

Supporting Information for

**Rh(III)-Catalyzed Atroposelective C-H Alkynylation of 1-Aryl  
Isoquinolines with Hypervalent Iodine-Alkyne Reagents**

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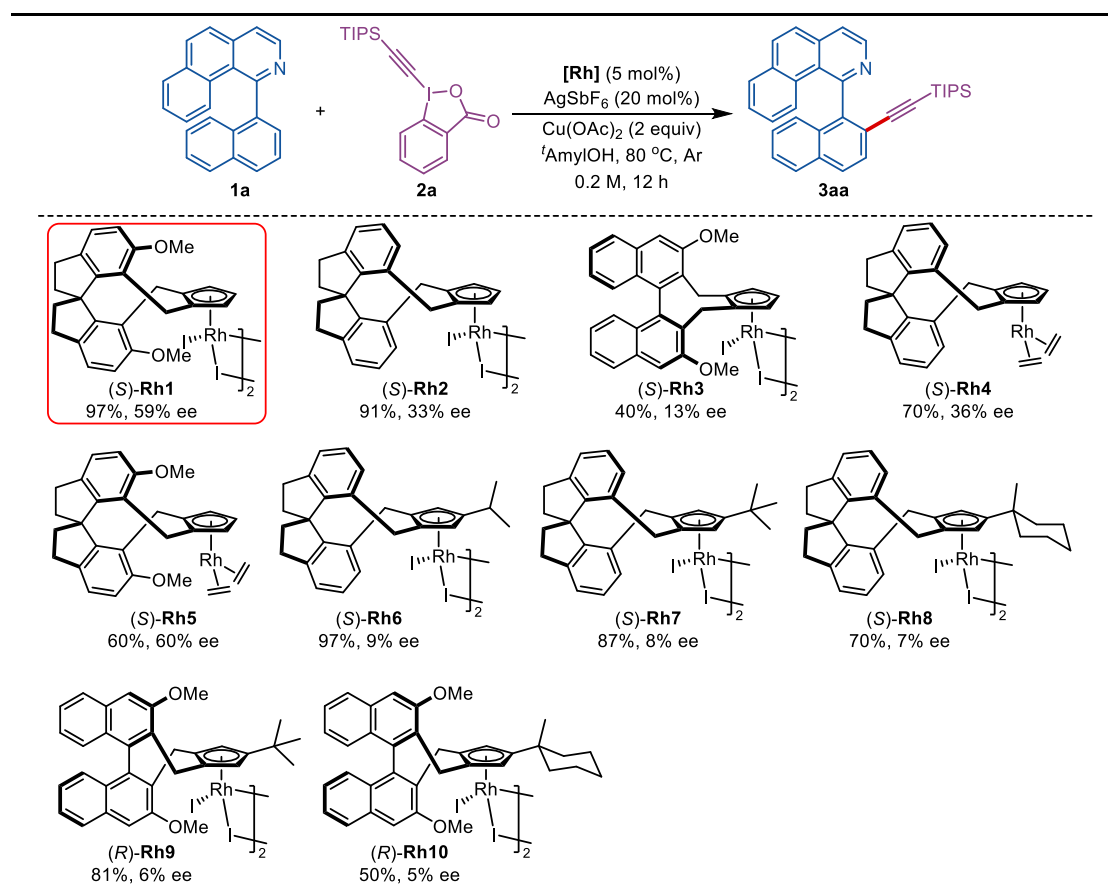
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## 1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods. Flash column chromatography was performed using 200-300 mesh silica gel.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) or an Agilent instrument (400, 600 MHz and 100, 151 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio-solvent signals. Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). All air- and moisture-sensitive reactions were performed under an atmosphere of argon in flame-dried glassware.

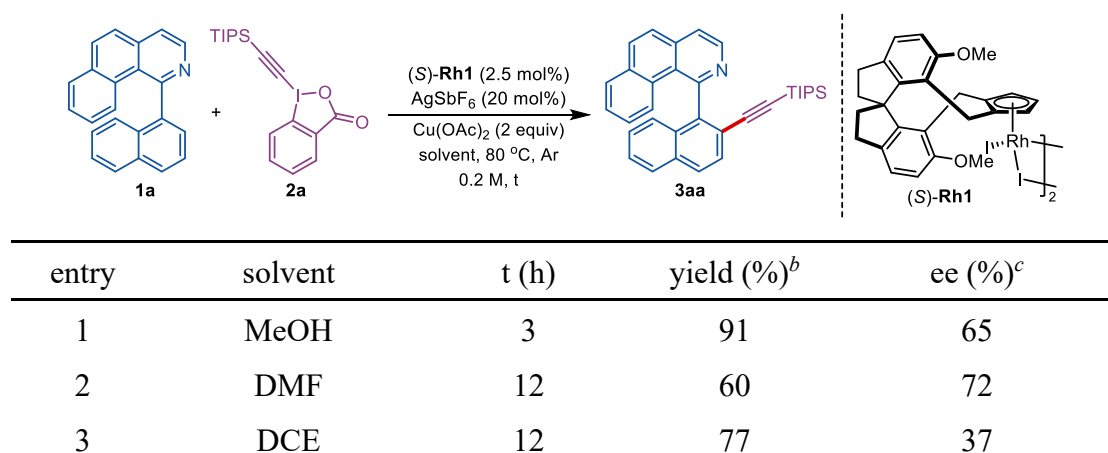
## 2. Complete Condition Optimization

**Table S1.** Screening of CpRh complexes<sup>a,b</sup>



<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), **[Rh]** (5 mol%), **AgSbF<sub>6</sub>** (20 mol%), **Cu(OAc)<sub>2</sub>** (0.1 mmol) in *t*AmylOH (0.25 mL). <sup>b</sup> Isolated yield. The ee values were determined by HPLC analysis on a chiral stationary phase.

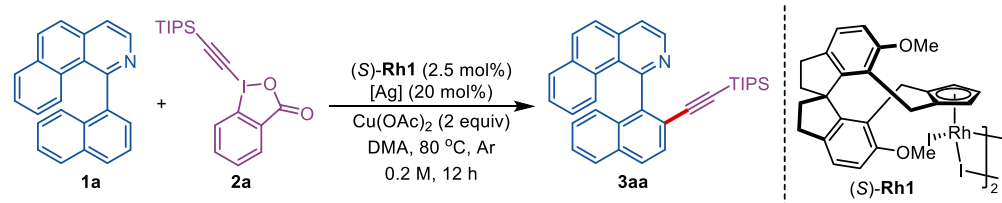
**Table S2.** Solvent effect<sup>a</sup>



4	HFIP	3	93	10
5	<sup>t</sup> AmylOH	12	97	59
6	toluene	12	74	52
7	dioxane	3	91	53
8	MeCN	12	86	54
9	THF	3	98	50
<b>10</b>	<b>DMA</b>	<b>12</b>	<b>86</b>	<b>72</b>

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), AgSbF<sub>6</sub> (20 mol%), Cu(OAc)<sub>2</sub> (0.1 mmol) in solvent (0.25 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase.

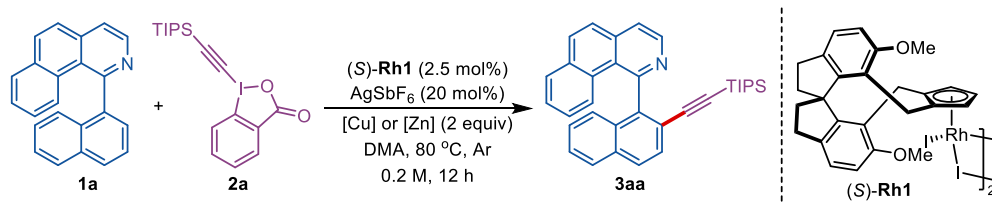
**Table S3.** Screening of silver salts<sup>a</sup>



entry	[Ag]	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
<b>1</b>	<b>AgSbF<sub>6</sub></b>	<b>86</b>	<b>72</b>
2	AgBF <sub>4</sub>	21	75
3	AgNTf <sub>2</sub>	92	70
4	AgOTf	89	69
5	AgPF <sub>6</sub>	66	73
6	AgNO <sub>3</sub>	24	65
7	AgF	12	15
8	AgOAc	20	32
9	<sup>t</sup> PrCOOAg	11	25
10	Ag <sub>2</sub> CO <sub>3</sub>	21	57

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), [Ag] (20 mol%), Cu(OAc)<sub>2</sub> (0.1 mmol) in DMA (0.25 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase.

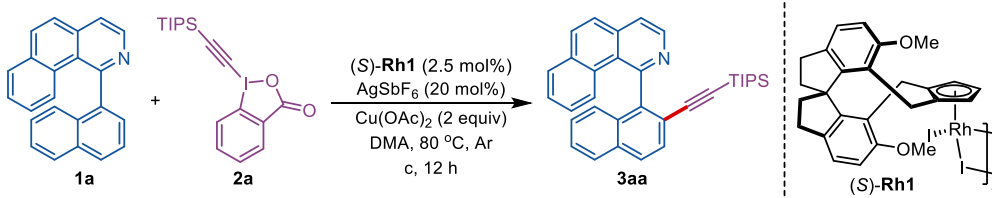
**Table S4.** Screening of copper salts or zinc salts<sup>a</sup>



entry	[Cu] or [Zn]	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
<b>1</b>	<b>Cu(OAc)<sub>2</sub></b>	<b>86</b>	<b>72</b>
2	Cu(OTf) <sub>2</sub>	95	67
3	Cu(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	14	61
4	Cu(NO <sub>2</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	30	67
5	CuBr <sub>2</sub>	16	33
6	CuCl <sub>2</sub>	27	36
7	Zn(OTf) <sub>2</sub>	93	65

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), AgSbF<sub>6</sub> (20 mol%), [Cu] or [Zn] (0.1 mmol) in DMA (0.25 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase.

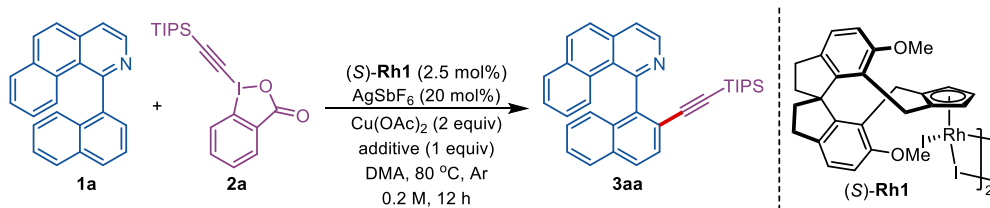
**Table S5.** Concentration effect<sup>a</sup>



entry	c (M)	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
<b>1</b>	<b>0.2</b>	<b>86</b>	<b>72</b>
2	0.1	88	70
3	0.05	88	71

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), AgSbF<sub>6</sub> (20 mol%), Cu(OAc)<sub>2</sub> (0.1 mmol) in DMA (x mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase.

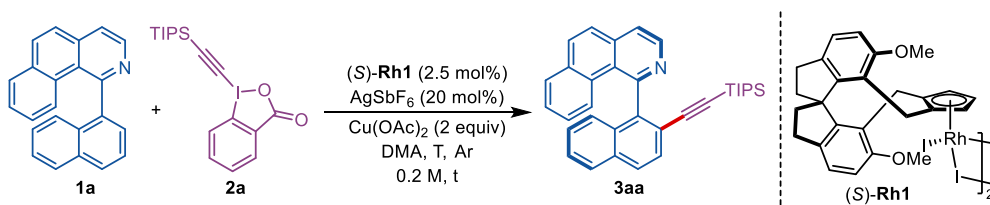
**Table S6.** Screening of additives<sup>a</sup>



entry	additive	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
<b>1</b>	-	<b>86</b>	<b>72</b>
2	NaOAc	10	11
3	NaOTf	92	69
4	PivOCs	79	58
5	NaBF <sub>4</sub>	70	72
6	PivOH	95	61
7	<sup>i</sup> PrCOOH	71	63
8	4-CF <sub>3</sub> PhCOOH	93	64

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), AgSbF<sub>6</sub> (20 mol%), Cu(OAc)<sub>2</sub> (0.1 mmol) and additive (0.05 mmol) in DMA (0.25 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase.

**Table S7.** Temperature effect<sup>a</sup>

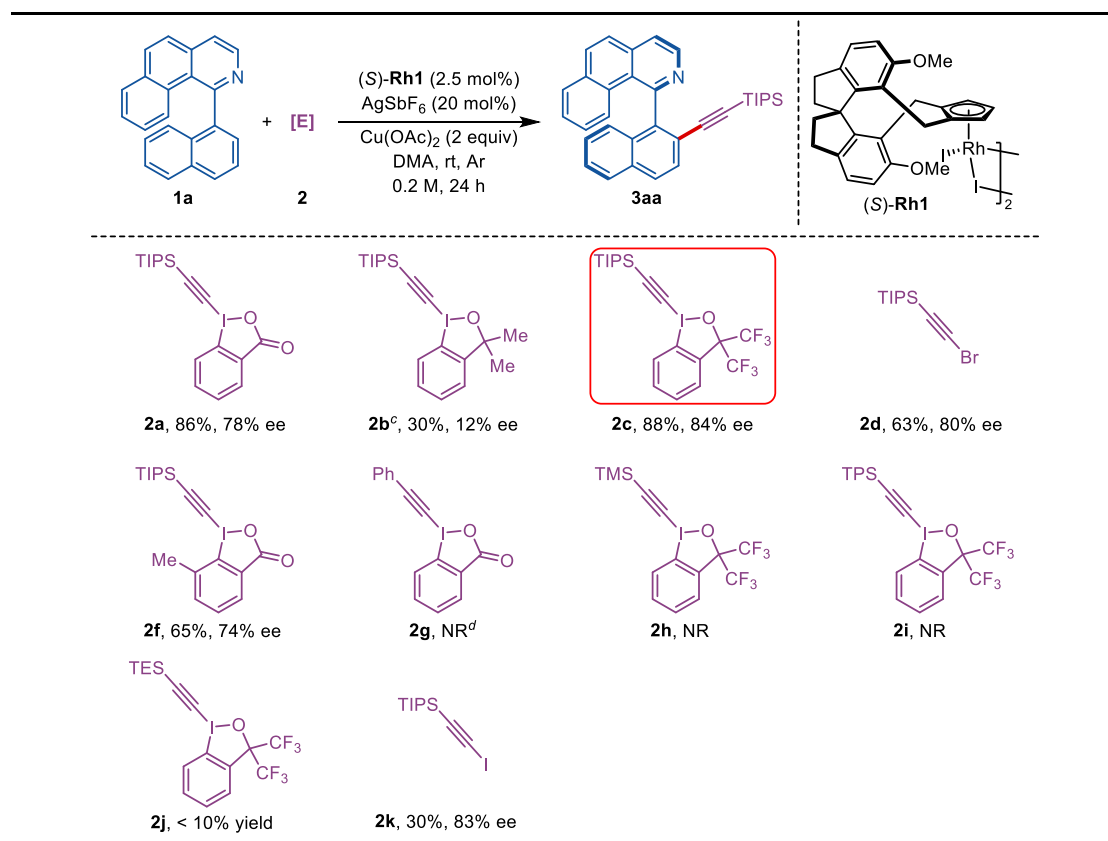


entry	T (°C)	t (h)	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	80	12	86	72
2	60	12	91	74
3	40	12	88	77
<b>4</b>	<b>rt</b>	<b>24</b>	<b>86</b>	<b>78</b>
5	10	24	59	85
6	0	24	46	87
7	0	48	51	88
8	-20	36	22	92

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), AgSbF<sub>6</sub> (20 mol%),

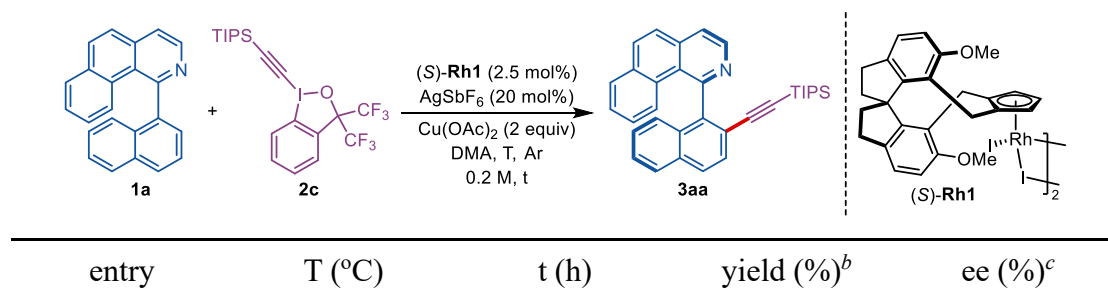
Cu(OAc)<sub>2</sub> (0.1 mmol) in DMA (0.25 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase.

**Table S8.** Screening of alkynylated reagents<sup>a,b</sup>



<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2** (0.1 mmol), **(S)-Rh1** (2.5 mol%), **AgSbF<sub>6</sub>** (20 mol%), **Cu(OAc)<sub>2</sub>** (0.1 mmol) in **DMA** (0.25 mL). <sup>b</sup> Isolated yield. The ee values were determined by HPLC analysis on a chiral stationary phase. <sup>c</sup> at 80 °C. <sup>d</sup> NR = no reaction.

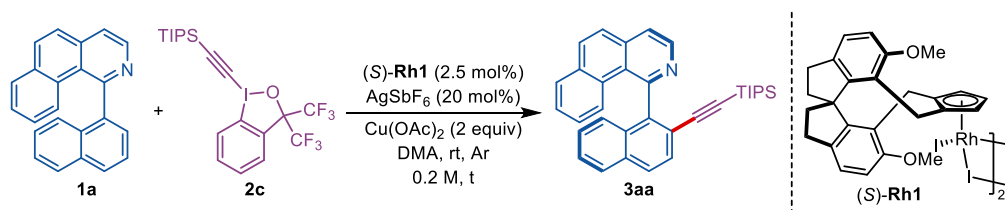
**Table S9.** Temperature effect<sup>a</sup>



4	0	24	68	89
5	-10	48	56	91

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2c** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), AgSbF<sub>6</sub> (20 mol%), Cu(OAc)<sub>2</sub> (0.1 mmol) in DMA (0.25 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase.

**Table S10.** Control experiments<sup>a</sup>

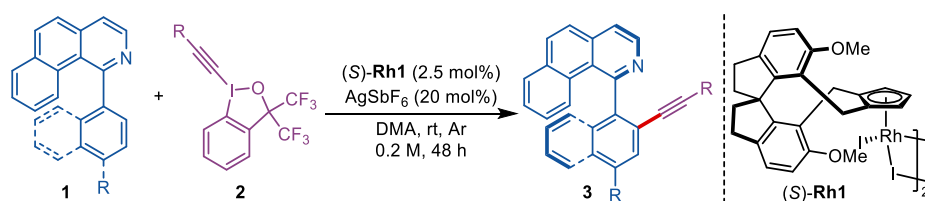


entry	variation from the “standard conditions”	t (h)	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	-	24	88	84
2	without AgSbF <sub>6</sub>	24	trace	-
3	without Cu(OAc) <sub>2</sub>	24	82	87
<b>4</b>	without <b>Cu(OAc)<sub>2</sub></b>	<b>48</b>	<b>88</b>	<b>87</b>
5 <sup>d</sup>	without Cu(OAc) <sub>2</sub>	48	52	90
6	without AgSbF <sub>6</sub> and Cu(OAc) <sub>2</sub>	24	trace	-

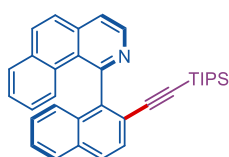
<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2c** (0.1 mmol), (*S*)-**Rh1** (2.5 mol%), AgSbF<sub>6</sub> (20 mol%), Cu(OAc)<sub>2</sub> (0.1 mmol) in DMA (0.25 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The ee values were determined by HPLC analysis on a chiral stationary phase. <sup>d</sup> Under air.



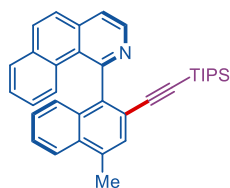
### 3. General Procedure for Rh-Catalyzed Atroposelective C-H Alkynylation of 1-Aryl Isoquinolines



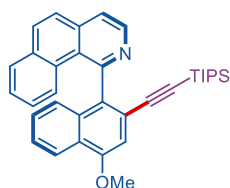
A sealed tube with a magnetic stir bar was charged with (*S*)-**Rh1** (7.2 mg, 0.0025 mmol), AgSbF<sub>6</sub> (13.8 mg, 0.04 mmol), **1** (0.2 mmol), **2** (0.4 mmol), and DMA (1 mL) under argon atmosphere. The resulting mixture was stirred at rt. After the reaction was complete (monitored by TLC), the mixture was cooled to room temperature and quenched with water (5 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL). Then the combined organic layer was washed with H<sub>2</sub>O and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Then the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product **3**.



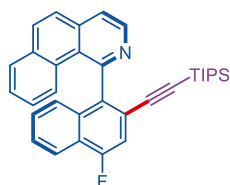
**3aa**, 85.5 mg, 88% yield, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.83 (d, *J* = 5.2 Hz, 1H), 8.02-7.88 (m, 3H), 7.86-7.74 (m, 3H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.51-7.45 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.34-7.27 (m, 2H), 7.05 (t, *J* = 8.4 Hz, 1H), 0.64-0.54 (m, 21H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.7, 144.7, 144.2, 138.3, 133.8, 133.4, 132.4, 131.7, 129.6, 128.9, 128.27, 128.25, 127.4, 127.2, 126.90, 126.86, 126.3, 126.1, 126.0, 125.7, 121.6, 120.0, 105.5, 95.1, 18.31, 18.29, 10.9. IR (ATR): ν<sub>max</sub> (cm<sup>-1</sup>) = 3056, 2943, 2891, 2864, 2148, 1588, 1555, 1507, 1464, 1432, 1384, 1300, 1232, 1210, 1181, 1145, 1114, 1073, 1015, 996, 960, 933, 918, 883, 868, 853, 819, 748, 731, 677, 664, 634; HRMS (ESI): exact mass calculated for: C<sub>34</sub>H<sub>36</sub>NSi [M+H]<sup>+</sup>: 486.2612, found 486.2619. [Phenomenex Lux 5u Cellulose-4 PC-4 column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t<sub>R</sub> (major) = 6.13 min, t<sub>R</sub> (minor) = 7.64 min, ee = 87%. [α]<sub>D</sub><sup>25</sup> = +237.4 (c = 0.2, CHCl<sub>3</sub>).



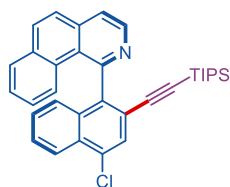
**3ba**, 79.2 mg, 79% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 5.2$  Hz, 1H), 8.09 (d,  $J = 8.4$  Hz, 1H), 7.93 (d,  $J = 8.8$  Hz, 1H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.80-7.74 (m, 2H), 7.59-7.48 (m, 3H), 7.42 (t,  $J = 7.6$  Hz, 1H), 7.36-7.28 (m, 2H), 7.11-7.04 (m, 1H), 2.81 (s, 3H), 0.63-0.55 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 144.1, 143.2, 138.3, 134.8, 133.4, 133.2, 132.3, 131.8, 129.9, 129.7, 128.9, 127.4, 127.0, 126.8, 126.8, 126.2, 126.1, 125.7, 124.5, 121.5, 119.6, 105.7, 94.6, 19.6, 18.33, 18.30, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2941, 2889, 2864, 2147, 1704, 1586, 1554, 1509, 1463, 1424, 1403, 1379, 1362, 1302, 1236, 1192, 1164, 1143, 1072, 1035, 1015, 994, 963, 917, 903, 881, 853, 836, 801, 757, 719, 691, 676, 661, 612; HRMS (ESI): exact mass calculated for:  $\text{C}_{35}\text{H}_{38}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 500.2768, found 500.2761. [Chiralpak IC column, hexane/*i*-PrOH, 98/2 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (minor) = 12.01 min,  $t_{\text{R}}$  (major) = 16.80 min,  $ee = 82\%$ .  $[\alpha]_{\text{D}}^{25} = +287.0$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



**3ca**, 81.6 mg, 79% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 5.2$  Hz, 1H), 8.35 (d,  $J = 8.4$  Hz, 1H), 7.93 (d,  $J = 8.8$  Hz, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 7.79-7.73 (m, 2H), 7.60 (d,  $J = 8.8$  Hz, 1H), 7.47 (t,  $J = 7.2$  Hz, 1H), 7.42 (t,  $J = 7.6$  Hz, 1H), 7.30 (t,  $J = 8.0$  Hz, 1H), 7.26-7.23 (m, 1H), 7.13-7.06 (m, 1H), 6.98 (s, 1H), 4.12 (s, 3H), 0.63-0.56 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 155.2, 144.2, 138.3, 133.4, 132.7, 132.3, 129.8, 128.9, 127.7, 127.4, 126.8, 126.44, 126.40, 126.36, 126.11, 126.09, 125.7, 122.2, 121.5, 119.8, 107.1, 105.9, 94.6, 55.9, 18.33, 18.31, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2924, 2863, 2145, 1613, 1590, 1556, 1509, 1462, 1423, 1409, 1385, 1363, 1347, 1301, 1248, 1230, 1211, 1183, 1145, 1132, 1112, 1015, 996, 964, 947, 933, 906, 883, 870, 852, 802, 754, 730, 700, 674, 642; HRMS (ESI): exact mass calculated for:  $\text{C}_{35}\text{H}_{38}\text{NOSi}$   $[\text{M}+\text{H}]^+$ : 516.2717, found 516.2709. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (minor) = 8.67 min,  $t_{\text{R}}$  (major) = 12.26 min,  $ee = 94\%$ .  $[\alpha]_{\text{D}}^{25} = +374.1$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

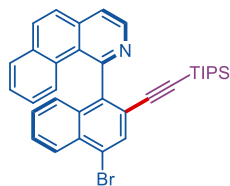


**3da**, 80.2 mg, 80% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 5.2$  Hz, 1H), 8.20 (d,  $J = 8.4$  Hz, 1H), 7.94 (d,  $J = 8.8$  Hz, 1H), 7.85-7.72 (m, 3H), 7.55 (t,  $J = 7.2$  Hz, 1H), 7.49 (d,  $J = 8.4$  Hz, 1H), 7.43 (t,  $J = 7.2$  Hz, 1H), 7.40-7.29 (m, 3H), 7.10 (t,  $J = 7.6$  Hz, 1H), 0.66-0.51 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3 (d,  $J = 251.5$  Hz), 156.0, 144.2, 141.1 (d,  $J = 4.2$  Hz), 138.3, 133.4, 133.1 (d,  $J = 5.4$  Hz), 132.4, 129.5, 129.0, 128.2, 127.4, 127.3 (d,  $J = 1.8$  Hz), 127.0, 126.4 (d,  $J = 2.9$  Hz), 126.2, 125.9, 125.7, 124.5 (d,  $J = 16.6$  Hz), 121.7, 120.9 (d,  $J = 5.1$  Hz), 120.0 (d,  $J = 10.2$  Hz), 113.0 (d,  $J = 21.3$  Hz), 104.5 (d,  $J = 2.9$  Hz), 96.1, 18.28, 18.26, 10.9.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -123.02 (d,  $J = 10.9$  Hz, 1F). IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2944, 2890, 2865, 2156, 1625, 1601, 1586, 1557, 1509, 1463, 1417, 1383, 1363, 1301, 1272, 1247, 1172, 1146, 1126, 1066, 1039, 1017, 994, 965, 908, 882, 866, 853, 837, 798, 762, 732, 695, 674, 610; HRMS (ESI): exact mass calculated for:  $\text{C}_{34}\text{H}_{35}\text{NFSi}$   $[\text{M}+\text{H}]^+$ : 504.2517, found 504.2513. [Phenomenex Lux 5u Cellulose-4 PC-4 column, hexane/*i*-PrOH, 98/2 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (major) = 6.68 min,  $t_{\text{R}}$  (minor) = 8.11 min,  $ee = 90\%$ .  $[\alpha]_{\text{D}}^{25} = +278.8$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

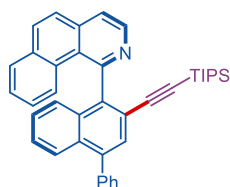


**3ea**, 88.2 mg, 85% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (d,  $J = 5.2$  Hz, 1H), 8.38 (d,  $J = 8.4$  Hz, 1H), 7.93 (d,  $J = 8.8$  Hz, 1H), 7.84-7.73 (m, 4H), 7.64-7.56 (m, 1H), 7.52 (d,  $J = 8.4$  Hz, 1H), 7.47-7.39 (m, 1H), 7.34 (d,  $J = 3.6$  Hz, 2H), 7.15-7.06 (m, 1H), 0.62-0.54 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 144.2, 144.0, 138.3, 133.4, 132.8, 132.5, 132.0, 131.3, 129.40, 129.36, 129.0, 128.0, 127.5, 127.0, 126.9, 126.1, 125.9, 125.7, 124.8, 121.8, 120.3, 104.2, 96.3, 18.27, 18.25, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2942, 2890, 2864, 2153, 1609, 1584, 1555, 1501, 1463, 1423, 1385, 1361, 1323, 1300, 1266, 1239, 1218, 1073, 1016, 994, 967, 937, 908, 881, 852, 836, 801, 780, 759, 734, 697, 675, 650; HRMS (ESI): exact mass calculated for:  $\text{C}_{34}\text{H}_{35}\text{NSiCl}$   $[\text{M}+\text{H}]^+$ : 520.2222, found 520.2213. [Phenomenex Lux 5u Cellulose-4 PC-4 column, hexane/*i*-PrOH, 98/2 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$

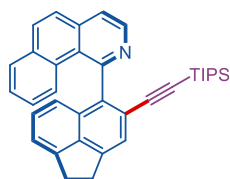
(major) = 7.18 min,  $t_R$  (minor) = 8.30 min,  $ee = 67\%$ .  $[\alpha]_D^{25} = +225.0$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



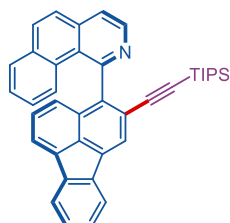
**3fa**, 94.7 mg, 84% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 5.2$  Hz, 1H), 8.35 (d,  $J = 8.8$  Hz, 1H), 8.01 (s, 1H), 7.95 (d,  $J = 8.8$  Hz, 1H), 7.87-7.73 (m, 3H), 7.64-7.56 (m, 1H), 7.52 (d,  $J = 8.8$  Hz, 1H), 7.44 (t,  $J = 7.2$  Hz, 1H), 7.38-7.28 (m, 2H), 7.11 (t,  $J = 8.4$  Hz, 1H), 0.67-0.47 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 144.1, 138.3, 133.3, 133.0, 132.6, 132.5, 132.3, 129.3, 129.0, 128.2, 128.0, 127.5, 127.0, 126.8, 125.9, 125.8, 125.6, 122.7, 121.7, 120.6, 103.9, 96.4, 18.19, 18.17, 10.8. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2943, 2923, 2890, 2864, 2153, 1586, 1557, 1499, 1463, 1423, 1385, 1360, 1319, 1299, 1232, 1213, 1183, 1145, 1115, 1072, 1058, 1016, 996, 964, 924, 908, 880, 853, 757, 732, 698, 671, 647; HRMS (ESI): exact mass calculated for:  $\text{C}_{34}\text{H}_{35}\text{NSiBr}$   $[\text{M}+\text{H}]^+$ : 564.1717, found 564.1707. [Chiralpak IC column, hexane/*i*-PrOH, 98/2 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 7.50 min,  $t_R$  (major) = 9.18 min,  $ee = 83\%$ .  $[\alpha]_D^{25} = +176.3$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



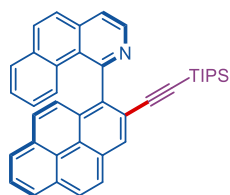
**3ga**, 91.4 mg, 81% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (d,  $J = 5.2$  Hz, 1H), 8.01-7.93 (m, 2H), 7.87-7.78 (m, 3H), 7.71 (d,  $J = 8.4$  Hz, 1H), 7.67-7.60 (m, 3H), 7.58-7.52 (m, 2H), 7.51-7.36 (m, 4H), 7.33-7.27 (m, 1H), 7.18-7.12 (m, 1H), 0.63-0.53 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 144.2, 140.7, 140.2, 138.3, 133.4, 132.4, 132.3, 132.1, 130.3, 129.6, 129.0, 128.5, 127.7, 127.5, 127.1, 127.0, 126.9, 126.7, 126.5, 126.2, 126.1, 125.7, 121.7, 119.6, 105.4, 95.1, 18.3, 18.3, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2942, 2891, 2864, 2152, 1687, 1587, 1555, 1509, 1493, 1463, 1446, 1423, 1405, 1384, 1366, 1346, 1302, 1267, 1237, 1194, 1144, 1100, 1073, 1016, 996, 969, 932, 917, 884, 853, 771, 757, 739, 690, 676, 646, 629; HRMS (ESI): exact mass calculated for:  $\text{C}_{40}\text{H}_{40}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 562.2925, found 562.2930. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 5.80 min,  $t_R$  (major) = 7.51 min,  $ee = 43\%$ .  $[\alpha]_D^{25} = +127.2$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



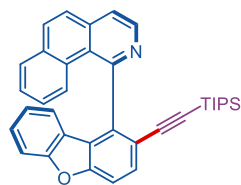
**3ha**, 93.2 mg, 91% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 5.2$  Hz, 1H), 7.91 (d,  $J = 8.8$  Hz, 1H), 7.82-7.70 (m, 3H), 7.66 (d,  $J = 8.4$  Hz, 1H), 7.49 (s, 1H), 7.42-7.36 (m, 1H), 7.30-7.25 (m, 2H), 7.11-7.01 (m, 2H), 3.56-3.40 (m, 4H), 0.64-0.55 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.0, 156.5, 146.1, 145.9, 144.0, 140.5, 139.6, 138.2, 133.3, 132.2, 129.9, 129.8, 129.0, 128.8, 127.3, 126.8, 126.1, 126.1, 125.7, 123.1, 121.5, 121.4, 121.3, 120.6, 106.5, 94.2, 30.7, 30.2, 18.31, 18.29, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2941, 2890, 2864, 2147, 1722, 1700, 1687, 1610, 1586, 1555, 1509, 1463, 1418, 1384, 1365, 1301, 1269, 1236, 1182, 1143, 1101, 1072, 997, 909, 883, 869, 849, 803, 760, 733, 665; HRMS (ESI): exact mass calculated for:  $\text{C}_{36}\text{H}_{38}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 512.2768, found 512.2773. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (minor) = 10.52 min,  $t_{\text{R}}$  (major) = 16.80 min,  $ee = 83\%$ .  $[\alpha]_{\text{D}}^{25} = +247.1$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



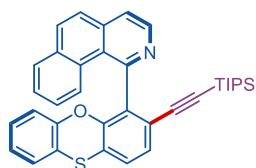
**3ia**, 93.7 mg, 84% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (d,  $J = 5.2$  Hz, 1H), 8.13 (s, 1H), 8.02-7.96 (m, 1H), 7.96-7.86 (m, 3H), 7.84-7.73 (m, 3H), 7.60 (d,  $J = 8.8$  Hz, 1H), 7.48-7.36 (m, 4H), 7.30 (d,  $J = 8.4$  Hz, 1H), 7.05-6.98 (m, 1H), 0.70-0.48 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 144.5, 143.8, 140.1, 138.9, 138.1, 137.1, 137.0, 133.4, 132.9, 132.4, 129.6, 129.2, 128.9, 128.7, 128.2, 127.9, 127.3, 126.9, 126.3, 126.2, 125.64, 125.61, 124.3, 122.1, 121.9, 121.8, 121.6, 121.1, 105.9, 95.2, 18.34, 18.32, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3054, 2942, 2890, 2864, 2146, 1611, 1585, 1554, 1509, 1451, 1408, 1368, 1299, 1237, 1189, 1148, 1110, 1074, 1016, 994, 970, 942, 908, 884, 869, 853, 837, 800, 778, 733, 680, 660, 629; HRMS (ESI): exact mass calculated for:  $\text{C}_{40}\text{H}_{38}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 560.2768, found 560.2761. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (minor) = 10.34 min,  $t_{\text{R}}$  (major) = 13.49 min,  $ee = 90\%$ .  $[\alpha]_{\text{D}}^{25} = +284.3$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



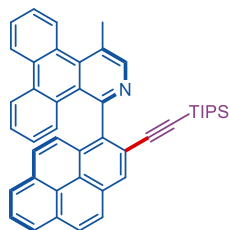
**3ja**, 98.3 mg, 88% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (d,  $J = 4.8$  Hz, 1H), 8.48 (s, 1H), 8.18 (d,  $J = 7.6$  Hz, 1H), 8.14-8.05 (m, 3H), 8.00-7.90 (m, 2H), 7.87-7.75 (m, 4H), 7.54 (d,  $J = 9.2$  Hz, 1H), 7.36-7.26 (m, 2H), 6.90-6.78 (m, 1H), 0.69-0.57 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.1, 144.2, 141.3, 138.3, 133.4, 132.4, 131.6, 131.3, 131.0, 129.7, 129.4, 129.2, 128.9, 128.7, 128.4, 127.4, 127.2, 126.8, 126.6, 126.3, 126.0, 125.72, 125.69, 125.6, 125.2, 124.7, 121.7, 120.4, 105.6, 94.7, 18.4, 18.3, 11.0. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3046, 2941, 2890, 2863, 2149, 1585, 1555, 1509, 1463, 1415, 1389, 1364, 1303, 1286, 1236, 1181, 1142, 1102, 1072, 1061, 1016, 993, 933, 882, 856, 839, 831, 813, 748, 686, 659, 639; HRMS (ESI): exact mass calculated for:  $\text{C}_{40}\text{H}_{38}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 560.2768, found 560.2764. [Chiralpak IC column, hexane/*i*-PrOH, 80/20 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (major) = 7.29 min,  $t_{\text{R}}$  (minor) = 14.74 min,  $ee = 61\%$ .  $[\alpha]_{\text{D}}^{25} = -54.3$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



**3ka**, 89.9 mg, 86% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (d,  $J = 5.6$  Hz, 1H), 7.95 (d,  $J = 8.8$  Hz, 1H), 7.86 (d,  $J = 5.2$  Hz, 1H), 7.84-7.74 (m, 3H), 7.74-7.64 (m, 2H), 7.52 (d,  $J = 8.4$  Hz, 1H), 7.43 (t,  $J = 7.6$  Hz, 1H), 7.29 (t,  $J = 8.4$  Hz, 1H), 7.17-7.06 (m, 1H), 6.87 (t,  $J = 7.6$  Hz, 1H), 6.41 (d,  $J = 7.6$  Hz, 1H), 0.63-0.55 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 156.5, 155.3, 144.3, 138.4, 133.4, 132.6, 132.5, 129.7, 129.0, 127.5, 127.1, 125.9, 125.6, 125.3, 123.4, 123.0, 122.9, 122.2, 122.1, 117.3, 111.63, 111.59, 104.6, 93.1, 18.29, 18.27, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2943, 2890, 2864, 2163, 2149, 1588, 1556, 1510, 1471, 1449, 1424, 1384, 1318, 1293, 1262, 1233, 1208, 1182, 1146, 1114, 1066, 1015, 996, 963, 933, 907, 885, 853, 838, 815, 783, 746, 732, 700, 678, 631; HRMS (ESI): exact mass calculated for:  $\text{C}_{36}\text{H}_{36}\text{NOSi}$   $[\text{M}+\text{H}]^+$ : 526.2561, found 526.2551. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (major) = 6.93 min,  $t_{\text{R}}$  (minor) = 10.85 min,  $ee = 90\%$ .  $[\alpha]_{\text{D}}^{25} = +193.3$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

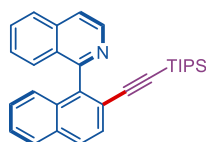


**3la**, 103.4 mg, 93% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 5.2$  Hz, 1H), 7.96 (d,  $J = 8.8$  Hz, 1H), 7.92 (d,  $J = 8.8$  Hz, 1H), 7.83 (d,  $J = 8.0$  Hz, 1H), 7.75 (s, 1H), 7.74 (d,  $J = 4.4$  Hz, 1H), 7.48-7.42 (m, 1H), 7.36 (d,  $J = 8.4$  Hz, 1H), 7.29-7.25 (m, 1H), 7.22 (d,  $J = 8.0$  Hz, 1H), 7.02 (dd,  $J = 7.6, 1.6$  Hz, 1H), 6.89-6.83 (m, 1H), 6.80-6.74 (m, 1H), 6.04 (dd,  $J = 8.4, 1.6$  Hz, 1H), 0.65-0.56 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 151.8, 149.6, 144.0, 138.0, 136.3, 133.3, 132.0, 129.7, 129.3, 128.9, 127.7, 127.5, 127.0, 126.5, 125.64, 125.63, 124.6, 122.9, 122.4, 121.6, 120.0, 118.0, 104.0, 95.3, 18.3, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2942, 2890, 2863, 2154, 1585, 1555, 1509, 1463, 1447, 1427, 1404, 1377, 1309, 1278, 1267, 1237, 1217, 1125, 1073, 1030, 1005, 952, 908, 883, 869, 852, 815, 784, 749, 732, 673, 642; HRMS (ESI): exact mass calculated for:  $\text{C}_{36}\text{H}_{36}\text{NOSiS}$   $[\text{M}+\text{H}]^+$ : 558.2281, found 558.2282. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (major) = 7.25 min,  $t_{\text{R}}$  (minor) = 9.68 min,  $ee = 79\%$ .  $[\alpha]_{\text{D}}^{24} = -93.4$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

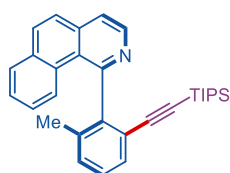


**3ma**, 100.8 mg, 81% yield, yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (s, 1H), 8.69 (d,  $J = 8.0$  Hz, 1H), 8.60 (d,  $J = 7.6$  Hz, 1H), 8.45 (d,  $J = 8.0$  Hz, 1H), 8.36 (s, 1H), 8.20 (d,  $J = 7.2$  Hz, 1H), 8.17-8.09 (m, 2H), 8.08-8.03 (m, 1H), 8.03-7.94 (m, 3H), 7.78-7.70 (m, 1H), 7.70-7.63 (m, 1H), 7.51 (dd,  $J = 8.8, 1.2$  Hz, 1H), 7.36-7.27 (m, 1H), 6.77-6.68 (m, 1H), 3.11 (s, 3H), 0.69-0.56 (m, 18H), 0.50-0.37 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 148.6, 141.6, 137.8, 132.9, 131.7, 131.3, 131.0, 130.9, 129.9, 129.6, 129.5, 129.3, 128.9, 128.8, 128.7, 128.3, 127.9, 127.40, 127.39, 127.35, 127.2, 126.9, 126.6, 126.2, 125.74, 125.67, 125.6, 125.3, 124.8, 123.7, 123.0, 120.8, 106.0, 94.4, 23.4, 18.34, 18.29, 11.0. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2942, 2888, 2864, 2151, 1685, 1596, 1577, 1548, 1528, 1462, 1442, 1418, 1383, 1363, 1292, 1262, 1239, 1178, 1142, 1101, 1073,

1013, 995, 904, 883, 831, 813, 788, 760, 727, 687, 636; HRMS (ESI): exact mass calculated for: C<sub>45</sub>H<sub>42</sub>NSi [M+H]<sup>+</sup>: 624.3081, found 624.3076. [Chiralpak IC column, hexane/*i*-PrOH, 80/20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t<sub>R</sub> (major) = 7.52 min, t<sub>R</sub> (minor) = 11.75 min, ee = 65%. [α]<sub>D</sub><sup>24</sup> = -46.4 (c = 0.2, CHCl<sub>3</sub>).



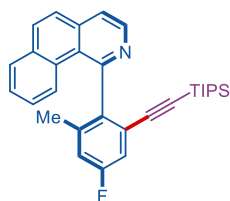
**3na**, 74.4 mg, 85% yield, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.70 (d, *J* = 5.6 Hz, 1H), 7.91 (t, *J* = 9.2 Hz, 3H), 7.74 (d, *J* = 5.6 Hz, 1H), 7.71-7.62 (m, 2H), 7.54-7.44 (m, 2H), 7.43-7.36 (m, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 0.82-0.62 (m, 21H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 142.6, 140.3, 136.6, 133.2, 132.5, 130.3, 128.9, 128.52, 128.50, 128.1, 127.5, 127.4, 127.0, 126.9, 126.7, 126.3, 121.4, 120.4, 105.8, 95.6, 18.41, 18.40, 11.0. IR (ATR): ν<sub>max</sub> (cm<sup>-1</sup>) = 3054, 2942, 2891, 2865, 2143, 1622, 1585, 1556, 1500, 1464, 1382, 1369, 1317, 1240, 1222, 1208, 1145, 1074, 1016, 995, 970, 935, 919, 882, 867, 827, 798, 749, 690, 676, 658, 634; HRMS (ESI): exact mass calculated for: C<sub>30</sub>H<sub>34</sub>NSi [M+H]<sup>+</sup>: 436.2455, found 436.2455. [Chiralpak IC column, hexane/*i*-PrOH, 98/2 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t<sub>R</sub> (major) = 9.06 min, t<sub>R</sub> (minor) = 16.60 min, ee = 34%. [α]<sub>D</sub><sup>24</sup> = -90.7 (c = 0.2, CHCl<sub>3</sub>).



