Supporting Information

Enantioselective Palladaelectro-Catalyzed C–H Olefinations and Allylations for N–C Axial Chirality

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General Remarks

Catalytic reactions were carried out in an undivided electrochemical cell (10 mL) using pre-dried glassware, if not noted otherwise. Hetero-biaryl aldehydes **1** were synthesized according to a known method,[1] acrylates and malimides were used as obtained by commercial sources, acrylates **2e**-**2f** were synthesized according to a known method.[2] Other chemicals were obtained from commercial sources and were used without further purification. Lithium acetate was stored in glovebox. Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and GF electrodes (10 mm × 15 mm × 6 mm, SIGRACELL®GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat in constant current mode. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR. Chromatography: Merck silica gel 60 (40–63 µm). NMR: Spectra were recorded on a Varian Unity 300, Mercury 300, Inova 500 or Bruker Avance III 300, Bruker Avance III HD 400 and Bruker Avance III HD 500 in the solvent indicated; chemical shifts (δ) are given in ppm relative to the residual solvent peak. All IR spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS- and ESI-MS-spectra were recorded with Finnigan MAT 95, 70 eV and Finnigan LCQ; High resolution mass spectrometry (HRMS) with APEX IV 7T FTICR. M. p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected. HPLC chromatograms were recorded on an Agilent 1290 Infinity using CHIRALPAK® IA-3, IB-3, IC-3, ID-3 and IE-3 columns (3.0 µm particle size; Ø: 4.6 mm and 250 mm length). Optical rotations were measured with Anton Paar MCP 150 at the stated temperature under a Na/Hg lamp, λ = 589 nm (c in g/100 ml). The structure of the major stereoisomer is shown.

General Procedure A: Atroposelective electrocatalyzed C–H olefinations and allylations

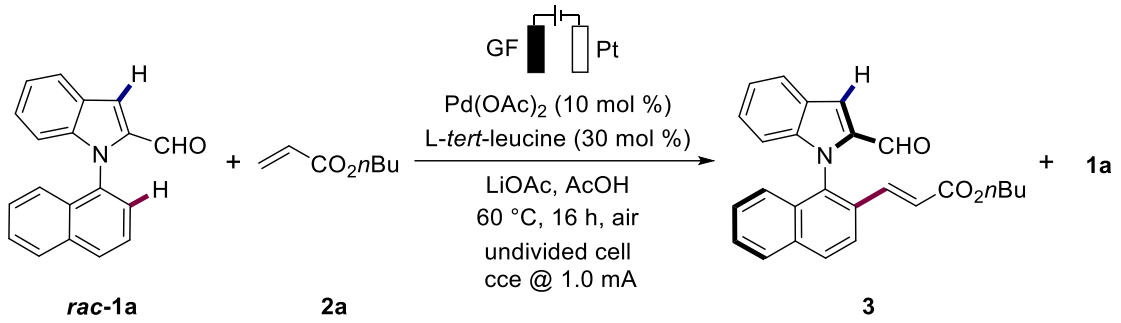
The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Hetero aryls aldehydes **1** (0.20 mmol, 1.0 equiv), alkenes (0.60 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.49 mg, 10 mol %), L-*tert*-leucine (7.9 mg, 30 mol %) and LiOAc (26.4 mg, 2.0 equiv) were placed in a 10 mL cell and dissolved in AcOH (4.5 mL). Electrocatalysis was performed at 60 °C with a constant current of 1.0 mA maintained for 16 h. At ambient temperature, the reaction mixture was diluted with EtOAc. The GF anode was washed with EtOAc (3 × 10 mL) in an ultrasonic bath. The washings were added to the reaction mixture and the solvents were removed *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel to yield the products.

General Procedure for the Synthesis of Racemic Products

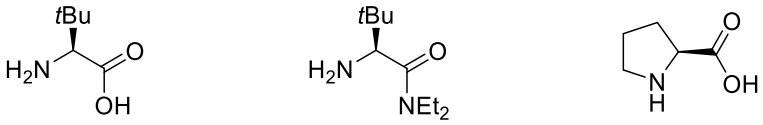
The racemic compounds were prepared using D/L-valine as transient directing group instead of L-*tert*-leucine.

Optimization Studies

Table S1 Optimization of the atroposelective electrocatalyzed C–H olefination.[a]



Entry	Deviation from standard conditions	Conv. (%)[b]	ee (**3**)	*S*[c]
1	None	42	97	138
2	L-*tert*-leucine diethylamide as TDG	23	99	264
3	L-proline as TDG	30[d]	---	---
4	TFE as solvent, no LiOAc	---	---	---
5	TFE/AcOH as solvent, no LiOAc	38	94	56
6	L-*tert*-leucine (20 mol %)	37	97	118
7	No electricity	29	97	97
8	No palladium	---	---	---
9	No L-*tert*-leucine	12[d]	---	---
10	Under O_2, No electricity	40	98	192
11	Under N_2	26	99	280
12	1,4-Benzoquinone	36[e]	99	347

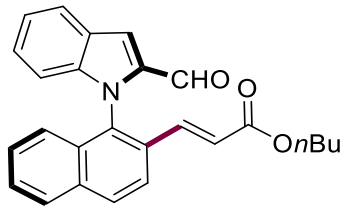


L-*tert*-leucine | L-*tert*-leucine diethylamide | L-proline

[a] Reaction conditions: Undivided cell, *rac*-**1a** (0.20 mmol), **2a** (0.60 mmol), [Pd] (10 mol %), L-*tert*-leucine (30 mol %), LiOAc (2.0 equiv), AcOH (4.5 mL), 60 °C, constant current at 1.0 mA, 16 h, graphite felt (GF) anode, Pt-plate cathode. [b] Calculated conversion, $C = ee_{1a}/(ee_{1a} + ee_{3a})$,

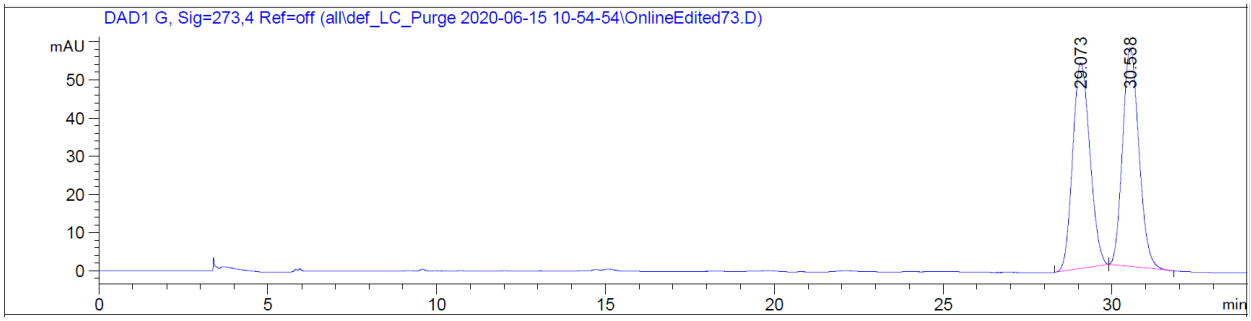
$ee_{\mathbf{1a}}$ = ee of **1a** and $ee_{\mathbf{3}}$ = ee of **3**. [c] Selectivity (s) = $\ln[(1 - C)(1 - ee_{\mathbf{1a}})]/\ln[(1 - C)(1 + ee_{\mathbf{1a}})]$. [d] C-3 alkenylated product was isolated. [e] 1,4-Benzoquinone (10 mol %) as additive.

Characterization Data of Products



(*E*)-Butyl-3-(1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)acrylate (3)

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and *n*-butyl acrylate (**2a**) (76.9 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **3** (32.8 mg, 40%) as a yellow oil and **1a** (29.0 mg, 55%) as yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 8.00–7.86 (m, 3H), 7.64 (s, 1H), 7.55 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.40–7.33 (m, 1H), 7.32–7.25 (m, 2H), 7.16 (d, *J* = 16.0 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.82–6.72 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 1.57 (dq, *J* = 8.5, 6.5 Hz, 2H), 1.31 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.2 (CH), 166.5 (C_q), 141.8 (C_q), 138.7 (CH), 137.7 (C_q), 135.0 (C_q), 134.1(C_q), 131.8 (C_q), 131.0 (C_q), 129.8 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 126.7 (C_q), 123.7 (CH), 123.5 (CH), 123.0 (CH), 122.2 (CH), 121.6 (CH), 116.6 (CH), 111.8 (CH), 64.5 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2980, 1705, 1622, 1432, 1295, 1145, 752 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 420 (100) $[M + Na]^+$, 398 (95) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{26}H_{23}NO_3 + H]^+$ 398.1751 found 398.1753. $[\alpha]_D^{20}$: +60.3 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 31.1 min, t_r (minor) = 30.1 min, 97% ee. The analytical data correspond with those reported in the literature.[3]



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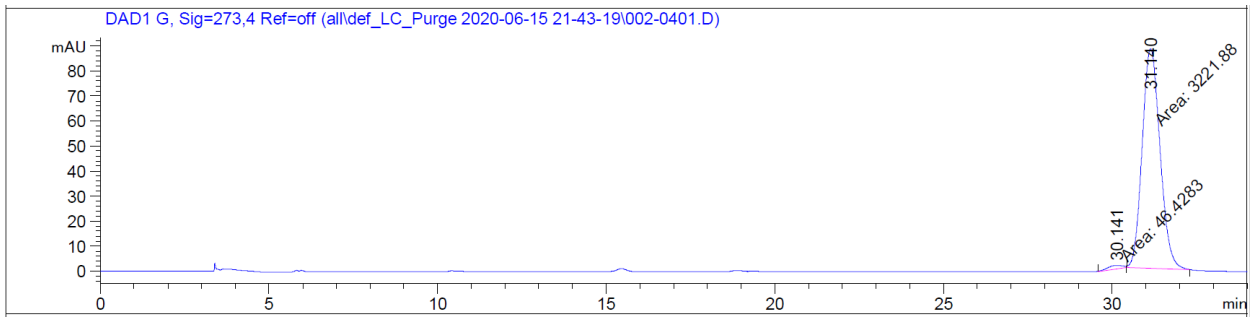

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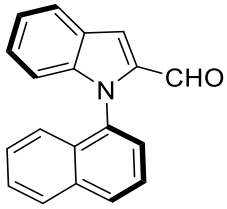
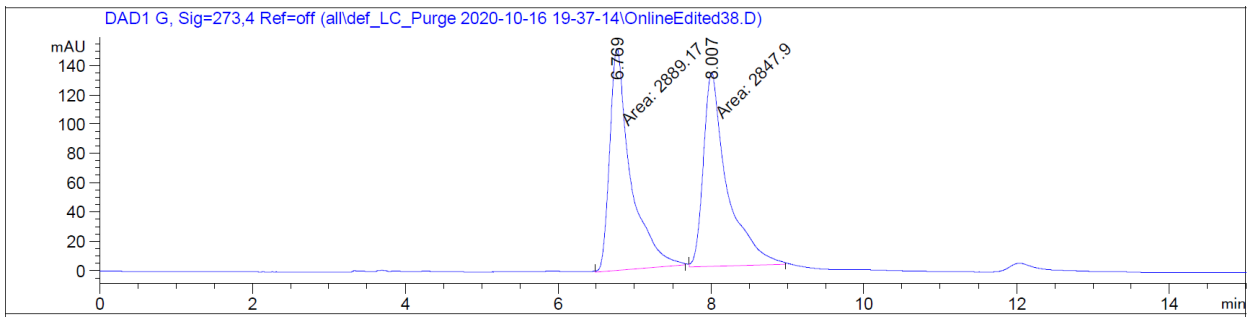
2	31.140	MM	0.6121	3221.87817	87.72165	98.5794



1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

M.p.: 90–92 °C (racemic sample). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.59–7.48 (m, 3H), 7.36 (t, J = 7.6 Hz, 1H), 7.33–7.18 (m, 2H), 7.09 (d, J = 8.5 Hz, 1H), 6.94–6.88 (m, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) (one carbon is missing due to overlap): δ = 181.6 (CH), 141.6 (C_q), 137.4 (C_q), 134.3 (C_q), 133.8 (C_q), 131.3 (C_q), 129.4 (CH), 128.4 (CH), 127.4 (CH), 127.1 (CH), 126.7 (CH), 126.4 (CH), 125.4 (CH), 123.3 (CH), 122.5 (CH), 121.8 (CH), 114.5 (CH), 111.8 (CH). IR (ATR): 2817, 1673, 798, 772, 752, 734, 484 cm^{-1}. MS (ESI) *m/z* (relative intensity): 294 (100) $[M+Na]^+$, 272 (70) $[M+H]^+$. HR-MS (ESI) *m/z* calc. for $[C_{19}H_{13}NO + H]^+$ 272.1070, found

272.1071. $[\alpha]_D^{20}$: +78.7 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.0 min, t_r (minor) = 6.8 min, 70% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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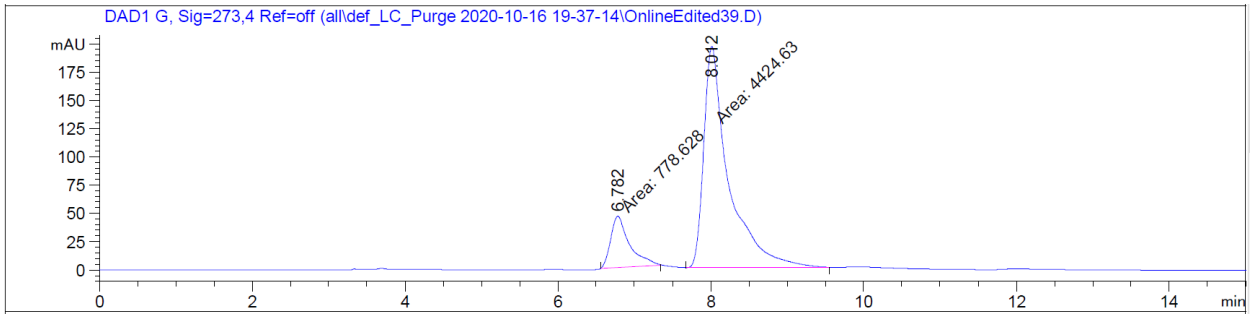
2	8.007	MM	0.3590	2847.90430	132.21581	49.6403



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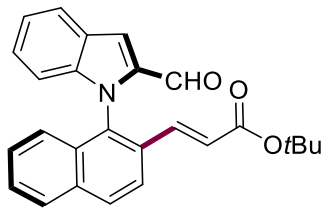
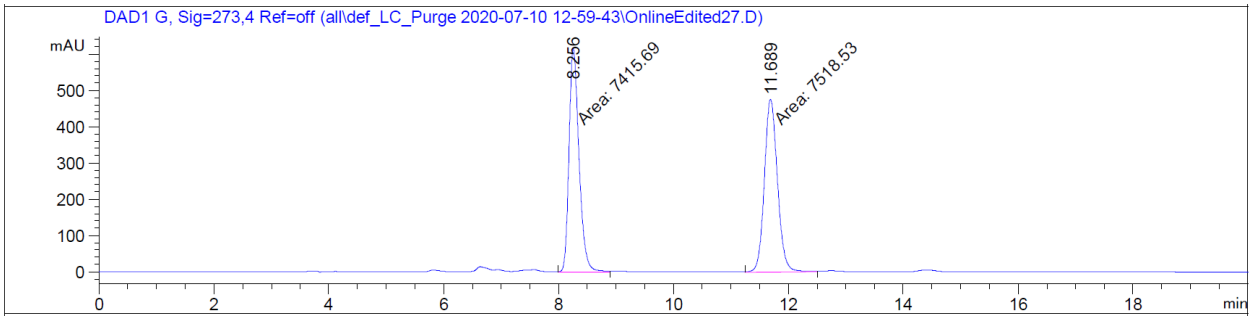
1	6.782	MM	0.2853	778.62787	45.49137	14.9642
2	8.012	MM	0.3766	4424.62695	195.82300	85.0358



(*E*)-*tert*-Butyl-3-(1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)acrylate (4)

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and *t*-butyl acrylate (**2b**) (76.9 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **4** (29.1 mg, 36%) as a yellow oil and **1a** (27.0 mg, 50%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.93–7.88 (m, 2H), 7.63 (s, 1H), 7.57–7.50 (m, 1H), 7.35 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.31–7.26 (m, 2H), 7.08 (d, *J* = 15.9 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.80–6.72 (m, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 1.42 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.2 (CH), 165.6 (C_q), 141.7 (C_q), 137.6 (C_q), 137.6 (CH), 134.8 (C_q), 133.8 (C_q), 131.7 (C_q), 131.0 (C_q), 129.6 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 126.5 (C_q), 123.6 (CH), 123.3 (CH), 122.9 (CH), 122.0 (CH), 116.3 (CH), 111.7 (CH), 80.6 (C_q), 28.1 (CH_3). IR (ATR): 2976, 1706, 1673, 1632, 1452, 1295, 1145, 752 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 420 (100) $[M + Na]^+$, 398 (95) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{26}H_{23}NO_3 + H]^+$ 398.1751 found 398.1750. $[\alpha]_D^{20}$: +43.5 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 11.7 min, t_r (minor) = 8.3 min, 92% ee.



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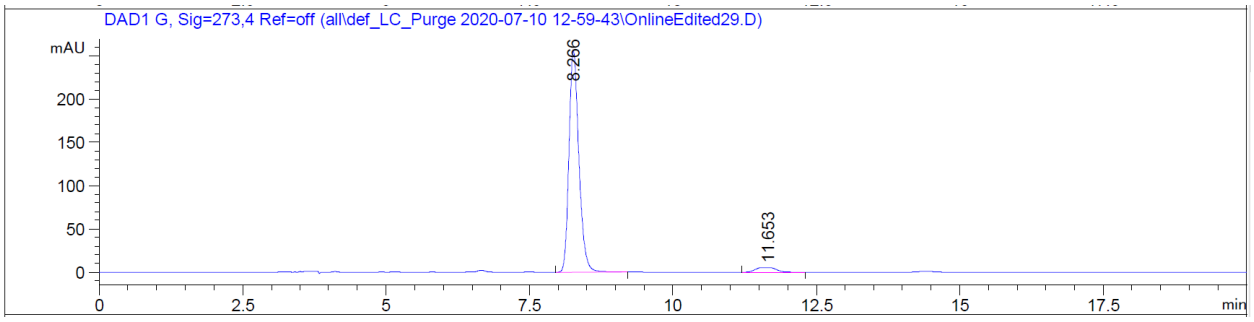

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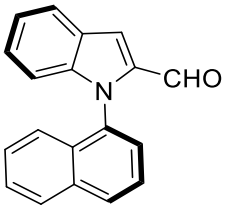
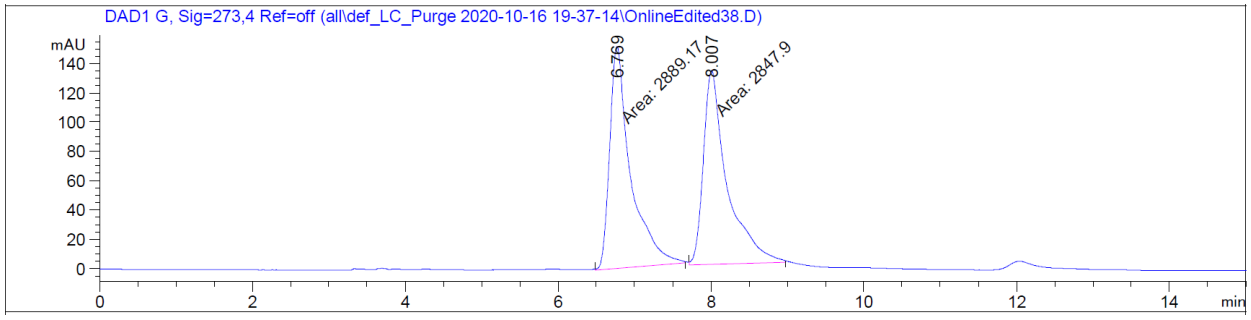
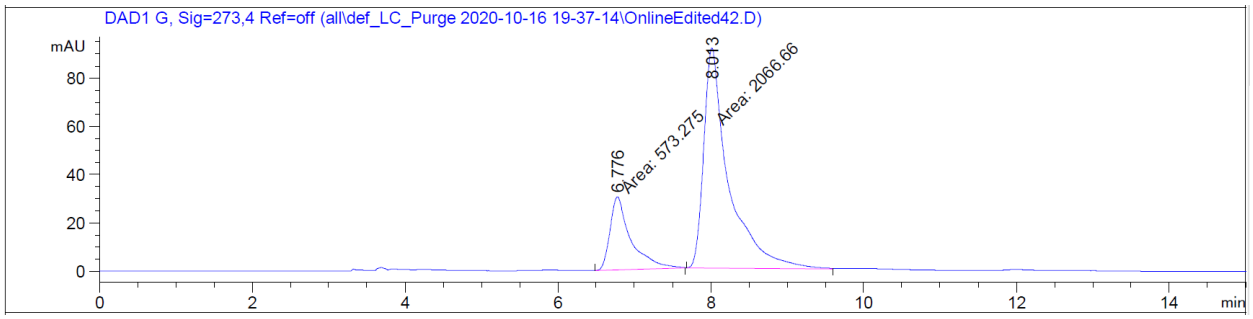


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

$[\alpha]_D^{20}$: +53.2 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.0 min, t_r (minor) = 6.8 min, 57% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.769	MM	0.3178	2889.17456	151.52682	50.3597
2	8.007	MM	0.3590	2847.90430	132.21581	49.6403



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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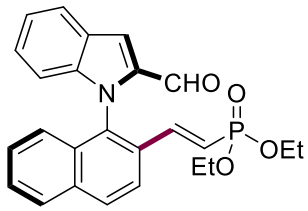
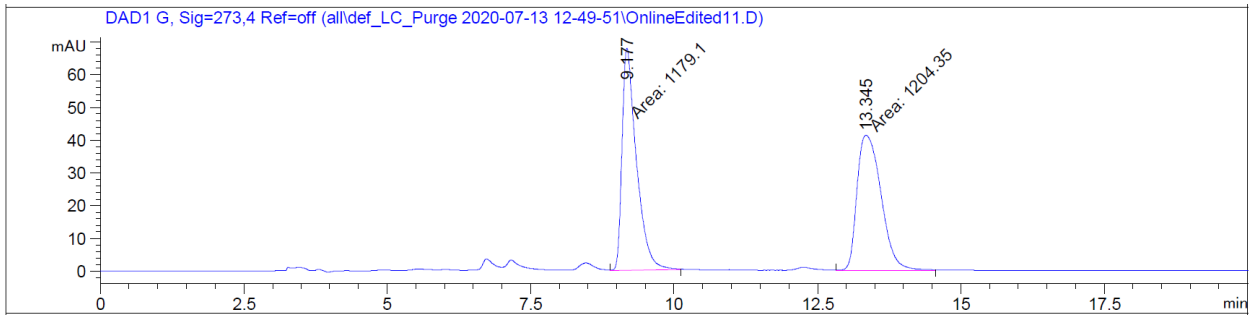
2	8.013	MM	0.3775	2066.65649	91.25343	78.2845



(*E*)-Diethyl-2-(1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)vinyl)phosphonate (5)

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and diethyl vinylphosphonate (**2c**) (98.4 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 1:1) yielded **5** (36.0 mg, 41%) as a yellow oil and **1a** (27.0 mg, 50%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1H), 8.01 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 1.1 Hz, 1H), 7.87–7.83 (m, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 1.1 Hz, 1H), 7.50 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.32 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.26–7.20 (m, 2H), 6.92 (dd, J = 8.6, 1.2 Hz, 1H), 6.83 (dd, J = 22.6, 17.6 Hz, 1H), 6.74–6.67 (m, 1H), 6.26 (t, J = 17.6 Hz, 1H), 3.95–3.78 (m, 3H), 3.77–3.64 (m, 1H), 1.16 (t, J = 7.0 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.0 (CH), 142.0 (J = 7.2 Hz, CH), 141.5 (C_q), 137.4 (C_q), 134.7 (C_q), 133.3 (C_q), 131.6 (C_q), 131.1 (J = 22.1 Hz, C_q), 129.7 (CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 126.5 (C_q), 123.5 (CH), 123.2 (CH), 122.8 (CH), 122.1 (CH), 119.0 (CH), 117.1 (CH), 116.2 (CH), 111.6 (CH), 62.0 (d, J = 5.4 Hz, CH_2), 61.8 (d, J = 5.4 Hz, CH_2), 16.2 (d, J = 6.6 Hz, CH_3), 16.0 (d, J = 6.6 Hz, CH_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 17.8. IR (ATR): 2984, 1672, 1614, 1409, 1245, 1021, 965, 734 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 456 (50) $[M + Na]^+$, 434

(100) $[M + H]^+$. HR-MS (ESI): *m/z* calcd. for $[C_{25}H_{24}NO_4{}^{31}P + H]^+$ 434.1516 found 434.1518. $[\alpha]_D^{20}$: +66.7 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 80:20, 1.0 mL/min, detection at 273 nm): t_r (major) = 13.7 min, t_r (minor) = 9.3 min, 93% ee.



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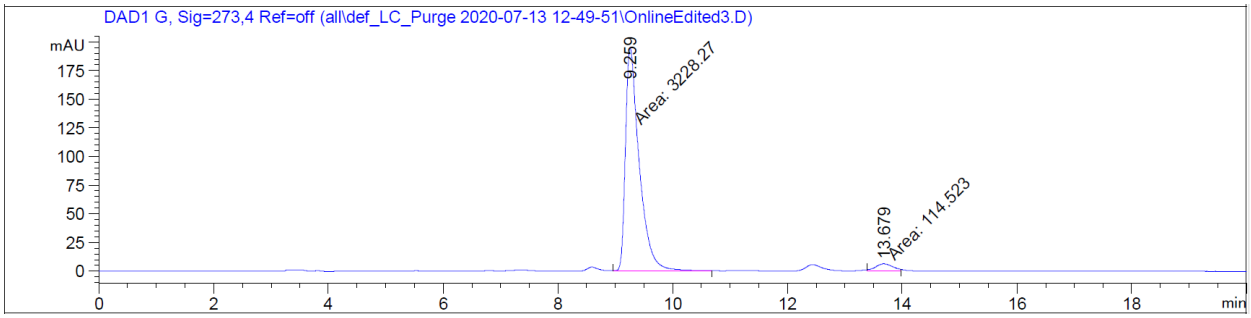
2	13.345	MM	0.4866	1204.34851	41.25092	50.5296



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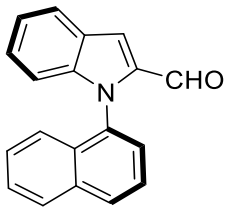
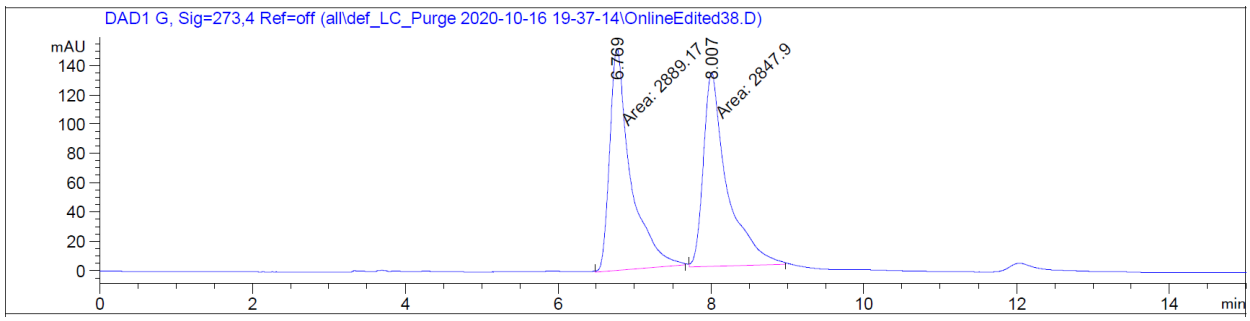
1	9.259	MM	0.2762	3228.26855	194.78714	96.5740
2	13.679	MM	0.3383	114.52299	5.64232	3.4260

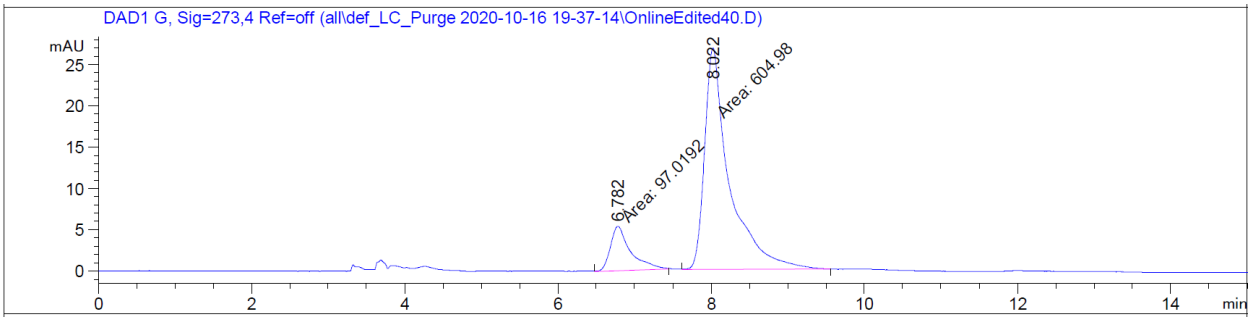


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

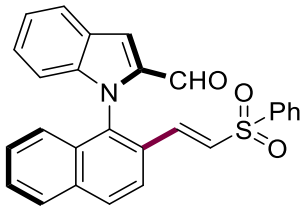
$[\alpha]_D^{20}$: +76.6 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.0 min, t_r (minor) = 6.8 min, 72% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.769	MM	0.3178	2889.17456	151.52682	50.3597
2	8.007	MM	0.3590	2847.90430	132.21581	49.6403

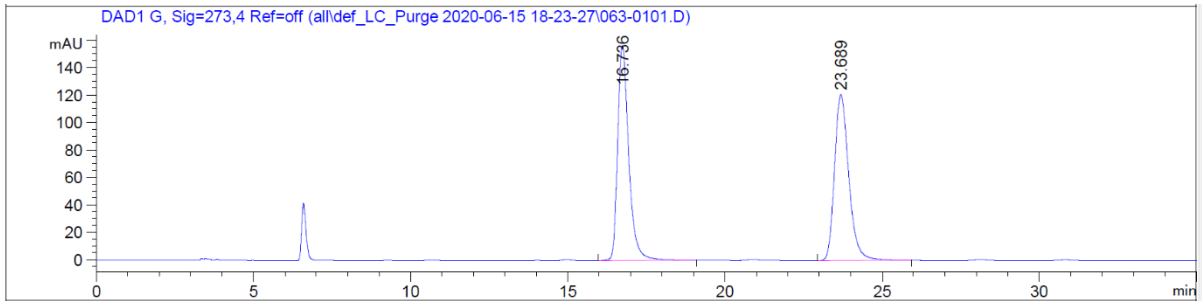


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.782	MM	0.3013	97.01921	5.36595	13.8204
2	8.022	MM	0.3758	604.97961	26.83046	86.1796

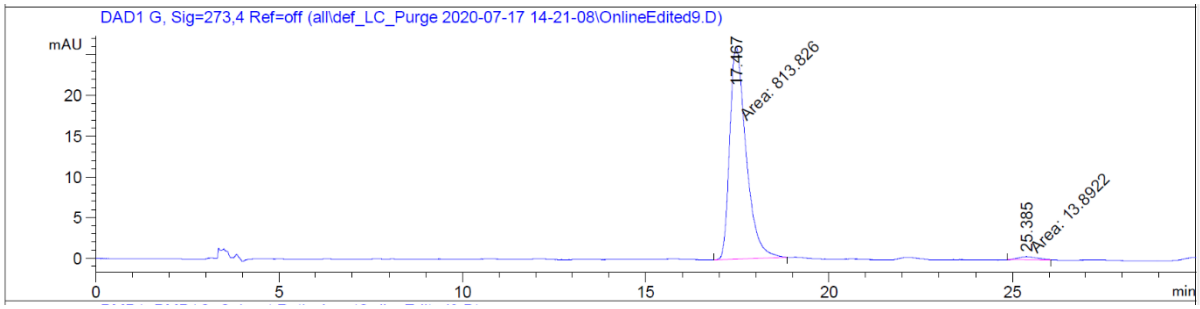


(*E*)-1-2-[2-(Phenylsulfonyl)vinyl]naphthalen-1-yl-1*H*-indole-2-carbaldehyde (6)

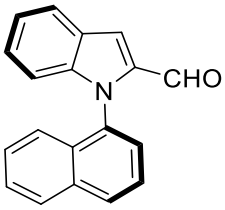
The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and phenyl vinyl sulfone (**2d**) (100.8 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 3:1) yielded **6** (27.0 mg, 31%) as a yellow oil and **1a** (30.0 mg, 56%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.90 (ddt, *J* = 12.0, 8.0, 1.0 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.62–7.56 (m, 3H), 7.56–7.49 (m, 2H), 7.45–7.38 (m, 2H), 7.33 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.29–7.21 (m, 2H), 7.05 (d, *J* = 15.5 Hz, 1H), 6.93 (dq, *J* = 8.6, 0.9 Hz, 1H), 6.72 (d, *J* = 15.5 Hz, 1H), 6.64 (dq, *J* = 7.8, 0.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 180.8 (CH), 141.7 (C_q), 140.0 (C_q), 137.3 (C_q), 137.2 (CH), 135.1 (C_q), 134.8 (C_q), 133.3 (CH), 131.5 (C_q), 130.8 (CH), 129.8 (CH), 129.2 (CH), 128.9 (C_q), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 126.5 (C_q), 123.7 (CH), 123.4 (CH), 123.2 (CH), 122.3 (CH), 117.3 (CH), 111.5 (CH). IR (ATR): 3033, 1738, 1673, 1611, 1306, 1146, 745 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 460 (100) $[M + Na]^+$, 438 (60) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{27}H_{19}NO_3S + H]^+$ 438.1158 found 438.1155. $[\alpha]_D^{20}$: +7.2 (c = 0.4, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 80:20, 1.0 mL/min, detection at 273 nm): t_r (major) = 17.5 min, t_r (minor) = 25.4 min, 97% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.736	BB	0.3733	3832.90967	156.72855	50.1128
2	23.689	BB	0.4832	3815.65234	120.90112	49.8872

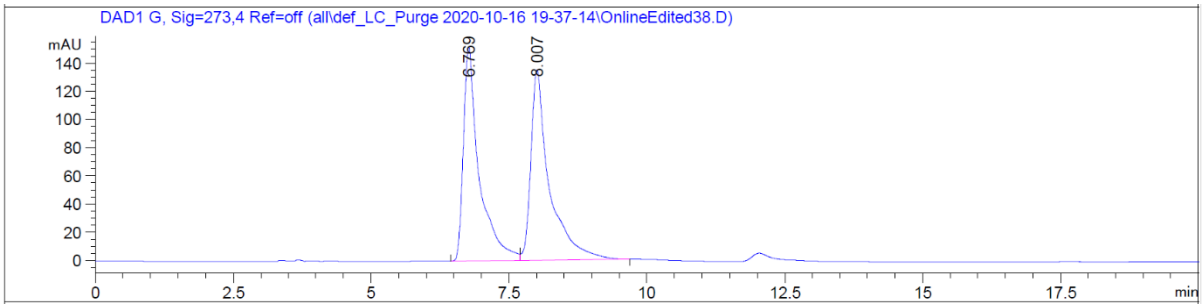


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.467	MM	0.5185	813.82623	26.15895	98.3216
2	25.385	MM	0.5953	13.89222	3.88927e-1	1.6784

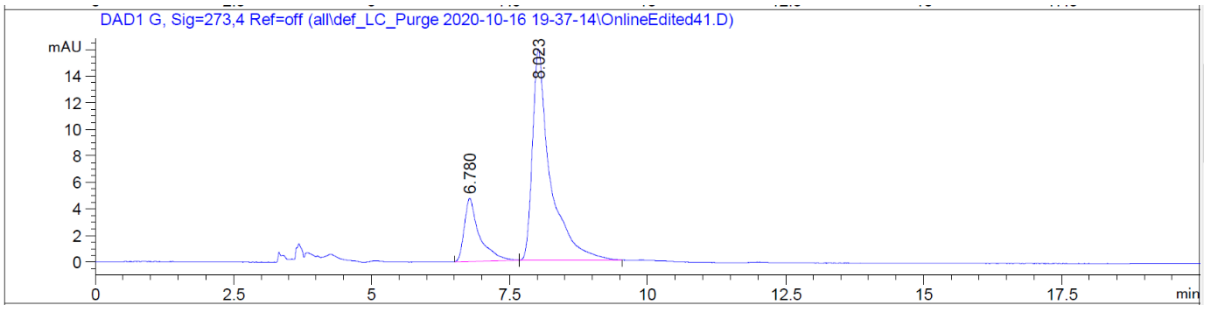


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

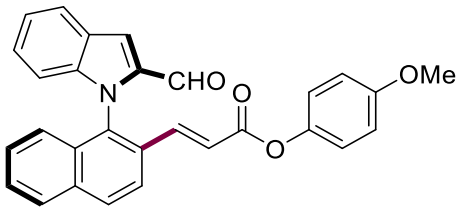
$[\alpha]_D^{20}$: +49.5 (c = 1.1, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.0 min, t_r (minor) = 6.8 min, 60% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.769	BV	0.2798	3021.69263	152.08777	48.8508
2	8.007	VB	0.3262	3163.86377	135.12547	51.1492



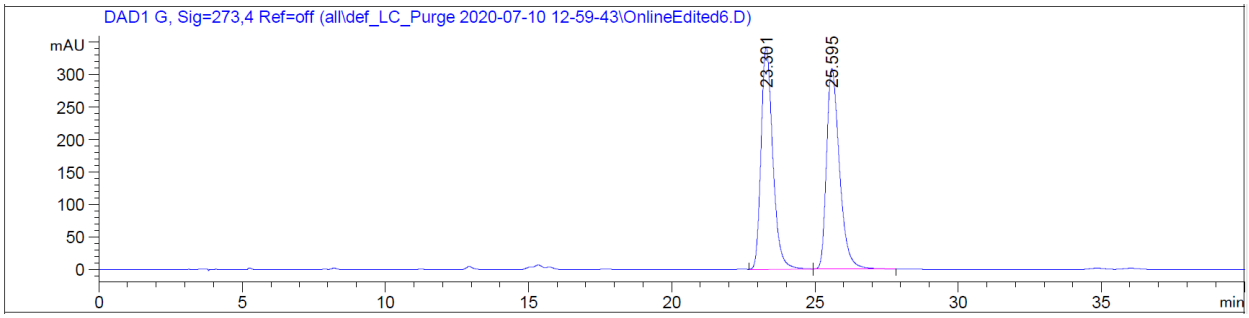
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.780	BB	0.2622	89.82868	4.75887	20.0919
2	8.023	BB	0.3107	357.25980	15.92416	79.9081



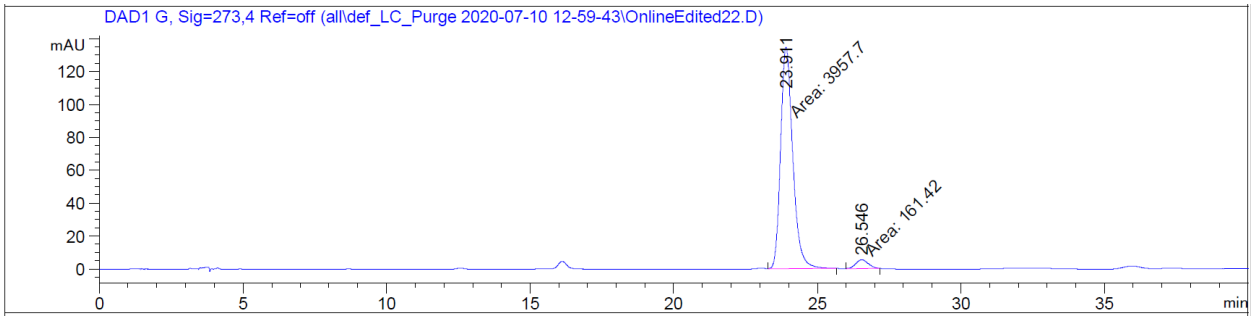
(*E*)-4-Methoxyphenyl-3-(1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)acrylate (7):

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and 4-methoxyphenyl acrylate (**2e**) (115.2 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **7** (36.0 mg, 40%) as a yellow oil and **1a** (22.1 mg, 41%) as yellow solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 8.09–8.04 (d, *J* = 8.2 Hz, 1H), 7.98–7.93 (m, 2H), 7.89 (ddd, *J* = 7.8, 1.4 Hz, 1H), 7.62 (d, *J* = 0.9 Hz, 1H), 7.54 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.36–7.31 (m, 2H), 7.30 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.28–7.24 (m, 1H), 6.99–6.94 (m, 2H), 6.90 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.85 (d, *J* = 9.1 Hz, 2H), 6.77 (dq, *J* = 8.2, 1.0 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 3.78 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 181.1 (CH), 165.1 (C_q), 157.1 (C_q), 144.1 (C_q), 141.8 (C_q), 140.4 (CH), 137.5 (C_q), 135.0 (C_q), 134.4 (C_q), 131.6 (C_q), 130.5 (C_q), 129.7 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 126.5

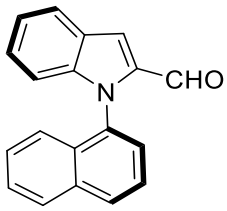
(C_q), 123.6 (CH), 123.4 (CH), 122.9 (CH), 122.2 (CH), 122.1 (CH), 120.5 (CH), 116.9 (CH), 114.3 (CH), 111.6 (CH), 55.5 (CH_3). IR (ATR): 2930, 1722, 1671, 1612, 1504, 1408, 1193, 752 cm^{-1}. MS (ESI) *m/z* (relative intensity): 470 (100) $[M + Na]^+$, 448 (50) $[M + H]^+$. HR-MS (ESI): *m/z* calcd. for $[C_{29}H_{21}NO_4 + H]^+$ 448.1543 found 448.1546. $[\alpha]_D^{20}$: +105.5 (c = 1.1, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 26.5 min, t_r (minor) = 23.9 min, 92% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.301	BB	0.4347	9715.03516	341.66299	50.1289
2	25.595	BB	0.4790	9665.08203	308.11127	49.8711

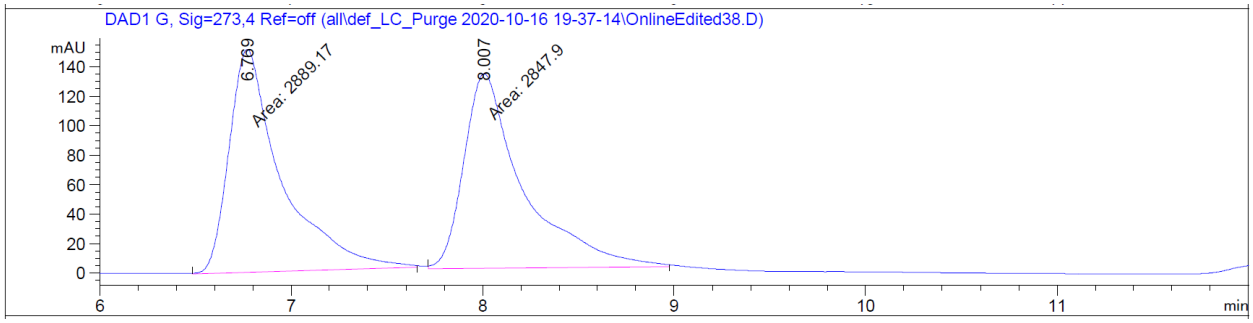


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.911	MM	0.4903	3957.70068	134.54184	96.0812
2	26.546	MM	0.5059	161.42030	5.31818	3.9188

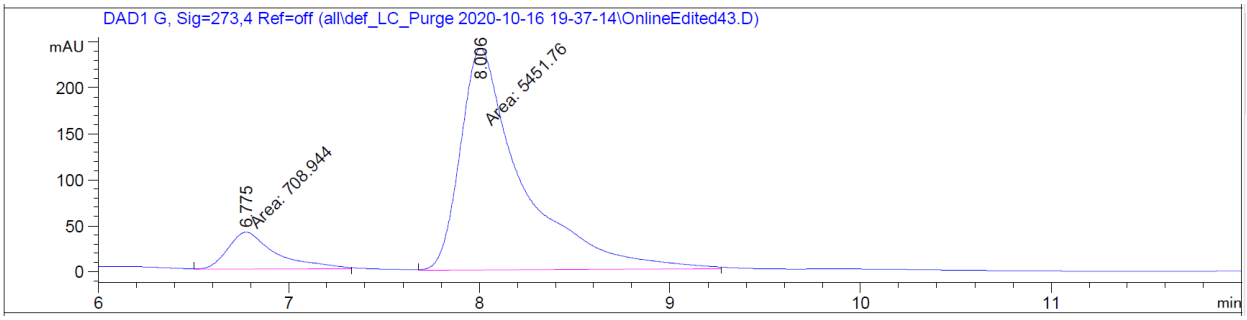


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

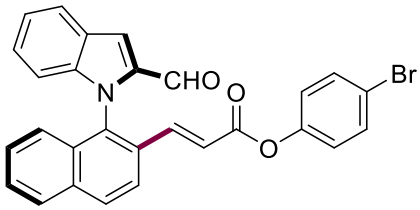
$[\alpha]_D^{20}$: +57.4 (c = 1.1, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.0 min, t_r (minor) = 6.8 min, 77% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.769	MM	0.3178	2889.17456	151.52682	50.3597
2	8.007	MM	0.3590	2847.90430	132.21581	49.6403

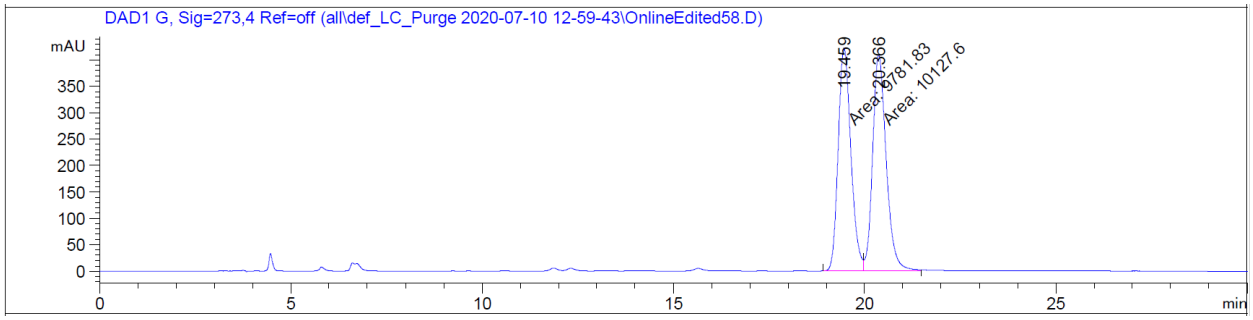


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.775	MM	0.2925	708.94360	40.39619	11.5075
2	8.006	MM	0.3772	5451.75635	240.87410	88.4925

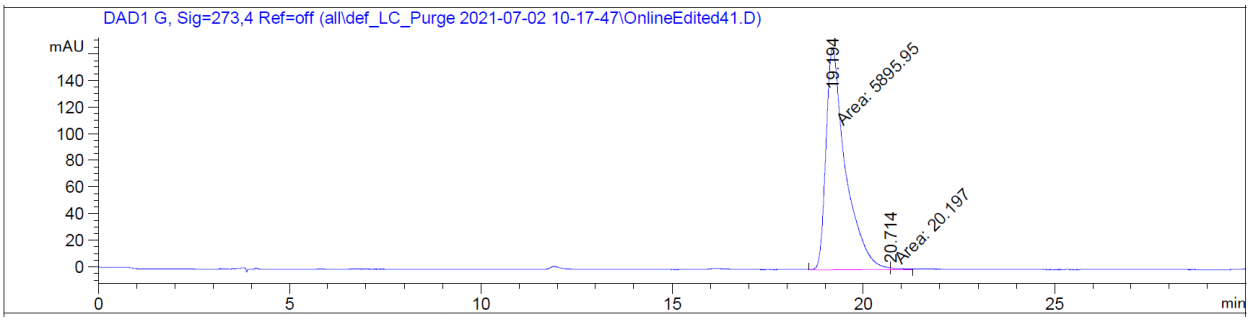


(*E*)-4-Bromophenyl 3-[1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl]acrylate (8)

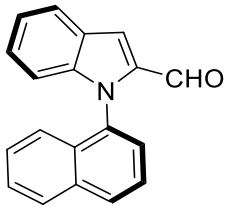
The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and 4-bromophenyl acrylate (**2f**) (136.2 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **8** (34.0 mg, 34%) as a yellow oil and **1a** (28.0 mg, 52%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.99–7.92 (m, 2H), 7.91–7.87 (m, 1H), 7.62 (d, *J* = 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.37–7.31 (m, 2H), 7.30–7.23 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.89 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.79–6.72 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.1 (CH), 164.4 (C_q), 149.6 (C_q), 141.8 (C_q), 141.1 (CH), 137.6 (C_q), 135.1 (C_q), 134.7 (C_q), 132.3 (CH), 131.6 (C_q), 130.4 (C_q), 129.8 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 126.5 (C_q), 123.6 (CH), 123.5 (CH), 123.3 (CH), 122.9 (CH), 122.2 (CH), 119.9 (CH), 118.8 (C_q), 117.0 (CH), 111.6 (CH). IR (ATR): 3061, 1732, 1672, 1613, 1482, 1198, 752 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 518 (80) $[M + Na]^+$, 496 (100) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{28}H_{18}NO_3{}^{79}Br + H]^+$ 496.0543 found 496.0542. $[\alpha]_D^{20}$: +70.7 (c = 1.1, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 19.2 min, t_r (minor) = 20.7 min, 99% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.459	MF	0.3855	9781.83008	422.86172	49.1315
2	20.366	FM	0.4122	1.01276e4	409.47269	50.8685

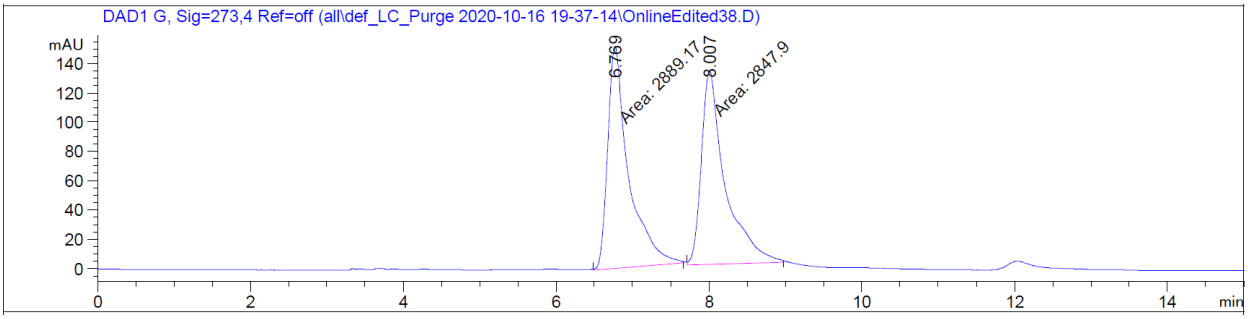


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.194	MF	0.5919	5895.94971	166.01936	99.6586
2	20.714	FM	0.3038	20.19699	1.10794	0.3414

