

Supporting Information

Remote Asymmetric amination of Naphthalene-Blocked Alkynes with various amines

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I General Information

Commercially available materials were used as received, unless otherwise noted, all reactions and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. Reactions were checked by TLC analysis and plates were visualized with short-wave UV light (254 nm). HPLC analysis of the compounds was done using chiralcel ADH, ODH, IA or OJH column using hexane and isopropanol as eluent, and the column temperature is 40 °C. The Rudolph Autopol V polarimeter was employed to gauge the optical rotation. The ¹H, ¹³C NMR and ¹⁹F spectra were obtained in CDCl₃ using a Bruker-Bio Spin AVANCE III HD NMR spectrometer at 400 MHz, 100 MHz and 376 MHz respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. The melting point was measured by Shanghai Instrument electrooptical SGW X-4A micro melting point instrument. High resolution mass spectra (HRMS) were recorded on Thermo Scientific Q Exactive mass spectrometry equipped with an APCI source. Crystal structure data was collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The following abbreviations are used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

II Optimization of Reaction Conditions

Table 1. Optimization of the Reaction Conditions

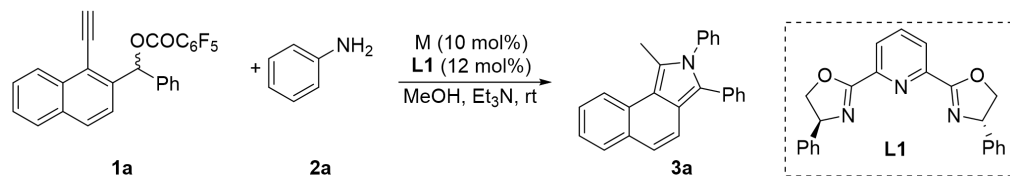


Table S1: Copper screening^a

Entry	M	Ligand	Solvent	T (°C)	Yield (%) ^b
1	Cu(CH ₃ CN) ₄ BF ₄	L1	MeOH	25	84
2	CuOTf	L1	MeOH	25	79
3	CuI	L1	MeOH	25	75
4	Cu(CH ₃ CN) ₄ PF ₆	L1	MeOH	25	80
5	Cu ₂ O	L1	MeOH	25	79
6	CuBr	L1	MeOH	25	95
7	CuCl	L1	MeOH	25	83
8	CuTc	L1	MeOH	25	76
9	CuOAc	L1	MeOH	25	76

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), **M** (10 mol%), **L1** (12 mol%), MeOH (1.0 mL) at 25 °C under Argon atmosphere for 24 h. ^bIsolated yields.

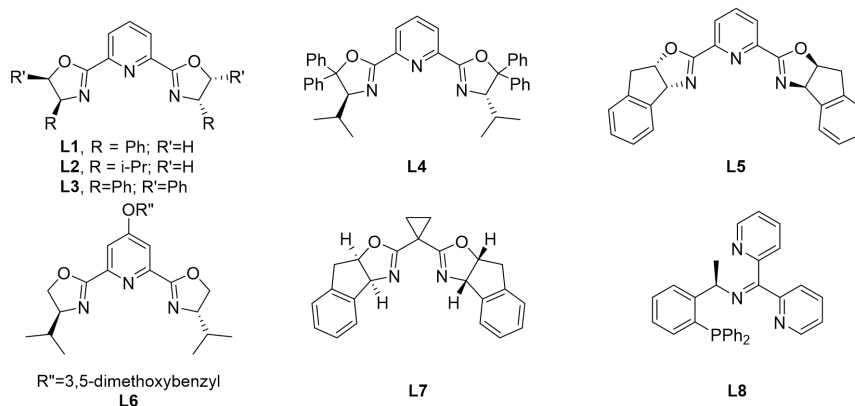
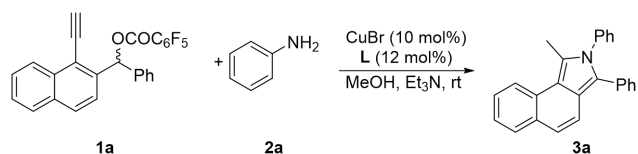


Table S2: Ligand screening^a

Entry	M	Ligand	Solvent	T (°C)	Yield (%) ^b
1	CuBr	L1	MeOH	25	95
2	CuBr	L2	MeOH	25	73
3	CuBr	L3	MeOH	25	85
4	CuBr	L4	MeOH	25	79
5	CuBr	L5	MeOH	25	83
6	CuBr	L6	MeOH	25	89
7	CuBr	L7	MeOH	25	89
8	CuBr	L8	MeOH	25	77

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), CuBr (10 mol%), **L** (12 mol%), MeOH (1.0 mL) at 25 °C under Argon atmosphere for 24 h. ^bIsolated yields.

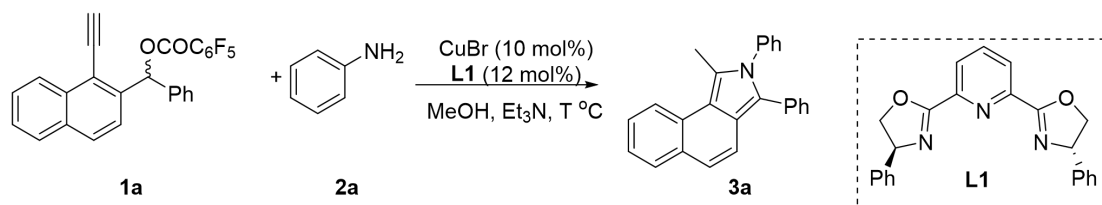
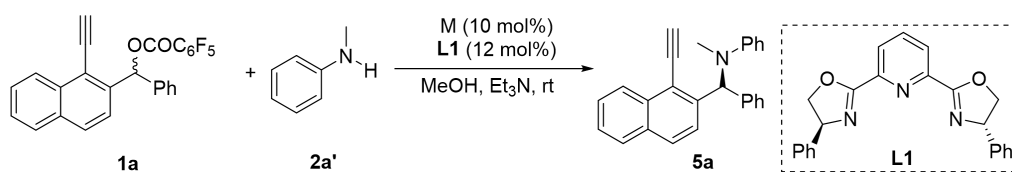


Table S3: Temperature screening^a

Entry	M	Ligand	Solvent	T (°C)	Yield (%) ^b
1	CuBr	L1	MeOH	0	83
2	CuBr	L1	MeOH	-20	74

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), CuBr (10 mol%), **L1** (12 mol%), MeOH (1.0 mL) at T °C under Argon atmosphere for 24 h. ^bIsolated yields.

Table 2. Optimization of the Reaction ConditionsTable S4: Copper screening^a

Entry	M	Base	Ligand	Solvent	Time (h)	Yield (%) ^b	Er ^c
1	Cu(CH ₃ CN) ₄ BF ₄	Et ₃ N	L1	MeOH	24	81	86:14
2	CuOTf	Et ₃ N	L1	MeOH	24	74	85:15
3	CuI	Et ₃ N	L1	MeOH	24	82	86:14
4	Cu(CH ₃ CN) ₄ PF ₆	Et ₃ N	L1	MeOH	24	80	87:13
5	Cu ₂ O	Et ₃ N	L1	MeOH	24	79	84:16
6	CuBr	Et ₃ N	L1	MeOH	24	82	85:15
7	CuCl	Et ₃ N	L1	MeOH	24	80	84:16
8	CuTc	Et ₃ N	L1	MeOH	24	79	85:15
9	CuOAc	Et ₃ N	L1	MeOH	24	74	85:15

^aReaction conditions: **1a** (0.1 mmol), **2a'** (0.2 mmol), M (10 mol%), **L1** (12 mol%), Et₃N (2.0 equiv), MeOH (1.0 mL) at rt under Argon atmosphere for 24 h. ^bisolated yield. ^cDetermined by chiral HPLC analysis.