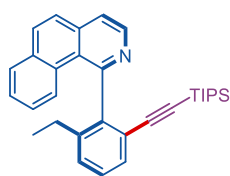
**3oa**, 76.7 mg, 85% yield, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (d, *J* = 5.2 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 4.4 Hz, 1H), 7.70 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.54-7.47 (m, 2H), 7.39-7.34 (d, *J* = 4.4 Hz, 2H), 7.29-7.25 (m, 1H), 1.99 (s, 3H), 0.61-0.52 (m, 21H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.6, 146.0, 143.9, 138.2, 136.0, 133.32, 132.26, 131.1, 131.0, 130.0, 129.0, 128.1, 127.7, 127.5, 126.9, 125.7, 125.6, 125.1, 122.6, 121.4, 105.2, 93.6, 20.0, 18.3, 18.2, 10.9. IR (ATR): ν<sub>max</sub> (cm<sup>-1</sup>) = 2942, 2891, 2864, 2150, 1611, 1588, 1556, 1510, 1461, 1421, 1380, 1235, 1211, 1182, 1145, 1113, 1070, 1016, 996, 963, 934, 909, 882, 852, 801, 786, 749, 731, 700, 676, 639; HRMS (ESI): exact mass calculated for: C<sub>31</sub>H<sub>36</sub>NSi [M+H]<sup>+</sup>: 450.2612, found 450.2605. [Phenomenex Lux 5u Cellulose-4 PC-4 column,



hexane/*i*-PrOH, 98/2 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 8.64 min,  $t_R$  (major) = 11.30 min,  $ee = 82\%$ .  $[\alpha]_D^{24} = +191.2$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

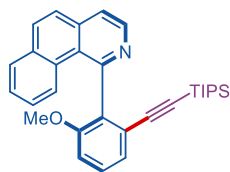


**3pa**, 82.9 mg, 89% yield, yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 4.8$  Hz, 1H), 7.92 (d,  $J = 8.8$  Hz, 1H), 7.86 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.73 (d,  $J = 3.2$  Hz, 1H), 7.71 (s, 1H), 7.69 (d,  $J = 8.8$  Hz, 1H), 7.56-7.49 (m, 1H), 7.35-7.28 (m, 1H), 7.22 (dd,  $J = 8.8, 2.4$  Hz, 1H), 7.11 (dd,  $J = 9.6, 2.8$  Hz, 1H), 1.98 (s, 3H), 0.58-0.51 (m, 21H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9 (d,  $J = 245.2$  Hz), 156.7, 144.2, 142.6 (d,  $J = 3.4$  Hz), 138.6 (d,  $J = 8.3$  Hz), 138.3, 133.4, 132.3, 129.8, 129.1, 127.6, 127.0, 125.7, 125.31, 125.26, 124.3 (d,  $J = 10.1$  Hz), 121.5, 118.2 (d,  $J = 21.0$  Hz), 117.5 (d,  $J = 22.5$  Hz), 104.0 (d,  $J = 3.3$  Hz), 95.1, 20.2 (d,  $J = 1.8$  Hz), 18.23, 18.20, 10.8.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.67 (t,  $J = 9.4$  Hz). IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2943, 2891, 2865, 2155, 1702, 1588, 1556, 1510, 1465, 1410, 1380, 1315, 1237, 1166, 1129, 1102, 1074, 1037, 1016, 989, 970, 919, 882, 854, 802, 750, 695, 675; HRMS (ESI): exact mass calculated for:  $\text{C}_{31}\text{H}_{35}\text{NFSi}$   $[\text{M}+\text{H}]^+$ : 468.2517, found 468.2516. [Phenomenex Lux 5u Cellulose-4 PC-2 column, hexane/*i*-PrOH, 99/1 v/v, flow rate 0.5 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 13.18 min,  $t_R$  (major) = 17.39 min,  $ee = 89\%$ .  $[\alpha]_D^{24} = +241.9$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

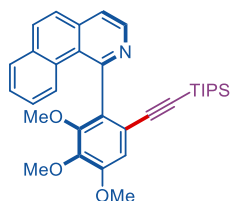


**3qa**, 82.6 mg, 89% yield, yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 5.2$  Hz, 1H), 7.90 (d,  $J = 8.8$  Hz, 1H), 7.83 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.74-7.67 (m, 3H), 7.55-7.45 (m, 2H), 7.45-7.40 (m, 2H), 7.28-7.23 (m, 1H), 2.31 (q,  $J = 7.6$  Hz, 2H), 0.95 (t,  $J = 7.2$  Hz, 3H), 0.59-0.50 (m, 21H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 145.9, 143.9, 141.6, 138.1, 133.3, 132.1, 131.1, 129.9, 129.4, 129.0, 128.2, 127.3, 126.8, 126.0, 125.8, 125.3, 122.6, 121.4, 105.3, 93.6, 26.5, 18.3, 18.2, 14.4, 10.9. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2960, 2941, 2891, 2864, 2146, 1609, 1585, 1555, 1510, 1461, 1412, 1380, 1310, 1236, 1103, 1074, 1015, 994, 916, 882, 852, 802, 746, 675, 640; HRMS (ESI): exact mass calculated for:  $\text{C}_{32}\text{H}_{38}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 464.2768, found 464.2772. [Phenomenex Lux 5u

Cellulose-4 PC-4 column, hexane/*i*-PrOH, 98/2 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 6.14 min,  $t_R$  (major) = 7.84 min,  $ee = 79\%$ .  $[\alpha]_D^{24} = +208.7$  ( $c = 0.2$ , CHCl<sub>3</sub>).

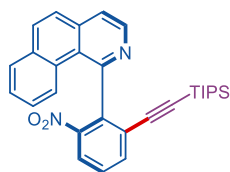


**3ra**, 58.9 mg, 63% yield, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.81 (d,  $J = 5.2$  Hz, 1H), 7.90 (d,  $J = 8.8$  Hz, 1H), 7.86-7.77 (m, 2H), 7.73-7.66 (m, 2H), 7.53-7.40 (m, 2H), 7.32-7.27 (m, 2H), 7.10 (d,  $J = 8.4$  Hz, 1H), 3.65 (s, 3H), 0.59-0.50 (m, 21H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.9, 155.2, 143.9, 138.3, 133.3, 132.2, 130.1, 129.5, 129.0, 127.3, 126.8, 125.9, 125.7, 125.7, 123.9, 121.5, 112.4, 104.5, 94.3, 56.2, 18.28, 18.25, 10.9. IR (ATR):  $\nu_{\max}$  (cm<sup>-1</sup>) = 2941, 2891, 2864, 2149, 1588, 1571, 1510, 1463, 1437, 1413, 1381, 1296, 1266, 1240, 1169, 1078, 1015, 994, 931, 916, 882, 852, 794, 748, 674, 658, 638; HRMS (ESI): exact mass calculated for: C<sub>31</sub>H<sub>36</sub>NOSi [M+H]<sup>+</sup>: 466.2561, found 466.2558. [Chiralpak IC column, hexane/*i*-PrOH, 90/10 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 6.12 min,  $t_R$  (major) = 11.01 min,  $ee = 71\%$ .  $[\alpha]_D^{24} = +131.2$  ( $c = 0.2$ , CHCl<sub>3</sub>).

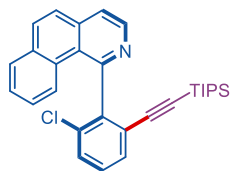


**3sa**, 96.7 mg, 92% yield, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.77 (d,  $J = 5.2$  Hz, 1H), 7.89 (dd,  $J = 8.4, 2.0$  Hz, 2H), 7.84 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.71 (d,  $J = 3.6$  Hz, 1H), 7.69 (s, 1H), 7.53-7.45 (m, 1H), 7.36-7.30 (m, 1H), 6.99 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.53 (s, 3H), 0.61-0.52 (m, 21H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.8, 153.5, 150.9, 143.8, 138.1, 135.0, 133.4, 132.0, 130.0, 129.0, 127.2, 126.8, 125.8, 125.68, 125.65, 121.4, 117.9, 112.1, 104.4, 93.4, 61.2, 60.9, 56.4, 18.23, 18.22, 10.9. IR (ATR):  $\nu_{\max}$  (cm<sup>-1</sup>) = 2941, 2892, 2865, 2149, 1587, 1556, 1486, 1459, 1416, 1403, 1374, 1337, 1309, 1262, 1236, 1196, 1134, 1105, 1065, 1047, 1027, 990, 948, 922, 883, 863, 845, 814, 749, 718, 674, 657, 626; HRMS (ESI): exact mass calculated for: C<sub>33</sub>H<sub>40</sub>NO<sub>3</sub>Si [M+H]<sup>+</sup>: 526.2772, found 526.2771. [Chiralpak AD-H column, hexane/*i*-PrOH, 90/10 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 3.87 min,  $t_R$  (major) = 5.36

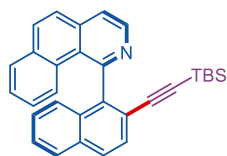
min,  $ee = 61\%$ .  $[\alpha]_D^{24} = +118.5$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



**3ta**, 76.7 mg, 80% yield, yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (d,  $J = 5.6$  Hz, 1H), 8.23 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.93 (d,  $J = 8.8$  Hz, 1H), 7.89-7.82 (m, 2H), 7.76-7.69 (m, 3H), 7.61 (t,  $J = 8.0$  Hz, 1H), 7.56-7.48 (m, 1H), 7.33-7.26 (m, 1H), 0.59-0.48 (m, 21H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 148.5, 143.7, 141.7, 138.1, 138.0, 133.5, 132.3, 129.4, 129.3, 128.8, 127.4, 127.1, 125.7, 125.6, 125.3, 125.1, 125.0, 121.9, 102.3, 97.7, 18.21, 18.18, 10.8. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2943, 2891, 2864, 2155, 1607, 1587, 1532, 1463, 1383, 1360, 1313, 1278, 1241, 1185, 1101, 1065, 1016, 995, 911, 883, 868, 852, 837, 821, 792, 750, 672, 638; HRMS (ESI): exact mass calculated for:  $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_2\text{Si}$   $[\text{M}+\text{H}]^+$ : 481.2306, found 481.2302. [Chiralcel OD-H column, hexane/*i*-PrOH, 90/10 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 3.20 min,  $t_R$  (major) = 4.96 min,  $ee = 95\%$ .  $[\alpha]_D^{24} = +591.8$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

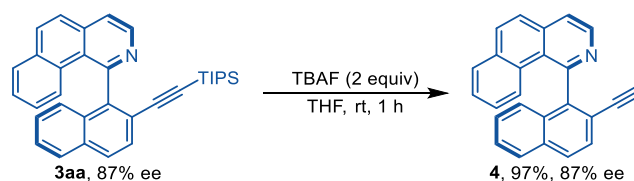


**3ua**, 84.7 mg, 90% yield, yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 5.2$  Hz, 1H), 7.91 (d,  $J = 8.4$  Hz, 1H), 7.85 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.75-7.68 (m, 3H), 7.61-7.56 (m, 2H), 7.54-7.49 (m, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.34-7.29 (m, 1H), 0.60-0.55 (m, 21H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 145.3, 144.1, 138.2, 133.3, 133.2, 132.2, 131.8, 130.3, 129.6, 129.2, 129.1, 127.6, 127.0, 125.7, 125.3, 125.1, 124.8, 121.9, 103.7, 95.8, 18.23, 18.20, 10.8. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2942, 2891, 2864, 2164, 1610, 1586, 1555, 1511, 1463, 1443, 1410, 1380, 1310, 1265, 1239, 1181, 1144, 1105, 1072, 1015, 994, 896, 869, 852, 790, 749, 735, 715, 674, 637; HRMS (ESI): exact mass calculated for:  $\text{C}_{30}\text{H}_{33}\text{NSiCl}$   $[\text{M}+\text{H}]^+$ : 470.2065, found 470.2061. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_R$  (minor) = 7.47 min,  $t_R$  (major) = 15.39 min,  $ee = 78\%$ .  $[\alpha]_D^{24} = +188.9$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

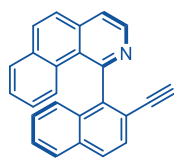


**3ae**, 21.3 mg, 24% yield, yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (d,  $J = 5.2$  Hz, 1H), 7.94 (t,  $J = 8.4$  Hz, 3H), 7.85-7.75 (m, 3H), 7.66 (d,  $J = 8.4$  Hz, 1H), 7.53-7.39 (m, 3H), 7.37-7.27 (m, 2H), 7.09-7.02 (m, 1H), 0.39 (s, 9H), -0.36 (s, 3H), -0.40 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 145.0, 144.2, 138.2, 133.9, 133.3, 132.4, 131.6, 129.6, 129.2, 128.9, 128.32, 128.28, 127.4, 127.3, 127.0, 126.9, 126.3, 126.2, 126.1, 125.7, 121.5, 119.8, 104.3, 97.0, 25.7, 16.1, -5.02, -5.06. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2953, 2926, 2887, 2854, 2149, 1586, 1555, 1506, 1466, 1430, 1393, 1362, 1335, 1301, 1249, 1222, 1007, 992, 956, 916, 868, 852, 824, 776, 747, 690, 677, 660, 647, 630; HRMS (ESI): exact mass calculated for:  $\text{C}_{31}\text{H}_{30}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 444.2142, found 444.2141. [Chiralpak IC column, hexane/*i*-PrOH, 95/5 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (major) = 8.65 min,  $t_{\text{R}}$  (minor) = 12.19 min,  $ee = 76\%$ .  $[\alpha]_{\text{D}}^{24} = +280.8$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

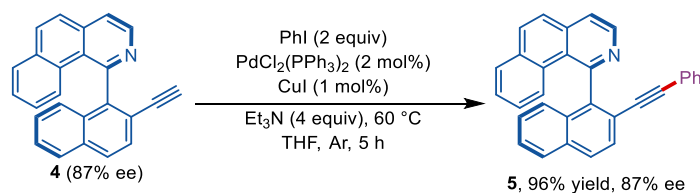
## 4. Synthetic Transformations



A sealed tube with a magnetic stir bar was charged with **3aa** (485.3 mg, 1 mmol), TBAF (2 mL, 2 mmol, 1M) and THF (5 mL) under argon atmosphere. The resulting mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), the mixture was quenched with water (5 mL). The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 $\times$ 15 mL). After the combined organic layer was washed with  $\text{H}_2\text{O}$  and brine, it was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. Then the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford terminal alkyne **4**.

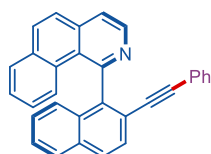


**4**, 318.2 mg, 97% yield, white solid, m.p. = 167.6-169.7 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (d,  $J$  = 5.2 Hz, 1H), 8.00-7.88 (m, 3H), 7.87-7.76 (m, 3H), 7.71 (d,  $J$  = 8.4 Hz, 1H), 7.50-7.37 (m, 3H), 7.29-7.21 (m, 2H), 7.08-6.98 (m, 1H), 2.61 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 145.3, 144.3, 138.0, 133.9, 133.2, 132.4, 131.4, 129.5, 129.4, 129.0, 128.5, 128.3, 127.4, 127.3, 127.2, 127.0, 126.1, 126.0, 125.8, 121.6, 118.7, 82.4, 81.1. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3292, 3054, 1608, 1585, 1555, 1506, 1428, 1395, 1363, 1333, 1301, 1238, 1197, 1144, 1102, 1026, 993, 908, 869, 854, 820, 748, 730, 693, 647, 622; HRMS (ESI): exact mass calculated for:  $\text{C}_{25}\text{H}_{16}\text{N}$   $[\text{M}+\text{H}]^+$ : 330.1277, found 330.1285. [Chiralpak IC column, hexane/*i*-PrOH, 80/20 v/v, flow rate 1 mL/min,  $\lambda$  = 254 nm, 25 °C).  $t_{\text{R}}$  (major) = 10.21 min,  $t_{\text{R}}$  (minor) = 20.16 min,  $ee$  = 87%.  $[\alpha]_{\text{D}}^{24}$  = +116.3 ( $c$  = 0.2,  $\text{CHCl}_3$ ).

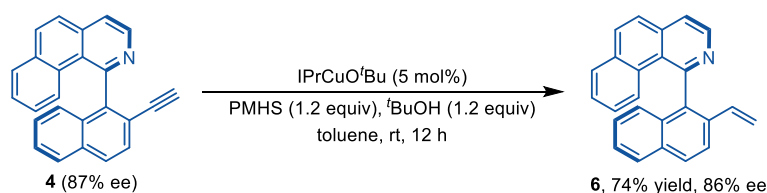


A sealed tube with a magnetic stir bar was charged with **4** (65.8 mg, 0.2 mmol),  $\text{CuI}$

(0.4 mg, 1 mol%), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (2.8 mg, 2 mol%), THF (2 mL), PhI (81.6 mg, 0.4 mmol) and Et<sub>3</sub>N (81.0 mg, 0.8 mmol) under argon atmosphere. The resulting mixture was stirred at 60 °C. After the reaction was complete (monitored by TLC), the mixture was cooled to room temperature and quenched with water (5 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL). After the combined organic layer was washed with H<sub>2</sub>O and brine, it was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Then the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product **5**.

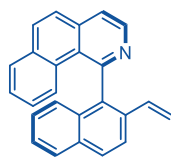


**5**, 77.8 mg, 96% yield, white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.88 (d, *J* = 5.2 Hz, 1H), 8.04-7.91 (m, 3H), 7.88-7.77 (m, 3H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.51-7.43 (m, 2H), 7.42-7.36 (m, 1H), 7.35-7.28 (m, 1H), 7.12-6.96 (m, 4H), 6.71-6.59 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.7, 144.4, 144.2, 138.0, 133.8, 133.2, 132.4, 131.6, 131.3, 129.6, 128.9, 128.8, 128.5, 128.3, 127.9, 127.4, 126.97, 126.96, 126.24, 126.19, 126.1, 125.7, 123.0, 121.4, 119.9, 93.6, 88.7. [Chiralpak IC column, hexane/*i*-PrOH, 80/20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). *t*<sub>R</sub> (major) = 8.01 min, *t*<sub>R</sub> (minor) = 10.97 min, *ee* = 87%. [α]<sub>D</sub><sup>24</sup> = +467.8 (c = 0.2, CHCl<sub>3</sub>).

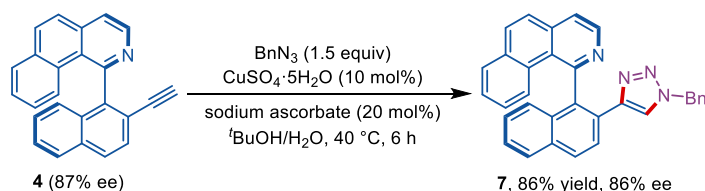


A sealed tube with a magnetic stir bar was charged with IPrCuCl (4.9 mg, 5 mol%), <sup>t</sup>BuONa (2.8 mg, 2 mol%) and THF (0.5 mL) under argon atmosphere. The resulting reaction mixture was stirred for 1 hour at room temperature, and then the solvent was removed under vacuum and anhydrous toluene (2 mL) was added and the solution was transferred via cannula to a dried sealed tube containing **4** (65.8 mg, 0.2 mmol). PMHS (53.4 mg, 0.24 mmol) and <sup>t</sup>BuOH (17.8 mg, 0.24 mmol) were added and the reaction mixture was stirred overnight at rt under argon atmosphere. After the reaction was complete (monitored by TLC), the mixture was quenched with water (5 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL). After the combined organic layer was washed with H<sub>2</sub>O and brine, it was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and

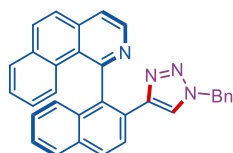
concentrated. Then the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford the alkene product **6**.



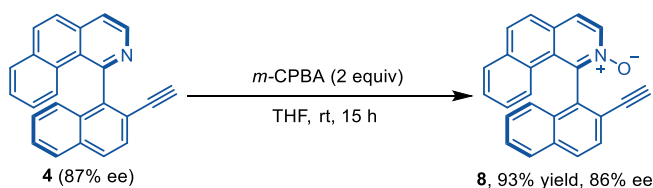
**6**, 49.0 mg, 74% yield, white solid, m.p. = 149.7-151.7 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.88 (d, *J* = 5.2 Hz, 1H), 8.04-7.95 (m, 2H), 7.94-7.87 (m, 2H), 7.86-7.78 (m, 3H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.43-7.36 (m, 2H), 7.20-7.14 (m, 1H), 7.09-6.99 (m, 2H), 6.26 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.72 (d, *J* = 17.2 Hz, 1H), 5.00 (d, *J* = 10.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.8, 144.4, 139.3, 138.0, 134.4, 133.8, 133.3, 132.63, 132.60, 132.0, 129.4, 129.0, 128.8, 128.1, 127.6, 127.0, 126.9, 126.31, 126.25, 126.2, 126.1, 125.8, 123.3, 121.5, 115.9. IR (ATR):  $\nu_{\text{max}}$  (cm<sup>-1</sup>) = 3047, 2972, 2926, 2855, 2161, 1586, 1555, 1509, 1466, 1420, 1391, 1364, 1300, 1267, 1237, 1202, 1101, 1056, 1028, 992, 909, 870, 851, 832, 819, 798, 753, 719, 666, 629; HRMS (ESI): exact mass calculated for: C<sub>25</sub>H<sub>18</sub>N [M+H]<sup>+</sup>: 332.1434, found 332.1436. [Chiralpak IC column, hexane/*i*-PrOH, 80/20 v/v, flow rate 1 mL/min,  $\lambda$  = 254 nm, 25 °C). *t*<sub>R</sub> (major) = 7.93 min, *t*<sub>R</sub> (minor) = 14.20 min, *ee* = 86%. [ $\alpha$ ]<sub>D</sub><sup>24</sup> = +95.8 (c = 0.2, CHCl<sub>3</sub>).



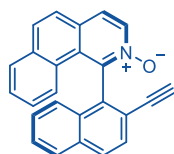
A sealed tube with a magnetic stir bar was charged with **4** (65.8 mg, 0.2 mmol), BnN<sub>3</sub> (40 mg, 0.3 mmol), <sup>t</sup>BuOH (6 mL) and water (0.48 mL), a solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.1 M in water, 5 mg, 0.02 mmol) and (L)-sodium ascorbate (0.1 M in water, 7.9 mg, 0.04 mmol) were then sequentially added under argon atmosphere. The resulting mixture was stirred at 40 °C. After the reaction was complete (monitored by TLC), the mixture was cooled to room temperature and quenched with water (5 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL). After the combined organic layer was washed with H<sub>2</sub>O and brine, it was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Then the residue was purified by silica gel column chromatography (DCM/EtOAc = 2/1) to afford triazole **7**.



**7**, 79.2 mg, 86% yield, yellow solid, m.p. = 174.3-176.5 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 (d, *J* = 5.2 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.76-7.67 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.47-7.37 (m, 2H), 7.36-7.26 (m, 2H), 7.23-7.12 (m, 4H), 7.01-6.92 (m, 1H), 6.76-6.67 (m, 2H), 5.70 (s, 1H), 5.06 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.0, 146.1, 144.1, 138.1, 137.9, 134.0, 133.8, 133.0, 132.7, 131.8, 129.0, 128.91, 128.87, 128.8, 128.4, 128.2, 127.9, 127.8, 127.2, 126.9, 126.6, 126.5, 126.4, 126.01, 125.96, 125.8, 125.4, 121.9, 121.7, 53.6. IR (ATR): ν<sub>max</sub> (cm<sup>-1</sup>) = 2956, 2927, 2855, 1585, 1555, 1505, 1474, 1457, 1423, 1396, 1354, 1309, 1255, 1234, 1223, 1202, 1144, 1088, 1051, 1027, 993, 949, 921, 868, 846, 804, 752, 727, 698, 669, 638; HRMS (ESI): exact mass calculated for: C<sub>32</sub>H<sub>23</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 463.1917, found 463.1921. [Chiralpak AD-H column, hexane/*i*-PrOH, 60/40 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). t<sub>R</sub> (minor) = 6.16 min, t<sub>R</sub> (major) = 7.47 min, ee = 86%. [α]<sub>D</sub><sup>24</sup> = +95.8 (c = 0.2, CHCl<sub>3</sub>).



A sealed tube with a magnetic stir bar was charged with **4** (65.8 mg, 0.2 mmol), *m*-CPBA (92 mg, 0.4 mmol) and THF (2 mL) under argon atmosphere. The resulting mixture was stirred at rt. After the reaction was complete (monitored by TLC), the mixture was quenched with water (5 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL). After the combined organic layer was washed with H<sub>2</sub>O and brine, it was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Then the residue was purified by silica gel column chromatography (DCM/MeOH = 30/1) to afford N-oxide **8**.



**8**, 64.2 mg, 93% yield, white solid, m.p. = 99.2-101.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



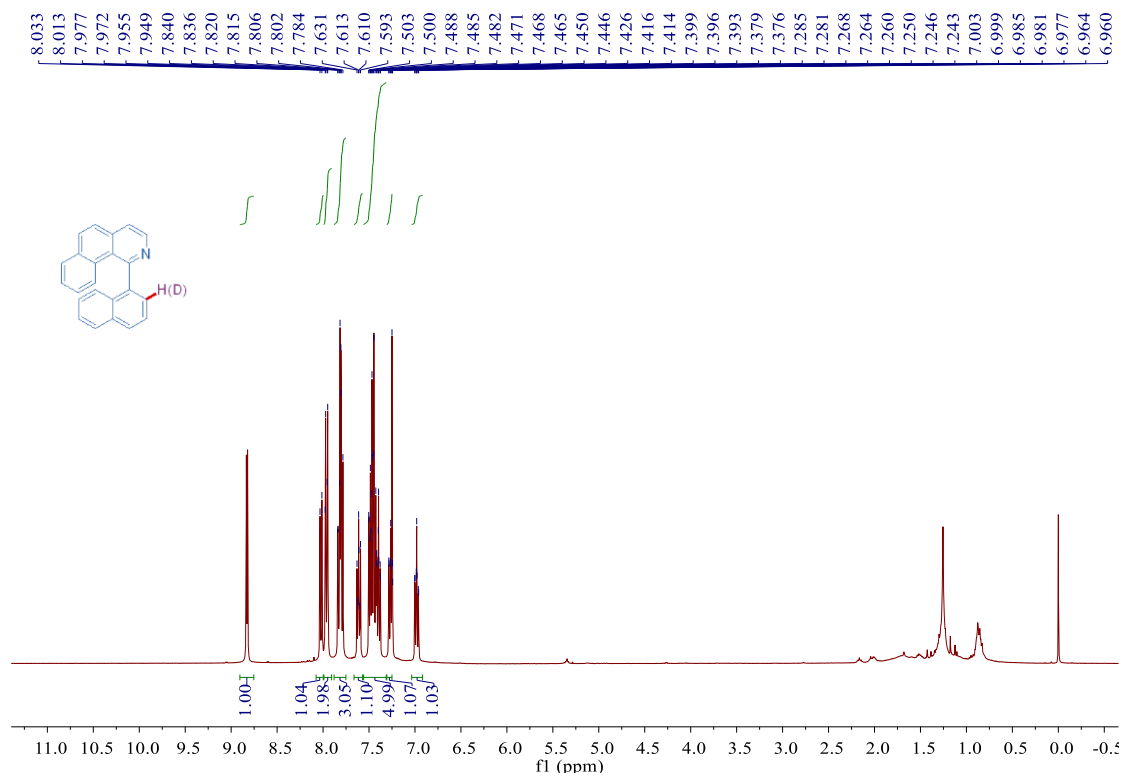
$\delta$  8.56 (d,  $J = 6.8$  Hz, 1H), 8.04 (d,  $J = 8.8$  Hz, 1H), 7.95 (d,  $J = 8.4$  Hz, 1H), 7.87-7.78 (m, 3H), 7.75 (d,  $J = 8.4$  Hz, 1H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.53-7.47 (m, 1H), 7.44-7.38 (m, 1H), 7.36-7.28 (m, 2H), 7.11 (d,  $J = 8.4$  Hz, 1H), 6.96 (m, 1H), 2.71 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.0, 137.6, 137.3, 134.0, 133.8, 130.9, 130.7, 129.8, 129.6, 129.5, 129.2, 128.8, 128.2, 128.0, 127.82, 127.76, 127.6, 127.4, 126.0, 125.0, 124.57, 124.55, 119.9, 81.5, 81.2. IR (ATR):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3294, 3060, 2923, 1701, 1573, 1502, 1432, 1394, 1289, 1249, 1210, 1178, 1147, 1121, 1086, 1074, 916, 868, 842, 822, 804, 749, 731, 710, 674, 647, 625; HRMS (ESI): exact mass calculated for:  $\text{C}_{25}\text{H}_{16}\text{NO}$   $[\text{M}+\text{H}]^+$ : 346.1226, found 346.1220. [Chiralpak AD-H column, hexane/*i*-PrOH, 60/40 v/v, flow rate 1 mL/min,  $\lambda = 254$  nm, 25 °C).  $t_{\text{R}}$  (minor) = 5.90 min,  $t_{\text{R}}$  (major) = 6.94 min,  $ee = 86\%$ .  $[\alpha]_{\text{D}}^{24} = +69.4$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

## 5. Mechanistic Studies

### 5.1 Deuterium labelling study with D<sub>2</sub>O

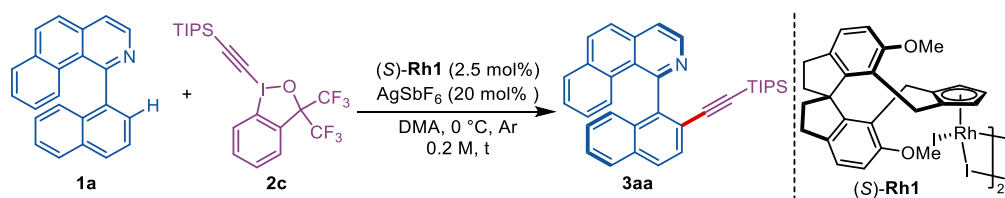


A sealed tube with a magnetic stir bar was charged with *(S)*-Rh1 (1.8 mg, 2.5 mol%), AgSbF<sub>6</sub> (3.4 mg, 20 mol%), **1a** (15.3 mg, 0.05 mmol), D<sub>2</sub>O (20 mg, 1.0 mmol) and DMA (0.25 mL) under argon atmosphere. The resulting mixture was stirred at rt for 48 h. Afterwards, the mixture was cooled to room temperature and diluted with DCM (10 mL), filtered through a thin pad of silica gel. The filter cake was washed with DCM and the combined filtrate was concentrated. The residue was then purified by short column chromatography on silica gel (petroleum ether/EtOAc, 10/1, v/v) to give the recovered **1a**. H/D exchange was not observed by <sup>1</sup>H NMR analysis.



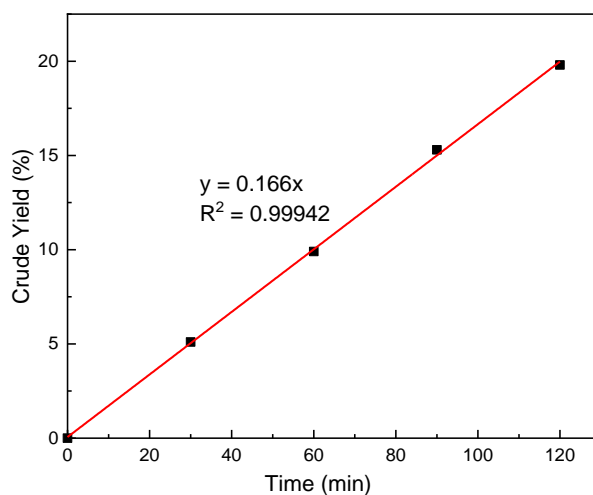
## 5.2 Intermolecular kinetic isotope effect of 1-(naphthalen-1-yl)benzo[h]isoquinoline

A sealed tube with a magnetic stir bar was charged with (*S*)-**Rh1** (1.8 mg, 0.0025 mmol), AgSbF<sub>6</sub> (3.4 mg, 0.01 mmol), **1a** (15.3 mg, 0.05 mmol) or **1a-D**<sub>1</sub> (15.6 mg, 0.05 mmol), **2c** (55 mg, 0.1 mmol) and DMA (0.25 mL) under argon atmosphere. The resulting mixture was stirred at 0 °C for specific time. The reaction mixture was transferred to a short pad of silica gel and washed with ethyl acetate. The solvent was evaporated, and analyzed by <sup>1</sup>H NMR using dibromomethane as an internal standard (the yields of **3aa** were shown in **Table S11** and **Table S12**). The initial reaction rate was obtained by plotting the five points to obtain KIE value ( $k_H/k_D$ ) to be 4.05 (shown in **Figure S1** and **Figure S2**).

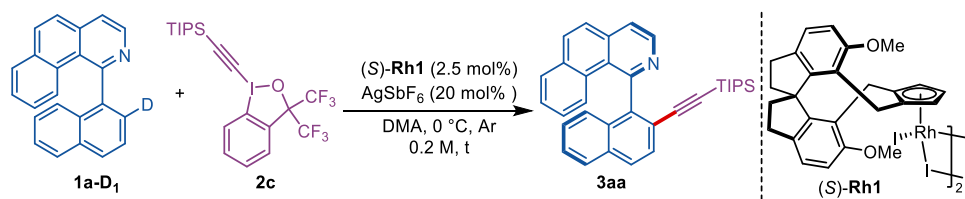


**Table S11.** Yield of **3aa** at specific time

Time (min)	0	30	60	90	120
Yield (%)	0	5.1	9.9	15.3	19.8

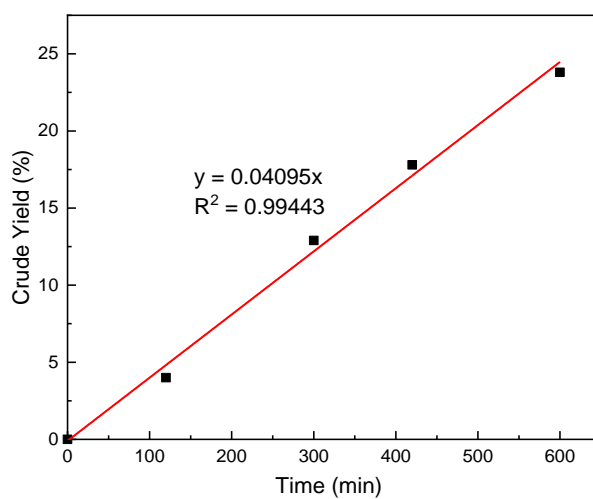


**Figure S1.** Initial rate of the reaction of **2a** with **2c**



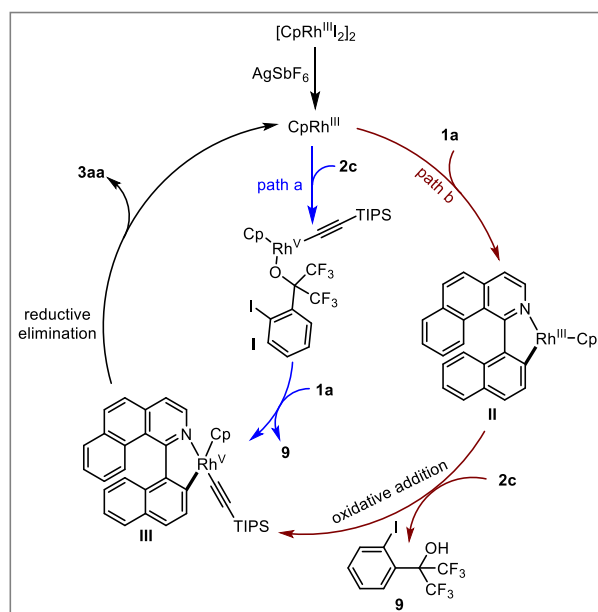
**Table S12.** Yield of **3aa** at specific time

Time (min)	0	120	300	420	600
Yield (%)	0	4.0	12.9	17.8	23.8



**Figure S2.** Initial rate of the reaction of **1a-D<sub>1</sub>** with **2c**

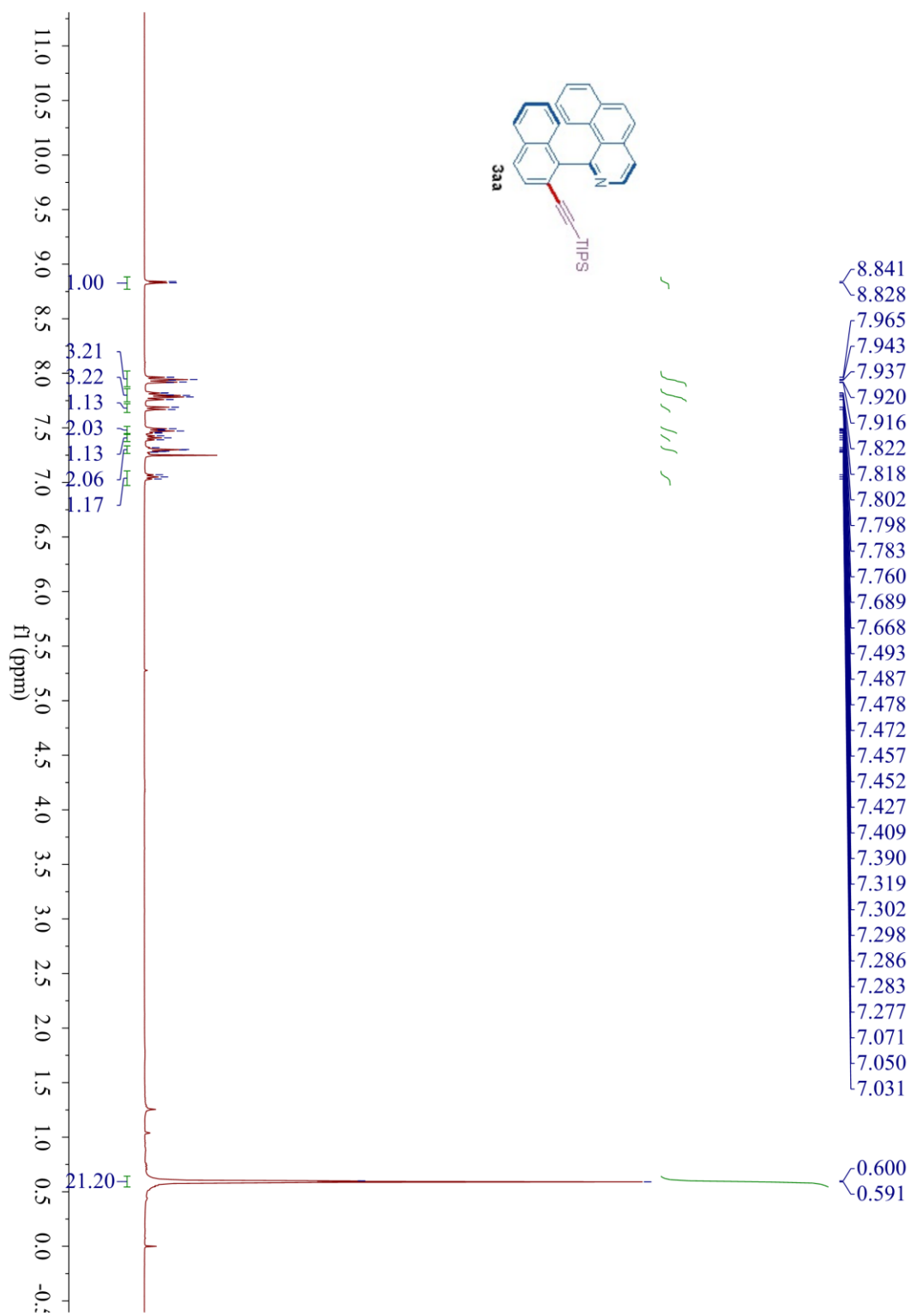
### 5.3 Plausible Catalytic Cycle



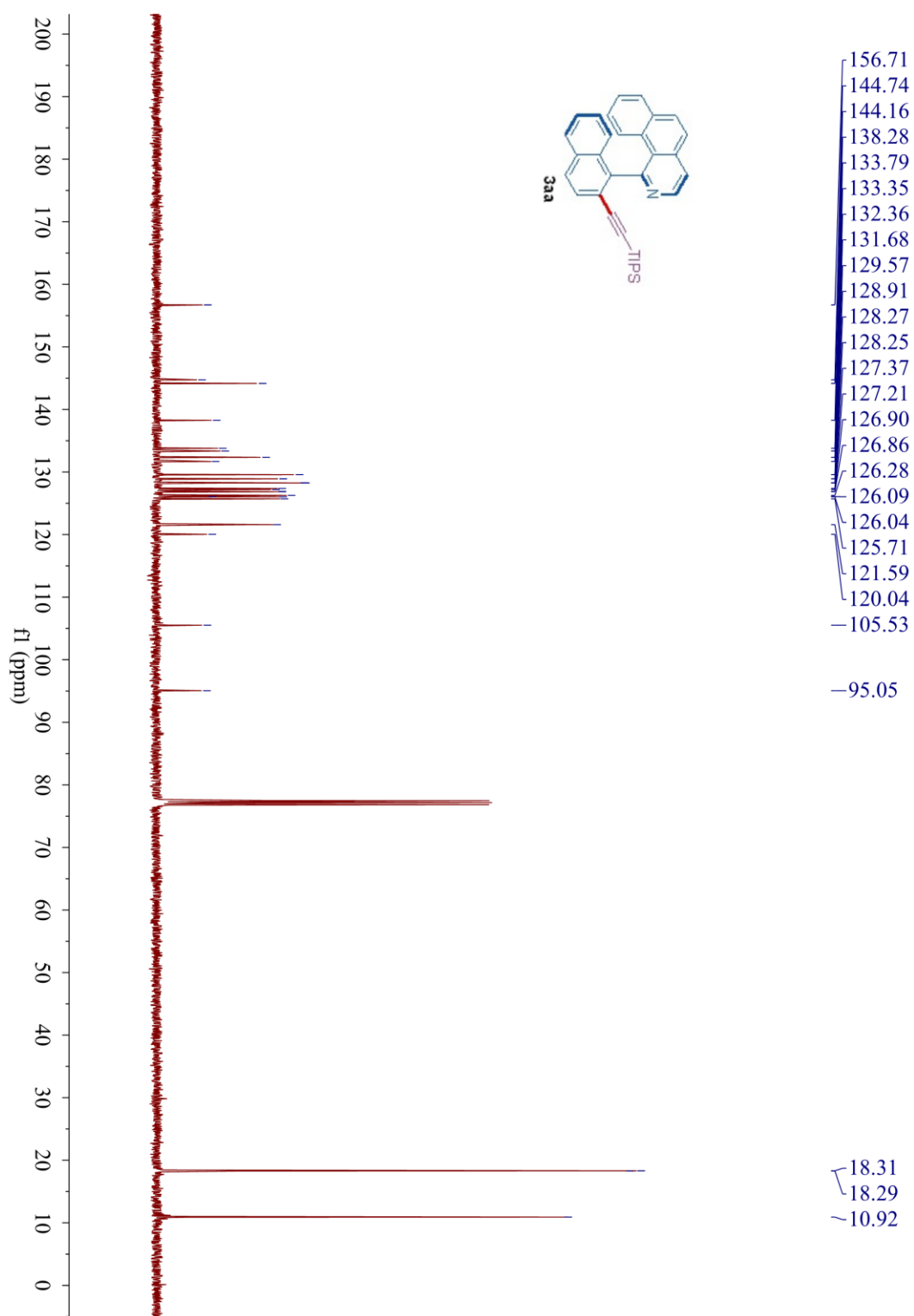
**Figure S3** Plausible Catalytic Cycle

## 6. Copies of NMR Spectra

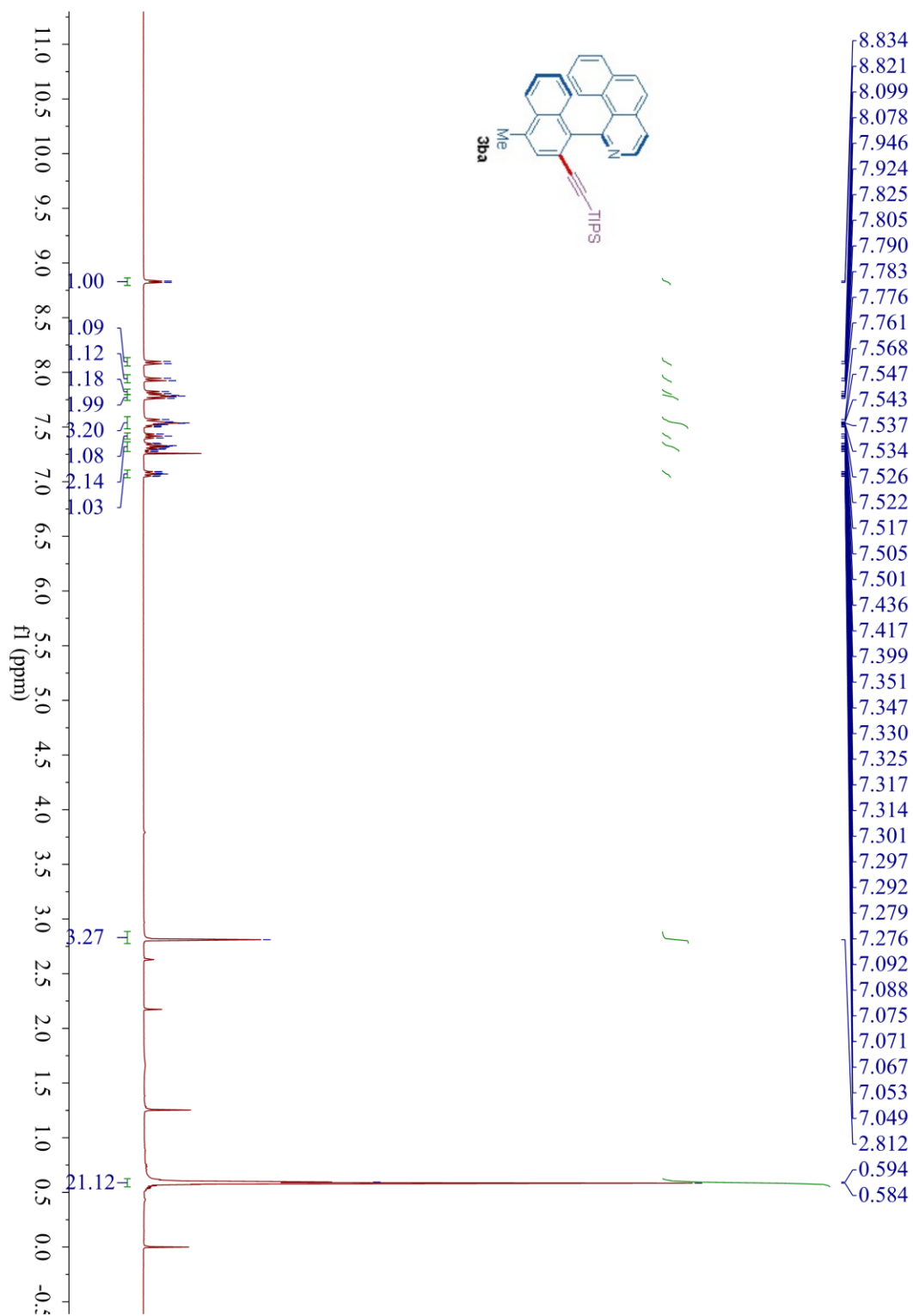
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3aa**



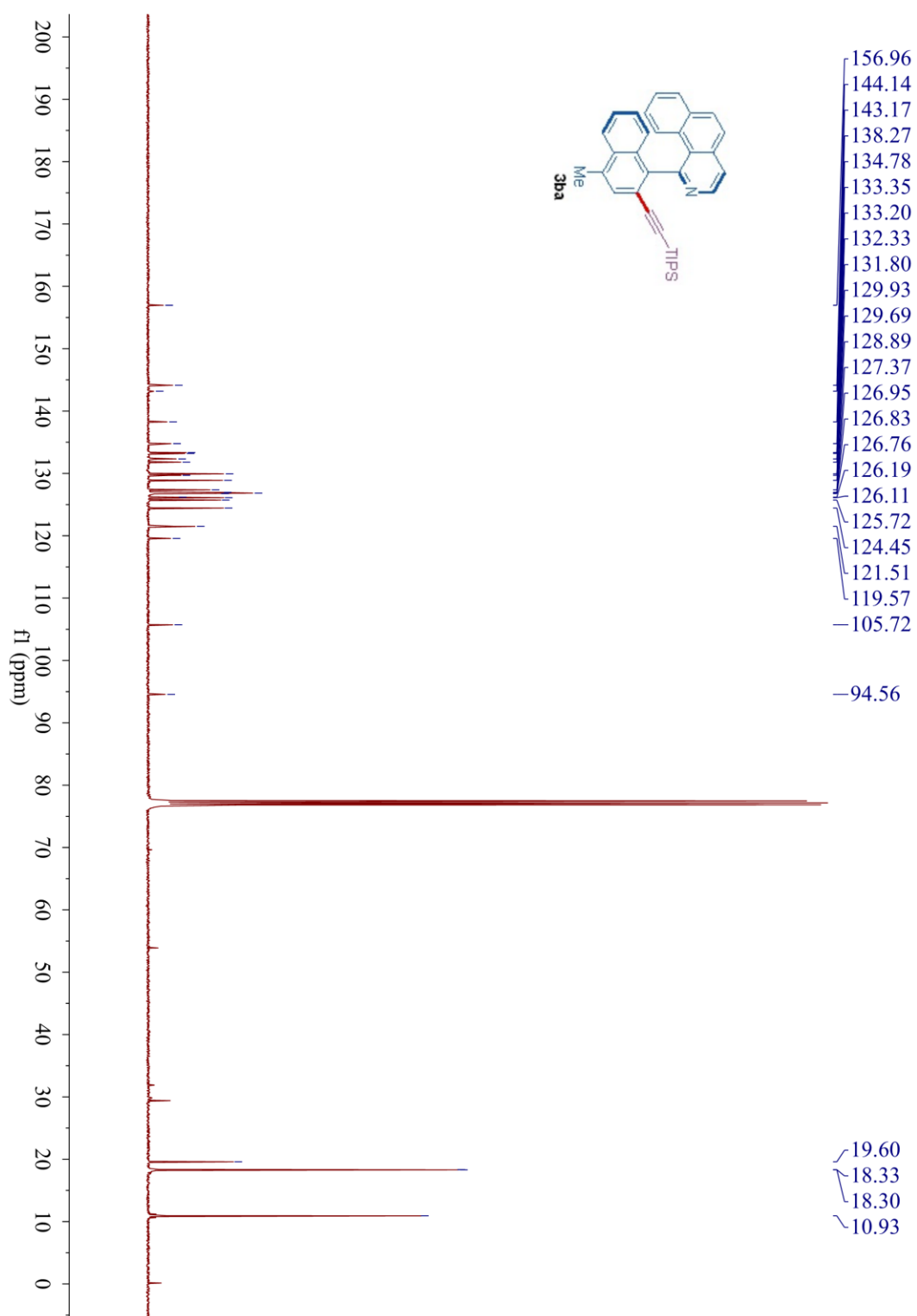
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3aa**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ba**