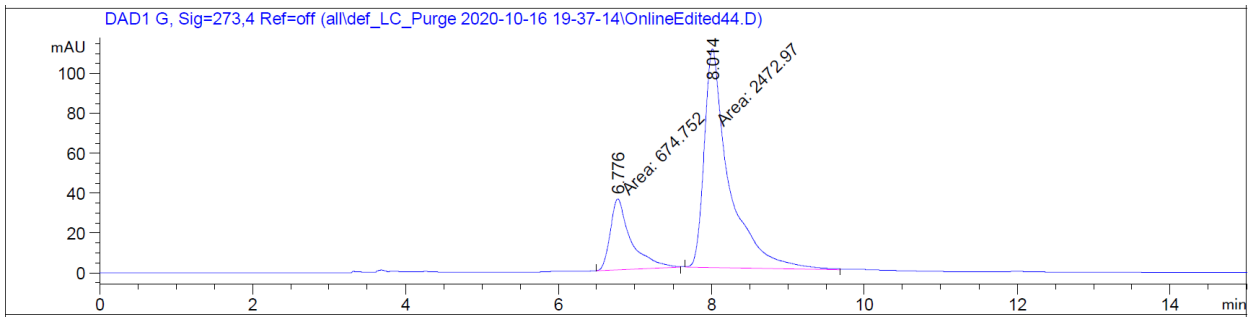


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

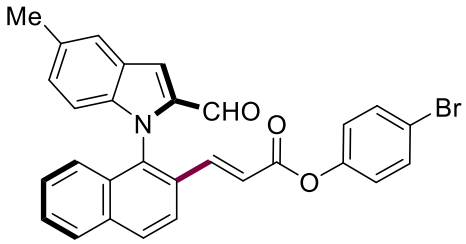
$[\alpha]_D^{20}$: +51.1 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.0 min, t_r (minor) = 6.8 min, 57% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.769	MM	0.3178	2889.17456	151.52682	50.3597
2	8.007	MM	0.3590	2847.90430	132.21581	49.6403



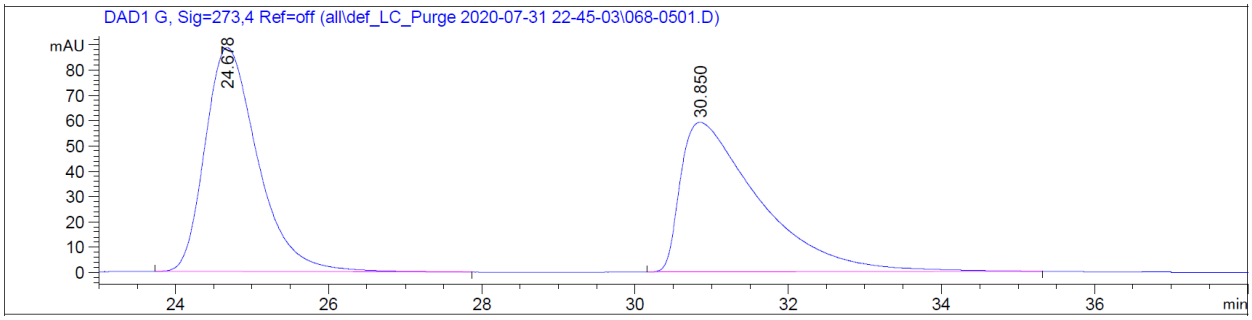
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.776	MM	0.3146	674.75220	35.74158	21.4362
2	8.014	MM	0.3758	2472.96680	109.66447	78.5638



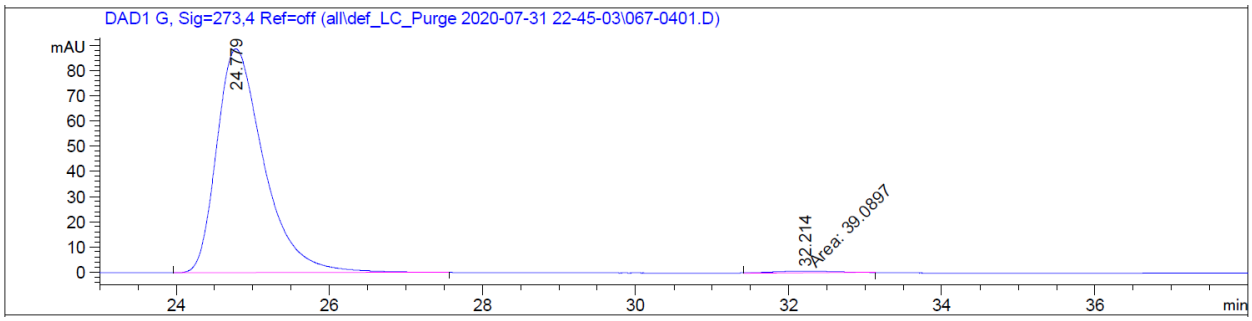
(*E*)-4-Bromophenyl-3-(1-(2-formyl-5-methyl-1*H*-indol-1-yl)naphthalen-2-yl)acrylate (9):

The general procedure **A** (reaction time = 20 h) was followed using 5-methyl-1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1b**) (57.1 mg, 0.20 mmol) and 4-bromophenyl acrylate (**2f**) (136.2 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **9** (30.3 mg, 30%) as a yellow oil and **1b** (23.4 mg, 41%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.98–7.94 (m, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.65 (dq, *J* = 2.3, 1.2 Hz, 1H), 7.57–7.50 (m, 2H), 7.48–7.41 (m, 2H), 7.37–7.29 (m, 2H), 7.12 (ddd, *J* = 8.6, 1.7, 0.5 Hz, 1H), 6.96–6.88 (m, 3H), 6.67–6.60 (m, 2H), 2.47 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 181.0 (CH), 164.4 (C_q), 149.6 (C_q), 141.2 (CH), 140.4 (C_q), 137.6 (C_q), 135.1 (C_q), 134.8 (C_q), 132.3 (CH), 131.6 (C_q), 130.3 (C_q), 129.9 (CH), 129.7 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 126.8 (C_q), 123.5 (CH), 123.3 (CH), 123.2 (C_q), 122.9 (CH), 122.8 (CH), 119.8 (CH), 118.8 (C_q), 116.5 (CH), 111.3 (CH), 21.4 (CH_3). IR (ATR): 2923, 1732, 1672, 1482, 1198, 1164, 1134 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 512 (40) $[M+H]^+$, 310 (70), 288 (100). HR-MS (ESI): *m*/*z* calcd. for $[C_{29}H_{20}NO_3{}^{79}Br + H]^+$ 510.0699 found 510.0701. $[\alpha]_D^{20}$: +72.5 (c = 0.8, $CHCl_3$). HPLC

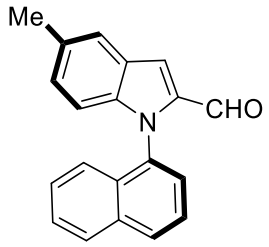
separation (Chiralpak® ID-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 24.8 min, t_r (minor) = 32.2 min, 98% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.678	BB	0.7105	4229.64648	88.51234	50.0209
2	30.850	BB	0.9641	4226.11230	59.10802	49.9791

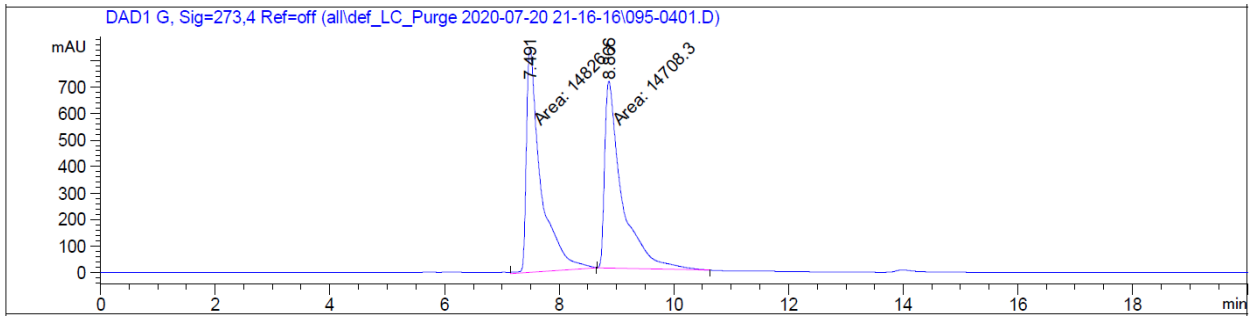


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.779	BB	0.6393	3801.27515	88.82663	98.9821
2	32.214	MM	0.9192	39.08968	7.08728e-1	1.0179

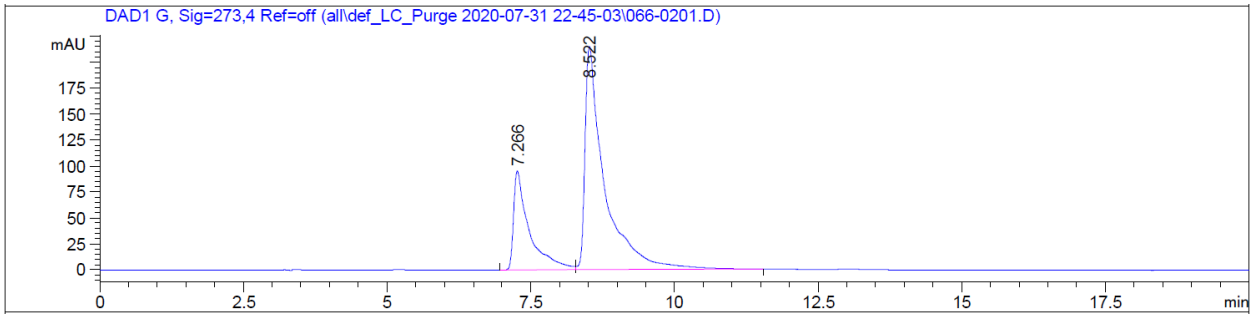


5-Methyl-1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1b)

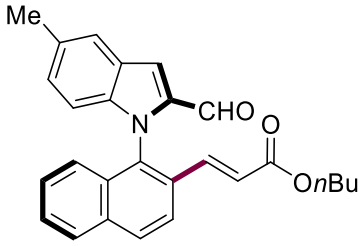
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.66–7.57 (m, 2H), 7.56–7.49 (m, 2H), 7.48 (d, J = 0.9 Hz, 1H), 7.36 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.11 (dd, J = 8.6, 1.4 Hz, 2H), 6.81 (d, J = 8.6 Hz, 1H), 2.47 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.6 (CH), 140.2 (C_q), 137.4 (C_q), 134.3 (C_q), 133.9 (C_q), 131.3 (C_q), 131.2 (C_q), 129.3 (CH), 129.2 (CH), 128.4 (CH), 127.3 (CH), 126.7 (CH), 126.6 (C_q), 126.3 (CH), 125.4 (CH), 122.5 (CH), 122.4 (CH), 113.9 (CH), 111.5 (CH), 21.4 (CH_3). IR (ATR): 3052, 2792, 1676, 1528, 1410, 774 cm^{-1}MS (ESI) m/z (relative intensity): 308 (70) $[M+Na]^+$, 286 (100). HR-MS (ESI): m/z calcd. for $[C_{20}H_{15}NO + H]^+$ 286.1226 found 286.1224. $[\alpha]_D^{20}$: +43.5 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.5 min, t_r (minor) = 7.3 min, 47% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.491	MM	0.2924	1.48261e4	844.99872	50.1994
2	8.866	MM	0.3482	1.47083e4	703.94916	49.8006

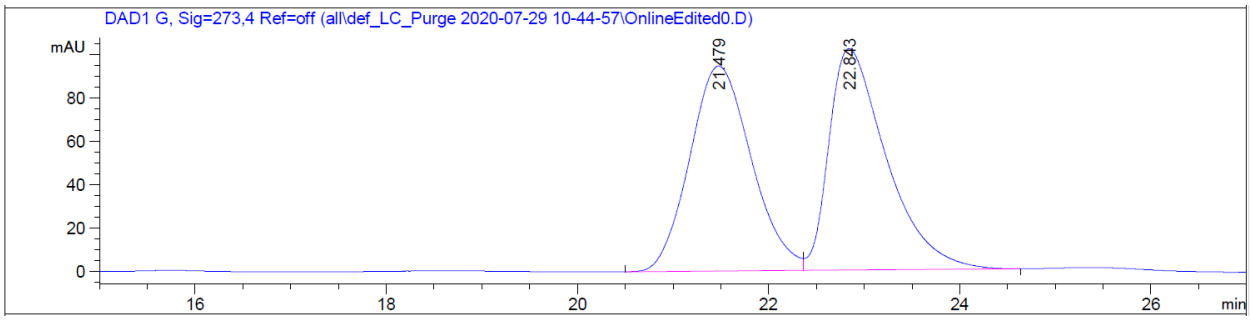


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.266	BV	0.2591	1826.17310	95.51523	26.3727
2	8.522	VB	0.3195	5098.30518	215.14488	73.6273

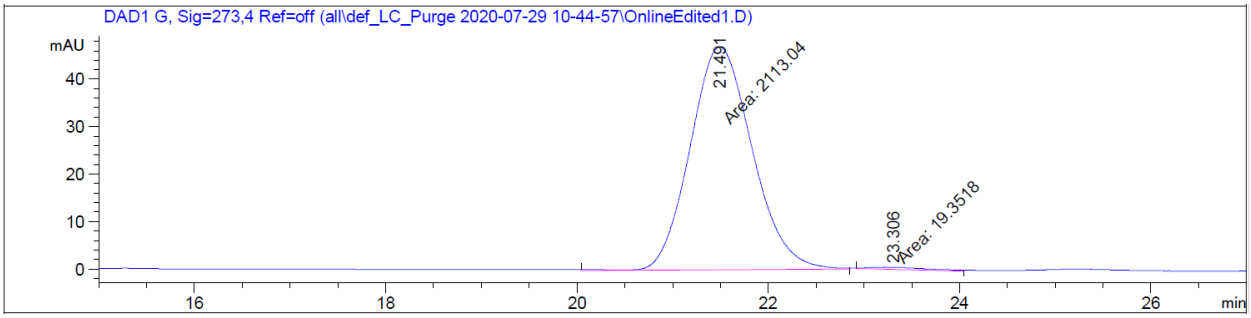


(*E*)-Butyl 3-(1-(2-formyl-5-methyl-1*H*-indol-1-yl)naphthalen-2-yl)acrylate (10)

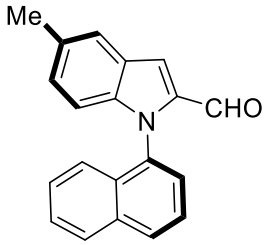
The general procedure **A** (reaction time = 20 h) was followed using 5-methyl-1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1b**) (57.1 mg, 0.20 mmol) and *n*-butyl acrylate (**2a**) (76.9 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **10** (19.1 mg, 23%) as a yellow oil and **1b** (25.0 mg, 44%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.68–7.62 (m, 1H), 7.57–7.48 (m, 2H), 7.33 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.18–7.08 (m, 2H), 6.92 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 4.06 (td, *J* = 6.6, 0.9 Hz, 2H), 2.47 (s, 3H), 1.57–1.49 (m, 2H), 1.32–1.23 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 181.0 (CH), 166.4 (CH), 140.3 (C_q), 138.6 (C_q), 137.6 (C_q), 134.8 (C_q), 134.1 (C_q), 131.7 (C_q), 131.5 (C_q), 130.8 (C_q), 129.8 (CH), 129.5 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 126.8 (C_q), 123.4 (CH), 122.9 (CH), 122.7 (CH), 121.4 (CH), 115.9 (CH), 111.3 (CH), 64.4 (CH_2), 30.6 (CH_2), 21.4 (CH_3), 19.1 (CH_2), 13.7 (CH_3). IR (ATR): 2958, 1711, 1672, 1175 cm^{-}1. MS (ESI) *m*/*z* (relative intensity): 840 (50), 434 (60) $[M+Na]^+$, 412 (100) $[M+H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{27}H_{25}NO_3 + H]^+$ 412.1907 found 412.1908. $[\alpha]_D^{20}$: +85.7 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® ID-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 21.5 min, t_r (minor) = 23.3 min, 98% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.479	BV	0.6820	4245.27832	94.52808	49.8488
2	22.843	VB	0.6061	4271.03906	102.08365	50.1512

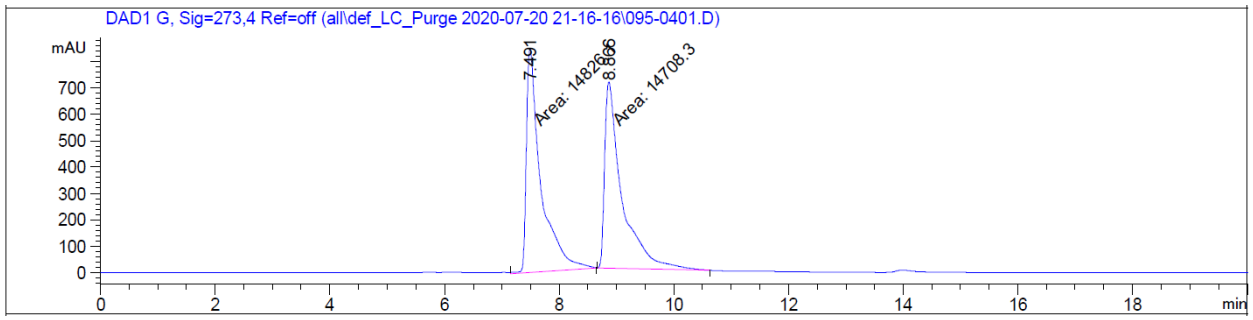


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.491	MM	0.7509	2113.03784	46.89743	99.0925
2	23.306	MM	0.7319	19.35180	4.40690e-1	0.9075

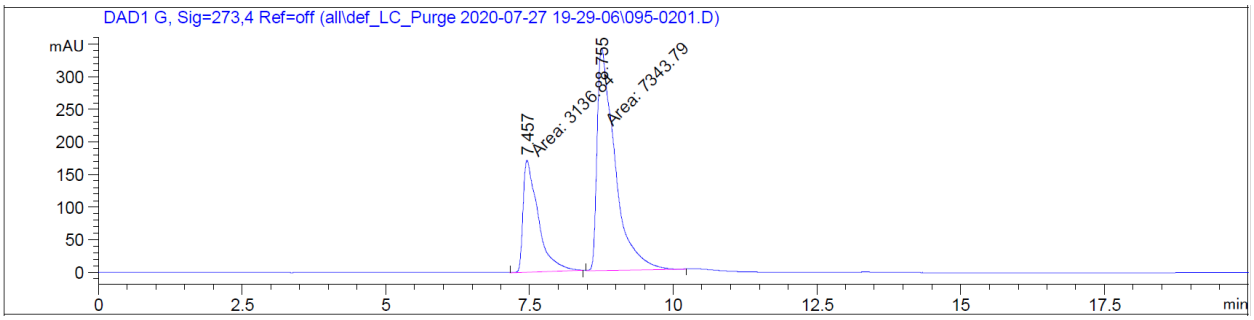


5-Methyl-1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1b)

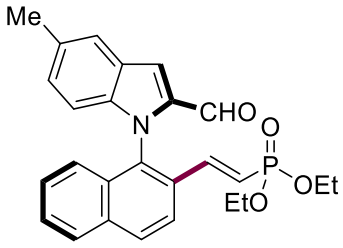
$[\alpha]_D^{20}$: +46.7 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.8 min, t_r (minor) = 7.5 min, 40% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.491	MM	0.2924	1.48261e4	844.99872	50.1994
2	8.866	MM	0.3482	1.47083e4	703.94916	49.8006



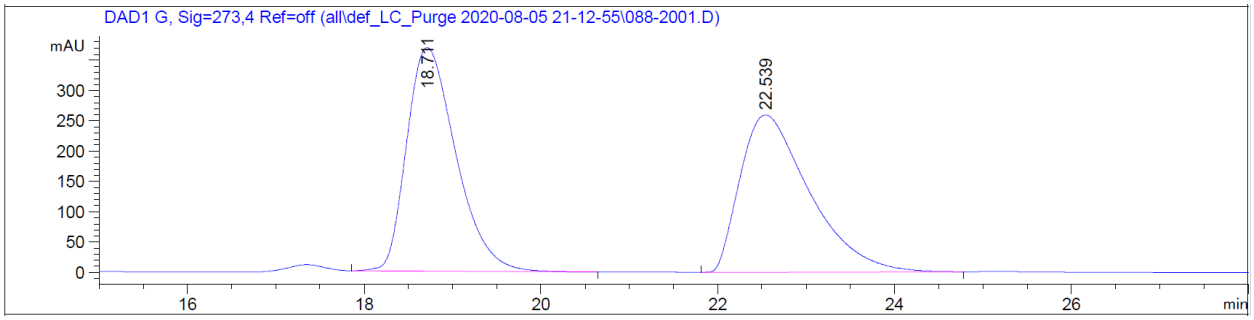
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.457	MM	0.3037	3136.83862	172.12798	29.9299
2	8.755	MM	0.3591	7343.79199	340.85080	70.0701



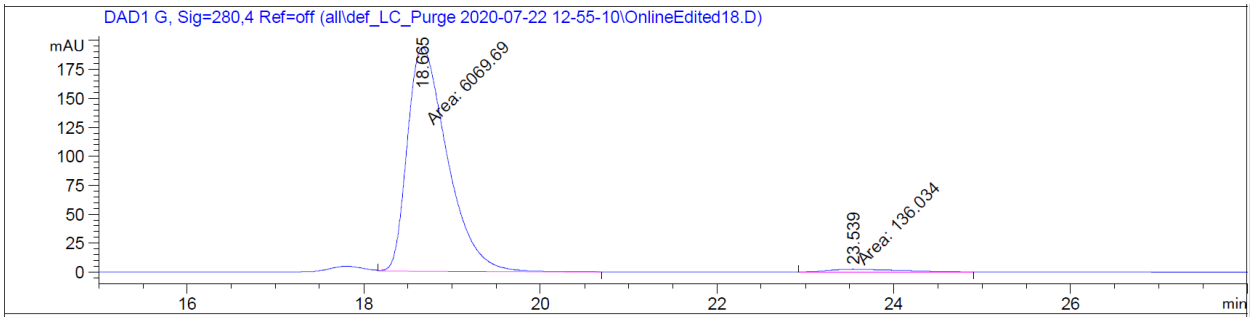
(*E*)-Diethyl {2-[1-(2-formyl-5-methyl-1*H*-indol-1-yl)naphthalen-2-yl]vinyl}phosphonate (11)

The general procedure **A** (reaction time = 20 h) was followed using 5-methyl-1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1b**) (57.1 mg, 0.20 mmol) and diethyl vinylphosphonate (**2c**) (98.4 mg,

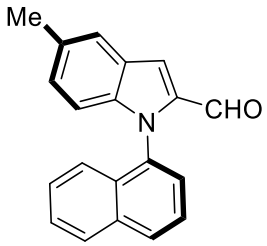
0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1 to EtOAc) yielded **11** (34.7 mg, 39%) as a colorless oil and **1b** (25.0 mg, 45%) as a yellow oil. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.63 (dt, *J* = 1.7, 0.9 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.34 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.09 (ddd, *J* = 8.6, 1.7, 0.6 Hz, 1H), 6.95 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.85 (dd, *J* = 22.6, 17.6 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 6.27 (t, *J* = 17.7 Hz, 1H), 3.94–3.81 (m, 3H), 3.79–3.69 (m, 1H), 2.45 (s, 3H), 1.19 (td, *J* = 7.1, 0.5 Hz, 3H), 1.08 (td, *J* = 7.1, 0.6 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 180.9 (CH), 142.2 (d, *J* = 7.2 Hz, CH), 140.1 (C_q), 137.5 (C_q), 134.7 (C_q), 133.5 (C_q), 131.63 (d, *J* = 1.6 Hz, C_q), 131.57 (C_q), 131.1 (d, *J* = 22.9 Hz, C_q), 129.7 (d, *J* = 21.1 Hz, CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 126.8 (C_q), 123.3 (CH), 122.8 (CH), 122.6 (CH), 118.6 (CH), 117.3 (CH), 115.7 (CH), 111.3 (CH), 62.0 (d, *J* = 5.5 Hz, CH_2), 61.9 (d, *J* = 5.7 Hz, CH_2), 21.3 (CH_3), 16.2 (d, *J* = 6.7 Hz, CH_3), 16.0 (d, *J* = 6.7 Hz, CH_3). ^{31}P-NMR (243 MHz, $CDCl_3$): δ = 17.8. IR (ATR): 2982, 1672, 1247, 1049, 1023, 964 cm^{-1}. MS (ESI) *m/z* (relative intensity): 448 (80) $[M+H]^+$, 165 (100). HR-MS (ESI): *m/z* calcd. for $[C_{26}H_{26}NO_4{}^{31}P + H]^+$ 448.1672 found 448.1672. $[\alpha]_D^{20}$: +86.4 (c = 0.9, $CHCl_3$). HPLC separation (Chiralpak® ID-3, *n*-hexane/*i*-PrOH 70:30, 1.0 mL/min, detection at 280 nm): t_r (major) = 18.7 min, t_r (minor) = 23.5 min, 96% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.711	BB	0.5970	1.42630e4	368.98788	50.2919
2	22.539	BB	0.8147	1.40975e4	259.52420	49.7081

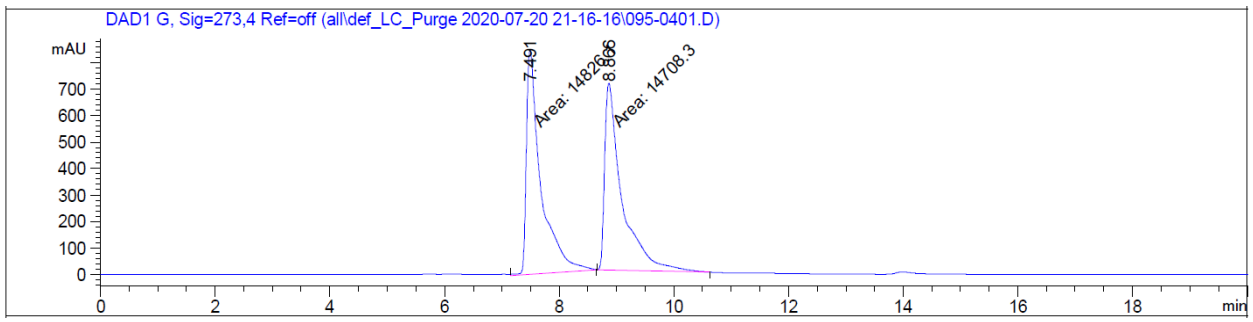


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.665	MM	0.5233	6069.68945	193.32231	97.8079
2	23.539	MM	0.9229	136.03410	2.45663	2.1921

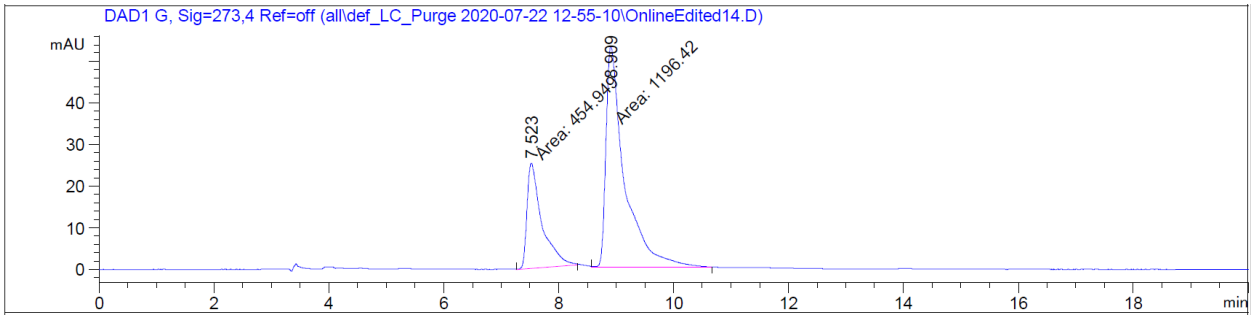


5-Methyl-1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1b)

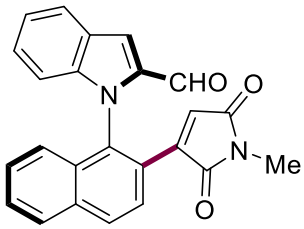
$[\alpha]_D^{20}$: +43.5 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 8.9 min, t_r (minor) = 7.5 min, 45% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.491	MM	0.2924	1.48261e4	844.99872	50.1994
2	8.866	MM	0.3482	1.47083e4	703.94916	49.8006



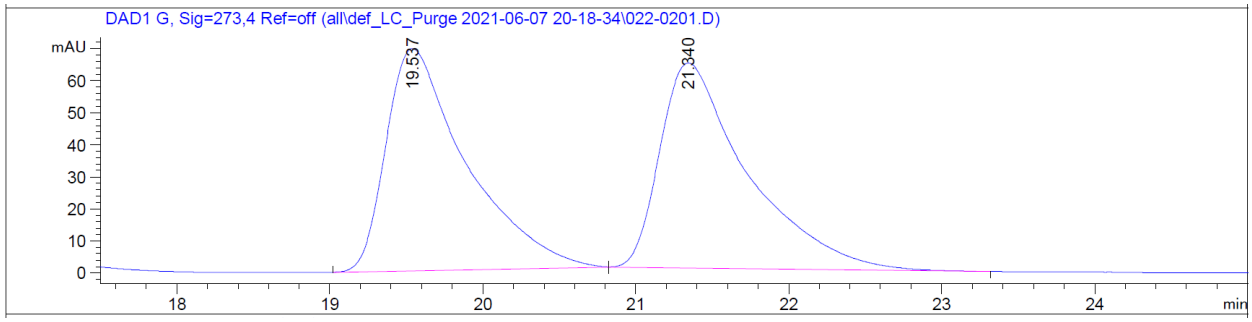
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.523	MM	0.2994	454.94934	25.32422	27.5499
2	8.909	MM	0.3758	1196.41772	53.06655	72.4501



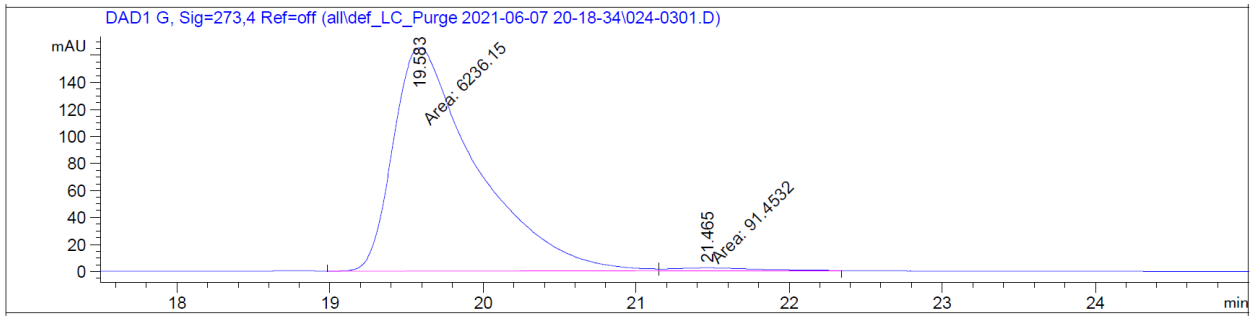
1-[2-(1-Methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)naphthalen-1-yl]-1*H*-indole-2-carbaldehyde (13)

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and *N*-methylmaleimide (**12a**) (66.6 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **13** (33.0 mg, 34%) as a yellow oil and **1a** (22.0 mg, 40%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 8.15–8.06 (m, 2H), 8.00–7.92 (m, 1H), 7.88–7.82 (m, 1H), 7.58 (s, 1H), 7.54 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.33 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.28–7.20 (m, 2H), 6.83 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.76–6.67 (m, 1H), 5.48 (s, 1H), 2.94 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) (one carbon is missing due to overlap): δ = 181.0 (CH), 170.3 (C_q), 170.1 (C_q), 141.0 (C_q), 140.7 (C_q), 136.6 (C_q), 134.9 (C_q), 134.0 (C_q), 131.5 (C_q), 129.2 (CH), 128.3 (CH), 128.1 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 126.5 (CH), 125.7 (C_q), 123.7 (CH), 123.1 (CH), 122.4 (CH), 117.3 (CH), 111.4 (CH), 24.0 (CH_3). IR (ATR): 2925, 1704, 1674, 1438, 1384, 751 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 403 (100) $[M + Na]^+$, 381 (25) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{24}H_{16}N_2O_3 + H]^+$ 381.1234 found 381.1234.

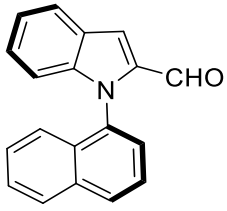
$[\alpha]_D^{20}$: –9.0 (c = 0.5, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 19.6 min, t_r (minor) = 21.5 min, 97% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.537	BB	0.5149	2519.67358	69.35225	49.8712
2	21.340	BB	0.5591	2532.69238	63.94244	50.1288

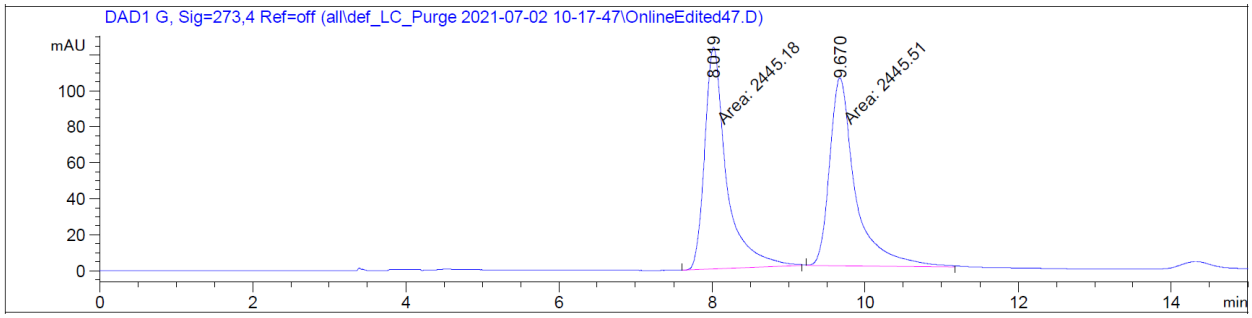


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.583	MF	0.6288	6236.15430	165.30261	98.5547
2	21.465	FM	0.6554	91.45322	2.32573	1.4453

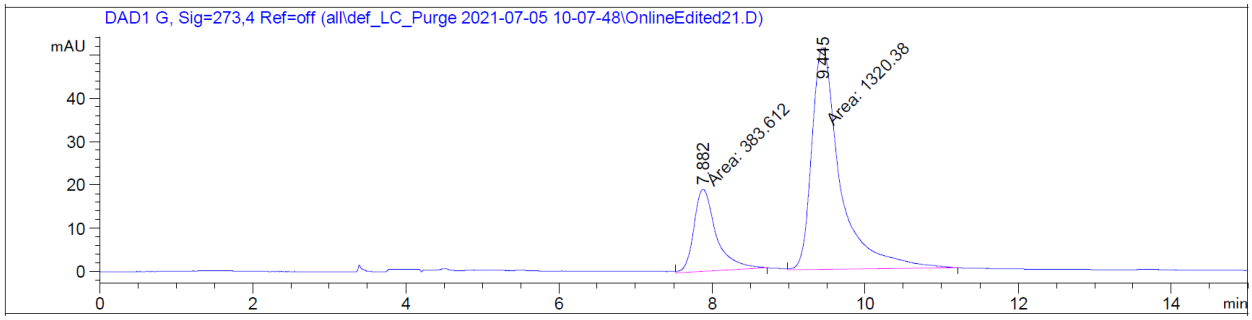


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

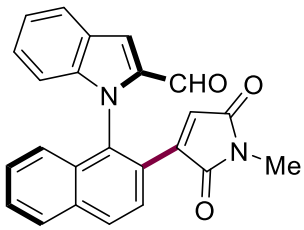
$[\alpha]_D^{20}$: +51.9 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.4 min, t_r (minor) = 7.9 min, 55% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.019	MM	0.3301	2445.17529	123.43890	49.9965
2	9.670	MM	0.3899	2445.51367	104.54658	50.0035

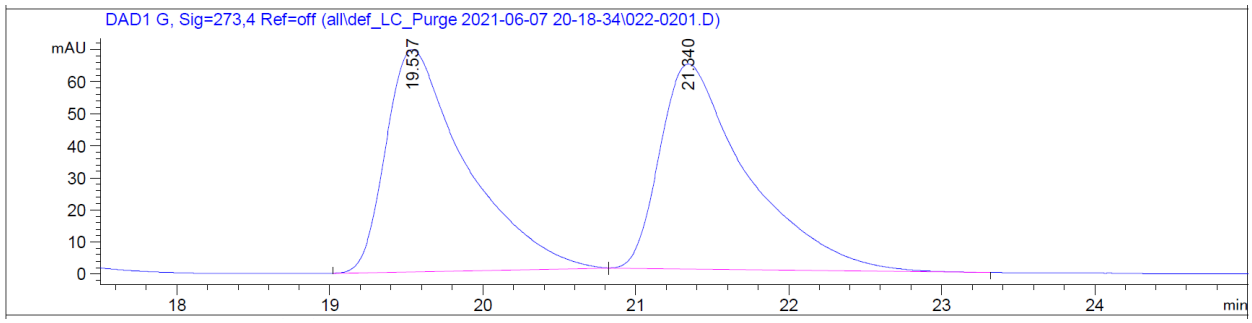


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.882	MM	0.3374	383.61203	18.94762	22.5126
2	9.445	MM	0.4307	1320.37903	51.09891	77.4874

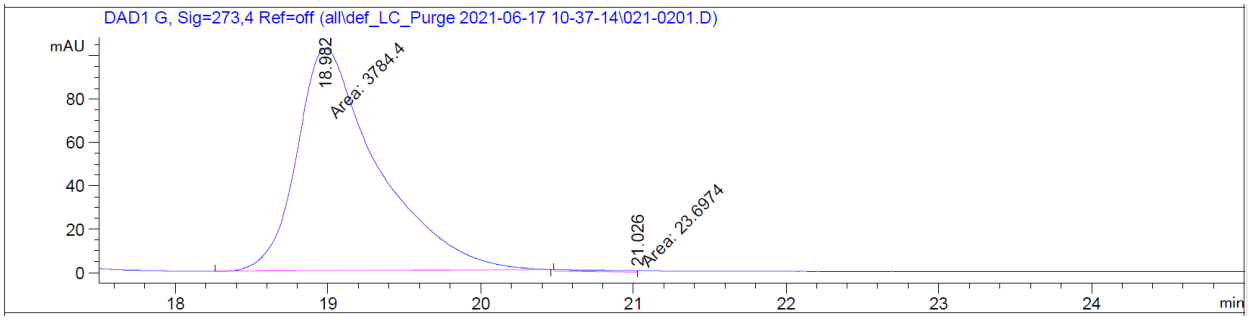


1-[2-(1-Methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)naphthalen-1-yl]-1*H*-indole-2-carbaldehyde (13)

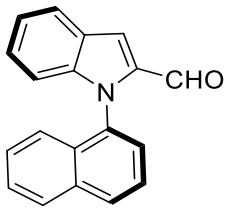
A modified procedure **A** was followed using L-*tert*-leucine diethylamide (11.2 mg, 30 mol %) as TDG. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **13** (15.0 mg, 20%) as a yellow oil and **1a** (33.0 mg, 60%) as yellow solid. $[\alpha]_D^{20}$: –9.8 (c = 0.50, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 19.0 min, t_r (minor) = 21.0 min, 99% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.537	BB	0.5149	2519.67358	69.35225	49.8712
2	21.340	BB	0.5591	2532.69238	63.94244	50.1288

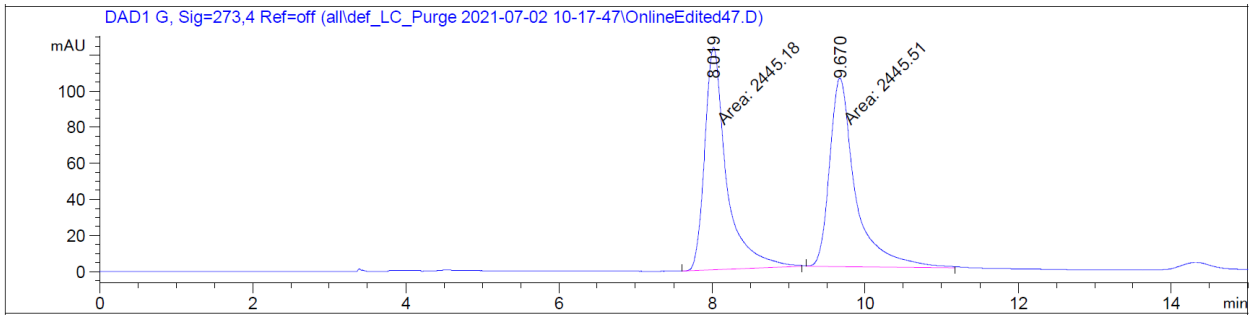


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.982	MM	0.6139	3784.40405	102.74258	99.3777
2	21.026	MM	0.5136	23.69745	7.69000e-1	0.6223

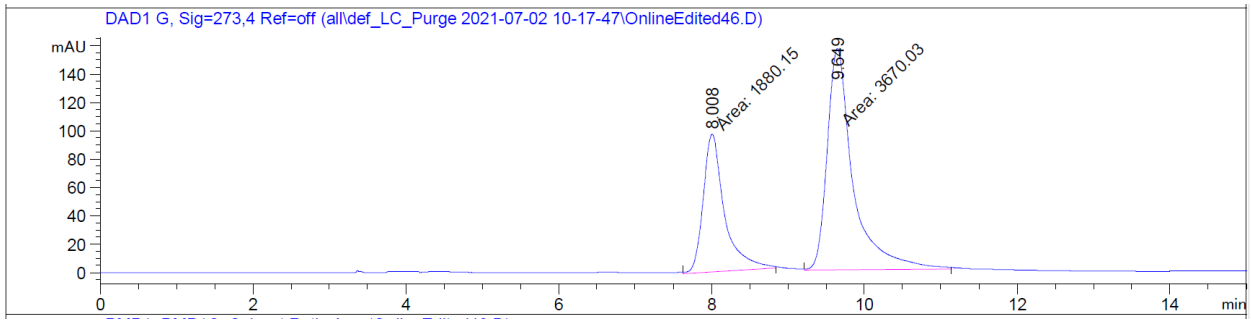


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

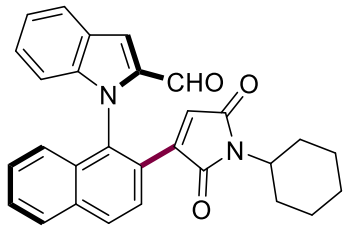
$[\alpha]_D^{20}$: +20.7 (c = 1.1, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.6 min, t_r (minor) = 8.0 min, 32% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.019	MM	0.3301	2445.17529	123.43890	49.9965
2	9.670	MM	0.3899	2445.51367	104.54658	50.0035

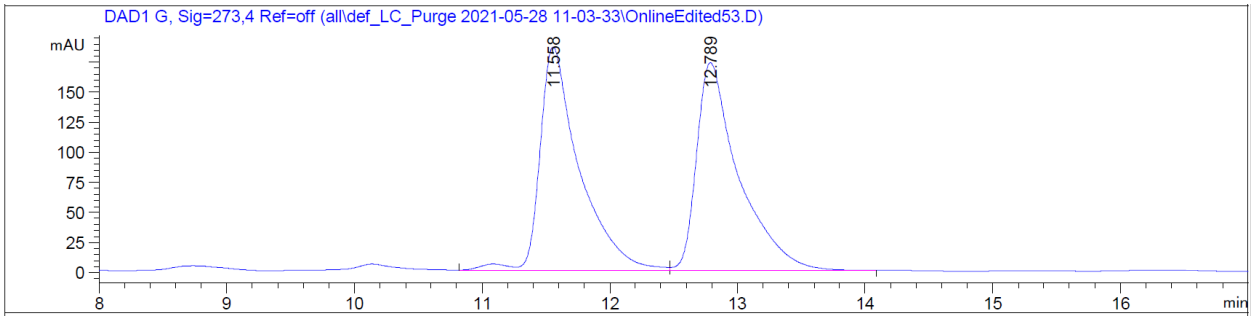


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.008	MM	0.3229	1880.14868	97.05759	33.8754
2	9.649	MM	0.3924	3670.03296	155.89415	66.1246

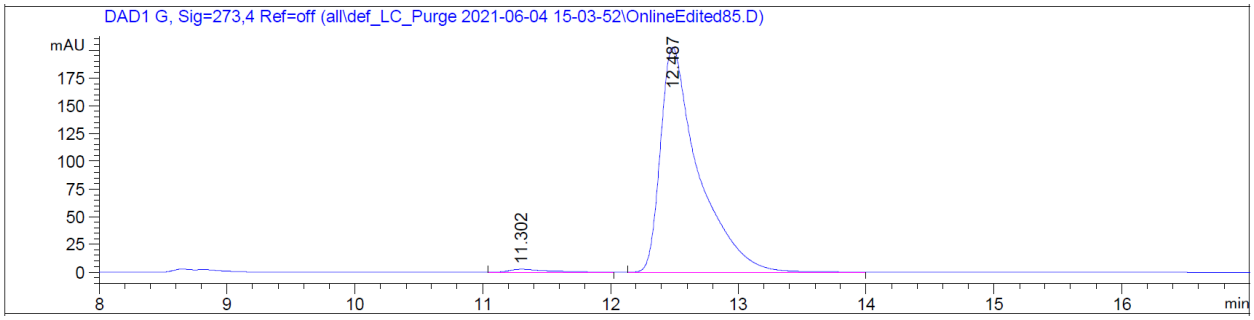


1-[2-(1-Cyclohexyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)naphthalen-1-yl]-1*H*-indole-2-carbaldehyde (14)

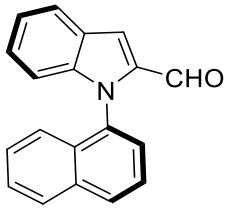
The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and *N*-cyclohexylmaleimide (**12b**) (107.5 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **14** (18.8 mg, 21%) as a yellow solid. M.p.: 215-217 °C. **1a** was isolated as a mixture (91.7 mg) with *N*-cyclohexylmaleimide (calculated yield based on NMR integration: 35%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 8.10 (s, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.90–7.80 (m, 1H), 7.62–7.51 (m, 2H), 7.35 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.31–7.19 (m, 2H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.76–6.68 (m, 1H), 5.50 (s, 1H), 3.82 (tt, *J* = 12.3, 3.9 Hz, 1H), 2.07–1.87 (m, 2H), 1.84–1.74 (m, 2H), 1.67–1.48 (m, 3H), 1.34–1.09 (m, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 181.0 (CH), 170.1 (C_q), 140.6 (C_q), 140.6 (C_q), 136.8 (C_q), 134.8 (C_q), 133.8 (C_q), 131.6 (C_q), 129.1 (CH), 128.2 (CH), 128.0 (CH), 127.98 (CH), 127.96 (CH), 127.6 (CH), 126.5 (CH), 126.5 (C_q), 125.9 (C_q), 123.7 (CH), 123.1 (CH), 122.3 (CH), 117.0 (CH), 111.4 (CH), 51.0 (CH), 29.8 (CH_2), 29.7 (CH_2), 25.9 (CH_2), 25.0 (CH_2). IR (ATR): 2933, 1701, 1676, 1398, 1376, 737 cm^{-1}.MS (ESI) *m*/*z* (relative intensity): 471 (100) $[M + Na]^+$, 449 (90) $[M + H]^+$, 352 (100), 288 (100). HR-MS (ESI): *m*/*z* calcd. for $[C_{29}H_{24}N_2O_3 + H]^+$ 449.1860 found 449.1849. $[\alpha]_D^{20}$: +10.0 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 12.5 min, t_r (minor) = 11.3 min, 98% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.558	VV R	0.3006	3987.34424	185.73163	50.1940
2	12.789	VB	0.3261	3956.52319	172.81795	49.8060

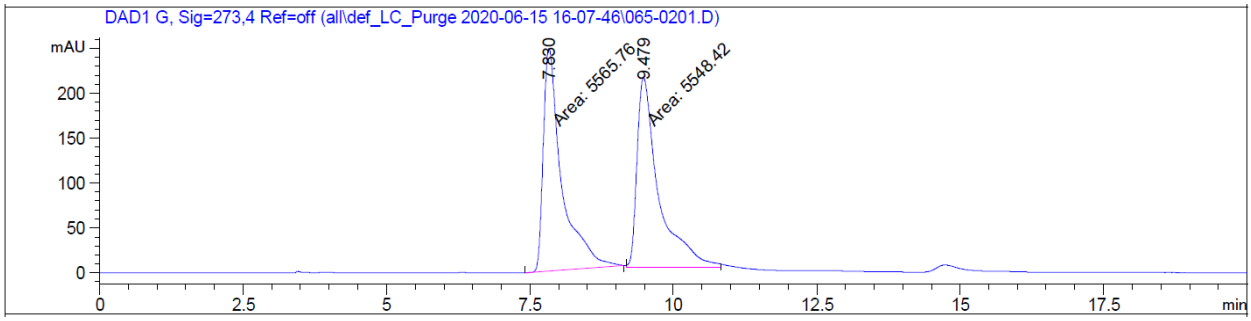


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.302	BB	0.2431	52.35242	2.70170	1.2383
2	12.487	BB	0.2924	4175.26270	202.59860	98.7617

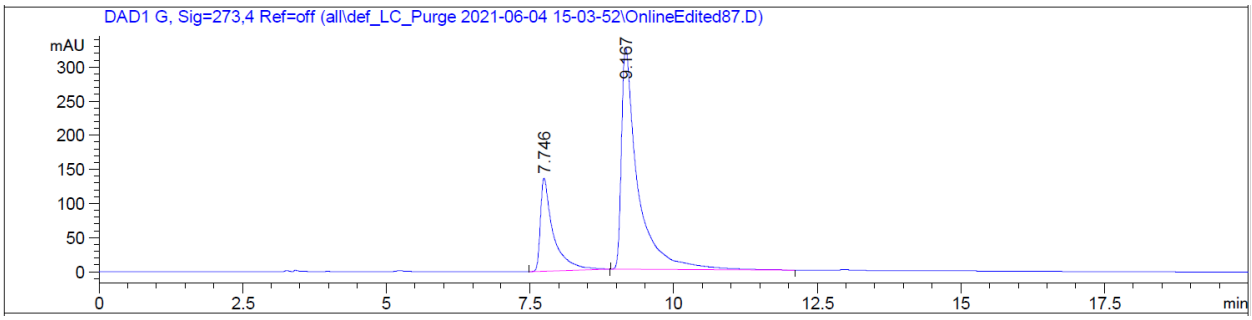


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

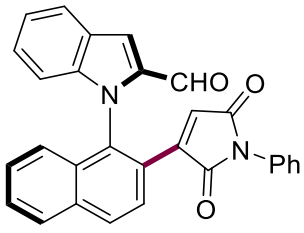
$[\alpha]_D^{20}$: +39.5 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.2 min, t_r (minor) = 7.7 min, 50% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	MM	0.3738	5565.76367	248.18161	50.0780
2	9.479	MM	0.4375	5548.42383	211.35017	49.9220