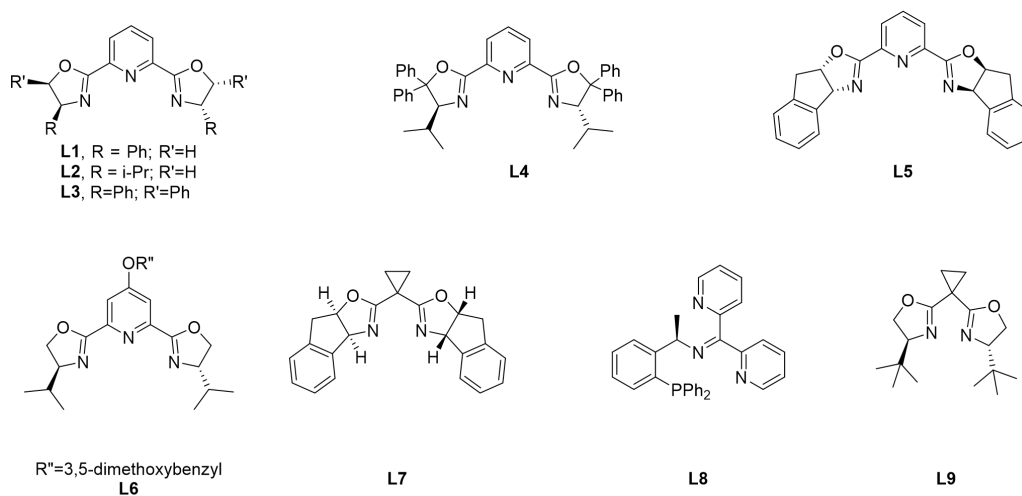
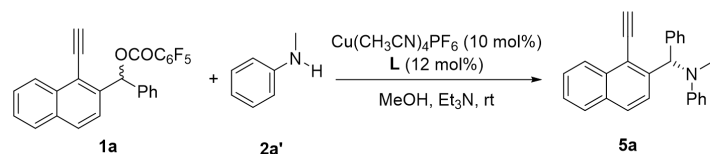


Table S5 Ligands screening^a

Entry	M	Base	Ligand	Solvent	Time (h)	Yield (%) ^b	Er ^c
1	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L1	MeOH	24	80	87:13
2	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L2	MeOH	24	79	86:14
3	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L3	MeOH	24	75	89:11
4	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L4	MeOH	24	76	86:14
5	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L5	MeOH	24	89	93:7
6	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L6	MeOH	24	71	87:13
7	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L7	MeOH	24	81	83:17
8	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L8	MeOH	24	86	77:23
9	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	Et_3N	L9	MeOH	24	79	67:33

^aReaction conditions: **1a** (0.1 mmol), **2a'** (0.2 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (10 mol%), **L** (12 mol%), Et_3N (2.0 equiv), MeOH (1.0 mL) at rt under Argon atmosphere for 24 h. ^bisolated yield. ^cDetermined by chiral HPLC analysis.

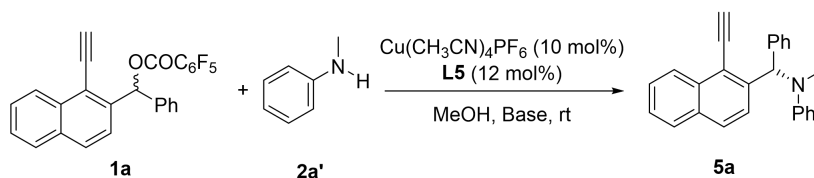


Table S6 Bases screening^a

Entry	M	Base	Ligand	Solvent	Time (h)	Yield (%) ^b	Er ^c
1	Cu(CH ₃ CN) ₄ PF ₆	Et ₃ N	L5	MeOH	24	89	93:7
2	Cu(CH ₃ CN) ₄ PF ₆	CS ₂ CO ₃	L5	MeOH	24	77	90:10
3	Cu(CH ₃ CN) ₄ PF ₆	DIPEA	L5	MeOH	24	85	89:11
4	Cu(CH ₃ CN) ₄ PF ₆	NMM	L5	MeOH	24	76	92:8
5	Cu(CH ₃ CN) ₄ PF ₆	Py	L5	MeOH	24	76	53:47

^aReaction conditions: **1a** (0.1 mmol), **2a'** (0.2 mmol), Cu(CH₃CN)₄PF₆ (10 mol%), **L5** (12 mol%), Bases (2.0 equiv), MeOH (1.0 mL) at rt under Argon atmosphere for 24 h. ^bisolated yield. ^cDetermined by chiral HPLC analysis.

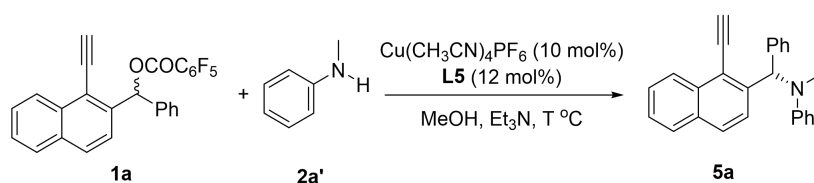


Table S7 Temperature screening^a

Entry	M	Base	Ligand	Solvent	Time (h)	Yield (%) ^b	Er ^c
1	Cu(CH ₃ CN) ₄ PF ₆	Et ₃ N	L5	MeOH	24	89	93:7
2 ^d	Cu(CH ₃ CN) ₄ PF ₆	Et ₃ N	L5	MeOH	24	62	92:8

^aReaction conditions: **1a** (0.1 mmol), **2a'** (0.2 mmol), Cu(CH₃CN)₄PF₆ (10 mol%), **L5** (12 mol%), Et₃N (2.0 equiv), MeOH (1.0 mL) under Argon atmosphere. ^bisolated yield. ^cDetermined by chiral HPLC analysis. ^d0 °C.

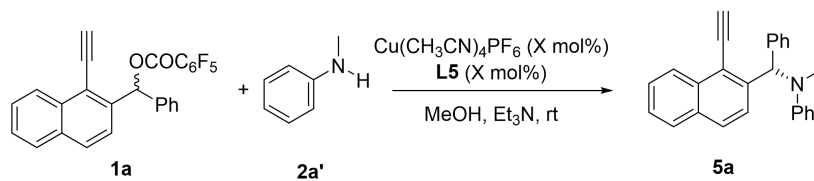


Table S8 Catalyst loading screening^a

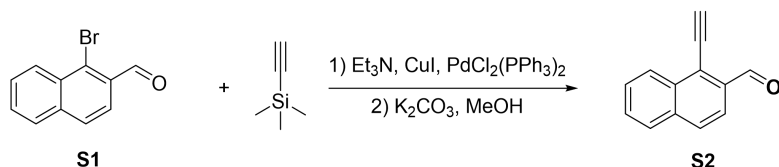
Entry	M	Base	Ligand	Solvent	Time (h)	Yield (%) ^b	Er ^c
1	Cu(CH ₃ CN) ₄ PF ₆	Et ₃ N	L5	MeOH	24	89	93:7
2 ^e	Cu(CH ₃ CN) ₄ PF ₆	Et ₃ N	L5	MeOH	24	78	90:10

^aReaction conditions: **1a** (0.1 mmol), **2a'** (0.2 mmol), Cu(CH₃CN)₄PF₆ (10 mol%), **L5** (12 mol%), Et₃N (2.0 equiv), MeOH (1.0 mL) under Argon atmosphere. ^bisolated yield. ^cDetermined by chiral HPLC analysis. ^eCu(CH₃CN)₄PF₆ (5 mol%), **L5** (6 mol%)

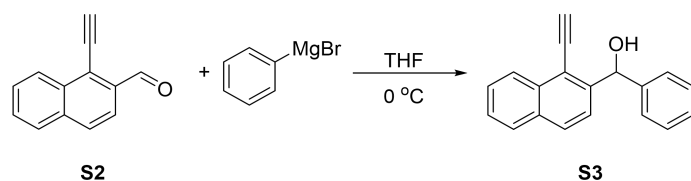
III Experimental Section

(1-ethynynaphthalen-2-yl)(phenyl)methyl 2,3,4,5,6-pentafluorobenzoate synthesized according to reported procedures.^[1-2]

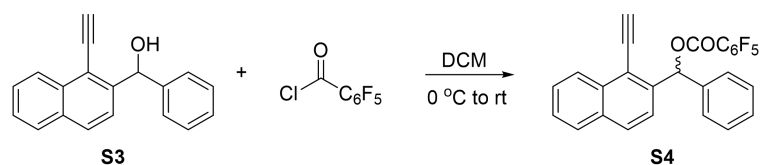
1. General procedure for synthesis of Compounds 1.



$PdCl_2(PPh_3)_2$ (0.5 mmol, 351 mg), CuI (1.0 mmol, 190 mg) and **S1** (10.0 mmol, 2.35 g) were dissolved in THF (40 mL) a Schlenk flask, followed by addition of trimethylsilylethyne (15.0 mmol, 2.1 mL) and Et_3N (30 mL). The reaction mixture was stirred at reflux for 3 hours, then cooled to 25 °C. The mixture was filtered through a pad of Celite/silica, and the pad was washed with Et_2O . The filtrate was concentrated under reduced pressure. The residue was treated with K_2CO_3 (2.7 g, 20 mmol) pellets in MeOH at 0 °C for 1 hour. The resulting mixture was quenched with 1M HCl and extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried over Na_2SO_4 filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (200-300 mesh, PE/EtOAc = 19/1) to obtain **S2**.