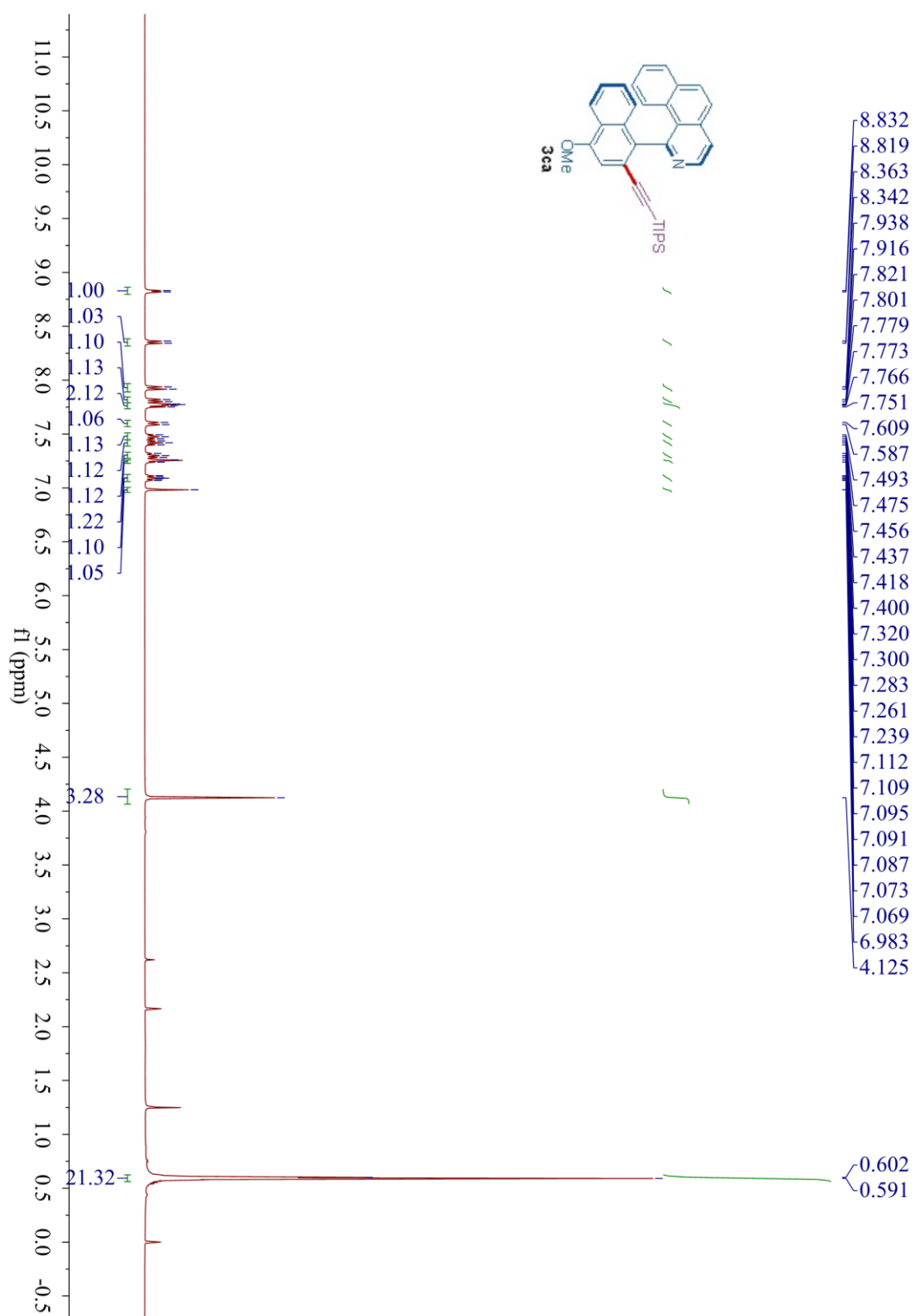


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ba**

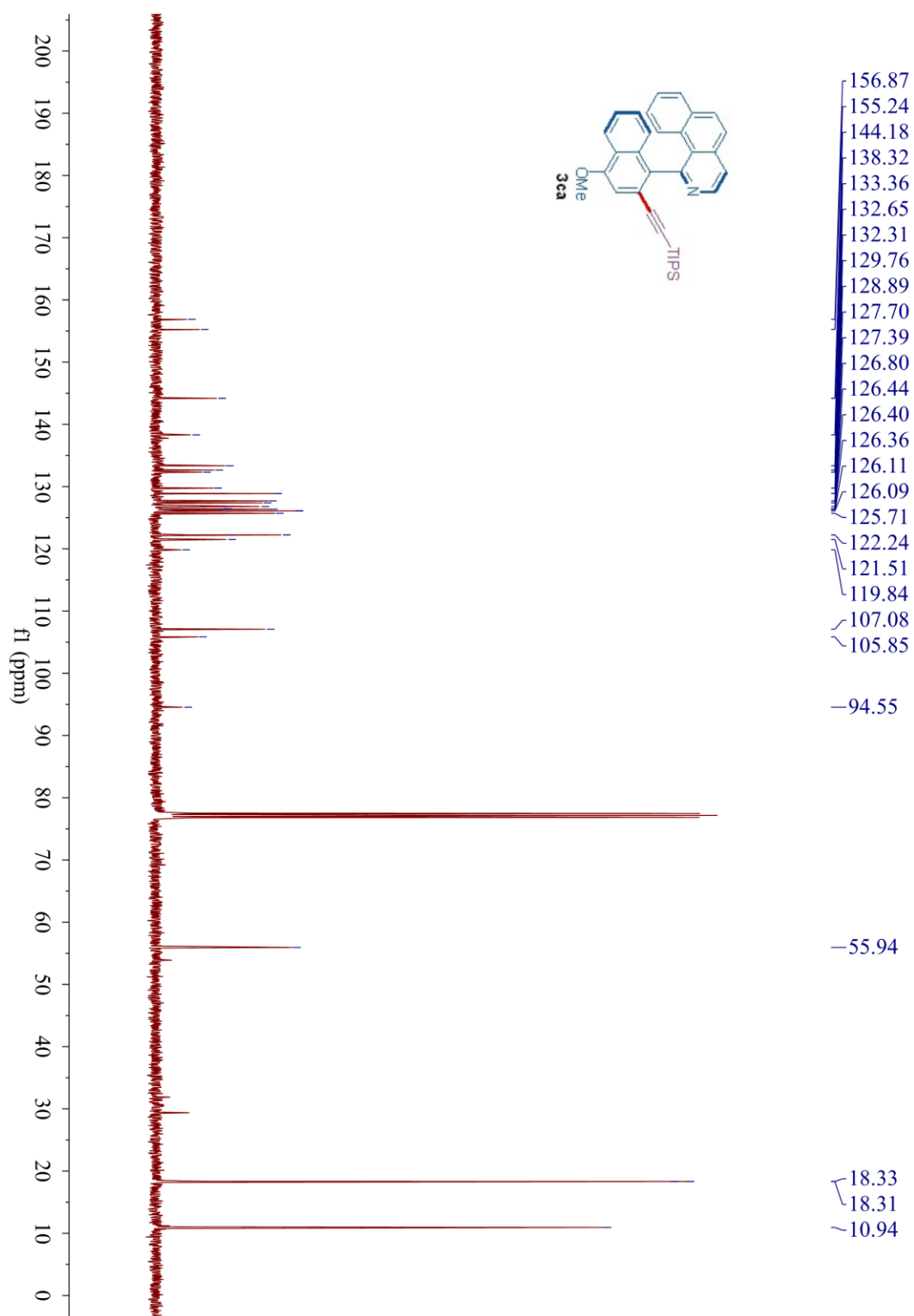




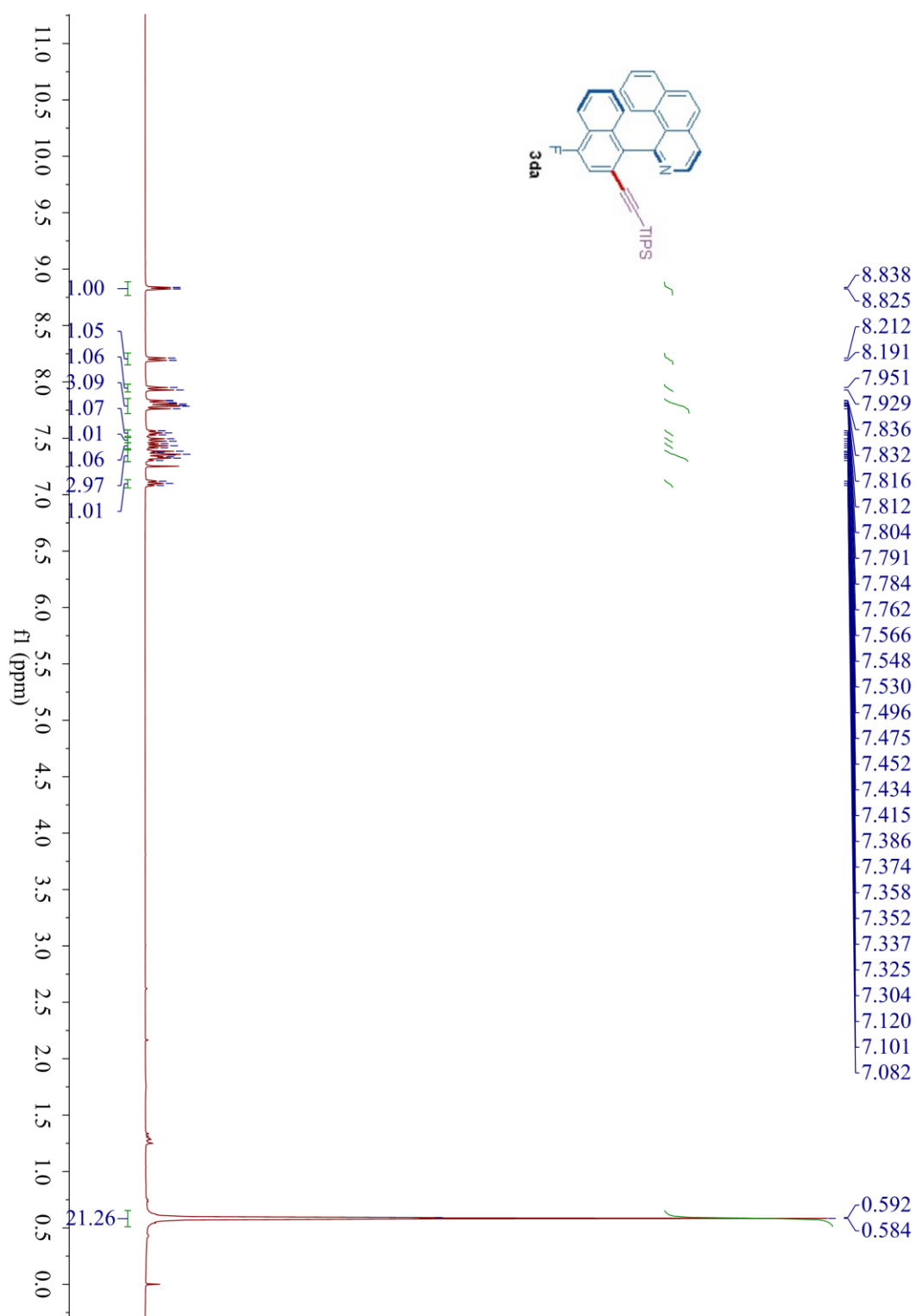
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ca**



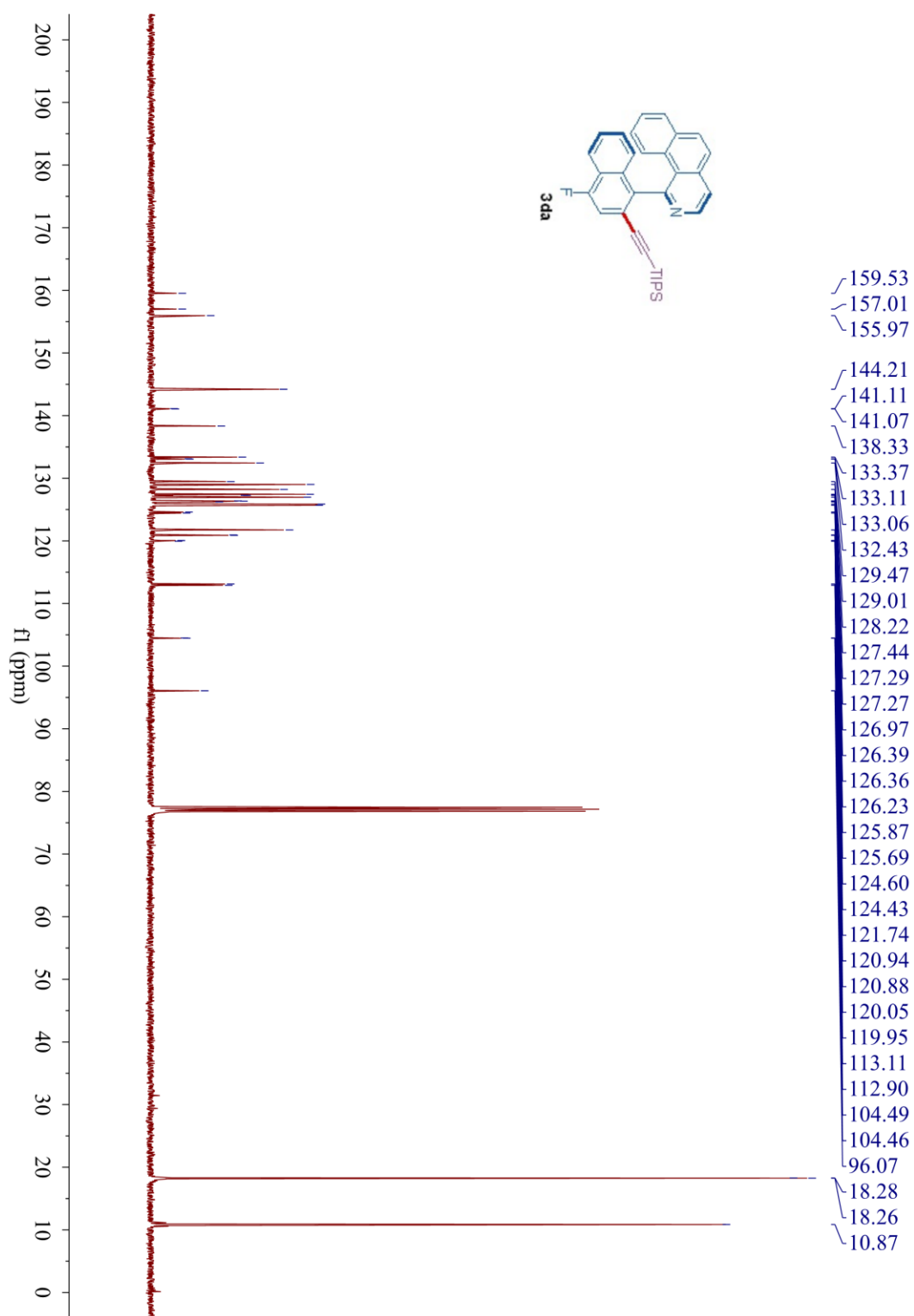
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ca**



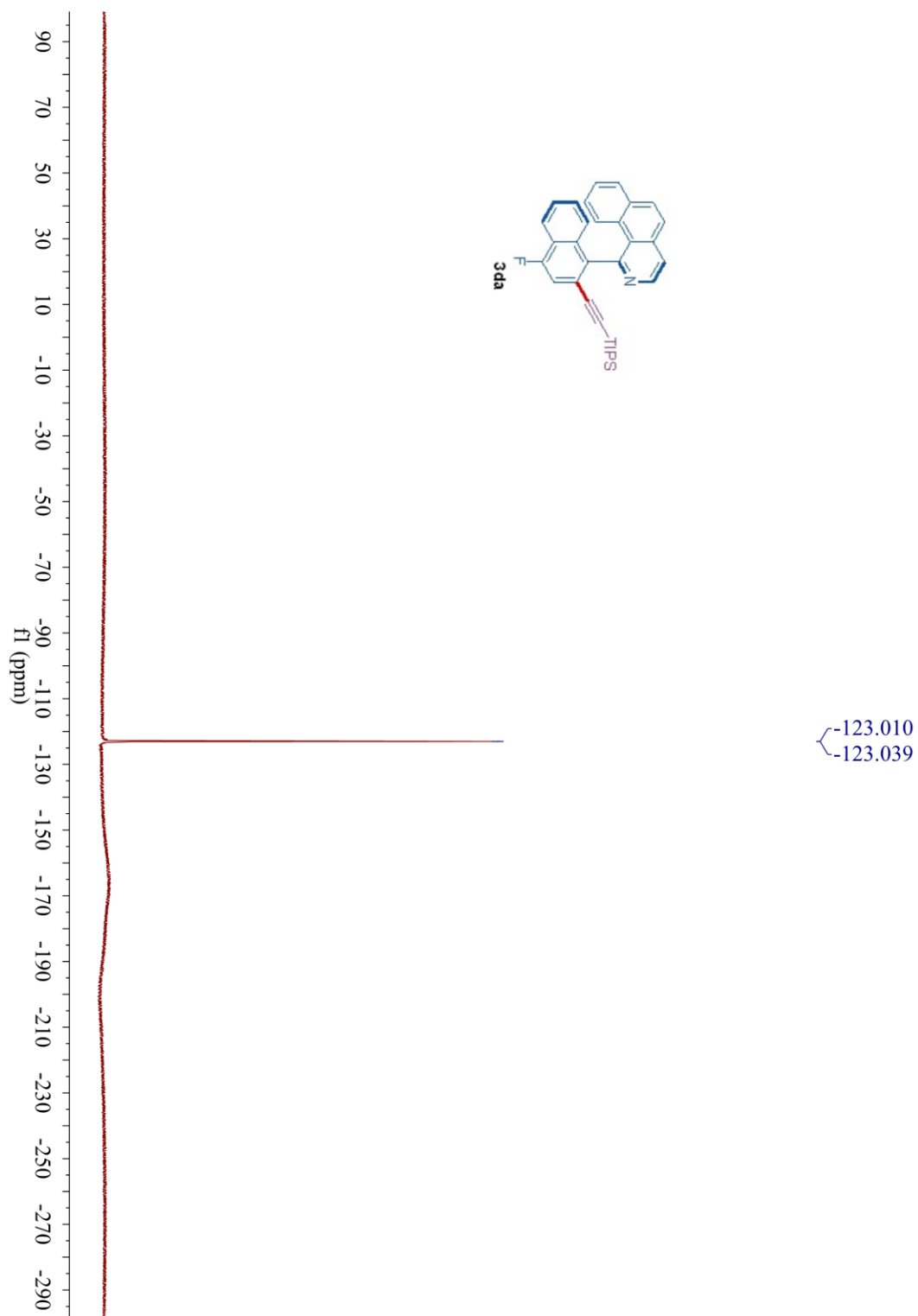
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3da**



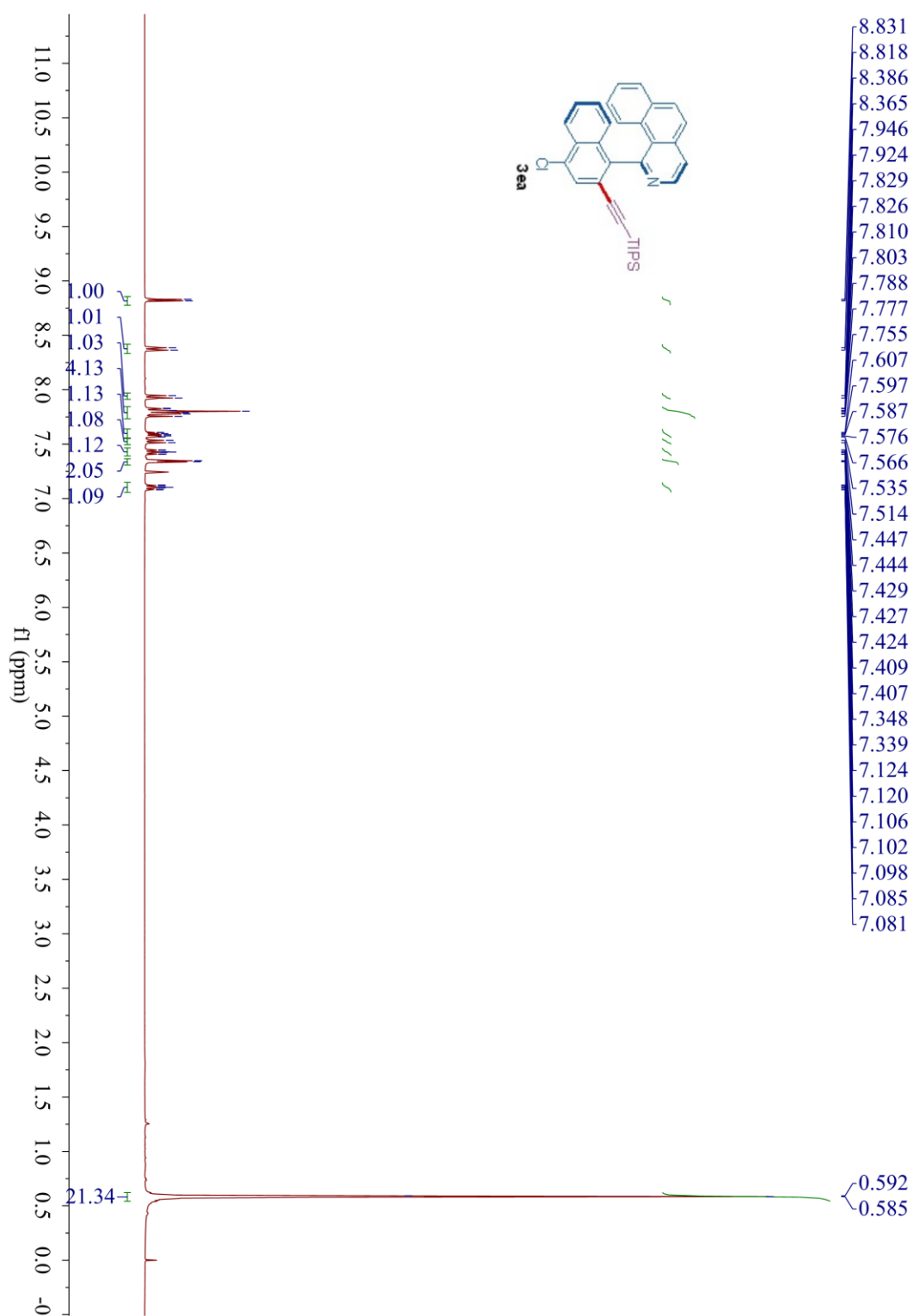
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3da**



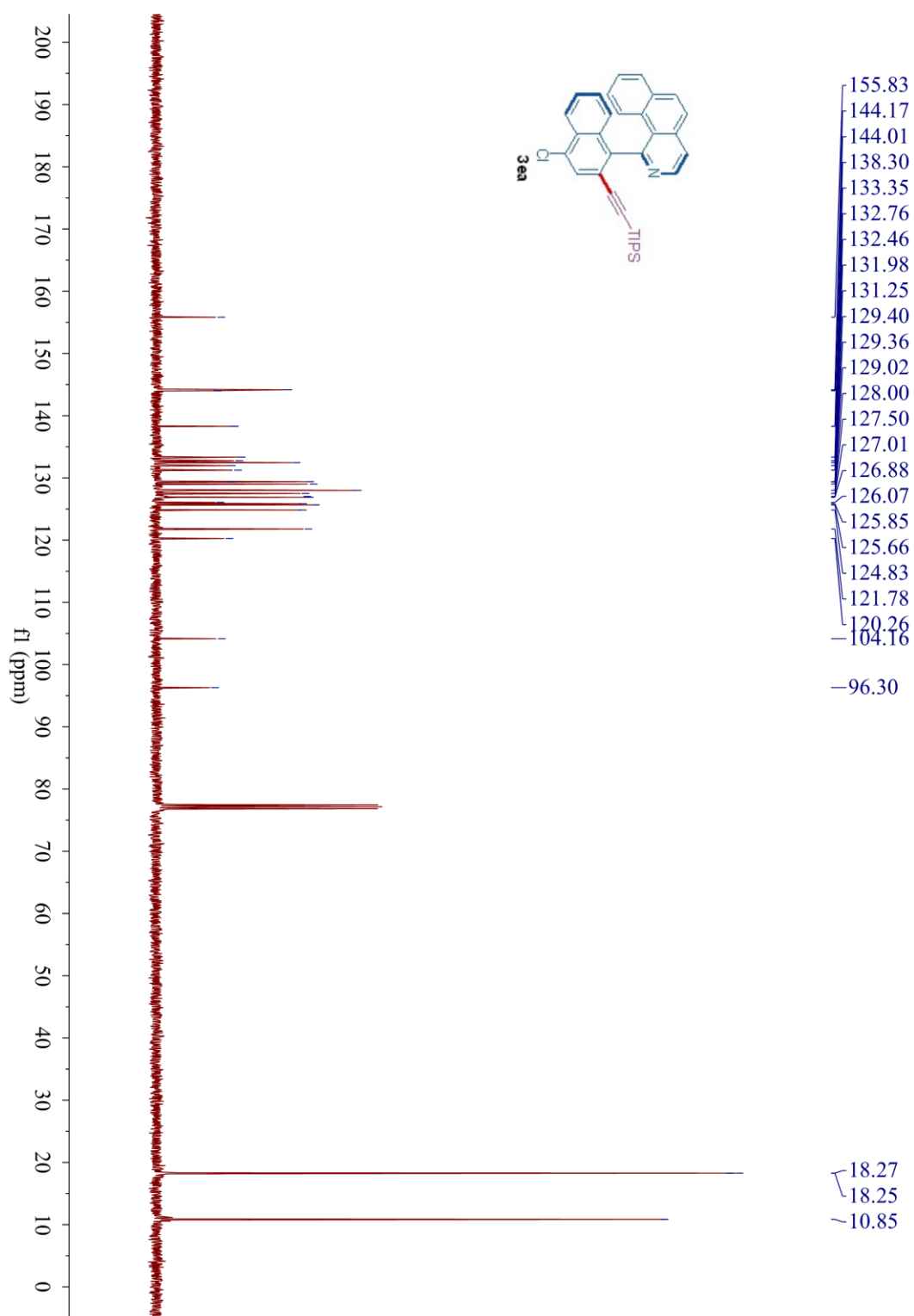
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3da**



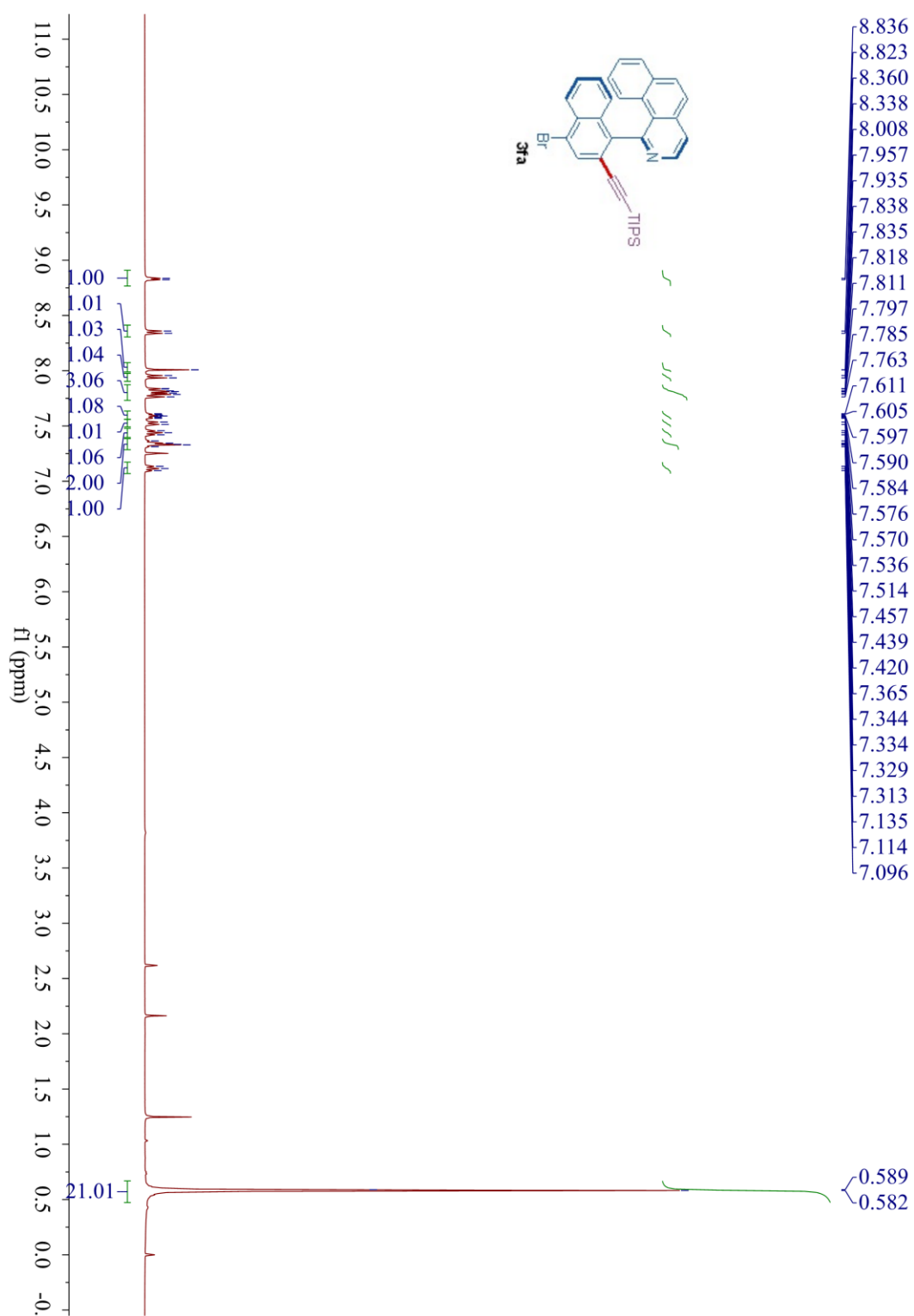
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ea**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3ea**

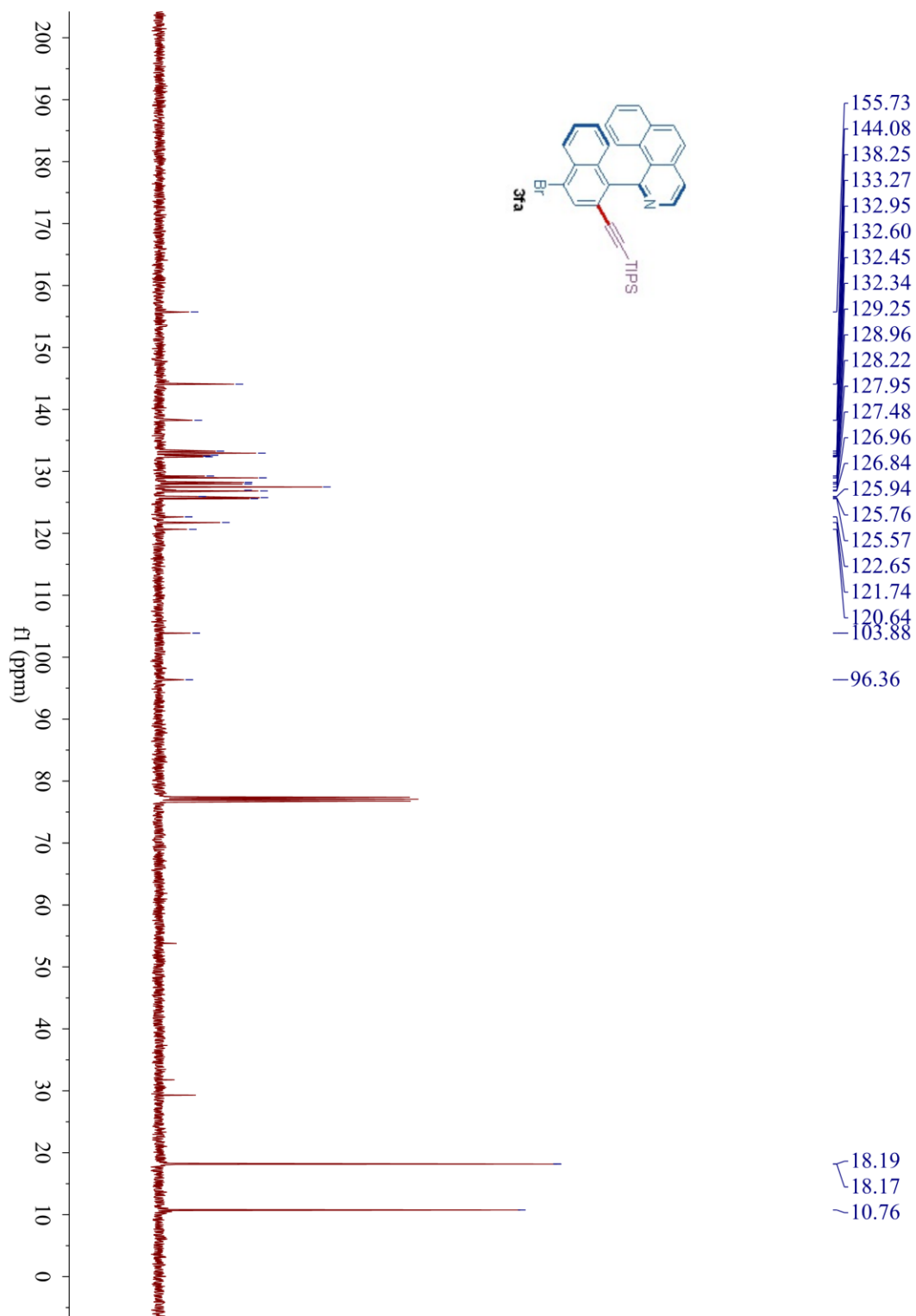


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3fa**

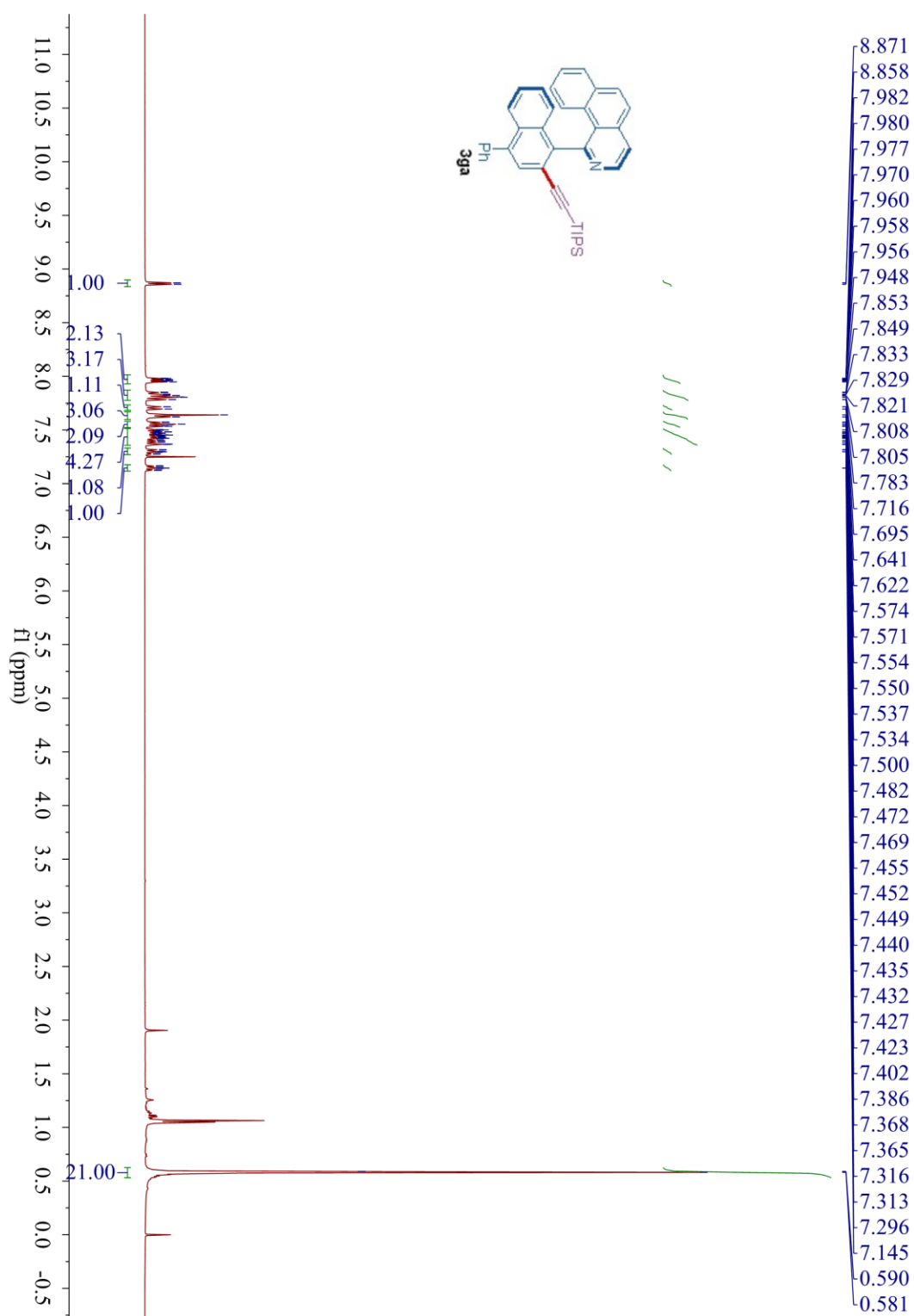




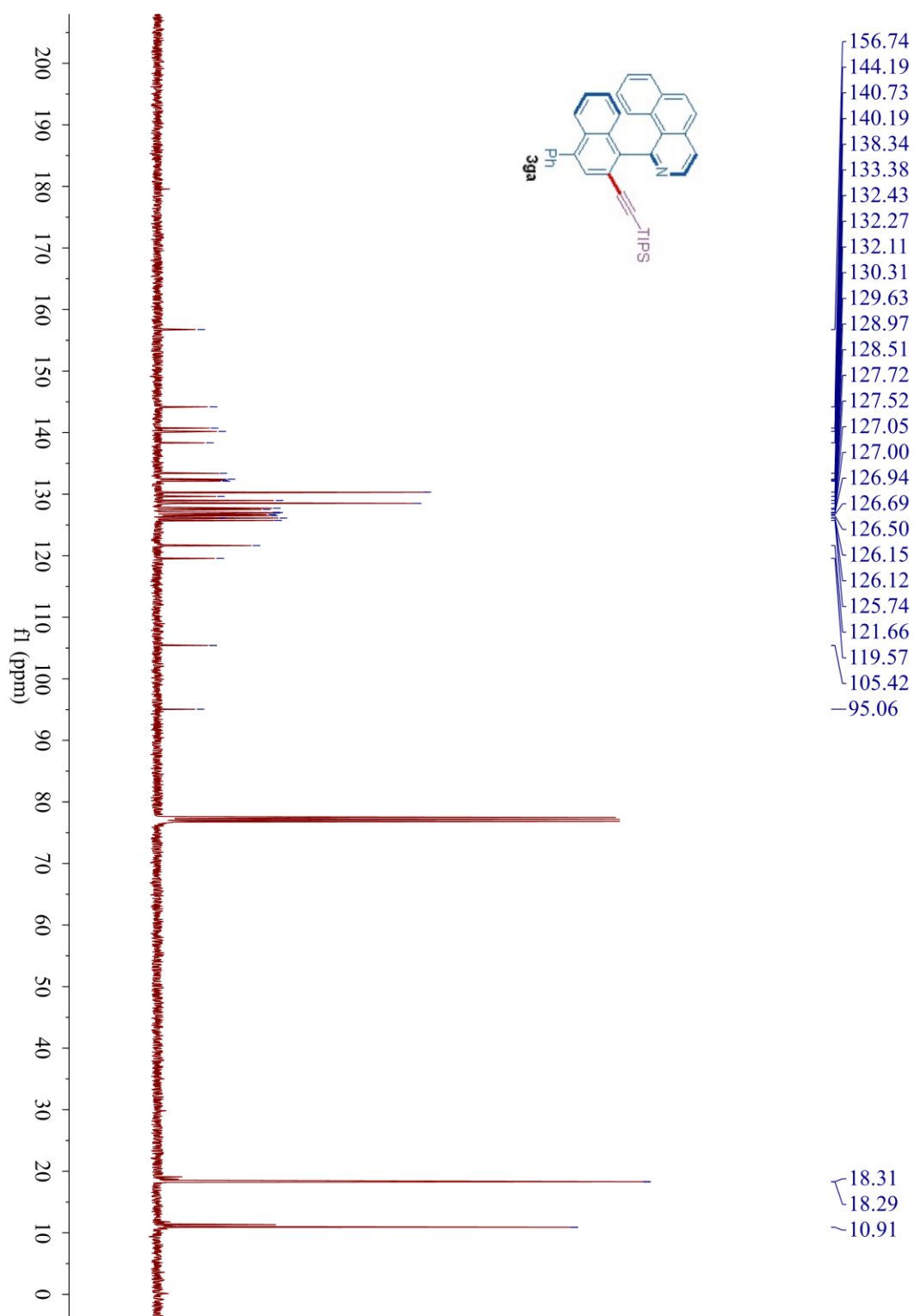
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3fa**



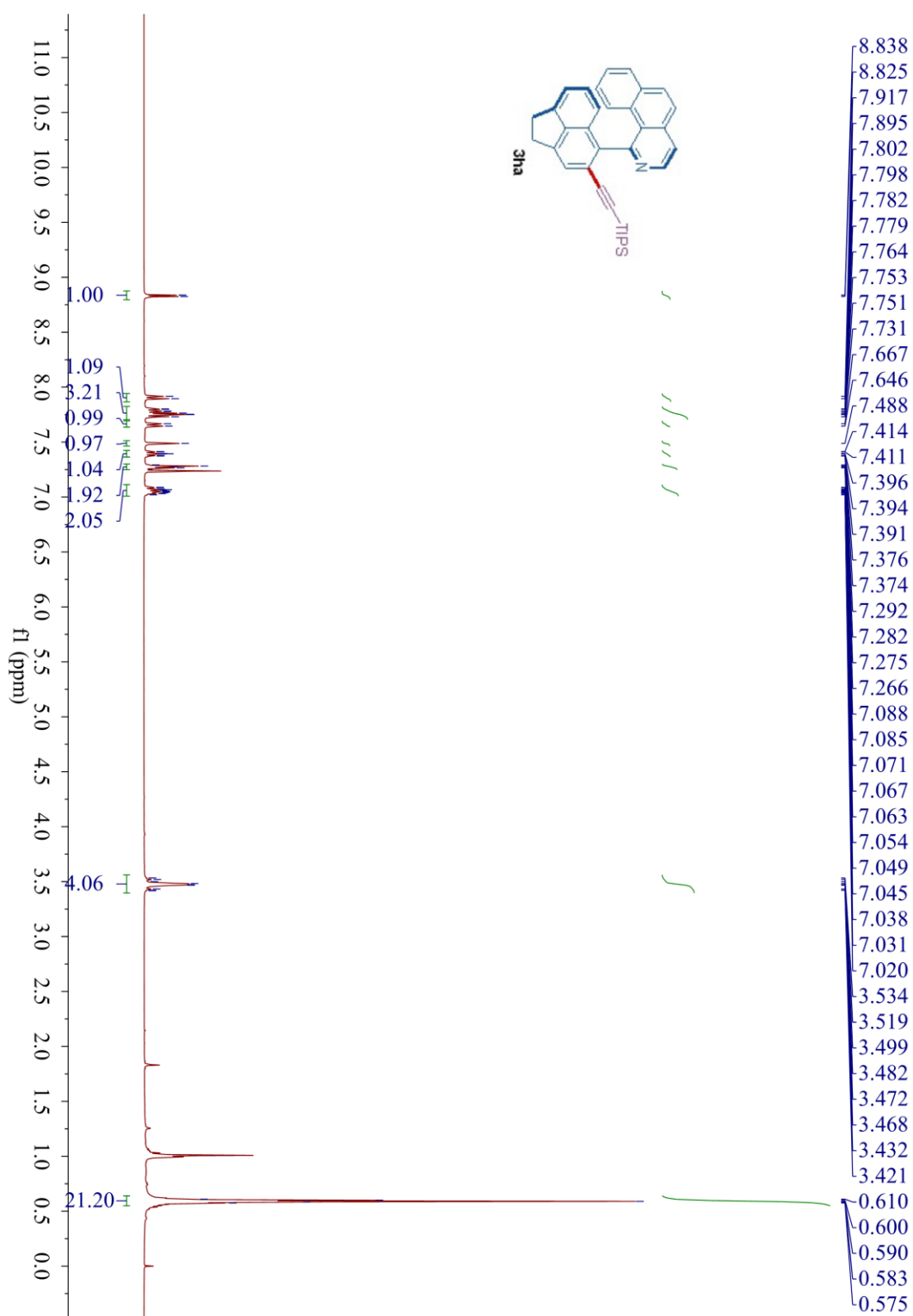
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ga**



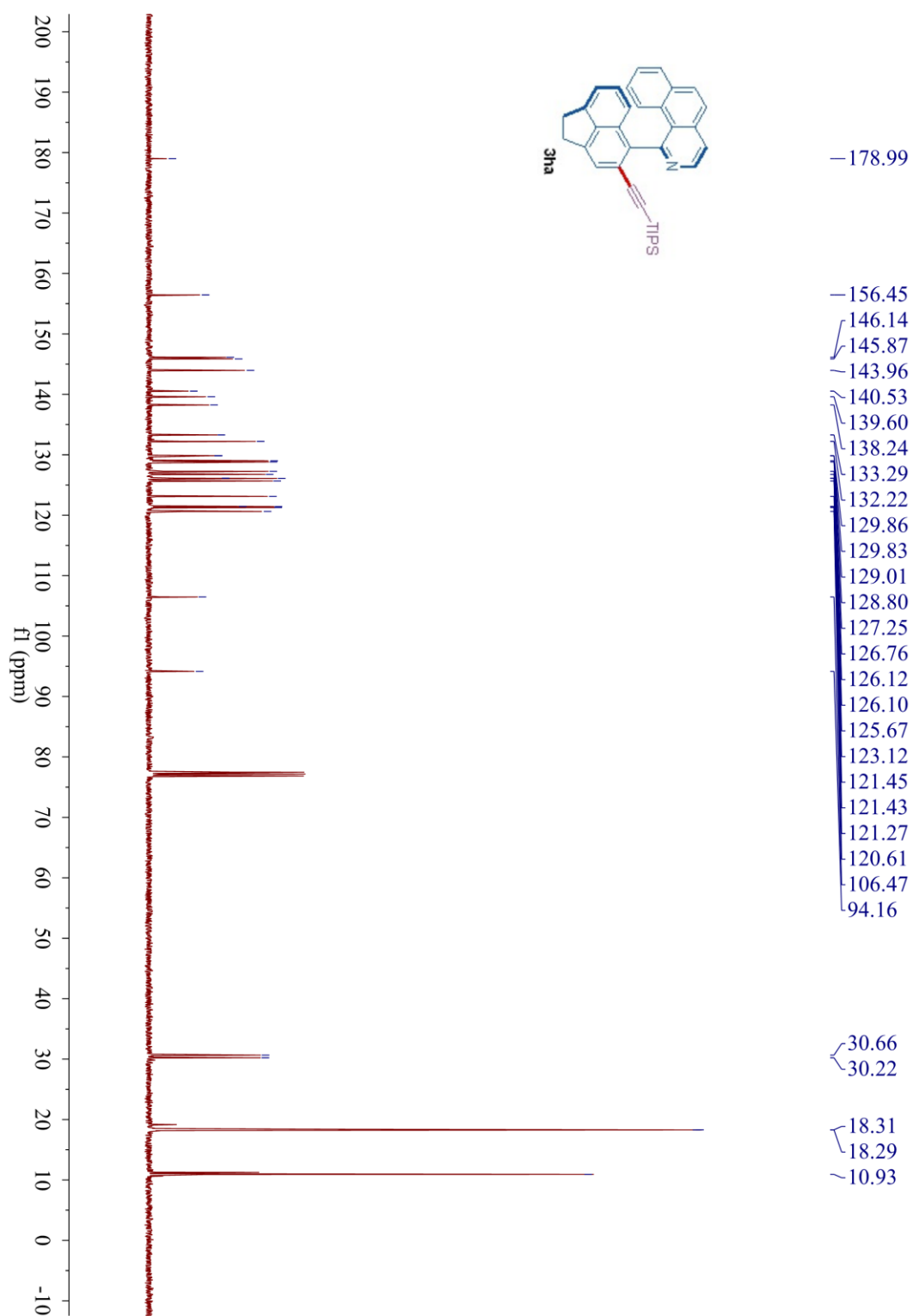
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ga**