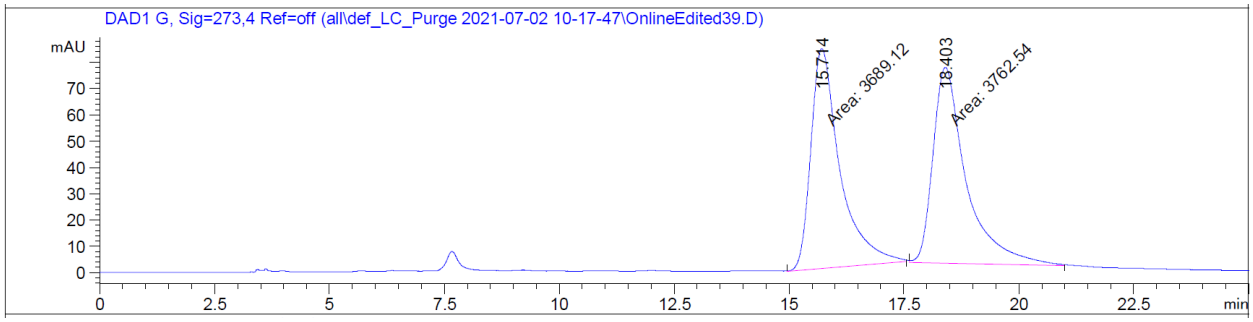
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.746	BB	0.2180	2125.90161	136.26164	24.9299
2	9.167	BB	0.2741	6401.63086	324.56186	75.0701



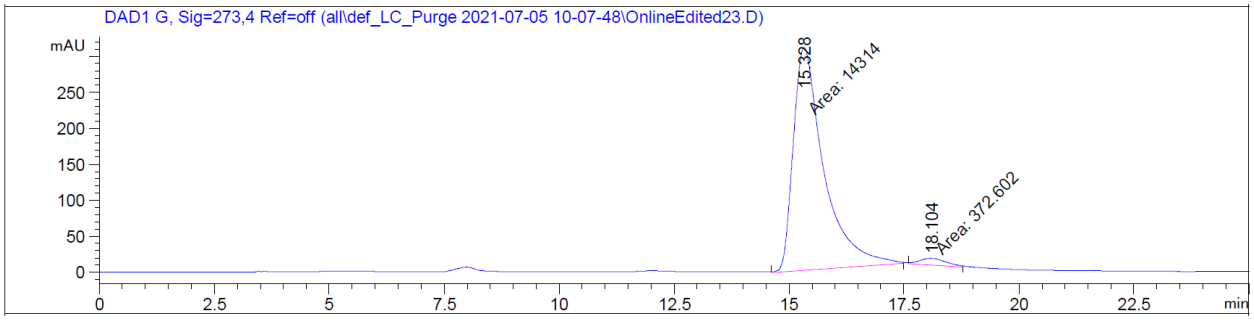
1-[2-(2,5-dioxo-1-phenyl-2,5-dihydro-1*H*-pyrrol-3-yl)naphthalen-1-yl]-1*H*-indole-2-carbaldehyde (15)

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and *N*-phenylmaleimide (**12c**) (103.8 mg, 0.60 mmol). Isolation by column

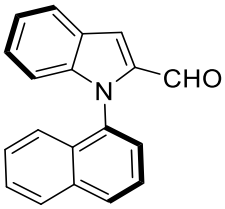
chromatography (*n*-hexane/EtOAc = 5:1) yielded **15** (27.0 mg, 30%) as a yellow solid and **1a** (32.0 mg, 59%) as yellow solid. M.P. of **15**: 84-87 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.95–7.87 (m, 1H), 7.66 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.50–7.42 (m, 2H), 7.42–7.35 (m, 2H), 7.33–7.22 (m, 4H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.73 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.1 (CH), 169.0 (C_q), 168.9 (C_q), 141.1 (C_q), 140.8 (C_q), 136.8 (C_q), 135.0 (C_q), 134.3 (C_q), 131.6 (C_q), 131.3 (C_q), 129.3 (CH), 129.1 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 126.6 (C_q), 126.5 (C_q), 126.1 (CH), 125. 6 (CH), 123.8 (CH), 123.2 (CH), 122.5 (CH), 117.5 (CH), 111.4 (CH). IR (ATR): 3061, 1713, 1673, 1502, 1390, 1134, 751 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 465 (100) $[M + Na]^+$, 443 (40) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{29}H_{18}N_2O_3 + H]^+$ 443.1390 found 443.1398. $[\alpha]_D^{20}$: +6.6 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 80:20, 1.0 mL/min, detection at 273 nm): t_r (major) = 15.3 min, t_r (minor) = 18.1 min, 95% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.714	MM	0.7339	3689.12231	83.78253	49.5074
2	18.403	MM	0.8401	3762.53955	74.64334	50.4926

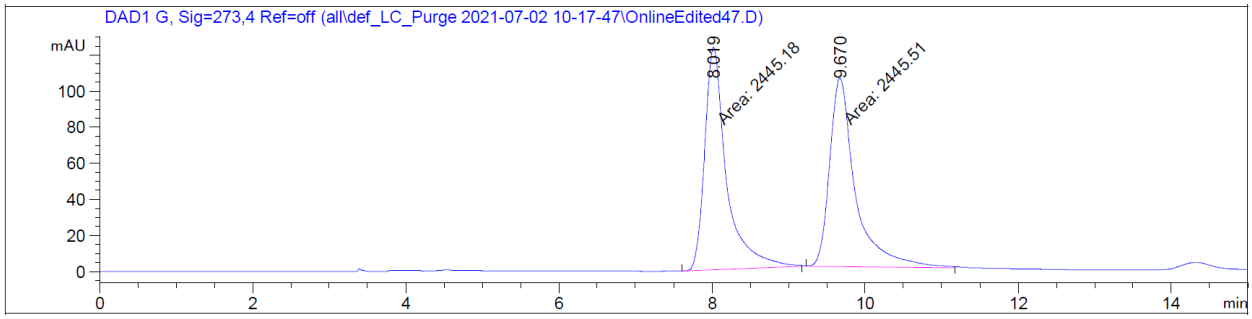


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.328	MM	0.7706	1.43140e4	309.57407	97.4630
2	18.104	MM	0.6613	372.60208	9.39006	2.5370

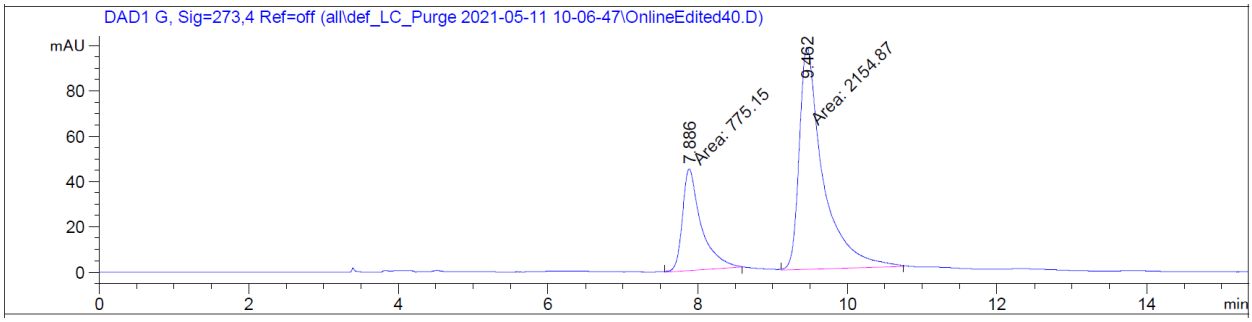


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

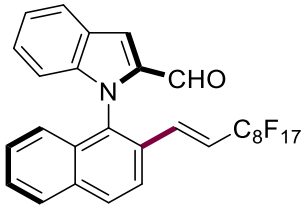
$[\alpha]_D^{20}$: +43.5 (c = 1.1, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.5 min, t_r (minor) = 7.9 min, 47% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.019	MM	0.3301	2445.17529	123.43890	49.9965
2	9.670	MM	0.3899	2445.51367	104.54658	50.0035

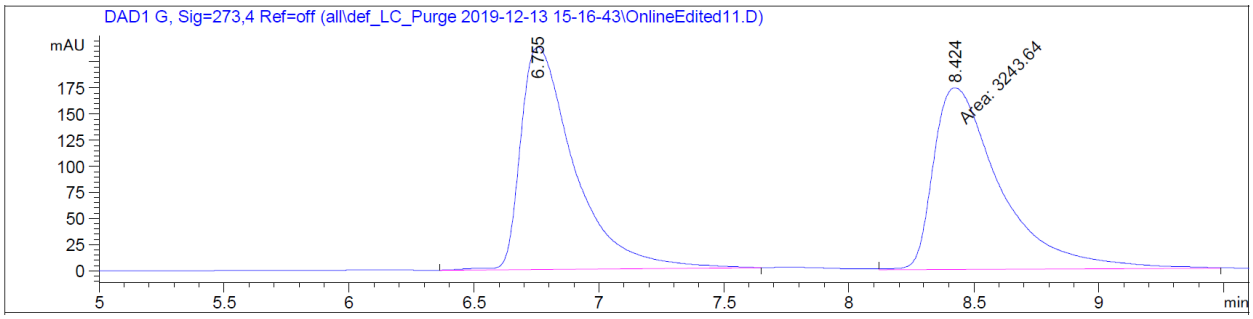


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.886	MM	0.2877	775.14954	44.90294	26.4554
2	9.462	MM	0.3666	2154.87378	97.96462	73.5446

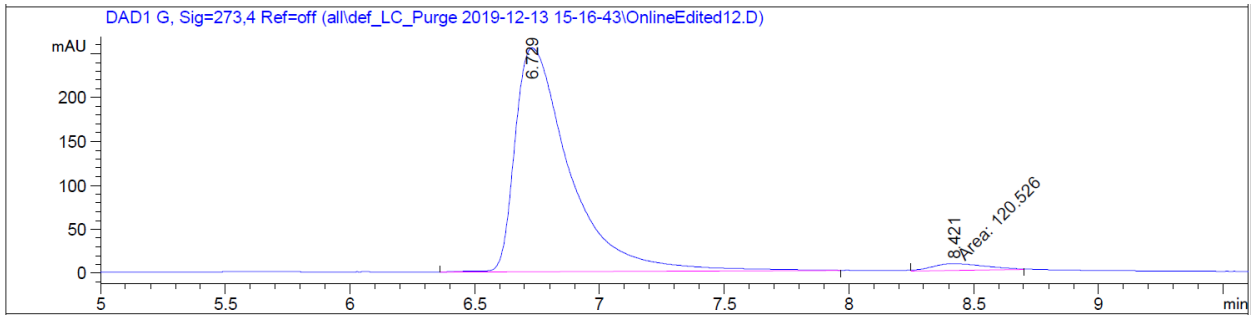


(*E*)-1-(2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodec-1-en-1-yl)naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (17)

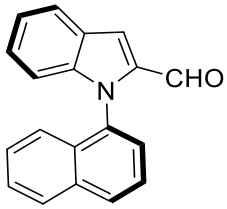
The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene (**16a**) (267.7 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/DCM = 1:1) yielded **17** (40.6 mg, 28%) as an off-white solid (M.p.: 64-65 °C) and **1a** (34.8 mg, 64%) as a yellow solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.93–7.87 (m, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 1.0 Hz, 1H), 7.54 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.36 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.32–7.24 (m, 2H), 6.95 (dd, J = 8.5, 1.0 Hz, 1H), 6.78–6.72 (m, 1H), 6.63 (dt, J = 16.2, 2.3 Hz, 1H), 6.17 (dt, J = 16.2, 11.9 Hz, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 180.8 (CH), 141.4 (C_q), 137.3 (C_q), 134.76 (C_q), 134.6 (t, $^{3}J_{C–F}$ = 9.7 Hz, CH), 133.7 (C_q), 131.5 (C_q), 129.9 (C_q), 129.8 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.8 (CH), 126.5 (C_q), 123.5 (CH), 123.3 (CH), 123.0 (CH), 122.2 (CH), 118.0 (m, C_q), 117.74 (t, $^{2}J_{C–F}$ = 23.1 Hz, CH), 116.8 (CH), 116.2 (m, C_q), 114.6 (m, C_q), 111.5 (CH), 112.7 (m, C_q), 110.7 (m, C_q). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = –80.8 (t, J = 9.9 Hz), –111.5 (m), –121.4 (m), –121.9 (m), –122.7 (m), –123.3 (m), –126.1 (m). IR (ATR): 2923, 1675, 1198, 1133, 1109, 738 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 738 (100) $[M + Na]^+$, 696 (40). HR-MS (ESI): *m*/*z* calcd. for $[C_{29}H_{14}{}^{19}F_{17}NO + H]^+$ 716.0877 found 716.0862. $[\alpha]_D^{20}$: +8.9 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 6.7 min, t_r (minor) = 8.4 min, 94% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.755	BB	0.2218	3169.64746	212.70924	49.4231
2	8.424	MM	0.3106	3243.63867	174.03014	50.5769

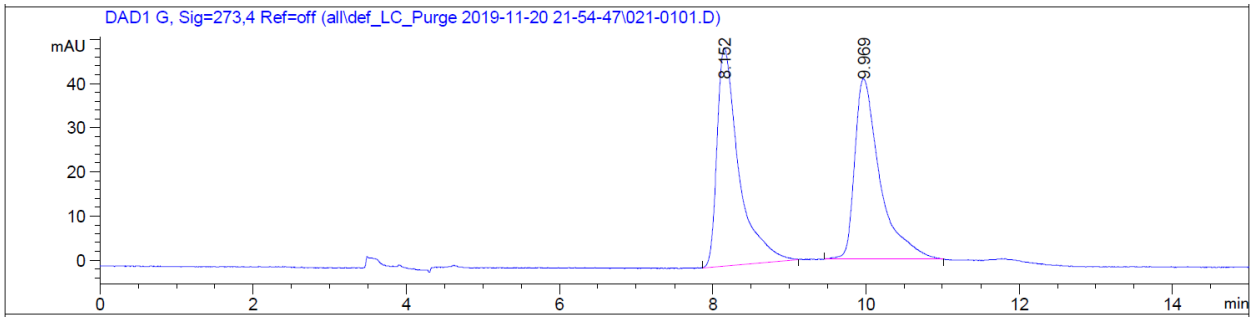


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.729	VV R	0.2265	3874.50195	254.68750	96.9831
2	8.421	MM	0.2502	120.52612	8.02763	3.0169

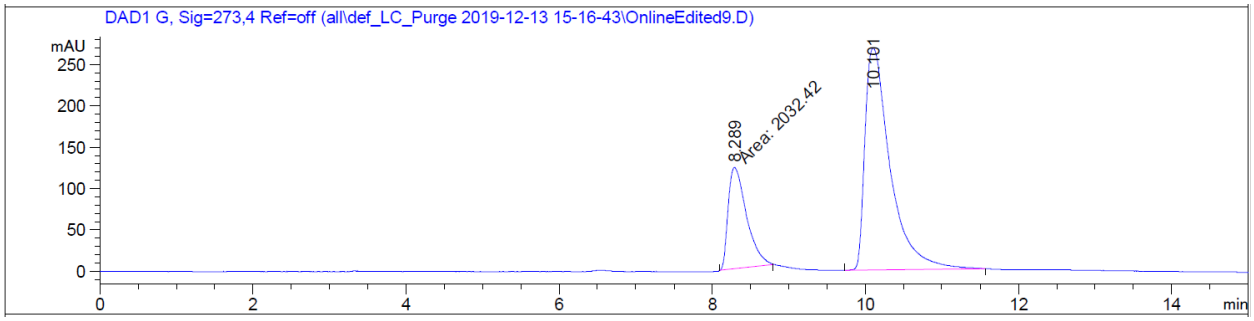


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

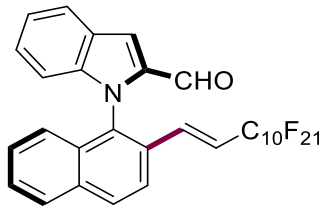
$[\alpha]_D^{20}$: +39.5 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 10.1 min, t_r (minor) = 8.3 min, 50% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.152	BB	0.2724	971.97015	49.42218	50.8362
2	9.969	VV R	0.3072	939.99512	40.89202	49.1638

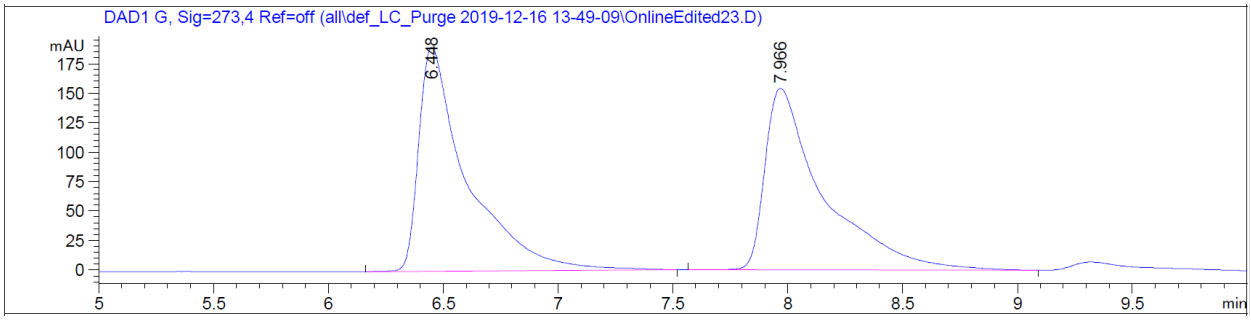


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.289	MM	0.2774	2032.42297	122.11781	24.8259
2	10.101	BV R	0.3369	6154.26611	268.02570	75.1741

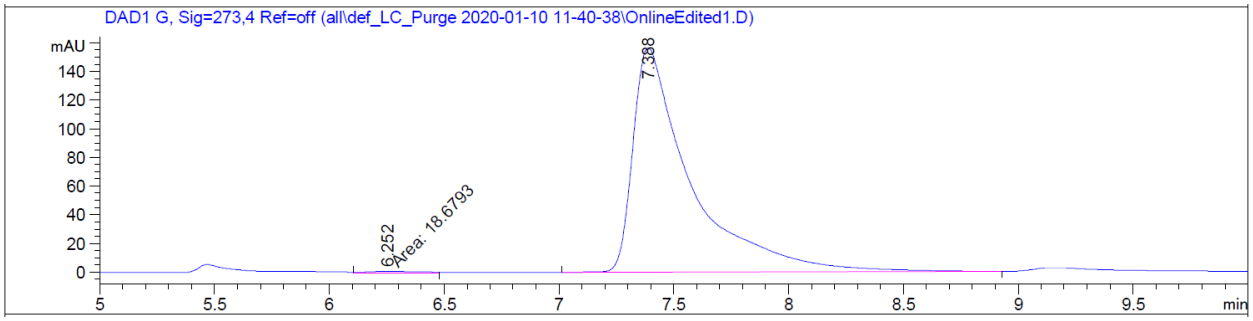


(*E*)-1-(2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,12,12,12-Nonadecafluorododec-1-en-1-yl)naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (18)

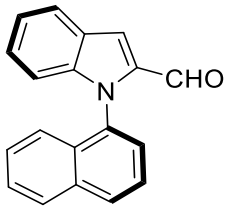
The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododec-1-ene (**16b**) (327.7 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/DCM = 1:1) yielded **18** (47.1 mg, 29%) as an off-white solid (M.p.: 91-92 °C) and **1a** (36.7 mg, 68%) as a yellow solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.92–7.87 (m, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 0.9 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.36 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.32–7.23 (m, 2H), 6.95 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.78–6.71 (m, 1H), 6.63 (dt, *J* = 16.2, 2.2 Hz, 1H), 6.17 (dt, *J* = 16.1, 11.8 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 180.9 (CH), 141.4 (C_q), 137.3 (C_q), 134.8 (C_q), 134.6 (t, $^{3}J_{C-F}$ = 9.8 Hz, CH), 133.7 (C_q), 131.5 (C_q), 129.9 (C_q), 129.8 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.8 (CH), 126.4 (C_q), 123.5 (CH), 123.3 (CH), 122.9 (CH), 122.2 (CH), 118.2 (m, C_q), 117.7 (t, $^{2}J_{C-F}$ = 23.2 Hz, CH), 116.8 (CH), 116.6 (m, C_q), 115.9 (m, C_q), 114.6 (m, C_q), 112.9 (m, C_q), 110.7 (m, C_q), 111.5 (CH), 108.5 (m, C_q). ^{19}F-NMR (565 MHz, $CDCl_3$) δ = –80.7 (t, *J* = 9.9 Hz), –111.5 (m), –121.4 (m), –121.8 (m), –122.7, –123.3 (m), –126.1 (m). IR (ATR): 1675, 1207, 1150, 735 cm^{-1}.MS (ESI) *m*/*z* (relative intensity): 838 (100) $[M + Na]^+$, 796 (30). HR-MS (ESI): *m*/*z* calcd. for $[C_{31}H_{14}{}^{19}F_{21}NO + H]^+$ 816.0813 found 816.0812. $[\alpha]_D^{20}$: +8.9 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 7.4 min, t_r (minor) = 6.3 min, 99% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.448	BB	0.2042	2788.03320	190.01219	50.4527
2	7.966	BV R	0.2492	2738.00488	154.19501	49.5473

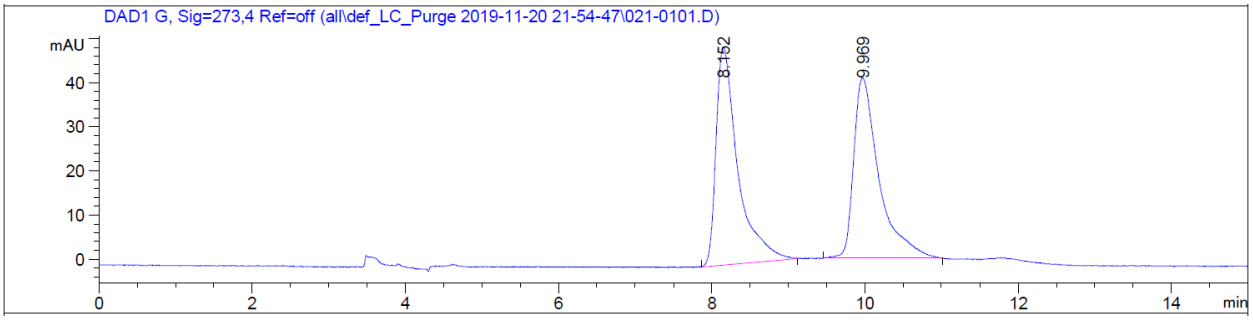


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.252	MM	0.2417	18.67928	1.28811	0.6781
2	7.388	BB	0.2413	2736.12964	156.25362	99.3219

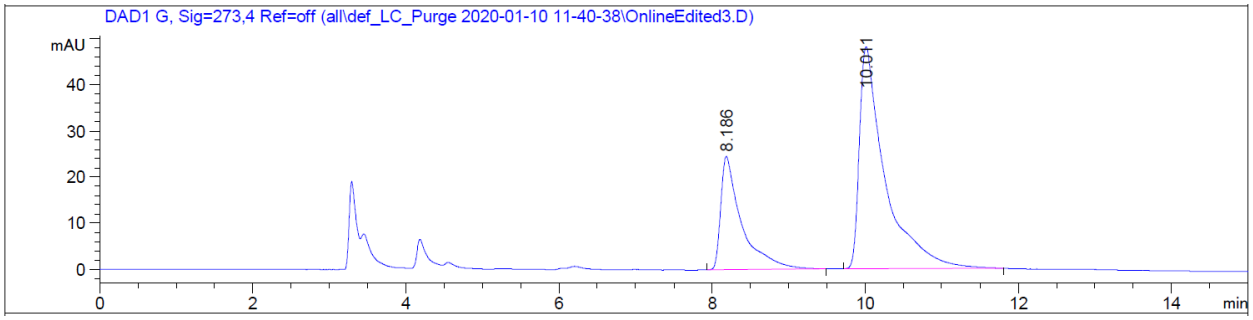


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

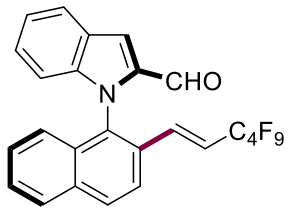
$[\alpha]_D^{20}$: +29.9 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 10.0 min, t_r (minor) = 8.2 min, 41% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.152	BB	0.2724	971.97015	49.42218	50.8362
2	9.969	VV R	0.3072	939.99512	40.89202	49.1638



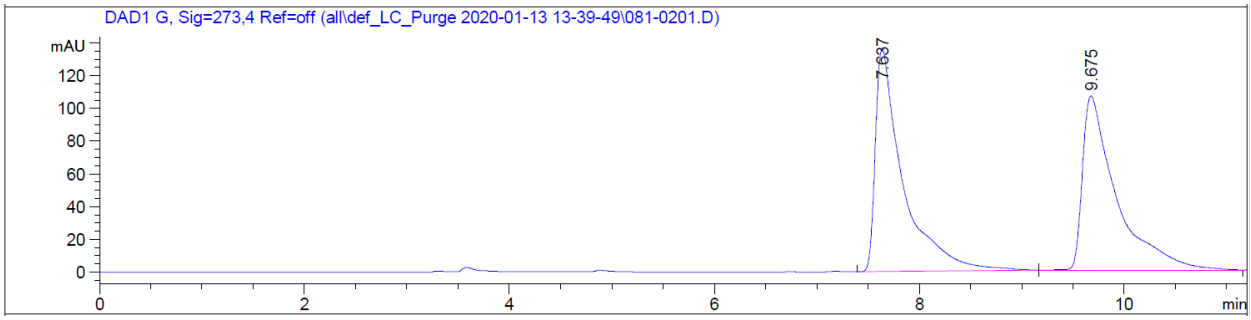
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.186	BB	0.2609	463.88345	24.50509	29.2857
2	10.011	BB	0.3201	1120.10925	48.02735	70.7143



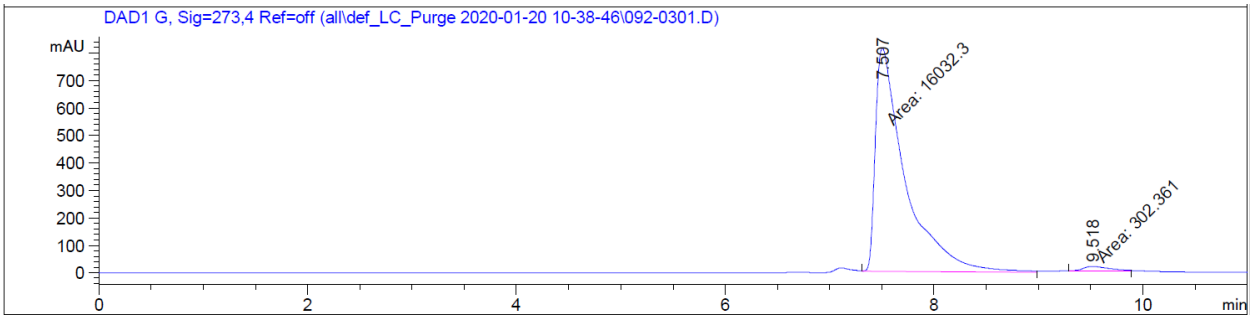
(*E*)-1-(2-(3,3,4,4,5,5,6,6,6-Nonafluorohex-1-en-1-yl)naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (19)

The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene (**16c**) (147.6 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/DCM = 1:1) yielded **19** (23.0 mg, 22%) as a yellow oil and **1a** (34.4 mg, 63%) as a yellow solid. ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 9.77 (s, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.91–7.89 (m, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 0.9 Hz, 1H), 7.54 (ddd, J = 8.1, 6.8, 1.1 Hz, 1H), 7.36 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.32–7.26 (m, 2H), 6.94 (dd, J = 8.4, 1.0 Hz, 1H), 6.77–6.72 (m, 1H), 6.63 (dt, J = 16.1, 2.4 Hz, 1H), 6.17 (dt, J = 16.2, 11.9 Hz, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ =

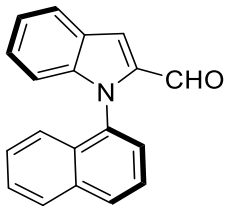
180.9 (CH), 141.4 (C_q), 137.3 (C_q), 134.8 (C_q), 134.7 (t, $^3J_{C–F}$ = 9.8 Hz, CH), 133.7 (C_q), 131.5 (C_q), 129.9 (C_q), 129.8 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.8(CH), 126.5 (C_q), 123.5 (CH), 123.3 (CH), 122.9 (CH), 122.2 (CH), 118.2 (m, C_q), 117.6 (t, $^2J_{C–F}$ = 23.1 Hz, CH), 116.8 (CH), 116.3 (m, C_q), 114.5 (m, C_q), 111.5 (CH). ^{19}F-NMR (565 MHz, $CDCl_3$) δ = –81.1 (t, J = 9.5 Hz), –111.9 (m), –124.2 (m), –125.7 (m). IR (ATR): 3065, 2804, 1673, 1229, 1130, 1107, 886, 813, 749, 739 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 538 (100) $[M + Na]^+$, 516 (20) [M + H]. HR-MS (ESI): *m*/*z* calcd. for $[C_{25}H_{14}{}^{19}F_9NO_3 + H]^+$ 516.1004 found 516.1004 . $[\alpha]_D^{20}$: +2.4 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 7.5 min, t_r (minor) = 9.5 min, 96% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.637	BB	0.2553	2546.29810	136.69742	50.9285
2	9.675	BB	0.3176	2453.45483	106.55094	49.0715

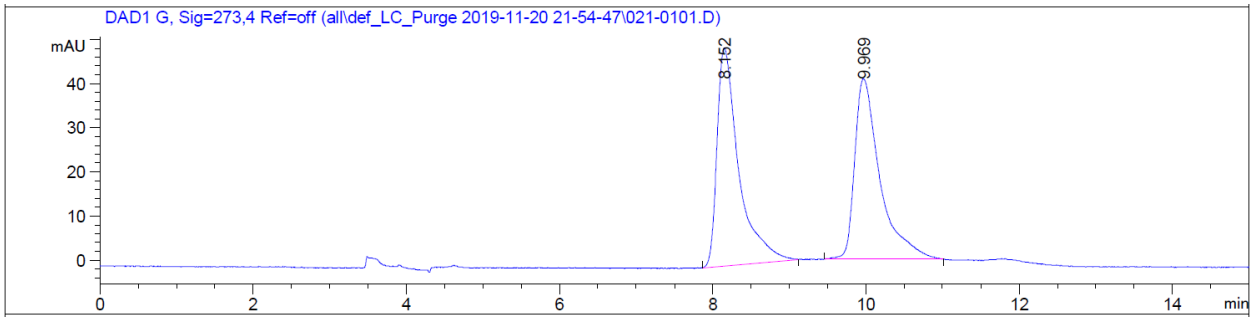


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.507	MM	0.3290	1.60323e4	812.19672	98.1490
2	9.518	MM	0.2925	302.36096	17.22758	1.8510

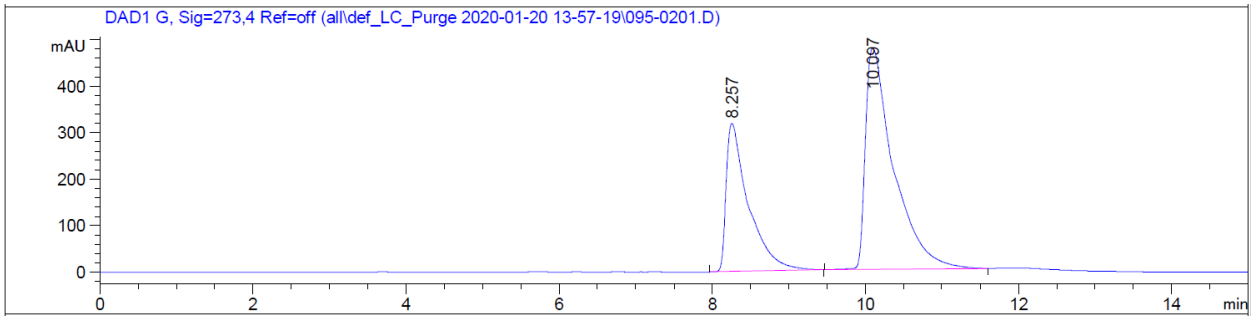


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

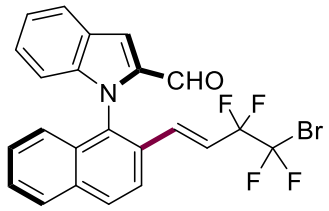
$[\alpha]_D^{20}$: +30.4 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 10.1 min, t_r (minor) = 8.2 min, 31% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.152	BB	0.2724	971.97015	49.42218	50.8362
2	9.969	VV R	0.3072	939.99512	40.89202	49.1638

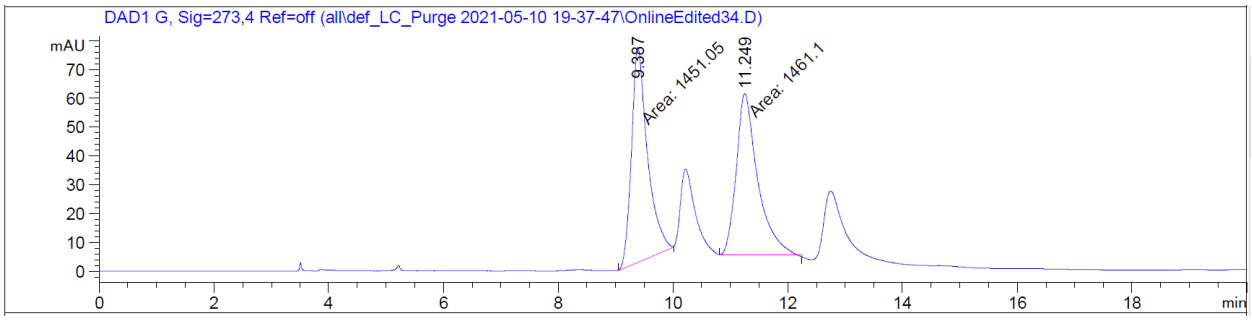


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.257	BB	0.2887	6402.04785	318.26682	34.5399
2	10.097	BB	0.3726	1.21332e4	475.58801	65.4601

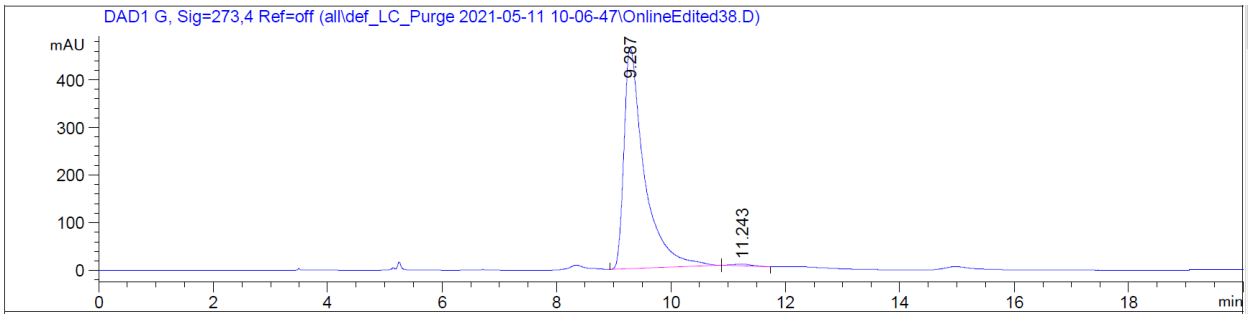


(*E*)-1-[2-(4-Bromo-3,3,4,4-tetrafluorobut-1-en-1-yl)naphthalen-1-yl]-1*H*-indole-2-carbaldehyde (20)

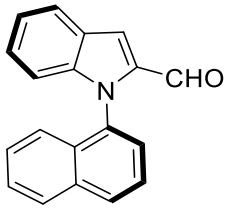
The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**xx**) (54.2 mg, 0.20 mmol) and 4-bromo-3,3,4,4-tetrafluorobut-1-ene (**16d**) (124.2 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 20:1) yielded **20** (25.5 mg, 27%) as a yellow oil and **1a** (33.0 mg, 62%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.95–7.89 (m, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.64 (s, 1H), 7.59–7.52 (m, 1H), 7.42–7.35 (m, 1H), 7.33–7.26 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.82–6.74 (m, 1H), 6.66 (dd, *J* = 16.1, 2.5 Hz, 1H), 6.21 (ddd, *J* = 16.1, 11.5, 2.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 180.9 (CH), 141.5 (C_q), 137.4 (C_q), 134.8 (t, $^{3}J_{C–F}$ = 9.2 Hz, CH), 134.7 (C_q), 133.5 (C_q), 131.5 (C_q), 130.1 (C_q), 129.8 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 126.5 (C_q), 123.6 (CH), 123.3 (CH), 123.0 (CH), 122.2 (CH), 117.9 (t, $^{2}J_{C–F}$ = 25.2 Hz, CH), 117.4 (t, $^{2}J_{C–F}$ = 45.5 Hz, C_q), 116.7 (CH), 114.0 (t, $^{2}J_{C–F}$ = 28.0 Hz, C_q), 111.7 (CH). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = –66.0 (m), –109.7 (m). IR (ATR): 3062, 1672, 1614, 1523, 1408, 1126, 752 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 498 (70) $[M + Na]^+$, 476 (100) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{23}H_{14}{}^{79}Br^{19}F_4N_2O_3 + H]^+$ 476.0268 found 476.0262. $[\alpha]_D^{20}$: +17.4 (c = 0.90, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.3 min, t_r (minor) = 11.2 min, 98% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.387	MM	0.3239	1451.05396	74.65611	49.8275
2	11.249	MM	0.4351	1461.09875	55.96720	50.1725

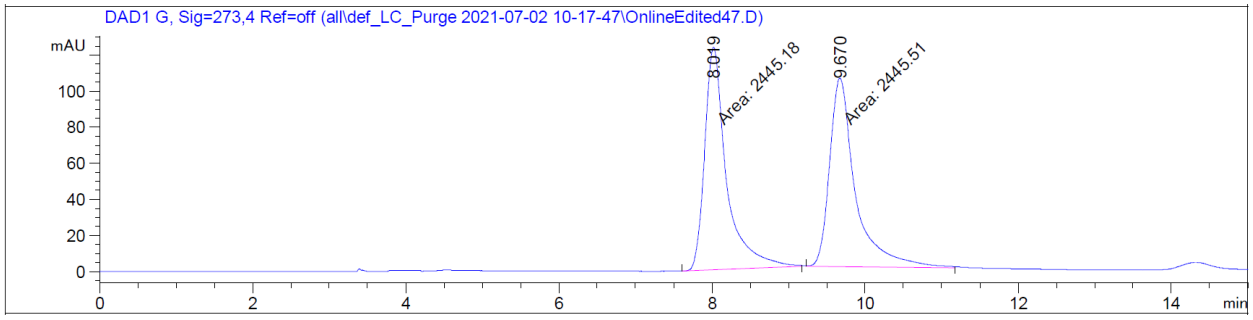


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.287	BB	0.3509	1.14362e4	464.99942	99.2005
2	11.243	BB	0.2812	92.16966	4.11760	0.7995

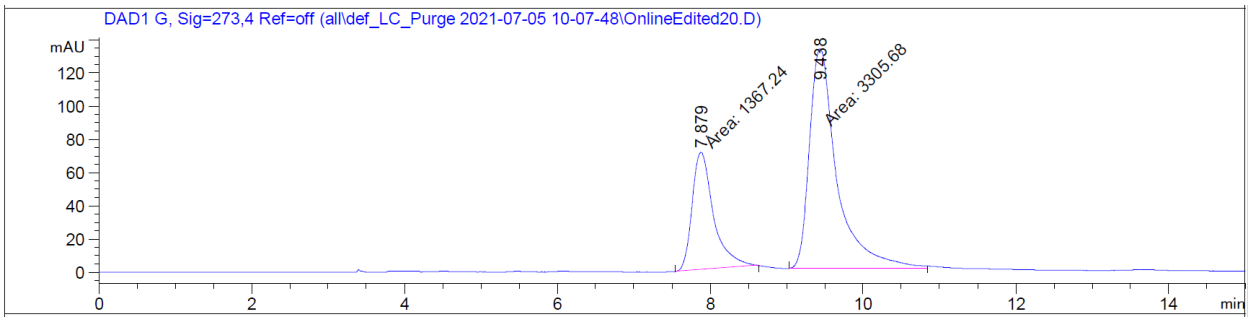


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

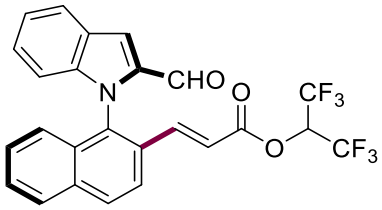
$[\alpha]_D^{20}$: +42.8 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.4 min, t_r (minor) = 7.9 min, 41% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.019	MM	0.3301	2445.17529	123.43890	49.9965
2	9.670	MM	0.3899	2445.51367	104.54658	50.0035



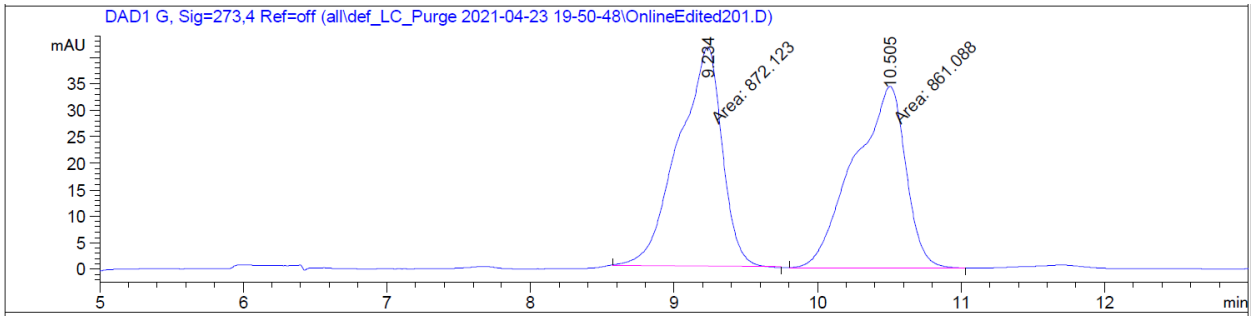
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.879	MM	0.3234	1367.24084	70.46983	29.2588
2	9.438	MM	0.4168	3305.68262	132.16966	70.7412



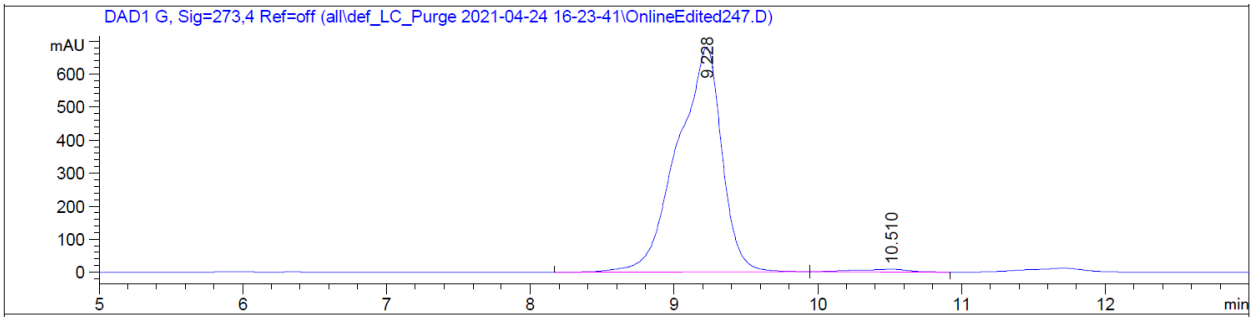
(*E*)-1,1,1,3,3,3-Hexafluoropropan-2-yl-3-(1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)acrylate (21)

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and 4-bromo-3,3,4,4-tetrafluorobut-1-ene (**16e**) (124.2 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 20:1) yielded **21** (26.5 mg, 27%) as a off-white solid and **1a** (30.0 mg, 55%) as yellow solid. M.p. of **21**: 123-126 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.79 (s, 1H), 8.06 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.93–7.87 (m, 2H), 7.63 (d, J = 0.9 Hz, 1H), 7.56 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.36 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.34–7.26 (m, 3H), 6.95 (dd, J = 8.5, 1.0 Hz, 1H), 6.78–6.70 (m, 1H), 6.57 (d, J = 16.0 Hz, 1H), 5.77–5.64 (m, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 181.0 (CH), 162.9 (C_q), 143.4 (CH),

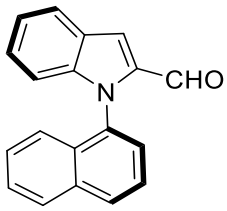
141.9 (C_q), 137.7 (C_q), 135.44 (C_q), 135.40 (C_q), 131.5 (C_q), 129.8 (CH), 129.7 (C_q), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 126.5 (C_q), 123.6 (CH), 123.6 (CH), 122.5 (CH), 122.3 (CH), 121.8 (m, C_q), 119.0 (m, C_q) 117.3 (CH), 116.94 (CH), 111.51 (CH), 66.5 (p, $^2J_{C–F}$ = 34.7 Hz, CH). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = –73.2 (m). IR (ATR): 2924, 1675, 1228, 1198, 1124, 1105, 1085, 815, 750, 736, 688 cm^{-1}.MS (ESI) *m*/*z* (relative intensity): 514 (60) $[M + Na]^+$, 492 (100) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{25}H_{15}{}^{19}F_6NO_3 + H]^+$ 492.1029 found 492.1029. $[\alpha]_D^{20}$: +88.1 (c = 0.7, $CHCl_3$). HPLC separation (Chiralpak® IE-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.2 min, t_r (minor) = 10.5 min, 97% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.234	MM	0.3517	872.12292	41.33110	50.3183
2	10.505	MM	0.4189	861.08771	34.26194	49.6817

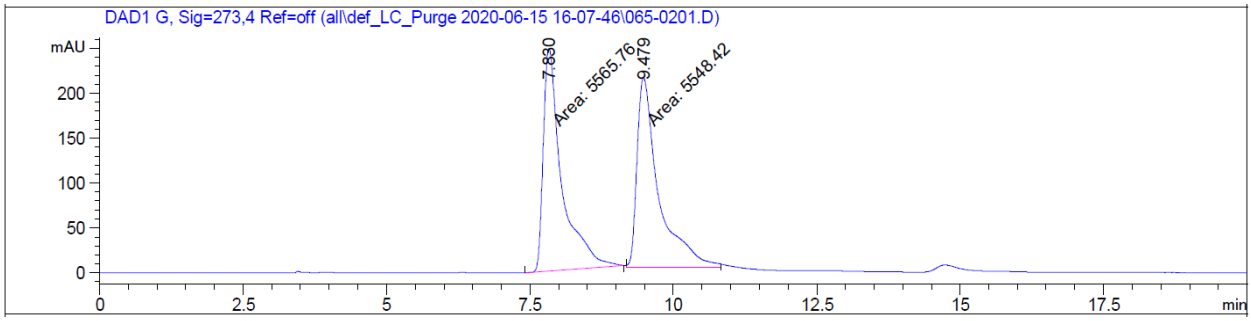


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.228	BB	0.2937	1.45528e4	679.94751	98.6981
2	10.510	BB	0.3151	191.96710	8.11260	1.3019

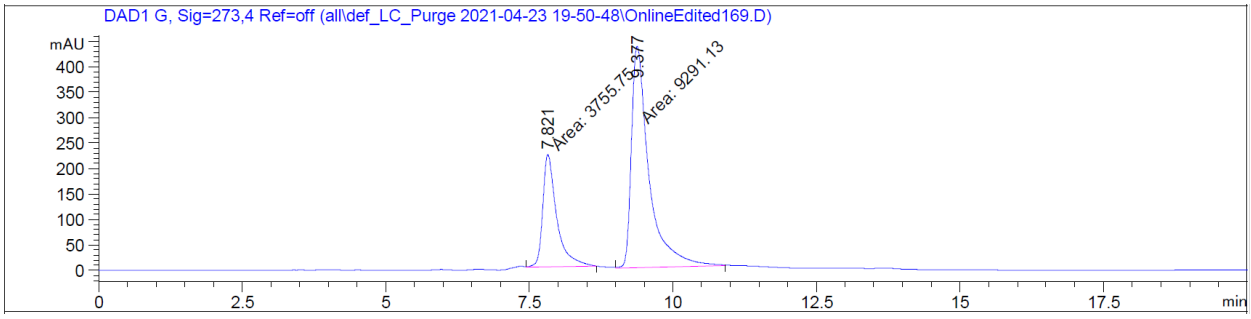


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

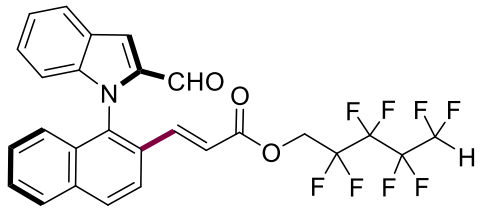
$[\alpha]_D^{20}$: +40.1 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.4 min, t_r (minor) = 7.8 min, 42% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	MM	0.3738	5565.76367	248.18161	50.0780
2	9.479	MM	0.4375	5548.42383	211.35017	49.9220

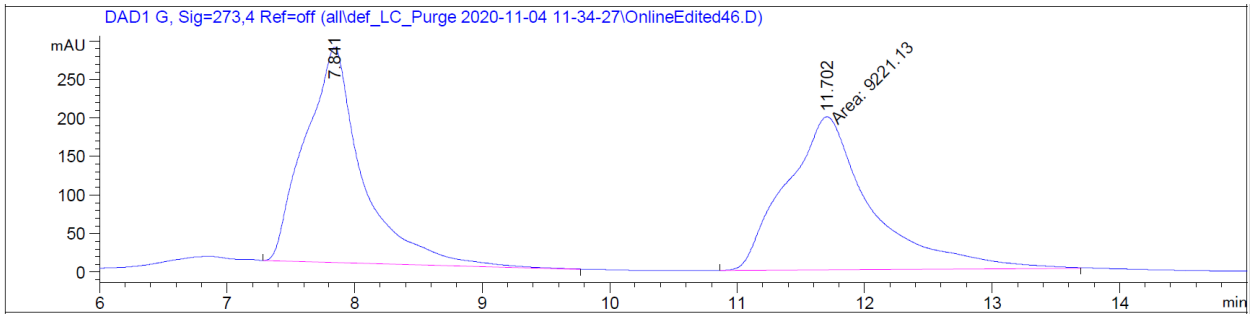


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.821	MM	0.2831	3755.75293	221.09750	28.7866
2	9.377	MM	0.3558	9291.13379	435.27673	71.2134

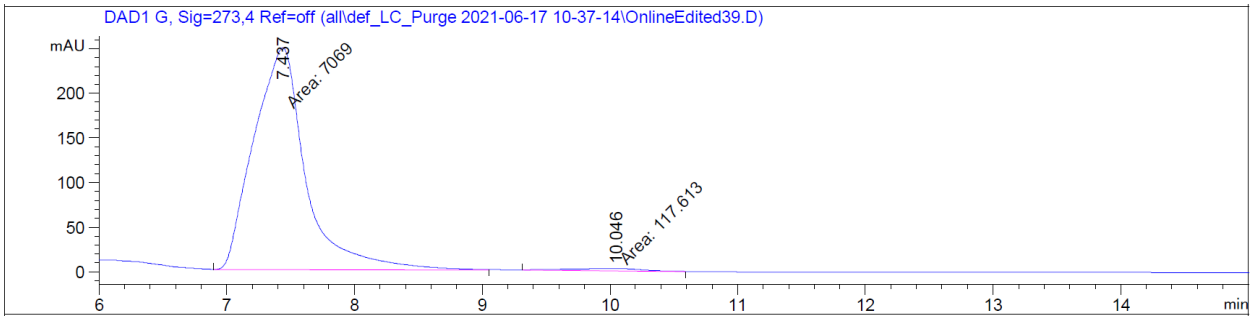


(*E*)-2,2,3,3,4,4,5,5-Octafluoropentyl-3-[1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl]acrylate (22):