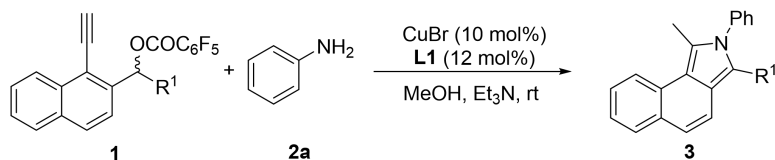


Add $PhMgBr$ (5.4 ml, 15 mmol, 2.8 M) to a solution of **S2** (10 mmol) in THF at 0 °C. Allow the reaction mixture to warm to room temperature and stir for 3 hours. After completion (TLC analysis), quench the reaction with saturated aqueous NH_4Cl solution. Extract the mixture with EtOAc. Wash the combined organic layer with brine. Dry the combined organic layers over Na_2SO_4 . Remove the solvent under reduced pressure. Purify the material by flash column chromatography using (200-300 mesh, PE/EtOAc = 9/1) to obtain **S3**.



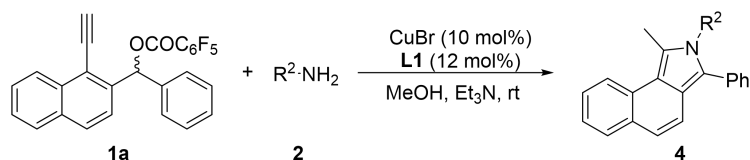
The **S3** (10 mmol) is dissolved in DCM, and pentafluorophenyl chloride (2.8 g, 12 mmol) is added dropwise at 0 °C, and then stirred at room temperature. After completion (TLC analysis), quench the reaction with saturated aqueous NH_4Cl solution. Extract the mixture with DCM. Wash the combined organic layer with brine. Dry the combined organic layers over Na_2SO_4 . Remove the solvent under reduced pressure. Purify the material by flash column chromatography using (200-300 mesh, PE/EtOAc = 10/1) to obtain **S4**.

2. General procedure for synthesis of Compounds 3.



An oven-dried 10 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with CuBr (1.4 mg, 0.01 mmol, 10 mol%) in an Argon atmosphere, followed by the addition of **L1** (3.7 mg, 0.012 mmol, 12 mol%) and MeOH (1.0 mL), with the mixture being stirred at room temperature for 1 hour. Following this, **1** (0.1 mmol, 1.0 equiv), **2a** (11.2 mg, 0.12 mmol, 1.2 equiv) and Et_3N (27.9 μL , 0.2 mmol, 2.0 equiv) were introduced into the aforementioned reaction mixture. Following the completion of the reaction (monitored using TLC), the crude product underwent direct flash column chromatography on silica gel (200-300 mesh, PE/EtOAc = 10/1 - 15/1) to produce the respective products **3**.

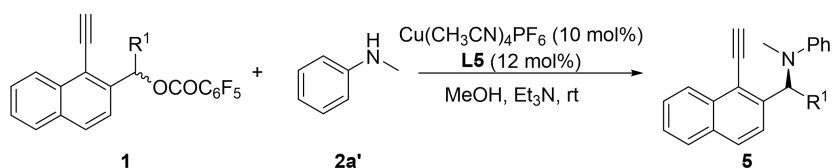
3. General procedure for synthesis of Compounds 4.



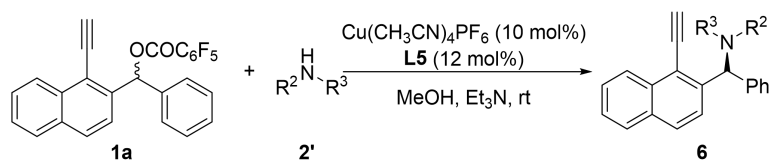
An oven-dried 10 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with CuBr (1.4 mg, 0.01 mmol, 10 mol%) in an Argon atmosphere, followed by the addition of **L1** (3.7 mg, 0.012 mmol, 12 mol%) and MeOH (1.0 mL), and the

mixture was stirred at room temperature for 1 hour. Following this, **1a** (45.2 mg, 0.1 mmol, 1.0 equiv), **2** (0.12 mmol, 1.2 equiv) and Et₃N (27.9 μL, 0.2 mmol, 2.0 equiv) were introduced into the aforementioned reaction mixture. Following the completion of the reaction (monitored using TLC), the crude product underwent direct flash column chromatography on silica gel (200-300 mesh, PE/EtOAc = 10/1-15/1) to produce the respective products **4**.

4. General procedure for synthesis of Compounds **5**.



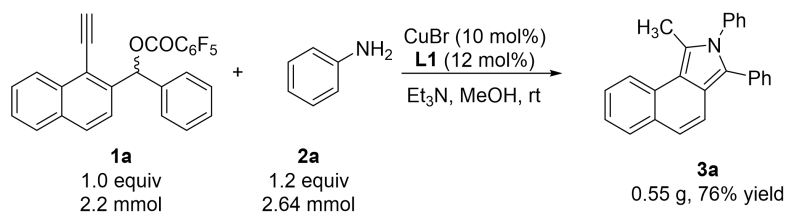
An oven-dried 10 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with Cu(CH₃CN)₄PF₆ (3.7 mg, 0.01 mmol, 10 mol%) under an argon atmosphere, followed by the addition of **L5** (3.9 mg, 0.012 mmol, 12 mol%) and MeOH (1.0 mL), and the mixture was stirred at room temperature for 1 hour. Following this, **1** (0.1 mmol, 1.0 equiv), **2a'** (12.9 mg, 0.12 mmol, 1.2 equiv) and Et₃N (27.9 μL, 0.2 mmol, 2.0 equiv) were introduced into the aforementioned reaction mixture. Following the completion of the reaction (monitored using TLC), the crude product underwent direct flash column chromatography on silica gel (200-300 mesh, PE/EtOAc = 10/1 - 15/1) to produce the respective products **5**.



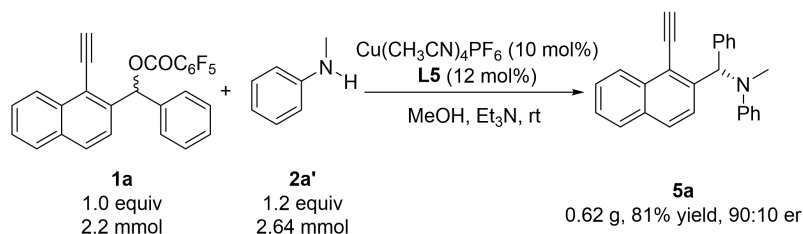
An oven-dried 10 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with Cu(CH₃CN)₄PF₆ (3.7 mg, 0.01 mmol, 10 mol%) under an argon atmosphere, followed by the addition of **L5** (3.9 mg, 0.012 mmol, 12 mol%) and MeOH (1.0 mL), and the mixture was stirred at room temperature for 1 hour. Following this, **1a** (45.2 mg, 0.1 mmol, 1.0 equiv), **2'** (0.12 mmol, 1.2 equiv) and Et₃N (27.9 μL, 0.2 mmol, 2.0 equiv) were introduced into the reaction mixture. Following the completion of the reaction (monitored using TLC), the crude product underwent direct flash column chromatography on silica gel (200-300 mesh,

PE/EtOAc v/v = 10:1 - 15:1 as the eluent) to produce the respective products **6**.

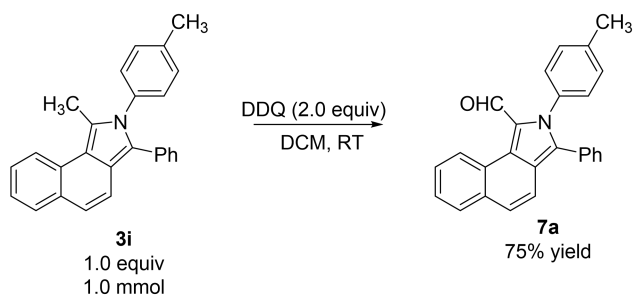
5. General procedure for gram-scale experiments with lower catalyst loading.