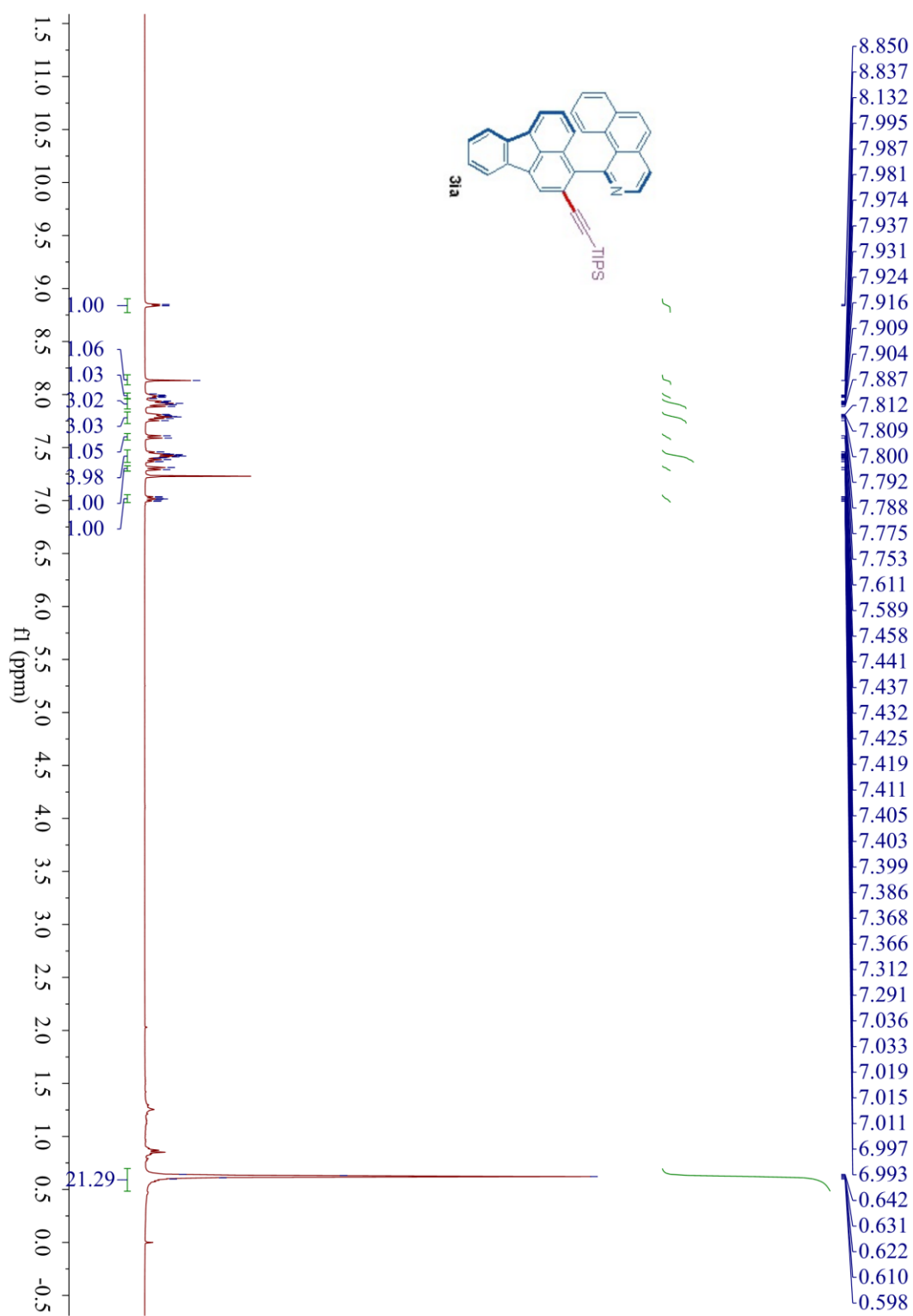
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ha**



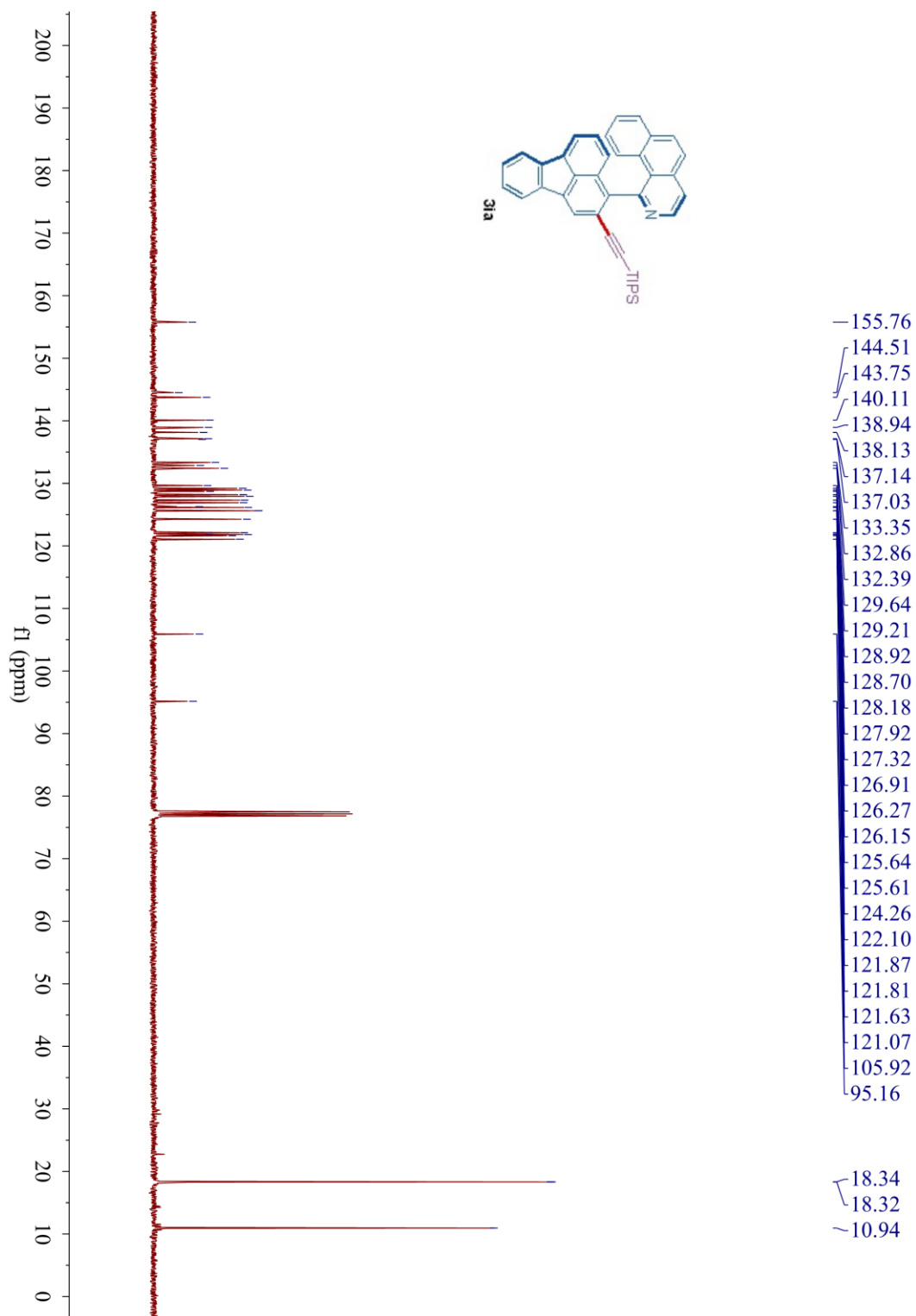
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ha**



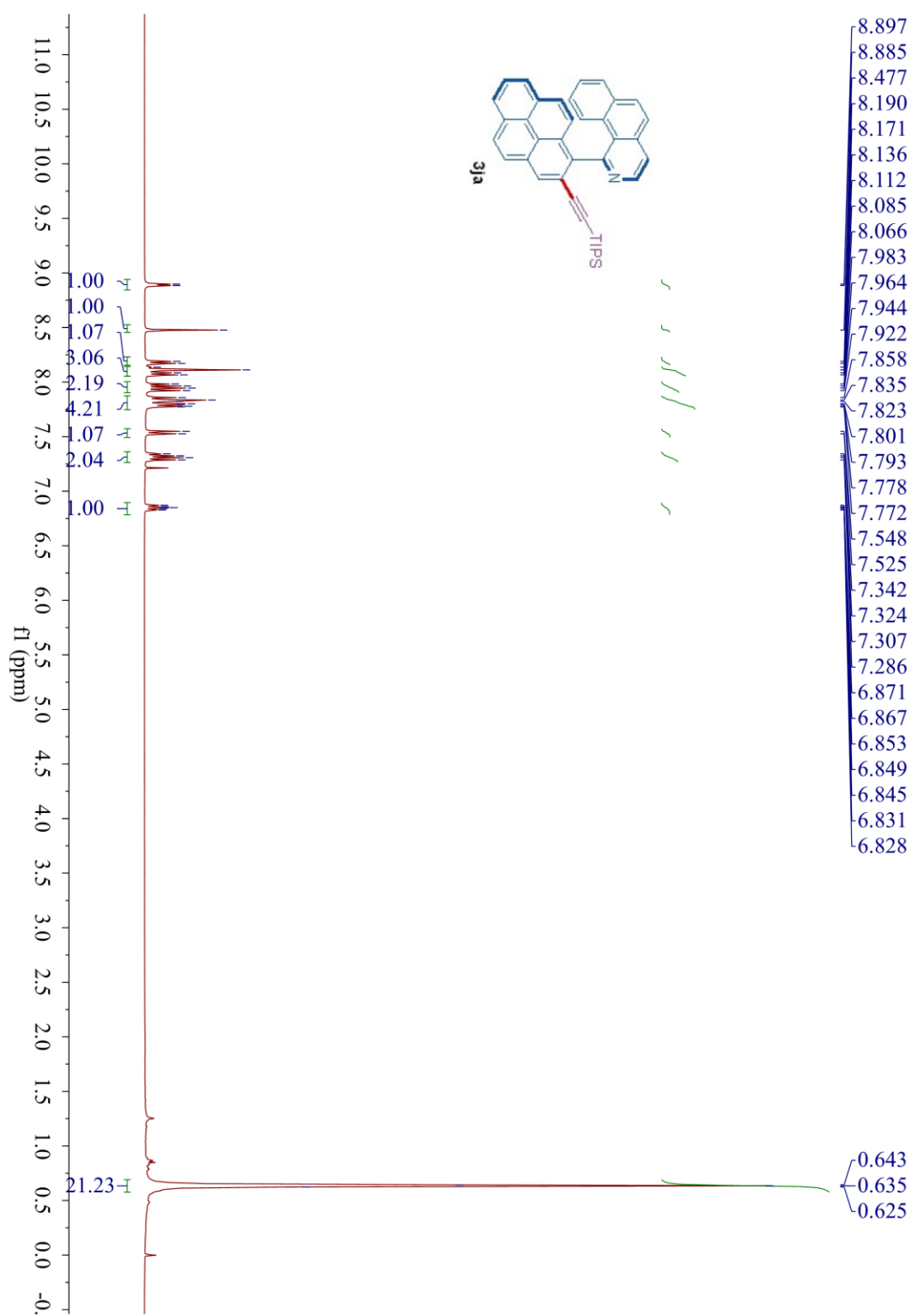
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ia**



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ia**

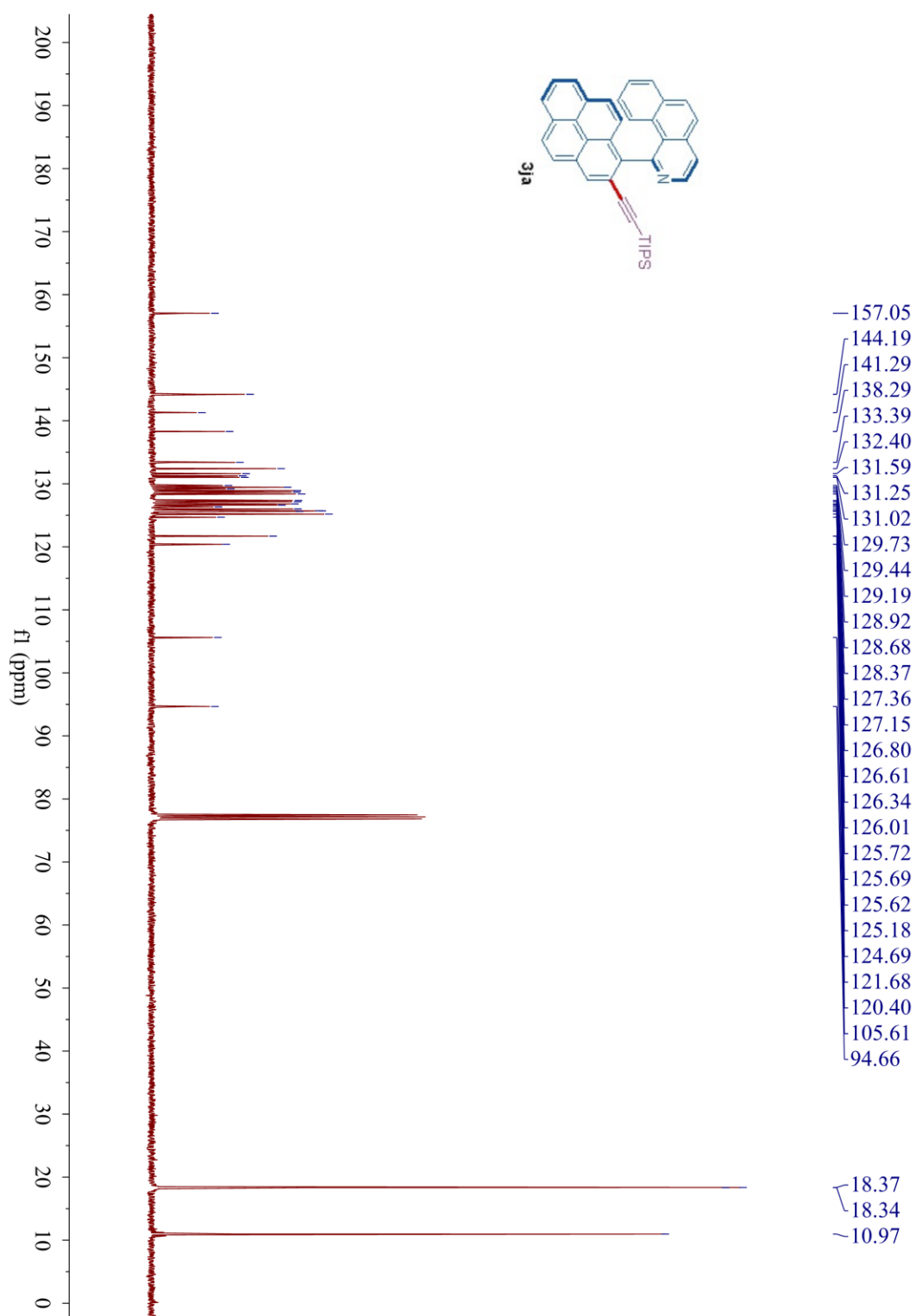


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ja**

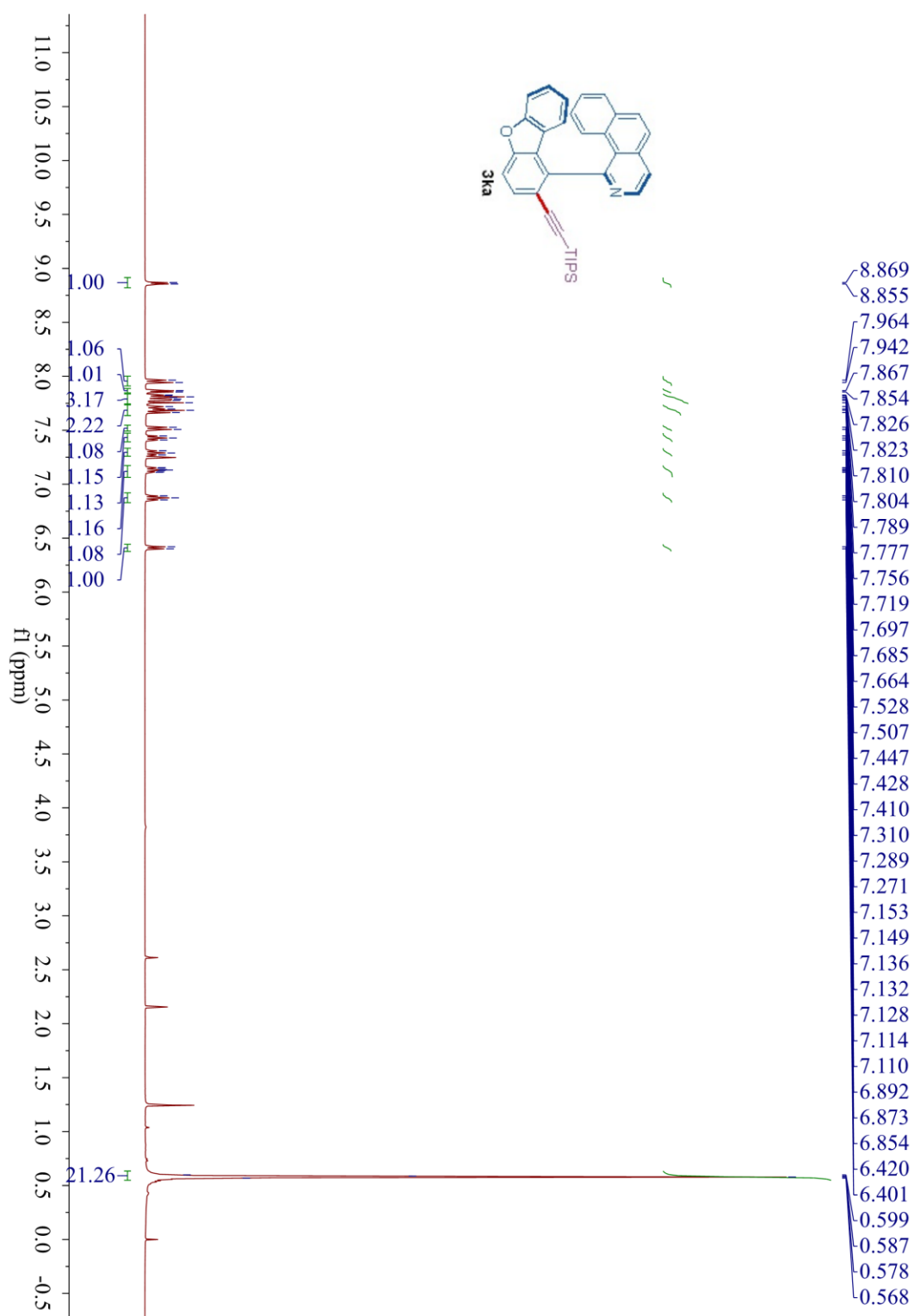




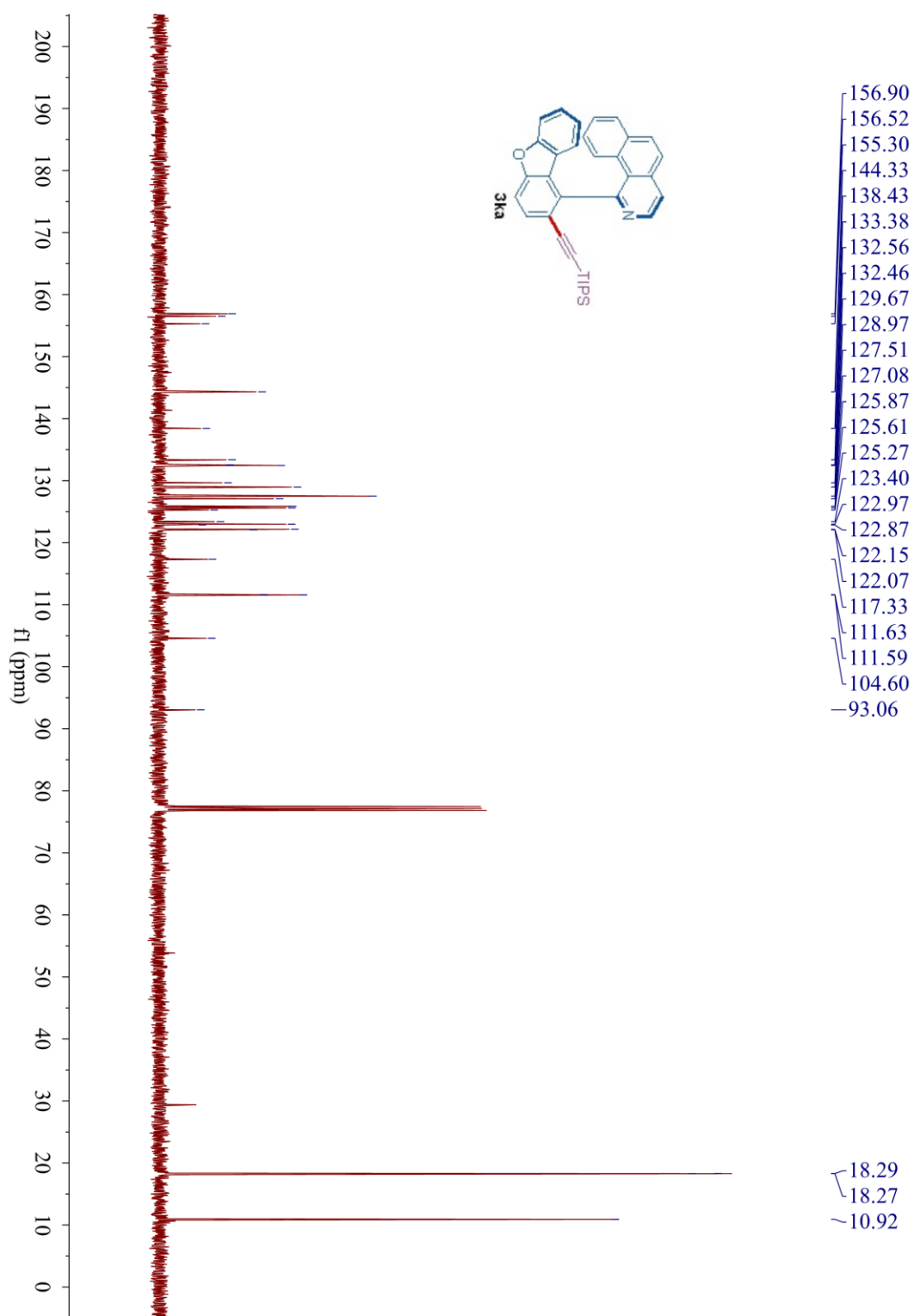
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ja**



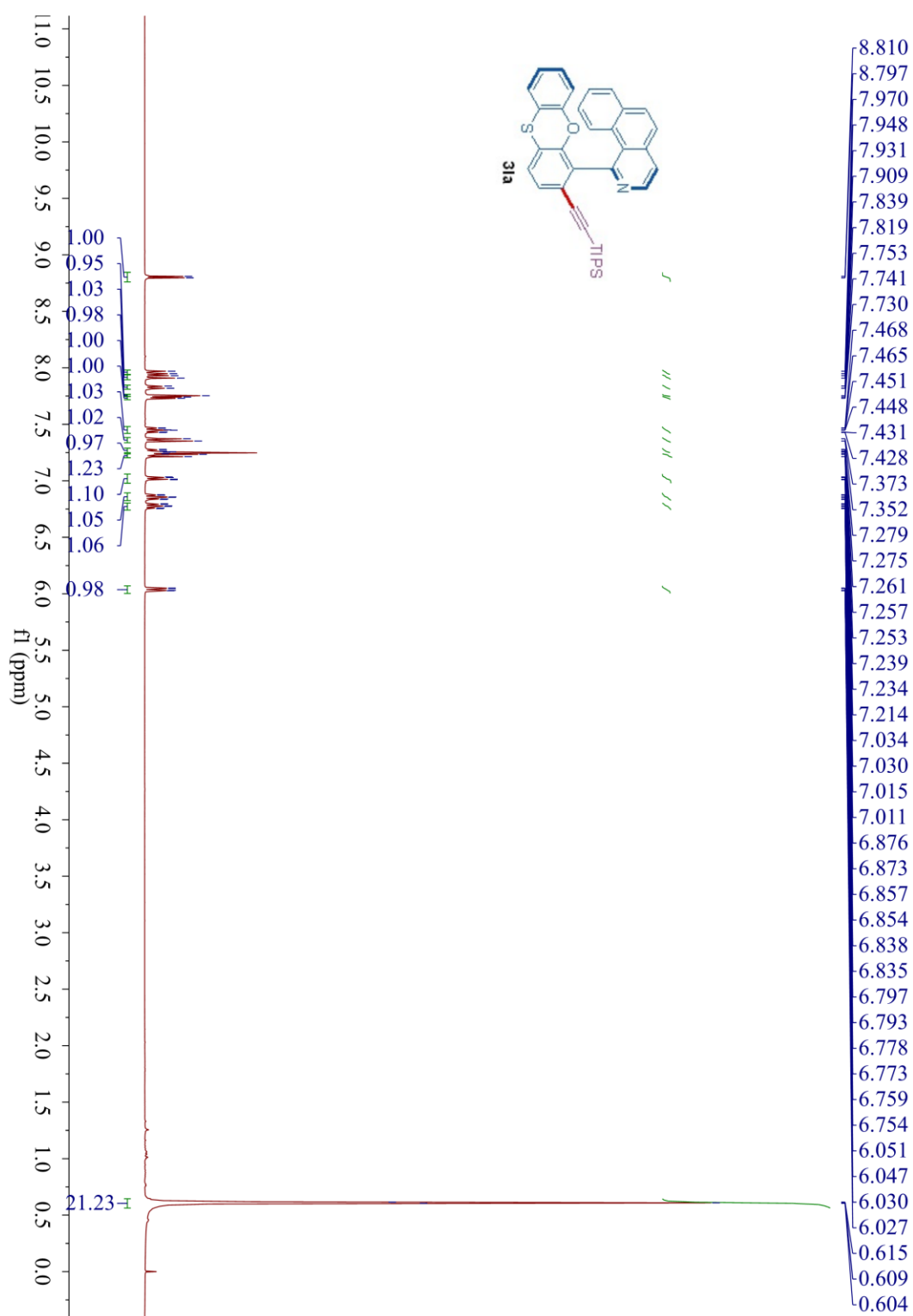
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ka**



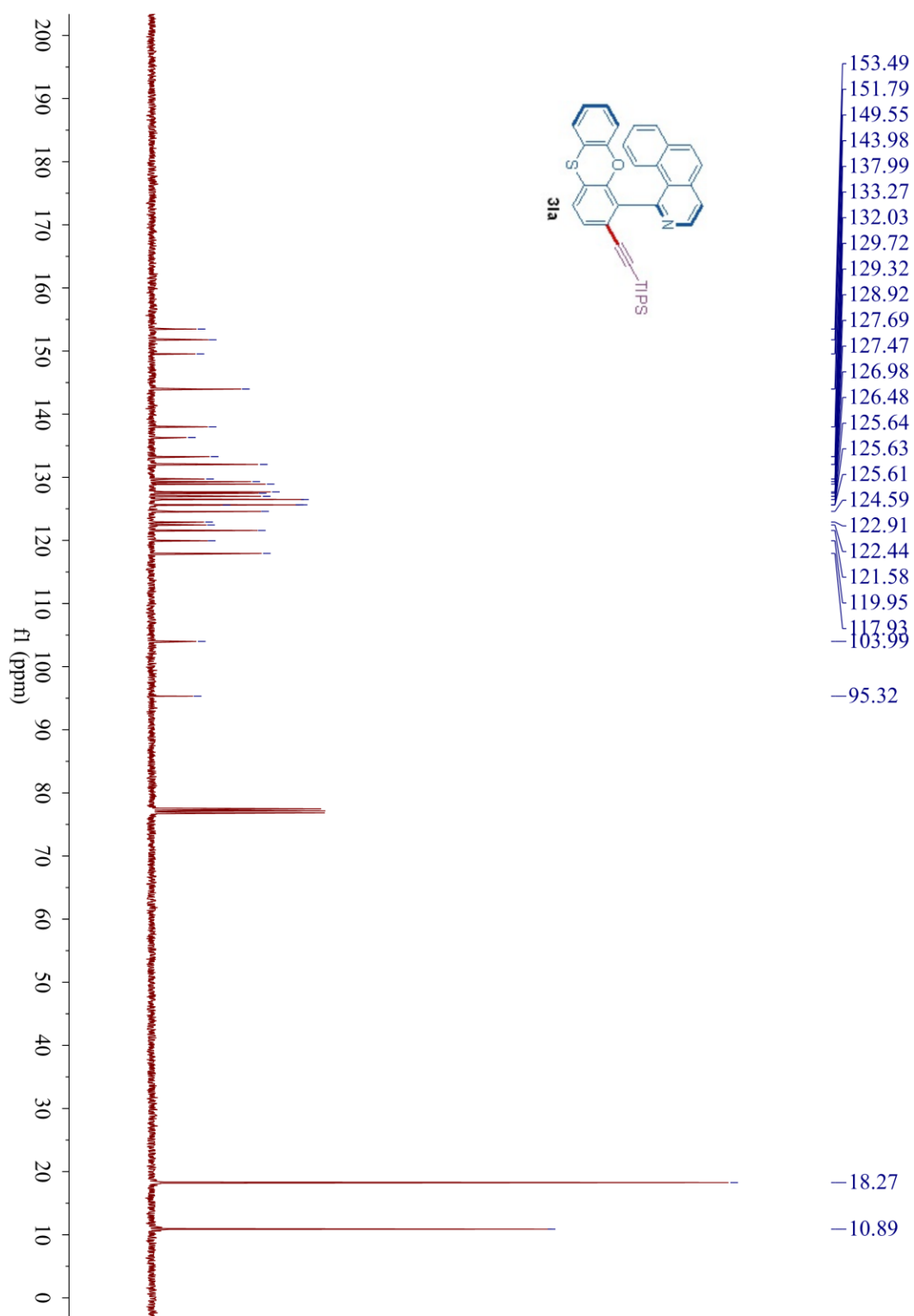
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ka**



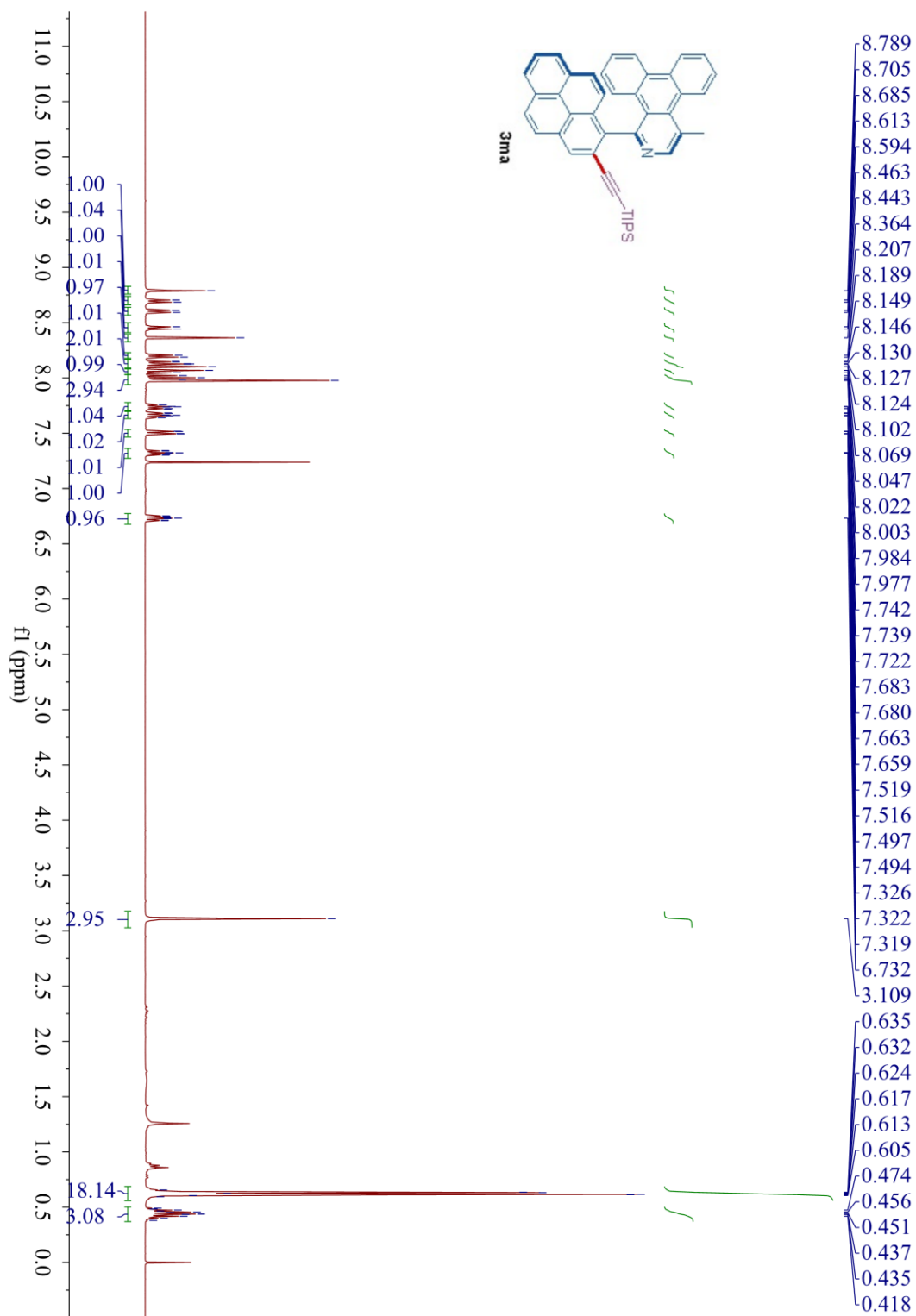
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **31a**



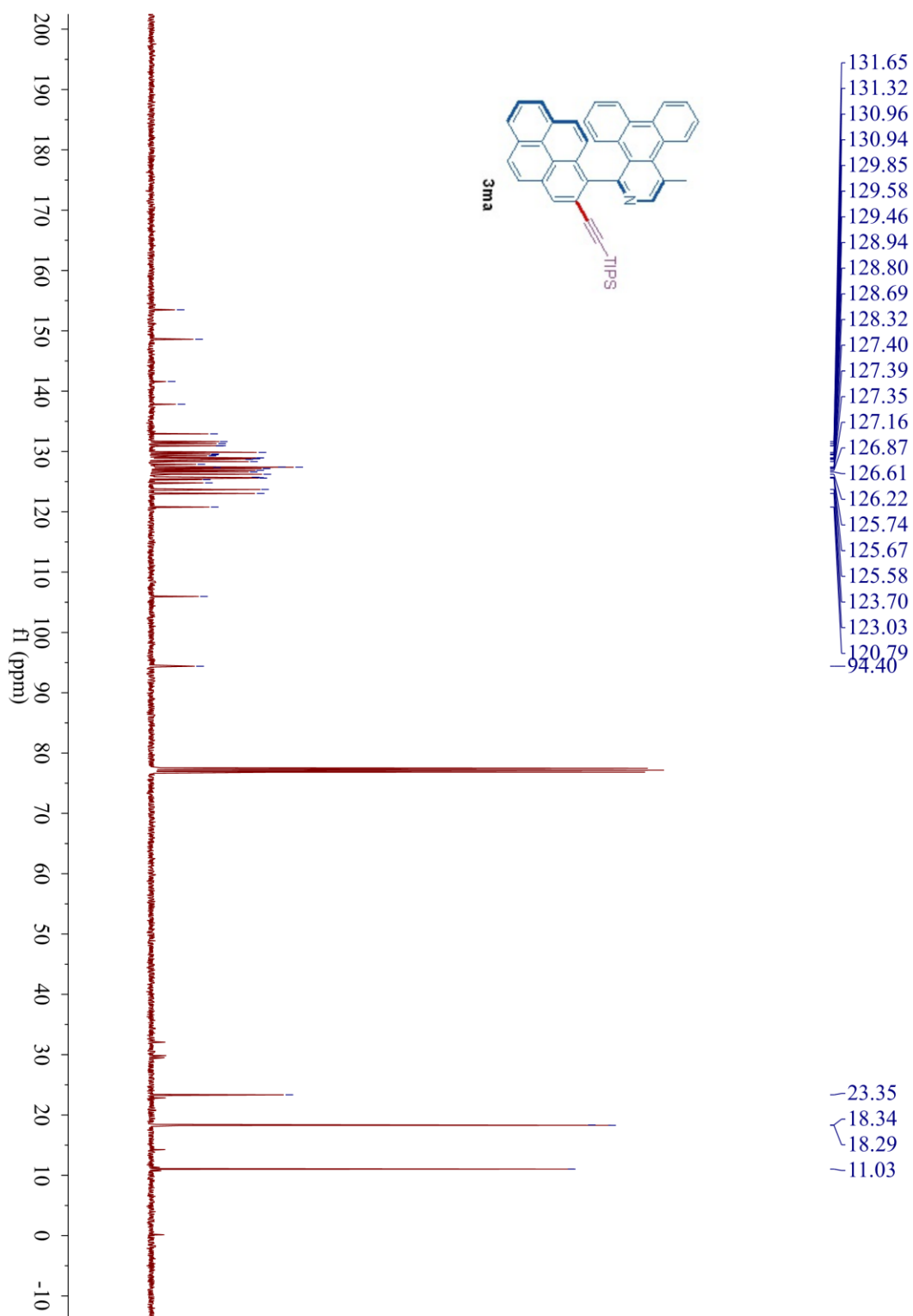
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **31a**



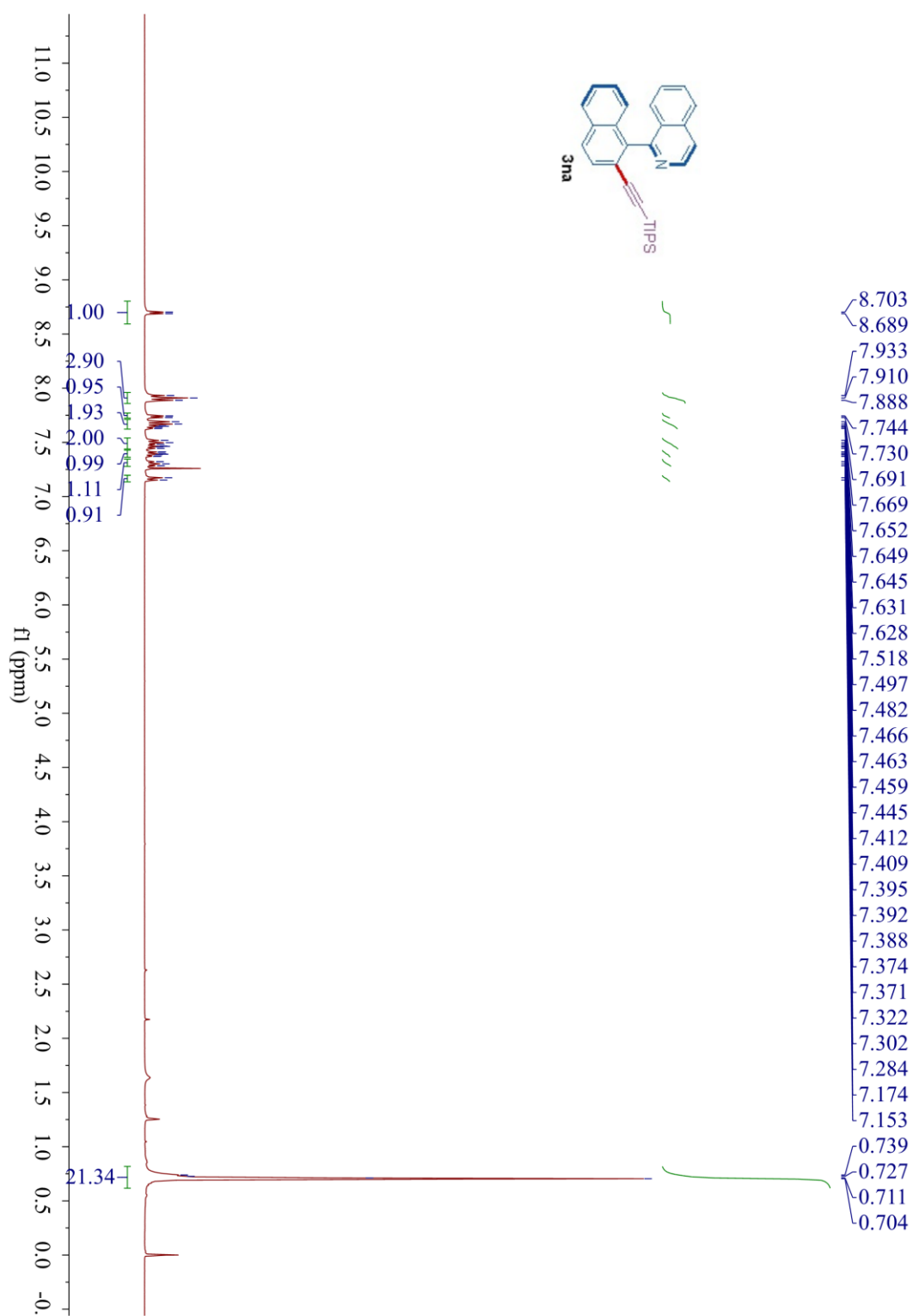
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ma**