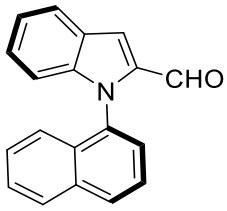
The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (**16f**) (171.6 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **22** (33.0 mg, 30%) as a yellow oil and **1a** (27.0 mg, 49%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 8.04 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.92–7.86 (m, 2H), 7.62 (s, 1H), 7.54 (ddd, J = 8.3, 6.8, 1.2 Hz, 1H), 7.35 (ddd, J = 8.3, 6.8, 1.2 Hz, 1H), 7.30–7.25 (m, 2H), 7.23 (d, J = 15.9 Hz, 1H), 6.92 (d, J = 8.5 Hz, 1H), 6.78–6.70 (m, 1H), 6.51 (d, J = 15.9 Hz, 1H), 6.17–5.82 (m, 1H), 4.63–4.47 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.0 (CH), 164.5 (C_q), 141.8 (C_q), 141.2 (CH), 137.6 (C_q), 135.2 (C_q), 134.8 (C_q), 131.6 (C_q), 130.2 (C_q), 129.8 (CH), 128.3 (CH), 128.1 (CH), 128.1 (CH), 127.9 (CH), 126.5 (C_q), 123.6 (CH), 123.5 (CH), 122.7 (CH), 122.2 (CH), 118.8 (CH), 117.0 (CH), 114.5 (t, $^{2}J_{C–F}$ = 32.4 Hz, C_q), 111.6 (CH), 110.3 (m, C_q), 107.9 (m, C_q), 107.6 (m, CH), 59.6 (t, $^{2}J_{C–F}$ = 27.1 Hz, CH_2). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = –119.5 (m), –125.3 (m), –130.0 (m), –137.1 (m). IR (ATR): 2922, 1733, 1673, 1632, 1410, 1230, 1169, 753 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 578 (100) $[M + Na]^+$, 556 (60) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{27}H_{17}F_8NO_3 + H]^+$ 556.1153 found 556.1157. $[\alpha]_D^{20}$: +53.1 (c = 0.80, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.3 min, t_r (minor) = 11.2 min, 98% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.841	BB	0.4115	8730.79297	279.41113	48.6343
2	11.702	MM	0.7732	9221.12500	198.75757	51.3657

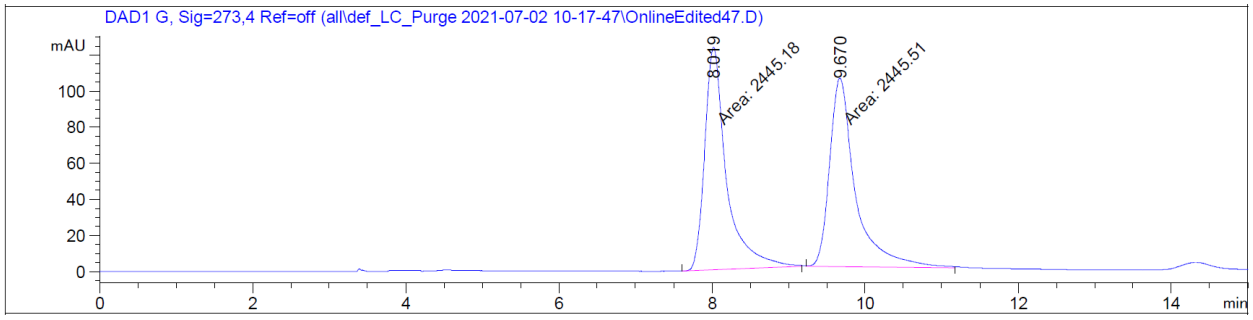


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.437	MM	0.4734	7068.99658	248.85547	98.3634
2	10.046	MM	0.6403	117.61257	3.06133	1.6366

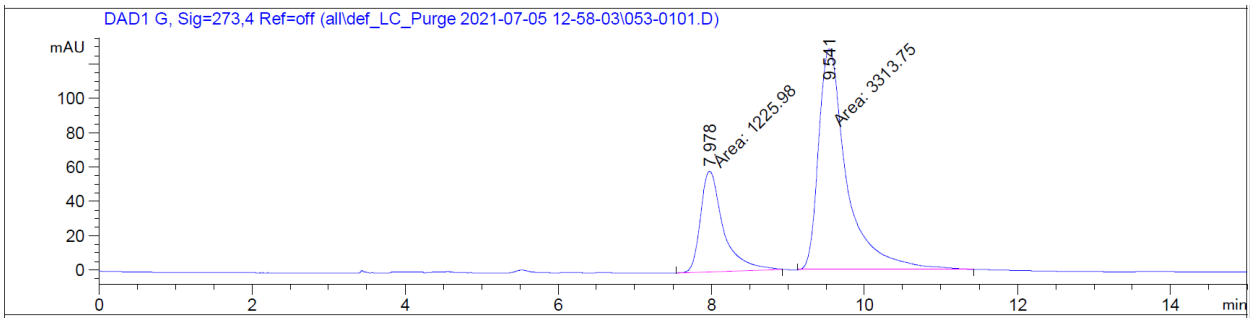


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

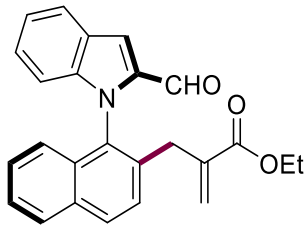
$[\alpha]_D^{20}$: +45.5 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.5 min, t_r (minor) = 8.0 min, 46% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.019	MM	0.3301	2445.17529	123.43890	49.9965
2	9.670	MM	0.3899	2445.51367	104.54658	50.0035



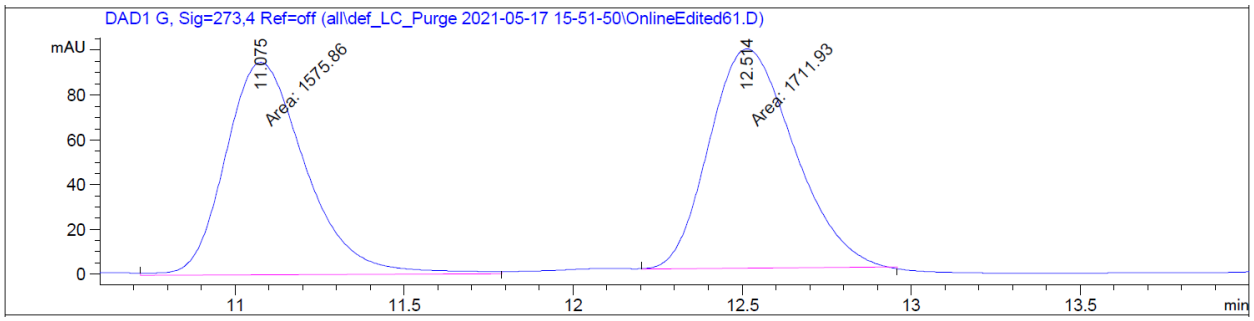
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.978	MM	0.3479	1225.97900	58.73999	27.0056
2	9.541	MM	0.4289	3313.74927	128.77022	72.9944



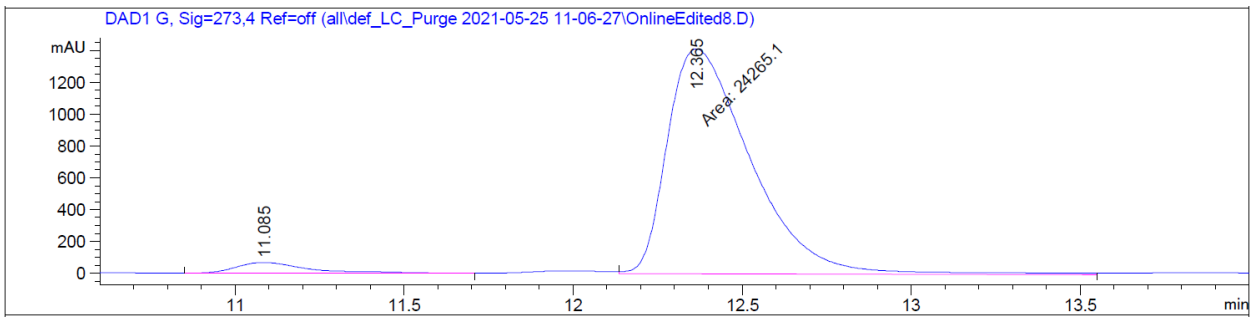
Ethyl 2-((1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)methyl)acrylate (24)

The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and ethyl methacrylate (**23a**) (68.5 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **24** (27.0 mg, 35%) as a yellow oil and **1a** (22.6 mg, 42%) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.66 (s, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.57 – 7.53 (m, 2H), 7.46 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.33 – 7.20 (m, 3H), 6.82 (dq, J = 8.5, 0.9 Hz, 1H), 6.80 – 6.76 (m, 1H), 6.08 (d, J = 1.1 Hz, 1H), 5.17 (q, J = 1.4 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H),

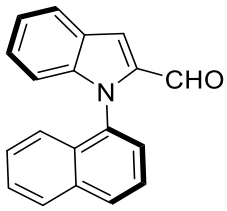
3.44 (ABq, J = 16.0 Hz, $\Delta\nu$ = 29.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 181.4 (CH), 166.4 (C_q), 140.8 (C_q), 138.1 (C_q), 137.0 (C_q), 135.7 (C_q), 133.1 (C_q), 131.9 (C_q), 131.6 (C_q), 129.3 (CH), 128.1 (CH), 127.7 (CH), 127.4 (CH), 127.19 (CH), 127.15 (CH_2), 126.4 (C_q), 126.2 (CH), 123.3 (CH), 122.3 (CH), 121.8 (CH), 114.6 (CH), 111.8 (CH), 60.7 (CH_2), 33.9 (CH_2), 14.1 (CH_3). IR (ATR): 2924, 1712, 1674, 1130, 815, 752, 738 cm^{-1} MS (ESI) *m*/*z* (relative intensity): 789 (60), 406 (100) $[M + Na]^+$, 384 (50) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{25}H_{21}NO_3 + H]^+$ 384.1594 found 384.1590. $[\alpha]_D^{20}$: –55.3 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® ID-3, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min, detection at 273 nm): t_r (major) = 12.4 min, t_r (minor) = 11.1 min, 92% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.075	MM	0.2766	1575.85974	94.94816	47.9306
2	12.514	MM	0.2914	1711.93213	97.92180	52.0694

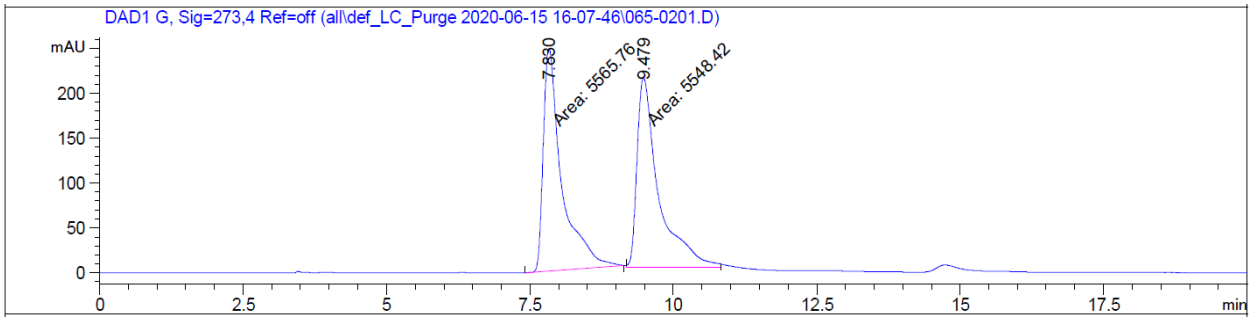


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.085	BB	0.2197	996.79712	67.32554	3.9459
2	12.365	MM	0.2865	2.42651e4	1411.79858	96.0541

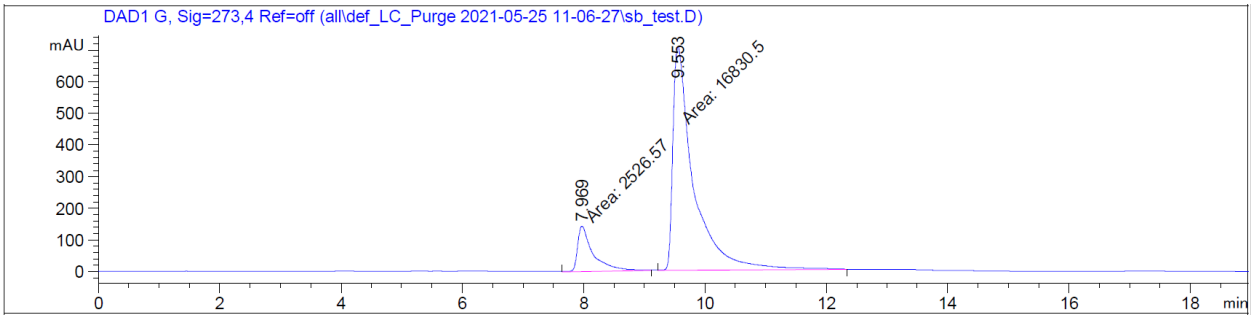


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

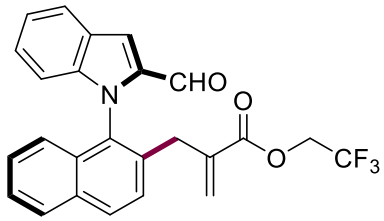
$[\alpha]_D^{20}$: +75.9 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.6 min, t_r (minor) = 8.0 min, 74% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	MM	0.3738	5565.76367	248.18161	50.0780
2	9.479	MM	0.4375	5548.42383	211.35017	49.9220

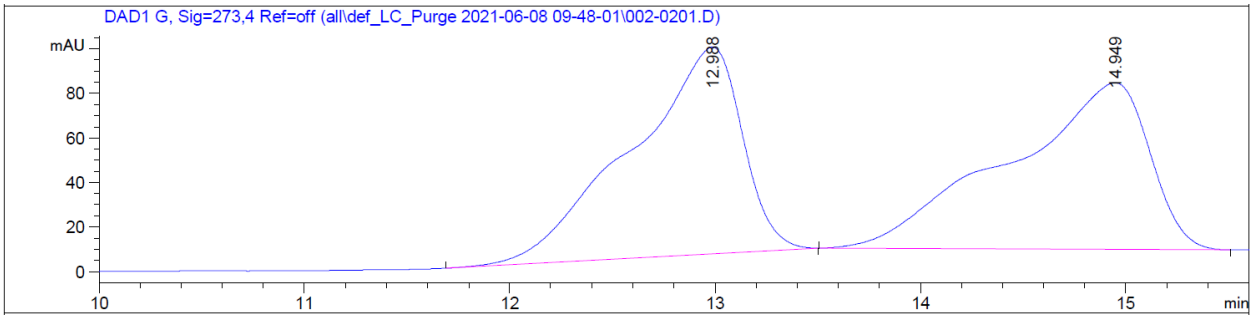


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.969	MM	0.2927	2526.56714	143.84387	13.0524
2	9.553	MM	0.3970	1.68305e4	706.54462	86.9476

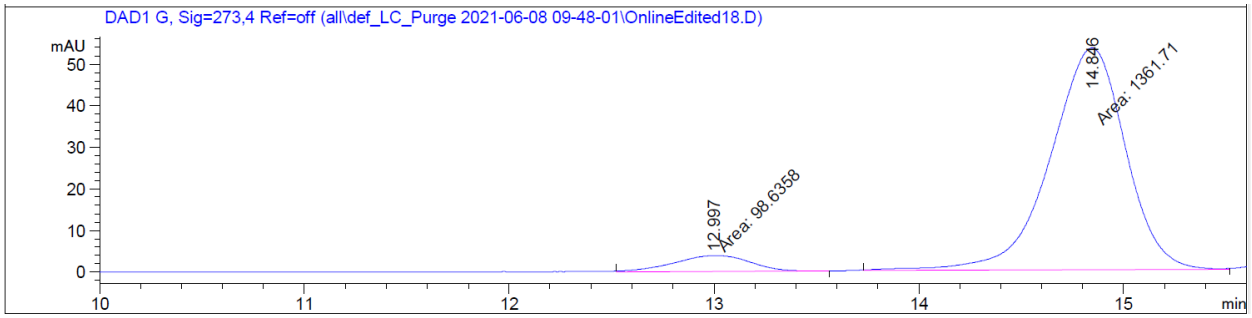


2,2,2-trifluoroethyl 2-((1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)methyl)acrylate (25)

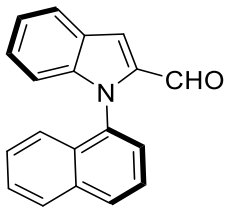
The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and 2,2,2-trifluoroethyl methacrylate (**23b**) (100.9 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **25** (33.4 mg, 38%) as a yellow oil and **1a** (28.6 mg, 53%) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.68 (s, 1H), 7.99 (d, J = 9.4 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.90–7.83 (m, 1H), 7.55 (d, J = 0.9 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.47 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.35–7.20 (m, 3H), 6.81 (dd, J = 8.5, 1.0 Hz, 1H), 6.80–6.73 (m, 1H), 6.14 (d, J = 0.8 Hz, 1H), 5.28 (q, J = 1.3 Hz, 1H), 4.47–4.29 (m, 2H), 3.47 (ABq, J = 16.0 Hz, $\Delta\nu$ = 30.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 181.4 (CH), 164.6 (C_q), 140.8 (C_q), 137.0 (C_q), 136.4 (C_q), 134.8 (C_q), 133.3 (C_q), 132.0 (C_q), 131.9 (C_q), 129.4 (CH), 129.4 (CH_2) 128.1 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.4 (C_q), 126.3 (CH), 123.4 (CH), 122.3 (CH), 121.9 (CH), 121.5 (C_q), 115.3 (CH), 111.8 (CH), 60.5 (q, $^{2}J_{C–F}$ = 36.7 Hz, CH_2), 34.0 (CH_2). ^{19}F-NMR (377 MHz, $CDCl_3$) δ = -73.69 (t, J = 8.4 Hz). IR (ATR): 3060, 1735, 1677, 1279, 1169, 1129 cm^{-1} MS (ESI) *m/z* (relative intensity): 460 (100) $[M + Na]^+$, 438 (80) $[M + H]^+$. HR-MS (ESI): *m/z* calcd. for $[C_{25}H_{18}NO_3{}^{19}F_3 + H]^+$ 438.1312 found 438.1304. $[\alpha]_D^{20}$: –49.6 (c = 1.1, $CHCl_3$). HPLC separation (Chiralpak® ID-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 14.8 min, t_r (minor) = 13.0 min, 86% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.988	BB	0.5177	3489.67505	92.80389	49.5527
2	14.949	BB	0.6451	3552.67627	74.80334	50.4473

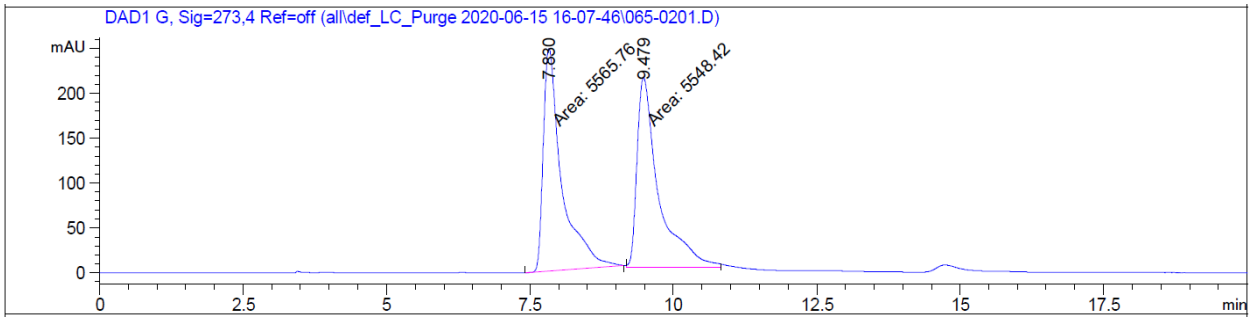


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.997	MM	0.4315	98.63578	3.80950	6.7543
2	14.846	MM	0.4252	1361.70923	53.37650	93.2457

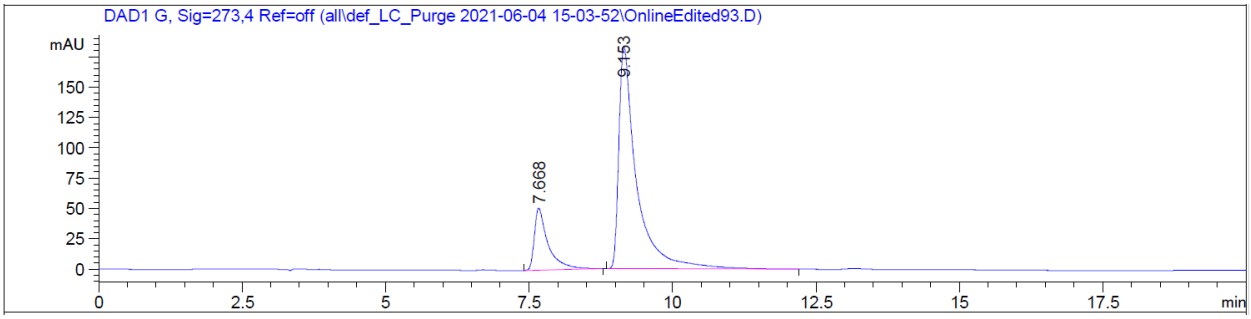


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

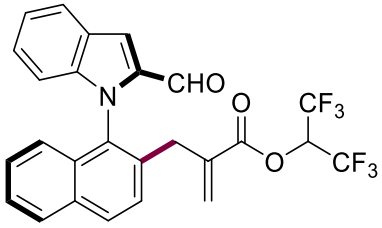
$[\alpha]_D^{20}$: +61.8 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.2 min, t_r (minor) = 7.7 min, 65% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	MM	0.3738	5565.76367	248.18161	50.0780
2	9.479	MM	0.4375	5548.42383	211.35017	49.9220

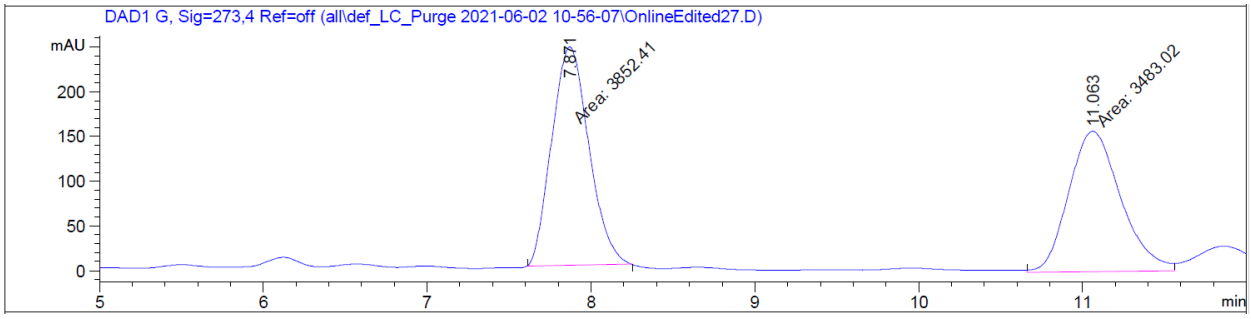


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.668	BB	0.2361	851.41022	51.17560	17.7517
2	9.153	BB	0.3028	3944.80933	183.49541	82.2483

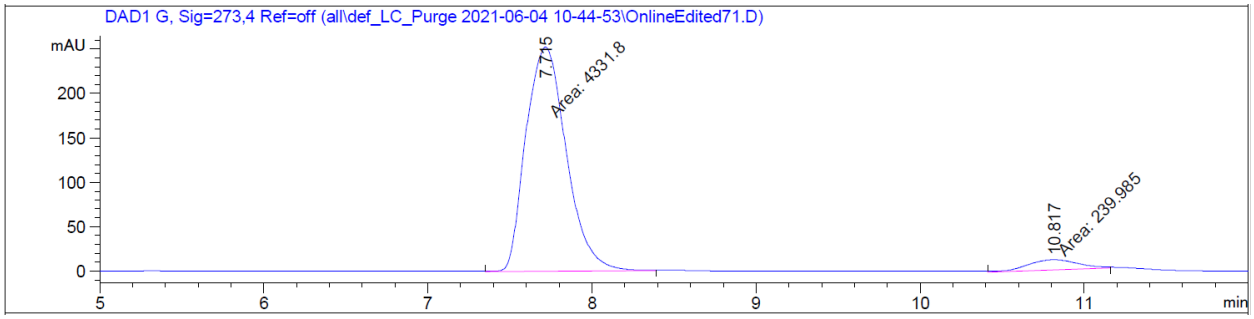


1,1,1,3,3,3-hexafluoropropan-2-yl 2-((1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)methyl)acrylate (26):

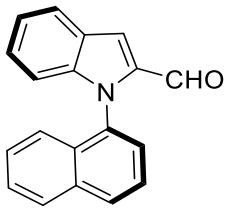
The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (**23c**) (68.5 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **26** (43.1 mg, 43%) as a yellow oil and **1a** (27.0 mg, 50%) as a yellow solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.70 (s, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.87 (ddd, J = 7.8, 1.4, 0.8 Hz, 1H), 7.56 (d, J = 1.0 Hz, 1H), 7.51 (d, J = 8.6 Hz, 1H), 7.48 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.34–7.22 (m, 3H), 6.81 (dq, J = 8.5, 0.9 Hz, 1H), 6.75 (dq, J = 8.3, 1.0 Hz, 1H), 6.23 (d, J = 0.6 Hz, 1H), 5.70 (p, J = 6.1 Hz, 1H), 5.41 (td, J = 1.5, 0.5 Hz, 1H), 3.49 (ABq, J = 16.2 Hz, $\Delta\nu$ = 34.3 Hz, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 181.3 (CH), 162.8 (C_q), 140.8 (C_q), 136.9 (C_q), 135.2 (C_q), 134.3 (C_q), 134.2 (C_q), 133.4 (C_q), 132.2 (C_q), 131.8 (C_q), 131.4 (CH_2), 129.5 (CH), 128.1 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.4 (CH), 123.4 (CH), 122.3 (CH), 121.9 (CH), 121.3 (m, C_q), 119.4 (m, C_q), 115.6 (CH), 111.7 (CH), 66.7 (p, $^{2}J_{C–F}$ = 34.8 Hz, CH), 33.91 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = –73.2 (m). IR (ATR): 2963, 1675, 1284, 1225, 1197, 1106, 752, 738, 690 cm^{-1} MS (ESI) *m*/*z* (relative intensity): 1033 (80), 528 (100) $[M + Na]^+$, 506 (80) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{26}H_{17}NO_3{}^{19}F_6 + H]^+$ 506.1185 found 506.1182. $[\alpha]_D^{20}$: –48.1 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IC-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 7.7 min, t_r (minor) = 10.8 min, 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.871	MM	0.2628	3852.40942	244.34843	52.5179
2	11.063	MM	0.3695	3483.01880	157.09473	47.4821

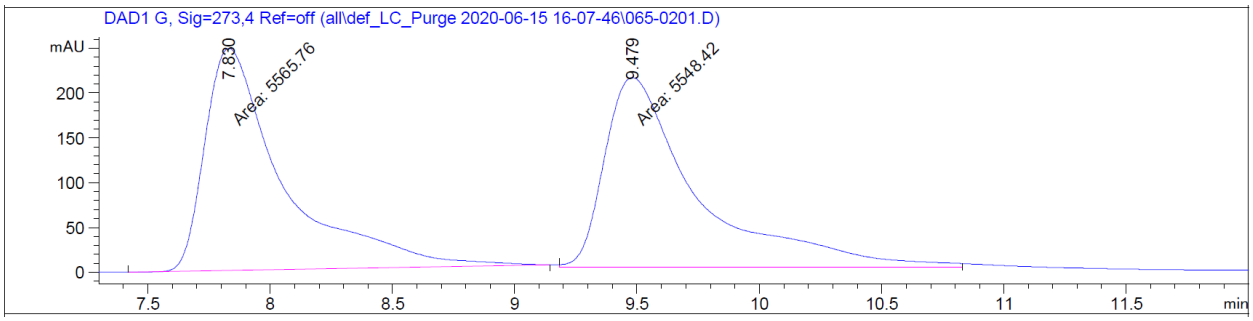


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.715	MM	0.2858	4331.80127	252.64749	94.7507
2	10.817	MM	0.3532	239.98474	11.32357	5.2493

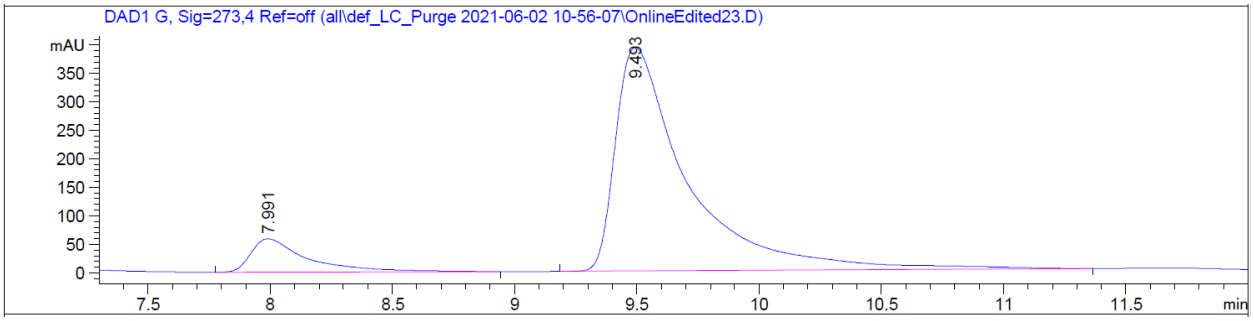


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

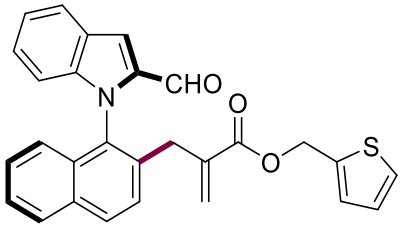
$[\alpha]_D^{20}$: +78.1 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.4 min, t_r (minor) = 8.0 min, 79% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	MM	0.3738	5565.76367	248.18161	50.0780
2	9.479	MM	0.4375	5548.42383	211.35017	49.9220



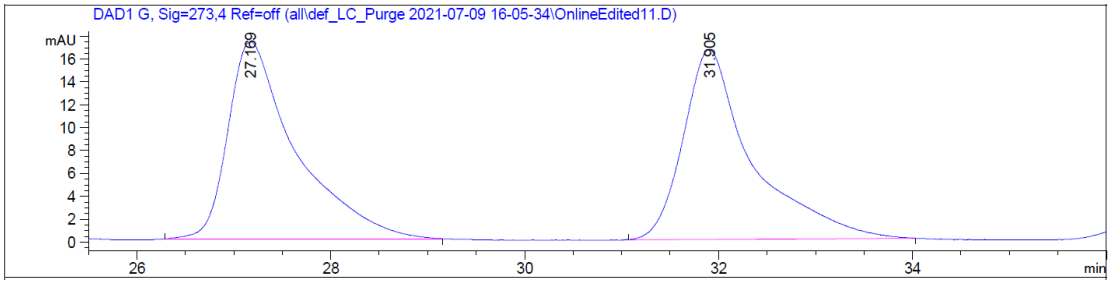
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.991	BB	0.2300	935.11871	58.65556	10.3724
2	9.493	BB	0.2960	8080.33301	392.72739	89.6276



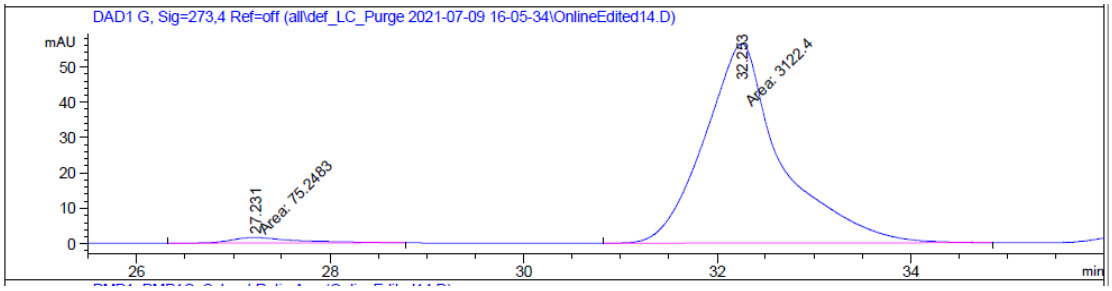
Thiophen-2-ylmethyl-2-[(1-(2-formyl-1*H*-indol-1-yl) naphthalen-2-yl] methyl acrylate (27)

The general procedure **A** was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.2 mg, 0.20 mmol) and thiophen-2-ylmethyl methacrylate (**23d**) (109.4 mg, 0.60 mmol).

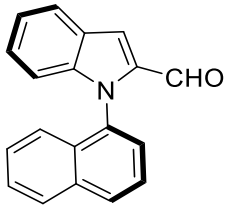
Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **27** (27.1 mg, 30%) as a yellow oil and **1a** (22.5 mg, 41%) as yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.93–7.90 (m, 1H), 7.87–7.83 (m, 1H), 7.54 (d, *J* = 0.9 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.46 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.32–7.27 (m, 2H), 7.26–7.22 (m, 2H), 6.99 (dd, *J* = 3.5, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.81 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.76–6.72 (m, 1H), 6.09 (d, *J* = 1.0 Hz, 1H), 5.20–5.18 (m, 3H), 3.44 (ABq, *J* = 16.1 Hz, Δν = 28.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 181.4 (C_q), 166.0 (CH), 140.8 (CH), 137.7 (CH), 137.6 (CH), 137.0 (CH), 135.5 (CH), 133.1 (CH), 131.8 (CH), 131.7 (CH), 129.3 (C_q), 128.1 (C_q), 128.1 (C_q), 128.0 (CH), 127.7 (C_q), 127.4 (C_q), 127.2 (C_q), 126.7 (C_q), 126.4 (CH), 126.2 (C_q), 123.3 (C_q), 122.3 (C_q), 121.8 (C_q), 114.8 (C_q), 111.8 (C_q), 60.8 (CH), 33.9 (CH). IR (ATR): 2957, 1714, 1673, 1405, 1314, 1106, 752 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 474 (100) $[M + Na]^+$, 452 (75) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{28}H_{21}NO_3S + H]^+$ 452.1315 found 452.1314. $[\alpha]_D^{20}$: –37.0 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IA-3, *n*-hexane/*i*-PrOH 98:2, 1.0 mL/min, detection at 273 nm): t_r (major) = 32.3 min, t_r (minor) = 27.2 min, 95% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.169	BB	0.6123	836.53931	17.23328	50.5299
2	31.905	BB	0.5987	818.99341	16.56907	49.4701

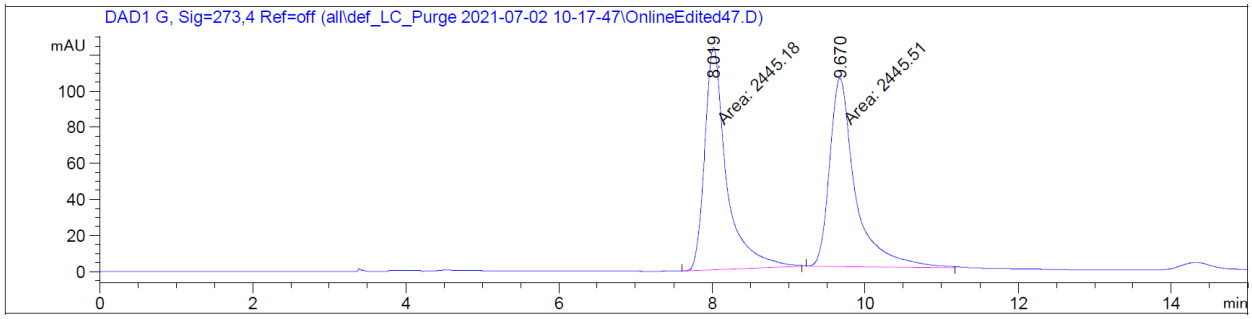


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.231	MM	0.7978	75.24831	1.57200	2.3532
2	32.253	MM	0.9225	3122.40063	56.41489	97.6468

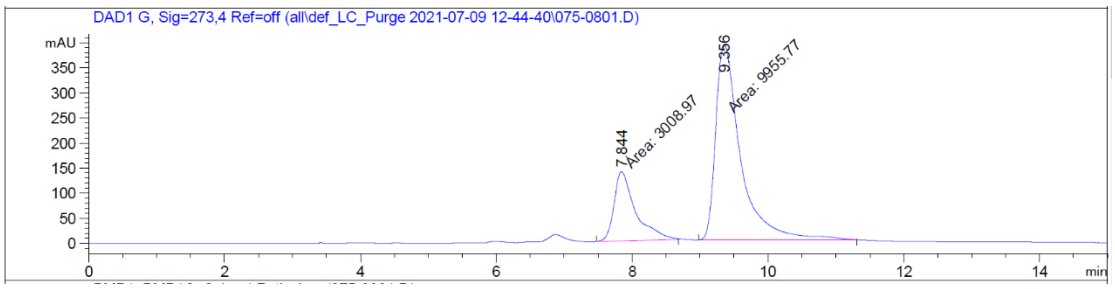


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

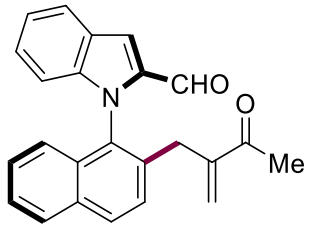
$[\alpha]_D^{20}$: +60.7 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.4 min, t_r (minor) = 7.8 min, 54% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.019	MM	0.3301	2445.17529	123.43890	49.9965
2	9.670	MM	0.3899	2445.51367	104.54658	50.0035

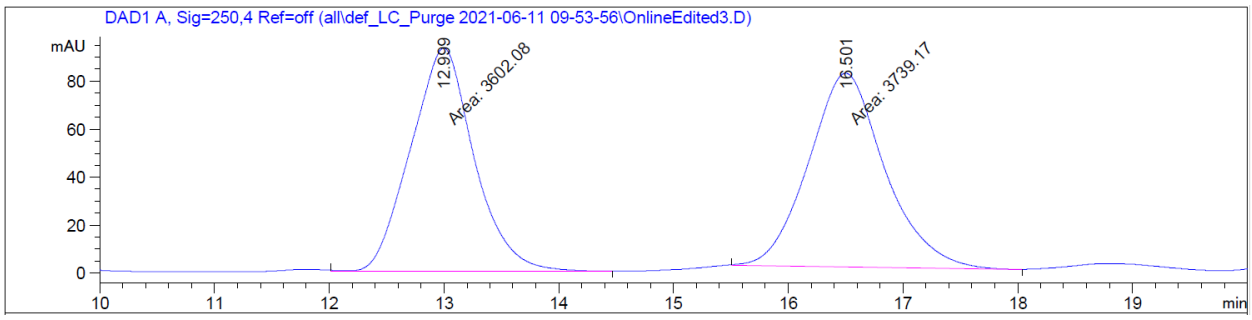


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.844	MM	0.3650	3008.97314	137.39168	23.2089
2	9.356	MM	0.4261	9955.76563	389.42172	76.7911

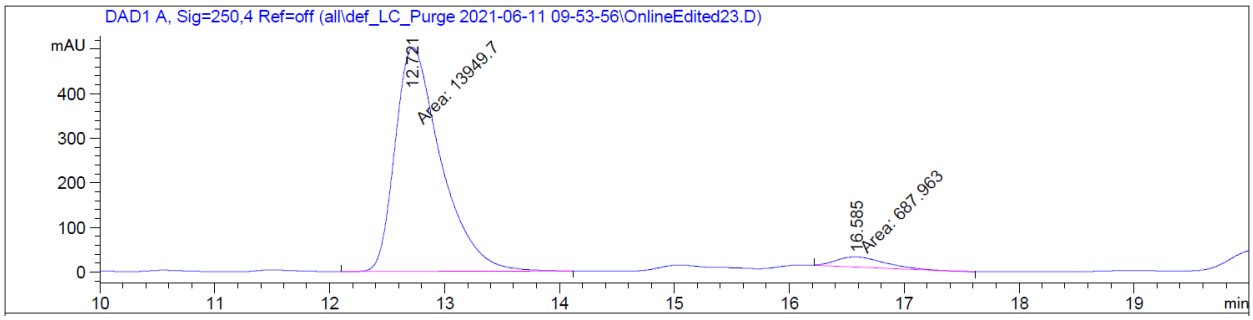


1-(2-(2-Methylene-3-oxobutyl)naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (28)

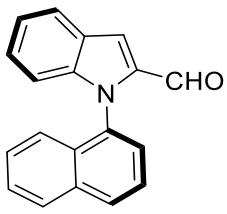
The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and ethyl methacrylate (**23e**) (68.5 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **28** (26.4 mg, 37%) as a yellow oil and **1a** (23.4 mg, 43%) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.67 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.85 (ddd, *J* = 7.7, 1.5, 0.8 Hz, 1H), 7.55 (d, *J* = 0.9 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.45 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.34–7.18 (m, 3H), 6.81 (dq, *J* = 8.5, 0.9 Hz, 1H), 6.77 (dq, *J* = 8.5, 1.0 Hz, 1H), 5.86 (d, *J* = 0.9 Hz, 1H), 5.37 (t, *J* = 1.4 Hz, 1H), 3.40 (ABq, *J* = 15.9 Hz, $\Delta\nu$ = 63.7 Hz, 2H), 2.14 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 198.7 (C_q), 181.5 (CH), 146.6 (C_q), 140.8 (C_q), 137.0 (C_q), 136.1 (C_q), 133.1 (C_q), 131.9 (C_q), 131.7 (C_q), 129.3 (CH), 128.2 (CH), 128.1 (CH), 127.4 (CH), 127.28 (CH_2), 127.25 (CH), 126.4 (C_q), 126.2 (CH), 123.4 (CH), 122.2 (CH), 121.8 (CH), 114.8 (CH), 111.9 (CH), 32.8 (CH_2), 25.5 (CH_3). IR (ATR): 3058, 1676, 1522, 1406 cm^{-1} MS (ESI) *m*/*z* (relative intensity): 376 (100) $[M + Na]^+$, 354 (60) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{24}H_{19}NO_2 + H]^+$ 354.1489 found 354.1482. $[\alpha]_D^{20}$: –59.2 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IC-3, *n*-hexane/*i*-PrOH 70:30, 1.0 mL/min, detection at 250 nm): t_r (major) = 12.3 min, t_r (minor) = 16.6 min, 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.999	MM	0.6437	3602.07861	93.25908	49.0663
2	16.501	MM	0.7707	3739.17041	80.86494	50.9337

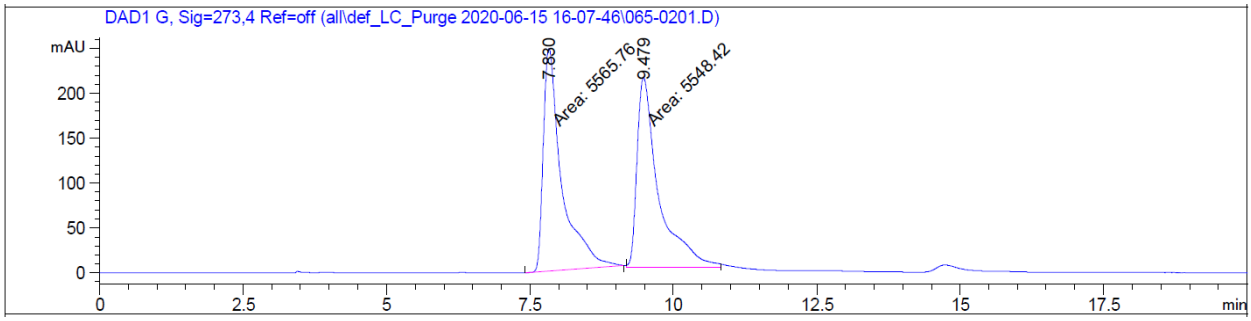


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.721	MM	0.4624	1.39497e4	502.82117	95.3001
2	16.585	MM	0.4979	687.96252	23.02838	4.6999

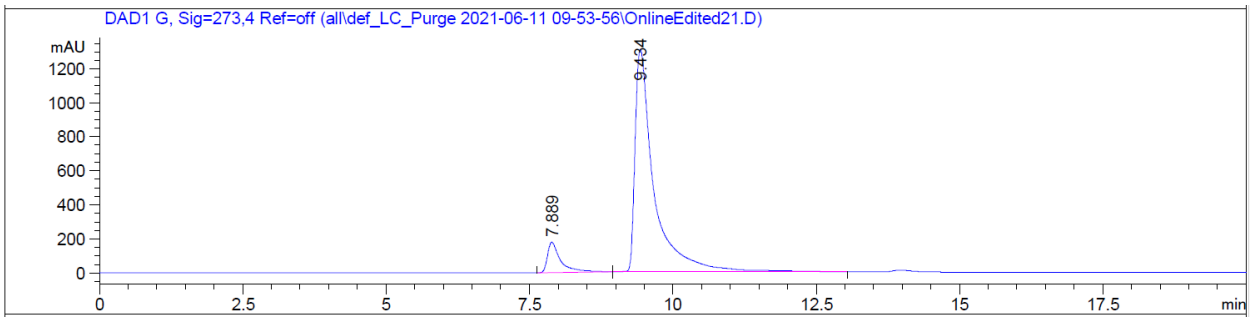


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

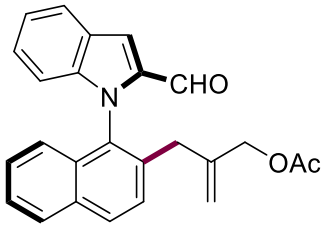
$[\alpha]_D^{20}$: +93.1 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.4 min, t_r (minor) = 7.9 min, 83% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	MM	0.3738	5565.76367	248.18161	50.0780
2	9.479	MM	0.4375	5548.42383	211.35017	49.9220

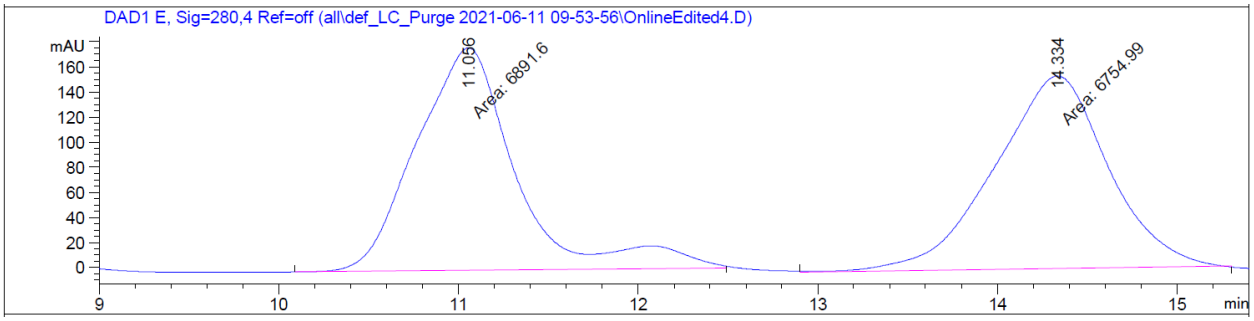


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.889	BB	0.2308	2846.91431	178.71854	8.6473
2	9.434	BB	0.3312	3.00757e4	1308.43604	91.3527

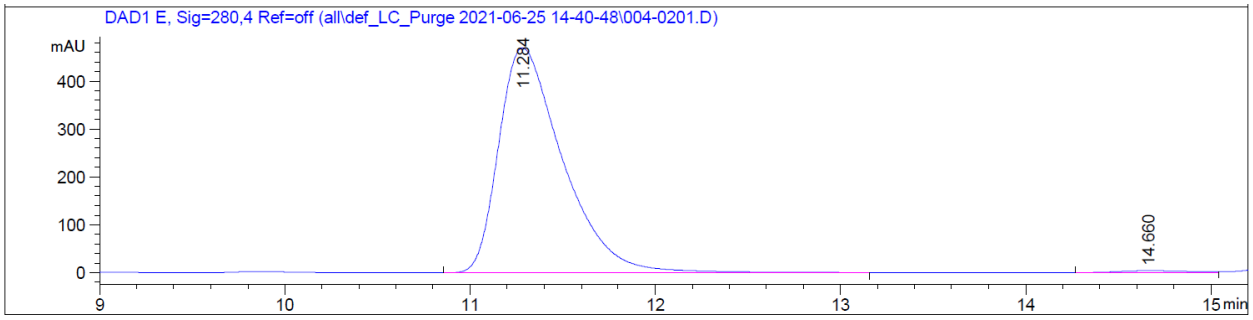


2-((1-(2-formyl-1*H*-indol-1-yl)naphthalen-2-yl)methyl)allyl acetate (29)

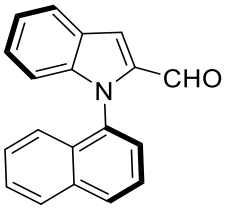
The general procedure **A** (reaction time = 20 h) was followed using 1-(naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (**1a**) (54.3 mg, 0.20 mmol) and ethyl methacrylate (**23f**) (68.5 mg, 0.60 mmol). Isolation by column chromatography (*n*-hexane/EtOAc = 9:1) yielded **29** (26.8 mg, 35%) as a yellow oil and **1a** (20.4 mg, 38%) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$) (one carbon is missing due to overlap): δ = 9.67 (s, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.90–7.83 (m, 1H), 7.56 (d, J = 0.9 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 7.47 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.34–7.20 (m, 3H), 6.88–6.81 (m, 1H), 6.79–6.72 (m, 1H), 5.07–4.99 (m, 1H), 4.75 (dq, J = 1.4, 0.7 Hz, 1H), 4.32–4.21 (m, 2H), 3.17 (s, 2H), 1.85 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 181.3 (CH), 170.4 (C_q), 141.3 (C_q), 140.8 (C_q), 137.1 (C_q), 135.1 (C_q), 133.2 (C_q), 131.8 (C_q), 129.3 (CH), 128.1 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 126.4 (C_q), 126.3 (CH), 123.3 (CH), 122.4 (CH), 121.8 (CH), 115.8 (CH_2), 114.7 (CH), 111.7 (CH), 66.2 (CH_2), 35.3 (CH_2), 20.7 (CH_3). IR (ATR): 3052, 2927, 1738, 1677, 1228 cm^{-}1. MS (ESI) *m*/*z* (relative intensity): 789 (50), 406 (100) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{25}H_{21}NO_3 + H]^+$ 384.1594 found 384.1580. $[\alpha]_D^{20}$: -65.3 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IC-3, *n*-hexane/*i*-PrOH 70:30, 1.0 mL/min, detection at 280 nm): t_r (major) = 11.3 min, t_r (minor) = 14.7 min, 98% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.056	MM	0.6480	6891.59570	177.25635	50.5005
2	14.334	MM	0.7335	6754.98584	153.48363	49.4995

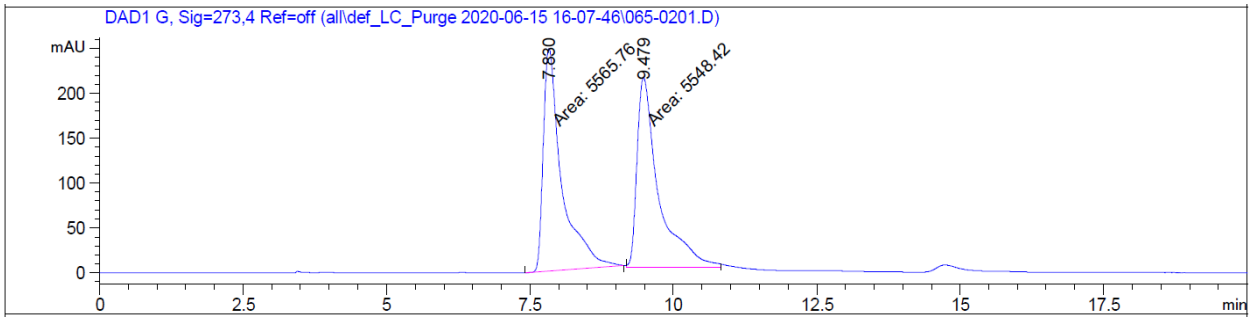


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.284	BB	0.3600	1.12628e4	469.35208	99.0439
2	14.660	BV	0.3182	108.72722	4.05004	0.9561

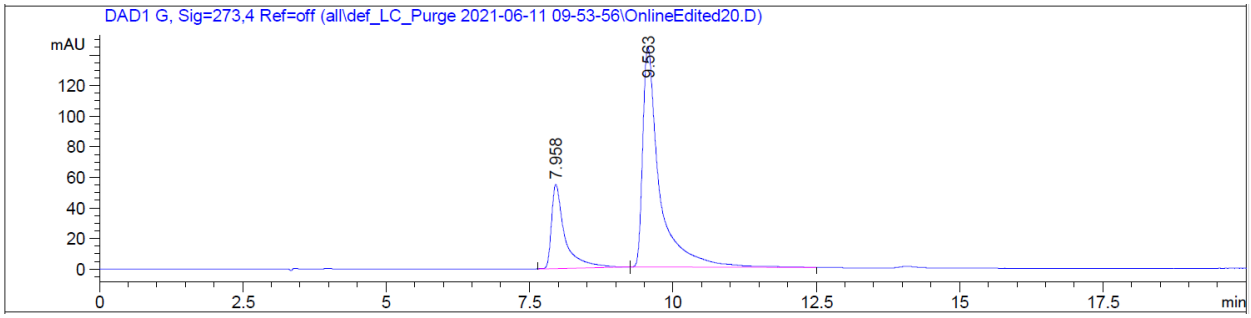


1-(Naphthalen-1-yl)-1*H*-indole-2-carbaldehyde (1a)

$[\alpha]_D^{20}$: +52.3 (c = 1.0, $CHCl_3$). HPLC separation (Chiralpak® IB-3, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min, detection at 273 nm): t_r (major) = 9.6 min, t_r (minor) = 8.0 min, 53% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	MM	0.3738	5565.76367	248.18161	50.0780
2	9.479	MM	0.4375	5548.42383	211.35017	49.9220

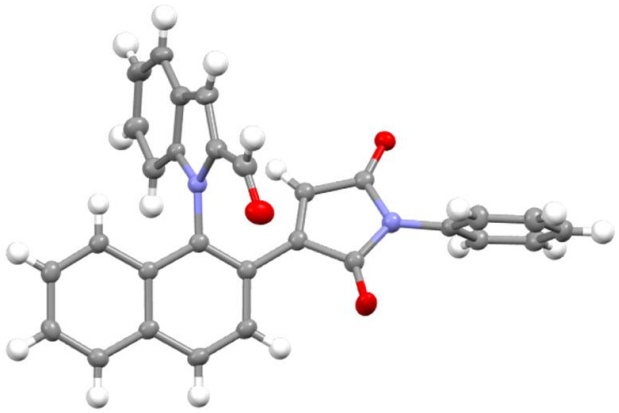


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.958	BB	0.2326	891.78760	54.86127	23.3164
2	9.563	BB	0.2914	2932.94287	144.16432	76.6836

Determination of Absolute Stereochemistry

Determination of Absolute Stereochemistry of 15

Crystals suitable for X-Ray crystallography were grown by slow evaporation of a $CDCl_3$ solution of **15** at ambient temperature.