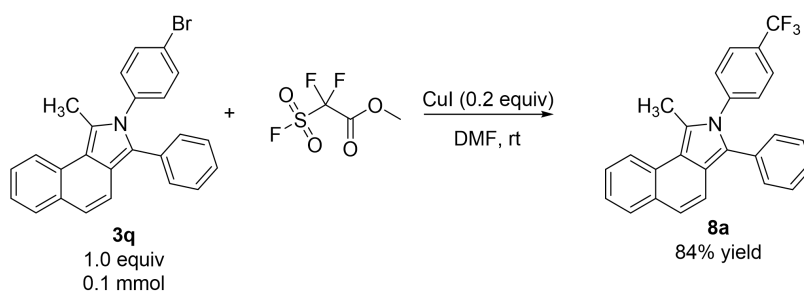
An oven-dried 50 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with CuBr (30.8 mg, 0.22 mmol, 10 mol%) under an argon atmosphere, followed by the addition of **L1** (97.7 mg, 0.26 mmol, 12 mol%) and MeOH (22.0 mL), and the mixture was stirred at room temperature for 1 hour. Following this, **1a** (1.0 g, 2.2 mmol, 1.0 equiv), **2a** (0.25 g, 2.64 mmol, 1.2 equiv) and Et₃N (0.61 mL, 4.4 mmol, 2.0 equiv) were introduced into the reaction mixture. Following the completion of the reaction (monitored using TLC), the crude product underwent direct flash column chromatography on silica gel (200-300 mesh, PE/EtOAc = 10/1 - 15/1 as the eluent) to produce the respective products **3a**.



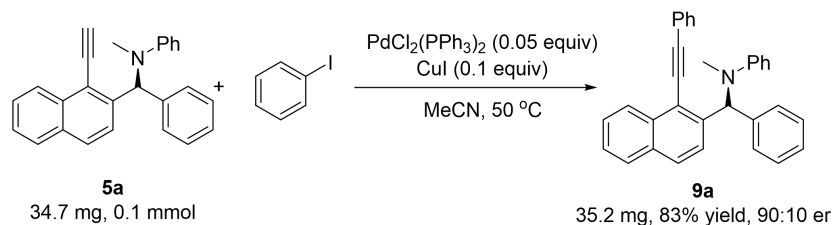
An oven-dried 50 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with Cu(CH₃CN)₄PF₆ (81.4 mg, 0.22 mmol, 10 mol%) under an Ar atmosphere, followed by the addition of **L5** (96.8 mg, 0.26 mmol, 12 mol%) and MeOH (22.0 mL), and the mixture was stirred at room temperature for 1 hour. Following this, **1a** (1.0 g, 2.2 mmol, 1.0 equiv), **2a'** (250 mg, 2.64 mmol, 1.2 equiv) and Et₃N (0.61 mL, 4.4 mmol, 2.0 equiv) were introduced into the reaction mixture. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200-300 mesh, PE/EtOAc = 10/1 - 15/1) to produce the respective products **5a**.



A dried 10 mL reaction tube containing a magnetic stir bar was charged with **3i** (34.7 mg, 0.1 mmol, 1.0 equiv), then DDQ was added (45.4 mg, 0.2 mmol, 2.0 equiv) and DCM (1.0 mL) and the mixture was stirred at room temperature for 1 hour. After the reaction was complete (monitored by TLC), purify the crude the crude product was directly purified by silica gel column chromatography (200-300 mesh, PE/EtOAc = 5/1 – 3/1) to obtain the corresponding product **7a** (27.1 mg, 75% yield).



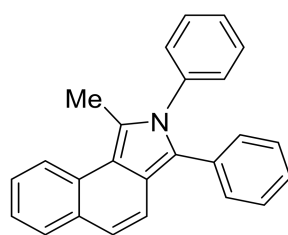
3q (41.2 mg, 0.1 mmol), methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (38.4 mg, 0.2 mmol) and CuI (3.8 mg, 0.02 mmol) was purified in DMF (1 mL). After completion of the reaction was confirmed by TLC, the reaction was quenched by water and the product was extracted with solvent EtOAc. The organic layers were dried over Na₂SO₄ and filtered. After concentration, the residue was purified by flash column chromatography (200-300 mesh, PE /EA = 5/1) to give the desired product amide **8a**.



A mixture **5a** (34.7 mg, 0.1 mmol, 1.0 equiv), iodobenzene (22.4 mg, 0.11 mmol, 1.1 equiv), PdCl₂(PPh₃)₂ (3.5 mg, 0.005 mmol, 0.05 equiv), CuI (1.9 mg, 0.01 mmol,

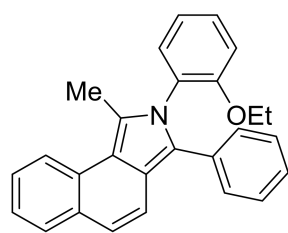
0.1 equiv) and Et₃N (42 μL, 3.0 equiv) in MeCN (1 mL) was dissolved under argon atmosphere. Stir the reaction mixture at 50 °C for 12 hours. Cool the reaction mixture to 25 °C. Pour the reaction mixture into water (3 mL). Extract the reaction mixture with EtOAc (3 × 5 mL). Wash the organic layer with brine (2 × 5 mL). Dry the combined organic layers over MgSO₄ and filter. After concentration, the residue was purified by flash column chromatography (200-300 mesh, PE /EA = 10/1) to give the desired product amide **9a**.

6. Characterization data of ligands **3a-3y**, **4a-4e**, **5a-5n**, **6a-6h**, **7a**, **8a**, **9a**.



3a

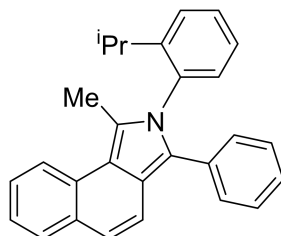
1-methyl-2,3-diphenyl-2H-benzo[e]isoindole (3a). Yellow oil (31.7 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.29 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.56-7.46 (m, 2H), 7.40-7.34 (m, 4H), 7.24-7.12 (m, 8H), 2.75-2.69 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 138.7, 132.4, 131.9, 130.1, 129.7, 129.3, 129.0, 128.6, 128.2, 128.1, 126.2, 126.2, 125.0, 124.1, 123.3, 123.1, 120.5, 120.0, 116.8, 14.3. HRMS (APCI) *m/z* calcd for C₂₅H₁₉NH⁺ (*M*+H)⁺ 334.1590, found 334.1590.



3b

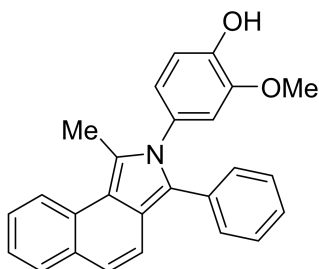
2-(2-ethoxyphenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3b). Yellow oil (32.5 mg, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.21 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29-7.21 (m, 2H), 7.15-7.09 (m, 5H), 7.06-7.02 (m, 1H), 6.98-6.96 (m, 1H), 6.87-6.79 (m, 2H), 3.93-3.84 (m, 1H), 3.78-3.71 (m, 1H), 2.57 (s, 3H), 1.07 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.1, 132.8, 131.8, 131.0, 130.0, 129.8, 129.6, 128.5, 128.0,

127.6, 126.1, 126.0, 125.1, 123.8, 123.6, 123.5, 123.3, 120.5, 120.3, 120.1, 116.4, 112.7, 63.9, 14.7, 13.9. HRMS (APCI) m/z calcd for $C_{27}H_{23}NOH^+$ ($M+H$) $^+$ 378.1852, found 378.1852.



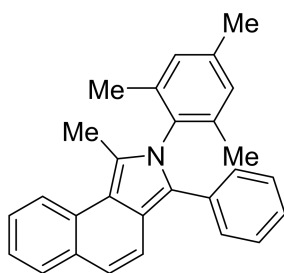
3c

2-(2-isopropylphenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3c). Yellow solid (30.3 mg, 81% yield). Mp: 110.9-111.3 °C. 1H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 9.1 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.43-7.36 (m, 3H), 7.33-7.18 (m, 7H), 7.12 (t, J = 7.0 Hz, 1H), 2.62 (s, 3H), 2.25-2.15 (m, 1H), 0.92 (d, J = 6.9 Hz, 3H), 0.57 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.2, 136.2, 131.8, 130.1, 130.1, 129.8, 129.5, 128.6, 128.1, 126.9, 126.3, 126.2, 126.0, 125.5, 124.1, 123.9, 123.3, 123.2, 120.3, 120.0, 27.5, 24.5, 22.4, 14.1. HRMS (APCI) m/z calcd for $C_{28}H_{25}NH^+$ ($M+H$) $^+$ 376.2060, found 376.2054.