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ma**

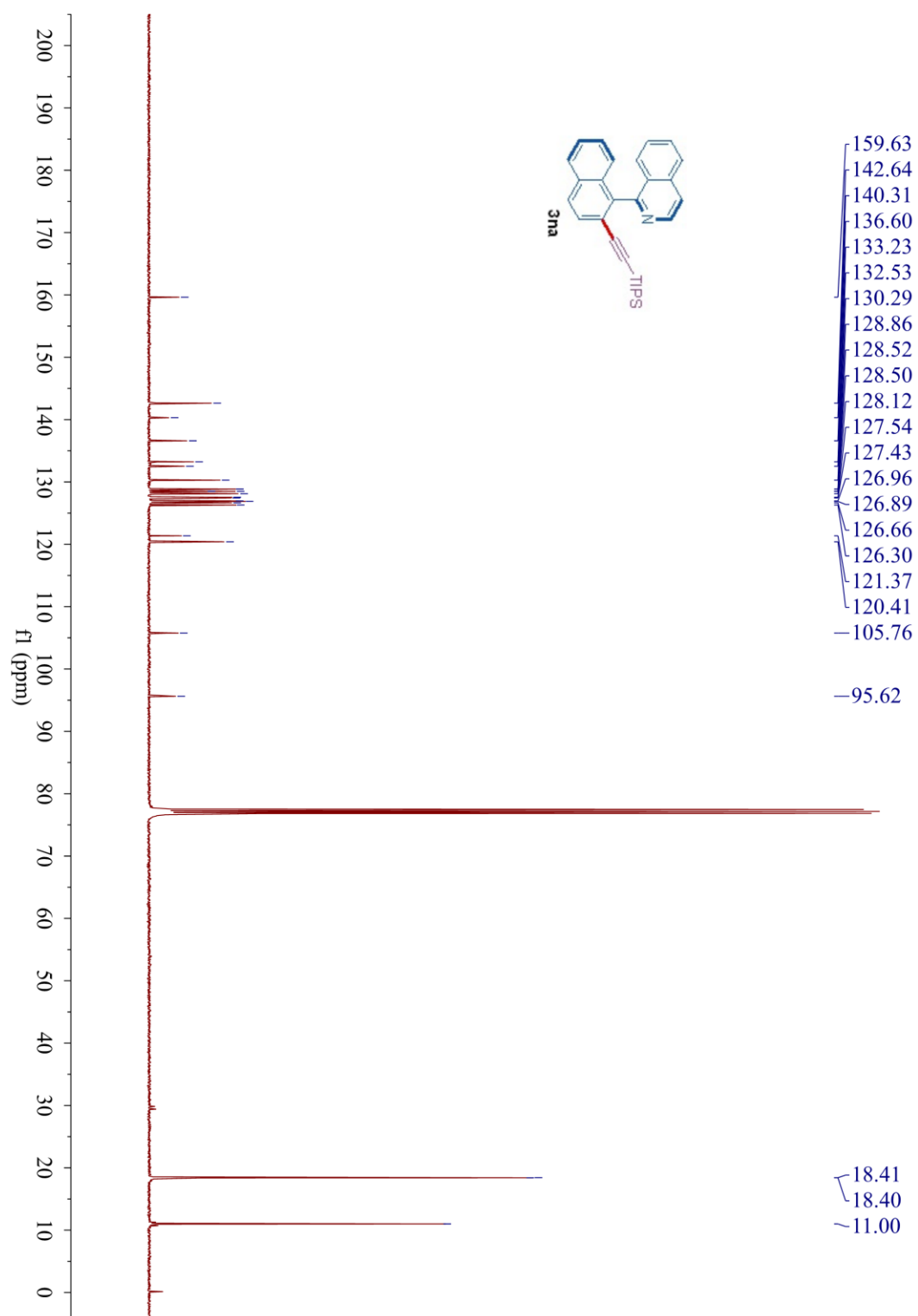


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3na**

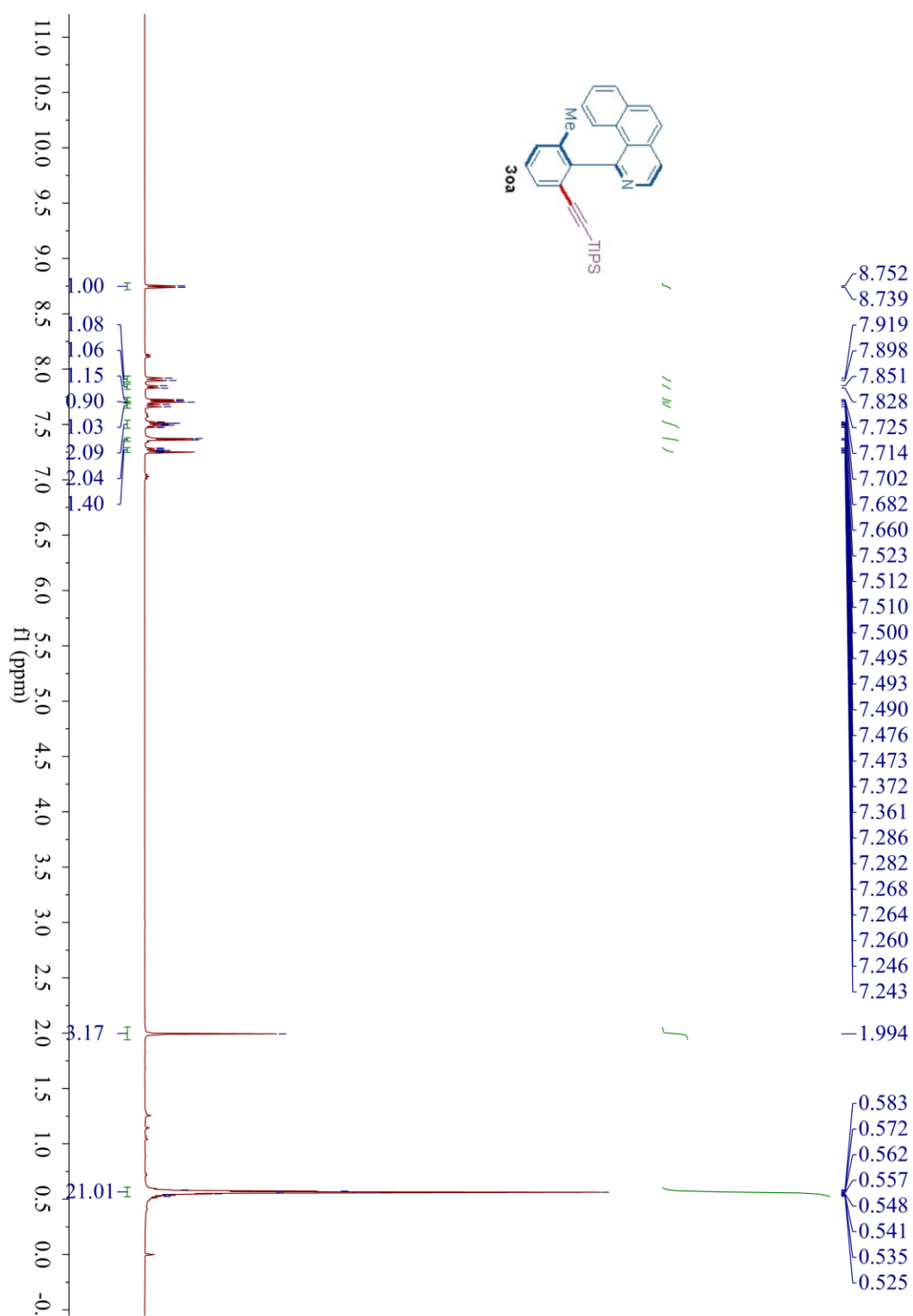




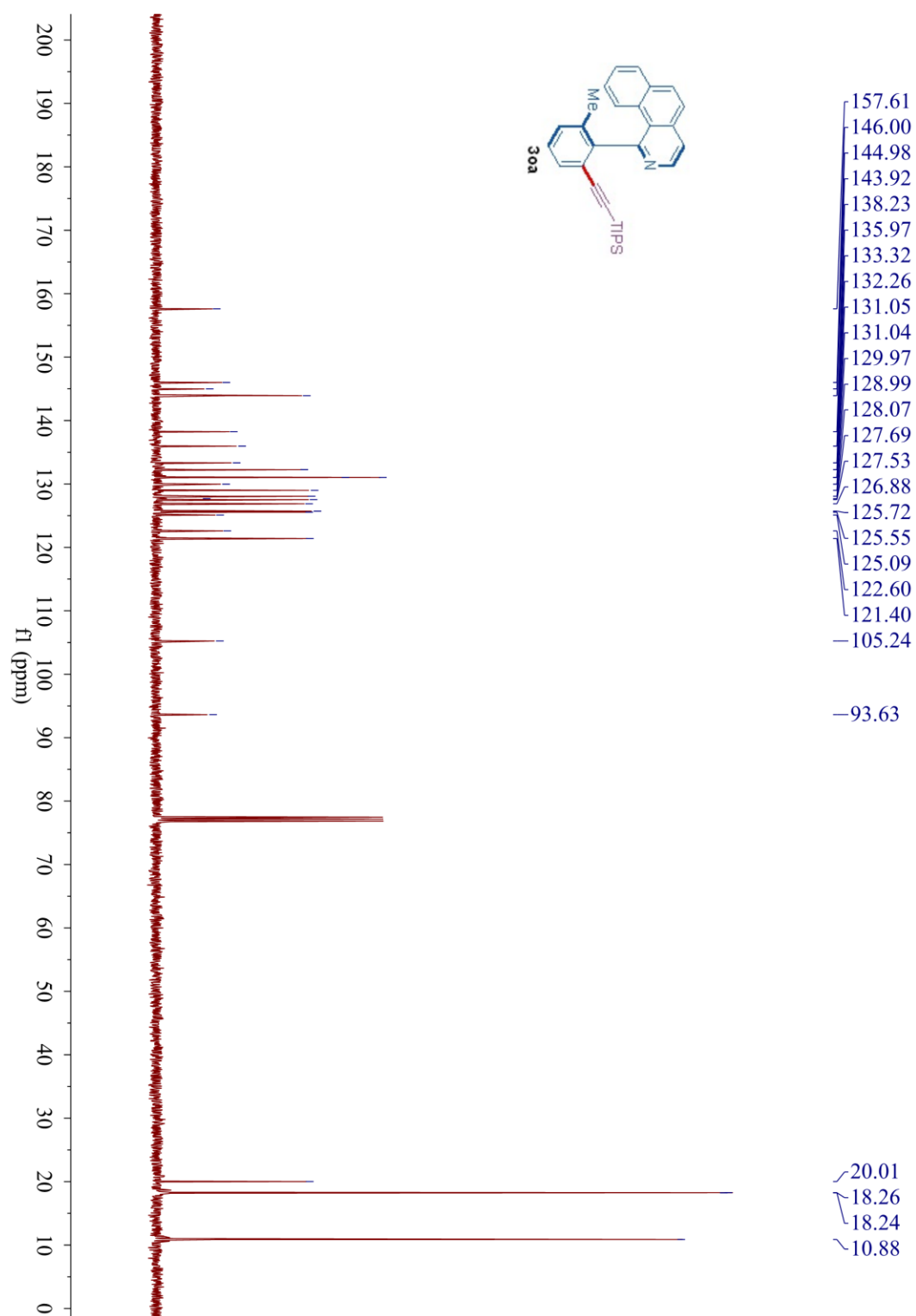
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3na**



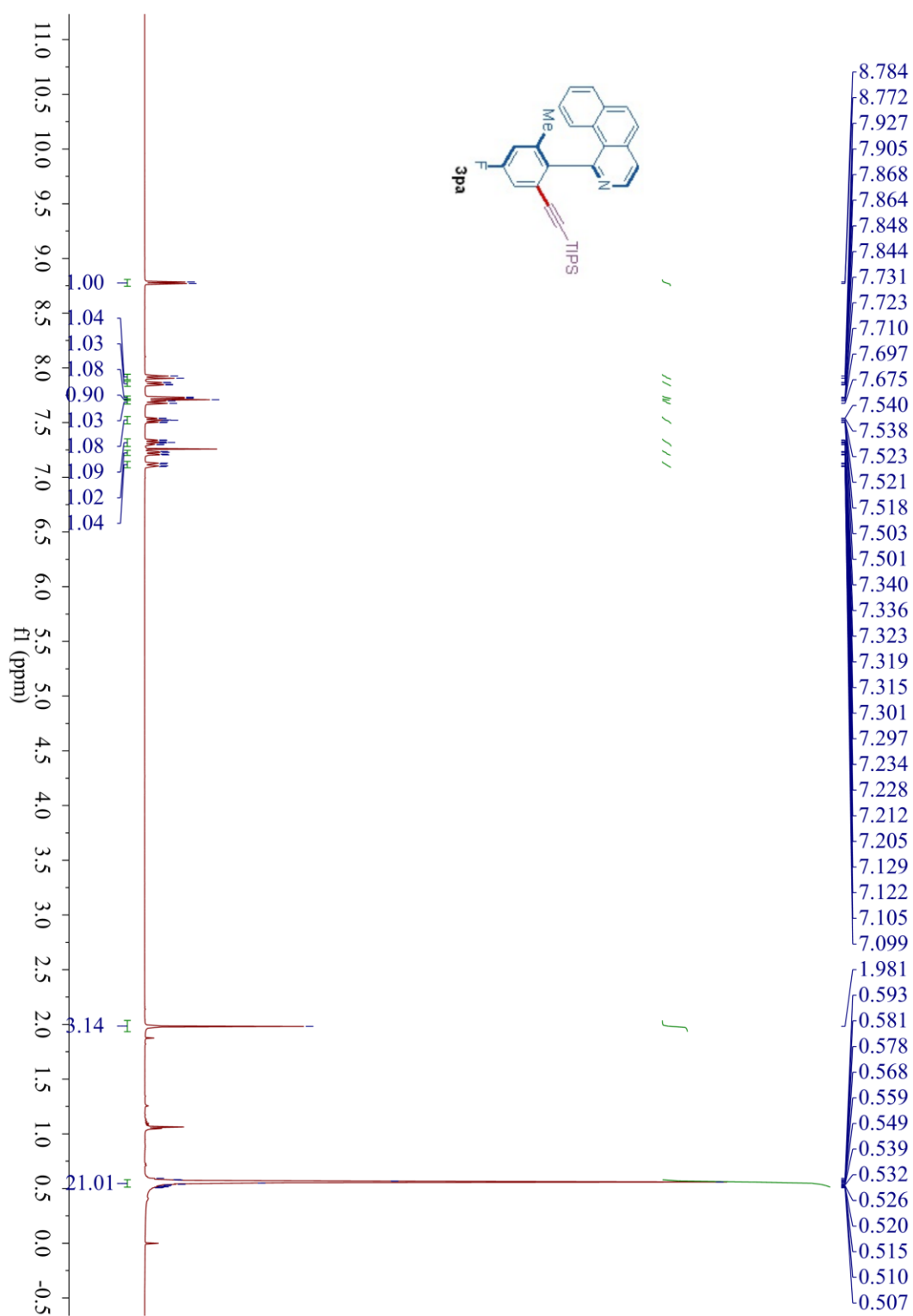
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3oa**



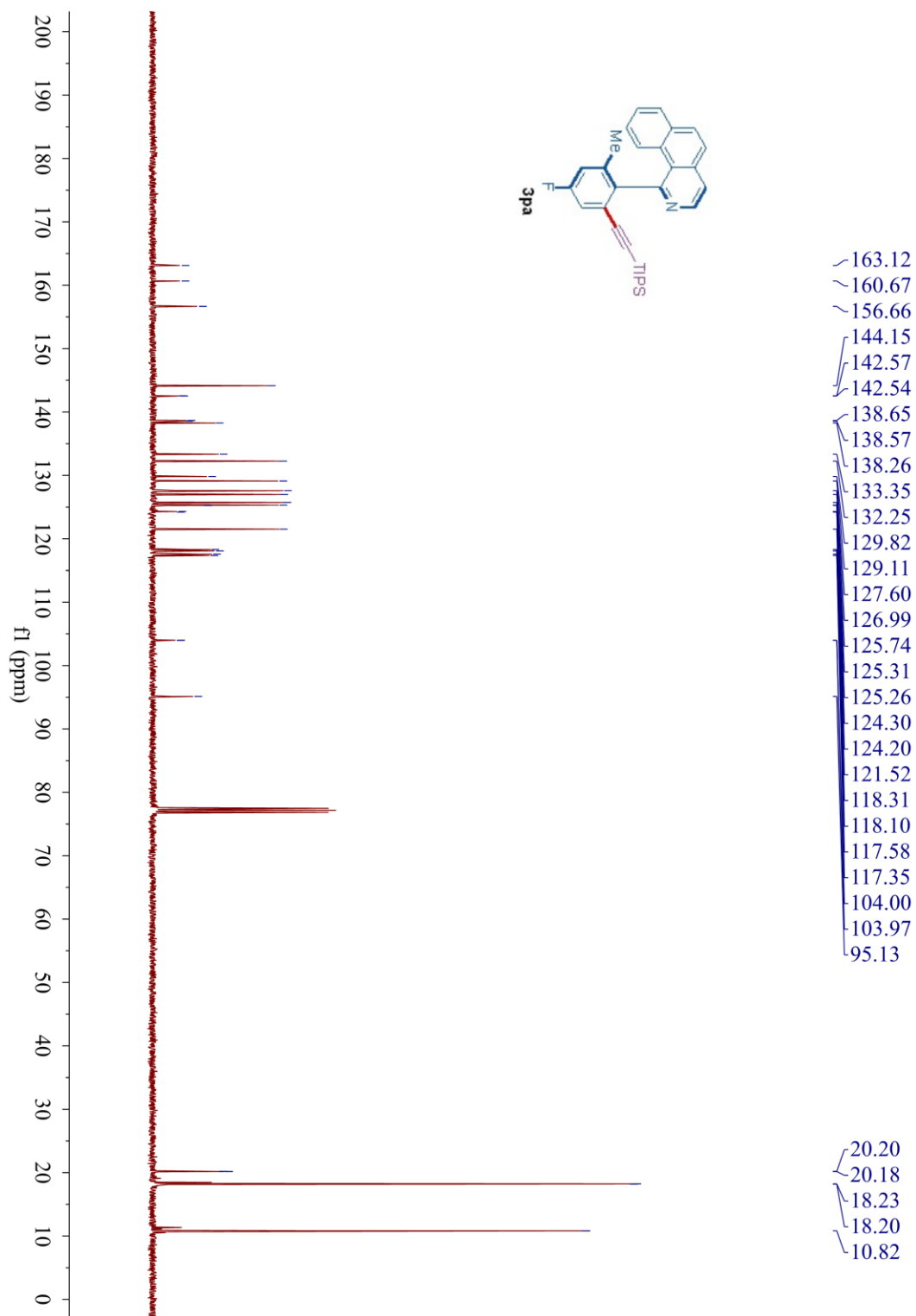
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **30a**



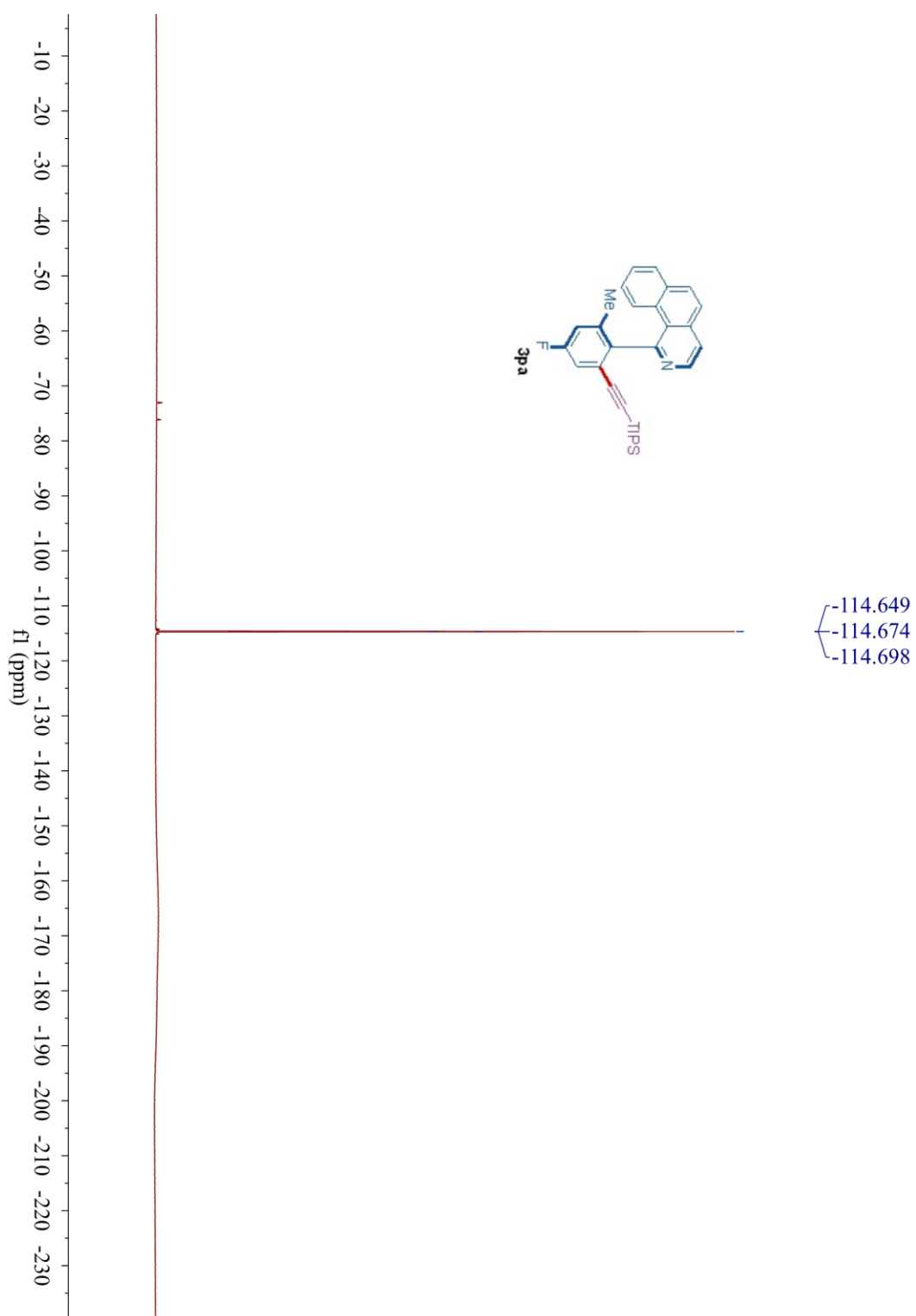
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3pa**



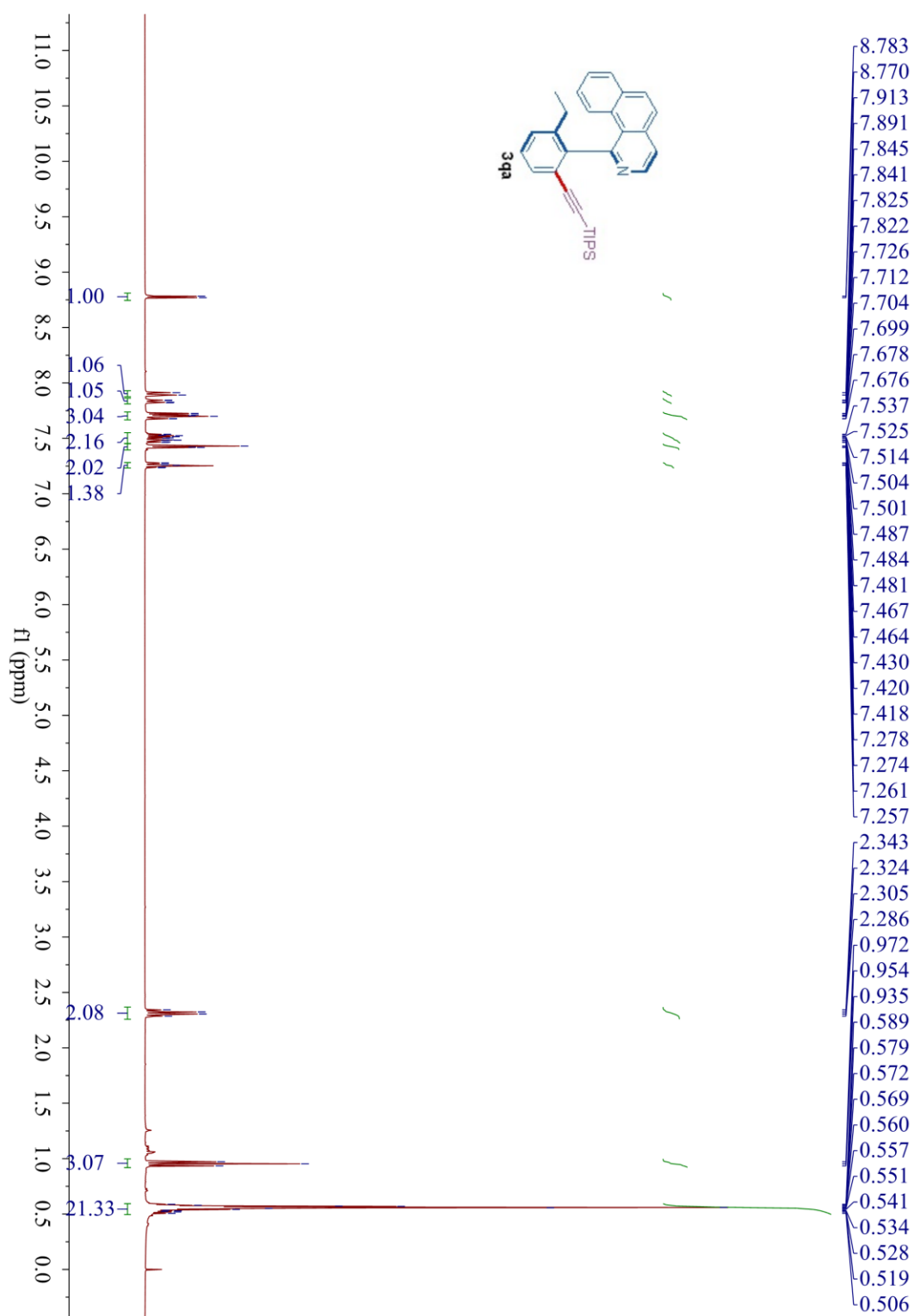
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3pa**



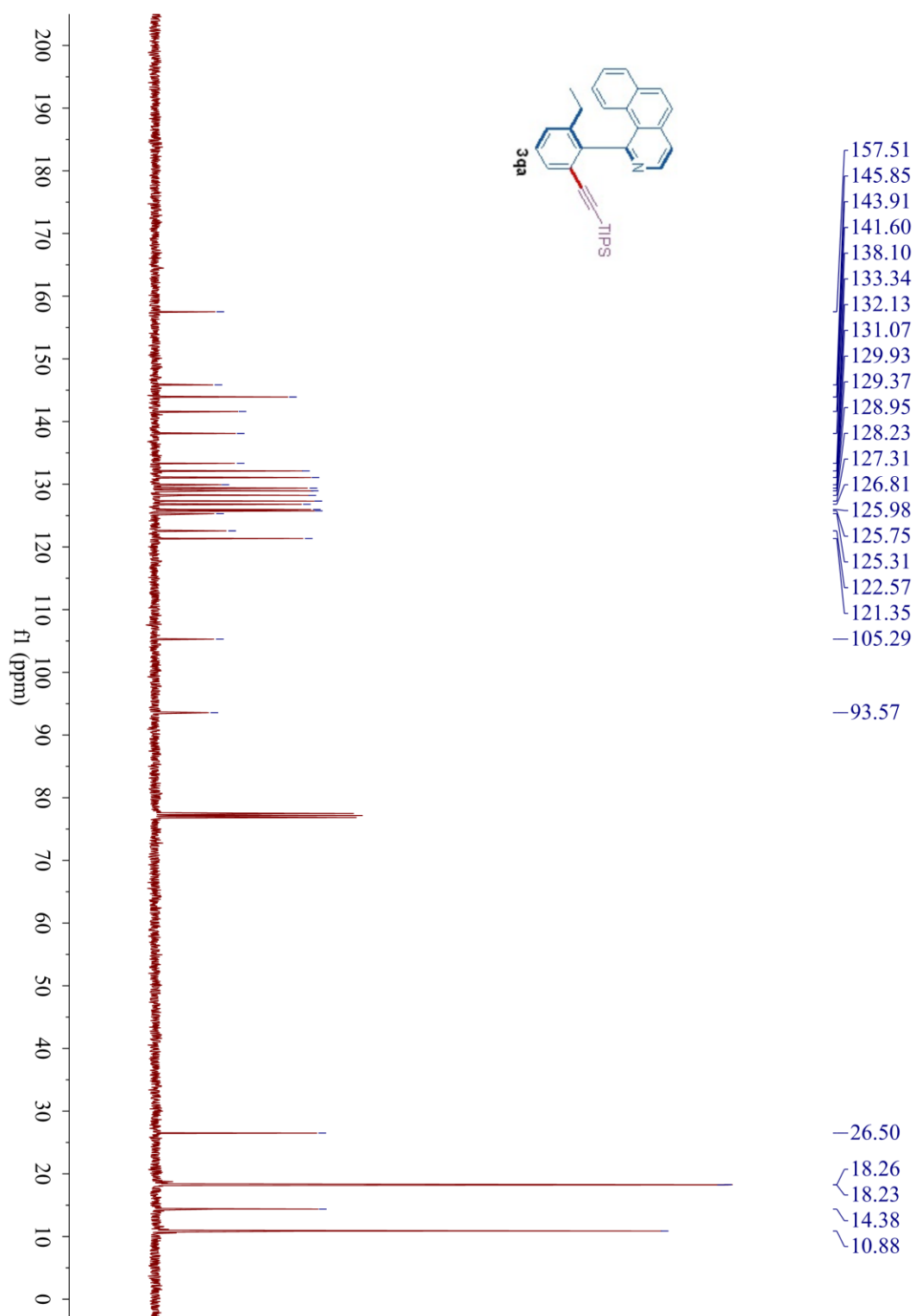
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3pa**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3qa**

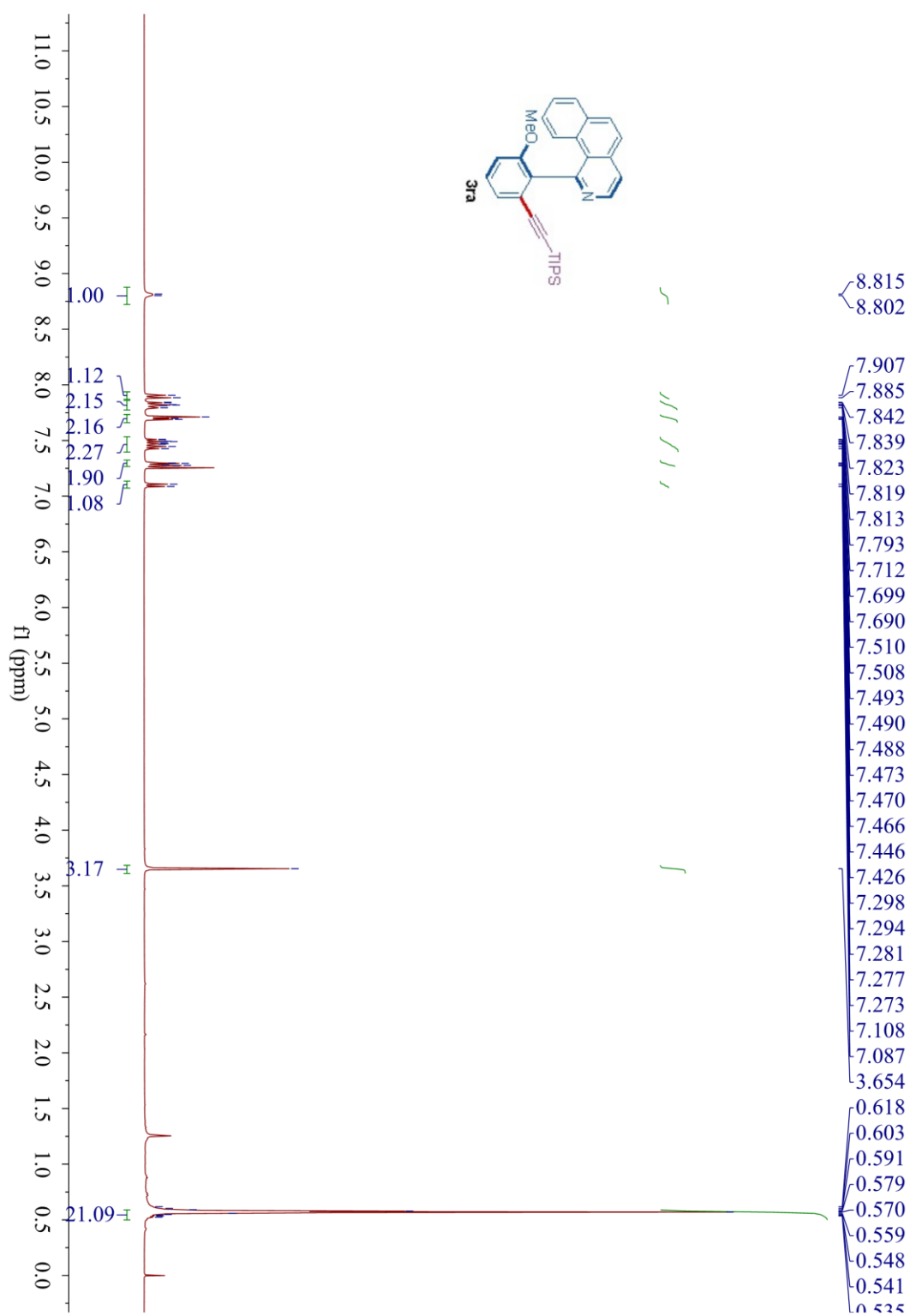


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3qa**

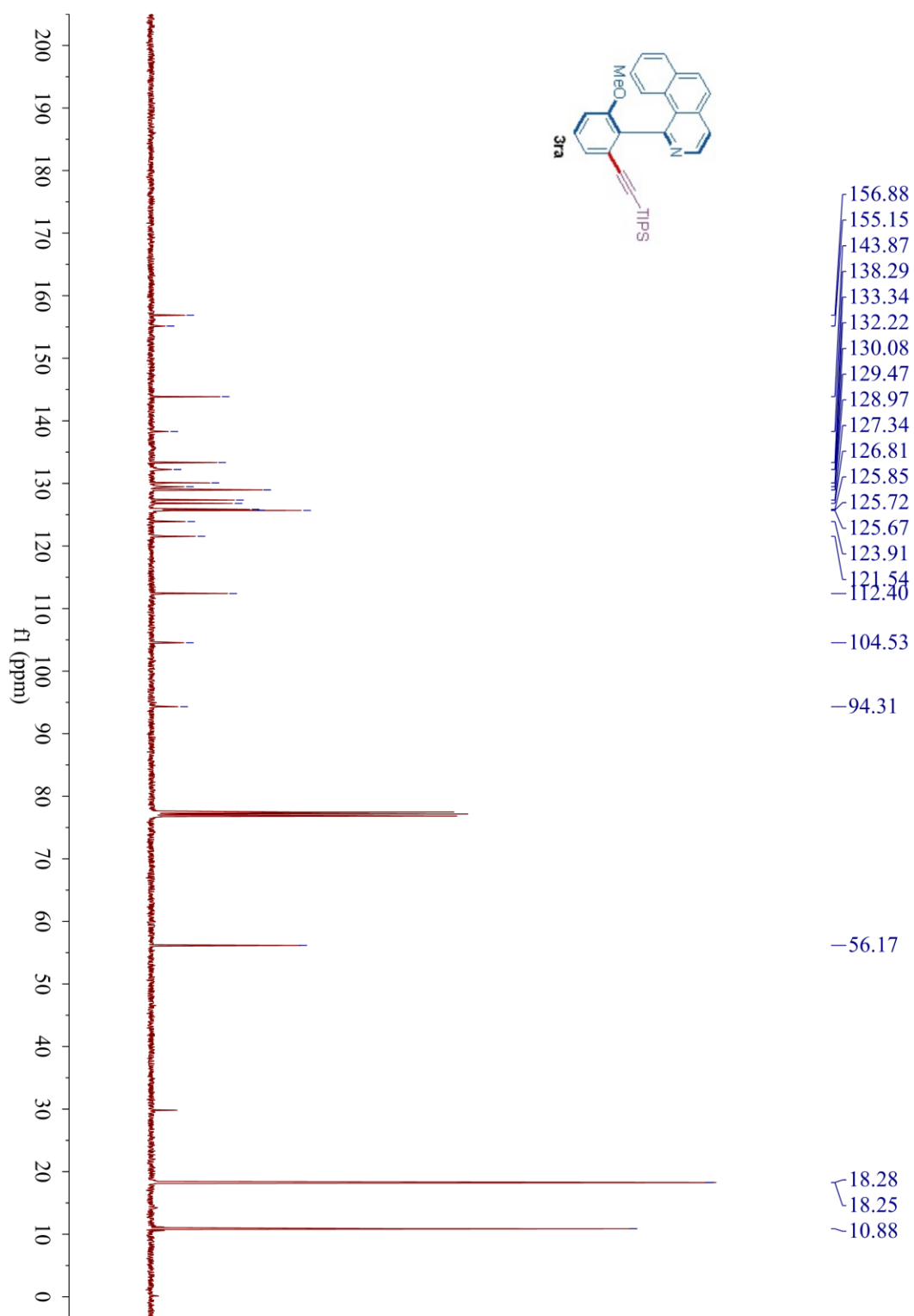




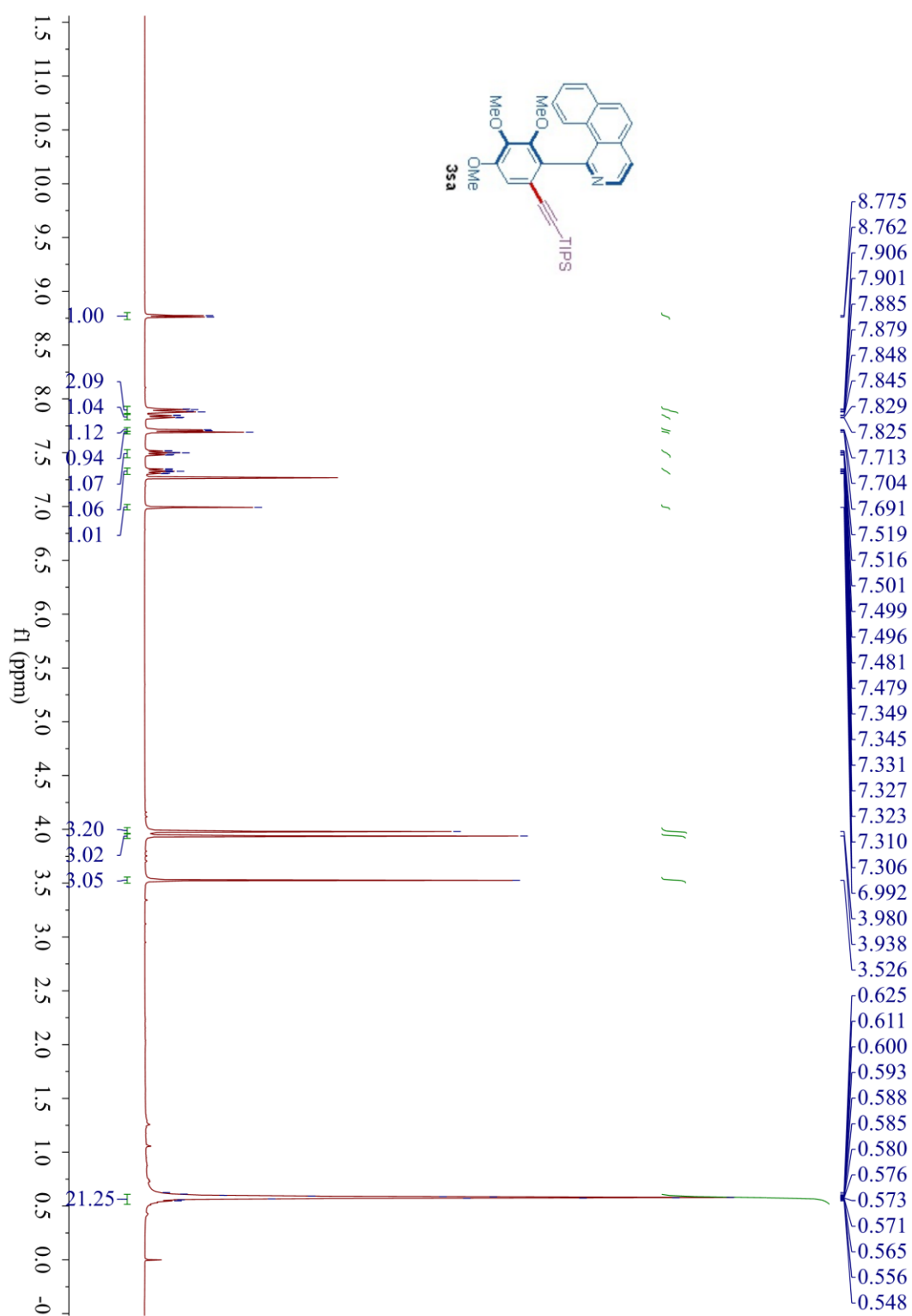
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ra**



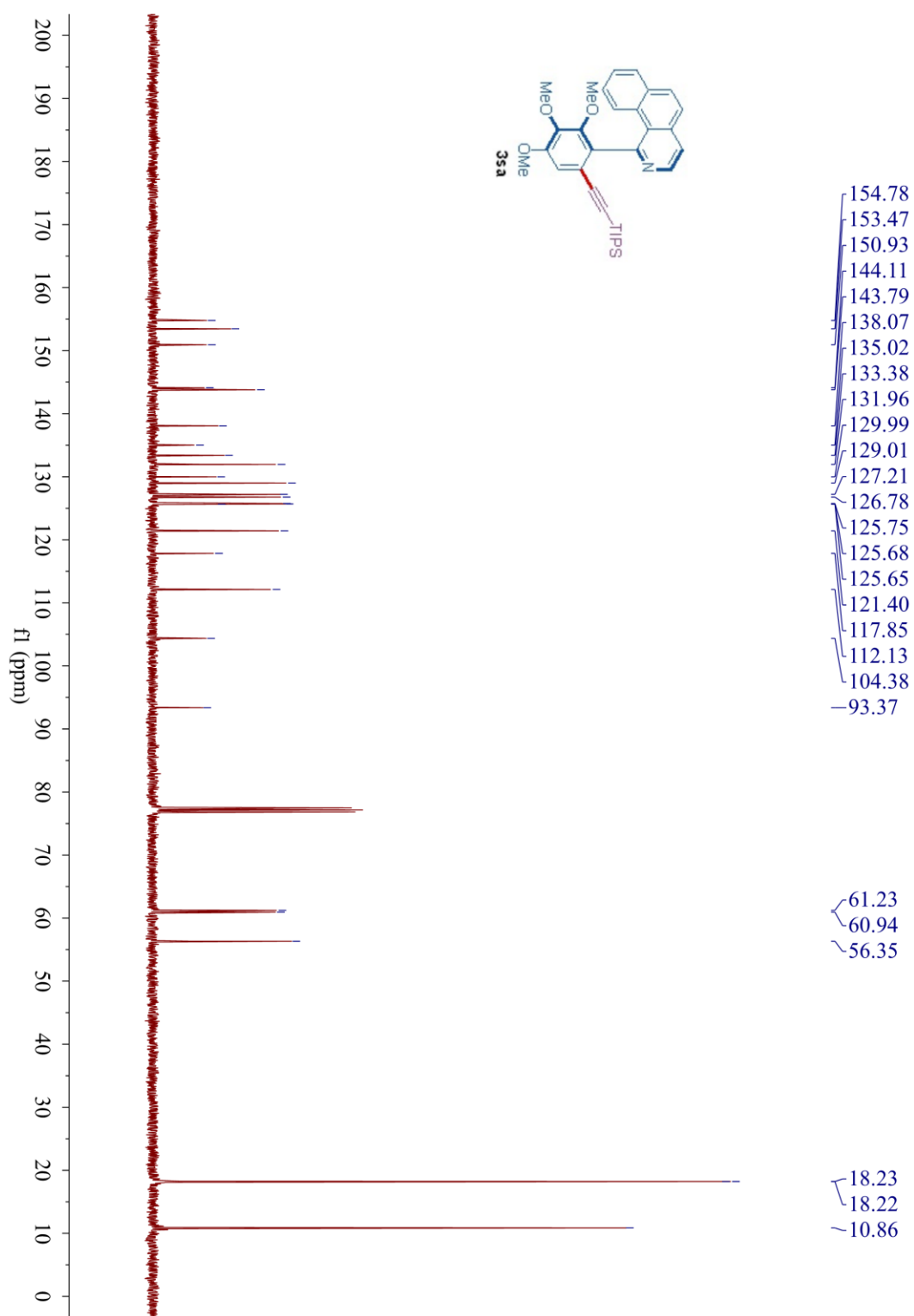
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ra**



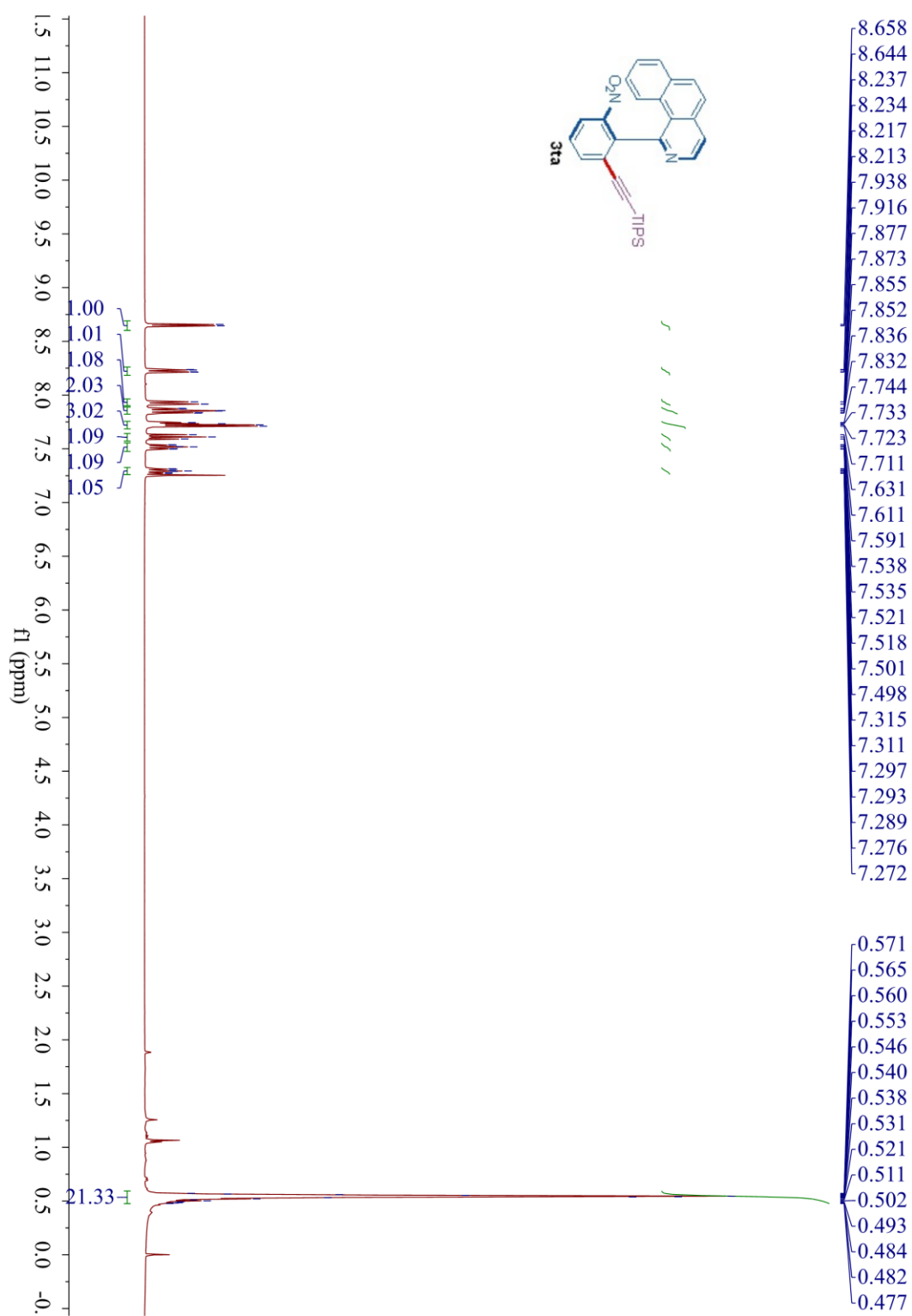
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3sa**



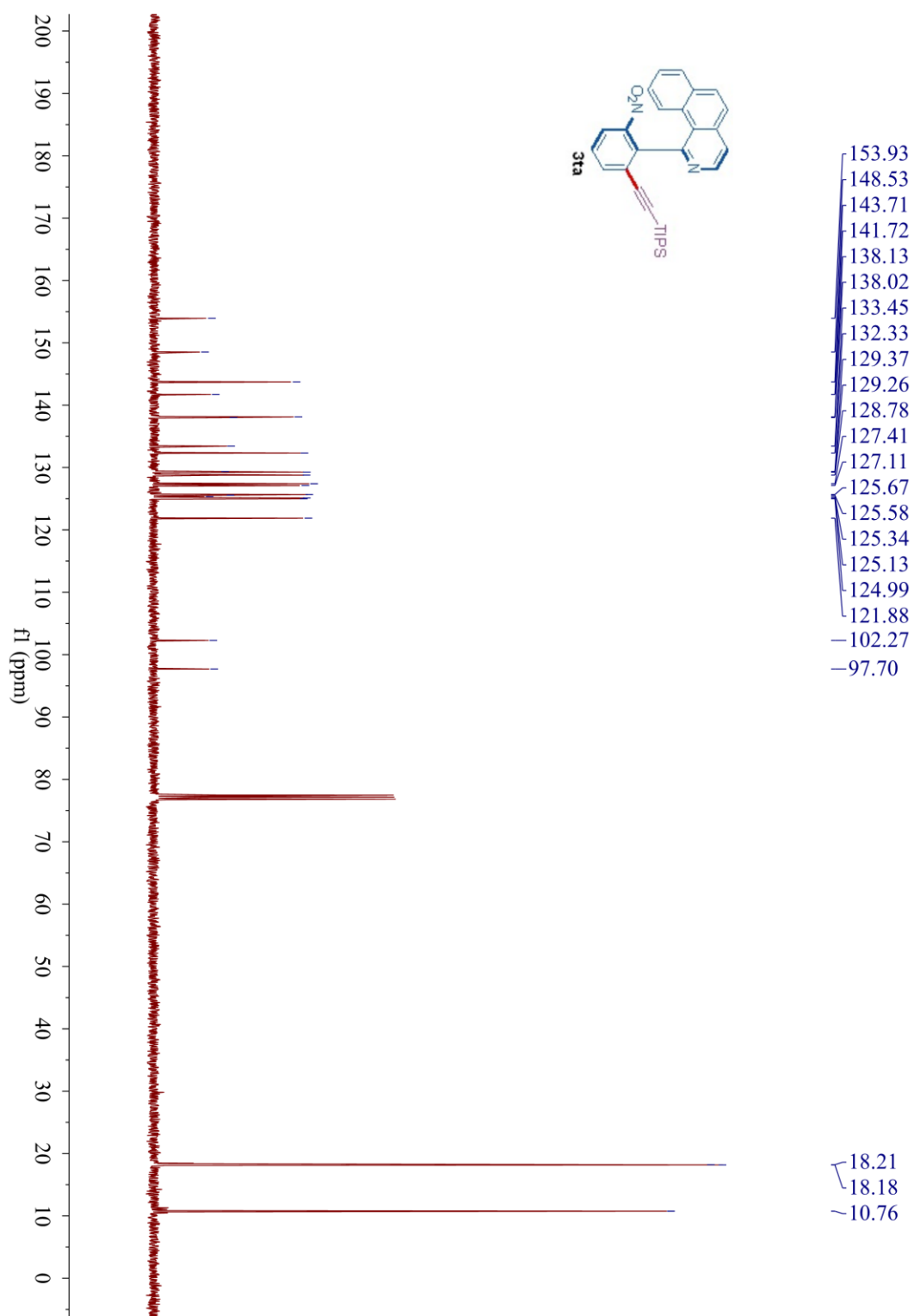
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3sa**