CCDC number	2090275
Empirical formula	$C_{29}H_{18}N_2O_3$
Formula weight	442.45
Temperature [K]	100.0
Crystal system	monoclinic
Space group (number)	$P2_1$ (4)
a [Å]	9.6726(8)
b [Å]	9.3885(6)
c [Å]	24.0690(15)
α [°]	90
β [°]	91.499(6)
γ [°]	90
Volume [Å^3]	2185.0(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.345
μ [mm^{-1}]	0.710
F(000)	920

Crystal size [mm^3]	0.213×0.121×0.101
Crystal colour	yellow
Crystal shape	block
Radiation	CuK_α (λ=1.54178 Å)
2Θ range [°]	3.67 to 158.68 (0.78 Å)
Index ranges	-12 ≤ h ≤ 12 -11 ≤ k ≤ 11 -30 ≤ l ≤ 30
Reflections collected	75722
Independent reflections	9220 R_{int} = 0.0381 R_{sigma} = 0.0181
Completeness to Θ = 67.679°	100.0 %
Data / Restraints / Parameters	9220/1/613
Goodness-of-fit on F^2	1.137
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0423 wR_2 = 0.1103
Final *R* indexes [all data]	R_1 = 0.0431 wR_2 = 0.1108
Largest peak/hole [e$Å^{-3}$]	0.23/-0.19
Flack X parameter	0.02(7)

Table S2 Atomic coordinates and U_{eq} [$Å^2$]

Atom	***x***	***y***	***z***	U_{eq}
O1	0.7565(3)	0.8390(3)	0.55530(12)	0.0418(7)
O2	0.7496(2)	0.3885(3)	0.40153(9)	0.0255(5)
O3	1.0860(3)	0.6795(3)	0.47590(10)	0.0342(6)
N1	0.6911(3)	0.5523(3)	0.60014(11)	0.0223(5)
N2	0.9274(3)	0.5473(3)	0.42364(11)	0.0243(6)

C1	0.6396(4)	0.7911(4)	0.55437(16)	0.0332(8)
H1	0.567504	0.850601	0.540208	0.040
C2	0.6019(4)	0.6489(4)	0.57342(14)	0.0271(7)
C3	0.4740(4)	0.5877(4)	0.56524(16)	0.0334(8)
H3	0.395190	0.631179	0.548010	0.040
C4	0.4812(3)	0.4469(4)	0.58738(14)	0.0290(7)
C5	0.6179(3)	0.4279(4)	0.60828(13)	0.0233(6)
C6	0.6644(4)	0.2996(4)	0.63164(15)	0.0297(7)
H6	0.756801	0.288496	0.645247	0.036
C7	0.5705(4)	0.1910(4)	0.63397(16)	0.0337(8)
H7	0.598980	0.102127	0.649276	0.040
C8	0.4335(4)	0.2068(4)	0.61447(16)	0.0350(8)
H8	0.371077	0.129279	0.617656	0.042
C9	0.3875(4)	0.3325(5)	0.59074(15)	0.0344(8)
H9	0.294912	0.341708	0.577011	0.041
C10	0.8335(3)	0.5705(3)	0.61675(13)	0.0215(6)
C11	0.8630(3)	0.5891(3)	0.67489(13)	0.0210(6)
C12	1.0041(3)	0.6041(3)	0.69250(13)	0.0227(6)
C13	1.1081(3)	0.6031(4)	0.65272(14)	0.0255(7)
H13	1.202037	0.613886	0.664518	0.031
C14	1.0764(3)	0.5869(4)	0.59720(14)	0.0254(7)
H14	1.147958	0.588648	0.570933	0.030
C15	0.9359(3)	0.5673(3)	0.57869(13)	0.0225(6)
C16	0.9042(3)	0.5391(3)	0.51961(13)	0.0225(6)
C17	0.8065(3)	0.4563(3)	0.49645(13)	0.0234(6)
H17	0.738673	0.405547	0.516325	0.028
C18	0.8191(3)	0.4549(3)	0.43542(13)	0.0221(6)
C19	0.9870(3)	0.6006(4)	0.47294(13)	0.0249(7)
C20	1.0345(3)	0.6222(3)	0.75059(14)	0.0255(7)
H20	1.127716	0.633078	0.763255	0.031
C21	0.9313(4)	0.6241(4)	0.78784(14)	0.0267(7)

H21	0.953183	0.635936	0.826267	0.032
C22	0.7919(4)	0.6086(4)	0.77004(14)	0.0267(7)
H22	0.720848	0.609443	0.796532	0.032
C23	0.7586(3)	0.5922(3)	0.71464(13)	0.0237(6)
H23	0.664443	0.582899	0.702990	0.028
C24	0.9770(3)	0.5715(3)	0.36881(13)	0.0231(6)
C25	0.9519(4)	0.6998(4)	0.34201(15)	0.0299(7)
H25	0.905280	0.774448	0.360451	0.036
C26	0.9954(4)	0.7184(4)	0.28806(15)	0.0320(8)
H26	0.979353	0.806435	0.269518	0.038
C27	1.0623(4)	0.6086(4)	0.26116(14)	0.0296(7)
H27	1.091062	0.620784	0.224020	0.035
C28	1.0871(4)	0.4813(4)	0.28853(15)	0.0285(7)
H28	1.132376	0.405977	0.269951	0.034
C29	1.0463(3)	0.4626(4)	0.34287(14)	0.0260(7)
H29	1.065794	0.376026	0.361965	0.031
O4	0.7314(3)	0.1619(3)	0.05817(13)	0.0414(7)
O5	0.4110(3)	0.3211(3)	-0.03200(10)	0.0306(5)
O6	0.7489(2)	0.6096(2)	-0.09915(9)	0.0257(5)
N3	0.8047(3)	0.4503(3)	0.10148(11)	0.0211(5)
N4	0.5696(3)	0.4524(3)	-0.08088(11)	0.0234(5)
C30	0.8476(4)	0.2098(4)	0.05712(16)	0.0326(8)
H30	0.917645	0.149919	0.042994	0.039
C31	0.8893(3)	0.3523(4)	0.07579(14)	0.0257(7)
C32	1.0184(3)	0.4104(4)	0.06922(15)	0.0309(7)
H32	1.095475	0.364592	0.053298	0.037
C33	1.0154(3)	0.5525(4)	0.09073(14)	0.0272(7)
C34	0.8806(3)	0.5736(3)	0.11000(13)	0.0224(6)
C35	0.8379(4)	0.7027(4)	0.13250(15)	0.0285(7)
H35	0.746506	0.715347	0.145155	0.034
C36	0.9335(4)	0.8109(4)	0.13562(16)	0.0321(8)

H36	0.907092	0.900537	0.150246	0.039
C37	1.0701(4)	0.7919(4)	0.11758(16)	0.0342(8)
H37	1.134637	0.867756	0.121374	0.041
C38	1.1106(4)	0.6653(4)	0.09466(15)	0.0337(8)
H38	1.201861	0.654120	0.081620	0.040
C39	0.6622(3)	0.4352(3)	0.11484(13)	0.0208(6)
C40	0.6324(3)	0.4194(3)	0.17220(13)	0.0202(6)
C41	0.4908(3)	0.4055(3)	0.18650(13)	0.0223(6)
C42	0.4602(3)	0.3900(4)	0.24381(14)	0.0255(7)
H42	0.366796	0.380097	0.254384	0.031
C43	0.5633(4)	0.3891(3)	0.28376(13)	0.0259(7)
H43	0.540426	0.378867	0.321697	0.031
C44	0.7032(4)	0.4032(4)	0.26938(14)	0.0259(7)
H44	0.773887	0.402838	0.297538	0.031
C45	0.7366(3)	0.4173(3)	0.21482(13)	0.0234(6)
H45	0.830981	0.425841	0.205290	0.028
C46	0.3866(3)	0.4049(4)	0.14392(14)	0.0247(6)
H46	0.292483	0.394024	0.153468	0.030
C47	0.4196(3)	0.4197(4)	0.08935(14)	0.0250(7)
H47	0.348516	0.417675	0.061378	0.030
C48	0.5596(3)	0.4381(3)	0.07406(13)	0.0223(6)
C49	0.5914(3)	0.4639(3)	0.01557(13)	0.0227(6)
C50	0.6901(3)	0.5461(3)	-0.00520(13)	0.0228(6)
H50	0.757483	0.597268	0.016143	0.027
C51	0.6782(3)	0.5450(3)	-0.06666(13)	0.0214(6)
C52	0.5086(3)	0.4009(3)	-0.03284(13)	0.0237(6)
C53	0.5183(3)	0.4299(3)	-0.13662(13)	0.0217(6)
C54	0.5371(4)	0.2995(4)	-0.16257(15)	0.0291(7)
H54	0.580632	0.222963	-0.143127	0.035
C55	0.4915(4)	0.2825(4)	-0.21719(15)	0.0322(8)
H55	0.503217	0.193385	-0.235144	0.039

C56	0.4292(4)	0.3937(4)	-0.24587(14)	0.0289(7)
H56	0.398786	0.381349	-0.283412	0.035
C57	0.4111(4)	0.5236(4)	-0.21954(15)	0.0288(7)
H57	0.369706	0.600851	-0.239264	0.035
C58	0.4534(3)	0.5407(4)	-0.16463(14)	0.0262(7)
H58	0.437867	0.628480	-0.146191	0.031

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S3 Bond lengths and angles

Atom–Atom	**Length [Å]**
O1–C1	1.216(5)
O2–C18	1.216(4)
O3–C19	1.211(4)
N1–C2	1.397(4)
N1–C5	1.382(4)
N1–C10	1.434(4)
N2–C18	1.395(4)
N2–C19	1.398(4)
N2–C24	1.434(4)
C1–H1	0.9500
C1–C2	1.461(5)
C2–C3	1.374(5)
C3–H3	0.9500
C3–C4	1.427(5)
C4–C5	1.413(5)
C4–C9	1.409(5)
C5–C6	1.398(5)
C6–H6	0.9500
C6–C7	1.368(5)
C7–H7	0.9500

C7–C8	1.402(5)
C8–H8	0.9500
C8–C9	1.380(6)
C9–H9	0.9500
C10–C11	1.432(4)
C10–C15	1.367(4)
C11–C12	1.426(4)
C11–C23	1.409(4)
C12–C13	1.407(4)
C12–C20	1.431(5)
C13–H13	0.9500
C13–C14	1.372(5)
C14–H14	0.9500
C14–C15	1.431(4)
C15–C16	1.471(4)
C16–C17	1.334(5)
C16–C19	1.511(4)
C17–H17	0.9500
C17–C18	1.477(4)
C20–H20	0.9500
C20–C21	1.359(5)
C21–H21	0.9500
C21–C22	1.411(5)
C22–H22	0.9500
C22–C23	1.372(5)
C23–H23	0.9500
C24–C25	1.384(5)
C24–C29	1.381(5)
C25–H25	0.9500
C25–C26	1.386(5)
C26–H26	0.9500

C26–C27	1.387(5)
C27–H27	0.9500
C27–C28	1.382(5)
C28–H28	0.9500
C28–C29	1.387(5)
C29–H29	0.9500
O4–C30	1.212(5)
O5–C52	1.206(4)
O6–C51	1.214(4)
N3–C31	1.388(4)
N3–C34	1.382(4)
N3–C39	1.431(4)
N4–C51	1.399(4)
N4–C52	1.398(4)
N4–C53	1.434(4)
C30–H30	0.9500
C30–C31	1.464(5)
C31–C32	1.376(5)
C32–H32	0.9500
C32–C33	1.432(5)
C33–C34	1.410(4)
C33–C38	1.406(5)
C34–C35	1.394(5)
C35–H35	0.9500
C35–C36	1.374(5)
C36–H36	0.9500
C36–C37	1.413(5)
C37–H37	0.9500
C37–C38	1.372(6)
C38–H38	0.9500
C39–C40	1.425(4)

C39–C48	1.378(4)
C40–C41	1.427(4)
C40–C45	1.420(4)
C41–C42	1.426(5)
C41–C46	1.419(4)
C42–H42	0.9500
C42–C43	1.366(5)
C43–H43	0.9500
C43–C44	1.412(5)
C44–H44	0.9500
C44–C45	1.367(5)
C45–H45	0.9500
C46–H46	0.9500
C46–C47	1.367(5)
C47–H47	0.9500
C47–C48	1.423(4)
C48–C49	1.469(4)
C49–C50	1.334(5)
C49–C52	1.517(4)
C50–H50	0.9500
C50–C51	1.481(4)
C53–C54	1.388(5)
C53–C58	1.382(5)
C54–H54	0.9500
C54–C55	1.385(5)
C55–H55	0.9500
C55–C56	1.381(5)
C56–H56	0.9500
C56–C57	1.387(5)
C57–H57	0.9500
C57–C58	1.383(5)

C58–H58	0.9500

Atom–Atom–Atom	**Angle [°]**
C2–N1–C10	128.9(3)
C5–N1–C2	107.5(3)
C5–N1–C10	123.6(3)
C18–N2–C19	110.2(3)
C18–N2–C24	123.8(3)
C19–N2–C24	125.7(3)
O1–C1–H1	117.6
O1–C1–C2	124.9(3)
C2–C1–H1	117.6
N1–C2–C1	125.6(3)
C3–C2–N1	109.7(3)
C3–C2–C1	124.6(3)
C2–C3–H3	126.3
C2–C3–C4	107.3(3)
C4–C3–H3	126.3
C5–C4–C3	106.7(3)
C9–C4–C3	134.6(3)
C9–C4–C5	118.7(3)
N1–C5–C4	108.7(3)
N1–C5–C6	128.6(3)
C6–C5–C4	122.7(3)
C5–C6–H6	121.6
C7–C6–C5	116.9(3)
C7–C6–H6	121.6
C6–C7–H7	119.0
C6–C7–C8	122.0(4)
C8–C7–H7	119.0
C7–C8–H8	119.3

C9–C8–C7	121.4(3)
C9–C8–H8	119.3
C4–C9–H9	120.8
C8–C9–C4	118.3(3)
C8–C9–H9	120.8
C11–C10–N1	116.9(3)
C15–C10–N1	121.2(3)
C15–C10–C11	121.9(3)
C12–C11–C10	117.9(3)
C23–C11–C10	122.5(3)
C23–C11–C12	119.6(3)
C11–C12–C20	118.2(3)
C13–C12–C11	119.5(3)
C13–C12–C20	122.3(3)
C12–C13–H13	119.4
C14–C13–C12	121.2(3)
C14–C13–H13	119.4
C13–C14–H14	119.9
C13–C14–C15	120.3(3)
C15–C14–H14	119.9
C10–C15–C14	119.2(3)
C10–C15–C16	121.0(3)
C14–C15–C16	119.7(3)
C15–C16–C19	123.3(3)
C17–C16–C15	129.5(3)
C17–C16–C19	107.2(3)
C16–C17–H17	124.9
C16–C17–C18	110.1(3)
C18–C17–H17	124.9
O2–C18–N2	126.0(3)
O2–C18–C17	127.8(3)

N2–C18–C17	106.2(3)
O3–C19–N2	125.2(3)
O3–C19–C16	128.6(3)
N2–C19–C16	106.2(3)
C12–C20–H20	119.6
C21–C20–C12	120.7(3)
C21–C20–H20	119.6
C20–C21–H21	119.7
C20–C21–C22	120.7(3)
C22–C21–H21	119.7
C21–C22–H22	119.8
C23–C22–C21	120.3(3)
C23–C22–H22	119.8
C11–C23–H23	119.7
C22–C23–C11	120.5(3)
C22–C23–H23	119.7
C25–C24–N2	120.5(3)
C29–C24–N2	118.5(3)
C29–C24–C25	121.0(3)
C24–C25–H25	120.2
C24–C25–C26	119.5(3)
C26–C25–H25	120.2
C25–C26–H26	120.0
C25–C26–C27	120.0(3)
C27–C26–H26	120.0
C26–C27–H27	120.1
C28–C27–C26	119.8(3)
C28–C27–H27	120.1
C27–C28–H28	119.7
C27–C28–C29	120.6(3)
C29–C28–H28	119.7

C24–C29–C28	119.1(3)
C24–C29–H29	120.5
C28–C29–H29	120.5
C31–N3–C39	128.1(3)
C34–N3–C31	107.8(3)
C34–N3–C39	124.1(3)
C51–N4–C53	124.0(3)
C52–N4–C51	110.1(3)
C52–N4–C53	125.4(3)
O4–C30–H30	117.2
O4–C30–C31	125.5(3)
C31–C30–H30	117.2
N3–C31–C30	125.6(3)
C32–C31–N3	109.6(3)
C32–C31–C30	124.8(3)
C31–C32–H32	126.2
C31–C32–C33	107.5(3)
C33–C32–H32	126.2
C34–C33–C32	106.1(3)
C38–C33–C32	135.0(3)
C38–C33–C34	118.8(3)
N3–C34–C33	109.0(3)
N3–C34–C35	128.6(3)
C35–C34–C33	122.4(3)
C34–C35–H35	121.4
C36–C35–C34	117.3(3)
C36–C35–H35	121.4
C35–C36–H36	119.2
C35–C36–C37	121.6(4)
C37–C36–H36	119.2
C36–C37–H37	119.6

C38–C37–C36	120.8(3)
C38–C37–H37	119.6
C33–C38–H38	120.5
C37–C38–C33	119.1(3)
C37–C38–H38	120.5
C40–C39–N3	116.6(3)
C48–C39–N3	121.2(3)
C48–C39–C40	122.2(3)
C39–C40–C41	117.6(3)
C45–C40–C39	122.9(3)
C45–C40–C41	119.5(3)
C42–C41–C40	117.9(3)
C46–C41–C40	119.6(3)
C46–C41–C42	122.5(3)
C41–C42–H42	119.5
C43–C42–C41	121.0(3)
C43–C42–H42	119.5
C42–C43–H43	119.6
C42–C43–C44	120.9(3)
C44–C43–H43	119.6
C43–C44–H44	120.1
C45–C44–C43	119.8(3)
C45–C44–H44	120.1
C40–C45–H45	119.5
C44–C45–C40	120.9(3)
C44–C45–H45	119.5
C41–C46–H46	119.5
C47–C46–C41	120.9(3)
C47–C46–H46	119.5
C46–C47–H47	119.7
C46–C47–C48	120.6(3)

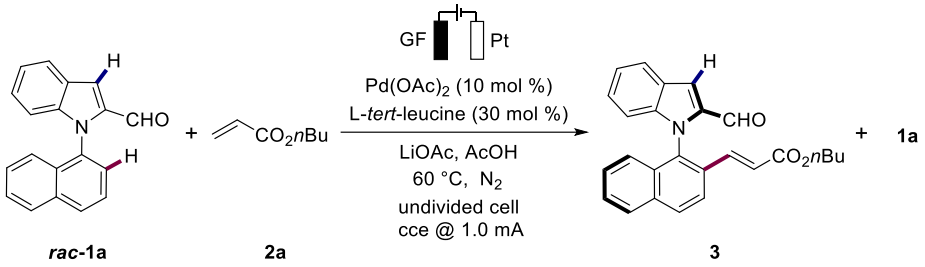
C48–C47–H47	119.7
C39–C48–C47	119.1(3)
C39–C48–C49	121.4(3)
C47–C48–C49	119.5(3)
C48–C49–C52	123.5(3)
C50–C49–C48	128.6(3)
C50–C49–C52	107.8(3)
C49–C50–H50	125.3
C49–C50–C51	109.4(3)
C51–C50–H50	125.3
O6–C51–N4	125.8(3)
O6–C51–C50	127.6(3)
N4–C51–C50	106.6(3)
O5–C52–N4	125.2(3)
O5–C52–C49	128.9(3)
N4–C52–C49	105.9(3)
C54–C53–N4	120.3(3)
C58–C53–N4	119.1(3)
C58–C53–C54	120.5(3)
C53–C54–H54	120.4
C55–C54–C53	119.1(3)
C55–C54–H54	120.4
C54–C55–H55	119.6
C56–C55–C54	120.8(3)
C56–C55–H55	119.6
C55–C56–H56	120.2
C55–C56–C57	119.6(3)
C57–C56–H56	120.2
C56–C57–H57	120.0
C58–C57–C56	120.1(3)
C58–C57–H57	120.0

C53–C58–C57	119.9(3)
C53–C58–H58	120.1
C57–C58–H58	120.1

On/off electricity experiment

On/off electricity reaction was carried out in an undivided cell, with a GF anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). ***rac*-1a** (81.4 mg, 0.30 mmol, 1.0 equiv), **2a** (115.5 mg, 0.90 mmol, 3.0 equiv), $Pd(OAc)_2$ (6.7 mg, 10 mol %), L-*tert*-leucine (11.7 mg, 30 mol %) and LiOAc (40.5 mg, 2.0 equiv) were placed in a 10 mL cell and dissolved in AcOH (6.0 mL) under nitrogen atmosphere. Electrocatalysis was performed at 60 °C with a constant current of 1.0 mA. Aliquots of 0.20 mL were removed from the cell every 1.0 h, and separately mixed with an aliquot (0.2 mL) of a solution of 1,3,5-trimethoxybenzene (0.30 mmol in 6.0 mL of AcOH). The mixture was extracted with EtOAc (3.0 mL). After evaporation of solvent, the crude mixture was analyzed by ^{1}H-NMR spectroscopy.

Table S4 Obtained data.



Time (h)	0	1.0	2.0	3.0	4.0	5.0	6.0
Yield **3** (%)	0	7	7	13	14	18	18

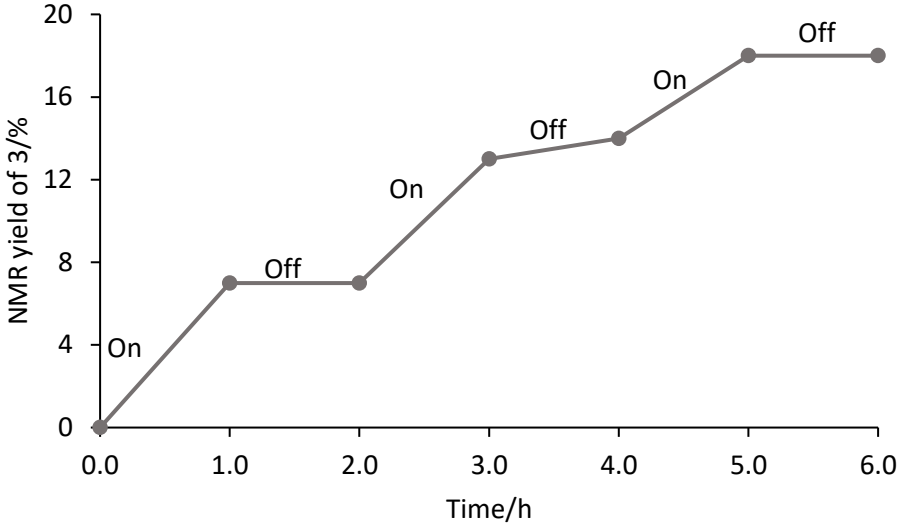


Fig. S1 On/off electricity experiment.

Cyclic voltammetric studies

CV measurements were conducted with a Metrohm Autolab PGSTAT204 potentiostat and Nova 2.1 software. A glassy carbon working electrode (disk, diameter: 3 mm), a coiled platinum wire counter electrode and a saturated calomel (SCE) reference electrode were employed. The voltammograms were recorded at room temperature in AcOH at a substrate concentration of 5.0 mmol/L and with 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte. The scan rate is 100 mV/s. Deviations from the general experimental conditions are indicated in the respective figures and descriptions.

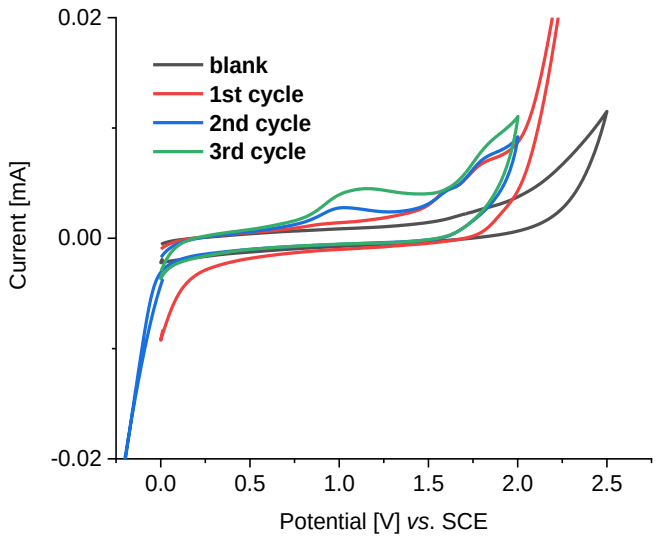


Fig. S2 Cyclic voltammogram of different scan cycles of Pd(OAc)$_2$ in AcOH with nBu$_4$NPF$_6$ (0.1 M) at 100 mV/s.

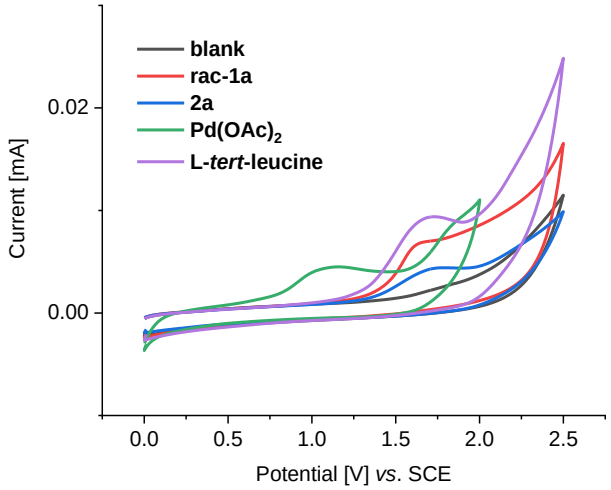


Fig. S3 Cyclic voltammogram of several reactants in AcOH with *n*Bu$_4$NPF$_6$ (0.1 M) at 100 mV/s.

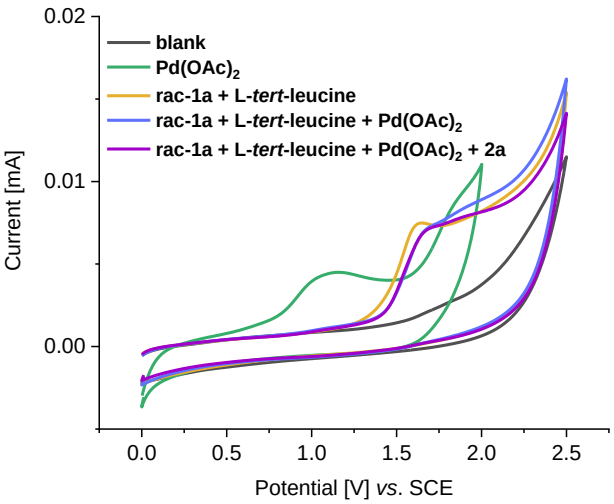


Fig. S4 Cyclic voltammogram of several reaction mixtures in AcOH with *n*Bu$_4$NPF$_6$ (0.1 M) at 100 mV/s.

Computational Studies

All DFT calculations were performed with Gaussian 16, Revision A.03 package.[4] All structures were optimized at the PBE0[5] level of theory in combination with D3 dispersion corrections with a Becke-Johnson damping scheme (D3BJ).[6] Analytical frequency calculations were carried out at the same level of theory in order to identify each stationary point as either an intermediate (no imaginary frequencies) or as a transition state (only one imaginary frequency) and to provide thermal and non-thermal corrections to the Gibbs free energy at 333.15 K and 1 atm. All atoms were described with a def2-SVP basis set,[7] while palladium was described also with a SSD pseudopotential.[8] The electronic energy was then improved through PW6B95[9] single-point calculations on the optimized geometries in combination with a standalone version of Grimme's D4 dispersion corrections,[10] with a def2-TZVP basis set combined with SSD pseudopotential for palladium.[11] Solvent effects were taken into consideration in the single-point calculations through the use of the SMD model[12] with a dielectric constant of $\varepsilon = 6.2528$, which corresponds to acetic acid, the solvent used in the experimental work. All reported energies are based on gas-phase Gibbs free energies with def2-SVP basis set for which the electronic energies were corrected to PW6B95-D4 with def2-TZVP basis set and solvent effects.

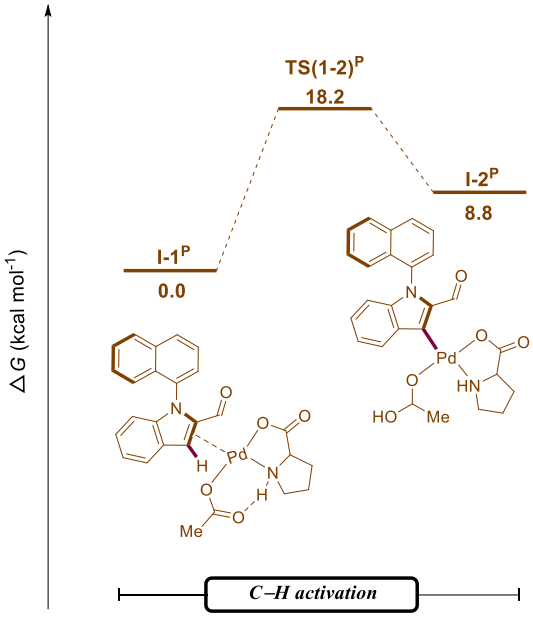


Fig. S5 Computed relative Gibbs free energies ($\Delta G_{333.15}$) in kcal mol^{-1} for C–H activation of indole's C-3 position at the PW6B95-D4/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory. Superscript P relates to structures with L-proline as a ligand.

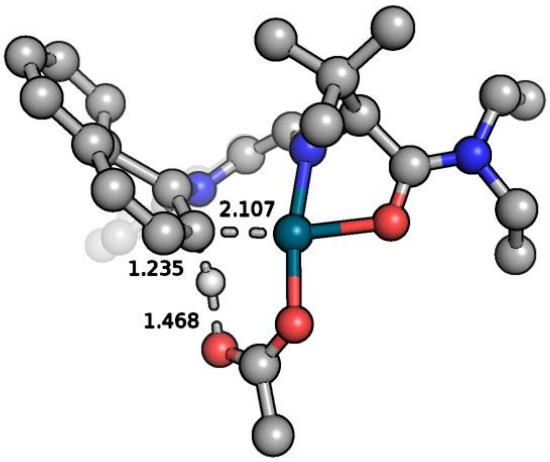


Fig. S6 Computed transition state structure for the C–H activation elementary step for the seven-membered ring pathway with *O*-coordination of the TDG, TS(1-2)[7]. Nonrelevant hydrogens were omitted for clarity.

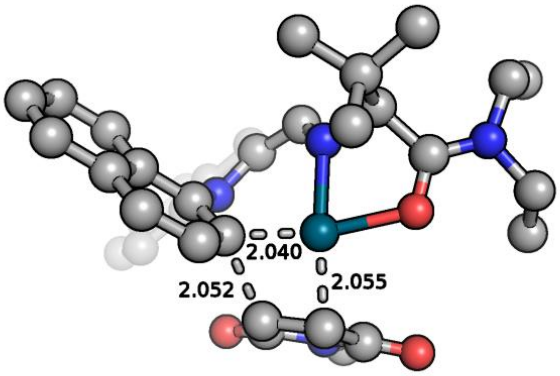


Fig. S7 Computed transition state structure for the migratory insertion elementary step for the seven-membered ring pathway with *O*-coordination of the TDG, TS(4-5). Nonrelevant hydrogens were omitted for clarity.

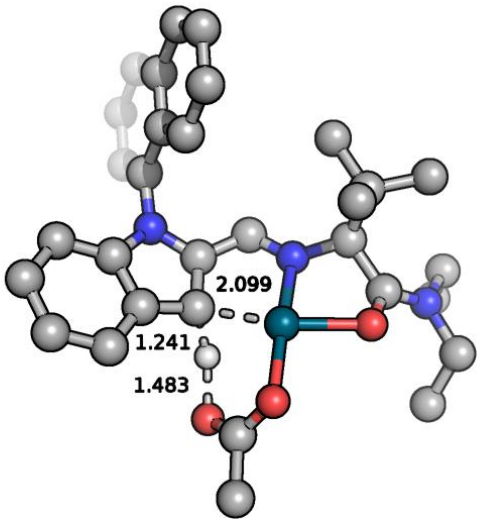


Fig. S8 Computed transition state structure for the C–H activation elementary step for the five-membered ring pathway with *O*-coordination of the TDG, TS(1-2)[5]. Nonrelevant hydrogens were omitted for clarity.

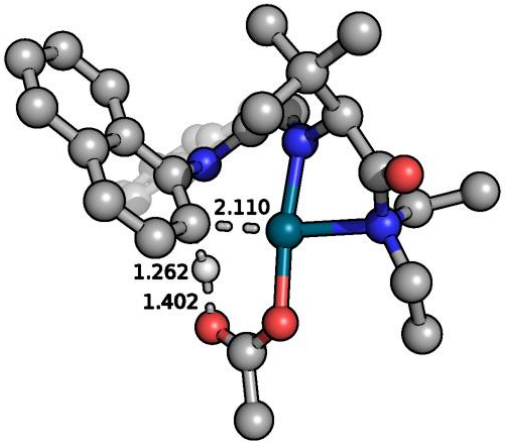


Fig. S9 Computed transition state structure for the C–H activation elementary step for the seven-membered ring pathway with *N*-coordination of the TDG, TS(1-2)'[7]. Nonrelevant hydrogens were omitted for clarity.

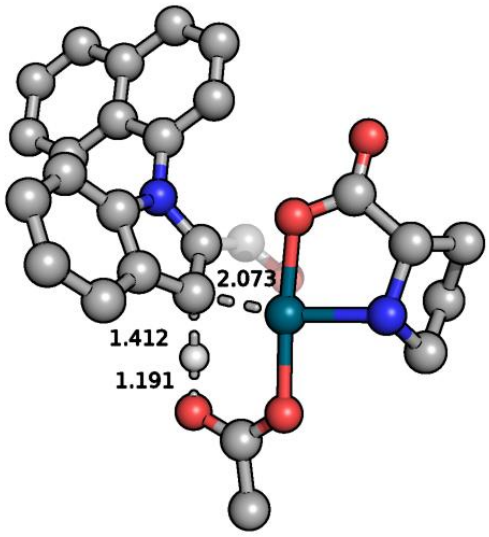


Fig. S10 Computed transition state structure for the C–H activation elementary step at indole's C-3 position with L-proline as a ligand, TS(1-2)^{P}. Nonrelevant hydrogens were omitted for clarity.

Table S5 Calculated electronic energies at the PW6B95-D4/def2-TZVP+SMD(AcOH) level of theory and Gibbs free energies with dispersion corrections for all structures in the present work (all in Hartree).[a]

Structure	Electronic Energy	Total Gibbs Free Energy
I-1^{5}	-1723.533894	-1722.998609
TS(1-2)^{5}	-1723.518017	-1722.985498
I-2^{5}	-1723.544208	-1723.008372
I-1'^{7}	-1723.525121	-1722.988313
TS(1-2)'^{7}	-1723.506879	-1722.971028
I-2'^{7}	-1723.531231	-1722.992187
I-1^{7}	-1723.546341	-1723.009262
TS(1-2)^{7}	-1723.523966	-1722.989254
I-2^{7}	-1723.548139	-1723.010954
I-3	-1494.050230	-1493.568479
I-4	-1893.497314	-1892.927722
TS(4-5)	-1893.475774	-1892.905948
I-5	-1893.509691	-1892.935256
Acetic acid	-229.455848	-229.424445
Maleimide	-399.402411	-399.341727

[a] Superscripts 5 and 7 correspond to structures, which lead to the formation of a 7-membered and 5-membered cyclometallated complex with *O*-coordination of the TDG. Superscripts '7 represents structures with *N*-coordination of the TDG.

Table S6 Calculated electronic energies at the PW6B95-D4/def2-TZVP+SMD(AcOH) level of theory and Gibbs free energies with dispersion corrections for C–H activation at the indole's C-3 position (all in Hartree).[a]

Structure	Electronic Energy	Total Gibbs Free Energy
I-1^{P}	-1621.451279	-1621.069778
TS(1-2)^{P}	-1621.419499	-1621.040839
I-2^{P}	-1621.438318	-1621.055699

[a] Superscripts P relates to structures with L-proline as a ligand.

Cartesian coordinates of the optimized structure

I-1[5]

Lowest frequency = 15.8310 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	3.195846	-0.734598	-1.066459
C	3.292154	-1.375677	0.200683
C	4.665213	-3.090825	-0.900140
H	5.238067	-4.018793	-0.832616
C	0.259241	-0.781995	-1.392096
N	-0.819434	-0.687128	-0.698797
C	-1.782305	-1.736600	-0.417871
H	-1.954414	-2.318449	-1.335577
O	-2.849725	0.013635	0.796467
H	0.575494	-1.684944	-1.926146
Pd	-1.023129	1.009882	0.295840
C	0.000358	-3.434725	0.186437
H	0.272480	-4.234563	0.890475
H	-0.149906	-3.903227	-0.799682
H	0.868571	-2.762046	0.139121
C	-2.341819	-3.789936	0.941583
H	-2.546328	-4.393959	0.044286
H	-1.993313	-4.480176	1.723320
H	-3.285398	-3.349540	1.295635
O	-1.255367	2.630716	1.372817
C	-1.426969	3.767639	0.758499
O	-1.414325	3.899472	-0.456700
C	-1.602318	4.930677	1.700752
H	-0.616663	5.204835	2.108291
H	-2.017776	5.788981	1.159921
H	-2.242062	4.656317	2.549577
C	1.057075	0.429481	-1.316459
C	0.509794	1.728181	-1.062868
C	2.801615	1.732480	-0.805540
C	1.656614	2.559598	-0.758389
H	-0.370944	2.144973	-1.576673
C	1.807516	3.927093	-0.495557
C	4.207904	3.549131	-0.250194
C	3.085623	4.401582	-0.236849
H	0.931539	4.577897	-0.496253
H	5.195061	3.964274	-0.036542
H	3.230417	5.461546	-0.017863
N	2.392872	0.444086	-1.156823
C	3.817457	-1.231345	-2.187949
H	3.723602	-0.699891	-3.137249

C	4.567821	-2.424490	-2.099159
H	5.064027	-2.814145	-2.989850
C	-1.262508	-2.733507	0.691703
C	-3.029652	-0.981778	0.056080
N	-4.262857	-1.350835	-0.273303
C	-5.369401	-0.535367	0.251527
H	-6.277972	-1.147445	0.160067
H	-5.183143	-0.376350	1.323347
C	-4.612043	-2.466328	-1.146596
H	-5.339524	-3.093989	-0.606485
H	-3.729072	-3.096518	-1.293609
C	-5.536152	0.801587	-0.449233
H	-6.384220	1.341881	-0.004488
H	-4.640744	1.425879	-0.325803
H	-5.738797	0.680728	-1.522595
C	-5.175771	-2.030200	-2.486509
H	-6.113959	-1.468646	-2.375509
H	-4.460716	-1.397372	-3.033495
H	-5.392831	-2.915728	-3.101075
C	4.089325	2.197252	-0.542087
H	4.954095	1.532385	-0.572235
C	-0.947020	-2.010662	2.002204
H	-0.191631	-1.223228	1.864060
H	-1.836701	-1.552777	2.454498
H	-0.533519	-2.735466	2.719052
C	4.034748	-2.594522	0.270575
C	2.678030	-0.864163	1.372486
C	4.117511	-3.270640	1.514944
C	2.785076	-1.545401	2.563332
H	2.130734	0.081055	1.332784
C	3.503810	-2.760326	2.635086
H	4.684223	-4.203170	1.569537
H	2.315866	-1.140690	3.462795
H	3.580025	-3.287322	3.588510

TS(1-2)[5]

Lowest frequency = -389.1099 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	-3.313437	-0.407232	1.170870
C	-3.619441	-1.230623	0.049275
C	-4.460587	-2.364761	0.266760
C	-4.975908	-2.606505	1.567064
H	-5.625478	-3.471641	1.720309
C	-0.359997	-0.681631	1.025344
N	0.764239	-0.675582	0.391199
C	1.625060	-1.815381	0.144965

H	1.614368	-2.475301	1.025441
O	3.054231	-0.120724	-0.740855
H	-0.769687	-1.575535	1.509519
Pd	1.337036	1.050528	-0.376374
C	-0.197087	-3.333874	-0.714672
H	-0.509073	-4.003268	-1.529809
H	-0.098205	-3.946719	0.195677
H	-1.018972	-2.617208	-0.576689
C	2.149267	-3.739511	-1.429197
H	2.284430	-4.454837	-0.604193
H	1.792253	-4.313931	-2.296230
H	3.129918	-3.320895	-1.699393
O	2.068408	2.823834	-0.931672
C	1.971168	3.751072	-0.052542
O	1.338635	3.635986	1.013816
C	2.675867	5.034856	-0.384212
H	2.296000	5.423321	-1.340104
H	2.527742	5.771084	0.412872
H	3.747680	4.834037	-0.523023
C	-1.064929	0.570299	0.951157
C	-0.461189	1.752134	0.449313
C	-2.764727	1.924662	0.453264
C	-1.570516	2.609342	0.103377
H	0.466554	2.441348	0.900073
C	-1.663685	3.914000	-0.409897
C	-4.093848	3.749747	-0.260711
C	-2.921082	4.461350	-0.596374
H	-0.764186	4.476187	-0.662156
H	-5.066111	4.220224	-0.421355
H	-3.013929	5.467515	-1.010125
N	-2.420192	0.686059	0.967427
C	-3.824688	-0.661890	2.421763
H	-3.567538	-0.001150	3.252126
C	-4.673039	-1.773935	2.618674
H	-5.081152	-1.968563	3.612202
C	1.121691	-2.656376	-1.093064
C	3.006544	-1.203675	-0.106016
N	4.132907	-1.774925	0.303891
C	5.392679	-1.086796	-0.017993
H	6.192650	-1.832108	0.095762
H	5.352946	-0.803252	-1.079523
C	4.228980	-3.011908	1.072055
H	4.898611	-3.693190	0.522012
H	3.250380	-3.501942	1.084905
C	5.661684	0.139590	0.836003
H	6.625044	0.582086	0.544190
H	4.883688	0.899989	0.684548
H	5.713427	-0.107712	1.905584
C	4.727402	-2.802463	2.490058
H	5.745418	-2.388811	2.513063

H	4.067457	-2.121773	3.048554
H	4.752698	-3.767060	3.017119
C	-4.037168	2.474371	0.275841
H	-4.936561	1.921337	0.551791
C	0.905125	-1.765417	-2.317731
H	0.151943	-0.985851	-2.128289
H	1.831832	-1.273257	-2.644224
H	0.537844	-2.382279	-3.151272
C	-3.118059	-0.974676	-1.253025
C	-4.754745	-3.214891	-0.830312
C	-3.429015	-1.819098	-2.294265
H	-2.496397	-0.093904	-1.430561
C	-4.248556	-2.950811	-2.081607
H	-5.397209	-4.082981	-0.664496
H	-3.045840	-1.609469	-3.295455
H	-4.487662	-3.610241	-2.918599

I-2[5]

Lowest frequency = 14.6716 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	-3.455617	-0.278480	1.071855
C	-3.877456	-1.278650	0.147818
C	-4.819995	-2.254012	0.598703
C	-5.326325	-2.170540	1.921432
H	-6.054223	-2.915274	2.252233
C	-0.440420	-0.857641	0.501247
N	0.783814	-0.778887	0.068307
C	1.708050	-1.875708	-0.118951
H	1.521017	-2.641139	0.650338
O	3.258604	-0.084707	-0.422622
H	-0.878380	-1.801359	0.847056
Pd	1.413348	1.027891	-0.430026
C	0.131078	-3.194232	-1.571176
H	0.014240	-3.755664	-2.509936
H	-0.024845	-3.903832	-0.742562
H	-0.675642	-2.447702	-1.546115
C	2.569009	-3.661620	-1.709222
H	2.463312	-4.462560	-0.961720
H	2.436000	-4.125545	-2.697450
H	3.597830	-3.273928	-1.668972
O	2.153060	2.919728	-0.792406
C	2.031351	3.856090	0.002020
O	1.288333	3.787264	1.072211
C	2.714725	5.158330	-0.207484
H	3.418443	5.088479	-1.042788

H	1.954199	5.925514	-0.419831
H	3.228369	5.461602	0.715455
C	-1.143216	0.375651	0.426842
C	-0.470964	1.489326	-0.095010
C	-2.688910	1.959390	0.260079
C	-1.456800	2.509364	-0.226876
H	0.791244	2.937316	1.067589
C	-1.457644	3.828414	-0.731872
C	-3.832002	3.988302	-0.222382
C	-2.633662	4.549656	-0.723200
H	-0.546252	4.259005	-1.151146
H	-4.744272	4.588715	-0.233627
H	-2.649596	5.567377	-1.118101
N	-2.474895	0.660881	0.654553
C	-3.965910	-0.221338	2.349362
H	-3.618883	0.560356	3.028252
C	-4.919562	-1.171450	2.774046
H	-5.321212	-1.113603	3.787546
C	1.522539	-2.560233	-1.526281
C	3.094185	-1.240961	0.032979
N	4.112553	-1.873323	0.613561
C	5.398389	-1.166138	0.671807
H	6.168507	-1.929581	0.853178
H	5.585813	-0.737373	-0.323133
C	4.055394	-3.196240	1.225177
H	4.852084	-3.808043	0.771007
H	3.114112	-3.678675	0.945420
C	5.458397	-0.072767	1.724048
H	6.452764	0.396649	1.708977
H	4.713669	0.707154	1.515638
H	5.285307	-0.465339	2.735800
C	4.199422	-3.171371	2.735947
H	5.174367	-2.773930	3.051743
H	3.411786	-2.559571	3.201061
H	4.118326	-4.194348	3.130896
C	-3.880321	2.695939	0.267809
H	-4.807936	2.257133	0.639458
C	1.653943	-1.544307	-2.662267
H	0.911181	-0.736620	-2.574588
H	2.652610	-1.086697	-2.698245
H	1.480948	-2.050495	-3.623647
C	-3.409389	-1.335276	-1.190629
C	-5.232707	-3.271499	-0.300091
C	-3.836806	-2.333272	-2.036257
H	-2.723257	-0.565631	-1.551379
C	-4.748484	-3.315258	-1.586128
H	-5.950423	-4.018602	0.047324
H	-3.479261	-2.361245	-3.068133
H	-5.078014	-4.101332	-2.268866

I-1'[7]
Lowest frequency = 13.7602 cm^{-1}
Charge = 1, Multiplicity = 1

74

C	-1.034542	-0.685353	1.689725
C	-0.648496	-0.079227	2.926225
C	-0.916481	1.242675	3.161204
H	-0.122551	-0.688094	3.661613
H	-0.606836	1.707683	4.099692
C	-0.361833	0.479474	-1.937847
N	0.579670	0.633341	-1.063126
C	1.752189	1.421423	-1.403442
H	1.883052	1.446331	-2.502469
H	-0.209050	0.890063	-2.946252
Pd	0.926387	-0.550554	0.540773
C	0.309934	3.475970	-1.488716
H	0.253828	4.549213	-1.256099
H	0.251628	3.379408	-2.585149
H	-0.575293	3.003815	-1.043247
C	2.770023	3.737212	-1.528610
H	2.782868	3.667649	-2.628304
H	2.621202	4.795964	-1.269652
H	3.748428	3.424493	-1.149158
O	1.501813	-1.815393	1.976046
C	1.200068	-3.044232	1.647477
O	0.595030	-3.320887	0.620325
C	1.688856	-4.082482	2.619527
H	1.620857	-3.724520	3.654911
H	1.120457	-5.010823	2.487629
H	2.750052	-4.292157	2.411925
H	-1.012285	-1.771413	1.553430
C	-1.598328	-0.194950	-1.734182
C	-2.452558	-0.683121	-2.715337
C	-3.524627	-1.337740	-2.057684
H	-2.287478	-0.607113	-3.788892
C	-3.295750	-1.203042	-0.659501
C	-4.677080	-2.015277	-2.507549
C	-4.197523	-1.684833	0.293916
C	-5.559089	-2.507591	-1.566757
H	-4.865162	-2.139303	-3.575853
C	-5.321664	-2.338773	-0.182959
H	-4.020718	-1.559223	1.363317
H	-6.458855	-3.034680	-1.889506
H	-6.045037	-2.739809	0.530395
N	-2.108840	-0.524068	-0.481816
C	-1.700497	0.082546	0.729421