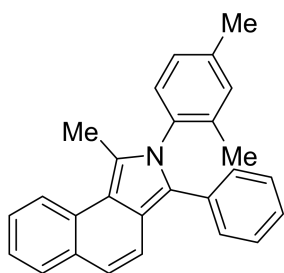
3d

2-methoxy-4-(1-methyl-3-phenyl-2H-benzo[e]isoindol-2-yl)phenol (3d). yellow solid (35.6 mg, 94% yield). Mp: 184.4-184.7 °C. 1H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, J = 8.0 Hz, 1H), 7.74-7.71 (m, 1H), 7.55-7.47 (m, 2H), 7.39-7.35 (m, 1H), 7.25-7.15 (m, 6H), 6.95 (d, J = 8.3 Hz, 1H), 6.81 (dd, J = 8.3, 2.3 Hz, 1H), 6.61 (d, J = 2.2 Hz, 1H), 3.70 (s, 3H), 2.75 (s, 3H), 1.08 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.6, 145.5, 132.6, 131.9, 130.9, 130.0, 129.7, 128.6, 128.2, 126.2, 126.1, 125.1, 124.1, 124.0, 123.3, 123.2, 122.2, 120.3, 120.0, 114.3, 112.2, 56.3, 14.3. HRMS (APCI) m/z calcd for $C_{26}H_{21}NO_2H^+$ ($M+H$) $^+$ 380.1645, found 380.1646.



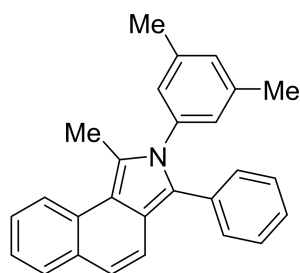
3e

2-mesityl-1-methyl-3-phenyl-2H-benzo[e]isoindole (3e). Yellow solid (33.8 mg, 90% yield). Mp: 94.7-95.1 °C. ¹H NMR (400 MHz, CDCl₃) δ = 8.30 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24-7.18 (m, 5H), 7.17-7.11 (m, 1H), 6.90 (s, 2H), 2.56 (s, 3H), 2.31 (s, 3H), 1.82 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 138.4, 136.5, 134.4, 132.6, 131.8, 130.0, 129.1, 129.0, 128.6, 128.3, 126.2, 126.1, 123.9, 123.9, 123.5, 123.3, 121.7, 120.5, 120.4, 116.9, 21.3, 17.9, 13.1. HRMS (APCI) *m/z* calcd for C₂₈H₂₅NH⁺ (M+H)⁺ 376.2060, found 376.2060.



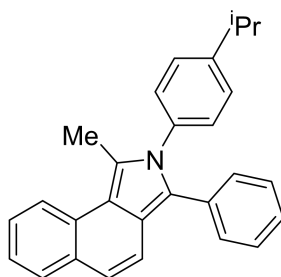
3f

2-(2,4-dimethylphenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3f). Yellow oil (33.1 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.21 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 9.1 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.15-7.13 (m, 5H), 7.08-7.03 (m, 2H), 6.96 (d, *J* = 10.4 Hz, 2H), 2.52 (s, 3H), 2.27 (s, 3H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 138.6, 136.4, 135.2, 132.5, 131.8, 131.5, 129.9, 129.7, 129.5, 128.6, 128.2, 127.2, 126.2, 126.1, 124.9, 124.0, 123.7, 123.3, 122.7, 116.6, 21.3, 17.5, 13.7. HRMS (APCI) *m/z* calcd for C₂₇H₂₃NH⁺ (M+H)⁺ 362.1903, found 362.1903.



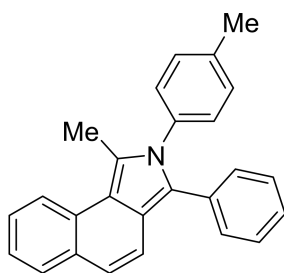
3g

2-(3,5-dimethylphenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3g). Yellow oil (30.5 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.29 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 9.1 Hz, 1H), 7.50-7.45 (m, 1H), 7.38-7.34 (m, 1H), 7.25-7.19 (m, 5H), 7.23-7.13 (m, 1H), 6.98 (s, 1H), 6.80 (s, 2H), 2.71 (s, 3H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ = 138.6, 138.5, 132.6, 131.9, 130.0, 129.8, 128.6, 128.1, 127.0, 126.1, 124.0, 123.8, 123.3, 123.1, 120.3, 120.1, 21.3, 14.3. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NH}^+$ ($\text{M}+\text{H}$) $^+$ 362.1903, found 362.1904.



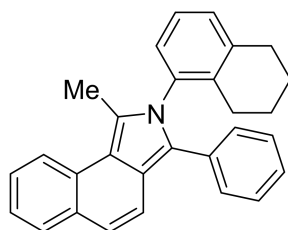
3h

2-(4-isopropylphenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3h). Yellow oil (31.7 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.21 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.48-7.45 (m, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 8.5 Hz, 7H), 7.09-7.04 (m, 1H), 7.01 (d, J = 8.3 Hz, 2H), 2.84 (p, J = 7.2 Hz, 1H), 2.63 (s, 3H), 1.17 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ = 148.9, 136.2, 132.6, 131.9, 130.1, 129.8, 129.0, 128.6, 128.1, 127.0, 126.1, 124.0, 123.9, 123.3, 123.2, 120.4, 120.0, 33.9, 24.1, 14.3. HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{NH}^+$ ($\text{M}+\text{H}$) $^+$ 376.2060, found 376.2061.



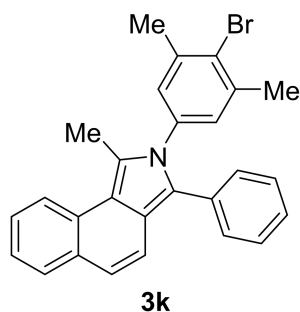
3i

1-methyl-3-phenyl-2-(p-tolyl)-2H-benzo[e]isoindole (3i). Yellow solid (31.0 mg, 89% yield). Mp: 173.3-174.0 °C. ^1H NMR (400 MHz, CDCl_3) δ = 8.22 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.48-7.39 (m, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.18-7.07 (m, 8H), 7.00 (d, J = 8.2 Hz, 2H), 2.64 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 138.0, 136.0, 132.6, 131.9, 130.1, 129.8, 129.7, 129.0, 128.6, 128.2, 126.1, 126.1, 124.0, 123.9, 123.3, 123.2, 116.7, 21.3, 14.3. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{21}\text{NH}^+$ ($\text{M}+\text{H}$) $^+$ 348.1747, found 348.1747.



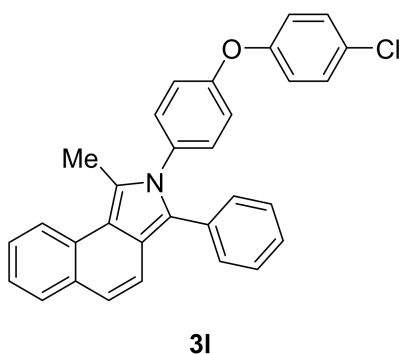
3j

1-methyl-3-phenyl-2-(5,6,7,8-tetrahydronaphthalen-1-yl)-2H-benzo[e]isoindole (3j). Yellow oil (33.9 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.29 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 9.1 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.23-7.21 (m, 5H), 7.17-7.07 (m, 4H), 2.76 (d, J = 6.4 Hz, 2H), 2.61 (s, 3H), 2.04-2.02 (m, 2H), 1.70-1.50 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ = 137.6, 136.2, 131.8, 129.9, 129.8, 129.7, 128.6, 128.2, 127.0, 126.2, 126.1, 125.6, 124.6, 124.0, 123.7, 123.3, 122.4, 120.3, 29.5, 24.9, 22.9, 22.5, 13.7. HRMS (APCI) m/z calcd for $\text{C}_{29}\text{H}_{25}\text{NH}^+$ ($\text{M}+\text{H}$) $^+$ 388.2060, found 388.2060.



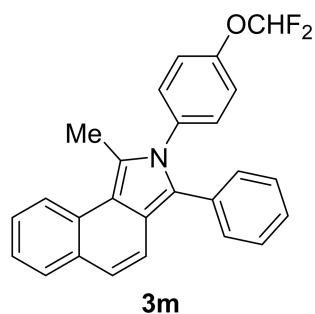
2-(4-bromo-3,5-dimethylphenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3k).

Yellow oil (36.7 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.28 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.53-7.46 (m, 2H), 7.39-7.35 (m, 1H), 7.28-7.16 (m, 6H), 6.92 (s, 2H), 2.70 (s, 3H), 2.38 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 139.2, 137.1, 132.3, 131.9, 130.0, 129.7, 128.7, 128.6, 128.3, 127.3, 126.3, 126.2, 124.9, 124.1, 124.1, 123.3, 123.0, 120.5, 120.0, 116.9, 24.1, 14.3. HRMS (APCI) *m/z* calcd for C₂₇H₂₂BrNH⁺ (M+H)⁺ 440.1008, found 440.1003.