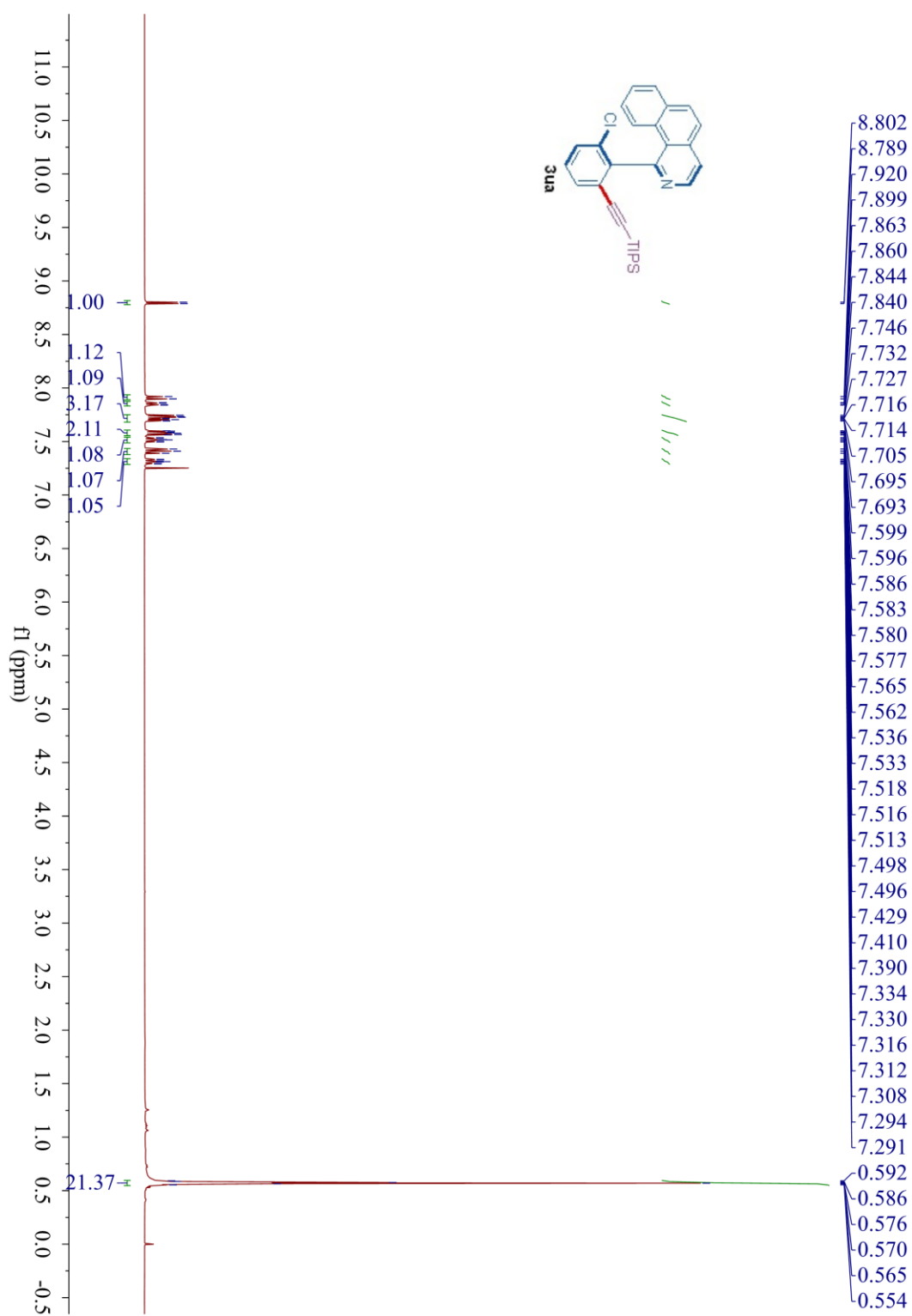
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ta**



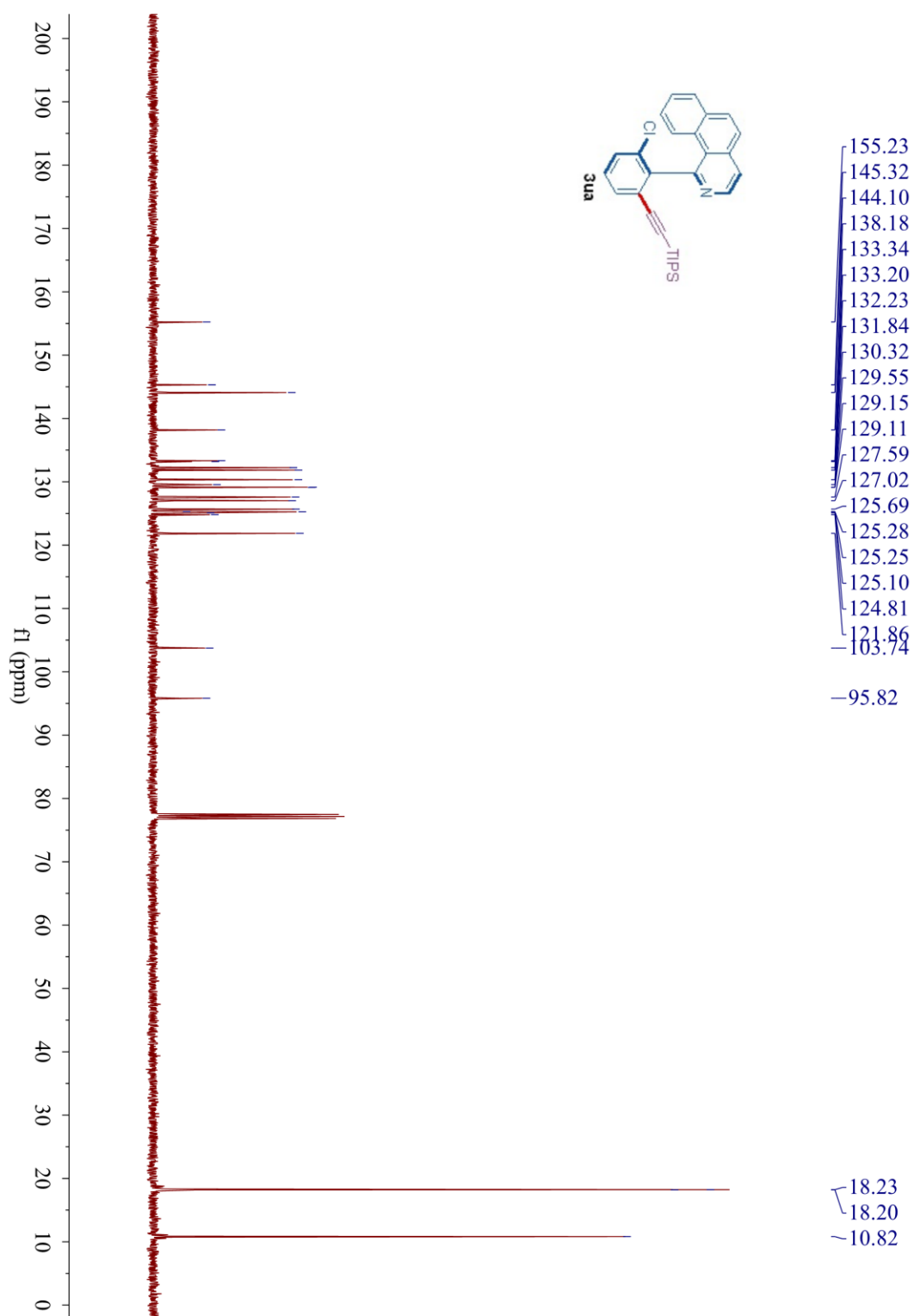
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ta**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ua**

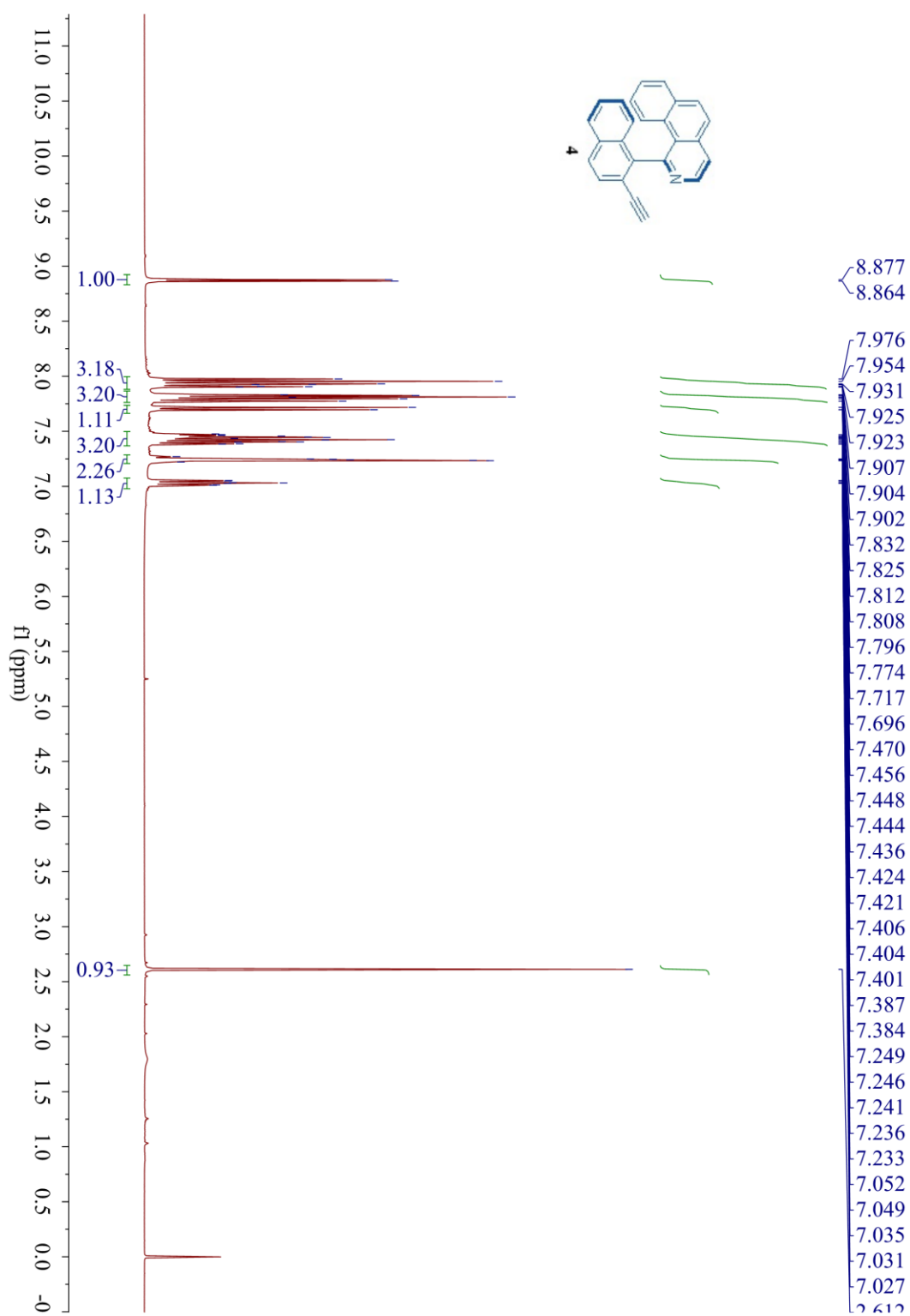


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3ua**

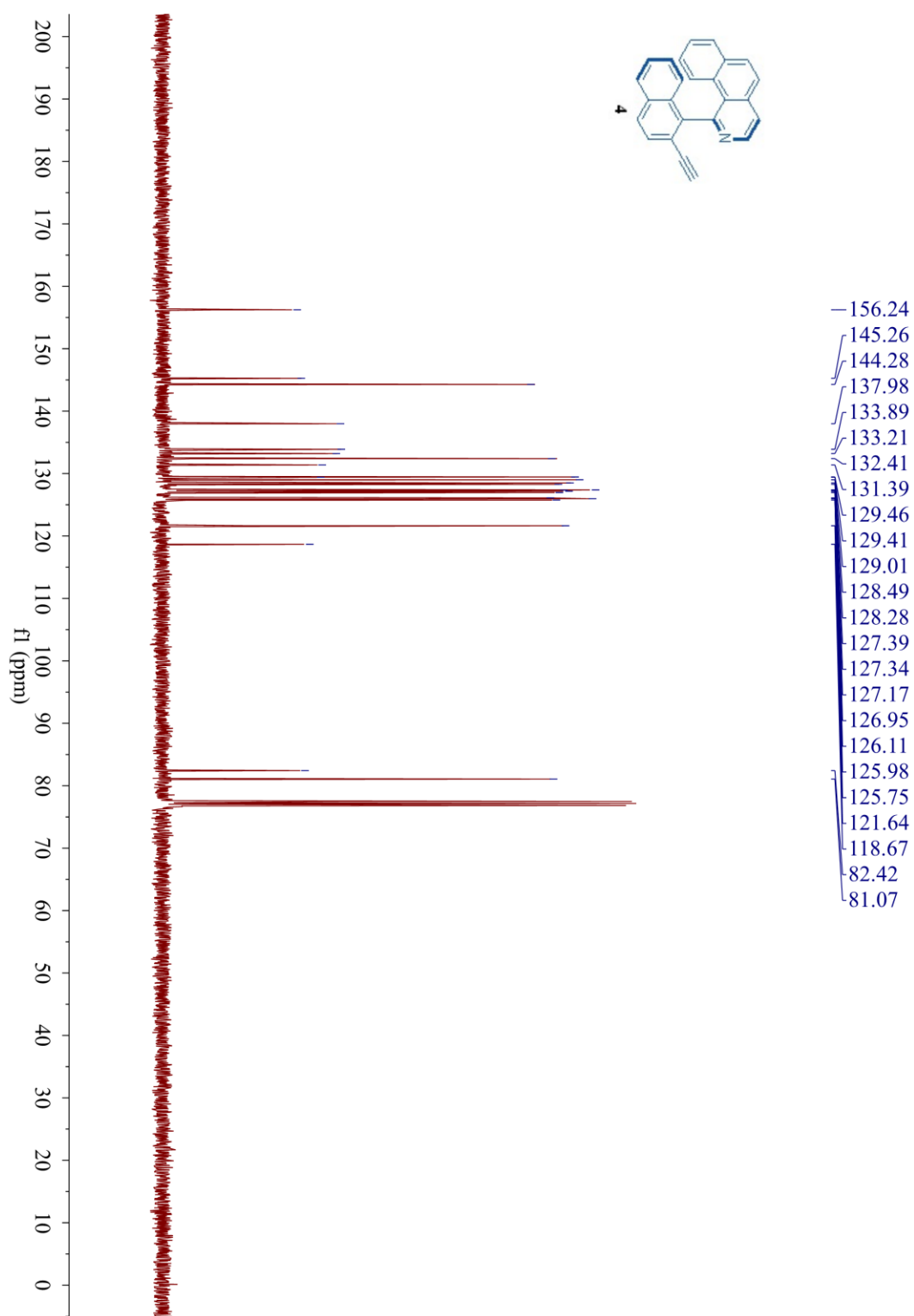




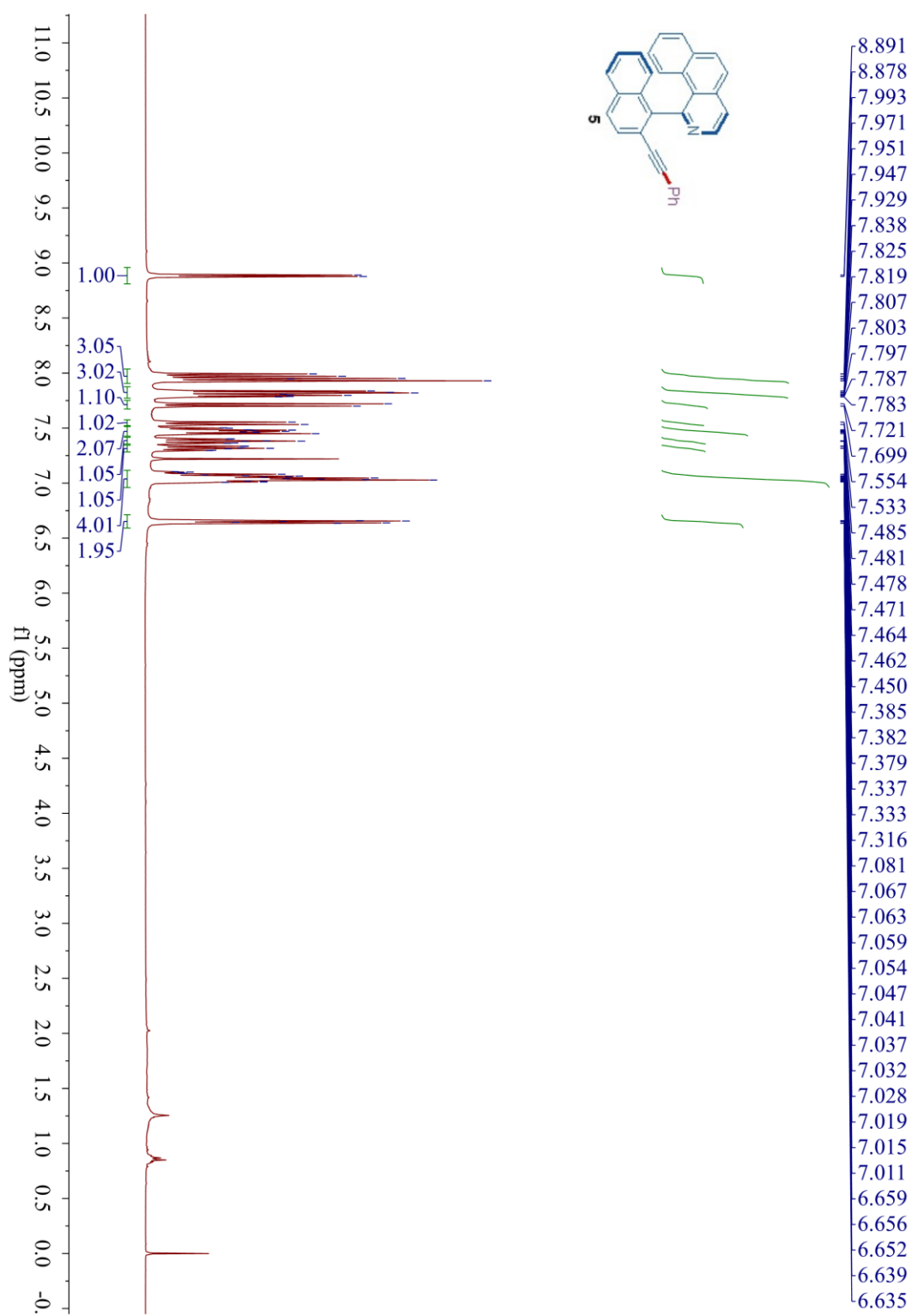
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **4**



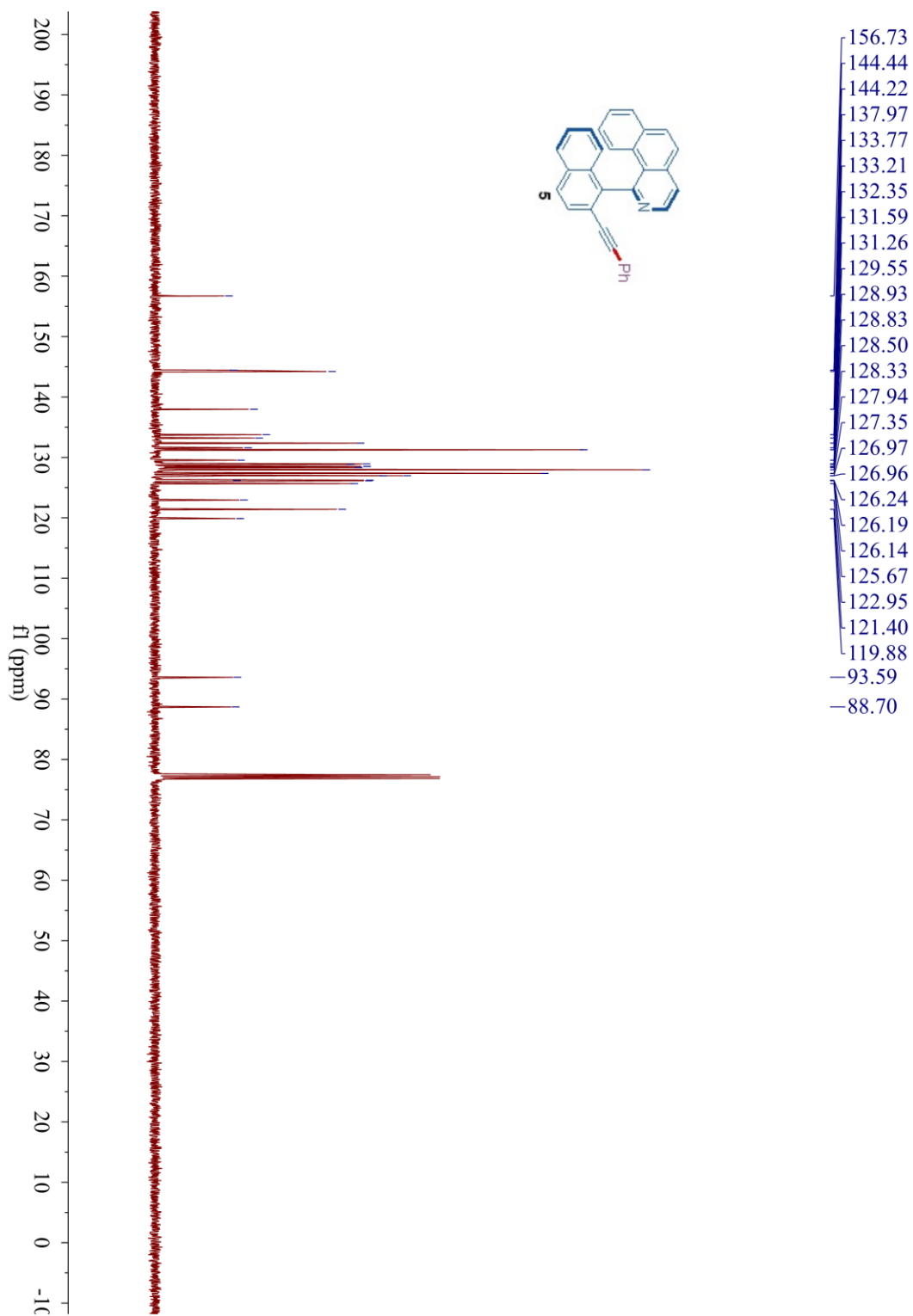
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **4**



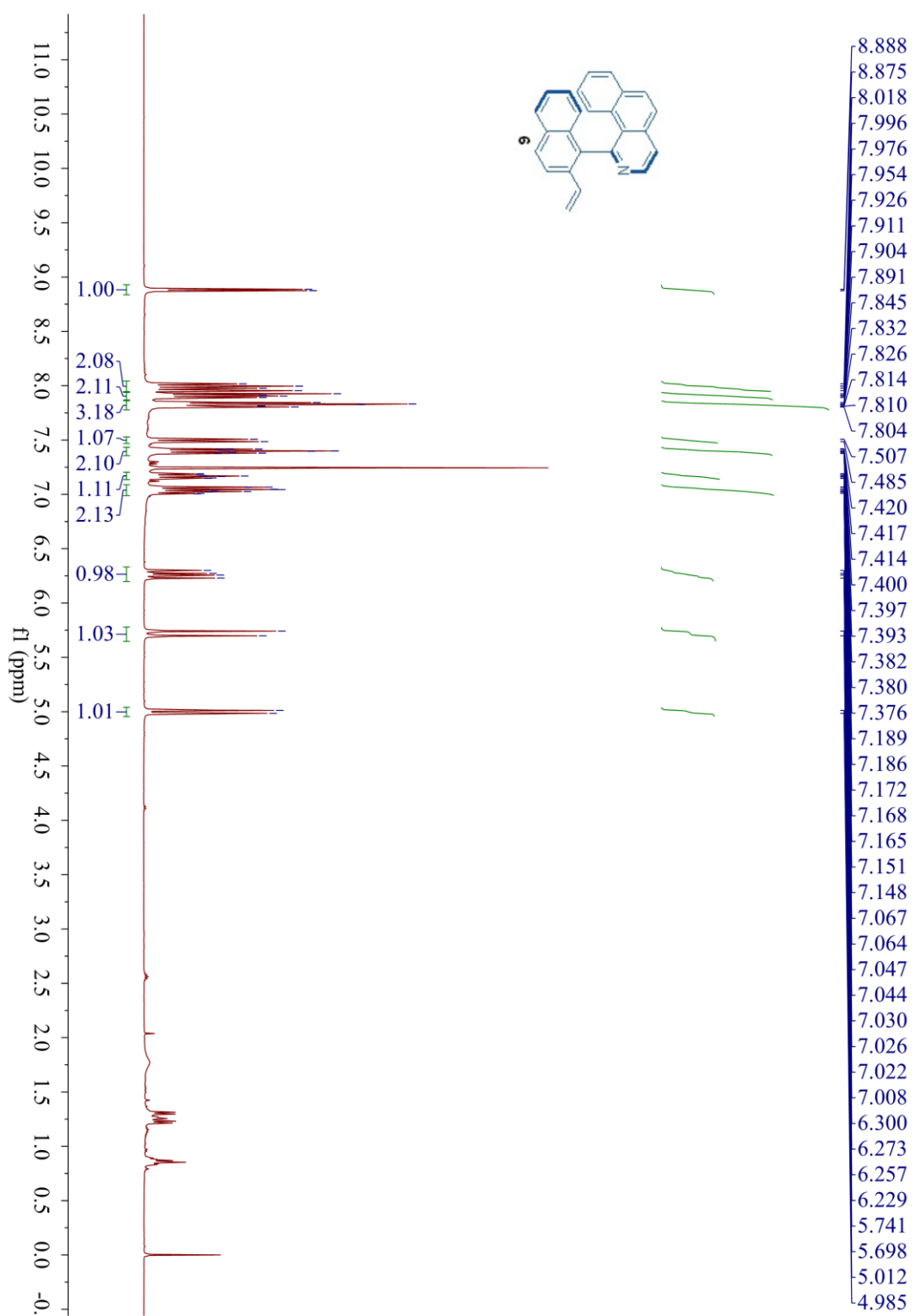
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **5**



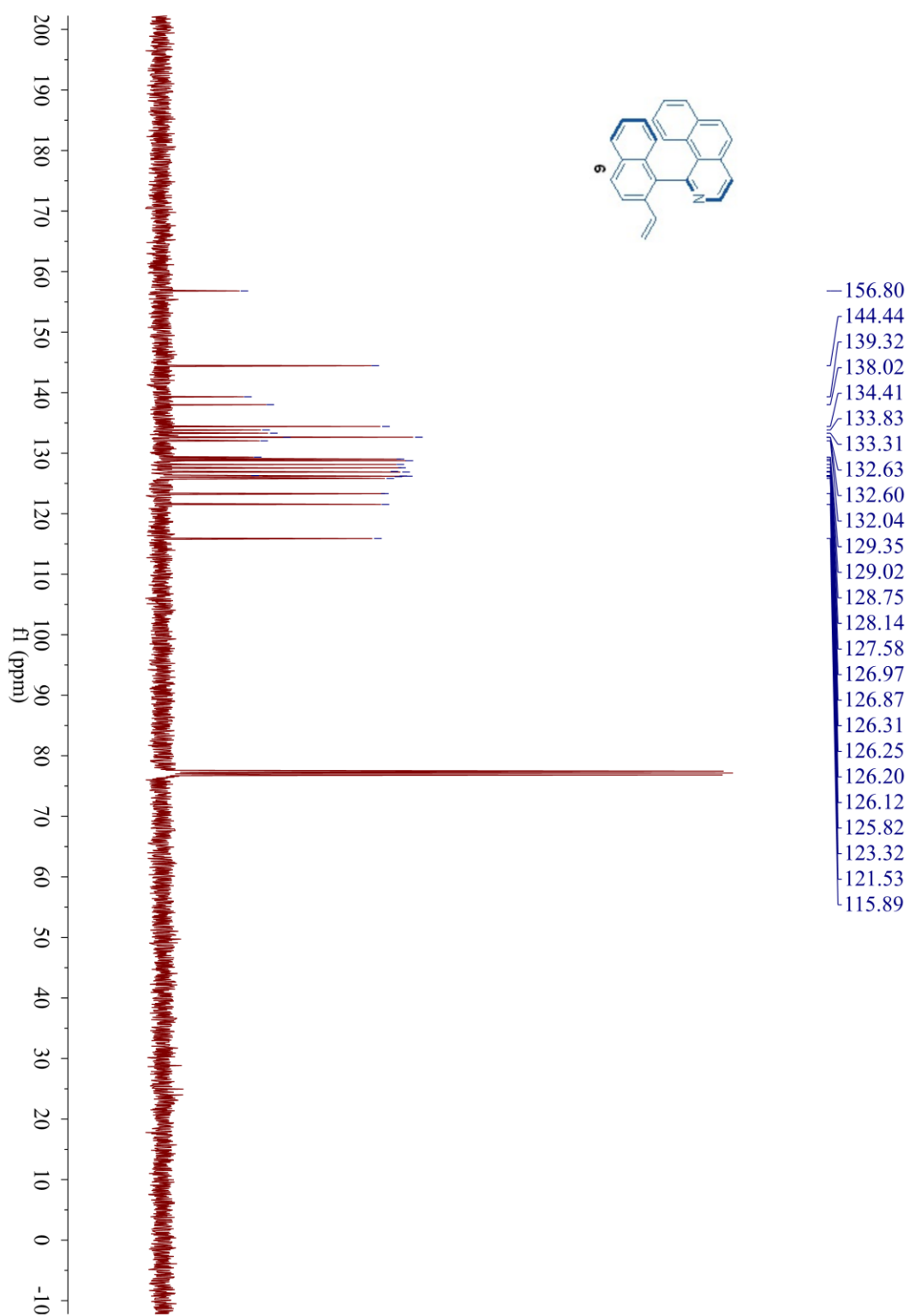
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **5**



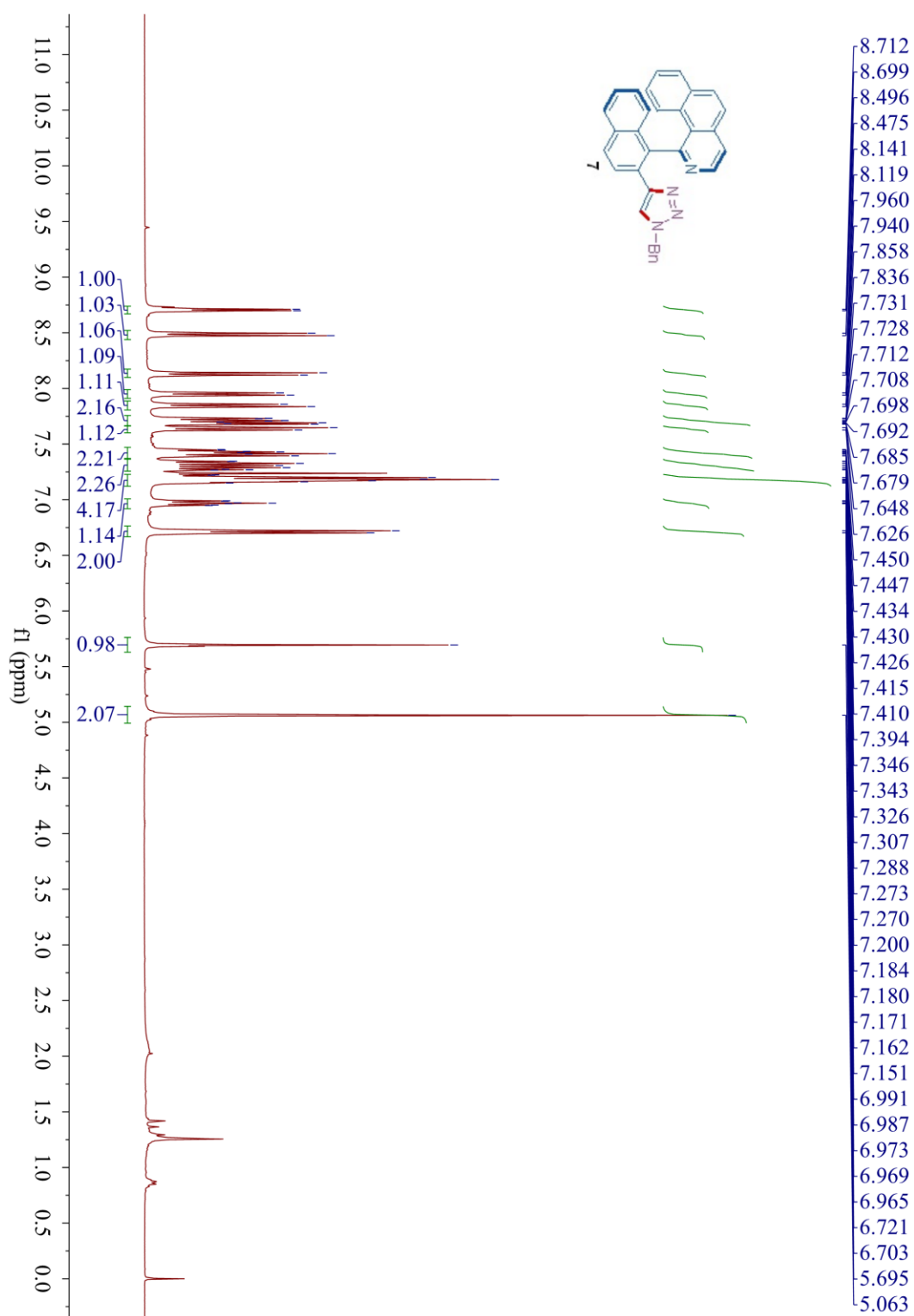
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **6**



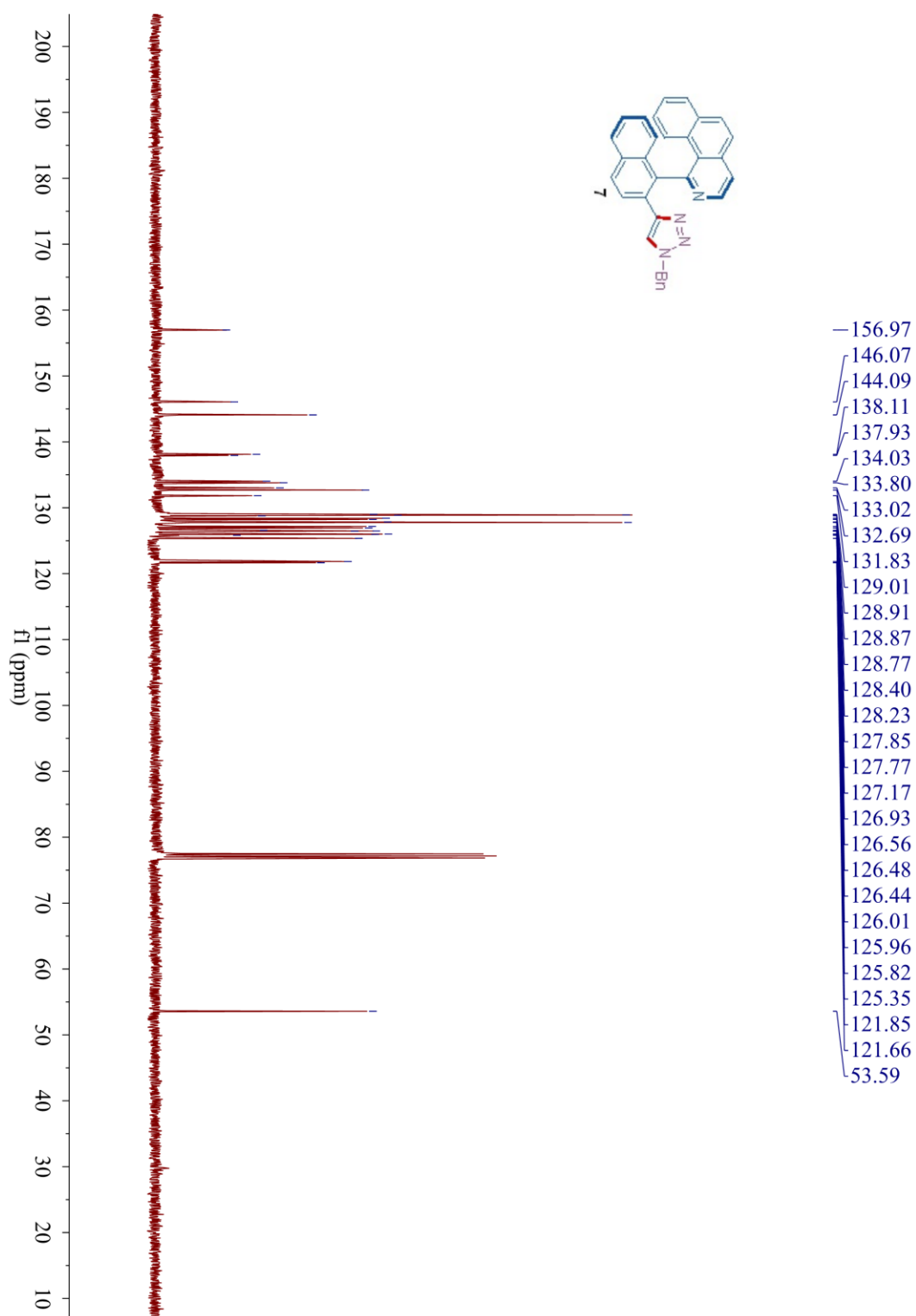
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **6**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **7**

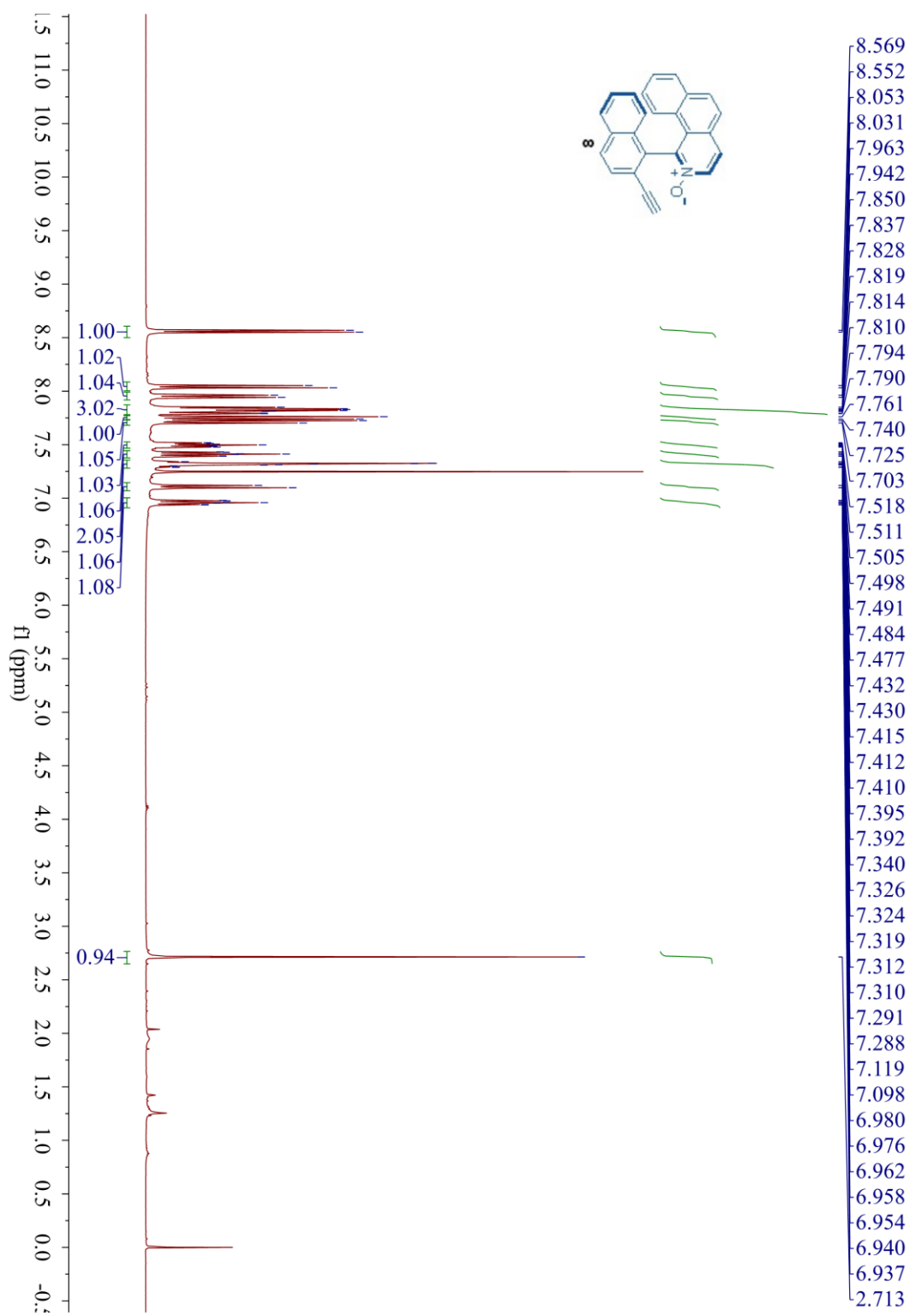


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 7

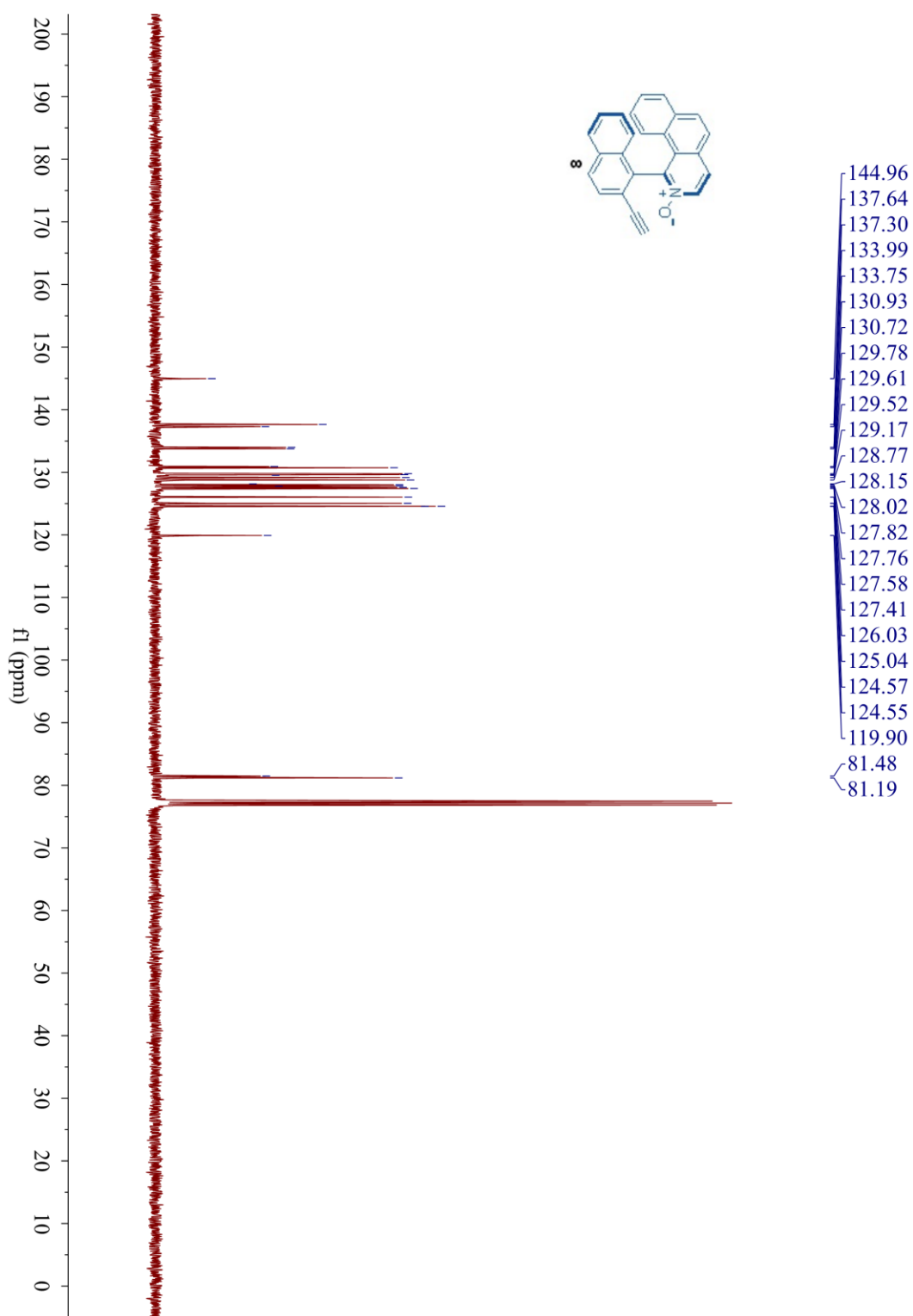




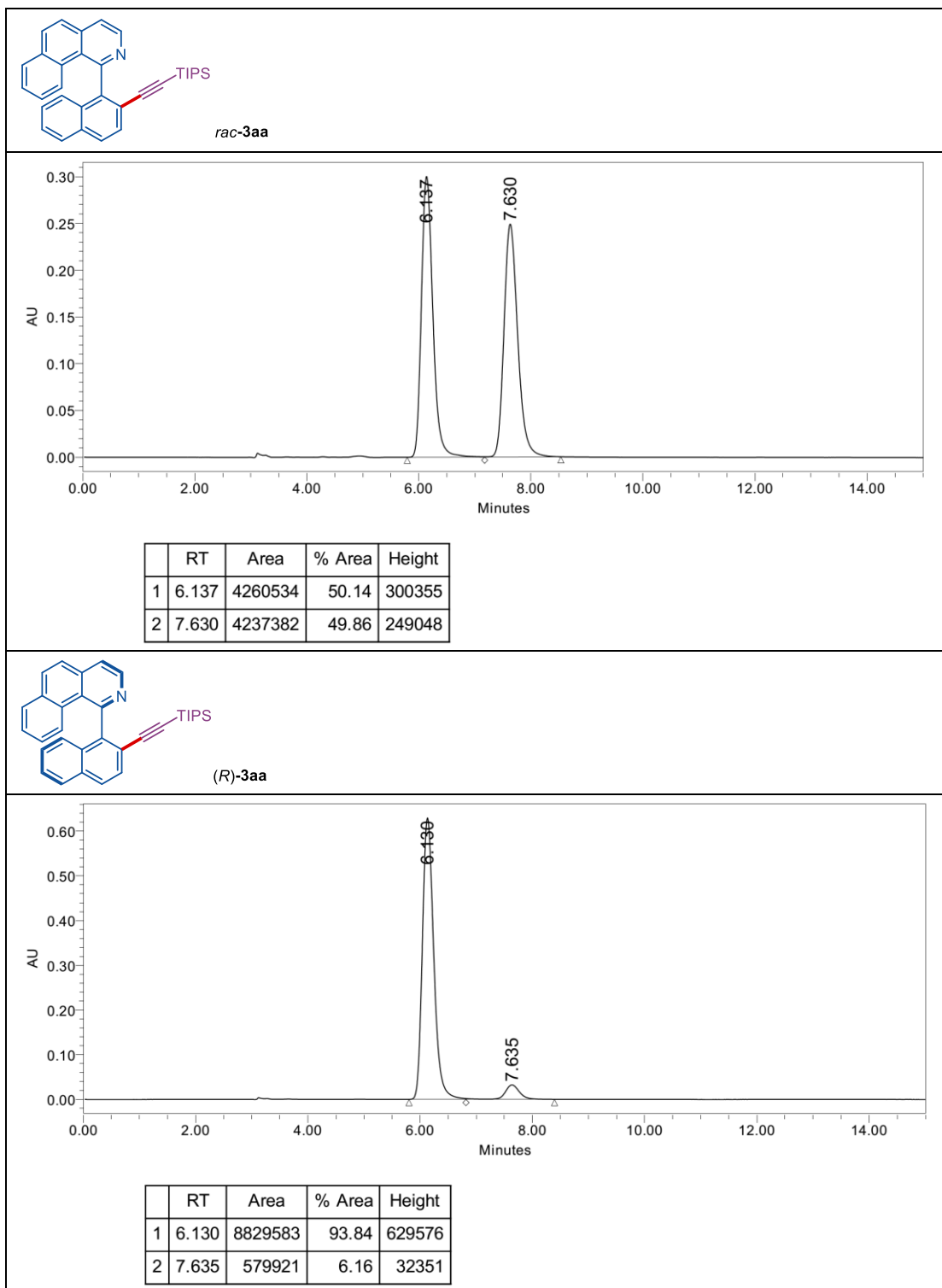
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **8**