C	-1.617188	2.032252	2.206901
C	-2.029856	1.445777	0.969238
C	1.620944	2.912785	-0.937796
C	2.973924	0.715989	-0.811795
O	4.007025	1.259681	-0.559849
N	2.787237	-0.692326	-0.483006
C	3.885432	-1.201641	0.389892
H	3.485046	-2.099728	0.871136
H	4.014856	-0.454415	1.183030
C	2.513311	-1.592156	-1.662112
H	2.726243	-2.607253	-1.301970
H	1.438066	-1.580825	-1.875121
C	5.213812	-1.505137	-0.275087
H	5.917111	-1.810736	0.513359
H	5.150321	-2.341682	-0.985188
H	5.639617	-0.627357	-0.777193
C	3.298562	-1.265599	-2.917945
H	3.077008	-2.030405	-3.676578
H	3.013945	-0.294038	-3.348642
H	4.382976	-1.258080	-2.756378
C	1.612457	2.999862	0.588194
H	0.803303	2.391437	1.020534
H	2.569048	2.676922	1.023292
H	1.441775	4.040198	0.901696
C	-2.786357	2.215216	0.048855
C	-1.932911	3.389465	2.452843
C	-3.097502	3.524777	0.332960
H	-3.134095	1.756756	-0.878660
C	-2.654973	4.119688	1.535295
H	-1.606406	3.845269	3.390277
H	-3.691402	4.108995	-0.372825
H	-2.901258	5.163349	1.742678

TS(1-2)'[7]

Lowest frequency = -486.7322 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	-0.659403	-0.260980	1.396887
C	-0.518467	0.429676	2.638066
C	-1.381679	1.435607	2.984617
H	0.285900	0.135820	3.316606
H	-1.270610	1.958079	3.937628
C	-0.126127	0.573400	-1.992978
N	0.775141	0.727242	-1.078008
C	1.864957	1.667766	-1.287474
H	2.061323	1.777790	-2.372611

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H     0.020378     1.080996    -2.957795
Pd    1.203250    -0.514436     0.437851
C     0.173043     3.533582    -1.330788
H    -0.014780     4.580573    -1.052319
H     0.159089     3.486449    -2.431824
H    -0.667163     2.941117    -0.939087
C     2.592207     4.080249    -1.248830
H     2.647813     4.083702    -2.349503
H     2.326381     5.099260    -0.931039
H     3.584935     3.845397    -0.848615
O     1.849559    -1.764185     1.877962
C     1.073553    -2.697136     2.287328
O    -0.129908    -2.773797     1.977378
C     1.695419    -3.745094     3.161067
H     0.946894    -4.154867     3.849528
H     2.046294    -4.565002     2.514686
H     2.557764    -3.341721     3.704697
H    -0.423219    -1.498721     1.472413
C    -1.300498    -0.223382    -1.886669
C    -2.013372    -0.789313    -2.935519
C    -3.052178    -1.570407    -2.367103
H    -1.773233    -0.681109    -3.992079
C    -2.956119    -1.415975    -0.956242
C    -4.076372    -2.376840    -2.906562
C    -3.866412    -2.010612    -0.076204
C    -4.968290    -2.973219    -2.038113
H    -4.160015    -2.519054    -3.985877
C    -4.863731    -2.788227    -0.639357
H    -3.783617    -1.876131     1.003423
H    -5.771052    -3.600163    -2.430918
H    -5.587617    -3.279456     0.014591
N    -1.873498    -0.609481    -0.677118
C    -1.705803     0.090921     0.548801
C    -2.431785     1.825867     2.110990
C    -2.608445     1.139139     0.865504
C     1.523075     3.100670    -0.752587
C     3.122015     1.057034    -0.650899
N     3.111364    -0.397617    -0.562346
C     4.255558    -0.889454     0.257246
H     5.171709    -0.403540    -0.109908
H     4.088712    -0.512862     1.274618
C     3.037467    -1.046367    -1.905761
H     2.125356    -0.699419    -2.403247
H     2.897912    -2.121159    -1.733213
C     4.250181    -0.777365    -2.776259
H     4.102227    -1.250166    -3.757840
H     4.405860     0.299500    -2.945532
H     5.174970    -1.188233    -2.348477
C     4.404440    -2.394110     0.270085
H     5.155277    -2.657358     1.028351
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H	3.466683	-2.890448	0.549221
H	4.759889	-2.798828	-0.687984
O	4.034273	1.687703	-0.207161
C	1.434457	3.114679	0.773422
H	1.157556	4.122579	1.115968
H	0.662457	2.421143	1.138101
H	2.393461	2.858992	1.245154
C	-3.645526	1.551120	-0.014268
C	-3.309749	2.889239	2.433489
C	-4.471791	2.593947	0.328594
H	-3.782377	1.035212	-0.966120
C	-4.306560	3.264612	1.562856
H	-3.180309	3.408740	3.385627
H	-5.264723	2.906847	-0.353818
H	-4.976442	4.087135	1.822861

I-2'[7]

Lowest frequency = 23.3782 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	-0.640383	0.408491	1.127011
C	-0.676698	1.135322	2.346233
C	-1.794821	1.849011	2.702154
H	0.191955	1.122138	3.009574
H	-1.821906	2.392459	3.649985
C	0.248061	0.617328	-2.088559
N	1.080156	0.728917	-1.107160
C	2.352759	1.415751	-1.290863
H	2.659619	1.341461	-2.352921
H	0.551454	1.003913	-3.072452
Pd	1.092509	-0.347662	0.565316
C	1.111965	3.549186	-1.771114
H	1.111083	4.639647	-1.630076
H	1.221580	3.364568	-2.852298
H	0.127079	3.182362	-1.446019
C	3.564664	3.619177	-1.411601
H	3.751243	3.451570	-2.484896
H	3.479128	4.705434	-1.260507
H	4.431373	3.261537	-0.844600
O	1.276176	-1.510479	2.265915
C	0.404794	-2.182733	2.831242
O	-0.850902	-2.146775	2.498028
C	0.735472	-3.092870	3.958558
H	1.820268	-3.176415	4.077961
H	0.288781	-2.689291	4.880363
H	0.281606	-4.078772	3.785816

H	-0.988961	-1.429200	1.831295
C	-1.004091	-0.066923	-2.054787
C	-1.536926	-0.764263	-3.130889
C	-2.610464	-1.548632	-2.634617
H	-1.143429	-0.753318	-4.146223
C	-2.719606	-1.259038	-1.246780
C	-3.497124	-2.473255	-3.223988
C	-3.699981	-1.852135	-0.441757
C	-4.456779	-3.065301	-2.427013
H	-3.422991	-2.711249	-4.287080
C	-4.553648	-2.756303	-1.050730
H	-3.788919	-1.610576	0.618576
H	-5.155171	-3.783764	-2.860416
H	-5.324293	-3.245670	-0.451010
N	-1.741174	-0.347016	-0.908837
C	-1.743314	0.420208	0.291694
C	-2.918442	1.921425	1.840503
C	-2.894499	1.217955	0.595756
C	2.263625	2.942678	-0.964434
C	3.398106	0.655574	-0.448534
N	3.145208	-0.752590	-0.282392
C	4.087081	-1.359788	0.689195
H	5.119591	-1.153080	0.366906
H	3.950847	-0.815909	1.633586
C	3.036848	-1.504957	-1.559273
H	2.256297	-1.037483	-2.169607
H	2.660758	-2.507245	-1.314711
C	4.338471	-1.580775	-2.335161
H	4.170451	-2.108722	-3.284945
H	4.730538	-0.579645	-2.573951
H	5.121004	-2.126291	-1.789279
C	3.868588	-2.842246	0.897219
H	4.481314	-3.171279	1.748395
H	2.819757	-3.068617	1.133566
H	4.173286	-3.445973	0.030551
O	4.324030	1.179393	0.102730
C	2.005189	3.184202	0.523353
H	1.928052	4.265374	0.710821
H	1.057701	2.726721	0.845687
H	2.820816	2.797289	1.149438
C	-3.989046	1.373645	-0.293351
C	-4.052861	2.704391	2.172200
C	-5.065837	2.157824	0.051916
H	-3.975314	0.877996	-1.264328
C	-5.108772	2.817545	1.299591
H	-4.066282	3.227248	3.131449
H	-5.895530	2.272952	-0.648921
H	-5.975950	3.427051	1.562037

I-1[7]

Lowest frequency = 13.7648 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	-1.737982	-1.285248	-1.426645
C	-2.012893	-2.643809	-1.237823
C	-2.270037	-3.120183	0.031872
H	-2.003681	-3.317276	-2.095675
H	-2.485332	-4.181297	0.180734
C	-0.024686	2.290085	-0.320102
N	0.756174	1.323822	0.024535
C	2.094216	1.633557	0.525923
H	2.406751	2.605104	0.113655
O	2.488394	-0.653076	0.080775
H	0.363707	3.317322	-0.326015
Pd	0.428886	-0.654951	-0.092774
C	1.193626	2.921568	2.492220
H	1.269471	3.093120	3.575954
H	1.472983	3.862469	1.991366
H	0.136799	2.708526	2.274217
C	3.537805	2.092543	2.551291
H	3.895513	3.048576	2.138941
H	3.556008	2.187215	3.646676
H	4.254201	1.301955	2.282548
O	0.505184	-2.625488	-0.045937
C	1.024855	-3.121375	-1.138663
O	1.243753	-2.451419	-2.134852
C	1.337003	-4.590766	-1.046201
H	0.552991	-5.129360	-0.497580
H	1.466160	-5.006505	-2.052569
H	2.275384	-4.717845	-0.484884
H	-1.597809	-0.881450	-2.431570
C	-1.390934	2.154514	-0.669734
C	-2.233974	3.201097	-1.024653
C	-3.524328	2.657040	-1.229800
H	-1.933333	4.243361	-1.116743
C	-3.418542	1.260466	-0.983888
C	-4.772299	3.206301	-1.591438
C	-4.522984	0.404687	-1.075707
C	-5.859300	2.361539	-1.688824
H	-4.870175	4.275959	-1.787362
C	-5.733012	0.976881	-1.430504
H	-4.438448	-0.664350	-0.874208
H	-6.835955	2.762330	-1.966676
H	-6.617198	0.340804	-1.511858
N	-2.112373	0.967710	-0.651544
C	-1.737137	-0.378822	-0.335658
C	-2.283504	-2.268533	1.166406

C	-2.063827	-0.869109	0.995056
C	2.113590	1.765347	2.095312
C	2.983395	0.501683	0.040226
N	4.221852	0.666291	-0.400869
C	4.944975	-0.535075	-0.851557
H	6.009181	-0.260545	-0.877402
H	4.822161	-1.304133	-0.075205
C	4.912440	1.945984	-0.521016
H	5.877587	1.850740	0.002508
H	4.350029	2.708188	0.027645
C	4.480205	-1.071138	-2.194541
H	5.098325	-1.939310	-2.466479
H	3.433215	-1.404678	-2.158808
H	4.589304	-0.321519	-2.991165
C	5.125202	2.380370	-1.959390
H	5.756186	1.671953	-2.514235
H	4.167494	2.475259	-2.492899
H	5.629612	3.357185	-1.978596
C	-2.202042	-0.004085	2.100741
C	-2.562057	-2.763174	2.464529
C	-2.486352	-0.517208	3.348949
H	-2.083407	1.071795	1.955764
C	-2.652659	-1.905821	3.537223
H	-2.710911	-3.837128	2.597712
H	-2.590635	0.158283	4.200970
H	-2.869619	-2.295176	4.533812
C	1.642928	0.486432	2.790154
H	0.614670	0.215468	2.506025
H	2.291868	-0.373031	2.573017
H	1.649744	0.646365	3.878686

TS(1-2)[7]

Lowest frequency = -225.8320 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	1.199263	-0.188554	-1.413910
C	1.244293	0.561886	-2.628133
C	2.017472	1.688035	-2.730198
H	0.653945	0.216351	-3.479988
H	2.046815	2.258225	-3.661686
C	-0.155725	0.315710	1.837140
N	-0.871081	0.458995	0.770208
C	-2.146629	1.163385	0.870443
H	-2.307312	1.442907	1.923934
O	-2.835769	-0.652252	-0.497973
H	-0.566239	0.682472	2.789807

Pd	-0.806326	-0.615953	-0.928006
C	-0.867384	3.262872	0.407640
H	-0.883492	4.255277	-0.065970
H	-0.781079	3.416893	1.495564
H	0.036683	2.742075	0.060204
C	-3.361440	3.335785	0.430222
H	-3.375146	3.574391	1.505514
H	-3.334225	4.291582	-0.112826
H	-4.306670	2.840672	0.162873
O	-1.038344	-1.802544	-2.518438
C	-0.144327	-2.692475	-2.754699
O	0.962467	-2.727873	-2.192750
C	-0.519206	-3.739489	-3.763433
H	-1.223458	-3.337029	-4.501147
H	0.381585	-4.136248	-4.246047
H	-1.017231	-4.563662	-3.229709
H	1.064402	-1.407656	-1.559793
C	1.120833	-0.308424	1.933389
C	1.665983	-0.865327	3.082951
C	2.892697	-1.476215	2.716525
H	1.196644	-0.868501	4.065477
C	3.073250	-1.229268	1.327808
C	3.876593	-2.197789	3.424412
C	4.214628	-1.649054	0.636723
C	4.998448	-2.621978	2.740900
H	3.750716	-2.410587	4.487913
C	5.164186	-2.346942	1.363196
H	4.340482	-1.446377	-0.427971
H	5.774852	-3.181111	3.266612
H	6.064446	-2.702720	0.857322
N	1.978749	-0.533114	0.860932
C	1.984925	0.223716	-0.341719
C	2.797844	2.136639	-1.630818
C	2.792795	1.388987	-0.408402
C	-2.141712	2.498615	0.040637
C	-3.186629	0.151305	0.401679
N	-4.418618	0.081858	0.892938
C	-5.322572	-0.921087	0.309202
H	-6.342864	-0.613480	0.579787
H	-5.233535	-0.846168	-0.784132
C	-4.927711	0.864749	2.014847
H	-5.864759	1.344034	1.687832
H	-4.231510	1.682003	2.224239
C	-5.045287	-2.347270	0.751271
H	-5.770294	-3.022316	0.273978
H	-4.039635	-2.663052	0.443339
H	-5.138260	-2.468224	1.839417
C	-5.161664	0.043355	3.269612
H	-5.930491	-0.728013	3.122903
H	-4.236664	-0.452694	3.600514

H	-5.507362	0.701809	4.079549
C	3.561036	1.853718	0.692915
C	3.582809	3.312864	-1.707386
C	4.304685	3.003922	0.583893
H	3.557742	1.291278	1.628059
C	4.319918	3.736430	-0.625748
H	3.593083	3.879065	-2.641531
H	4.891588	3.355002	1.435152
H	4.921907	4.644900	-0.698093
C	-2.177036	2.261117	-1.469323
H	-1.295687	1.705982	-1.823752
H	-3.077117	1.715711	-1.789036
H	-2.177075	3.232879	-1.985095

I-2[7]

Lowest frequency = 18.4300 cm^{-1}

Charge = 1, Multiplicity = 1

74

C	1.072670	-1.156452	0.371755
C	1.353039	-2.542749	0.514783
C	2.506848	-3.085435	0.005766
H	0.643905	-3.183654	1.045465
H	2.719579	-4.149383	0.137362
C	-0.462293	1.157606	-1.518340
N	-1.100712	0.201515	-0.931290
C	-2.454506	-0.123086	-1.374237
H	-2.714491	0.558607	-2.199513
O	-2.843115	-0.128803	0.974121
H	-0.968933	1.690475	-2.337068
Pd	-0.736988	-0.577854	0.866112
C	-1.406799	-1.786296	-2.919228
H	-1.512954	-2.758719	-3.421856
H	-1.392384	-1.009568	-3.701012
H	-0.433907	-1.778158	-2.406374
C	-3.890845	-1.727228	-2.691161
H	-3.977625	-1.007313	-3.520502
H	-3.953911	-2.734040	-3.128948
H	-4.758800	-1.609656	-2.025419
O	-0.573516	-1.259088	2.808273
C	0.372112	-1.077393	3.581863
O	1.507963	-0.560165	3.210917
C	0.287698	-1.450269	5.018255
H	-0.725706	-1.780172	5.267032
H	1.009116	-2.256487	5.220187
H	0.581483	-0.591739	5.638719
H	1.501843	-0.449190	2.229713

C	0.808785	1.692038	-1.148721
C	1.142608	3.032302	-1.295779
C	2.320459	3.258750	-0.537944
H	0.552109	3.773841	-1.831701
C	2.691146	2.005393	0.021419
C	3.103935	4.399872	-0.268919
C	3.829988	1.861114	0.823843
C	4.220933	4.258264	0.530234
H	2.828789	5.371171	-0.685103
C	4.576255	3.000780	1.070302
H	4.116140	0.892494	1.236477
H	4.843274	5.127068	0.753160
H	5.464790	2.927277	1.701293
N	1.768639	1.057460	-0.369889
C	1.986089	-0.347721	-0.280668
C	3.426280	-2.289233	-0.722581
C	3.158346	-0.896061	-0.897720
C	-2.565310	-1.583150	-1.940440
C	-3.331670	0.134131	-0.146115
N	-4.568391	0.623601	-0.235377
C	-5.314515	0.791680	1.018730
H	-6.376036	0.869557	0.742526
H	-5.191677	-0.132993	1.600915
C	-5.212509	1.085903	-1.459774
H	-6.205789	0.611248	-1.512512
H	-4.657116	0.705916	-2.321993
C	-4.879601	1.984105	1.853134
H	-5.490932	2.033385	2.765965
H	-3.828767	1.883762	2.155818
H	-5.003632	2.933297	1.313583
C	-5.342486	2.596099	-1.546271
H	-5.981415	3.002718	-0.749934
H	-4.358705	3.085162	-1.478547
H	-5.798720	2.872924	-2.507765
C	-2.509761	-2.654897	-0.851188
H	-1.561885	-2.629852	-0.292392
H	-3.334487	-2.562024	-0.129474
H	-2.585895	-3.647428	-1.319682
C	4.042020	-0.132664	-1.703749
C	5.151451	-0.714290	-2.273536
H	3.836971	0.922632	-1.885232
C	4.589104	-2.851332	-1.307104
C	5.439537	-2.080391	-2.063199
H	5.815017	-0.111913	-2.897802
H	4.790317	-3.914378	-1.154450
H	6.330398	-2.523489	-2.513140

I-3

Lowest frequency = 20.1286 cm^{-1}

Charge = 1, Multiplicity = 1

66

C	-3.273614	-1.140575	0.130934
C	-1.102669	-1.085758	-0.975225
C	-1.317841	-2.389995	-1.477774
C	-2.511453	-3.032353	-1.246583
H	-0.542900	-2.892965	-2.067727
H	-2.692513	-4.025865	-1.663814
C	0.350415	0.845272	1.337982
N	1.039748	0.068067	0.567606
C	2.416801	-0.268093	0.922098
H	2.665291	0.287652	1.839462
C	3.266143	0.208382	-0.262376
O	2.763924	0.098641	-1.404307
H	0.848200	1.233504	2.239527
Pd	0.675995	-0.425502	-1.327206
C	2.497324	-2.694564	0.039363
H	1.507999	-2.633176	-0.441214
H	3.266817	-2.466813	-0.712873
H	2.635841	-3.740485	0.351205
C	3.969215	-1.981511	1.906983
H	4.094593	-1.368080	2.813179
H	4.091853	-3.032684	2.205307
H	4.781459	-1.745537	1.205270
C	-0.952583	1.367099	1.110195
C	-1.331096	2.629729	1.558523
C	-2.508659	2.989020	0.860546
H	-0.763598	3.246801	2.253678
C	-2.835192	1.889200	0.019404
C	-3.320917	4.143145	0.850651
C	-3.953674	1.913380	-0.824177
C	-4.420144	4.164894	0.017745
H	-3.077996	4.996308	1.487280
C	-4.726783	3.060764	-0.812610
H	-4.198970	1.066648	-1.466008
H	-5.064453	5.045693	-0.010367
H	-5.598604	3.118448	-1.468135
N	-1.893962	0.896996	0.201020
C	-2.070196	-0.449077	-0.227023
C	2.594990	-1.787709	1.266231
N	4.483478	0.734719	-0.119773
C	5.147375	1.205584	-1.342511
H	6.229485	1.153576	-1.167511
H	4.909296	0.495334	-2.143776
C	5.110242	1.111554	1.146490
H	5.140239	2.214079	1.188735
H	4.465157	0.787899	1.969343
C	4.724425	2.610188	-1.733611

H	5.263945	2.923119	-2.639004
H	3.647805	2.648315	-1.952384
H	4.951154	3.342859	-0.944235
C	6.507776	0.554972	1.352400
H	6.528321	-0.541109	1.278141
H	7.233236	0.961658	0.634528
H	6.859638	0.832849	2.356207
C	-3.501406	-2.439907	-0.424415
C	1.506314	-2.165688	2.272203
H	1.524970	-1.510927	3.158515
H	0.502297	-2.116170	1.826153
H	1.666411	-3.196233	2.621051
C	-4.231378	-0.617321	1.038880
C	-4.698567	-3.130881	-0.105767
C	-5.370767	-1.325149	1.343728
H	-4.058701	0.348593	1.513571
C	-5.619865	-2.584200	0.754291
H	-4.867869	-4.115027	-0.549080
H	-6.089231	-0.909083	2.053374
H	-6.536458	-3.126106	0.996127

I-4

Lowest frequency = 21.1833 cm^{-1}

Charge = 1, Multiplicity = 1

79

C	1.029206	1.039586	-1.010681
C	1.232094	2.111294	-1.909667
C	2.332673	2.924080	-1.777713
H	0.524566	2.294841	-2.721933
H	2.498143	3.739134	-2.486653
C	-0.505472	0.386164	1.875220
N	-1.112836	0.819058	0.819121
C	-2.478138	1.313109	0.934985
H	-2.732742	1.376751	2.004893
O	-2.808784	-0.313638	-0.773344
H	-1.027392	0.458318	2.842044
C	-1.507094	3.609400	0.895195
H	-1.642044	4.654799	0.581412
H	-1.489575	3.593194	1.996846
H	-0.526120	3.271275	0.530071
C	-3.987233	3.330104	0.785761
H	-4.067676	3.383644	1.883124
H	-4.088985	4.356273	0.403767
H	-4.839184	2.753998	0.394326
C	0.750252	-0.287215	1.917123
C	1.068867	-1.265792	2.852033

C	2.246592	-1.911082	2.398111
H	0.470992	-1.523681	3.724944
C	2.638115	-1.253535	1.197995
C	3.017369	-2.988515	2.884907
C	3.794875	-1.615743	0.496191
C	4.147424	-3.356237	2.182966
H	2.724344	-3.511991	3.797254
C	4.529858	-2.672357	1.004275
H	4.080264	-1.106567	-0.424097
H	4.762325	-4.184994	2.539397
H	5.430376	-2.992624	0.475417
N	1.714071	-0.269848	0.916181
C	1.923193	0.807758	0.008751
Pd	-0.723069	0.102206	-1.052187
C	3.258096	2.735321	-0.722067
C	3.043639	1.676120	0.213179
C	-2.644446	2.751007	0.336891
C	-3.314858	0.242193	0.231859
N	-4.521990	-0.124572	0.645624
C	-5.217017	-1.168817	-0.124252
H	-6.275748	-1.108725	0.165757
H	-5.152132	-0.892228	-1.186640
C	-5.184483	0.363073	1.851616
H	-4.689588	1.279185	2.186919
H	-6.206438	0.661959	1.568434
C	-4.674204	-2.572922	0.078950
H	-4.698403	-2.871364	1.136507
H	-5.299158	-3.283081	-0.482030
H	-3.646994	-2.668832	-0.297809
C	-5.220928	-0.658181	2.973928
H	-5.705464	-0.218509	3.857653
H	-5.790783	-1.556139	2.697144
H	-4.205408	-0.973032	3.259021
N	0.699910	-2.749809	-1.728941
C	1.350749	-3.825420	-1.021055
H	0.800922	-4.757693	-1.201836
H	2.379035	-3.910561	-1.392905
H	1.380970	-3.627445	0.061434
C	-0.915320	-1.352777	-2.630313
H	-1.873901	-1.144167	-3.107476
C	1.371976	-1.681312	-2.312926
C	-0.675097	-2.639095	-1.869582
O	2.562614	-1.547598	-2.385793
O	-1.494702	-3.418630	-1.461223
C	0.306167	-0.760294	-2.854558
H	0.555503	0.024608	-3.567561
C	-2.597997	2.766821	-1.191271
H	-1.647656	2.371431	-1.581184
H	-3.420856	2.191644	-1.640685
H	-2.684714	3.804977	-1.544389

C	3.926351	1.556668	1.317058
C	4.372857	3.595221	-0.553102
C	4.989326	2.418985	1.460033
H	3.761725	0.779367	2.063676
C	5.226464	3.438590	0.512410
H	4.534946	4.392303	-1.282634
H	5.656810	2.313347	2.318089
H	6.080985	4.107061	0.635805

TS(4-5)

Lowest frequency = -251.9944 cm^{-1}

Charge = 1, Multiplicity = 1

79

C	1.133136	0.424407	-1.444001
C	1.230415	1.350986	-2.518673
C	2.154804	2.361491	-2.491771
H	0.565835	1.245381	-3.380023
H	2.223505	3.064499	-3.325307
C	-0.209320	0.528047	1.830262
N	-0.909994	0.842452	0.795210
C	-2.208669	1.469185	0.976923
H	-2.395141	1.603942	2.055029
O	-2.840291	-0.173001	-0.637019
H	-0.609483	0.755332	2.831606
C	-1.058522	3.680680	0.854042
H	-1.107622	4.719840	0.497098
H	-1.048088	3.708577	1.955692
H	-0.105368	3.252502	0.510930
C	-3.550186	3.600355	0.725369
H	-3.629785	3.722458	1.817044
H	-3.568435	4.608311	0.285896
H	-4.444165	3.072340	0.360862
C	1.043650	-0.157323	1.842779
C	1.541275	-0.835008	2.945823
C	2.741899	-1.477956	2.549930
H	1.060218	-0.882288	3.921822
C	2.957420	-1.133812	1.189356
C	3.680573	-2.287082	3.223336
C	4.104671	-1.535199	0.498566
C	4.805312	-2.695458	2.535714
H	3.520567	-2.572326	4.265097
C	5.013980	-2.316104	1.189426
H	4.261005	-1.262800	-0.544580
H	5.550779	-3.318488	3.033735
H	5.916161	-2.657734	0.677382
N	1.900004	-0.352114	0.755329
C	1.994191	0.524857	-0.362401

Pd	-0.789618	-0.127644	-1.044580
C	3.031629	2.514084	-1.387442
C	2.941774	1.595813	-0.294462
C	-2.256563	2.892736	0.319561
C	-3.206244	0.480218	0.371444
N	-4.423871	0.280565	0.863080
C	-5.287607	-0.686740	0.166524
H	-6.312602	-0.481106	0.506830
H	-5.243329	-0.455097	-0.907466
C	-4.955526	0.887572	2.078955
H	-4.317171	1.727006	2.369222
H	-5.934370	1.327521	1.828610
C	-4.919740	-2.143004	0.391979
H	-4.909258	-2.402882	1.459980
H	-5.666056	-2.781559	-0.102517
H	-3.943749	-2.380096	-0.051165
C	-5.091809	-0.091334	3.230989
H	-5.470787	0.434830	4.119026
H	-5.796745	-0.902921	3.002537
H	-4.121218	-0.543045	3.486624
N	-0.161143	-3.258852	-1.286529
C	-0.244821	-4.455041	-0.487611
H	-1.185597	-4.962029	-0.735568
H	0.610041	-5.106876	-0.710824
H	-0.231238	-4.212574	0.586097
C	-0.739291	-1.445097	-2.620351
H	-1.225381	-1.079133	-3.528103
C	1.014504	-2.565723	-1.497950
C	-1.248618	-2.696040	-1.963117
O	2.108408	-2.899251	-1.131660
O	-2.359630	-3.154841	-1.984605
C	0.657202	-1.357247	-2.344118
H	1.399244	-1.069391	-3.088291
C	-2.185876	2.834412	-1.206485
H	-1.255371	2.362037	-1.556213
H	-3.036725	2.293654	-1.646115
H	-2.199060	3.858656	-1.607997
C	3.766649	1.810354	0.841044
C	4.659956	2.856355	0.869104
H	3.695334	1.141480	1.698958
C	3.972327	3.571121	-1.331466
C	4.775458	3.738073	-0.227710
H	5.287555	3.005291	1.750346
H	4.041713	4.257622	-2.178499
H	5.496182	4.557644	-0.191843

I-5

Lowest frequency = 20.0041 cm^{-1}

Charge = 1, Multiplicity = 1

79

C	1.567091	-0.063901	-1.804456
C	1.508493	0.794207	-2.963611
C	1.528984	2.149264	-2.872882
H	1.450292	0.311496	-3.941183
H	1.486699	2.760449	-3.777187
C	-0.264506	0.340290	1.884852
N	-0.961537	0.711088	0.866815
C	-2.364313	1.050408	0.973932
H	-2.663379	1.068419	2.035277
O	-2.514535	-0.603319	-0.758927
H	-0.706606	0.361102	2.893595
C	-1.766191	3.461619	1.164037
H	-1.966280	4.488648	0.824749
H	-1.984563	3.419792	2.243414
H	-0.694931	3.264932	1.018546
C	-4.103532	2.857413	0.542085
H	-4.407011	2.892174	1.599539
H	-4.264275	3.863909	0.129084
H	-4.775670	2.174117	0.001968
C	1.092764	-0.112287	1.830663
C	1.845612	-0.496392	2.929204
C	3.175579	-0.720916	2.488979
H	1.464926	-0.591630	3.945044
C	3.195091	-0.453209	1.094898
C	4.369506	-1.078433	3.147536
C	4.377297	-0.476892	0.353339
C	5.535882	-1.119839	2.410199
H	4.368048	-1.301016	4.216419
C	5.537151	-0.811491	1.031299
H	4.386827	-0.260813	-0.714773
H	6.476594	-1.386924	2.895417
H	6.480314	-0.846716	0.481996
N	1.904175	-0.155116	0.684789
C	1.629985	0.550551	-0.525207
Pd	-0.484435	-0.202103	-0.944635
C	-2.632204	2.476208	0.377105
C	-3.093925	-0.071219	0.223492
N	-4.306837	-0.492468	0.563168
C	-4.933116	-1.529750	-0.273266
H	-6.014847	-1.456229	-0.088361
H	-4.758040	-1.253148	-1.322660
C	-5.065439	-0.039916	1.725209
H	-4.570115	0.833376	2.158307
H	-6.044643	0.316334	1.365824
C	-4.426092	-2.938160	-0.021641
H	-4.569084	-3.245736	1.023603
H	-4.990071	-3.637894	-0.655775

H	-3.366042	-3.036473	-0.289818
C	-5.247678	-1.110509	2.785567
H	-5.789321	-0.685947	3.643181
H	-5.832280	-1.964621	2.417028
H	-4.277711	-1.487655	3.143151
N	0.855360	-3.303872	-0.734968
C	0.934777	-4.398890	0.197466
H	-0.028286	-4.923664	0.179552
H	1.746450	-5.080376	-0.091333
H	1.139539	-4.026866	1.212679
C	-0.008470	-1.731084	-2.217108
H	-0.524783	-1.665845	-3.180913
C	1.960065	-2.577902	-1.125664
C	-0.325675	-2.931044	-1.386826
O	3.088776	-2.785785	-0.765264
O	-1.376299	-3.509234	-1.257832
C	1.490911	-1.548438	-2.147670
H	2.045687	-1.740851	-3.079721
C	-2.266036	2.548348	-1.106406
H	-1.201870	2.325376	-1.277561
H	-2.868556	1.863014	-1.720540
H	-2.445920	3.569627	-1.473675
C	1.737960	2.001979	-0.432719
C	1.983158	2.645614	0.798760
C	1.642004	2.796974	-1.606427
C	2.074688	4.022815	0.869697
H	2.116800	2.057838	1.706856
C	1.715829	4.202452	-1.505646
C	1.920762	4.810252	-0.283988
H	2.273238	4.500446	1.831375
H	1.627520	4.800477	-2.415603
H	1.985238	5.898154	-0.215552

Acetic acid
Lowest frequency = 80.3907 cm^{-1}
Charge = 0, Multiplicity = 1

8

C	0.092812	0.121660	0.000004
O	0.776498	-1.034021	0.000002
O	0.637848	1.192811	0.000001
C	-1.388123	-0.110409	-0.000001
H	-1.673482	-0.698172	0.884698
H	-1.911593	0.851449	-0.000114
H	-1.673448	-0.698350	-0.884594
H	1.715612	-0.792755	-0.000026

Maleimide
Lowest frequency = 59.2016 cm^{-1}
Charge = 0, Multiplicity = 1

```
  13

C     0.677873    -1.617181    -0.000010
C    -0.658070    -1.625990     0.000002
N    -0.004891     0.587870     0.000047
H     1.376374    -2.453228    -0.000011
H    -1.344819    -2.471715     0.000006
C    -1.144402    -0.206794     0.000005
C     1.146419    -0.192662     0.000005
O    -2.278706     0.195619    -0.000017
O     2.277282     0.219583    -0.000013
C    -0.015264     2.025645    -0.000011
H    -0.526916     2.413698    -0.892831
H    -0.527615     2.413725     0.892413
H     1.029270     2.362703     0.000384
```

I-1[P]
Lowest frequency = 7.1141 cm^{-1}
Charge = 0, Multiplicity = 1

```
  58

C    -2.550775     0.500087     0.098658
C    -3.778914     0.111797    -0.512630
C    -2.325670     1.793669     0.514021
C    -4.052149    -1.219518    -0.918832
C    -4.771415     1.119032    -0.721850
C    -3.324202     2.772332     0.315604
C    -5.247905    -1.535505    -1.521166
H    -3.306825    -1.997305    -0.740332
C    -5.991545     0.756711    -1.348168
C    -4.512429     2.446357    -0.293447
H    -3.133272     3.795369     0.646234
C    -6.225331    -0.539363    -1.742839
H    -5.445363    -2.565241    -1.827427
H    -6.745862     1.530747    -1.510738
H    -5.280039     3.207484    -0.455076
H    -7.169091    -0.804219    -2.224743
C    -0.834106    -0.675585    -2.066562
H    -1.531032     0.168141    -2.284301
H    -1.371703     2.047724     0.982265
O     2.691847    -1.596251    -1.251068
C     3.967498    -1.721297    -1.111503
```

O	4.693062	-1.011500	-0.411719
C	4.546248	-2.872436	-1.900136
H	4.169250	-2.852236	-2.931932
H	5.641545	-2.830126	-1.885593
H	4.210619	-3.819494	-1.451044
C	-0.702287	-1.010512	-0.631046
C	-1.282929	-1.083656	1.532711
C	-0.228743	-2.012329	1.359705
C	-1.887733	-0.861805	2.771935
C	0.221772	-2.757768	2.459300
C	-1.420959	-1.609317	3.842092
H	-2.686651	-0.127734	2.885256
C	-0.380988	-2.549119	3.689539
H	1.033425	-3.478879	2.342851
H	-1.867896	-1.465341	4.828333
H	-0.045180	-3.117218	4.559712
N	-1.557046	-0.501325	0.310278
O	-0.250771	-1.264780	-2.939665
C	2.843635	2.078409	0.982178
C	3.388295	3.408157	0.484819
C	3.079058	3.331155	-1.007474
H	3.320455	1.727561	1.911094
H	2.891405	4.240259	1.001588
H	4.473849	3.474567	0.659899
H	2.011487	3.547117	-1.175882
H	3.659593	4.037470	-1.617164
N	3.120436	1.113618	-0.107855
C	1.331027	2.145631	1.250180
O	0.821463	3.112388	1.773771
O	0.660728	1.092069	0.883937
Pd	1.628330	-0.268708	-0.176126
H	3.914627	0.460262	0.060232
C	0.162518	-1.947732	-0.026211
H	0.756258	-2.671749	-0.582672
C	3.390477	1.879412	-1.355971
H	4.452814	1.740539	-1.612447
H	2.795386	1.490538	-2.192770

TS(1-2)^{P}

Lowest frequency = -1011.5504 cm^{-1}

Charge = 0, Multiplicity = 1

58

C	-2.746131	0.633220	-0.013681
C	-4.040413	0.322782	-0.516998
C	-2.432013	1.893008	0.452945
C	-4.379648	-0.957695	-1.023817

C	-5.026000	1.358237	-0.517549
C	-3.411347	2.908920	0.430144
C	-5.646795	-1.206575	-1.497085
H	-3.619959	-1.741834	-1.032144
C	-6.323079	1.063436	-1.011340
C	-4.678007	2.646858	-0.036988
H	-3.150245	3.903158	0.798451
C	-6.628834	-0.189494	-1.487778
H	-5.896938	-2.196532	-1.885378
H	-7.076798	1.855002	-1.008228
H	-5.438489	3.431865	-0.046253
H	-7.631731	-0.402148	-1.865099
C	-0.323384	0.638697	-1.725016
H	-1.238826	1.162013	-2.089904
H	-1.428181	2.093703	0.842770
O	3.418004	-1.564872	-0.707822
C	3.017847	-2.477859	-1.472710
O	1.803337	-2.769482	-1.663663
C	4.042706	-3.265945	-2.233147
H	5.044012	-3.107249	-1.817590
H	3.777137	-4.331121	-2.223309
H	4.026988	-2.931867	-3.281890
C	-0.541777	-0.314078	-0.631772
C	-1.664550	-1.363535	0.992950
C	-0.365472	-1.929141	0.923956
C	-2.620344	-1.775452	1.926046
C	-0.029954	-2.960348	1.816726
C	-2.254504	-2.793619	2.793963
H	-3.608943	-1.314734	1.966056
C	-0.974081	-3.382256	2.739254
H	0.965053	-3.410239	1.782168
H	-2.973317	-3.146031	3.537337
H	-0.725950	-4.180566	3.442527
N	-1.744810	-0.375827	0.027540
O	0.755757	0.848900	-2.234211
C	3.087900	2.351711	1.161023
C	3.531274	3.425480	0.163058
C	3.828226	2.624302	-1.099958
H	3.442701	2.572028	2.179981
H	2.746634	4.185730	0.054303
H	4.445457	3.928516	0.516283
H	2.895675	2.331339	-1.610476
H	4.459053	3.160377	-1.822662
N	3.706534	1.079031	0.669983
C	1.552791	2.264625	1.264397
O	0.912685	3.275663	1.464368
O	1.035034	1.083382	1.157153
Pd	2.157108	-0.271745	0.241739
H	4.282749	0.651249	1.391416
C	0.365109	-1.250115	-0.118217

H	1.133569	-2.048775	-0.992427
C	4.514345	1.395051	-0.533173
H	5.549276	1.637406	-0.232677
H	4.540282	0.526545	-1.203945

I-2^{P}

Lowest frequency = 12.8876 cm^{-1}
Charge = 0, Multiplicity = 1

58

C	3.219220	0.804008	0.834304
C	4.109348	-0.211402	0.372427
C	3.608187	1.692574	1.813127
C	3.762252	-1.124919	-0.655682
C	5.403182	-0.301900	0.973985
C	4.895542	1.608741	2.385048
C	4.650502	-2.095229	-1.057434
H	2.781944	-1.053806	-1.128662
C	6.291500	-1.317963	0.536305
C	5.769562	0.628101	1.980604
H	5.185952	2.321507	3.159779
C	5.924440	-2.197524	-0.454394
H	4.368992	-2.790305	-1.851705
H	7.277858	-1.386898	1.002084
H	6.763372	0.551991	2.428764
H	6.618557	-2.974993	-0.781650
C	0.987229	-1.128717	1.295661
H	1.889674	-1.124987	1.954234
H	2.900311	2.456044	2.141994
O	-1.735722	-2.210844	-0.911802
C	-0.706180	-2.702147	-1.374173
O	0.311740	-1.997956	-1.771164
C	-0.541088	-4.176580	-1.496526
H	-1.519271	-4.668641	-1.524065
H	0.063093	-4.434282	-2.375103
H	-0.001535	-4.509426	-0.595391
C	0.866404	0.021015	0.413132
C	1.539046	1.906676	-0.607698
C	0.201129	1.637844	-1.005960
C	2.257695	3.007006	-1.094393
C	-0.441142	2.528661	-1.886376
C	1.598413	3.852892	-1.970845
H	3.289872	3.188365	-0.789177
C	0.259879	3.622168	-2.360048
H	-1.481127	2.351538	-2.165759
H	2.125124	4.724621	-2.366895
H	-0.225156	4.326118	-3.039816

N	1.927977	0.920027	0.264154
O	0.196470	-2.051226	1.341840
C	-4.867930	0.510123	0.283201
C	-5.706420	0.150821	1.507370
C	-4.851872	-0.917313	2.180100
H	-5.487221	0.836620	-0.566405
H	-5.889758	1.045600	2.116436
H	-6.679616	-0.270920	1.206963
H	-3.991584	-0.453560	2.689978
H	-5.394326	-1.522125	2.920248
N	-4.140248	-0.741186	-0.075258
C	-3.918488	1.690325	0.587405
O	-4.387902	2.697253	1.067167
O	-2.665483	1.535764	0.282002
Pd	-2.091843	-0.255501	-0.310035
H	-4.466652	-1.102804	-0.967813
C	-0.223372	0.428783	-0.361078
H	0.179062	-1.054341	-1.466871
C	-4.374879	-1.744213	0.996684
H	-5.163196	-2.447803	0.678835
H	-3.459463	-2.321251	1.186536

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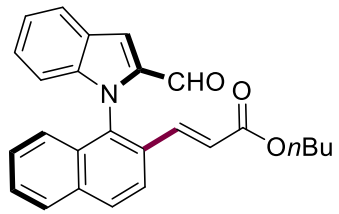

3
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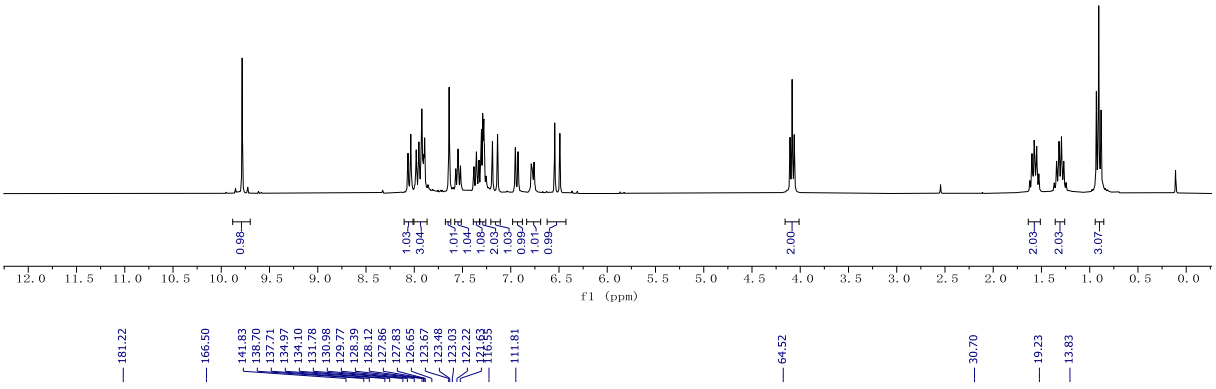

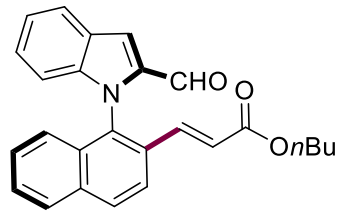

3
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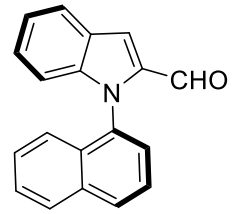
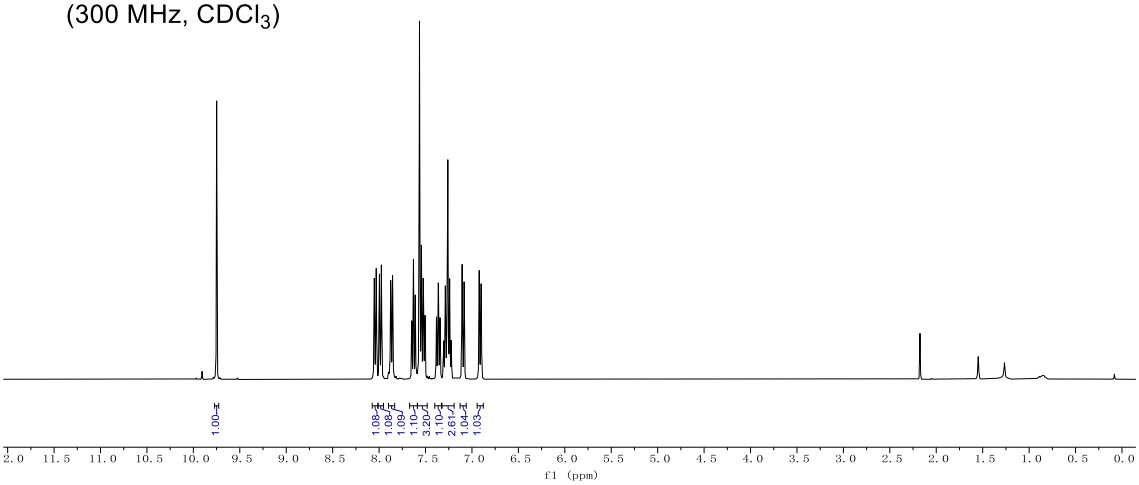
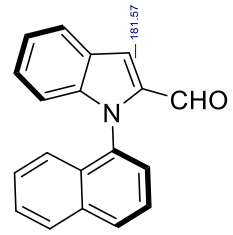
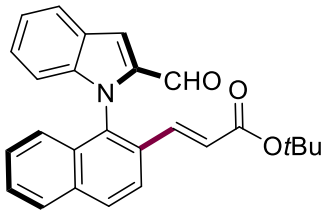


1a
(300 MHz, $CDCl_3$)



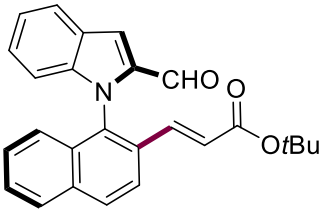


1a
(100 MHz, $CDCl_3$)



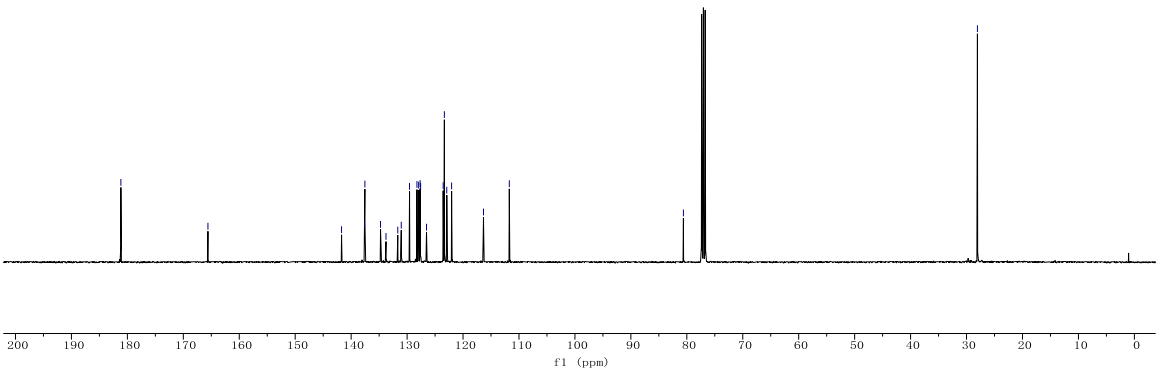
4

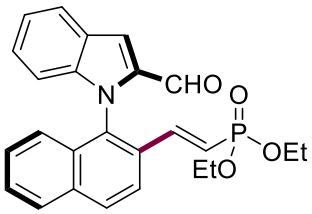
(400 MHz, $CDCl_3$)



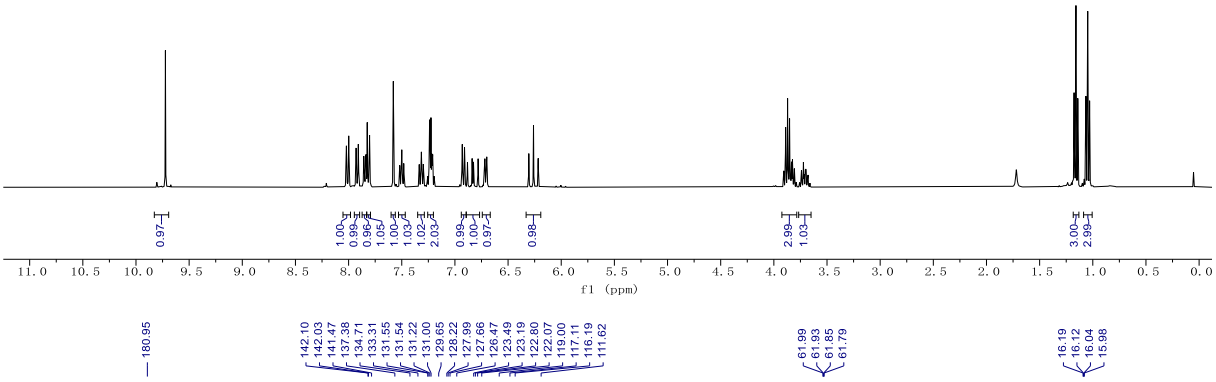
4

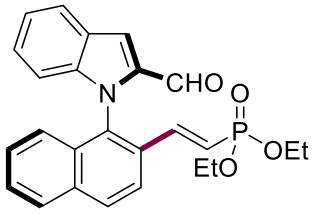
(100 MHz, $CDCl_3$)



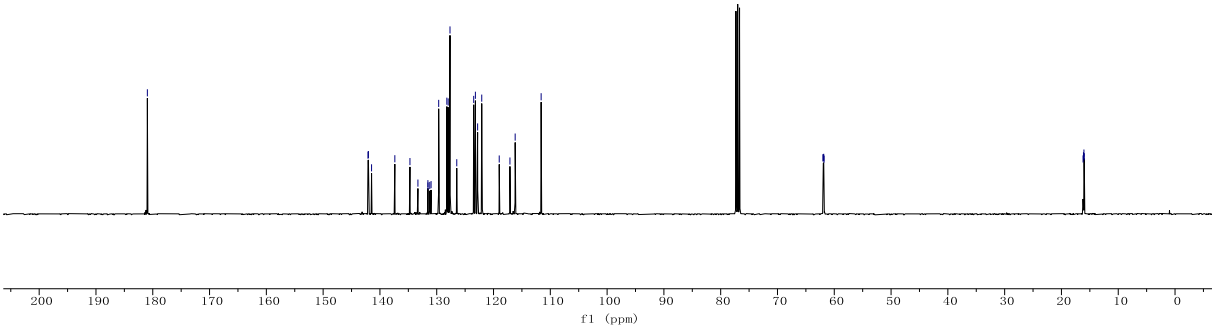


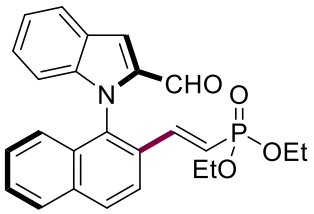
5
(400 MHz, $CDCl_3$)