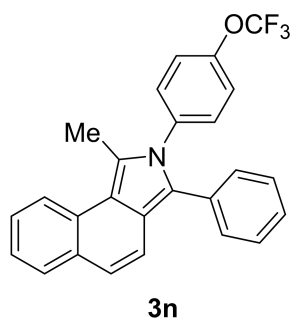
2-(4-(4-chlorophenoxy)phenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3l).

Yellow oil (36.1 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.21 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.46-7.40 (m, 2H), 7.31-7.30 (m, 1H), 7.25-7.06 (m, 10H), 6.92-6.86 (m, 4H), 2.66 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 156.8, 155.3, 133.9, 132.4, 131.9, 130.7, 130.2, 130.1, 129.7, 129.1, 128.8, 128.7, 128.3, 126.9, 126.3, 126.2, 124.2, 123.3, 123.1, 120.5, 119.9, 118.8, 14.3. HRMS (APCI) *m/z* calcd for C₃₁H₂₂ClNOH⁺ (M+H)⁺ 460.1463, found 460.1463.



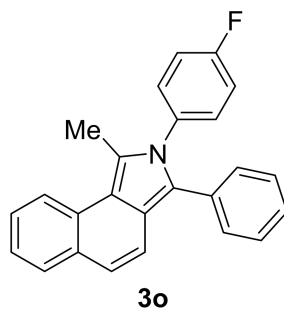
2-(4-(difluoromethoxy)phenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3m).

Yellow oil (30.8 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.29 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.54-7.48 (m, 2H), 7.38 (d, *J* = 6.7 Hz, 1H), 7.28-7.12 (m, 11H), 2.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 150.6, 135.8, 132.2, 130.6, 129.6, 128.7, 128.4, 126.4, 126.3, 124.3, 123.4, 123.0, 120.6, 119.9, 118.4, 117.0, 115.8, 14.3. ¹⁹F NMR (376 MHz, CDCl₃) δ = -81.3. HRMS (APCI) *m/z* calcd for C₂₆H₁₉F₂NOH⁺ (M+H)⁺ 400.1507, found 400.1509.

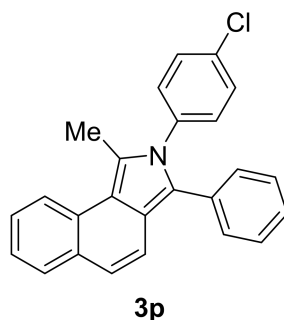


1-methyl-3-phenyl-2-(4-(trifluoromethoxy)phenyl)-2H-benzo[e]isoindole (3n).

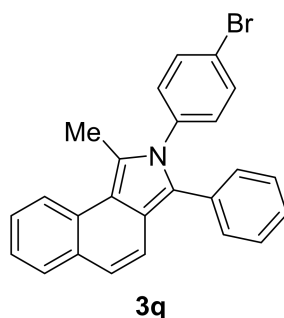
Yellow oil (33.7 mg, 81% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.19 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.45-7.38 (m, 2H), 7.32-7.27 (m, 1H), 7.17-7.05 (m, 10H), 2.62 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 148.7, 137.2, 132.1, 130.7, 130.1, 129.6, 128.7, 128.4, 126.5, 126.3, 125.1, 124.4, 123.4, 123.0, 121.4, 120.7, 119.8, 117.1, 14.3. ¹⁹F NMR (376 MHz, CDCl₃) δ = -58.4. HRMS (APCI) *m/z* calcd for C₂₆H₁₈F₃NOH⁺ (M+H)⁺ 418.1413, found 418.1416.



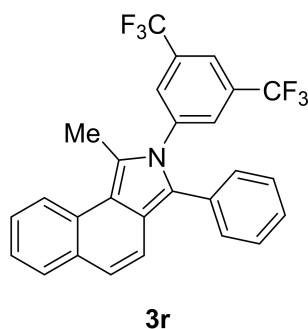
2-(4-fluorophenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3o). Yellow solid (32.3 mg, 92% yield). Mp: 124.3-124.6 °C. ¹H NMR (400 MHz, CDCl₃) δ = 8.29 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.53-7.47 (m, 2H), 7.40-7.36 (m, 1H), 7.29-7.22 (m, 3H), 7.20-7.15 (m, 5H), 7.11-7.05 (m, 2H), 2.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 132.0, 130.9, 130.8, 130.2, 129.6, 128.7, 128.3, 126.4, 126.2, 125.2, 124.2, 123.3, 123.1, 120.5, 119.9, 116.9, 116.2, 116.0, 14.2. ¹⁹F NMR (376 MHz, CDCl₃) δ = -113.1. HRMS (APCI) *m/z* calcd for C₂₅H₁₈FNH⁺ (M+H)⁺ 352.1496, found 352.1496.



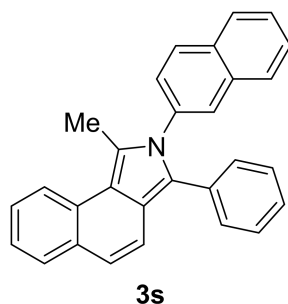
2-(4-chlorophenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3p). Yellow oil (30.9 mg, 84% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.29 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.52-7.48 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 3H), 7.30-7.27 (m, 1H), 7.23-7.25 (s, 1H), 7.22-7.13 (m, 6H), 2.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 137.3, 134.1, 132.1, 132.0, 130.5, 130.2, 129.6, 129.3, 128.7, 128.4, 126.5, 126.3, 124.3, 124.3, 123.4, 120.7, 14.3. HRMS (APCI) *m/z* calcd for C₂₅H₁₈ClNH⁺ (M+H)⁺ 368.1201, found 368.1206.



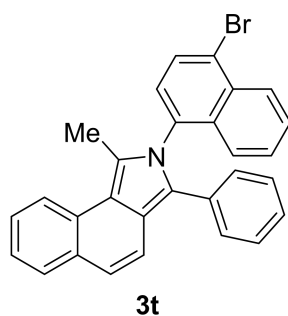
2-(4-bromophenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3q). Yellow oil (36.3 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.20 (d, J = 8.1 Hz, 1H), 7.66-7.62 (m, 1H), 7.45-7.39 (m, 4H), 7.32-7.28 (m, 1H), 7.22-7.13 (m, 3H), 7.12-7.08 (m, 3H), 7.01-6.95 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 137.8, 132.3, 132.1, 132.0, 130.8, 130.1, 129.6, 128.7, 128.4, 126.5, 126.3, 125.0, 124.3, 124.3, 123.4, 122.9, 120.7, 119.8, 117.1, 14.3. HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{18}\text{BrNH}^+$ ($\text{M}+\text{H}$) $^+$ 412.0695, found 412.0694.



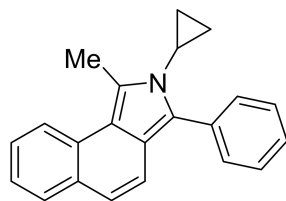
2-(3,5-bis(trifluoromethyl)phenyl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3r). Yellow solid (27.5 mg, 59% yield). Mp: 137.1-137.4 °C. ^1H NMR (400 MHz, CDCl_3) δ = 8.28 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.65 (s, 2H), 7.51-7.39 (m, 3H), 7.29-7.22 (m, 4H), 7.14-7.10 (m, 2H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 140.3, 132.8, 132.4, 132.1, 131.3, 130.3, 129.5, 129.3, 128.9, 128.7, 127.1, 126.5, 125.0, 124.7, 123.5, 122.4, 119.6, 117.8, 14.4. ^{19}F NMR (376 MHz, CDCl_3) δ = -63.0. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{17}\text{F}_6\text{N}$ H^+ ($\text{M}+\text{H}$) $^+$ 470.1338, found 470.1334.



1-methyl-2-(naphthalen-2-yl)-3-phenyl-2H-benzo[e]isoindole (3s). Yellow solid (36.0 mg, 94% yield). Mp: 89.6-90.0 °C. ¹H NMR (400 MHz, CDCl₃) δ = 8.23 (d, *J* = 8.1 Hz, 1H), 7.82-7.76 (m, 1H), 7.75-7.68 (m, 2H), 7.67-7.60 (m, 2H), 7.50-7.38 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.20-7.13 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 7.0 Hz, 1H), 2.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 136.2, 133.2, 132.6, 132.4, 132.0, 130.1, 129.7, 128.9, 128.6, 128.3, 128.2, 128.0, 127.8, 127.1, 126.9, 126.2, 125.2, 124.1, 123.4, 120.6, 120.0, 116.9, 14.4. HRMS (APCI) *m/z* calcd for C₂₉H₂₁NH⁺ (M+H)⁺ 384.1747, found 384.1748.