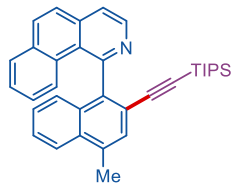


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **8**

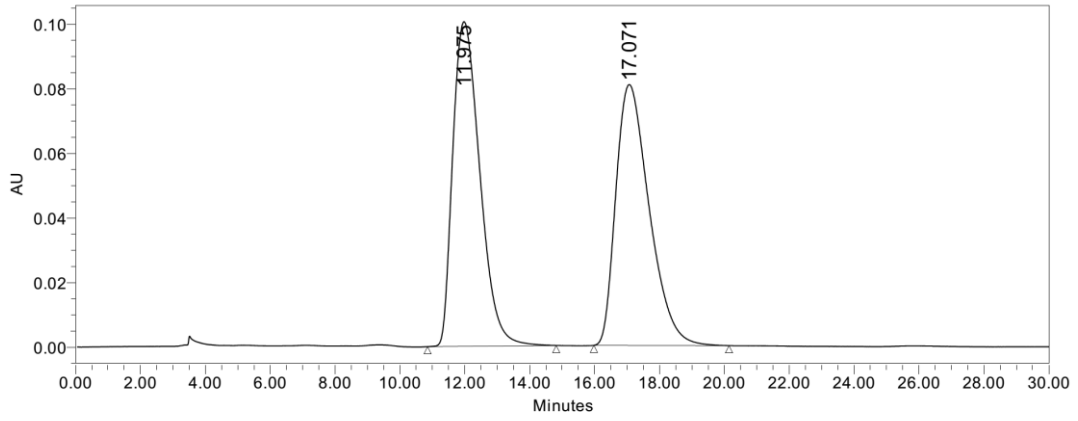


## 7. Copies of HPLC Chromatograms

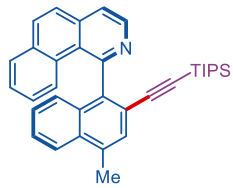




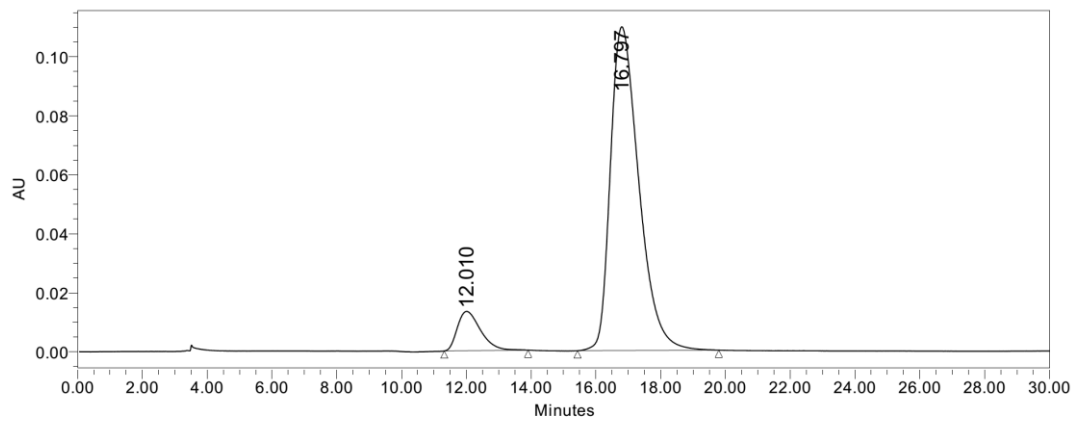
**rac-3ba**



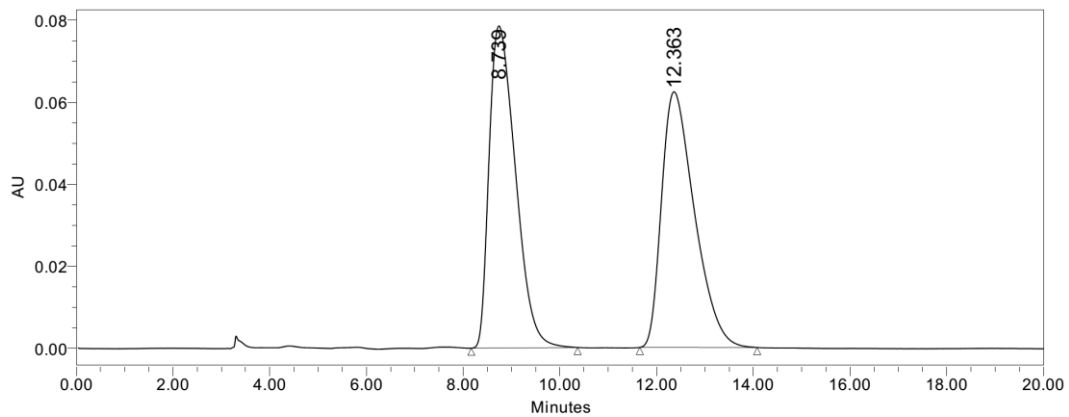
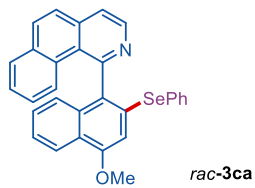
	RT	Area	% Area	Height
1	11.975	5827738	50.27	100531
2	17.071	5766276	49.73	80783



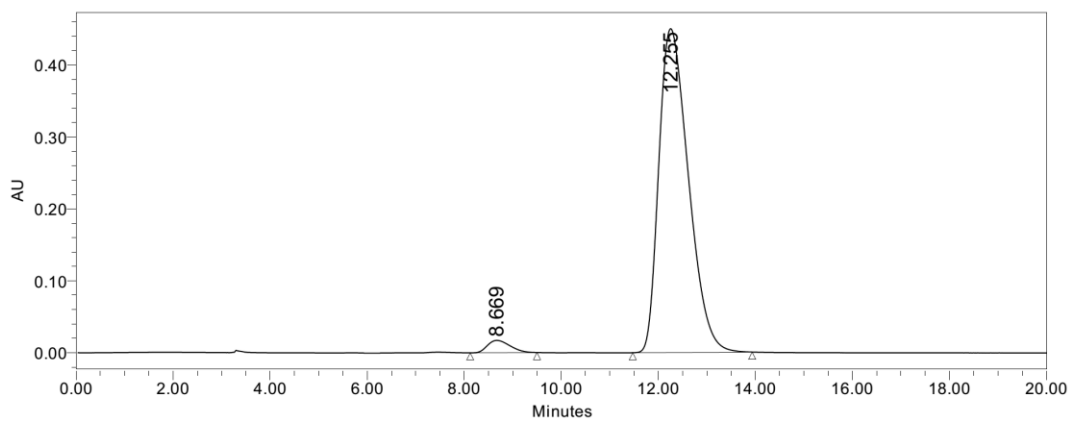
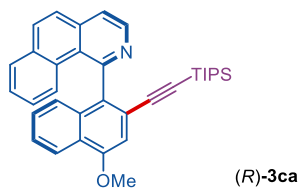
**(R)-3ba**



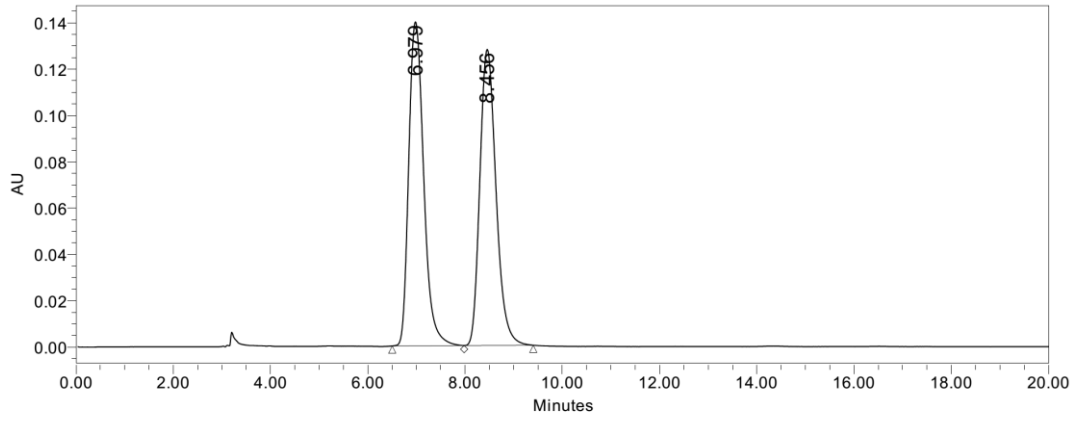
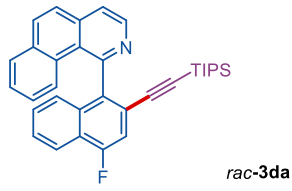
	RT	Area	% Area	Height
1	12.010	663181	9.02	13330
2	16.797	6685473	90.98	109740



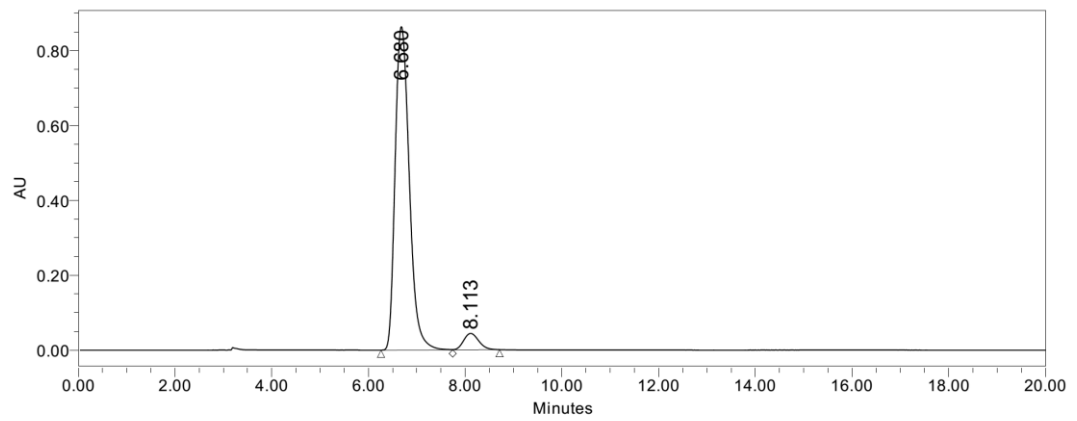
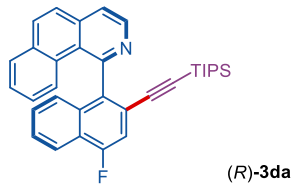
	RT	Area	% Area	Height
1	8.739	2971396	50.17	78531
2	12.363	2951349	49.83	62333



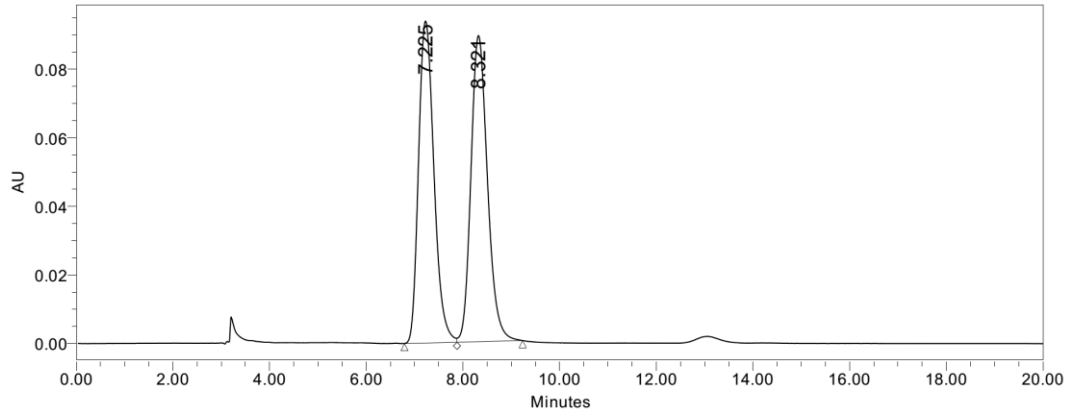
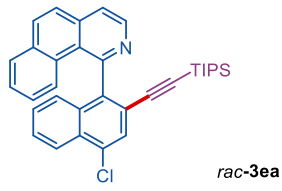
	RT	Area	% Area	Height
1	8.669	554473	2.82	17133
2	12.255	19074061	97.18	450142



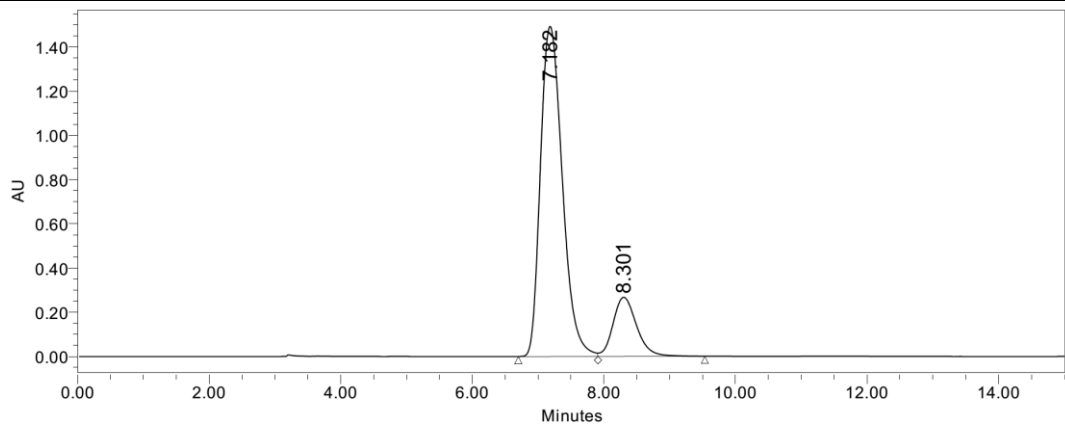
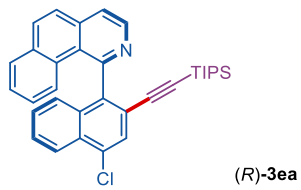
	RT	Area	% Area	Height
1	6.979	2985177	50.31	139903
2	8.456	2948915	49.69	127849



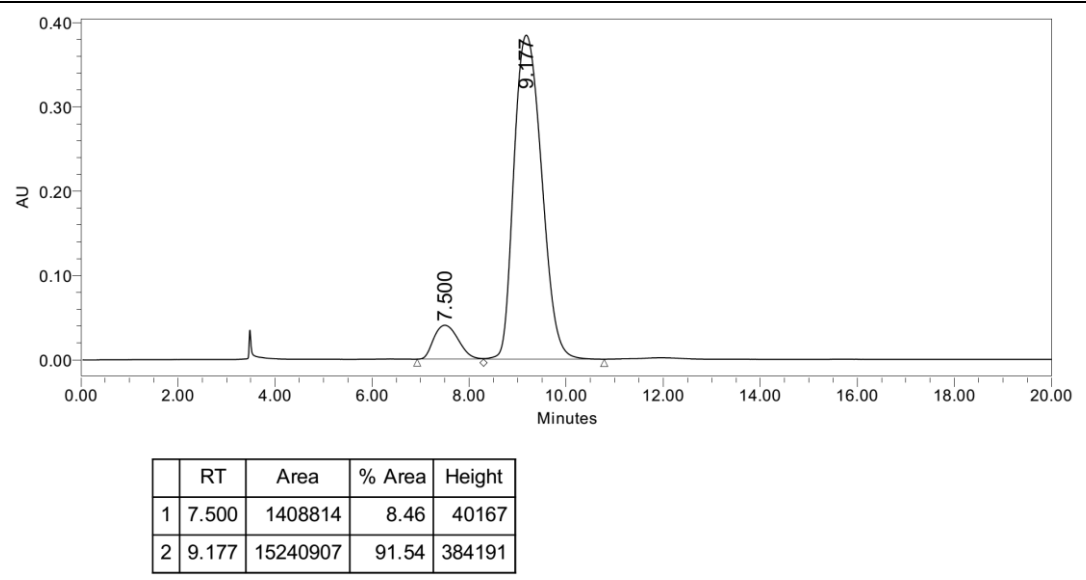
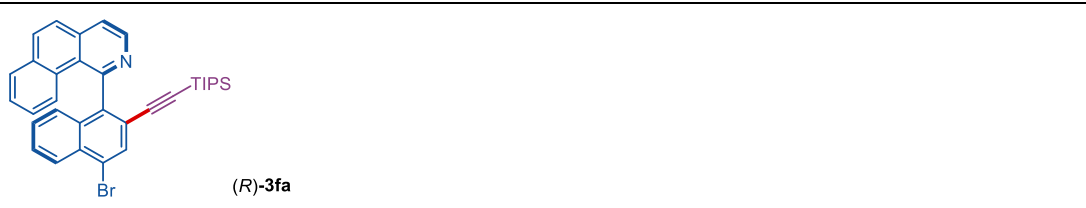
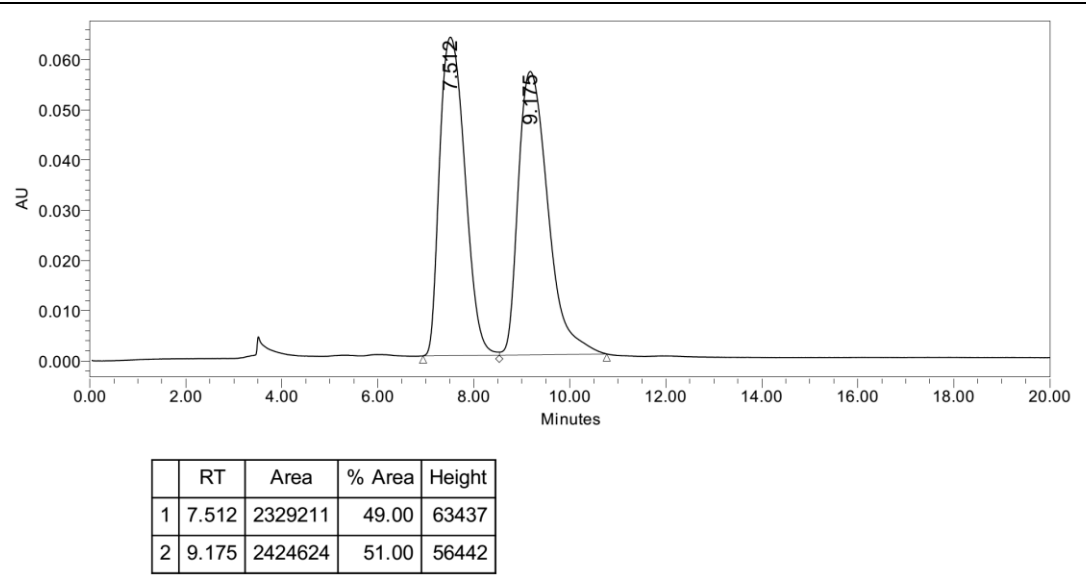
	RT	Area	% Area	Height
1	6.680	17584153	94.87	864042
2	8.113	950758	5.13	43726



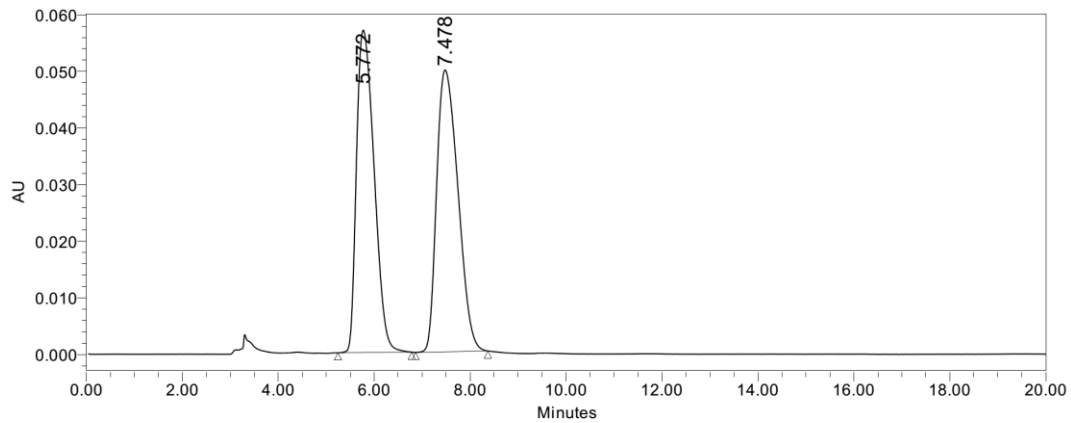
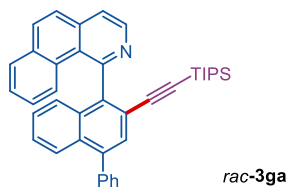
	RT	Area	% Area	Height
1	7.225	2076187	49.46	93871
2	8.321	2121856	50.54	89260



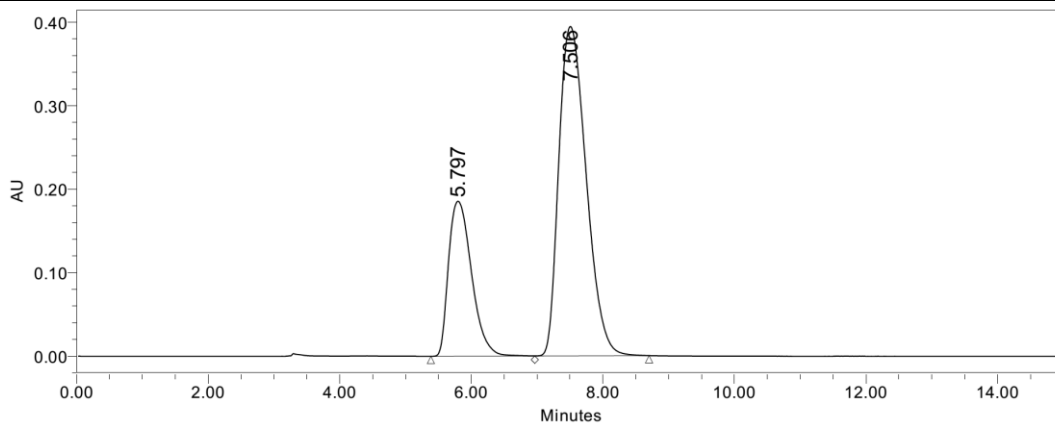
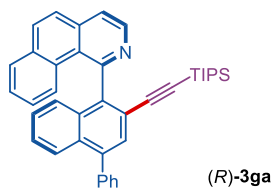
	RT	Area	% Area	Height
1	7.182	34513877	83.84	1493241
2	8.301	6652168	16.16	267242



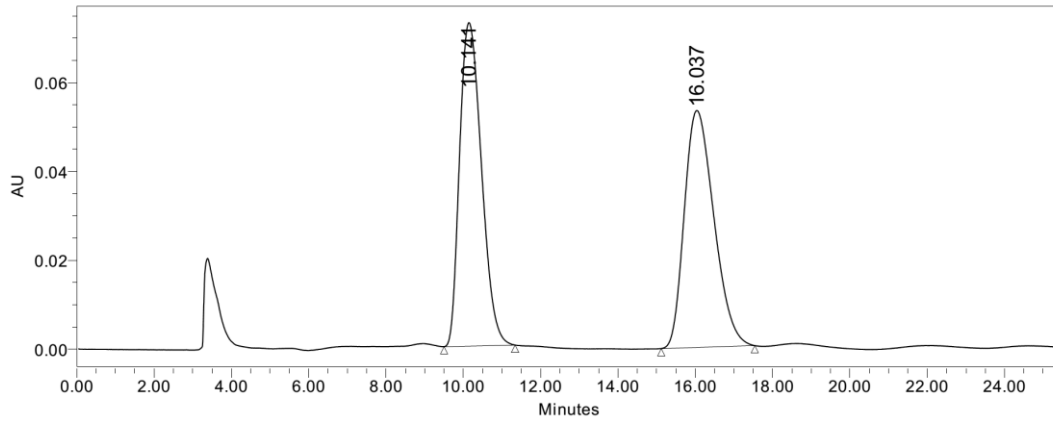
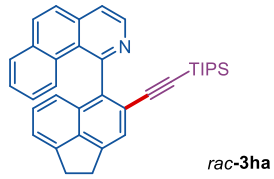




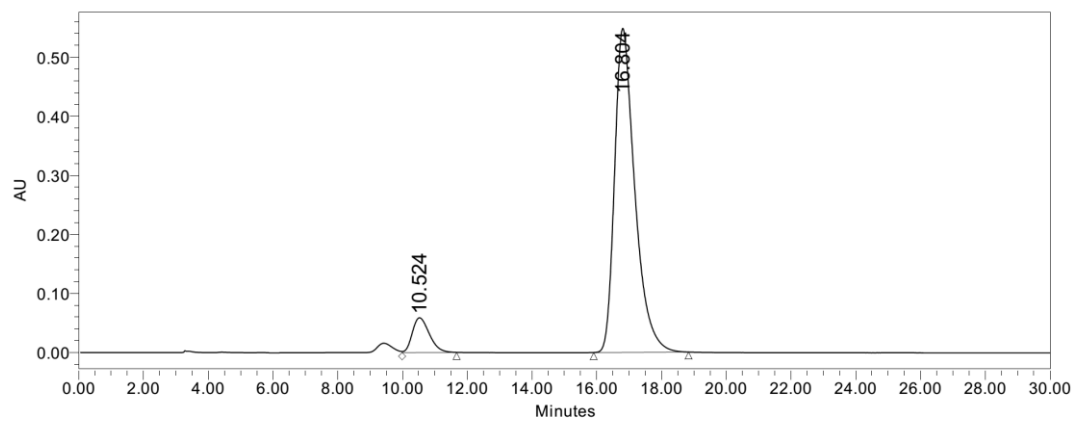
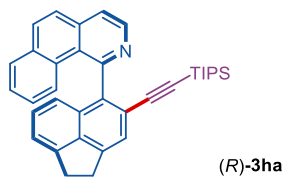
	RT	Area	% Area	Height
1	5.772	1456621	48.68	56978
2	7.478	1535509	51.32	49804



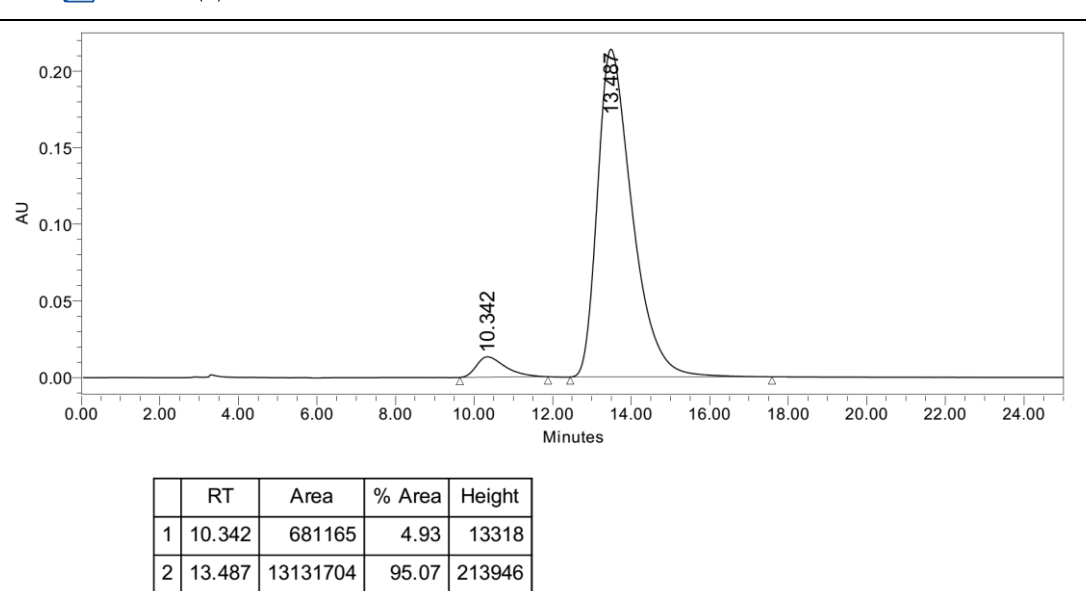
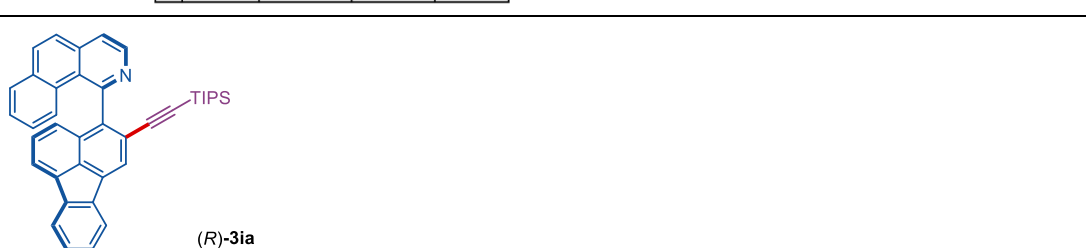
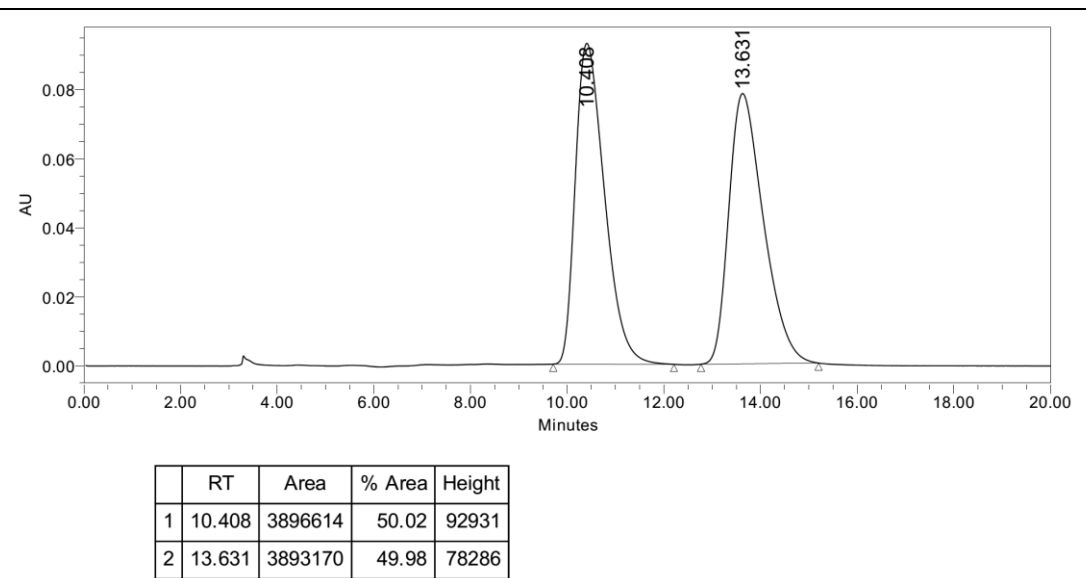
	RT	Area	% Area	Height
1	5.797	4512803	28.35	185539
2	7.506	11408022	71.65	394474

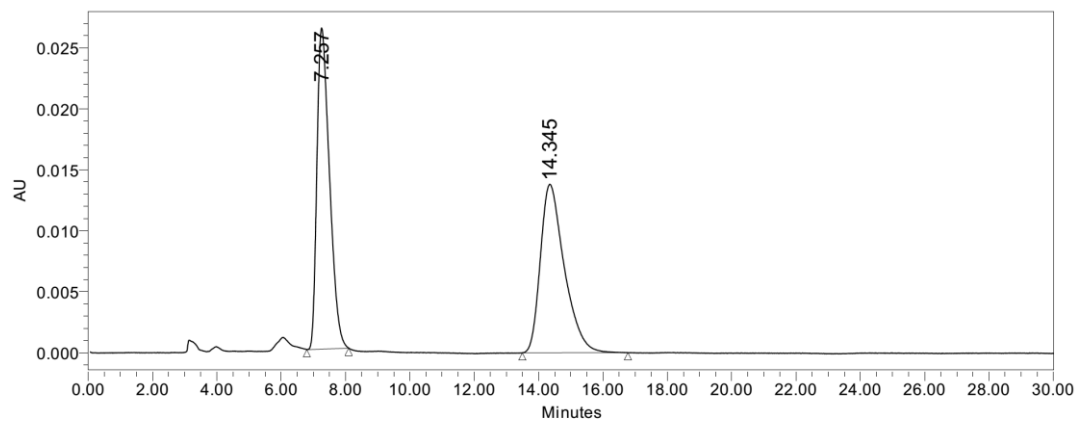
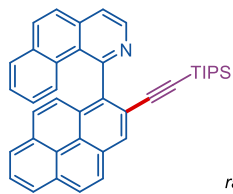


	RT	Area	% Area	Height
1	10.141	2862817	50.24	72831
2	16.037	2835075	49.76	53340

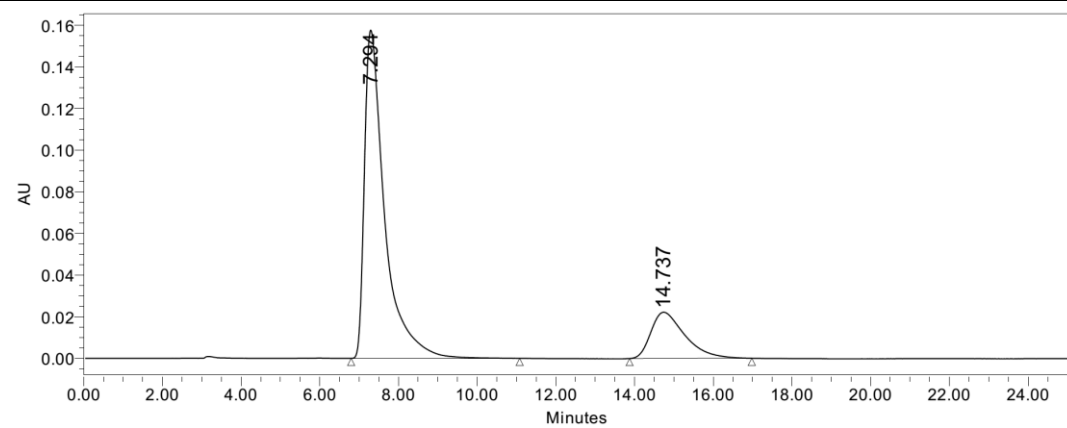
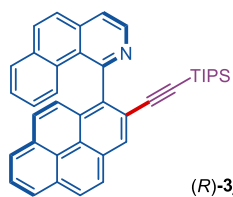


	RT	Area	% Area	Height
1	10.524	2140537	8.25	58765
2	16.804	23807378	91.75	548648

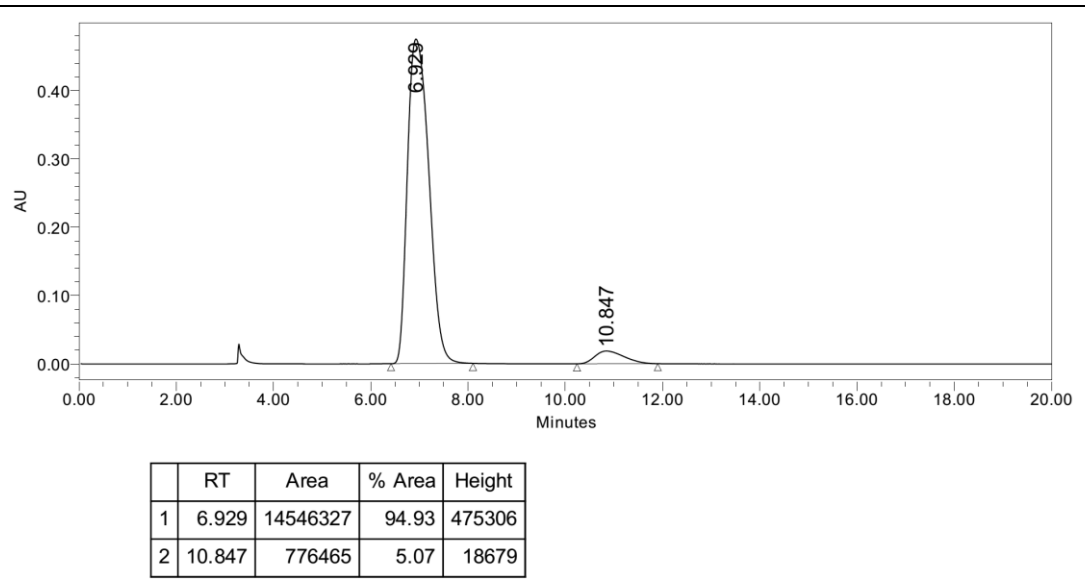
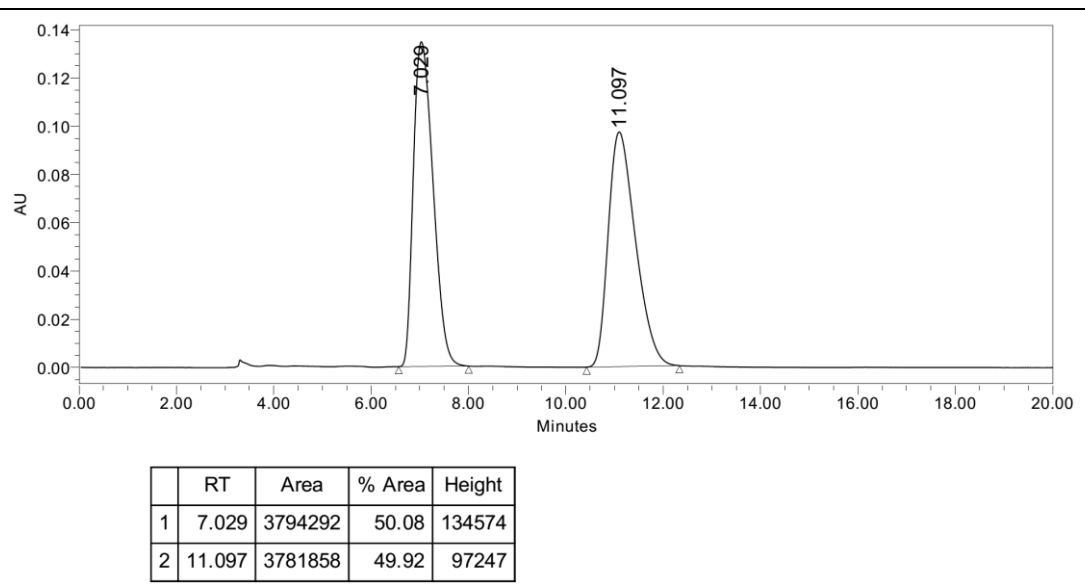


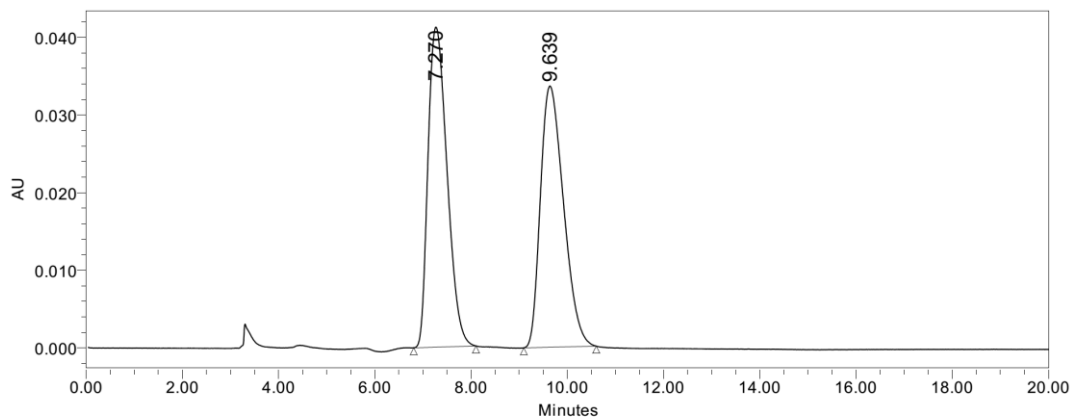
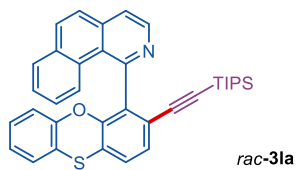


	RT	Area	% Area	Height
1	7.257	713463	49.97	26341
2	14.345	714200	50.03	13826

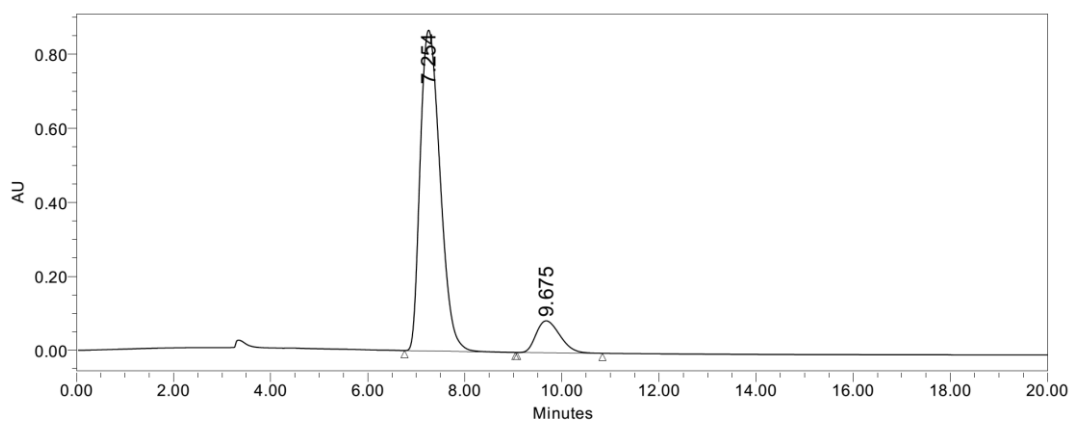
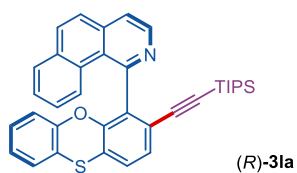


	RT	Area	% Area	Height
1	7.294	5618641	80.87	157624
2	14.737	1329388	19.13	22221

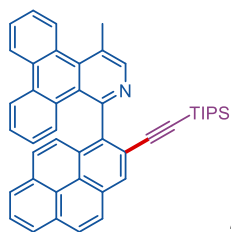




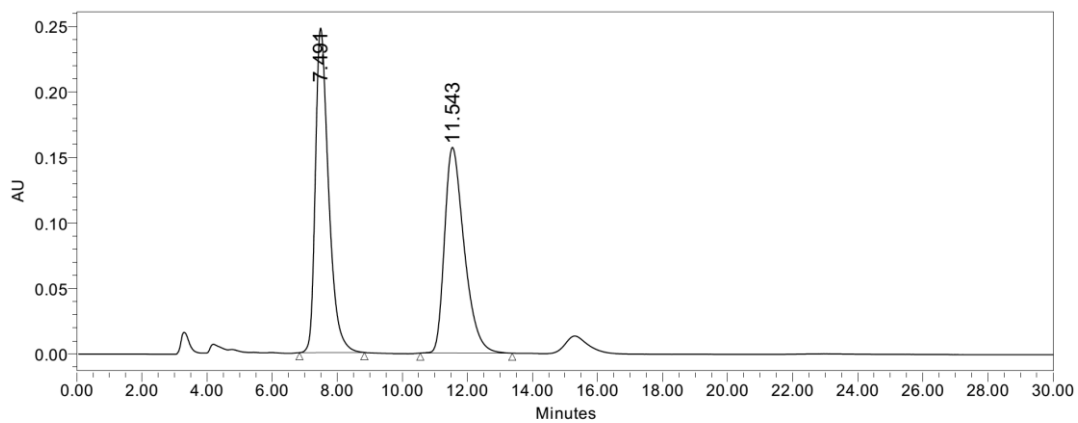
	RT	Area	% Area	Height
1	7.270	1132570	50.22	41234
2	9.639	1122576	49.78	33651



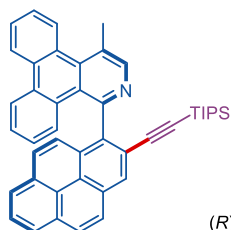
	RT	Area	% Area	Height
1	7.254	24665408	89.39	866808
2	9.675	2927210	10.61	86171



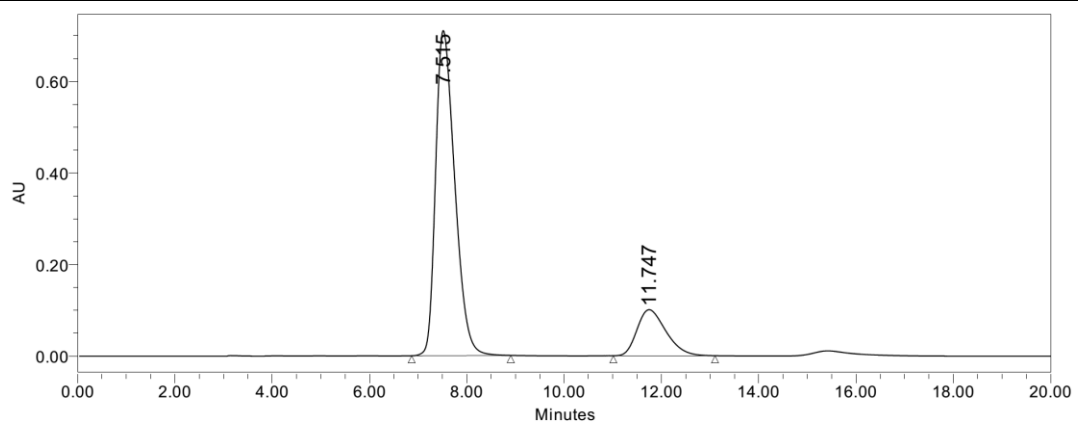
*rac*-3ma



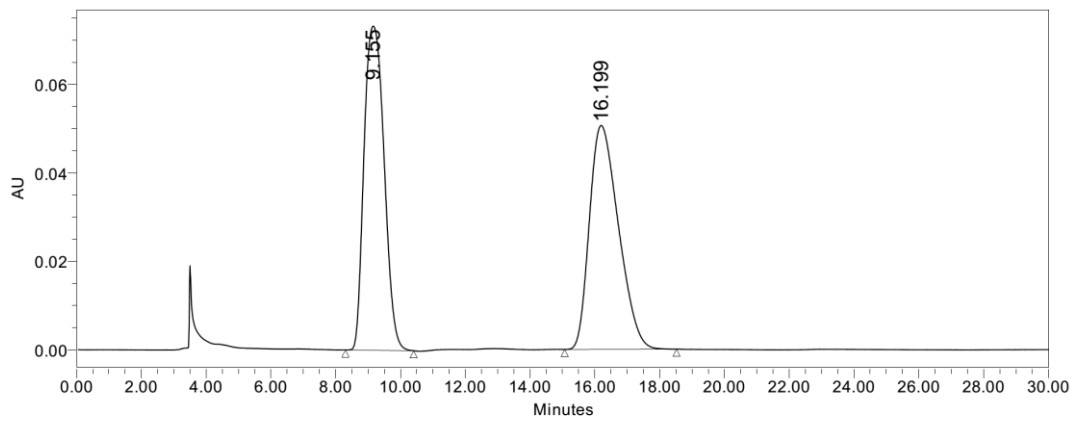
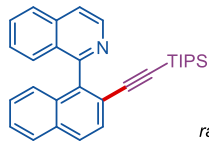
	RT	Area	% Area	Height
1	7.491	6989248	51.40	247743
2	11.543	6607271	48.60	157034