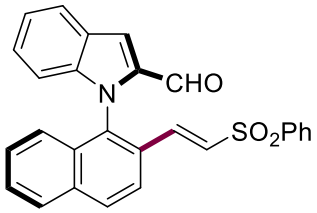
5
(100 MHz, $CDCl_3$)



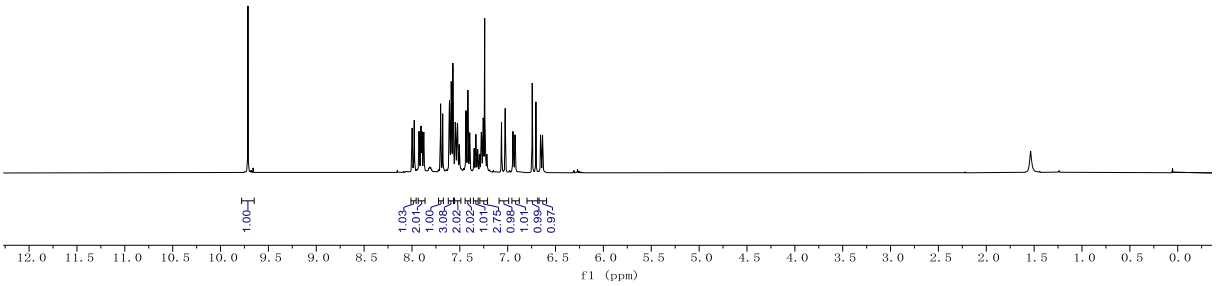


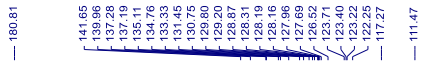
5

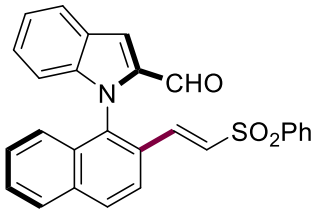
(162 MHz, $CDCl_3$)



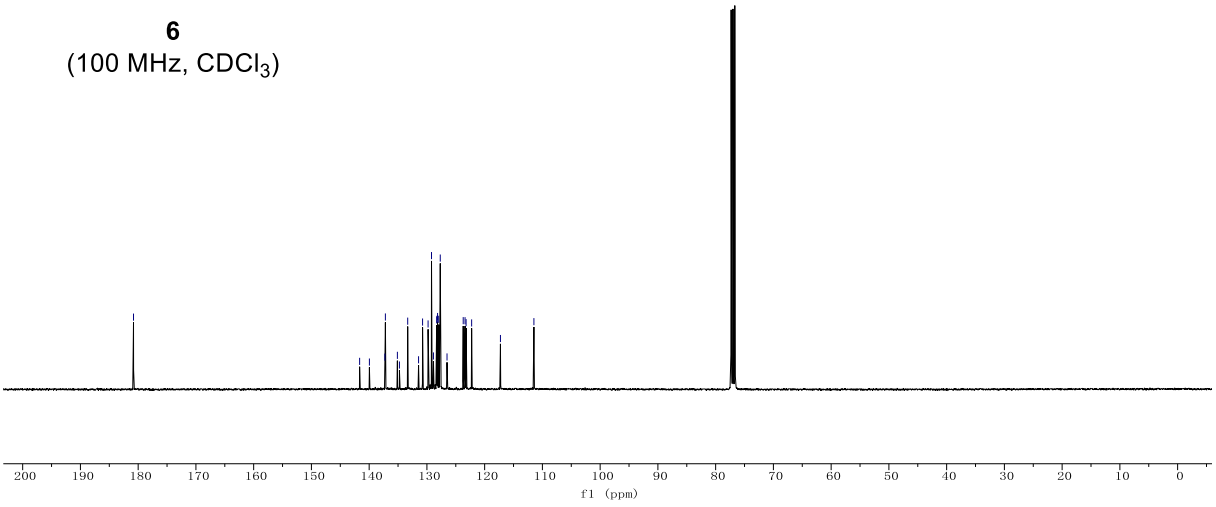
6
(400 MHz, $CDCl_3$)

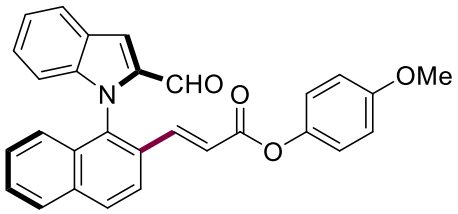






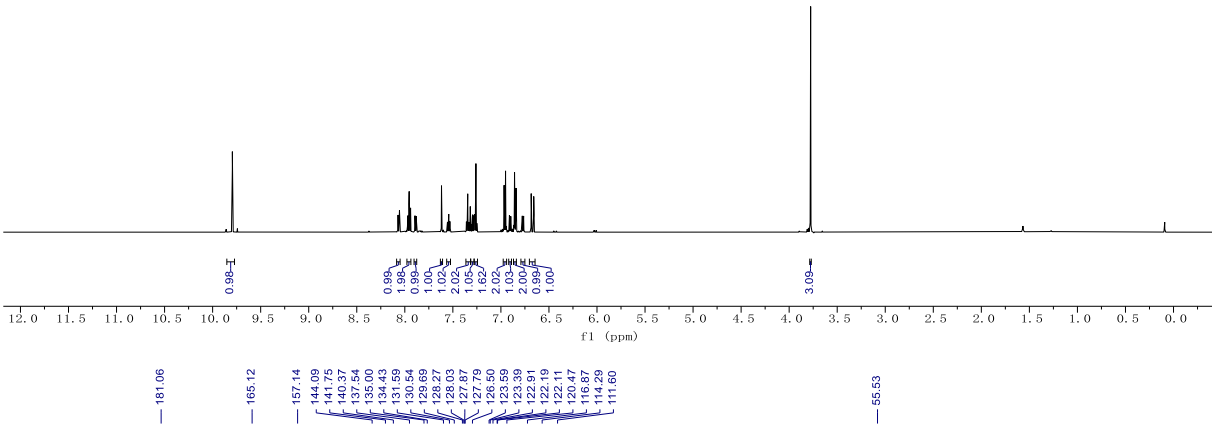
6
(100 MHz, $CDCl_3$)

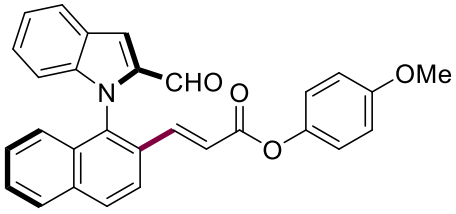




7

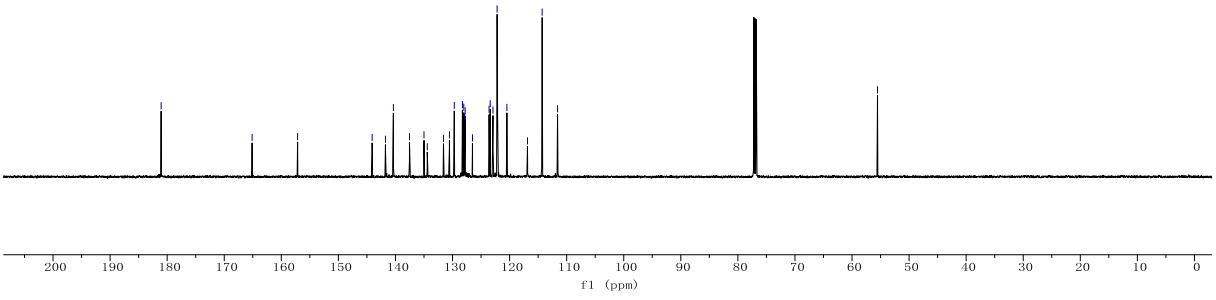
(600 MHz, $CDCl_3$)

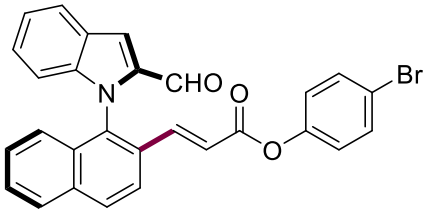




7

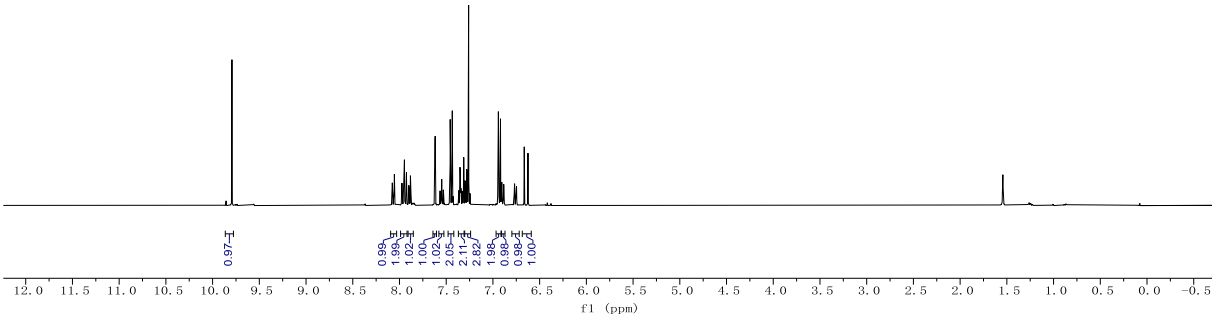
(150 MHz, $CDCl_3$)

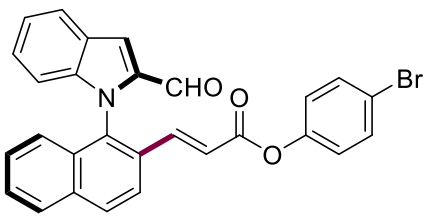




8

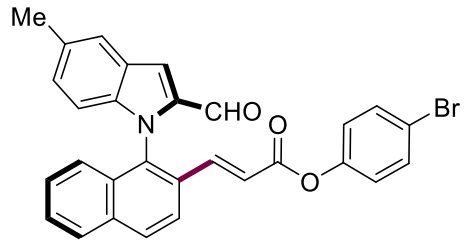
(400 MHz, $CDCl_3$)



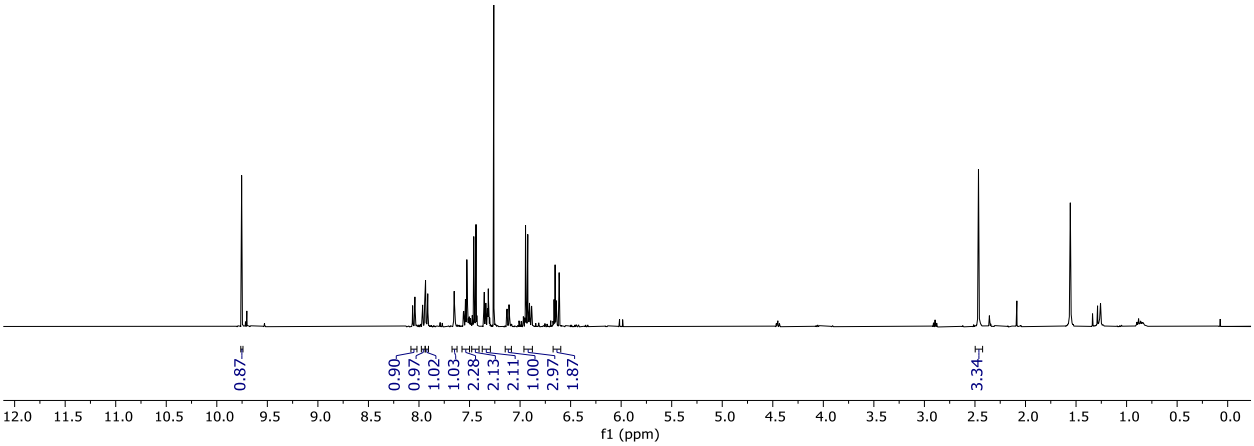


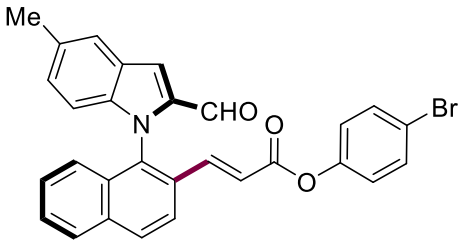
8

(100 MHz, $CDCl_3$)

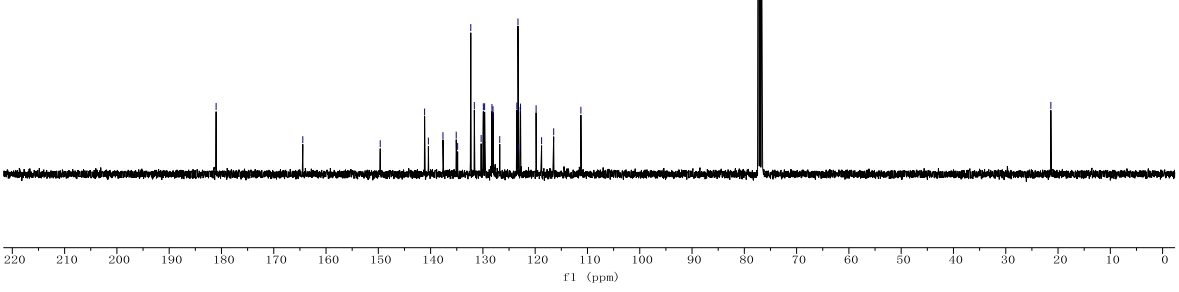


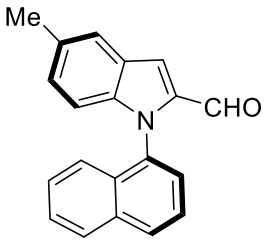
9
(400 MHz, $CDCl_3$)



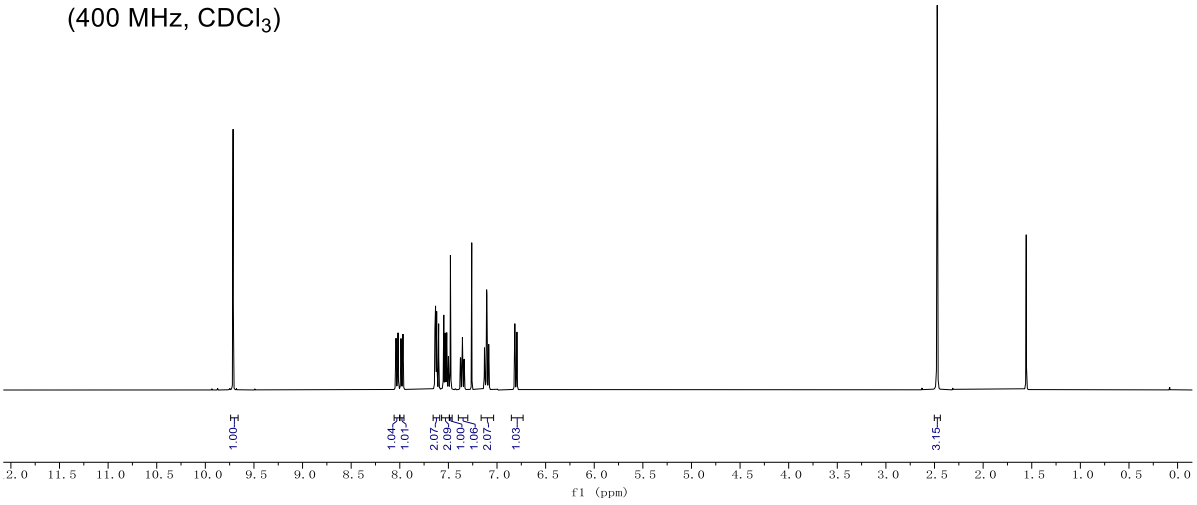


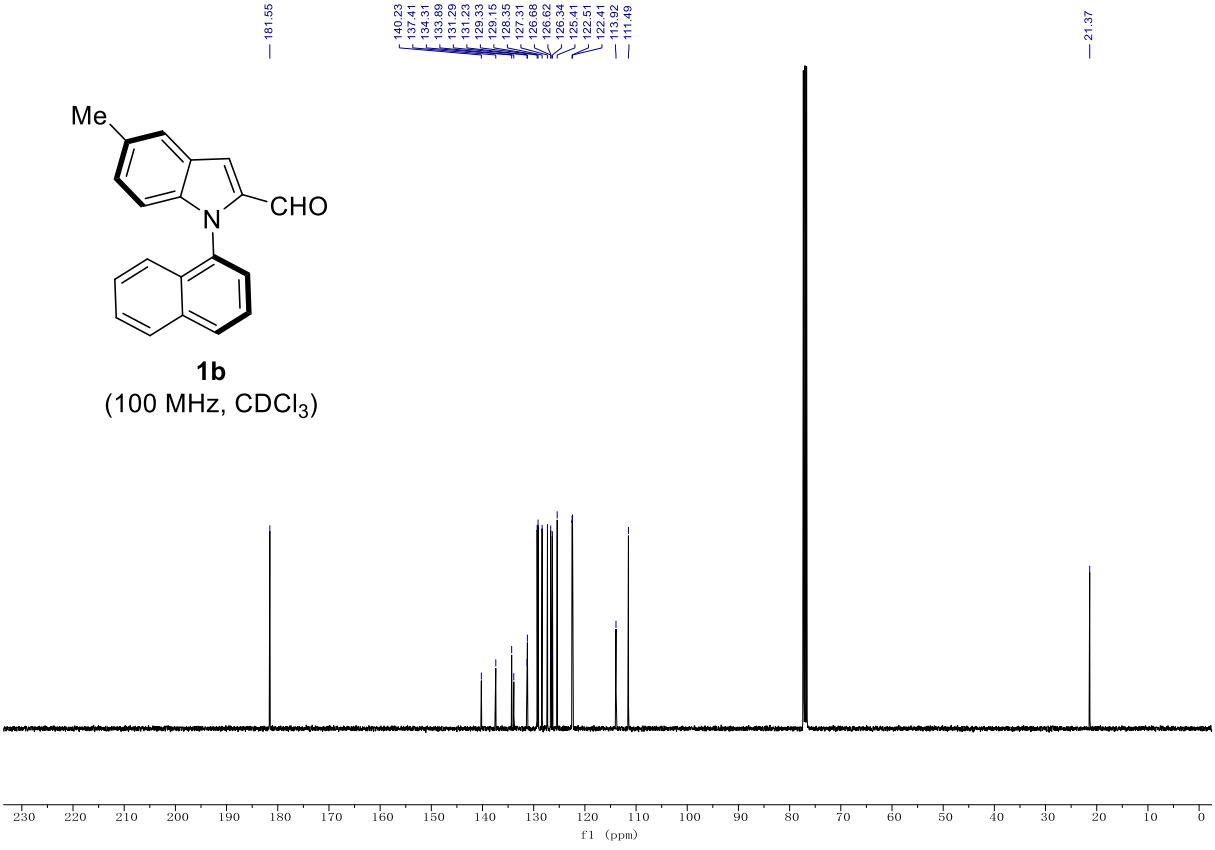
9
(100 MHz, $CDCl_3$)



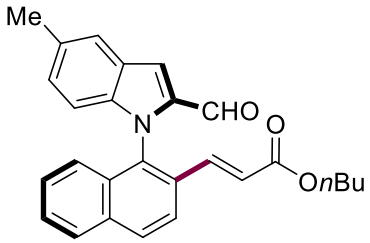


1b
(400 MHz, $CDCl_3$)

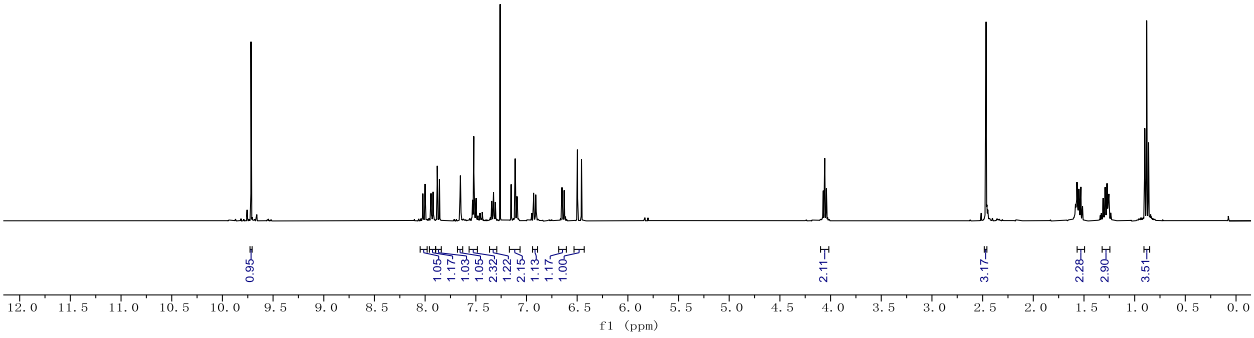


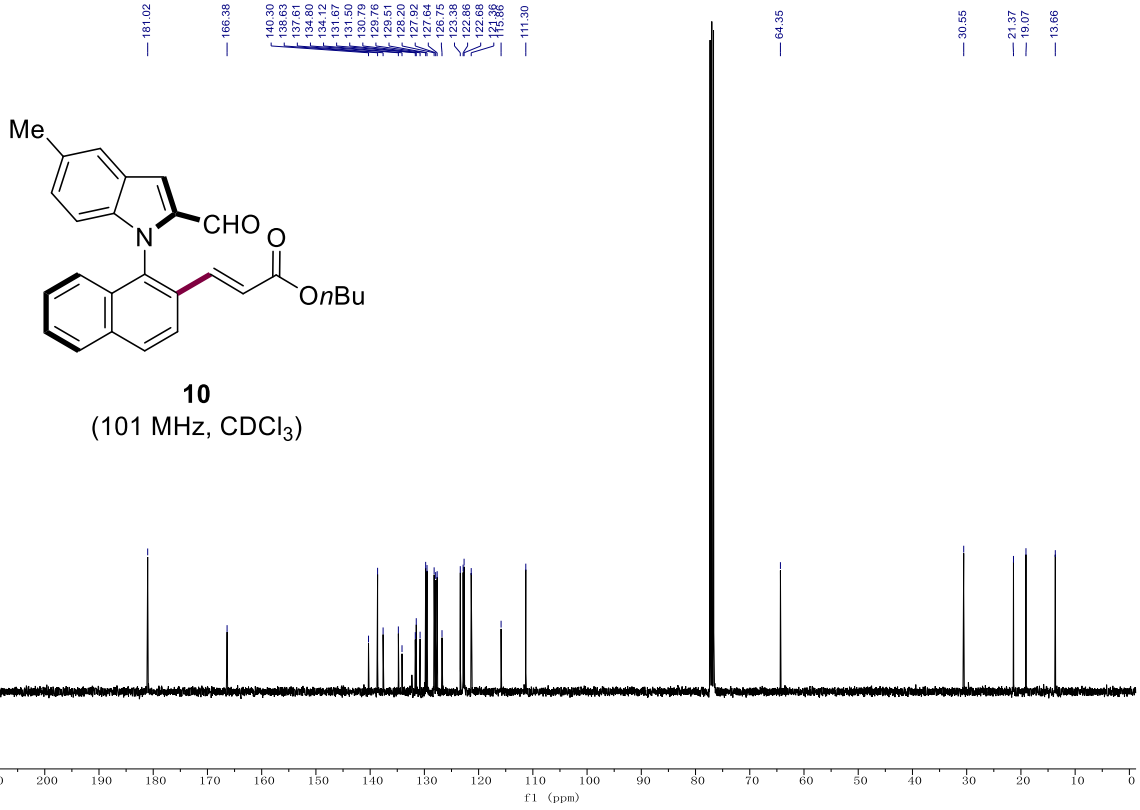


1b
(100 MHz, $CDCl_3$)

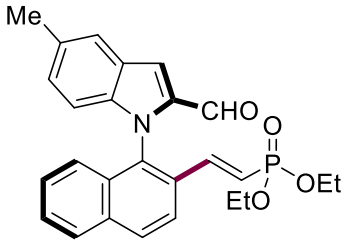


10
(400 MHz, $CDCl_3$)

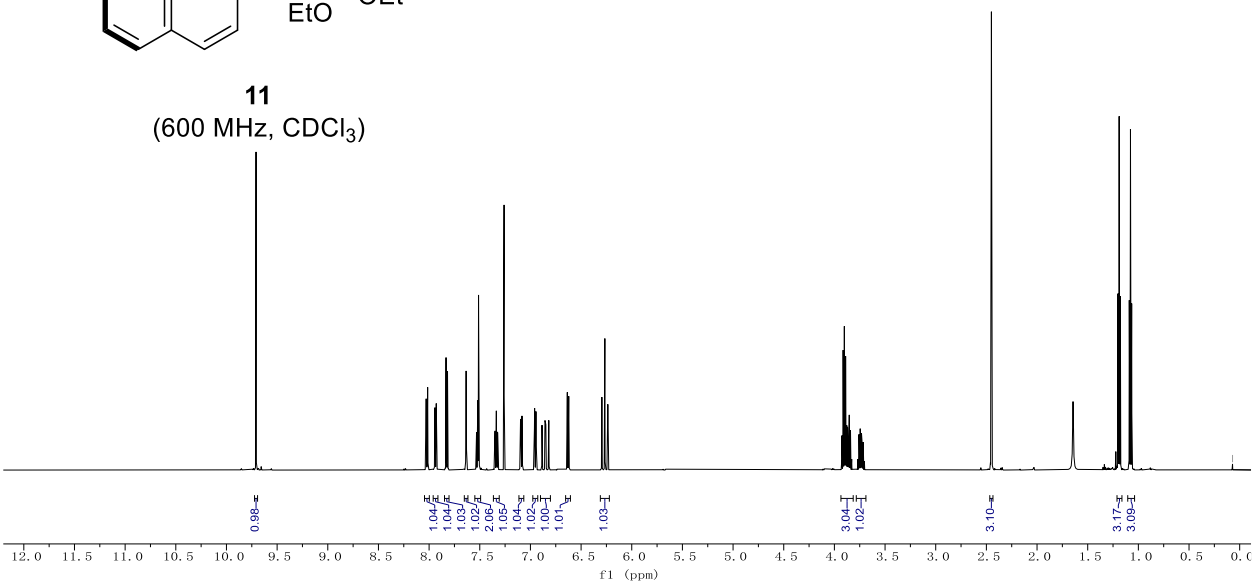


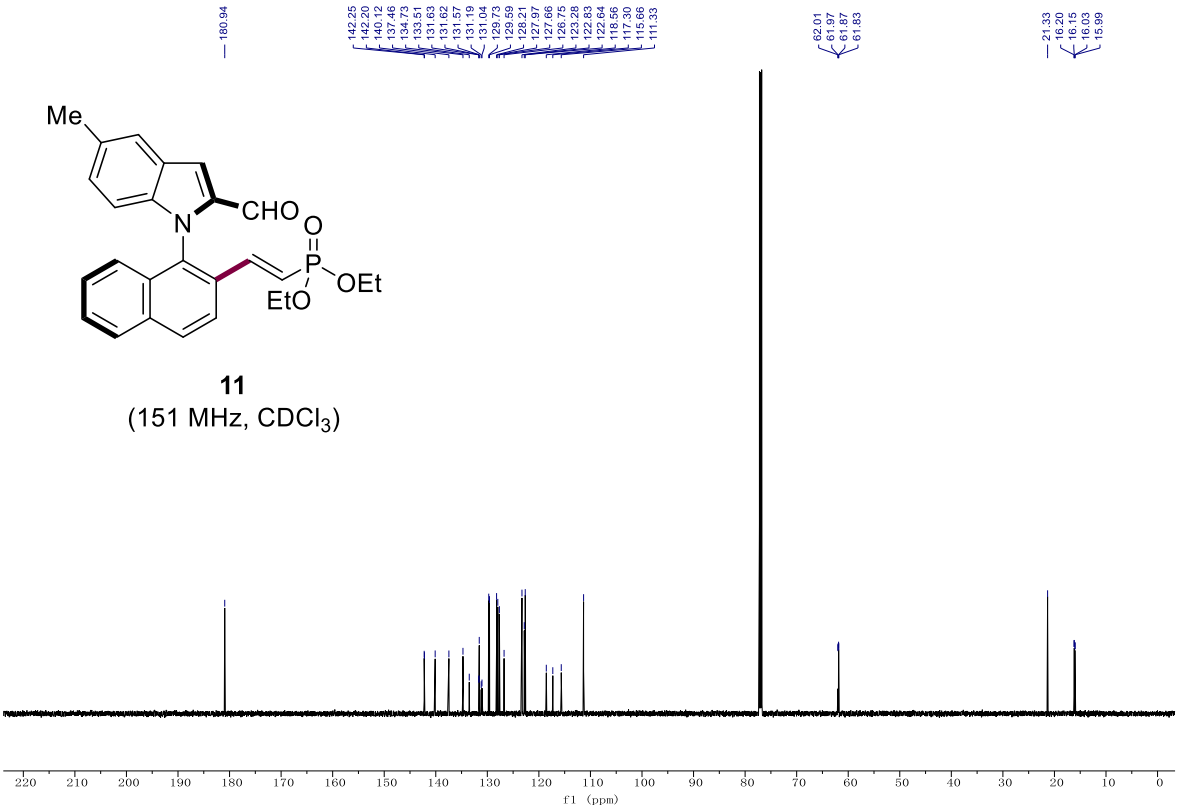


10
(101 MHz, $CDCl_3$)

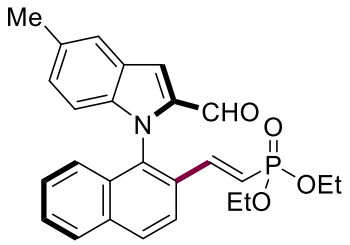


11
(600 MHz, $CDCl_3$)



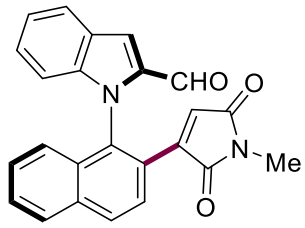


11
(151 MHz, $CDCl_3$)

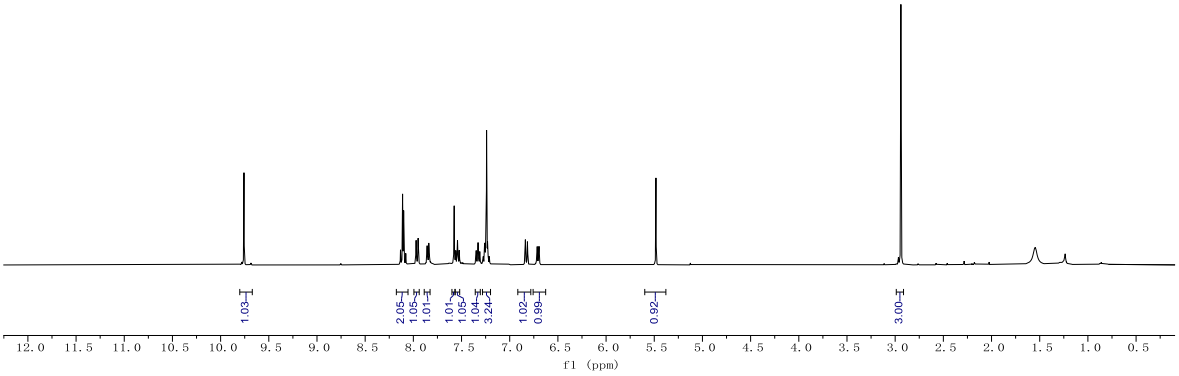


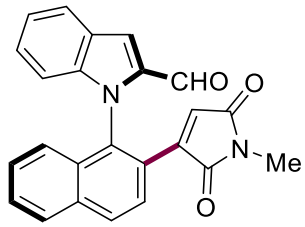
11

(243 MHz, $CDCl_3$)

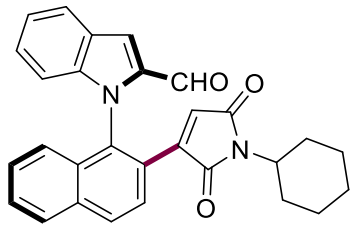


13
(400 MHz, $CDCl_3$)

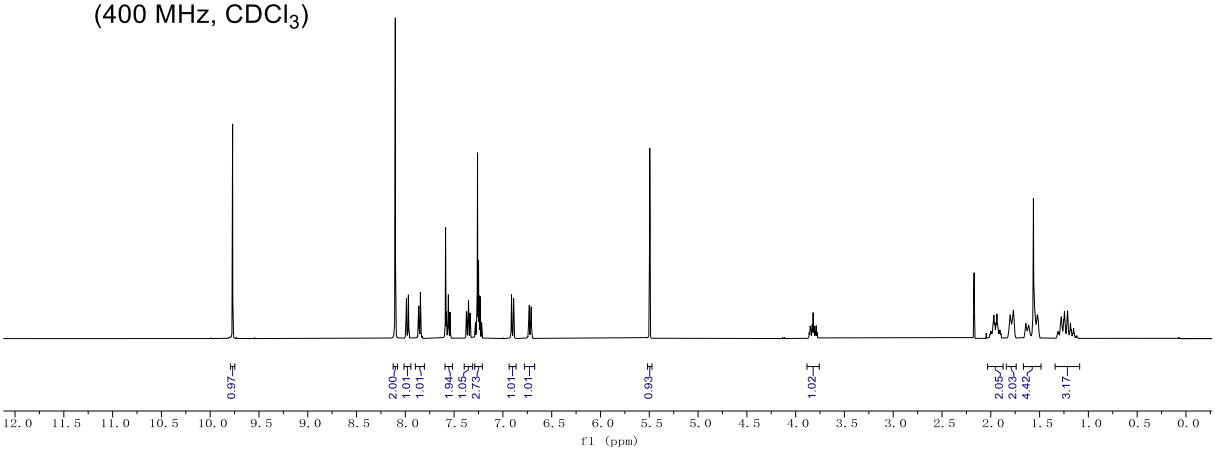


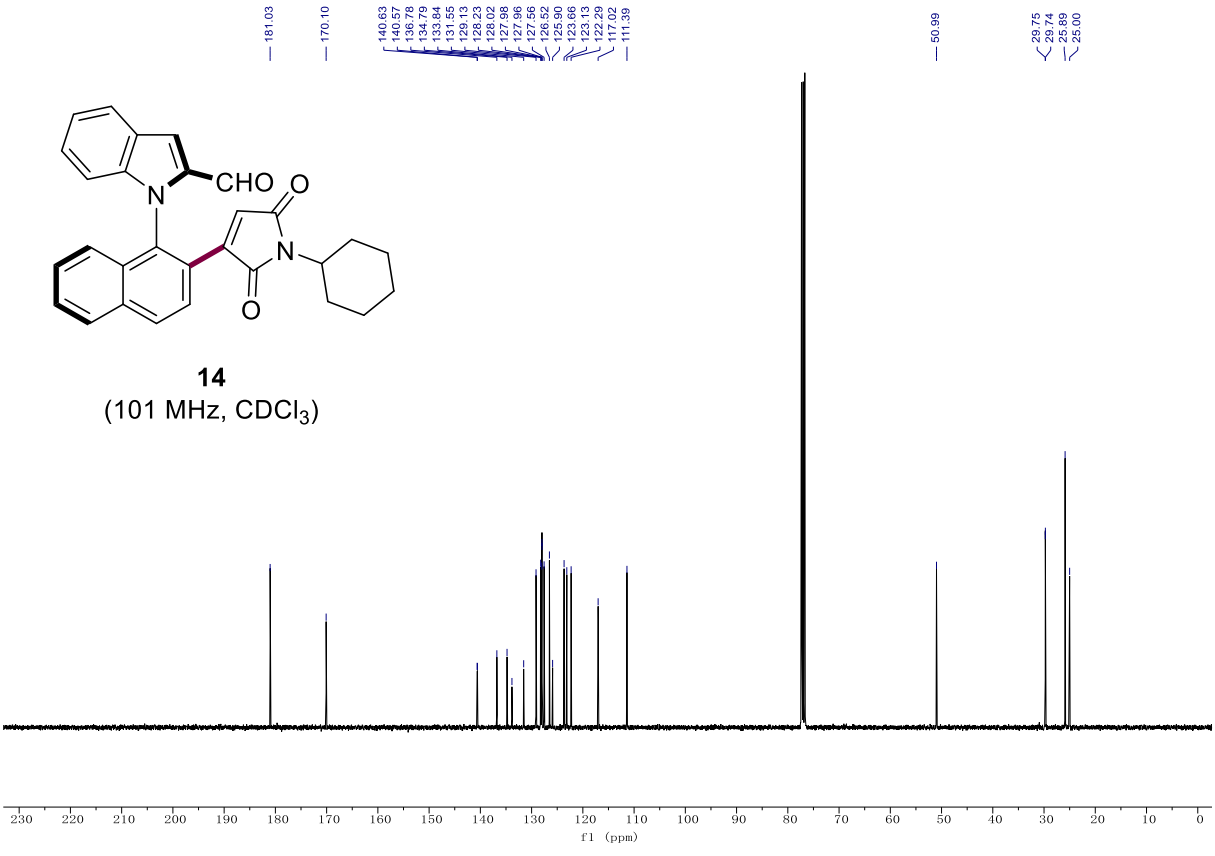


13
(100 MHz, $CDCl_3$)

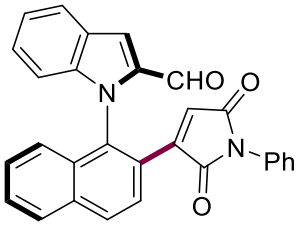


14
(400 MHz, $CDCl_3$)

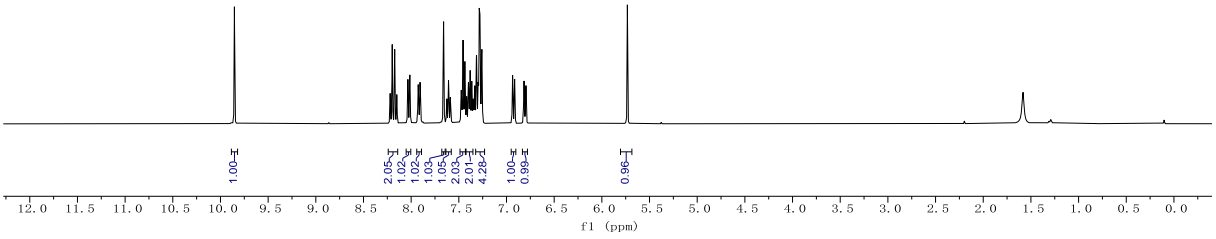


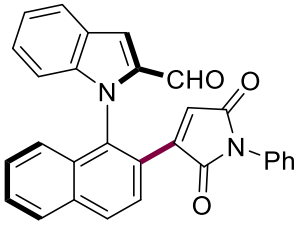


14
(101 MHz, $CDCl_3$)

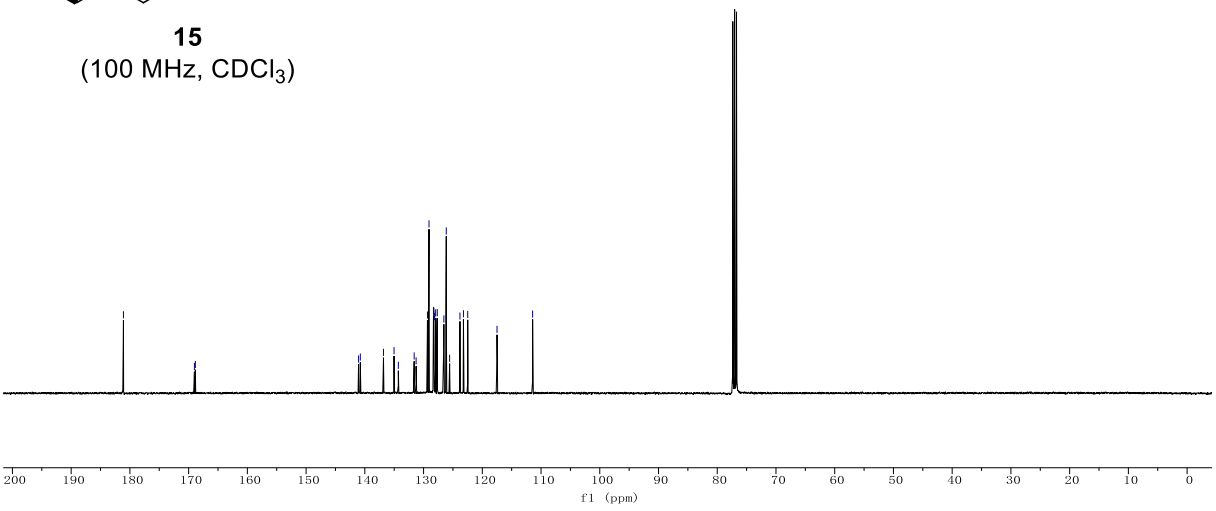


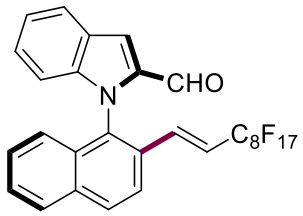
15
(400 MHz, $CDCl_3$)



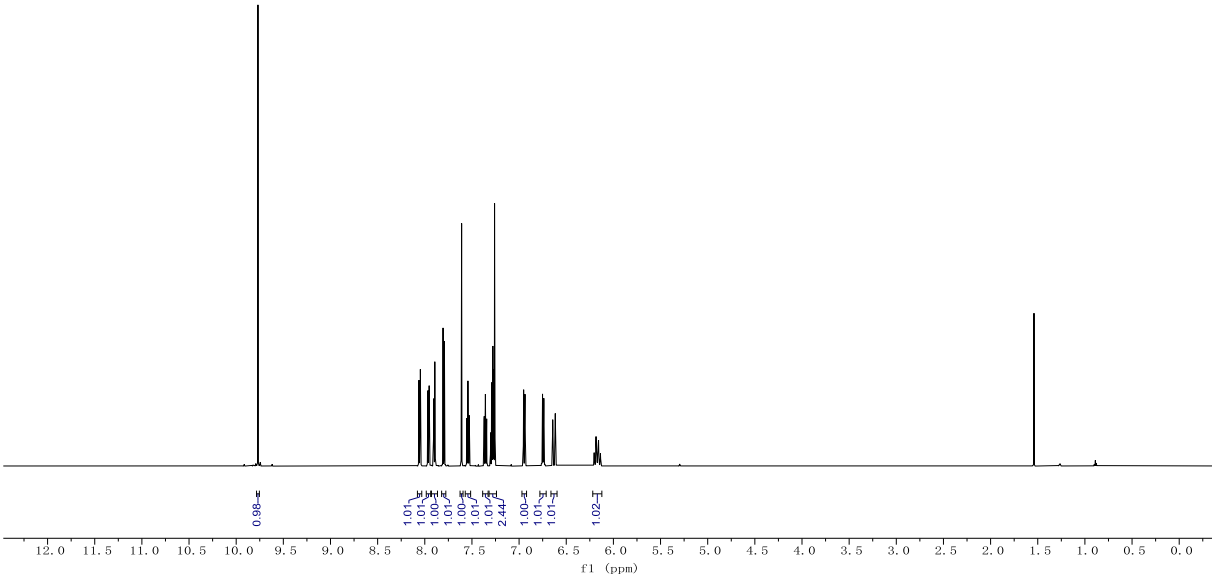


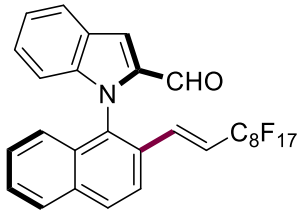
15
(100 MHz, $CDCl_3$)



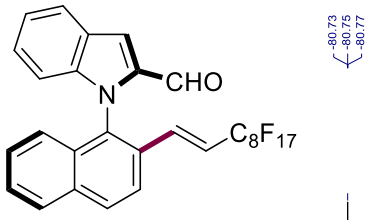


17
(600 MHz, $CDCl_3$)



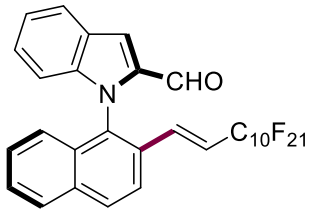


17
(151 MHz, $CDCl_3$)

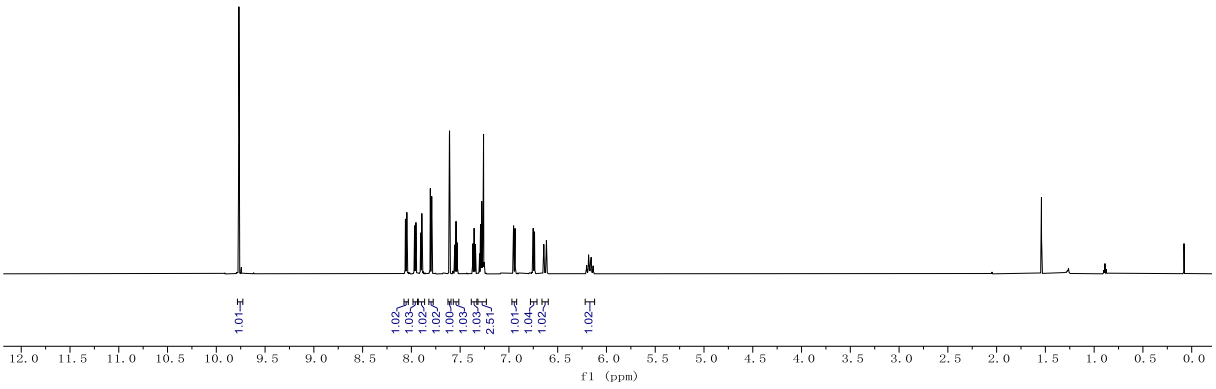


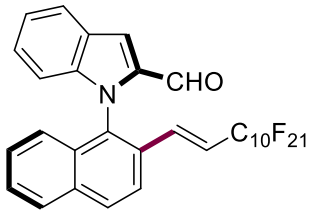
17

(565 MHz, $CDCl_3$)

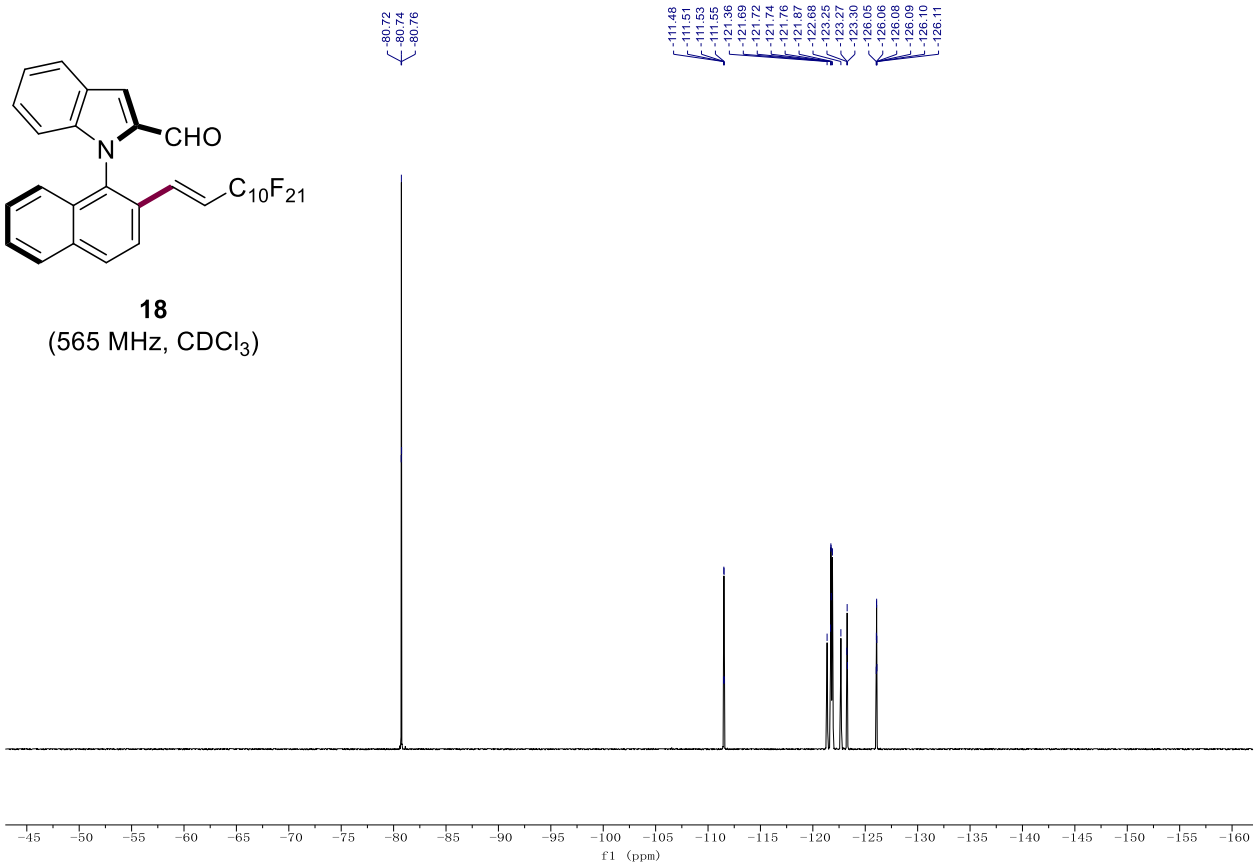


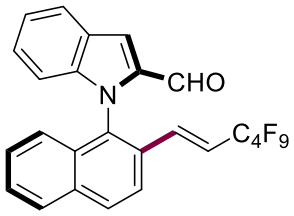
18
(600 MHz, $CDCl_3$)