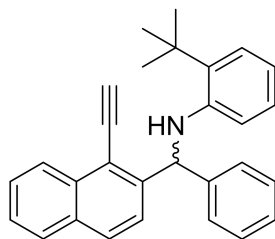


2-(4-bromonaphthalen-1-yl)-1-methyl-3-phenyl-2H-benzo[e]isoindole (3t). Yellow oil (40.2 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.30 (d, *J* = 8.3 Hz, 2H), 7.78 (t, *J* = 8.6 Hz, 2H), 7.64-7.37 (m, 6H), 7.28-7.20 (m, 3H), 7.14-7.09 (m, 4H), 2.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 135.4, 133.1, 132.1, 132.0, 129.7, 129.6, 128.6, 128.3, 127.8, 127.8, 126.6, 126.3, 124.3, 124.3, 124.0, 123.8, 123.4, 120.6, 120.1, 116.9, 14.0. HRMS (APCI) *m/z* calcd for C₂₉H₂₀BrNH⁺ (M+H)⁺ 462.0852, found 462.0850.



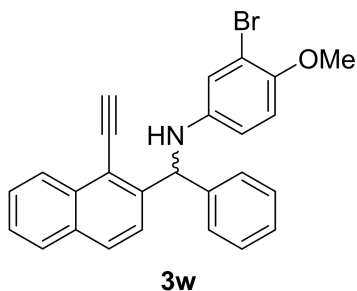
3u

2-cyclopropyl-1-methyl-3-phenyl-2H-benzo[e]isoindole (3u). Yellow solid (25.3 mg, 85% yield). Mp: 100.1-100.7 °C. ¹H NMR (400 MHz, CDCl₃) δ = 8.26 (d, *J* = 8.1 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.56-7.53 (m, 2H), 7.49-7.43 (m, 4H), 7.36-7.31 (m, 2H), 7.13 (d, *J* = 9.1 Hz, 1H), 3.50-3.45 (m, 1H), 3.02 (s, 3H), 1.04-0.98 (m, 2H), 0.70-0.64 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 133.2, 131.9, 130.0, 129.6, 128.5, 128.3, 126.0, 125.3, 124.4, 123.8, 123.3, 119.8, 119.5, 27.7, 14.4, 10.4. HRMS (APCI) *m/z* calcd for C₂₂H₁₉NH⁺ (M+H)⁺ 298.1590, found 298.1591.



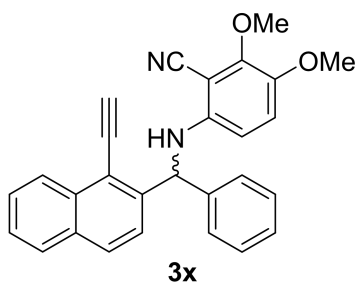
3v

2-(tert-butyl)-N-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)aniline (3v). Yellow solid (30.3 mg, 78% yield). Mp: 117.3-118.2 °C. ¹H NMR (400 MHz, CDCl₃) δ = 8.33 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43-7.38 (m, 3H), 7.20 (dt, *J* = 22.4, 6.9 Hz, 4H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.63-6.56 (m, 1H), 6.43 (d, *J* = 7.7 Hz, 1H), 6.29 (s, 1H), 4.56 (s, 1H), 3.72 (s, 1H), 1.37 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 145.3, 145.0, 142.8, 133.5, 129.9, 128.9, 128.3, 127.7, 127.6, 127.3, 127.3, 126.5, 126.4, 126.2, 124.1, 118.0, 117.6, 113.0, 88.7, 79.8, 61.3, 34.3, 30.1. HRMS (APCI) *m/z* calcd for C₂₉H₂₇NH⁺ (M+H)⁺ 390.2216, found 390.2215.



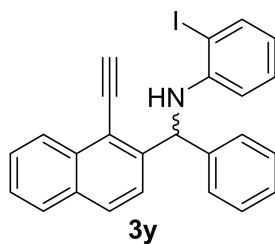
3-bromo-N-((1-ethynyl)naphthalen-2-yl)(phenyl)methyl-4-methoxyaniline (3w).

Yellow oil (36.7 mg, 83% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.30 (d, J = 8.27 Hz, 2H), 7.78 (t, J = 8.57 Hz, 2H), 7.64-7.37 (m, 6H), 7.28-7.20 (m, 3H), 7.14-7.09 (m, 4H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 135.4, 133.1, 132.1, 132.0, 129.7, 129.6, 128.6, 128.3, 127.8, 127.8, 126.6, 126.3, 124.3, 124.3, 124.0, 123.8, 123.4, 120.6, 120.1, 116.9, 14.0. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{20}\text{BrNOH}^+$ ($\text{M}+\text{H}$) $^+$ 442.0801, found 442.0800.

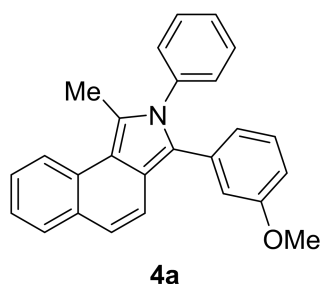


6-(((1-ethynyl)naphthalen-2-yl)(phenyl)methyl)amino)-2,3-dimethoxybenzonitrile (3x).

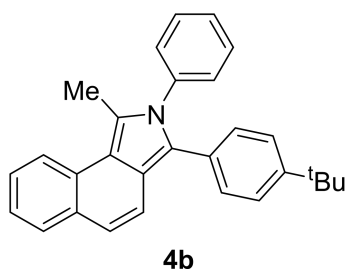
Yellow oil (38.9 mg, 93% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.30 (d, J = 8.4 Hz, 1H), 7.75 (dd, J = 16.4, 8.7 Hz, 2H), 7.55-7.48 (m, 2H), 7.45-7.36 (m, 3H), 7.28-7.18 (m, 3H), 6.74 (s, 1H), 6.40 (d, J = 5.1 Hz, 1H), 6.17 (s, 1H), 5.09 (s, 1H), 3.78 (s, 1H), 3.65 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 154.7, 146.4, 143.4, 141.2, 140.8, 133.7, 132.5, 130.4, 129.1, 128.4, 128.1, 127.6, 127.3, 126.9, 126.2, 123.8, 118.5, 114.3, 97.0, 88.6, 86.3, 79.6, 60.2, 56.6, 55.9. HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2\text{H}^+$ ($\text{M}+\text{H}$) $^+$ 419.1754, found 419.1758.



N-((1-ethynyl)naphthalen-2-yl)(phenyl)methyl)-2-iodoaniline (3u). Yellow oil (34.9 mg, 76% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.33 (d, J = 8.4 Hz, 1H), 7.73 (t, J = 8.6 Hz, 2H), 7.61-7.48 (m, 3H), 7.44-7.38 (m, 3H), 7.25 (t, J = 7.5 Hz, 2H), 7.20-7.16 (m, 1H), 7.00-6.91 (m, 1H), 6.40 (d, J = 7.9 Hz, 1H), 6.36-6.26 (m, 2H), 4.91 (d, J = 4.4 Hz, 1H), 3.74 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ = 146.3, 144.0, 141.8, 133.9, 132.5, 129.6, 128.9, 128.3, 127.8, 127.5, 127.4, 126.6, 126.4, 123.9, 119.3, 112.2, 88.7, 85.9, 79.7, 60.8. HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{18}\text{INH}^+$ ($\text{M}+\text{H}$) $^+$ 460.0557, found 460.0559.

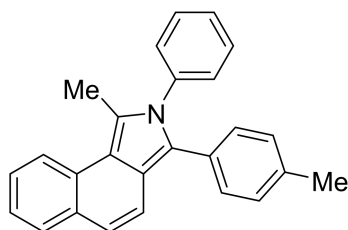


3-(3-methoxyphenyl)-1-methyl-2-phenyl-2H-benzo[e]isoindole (4a). Yellow oil (25.5 mg, 70% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.29 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 9.1 Hz, 1H), 7.51-7.46 (m, 1H), 7.43-7.35 (m, 4H), 7.24-7.20 (m, 3H), 7.15 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.72-6.70 (m, 2H), 3.61 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 159.3, 138.8, 133.6, 131.9, 129.7, 129.3, 129.1, 128.6, 128.2, 126.2, 124.1, 123.3, 122.6, 120.5, 120.0, 116.8, 115.0, 112.4, 55.2, 14.3. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{21}\text{NOH}^+$ ($\text{M}+\text{H}$) $^+$ 364.1696, found 364.1693.