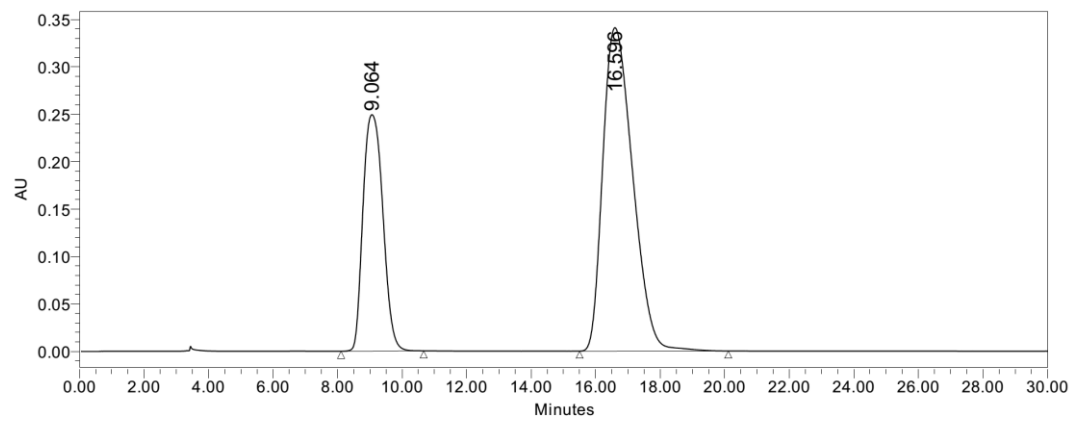
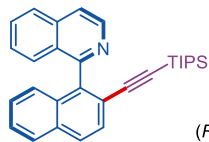
(*R*)-3ma



	RT	Area	% Area	Height
1	7.515	19415056	82.35	710431
2	11.747	4159923	17.65	100668

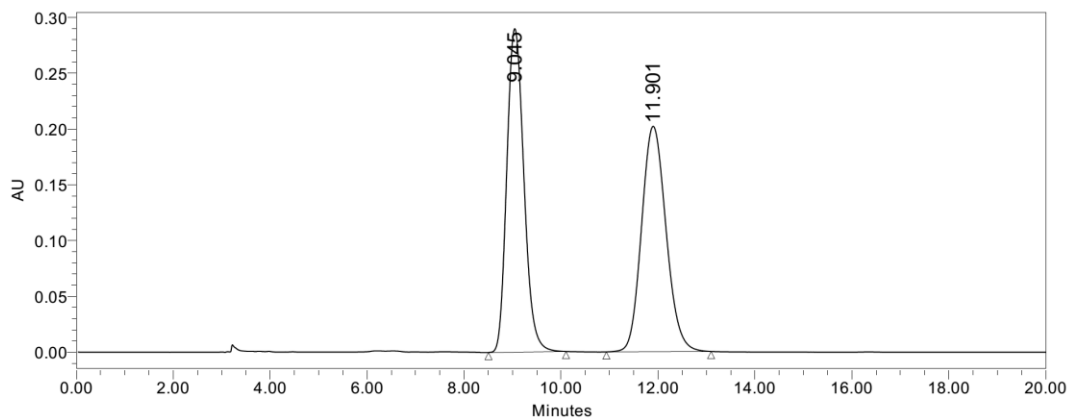
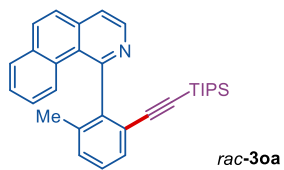


	RT	Area	% Area	Height
1	9.155	3160022	50.05	73275
2	16.199	3154141	49.95	50608

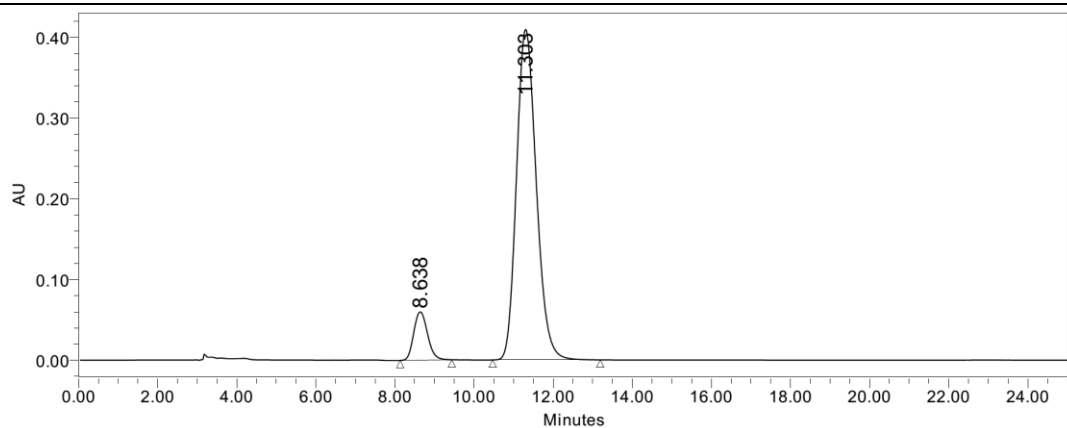
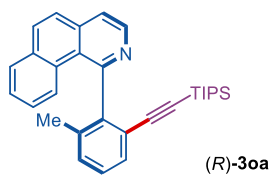


	RT	Area	% Area	Height
1	9.064	10690692	32.77	249309
2	16.596	21927962	67.23	341028

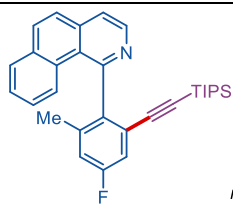




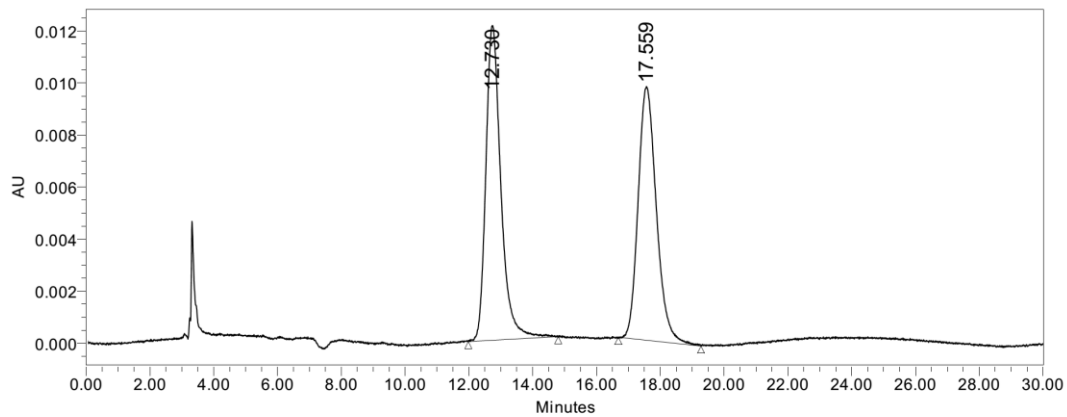
	RT	Area	% Area	Height
1	9.045	7105393	50.05	289881
2	11.901	7090971	49.95	202039



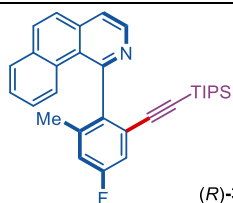
	RT	Area	% Area	Height
1	8.638	1447979	9.24	59826
2	11.303	14226155	90.76	409507



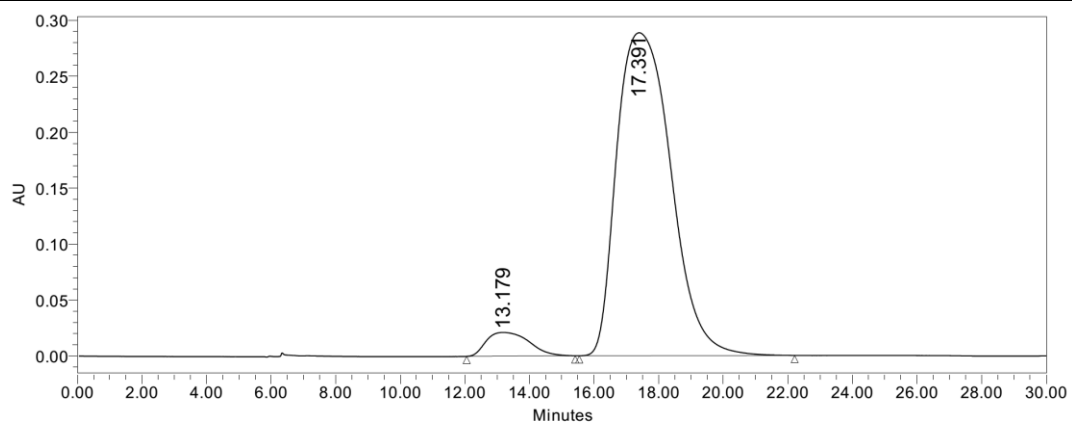
*rac*-3pa



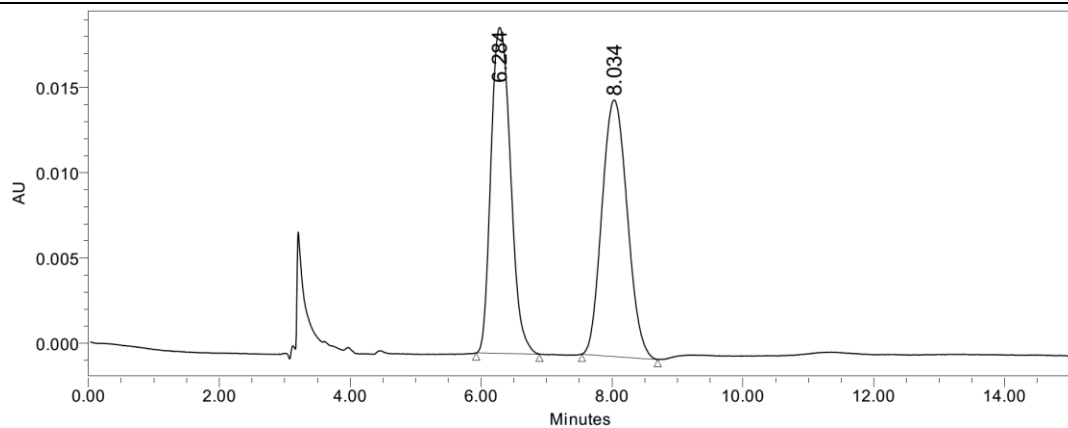
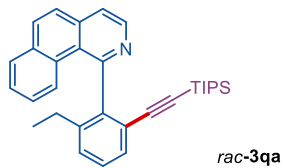
	RT	Area	% Area	Height
1	12.730	396920	50.66	12091
2	17.559	386572	49.34	9745



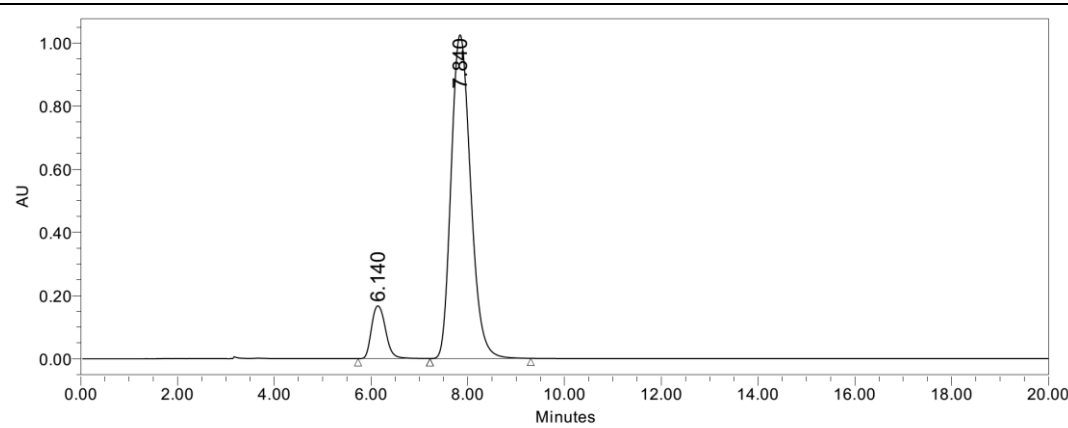
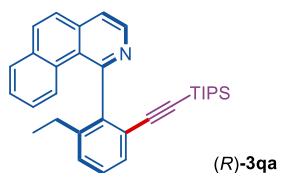
*(R)*-3pa



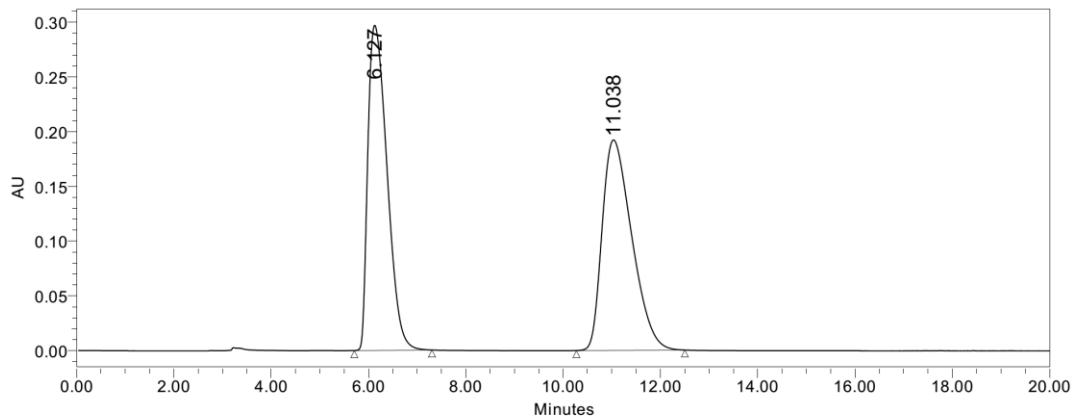
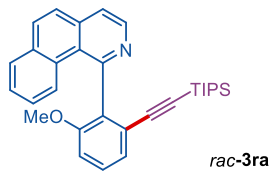
	RT	Area	% Area	Height
1	13.179	1950695	5.46	21205
2	17.391	33754725	94.54	288556



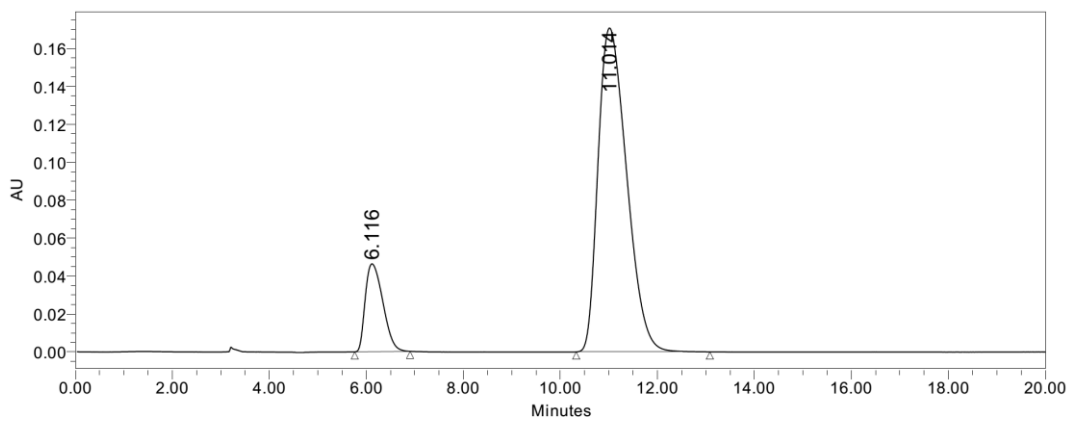
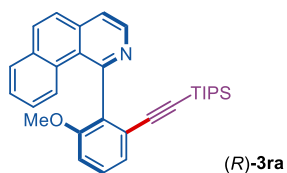
	RT	Area	% Area	Height
1	6.284	397445	49.50	19127
2	8.034	405549	50.50	15062



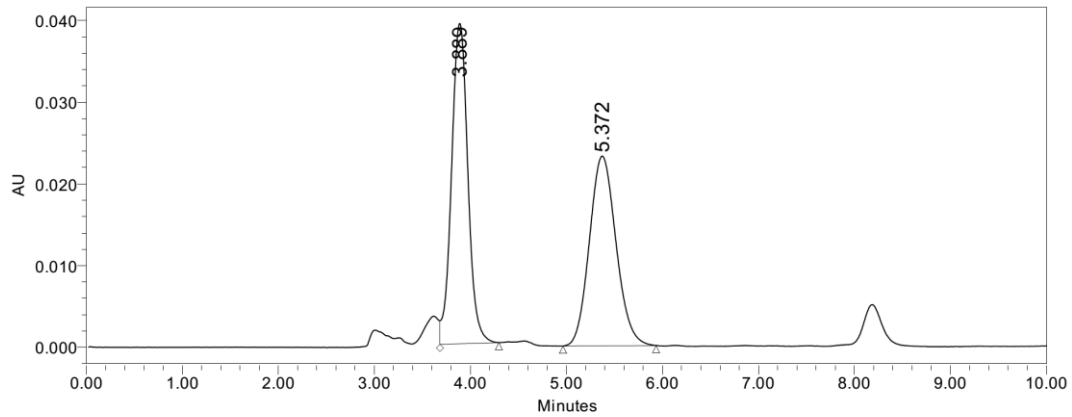
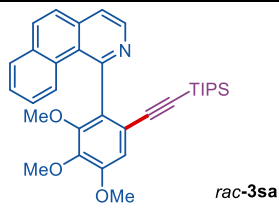
	RT	Area	% Area	Height
1	6.140	3376978	10.52	167034
2	7.840	28712784	89.48	1024835



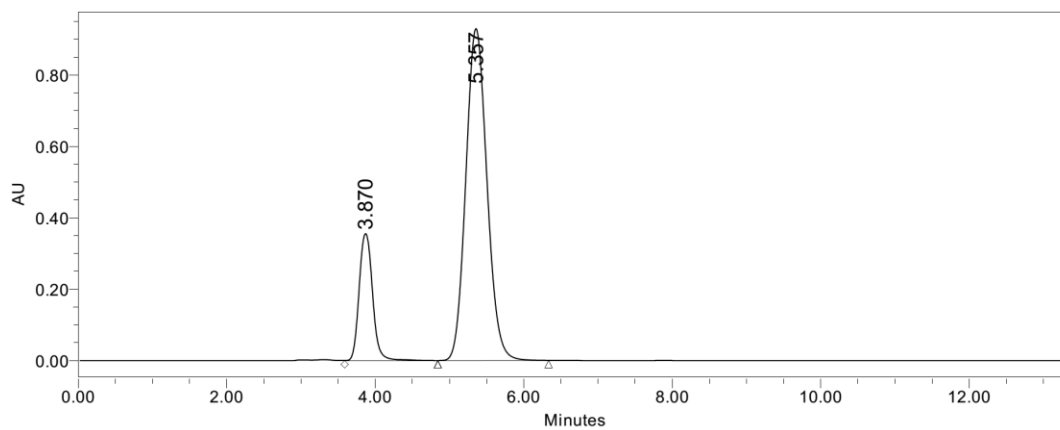
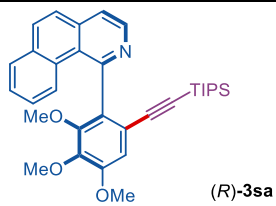
	RT	Area	% Area	Height
1	6.127	8133941	50.02	296995
2	11.038	8126198	49.98	192215



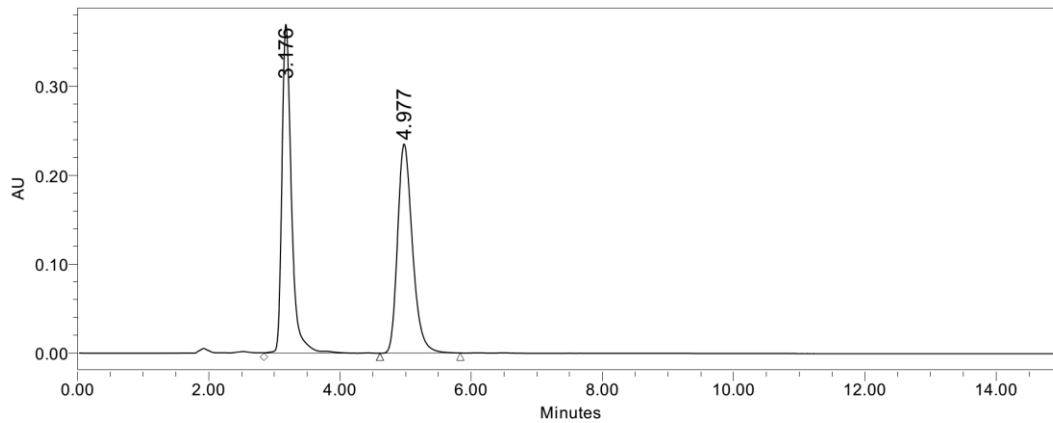
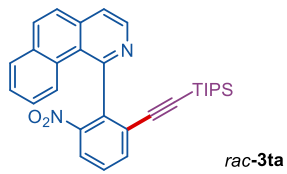
	RT	Area	% Area	Height
1	6.116	1168656	14.33	46345
2	11.014	6988256	85.67	170860



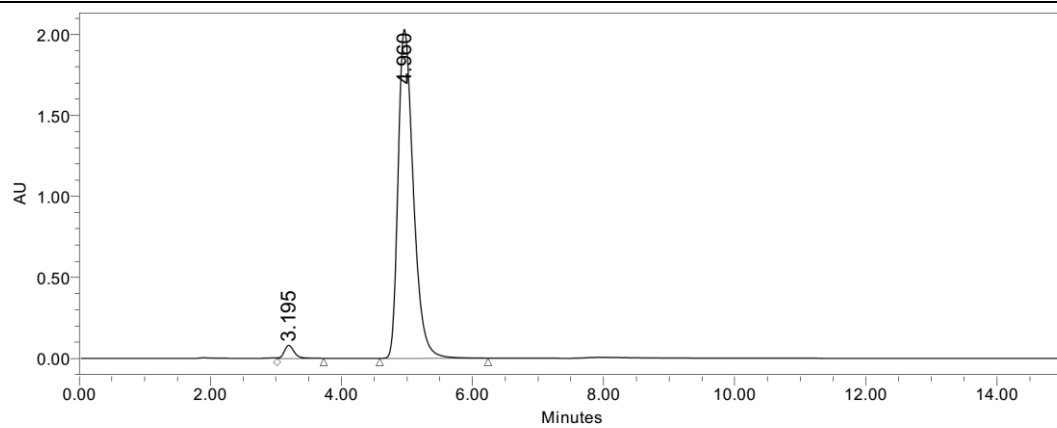
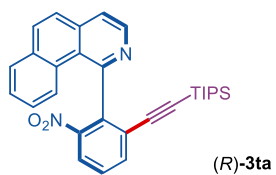
	RT	Area	% Area	Height
1	3.889	462378	50.80	39195
2	5.372	447807	49.20	23226



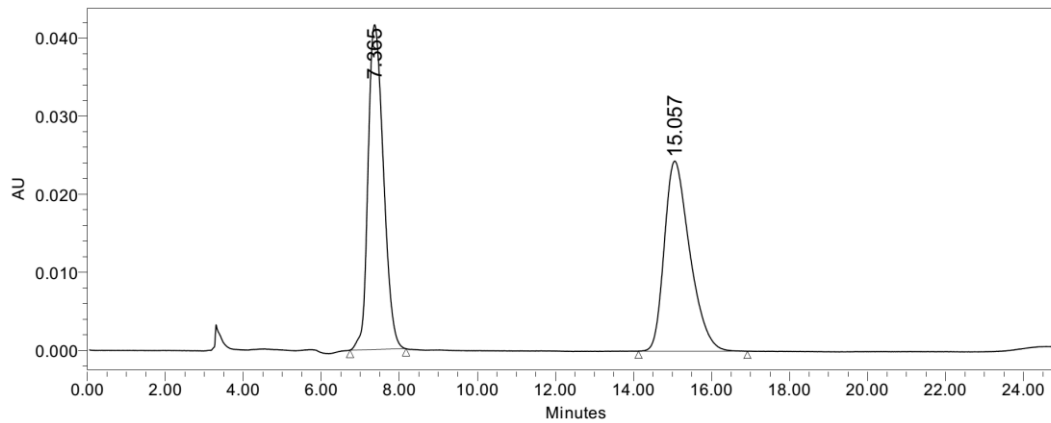
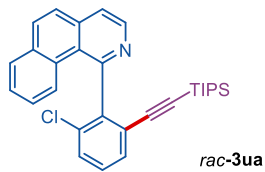
	RT	Area	% Area	Height
1	3.870	4464980	19.55	355666
2	5.357	18372461	80.45	930133



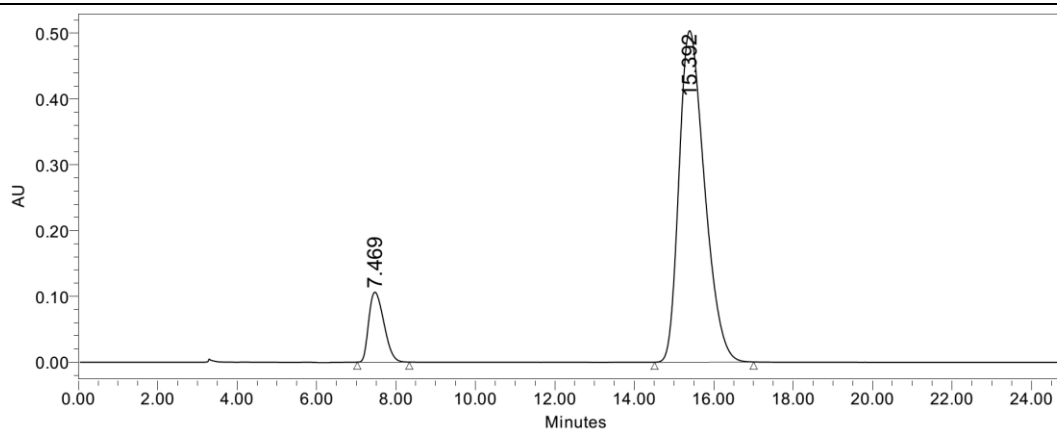
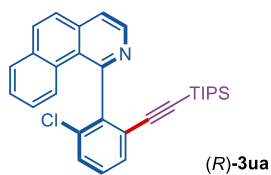
	RT	Area	% Area	Height
1	3.176	3742041	50.24	369800
2	4.977	3706451	49.76	235140



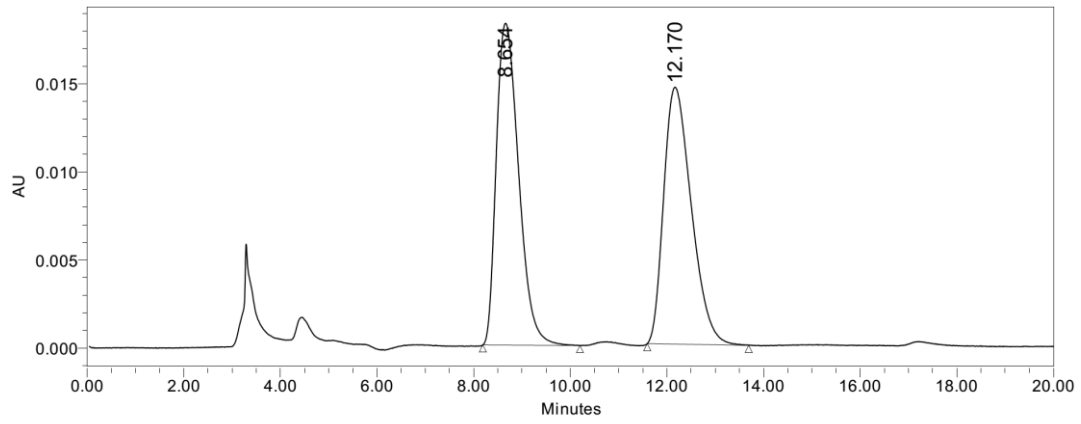
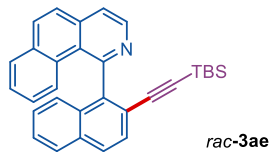
	RT	Area	% Area	Height
1	3.195	824972	2.45	80001
2	4.960	32817075	97.55	2031801



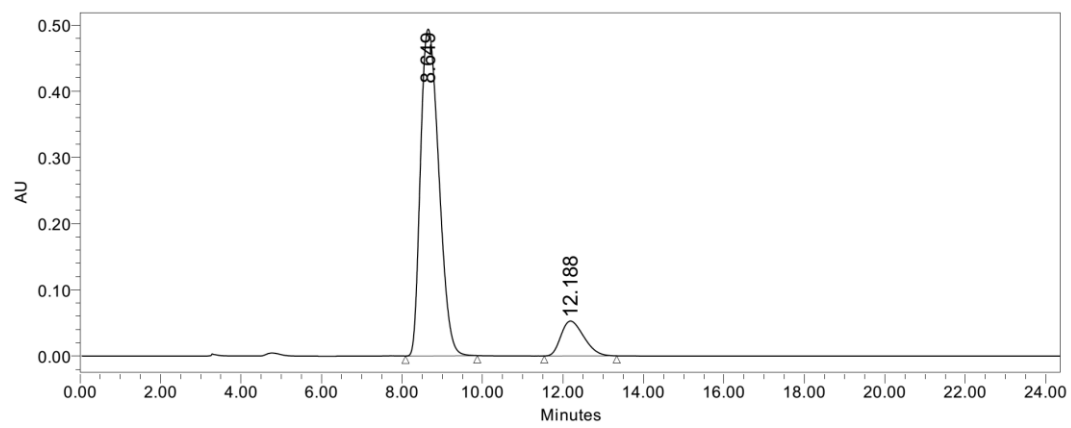
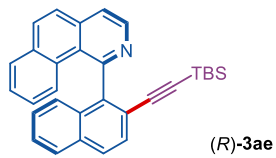
	RT	Area	% Area	Height
1	7.365	1138788	50.75	41585
2	15.057	1105319	49.25	24343



	RT	Area	% Area	Height
1	7.469	2813011	11.12	106315
2	15.392	22485061	88.88	503759

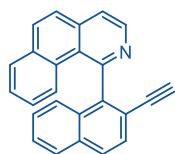


	RT	Area	% Area	Height
1	8.654	587322	50.32	18275
2	12.170	579799	49.68	14595

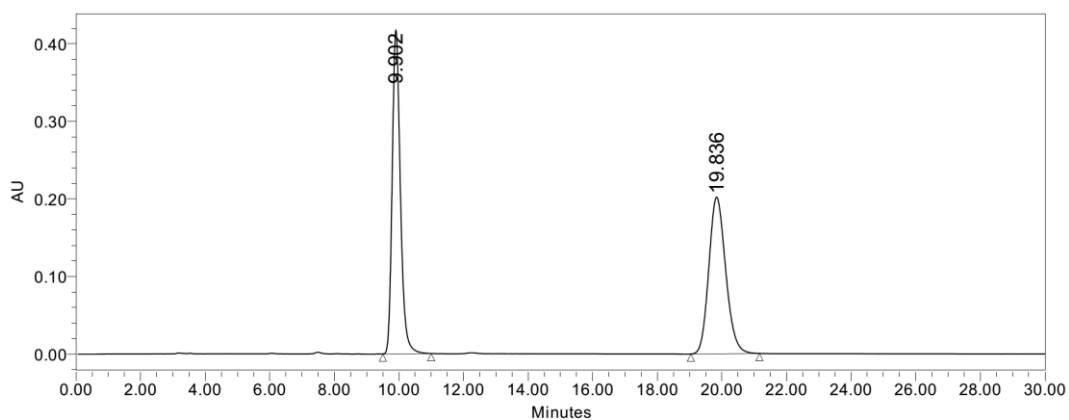


	RT	Area	% Area	Height
1	8.649	15608237	88.24	493690
2	12.188	2079315	11.76	52641

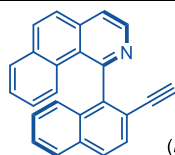




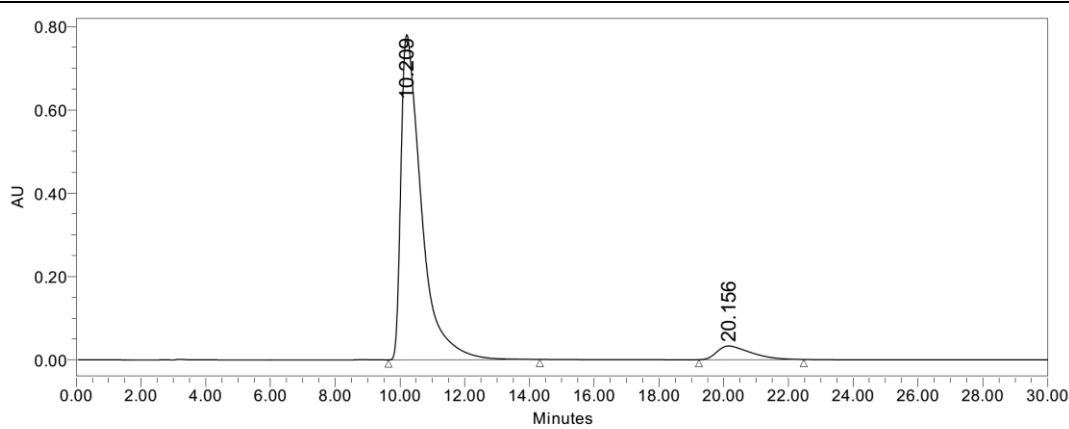
rac-4



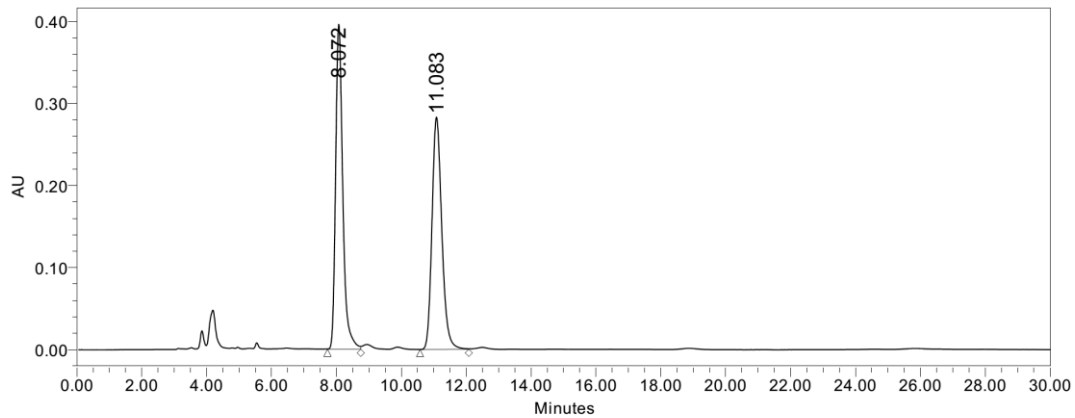
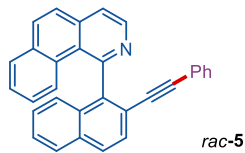
	RT	Area	% Area	Height
1	9.902	7359693	50.14	417345
2	19.836	7318944	49.86	201933



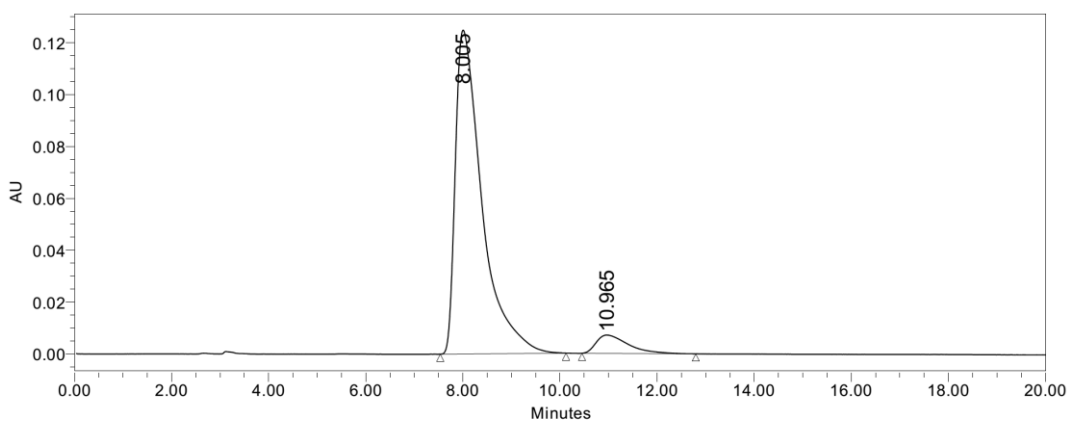
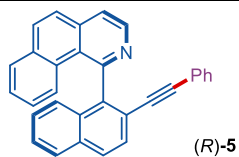
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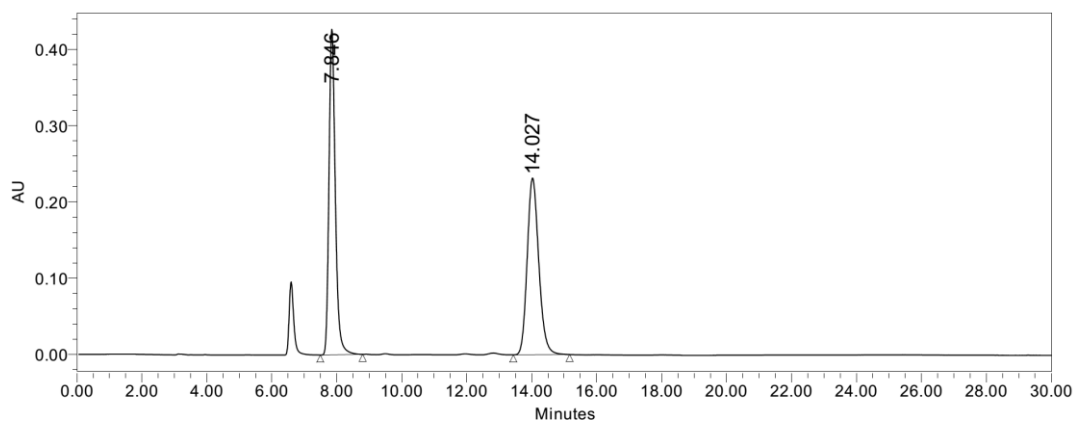
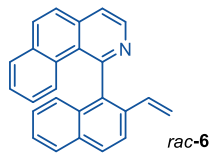
	RT	Area	% Area	Height
1	10.209	34197657	93.53	780719
2	20.156	2367137	6.47	32786



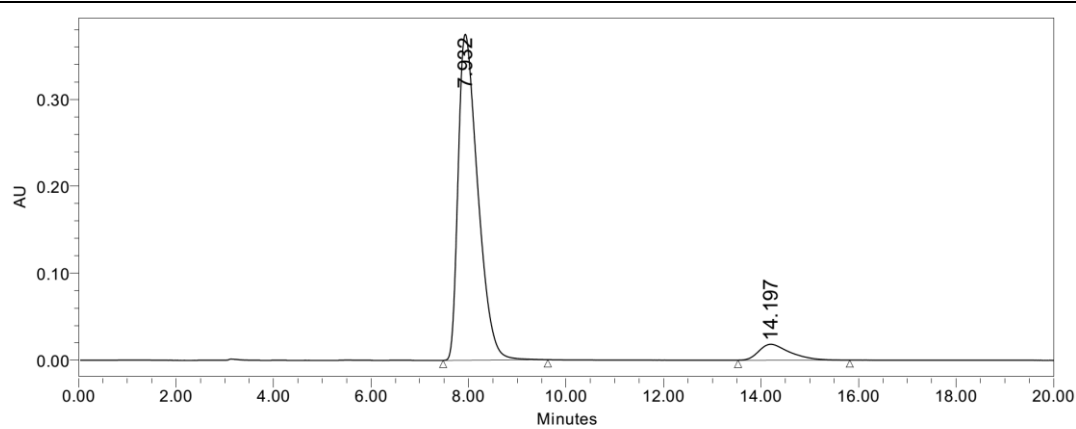
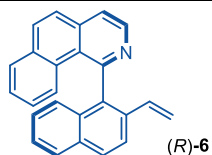
	RT	Area	% Area	Height
1	8.072	6044165	50.45	395704
2	11.083	5935812	49.55	282951



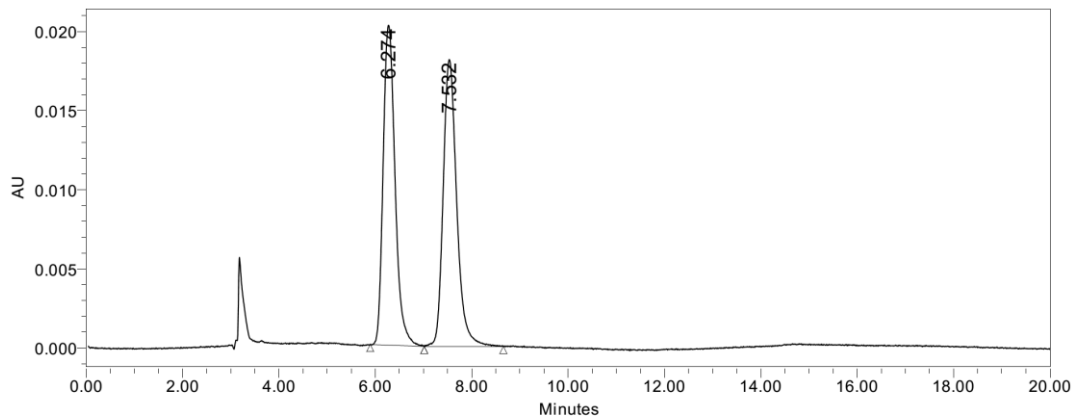
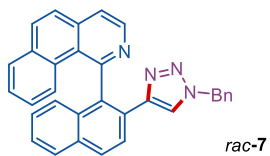
	RT	Area	% Area	Height
1	8.005	4740524	93.62	124928
2	10.965	323087	6.38	7063



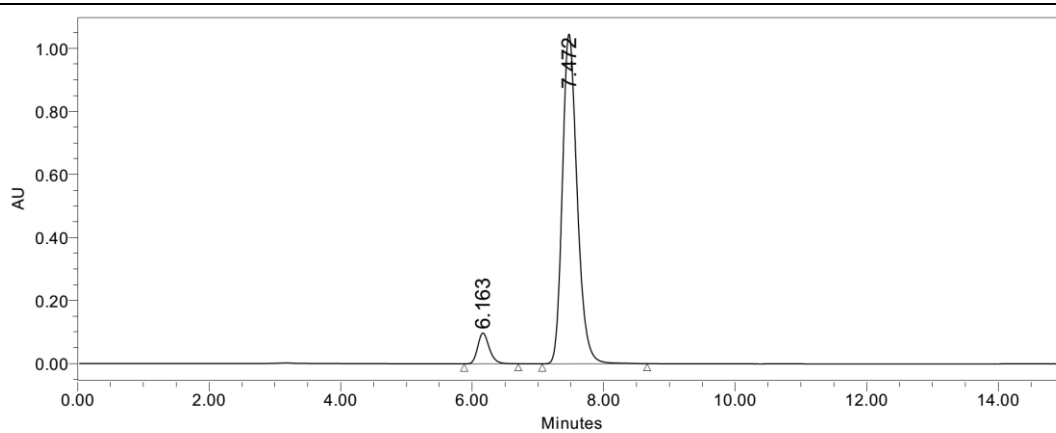
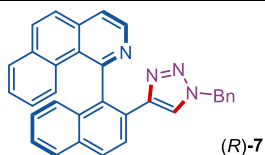
	RT	Area	% Area	Height
1	7.846	5795399	50.22	427210
2	14.027	5744063	49.78	231861



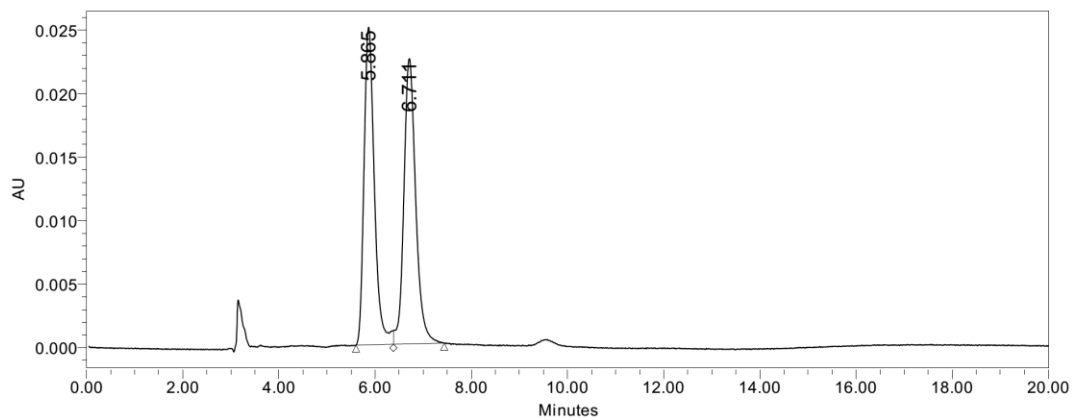
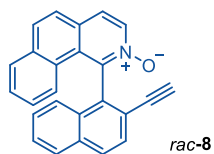
	RT	Area	% Area	Height
1	7.932	10469640	92.85	374802
2	14.197	805893	7.15	18281



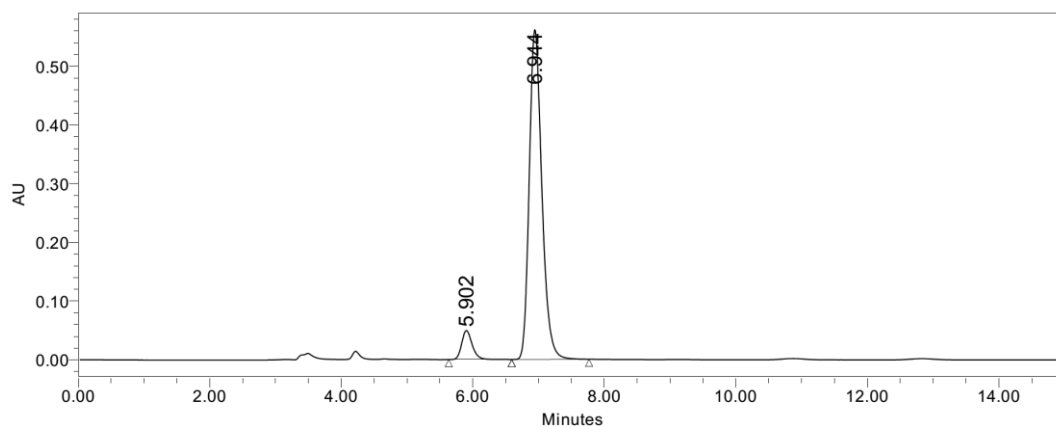
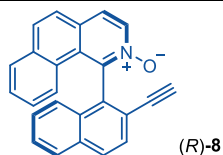
	RT	Area	% Area	Height
1	6.274	346694	49.53	20214
2	7.532	353240	50.47	18125



	RT	Area	% Area	Height
1	6.163	1194367	6.80	97660
2	7.472	16371904	93.20	1046273



	RT	Area	% Area	Height
1	5.865	374549	49.40	25006
2	6.711	383668	50.60	22471



	RT	Area	% Area	Height
1	5.902	550896	6.87	49407
2	6.944	7470770	93.13	561686