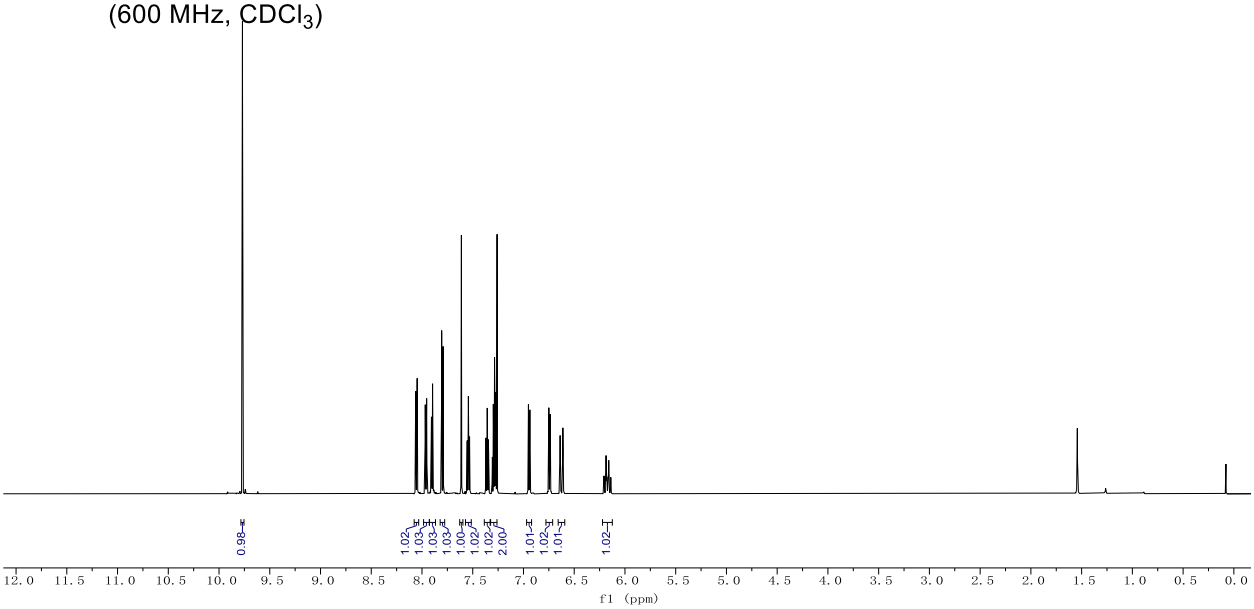


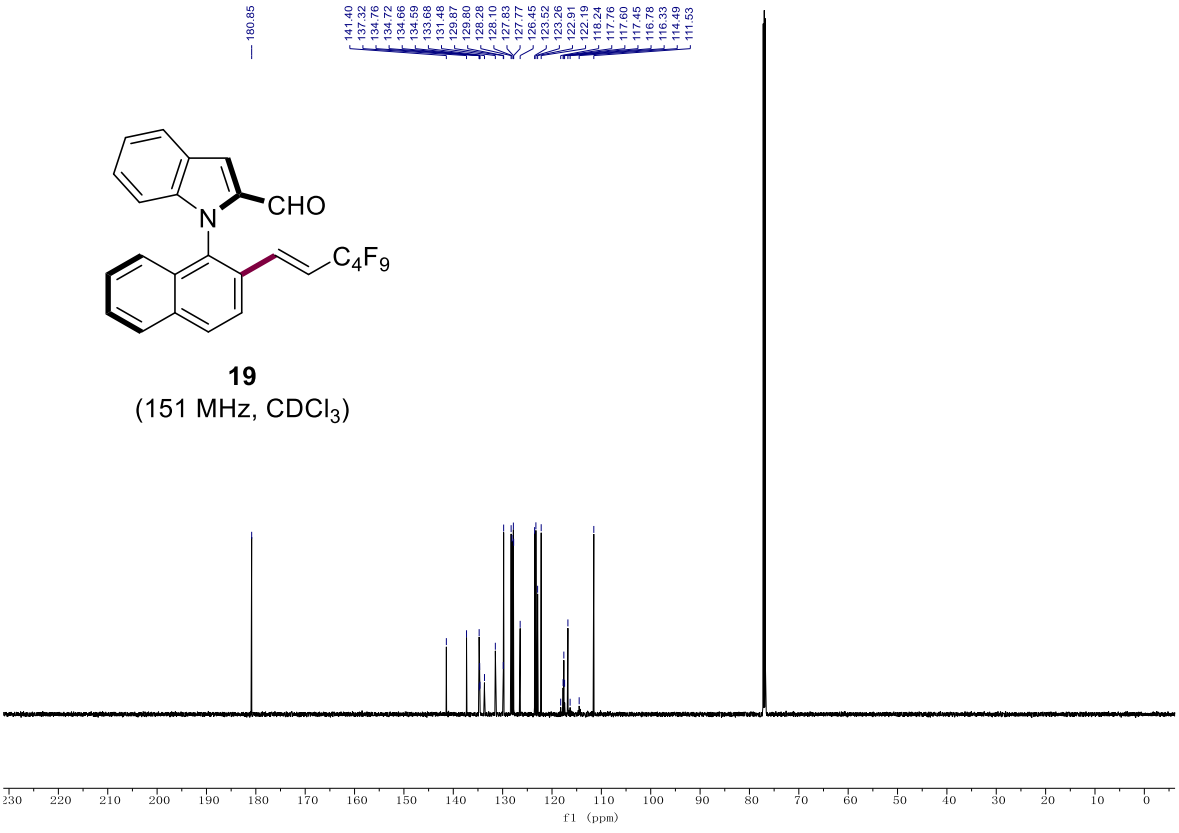
18
(126 MHz, $CDCl_3$)


-80.72
-80.74
-80.76
-111.48
-111.51
-111.53
-111.55
-121.36
-121.69
-121.72
-121.74
-121.76
-121.87
-122.68
-123.25
-123.27
-123.30
-126.05
-126.06
-126.08
-126.09
-126.10
-126.11
CHO
N
C10F21
18
(565 MHz, CDCl3)
−45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160
f1 (ppm)

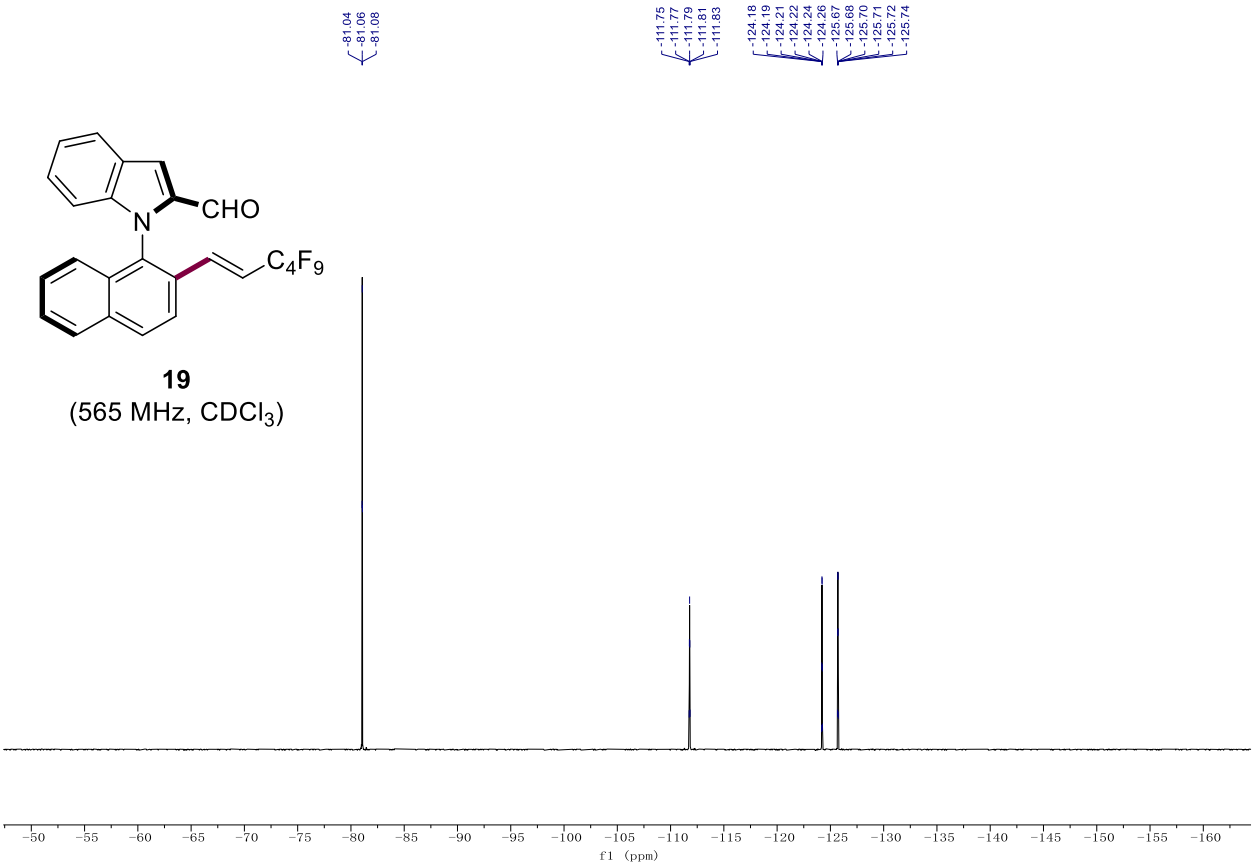


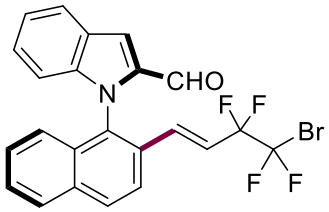
19
(600 MHz, $CDCl_3$)



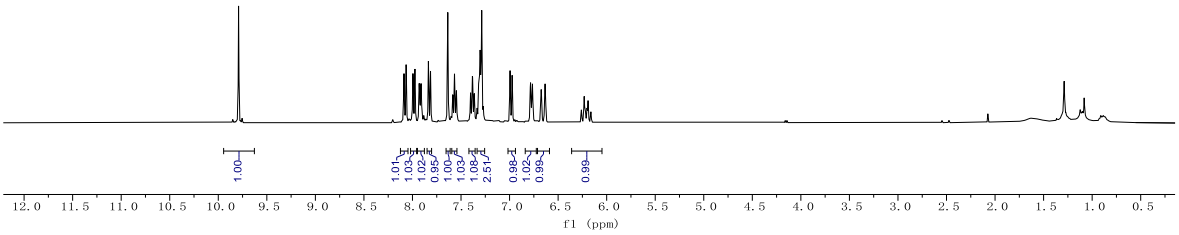


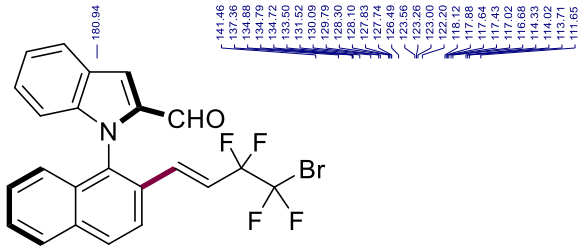
19
(151 MHz, $CDCl_3$)


-81.04
-81.06
-81.08
-111.75
-111.77
-111.79
-111.81
-111.83
-124.18
-124.19
-124.21
-124.22
-124.24
-124.26
-125.67
-125.68
-125.70
-125.71
-125.72
-125.74
CHO
N
C4F9
19
(565 MHz, CDCl3)
−50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160
f1 (ppm)

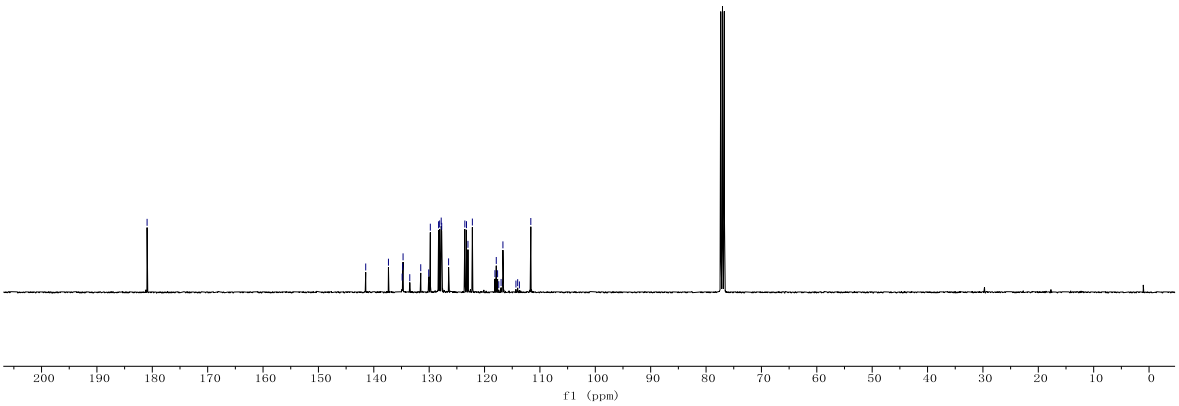


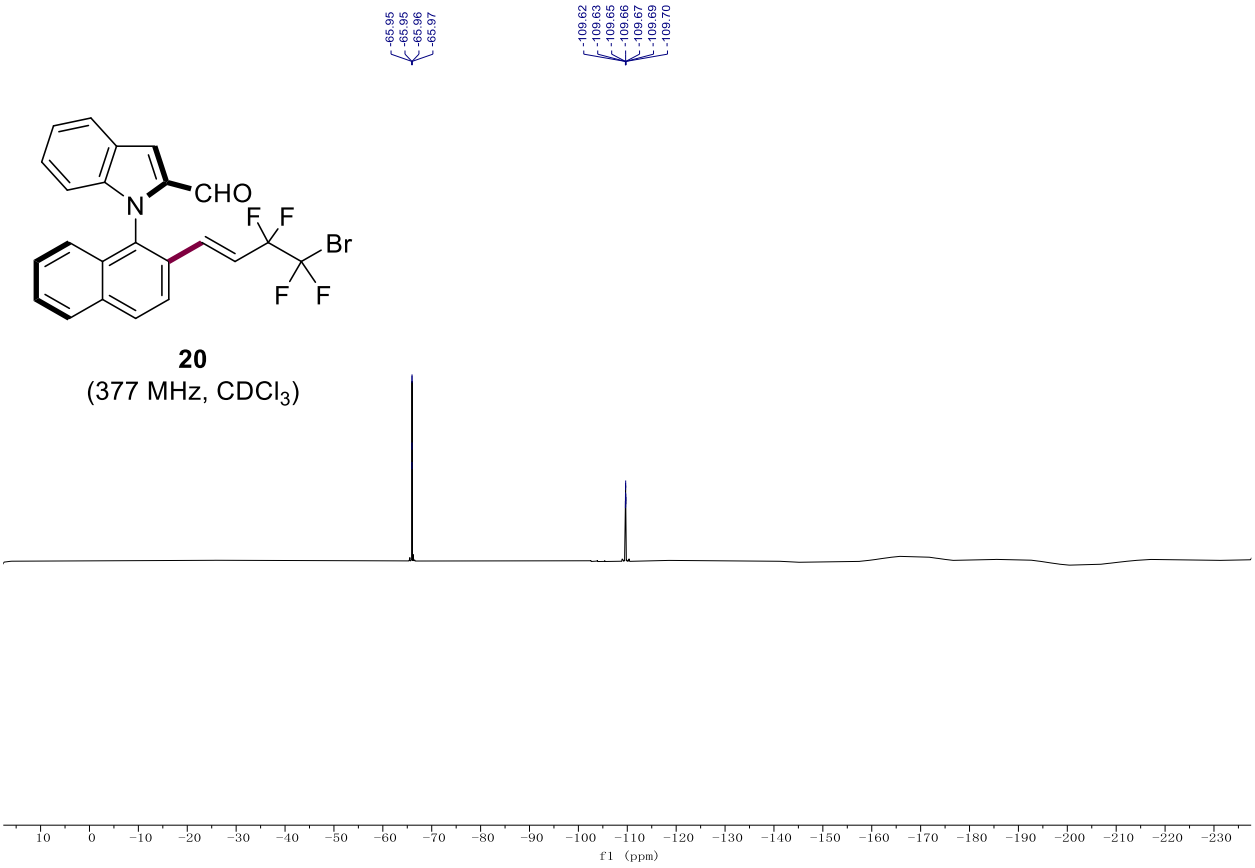
20
(400 MHz, $CDCl_3$)

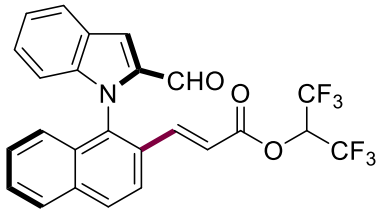




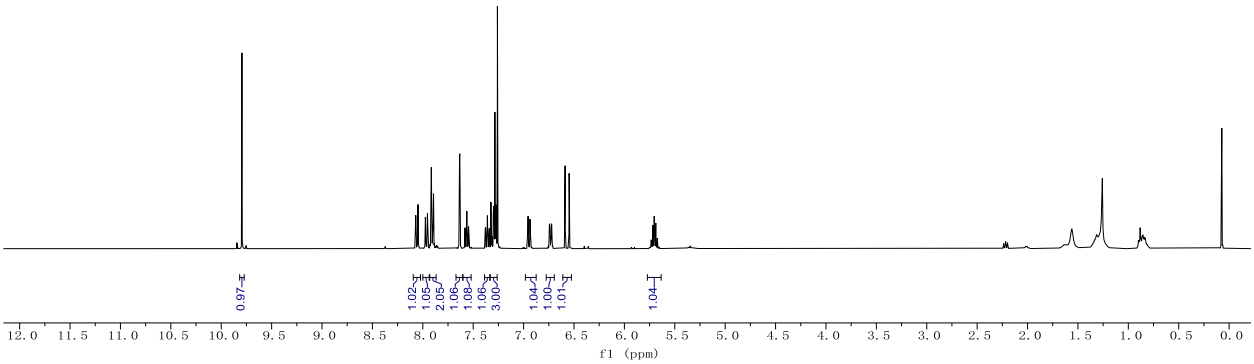
20
(100 MHz, $CDCl_3$)

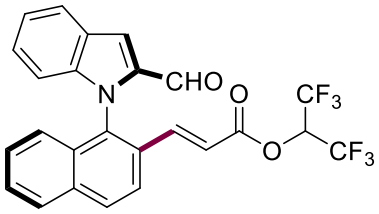



-65.95
-65.95
-65.96
-65.97
-109.62
-109.63
-109.65
-109.66
-109.67
-109.69
-109.70
CHO
N
F F
Br
F F
20
(377 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230
f1 (ppm)

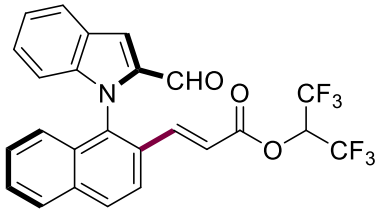


21
(400 MHz, $CDCl_3$)



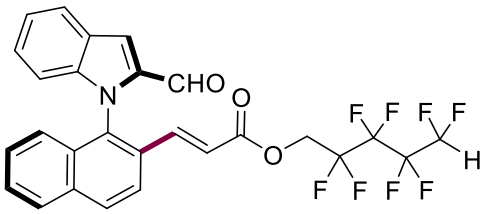


21
(101 MHz, $CDCl_3$)

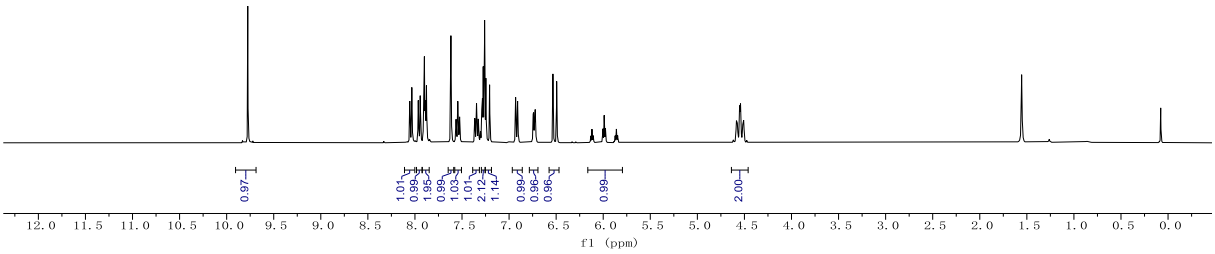


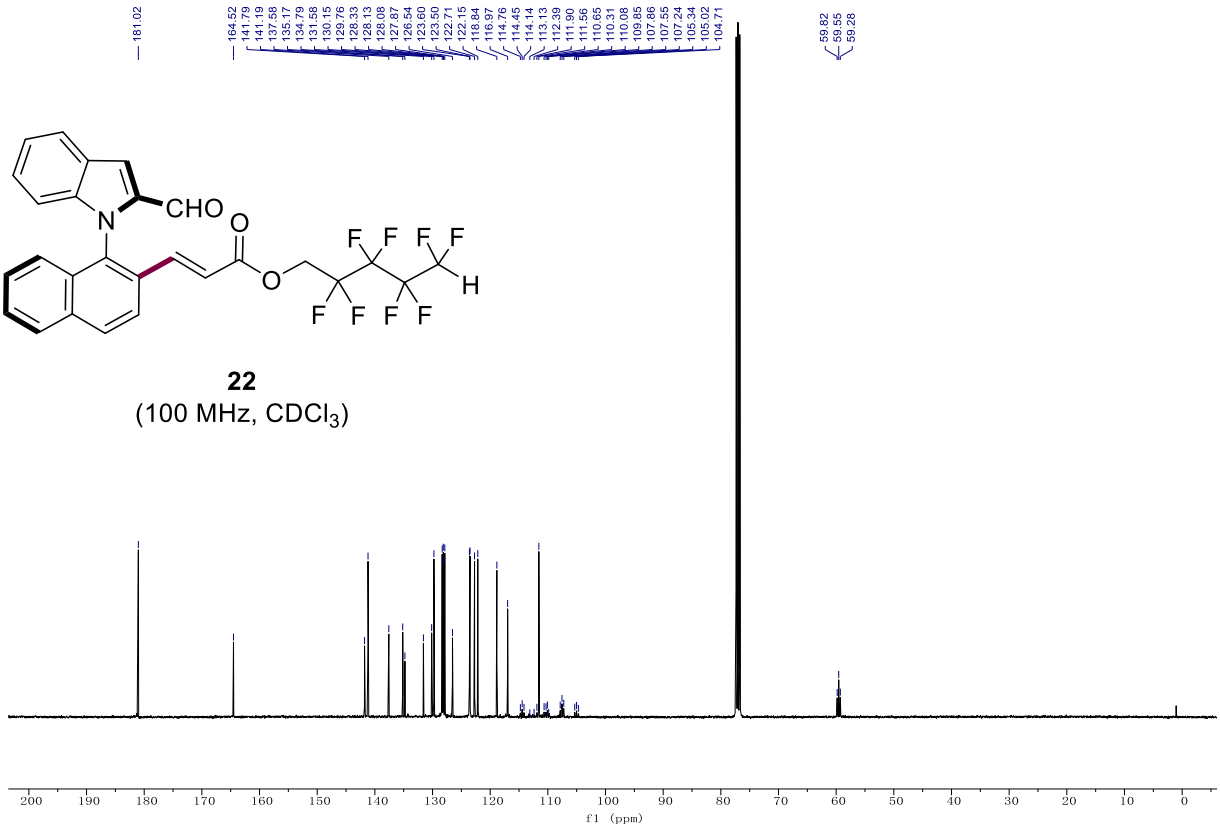
21

(377 MHz, $CDCl_3$)

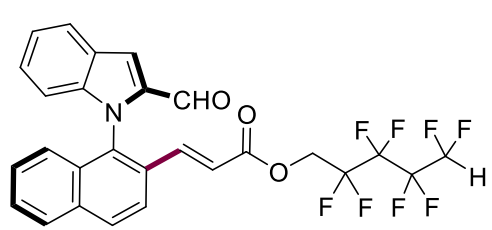


22
(400 MHz, $CDCl_3$)



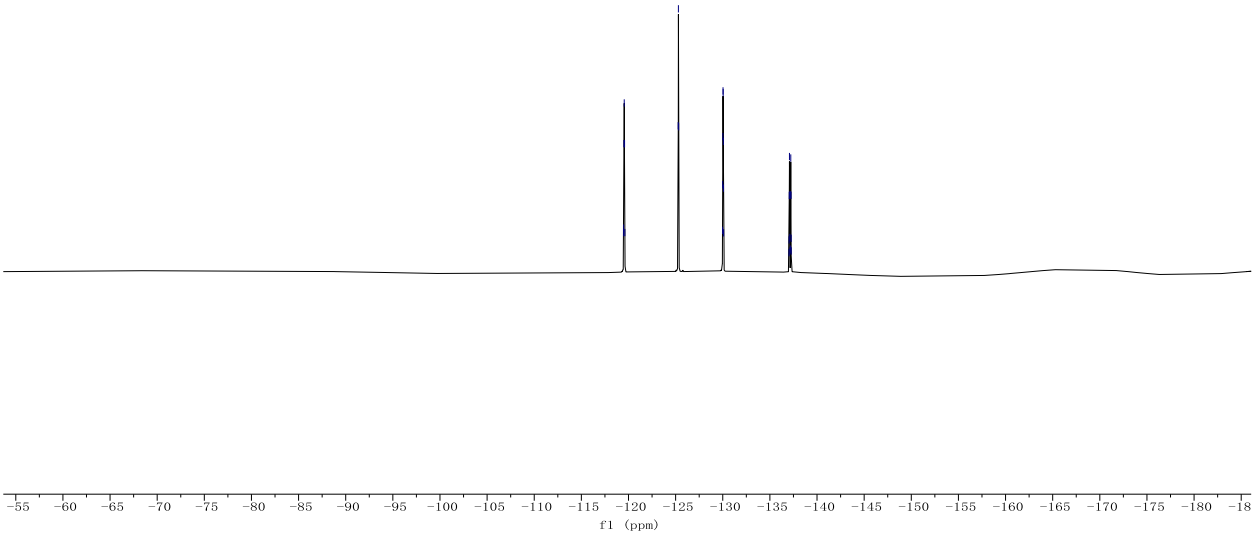


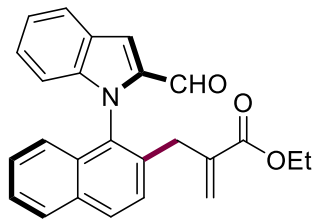
22
(100 MHz, $CDCl_3$)



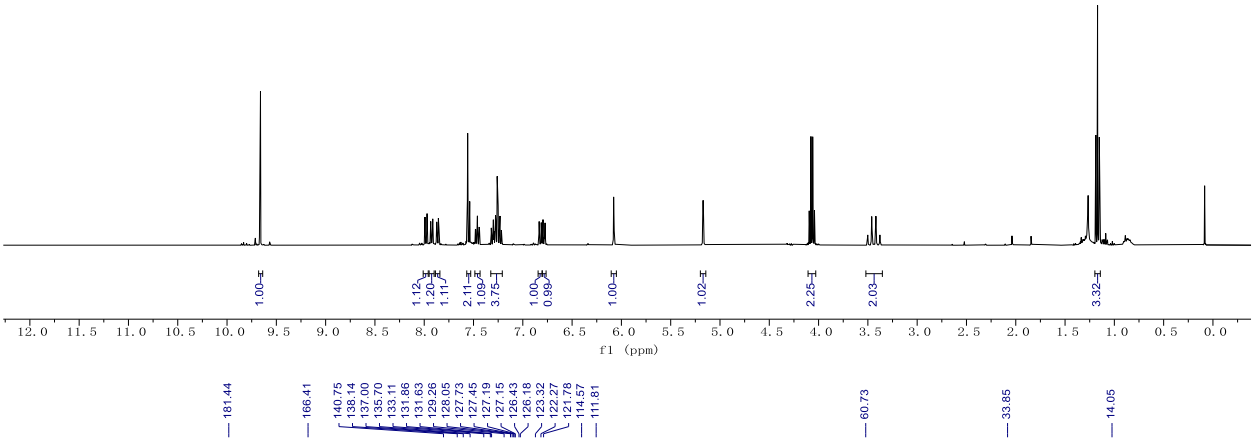
22

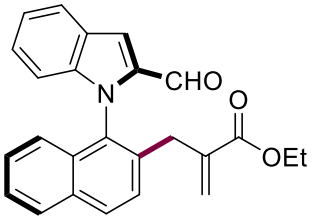
(377 MHz, $CDCl_3$)



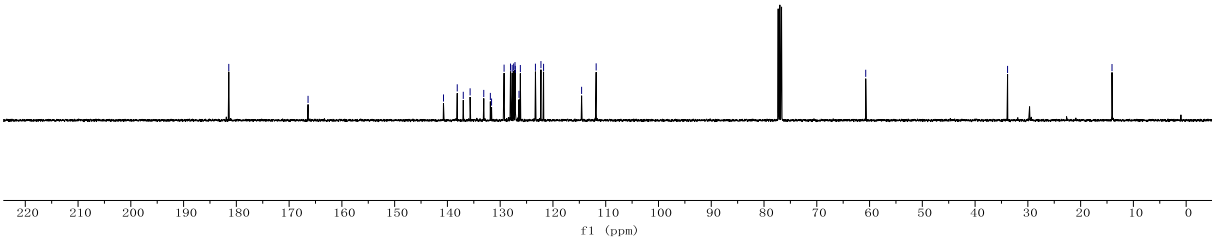


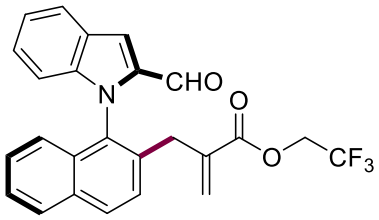
24
(400 MHz, $CDCl_3$)



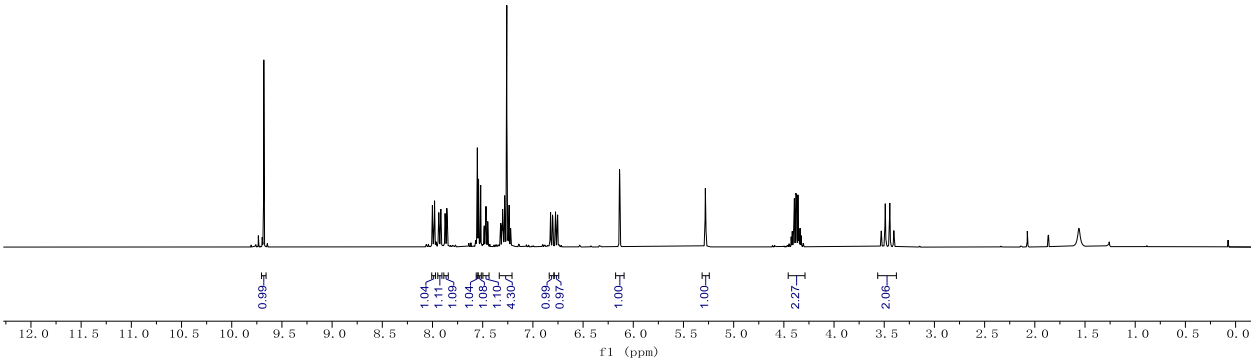


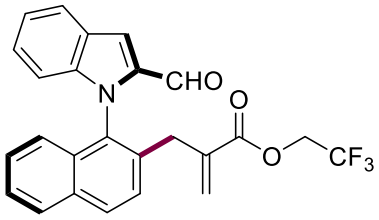
24
(101 MHz, $CDCl_3$)



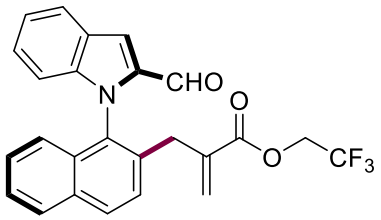


25
(400 MHz, $CDCl_3$)



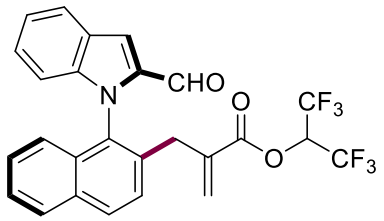


25
(101 MHz, $CDCl_3$)

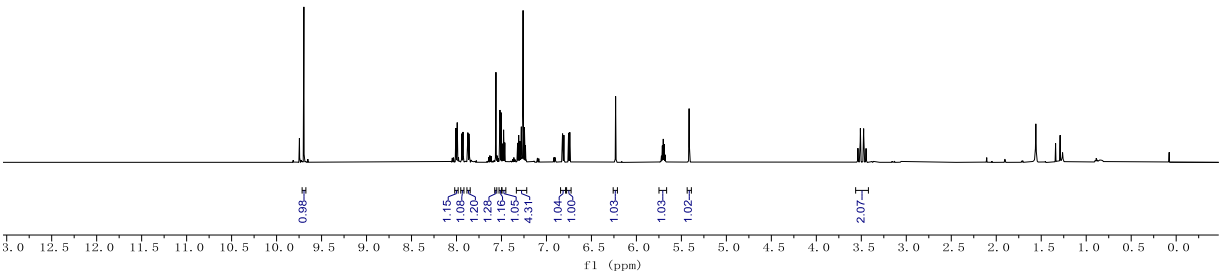


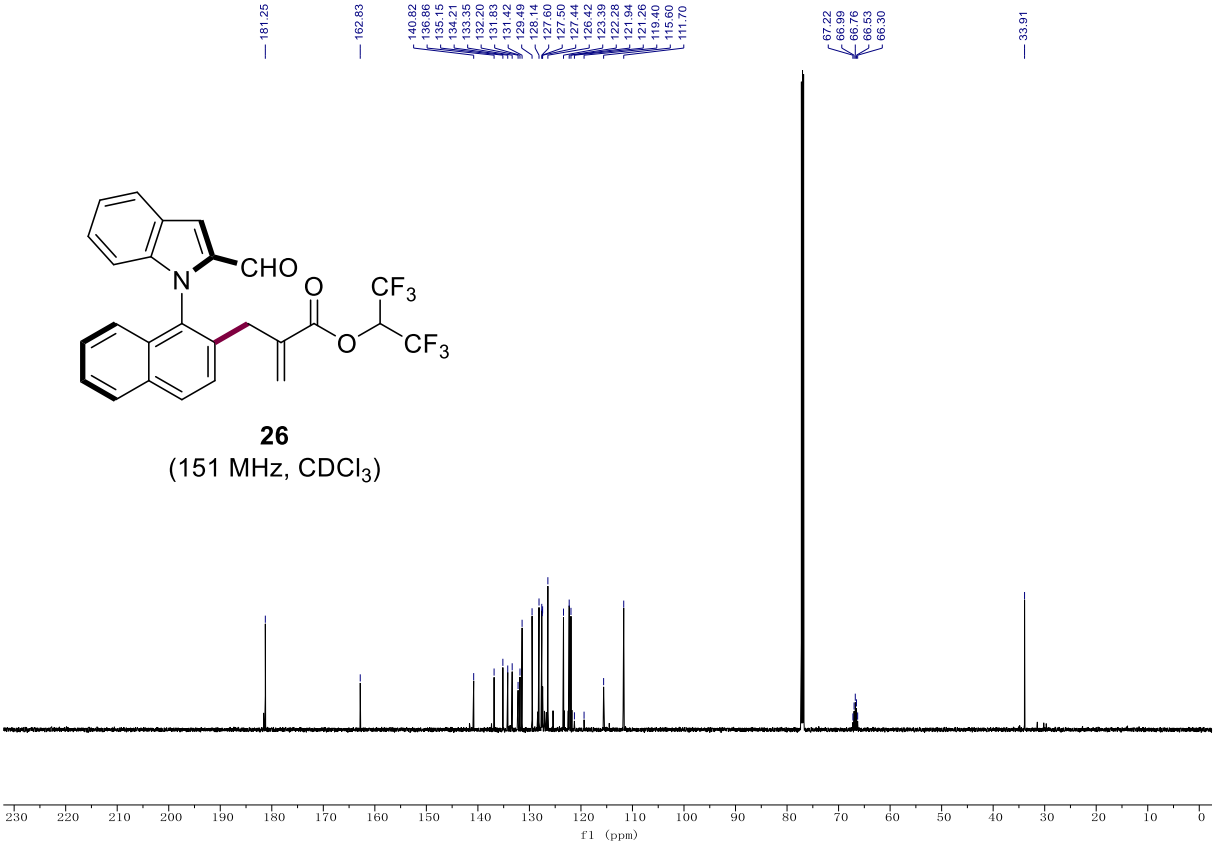
25

(377 MHz, $CDCl_3$)

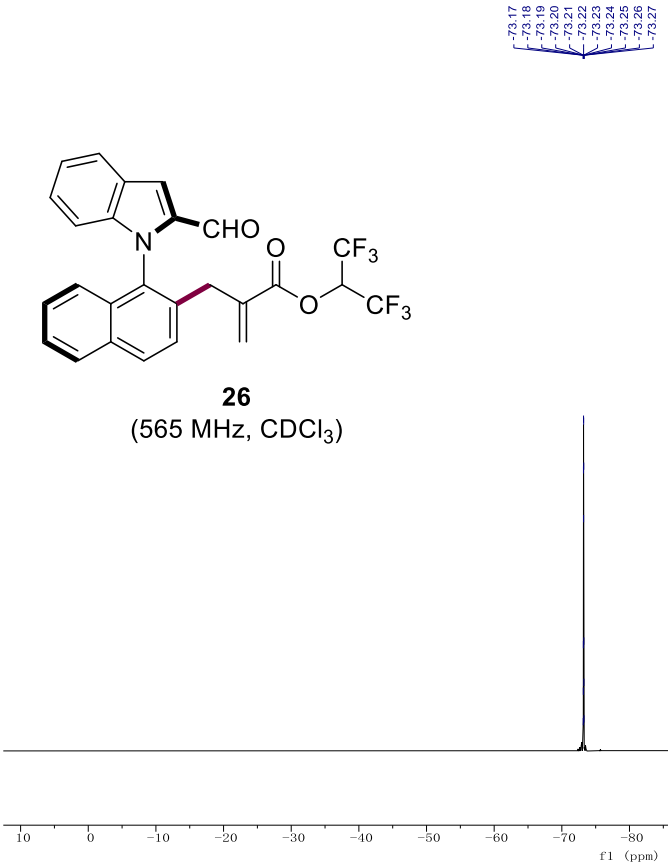


26
(600 MHz, $CDCl_3$)



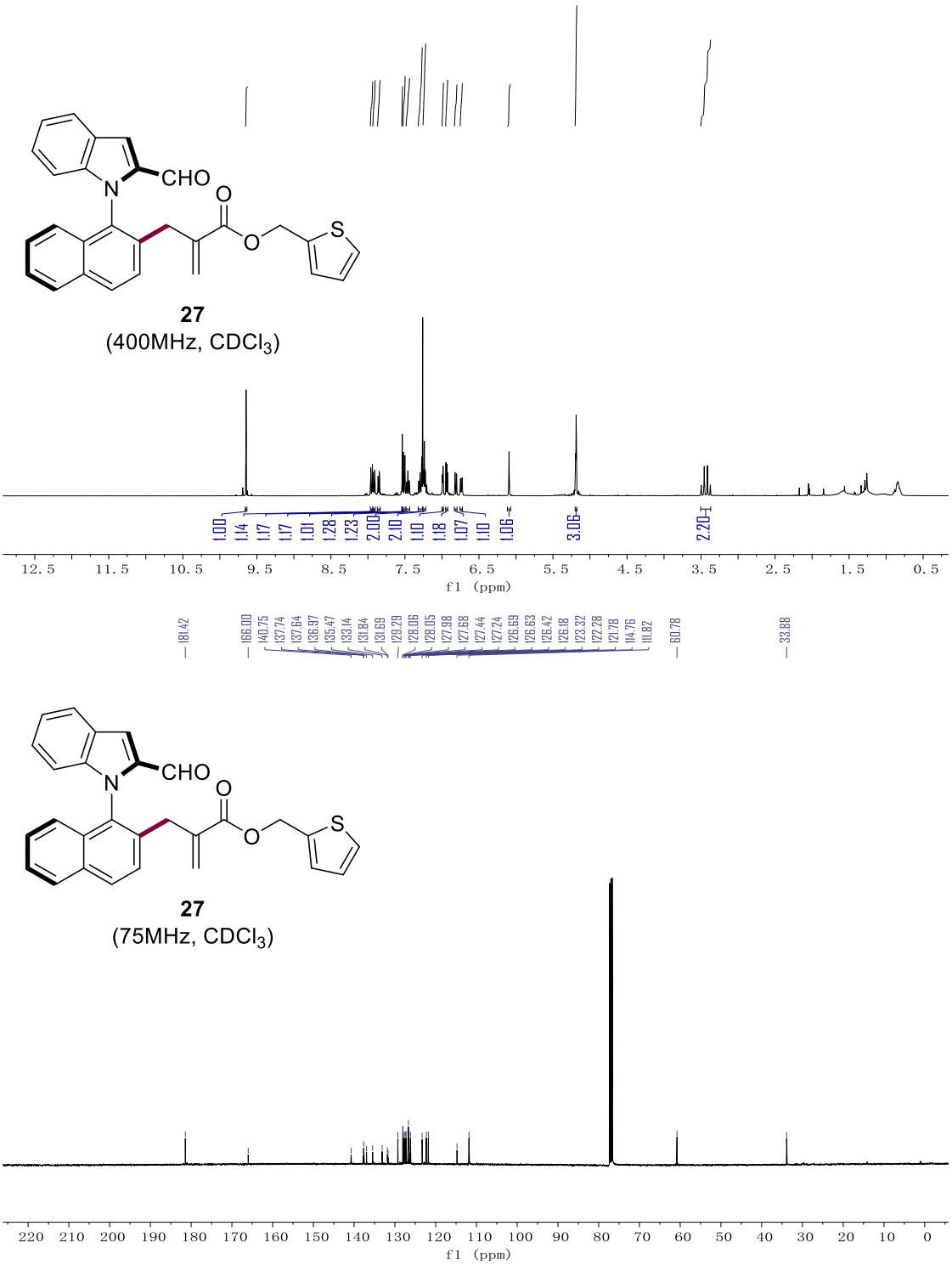


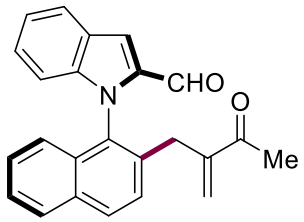
26
(151 MHz, $CDCl_3$)



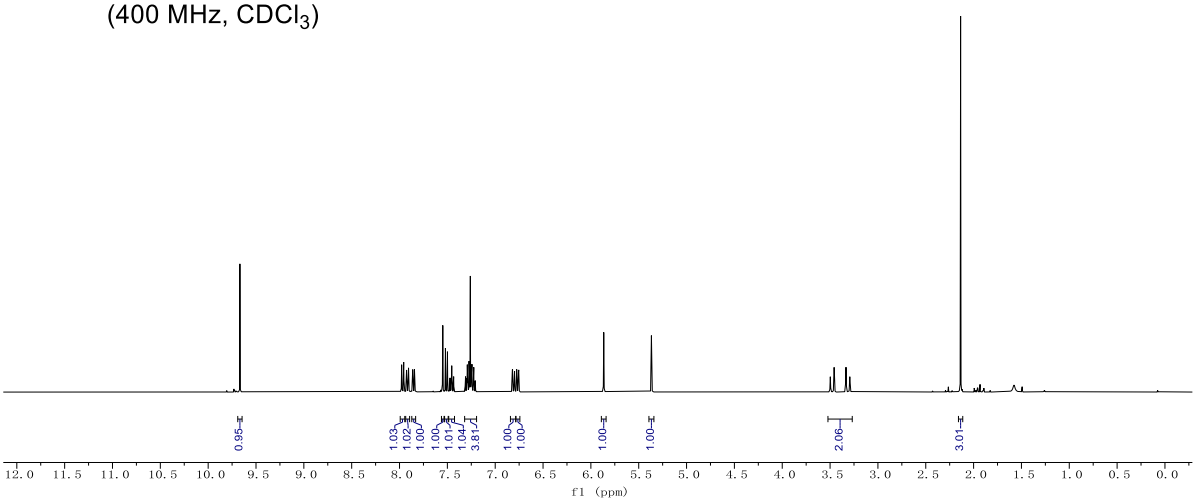
26

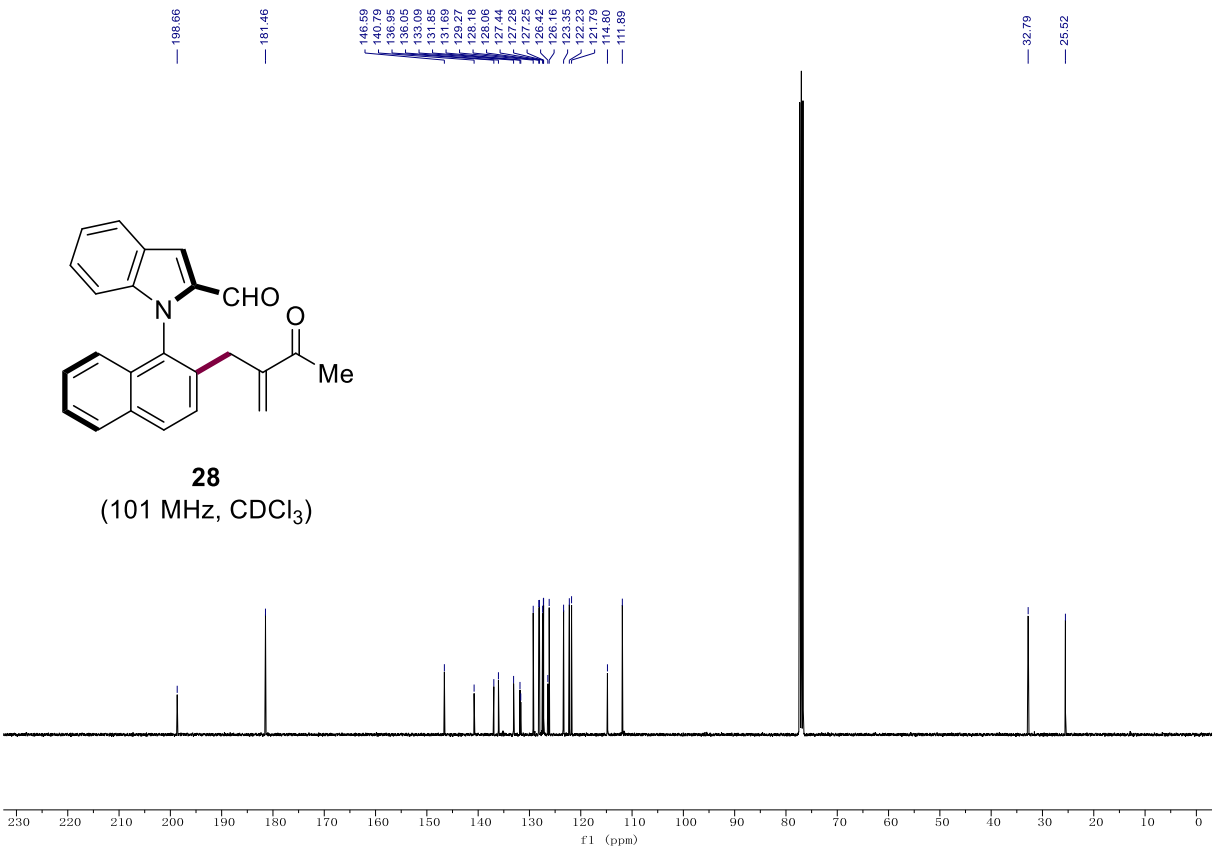
(565 MHz, $CDCl_3$)


CHO
N
O
O
S
27
(400MHz, CDCl3)
1.00
1.14
1.17
1.17
1.01
1.28
1.23
2.00
2.10
1.10
1.18
1.07
1.10
1.06
3.06
2.20
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
181.42
166.00
140.75
137.74
137.64
136.97
135.47
133.14
131.84
131.69
129.29
128.06
128.05
127.98
127.68
127.44
127.24
126.69
126.63
126.42
126.18
123.32
122.28
121.78
114.76
111.82
60.78
33.88
CHO
N
O
O
S
27
(75MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

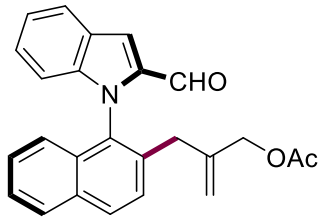


28
(400 MHz, $CDCl_3$)

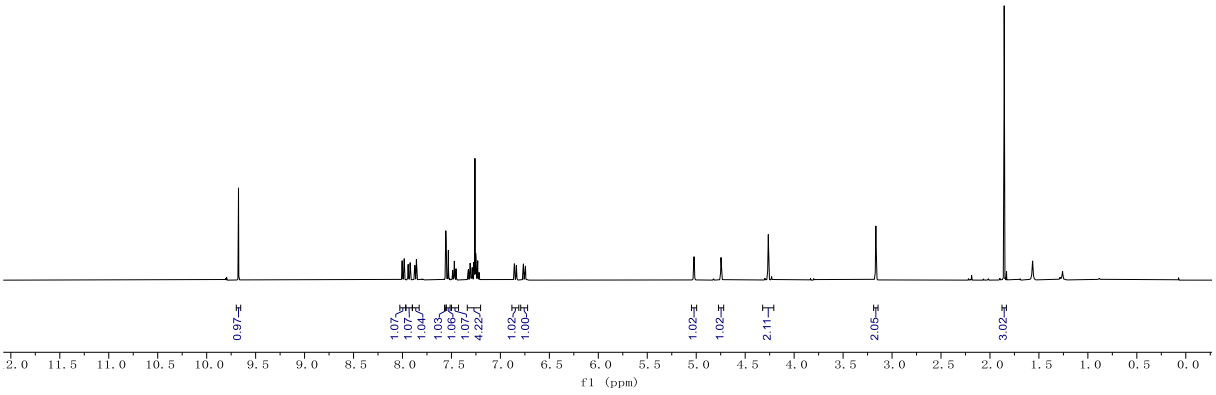


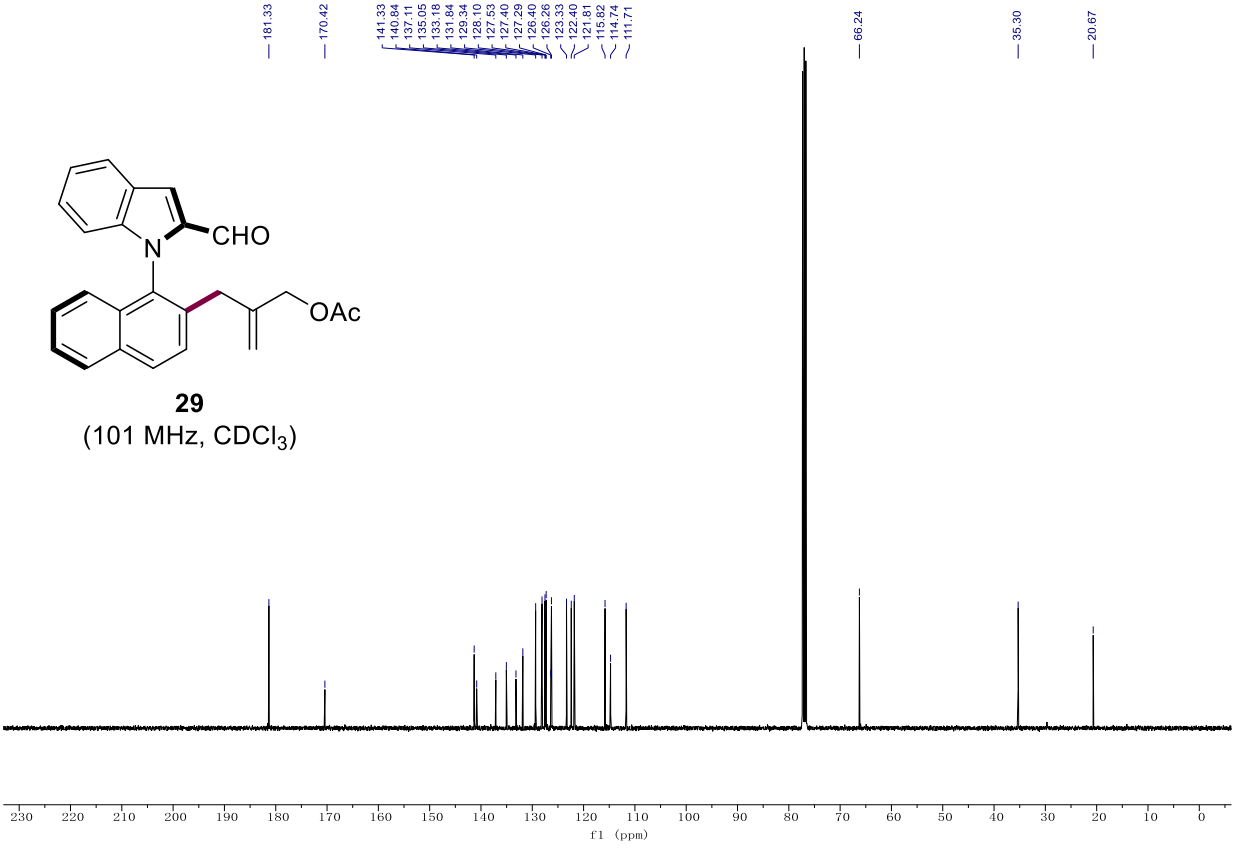


28
(101 MHz, $CDCl_3$)



29
(400 MHz, $CDCl_3$)





29
(101 MHz, $CDCl_3$)