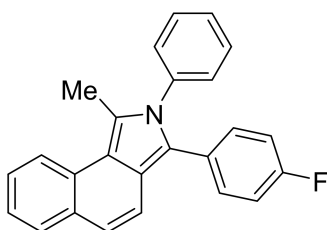
3-(4-(tert-butyl)phenyl)-1-methyl-2-phenyl-2H-benzo[e]isoindole (4b). Yellow oil (30.5 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.29 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 9.1 Hz, 1H), 7.50-7.46 (m, 1H), 7.41-7.34 (m, 4H), 7.25-7.19 (m, 5H), 7.14-7.10 (m, 2H), 2.71 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (100 MHz,

CDCl₃) δ = 149.0, 138.8, 132.0, 129.8, 129.6, 129.3, 129.0, 128.6, 128.1, 126.1, 125.1, 124.0, 123.7, 123.4, 122.8, 120.3, 34.6, 31.4, 14.3. HRMS (APCI) m/z calcd for C₂₉H₂₇NH⁺ (M+H)⁺ 390.2216, found 390.2219.



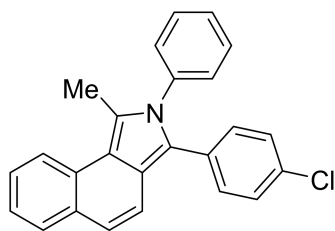
4c

1-methyl-2-phenyl-3-(p-tolyl)-2H-benzo[e]isoindole (4c). Yellow oil (25.7 mg, 73.9% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.29 (d, J = 8.0 Hz, 1H), 7.73-7.70 (m, 1H), 7.54-7.46 (m, 2H), 7.42-7.35 (m, 4H), 7.22-7.18 (m, 3H), 7.09 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 2.71 (s, 3H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 138.8, 135.9, 132.0, 130.0, 129.8, 129.5, 129.3, 129.0, 128.6, 128.1, 126.1, 124.1, 123.8, 123.3, 122.7, 120.3, 120.1, 116.7, 21.3, 14.3. HRMS (APCI) m/z calcd for C₂₆H₂₁NH⁺ (M+H)⁺ 348.1747, found 348.1744.



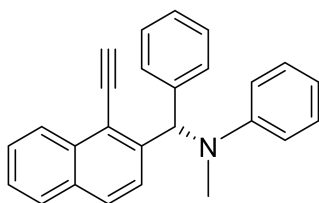
4d

3-(4-fluorophenyl)-1-methyl-2-phenyl-2H-benzo[e]isoindole (4d). Yellow oil (21.7 mg, 62% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.30 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.52-7.45 (m, 2H), 7.43-7.36 (m, 4H), 7.22-7.13 (m, 4H), 6.96-6.90 (m, 2H), 2.73 (s, 3H), 1.53 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 138.5, 131.9, 131.7, 131.7, 129.7, 129.3, 129.1, 128.7, 126.3, 124.2, 123.4, 123.0, 119.6, 116.7, 115.4, 115.2, 29.9, 14.3. ¹⁹F NMR (376 MHz, CDCl₃) δ = -115.8. HRMS (APCI) m/z calcd for C₂₅H₁₈FNH⁺ (M+H)⁺ 352.1496, found 352.1496.



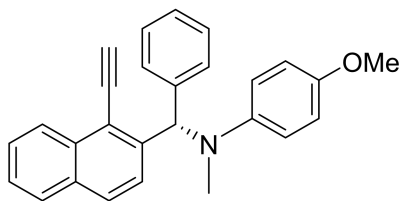
4e

3-(4-chlorophenyl)-1-methyl-2-phenyl-2H-benzo[e]isoindole (4e). Yellow oil (27.3 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.29 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.52-7.48 (m, 2H), 7.44-7.37 (m, 4H), 7.26-7.23 (m, 1H), 7.22-7.17 (m, 4H), 7.11 (d, J = 8.6 Hz, 2H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 132.1, 131.9, 131.1, 131.0, 129.6, 129.2, 128.7, 128.5, 128.4, 126.3, 124.5, 124.2, 123.3, 120.7, 119.5, 14.3. HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{18}\text{ClNH}^+$ ($\text{M}+\text{H}$) $^+$ 368.1201, found 368.1200.



5a

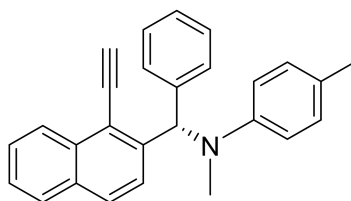
(S)-N-((1-ethynynaphthalen-2-yl)(phenyl)methyl)-N-methylaniline (5a). Light yellow solid (30.9 mg, 89% yield). Mp:113.1-114.3 °C. HPLC: 93:7 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, t_r (major) = 7.31 min, t_r (minor) = 6.59 min. $[\alpha]_{\text{D}}^{25}$ = 80.0 (c = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ = 8.30 (d, J = 8.4 Hz, 1H), 7.71 (dd, J = 16.8, 8.1 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.20 (m, 4H), 7.11 (m, 4H), 6.73 (d, J = 7.9 Hz, 2H), 6.63 (m, 2H), 3.43 (s, 1H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 150.5, 144.1, 140.9, 133.9, 132.4, 129.1, 128.8, 128.6, 128.3, 127.3, 126.6, 126.4, 125.8, 119.7, 117.0, 113.2, 88.7, 79.7, 65.9, 35.8. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{21}\text{NH}^+$ ($\text{M}+\text{H}$) $^+$ 348.1747, found 348.1742.



5b

(S)-N-((1-ethynyl-2-phenylnaphthalen-2-yl)(phenyl)methyl)-4-methoxy-N-methylaniline

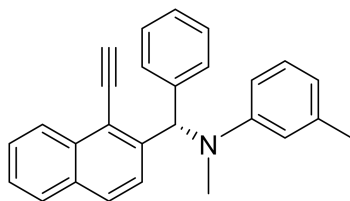
(5b). Yellow oil (28.7 mg, 76% yield). HPLC: 82:18 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 9.30 min, tr (minor) = 10.16 min. $[\alpha]_{\text{D}}^{25} = 34.5$ (c = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.29$ (d, $J = 8.4$ Hz, 1H), 7.69 (dd, $J = 15.4, 8.4$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.42-7.35 (m, 2H), 7.24-7.19 (m, 4H), 7.16-7.14 (m, 1H), 6.80-6.74 (m, 2H), 6.71-6.65 (m, 2H), 6.44 (s, 1H), 3.63 (s, 3H), 3.54 (s, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 152.6, 145.5, 144.6, 141.7, 133.9, 132.3, 129.1, 128.6, 128.5, 128.2, 127.2, 126.4, 125.7, 117.0, 114.5, 88.5, 80.0, 67.2, 55.7$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NOH}^+$ (M+H) $^+$ 378.1852, found 378.1850.



5c

(S)-N-((1-ethynyl-2-phenylnaphthalen-2-yl)(phenyl)methyl)-N,4-dimethylaniline (5c).

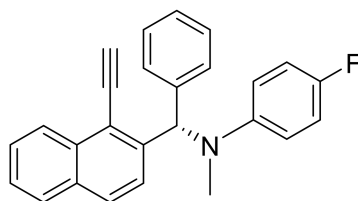
Yellow oil (33.3 mg, 92% yield). HPLC: 91:9 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 6.58 min, tr (minor) = 7.26 min. $[\alpha]_{\text{D}}^{25} = 50.8$ (c = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.38$ (d, $J = 8.4$ Hz, 1H), 7.77 (dd, $J = 16.5, 8.3$ Hz, 2H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.51-7.46 (m, 1H), 7.34 (d, $J = 8.6$ Hz, 1H), 7.31-7.18 (m, 5H), 6.99 (d, $J = 8.4$ Hz, 2H), 6.74 (d, $J = 8.3$ Hz, 2H), 6.65 (s, 1H), 3.55 (s, 1H), 2.81 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 148.5, 144.4, 141.2, 133.9, 132.3, 129.6, 129.1, 128.8, 128.5, 128.2, 127.3, 127.2, 126.5, 126.4, 126.4, 125.8, 119.5, 113.9, 88.6, 79.8, 66.2, 36.5, 20.4$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NH}^+$ (M+H) $^+$ 362.1903, found 362.1907.



5d

(S)-N-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)-N,3-dimethylaniline (5d).

Yellow oil (20.7 mg, 57% yield). HPLC: 87:13 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 5.69 min, tr (minor) = 4.95 min. $[\alpha]_{\text{D}}^{25} = 73.1$ (c = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.32$ (d, $J = 8.2$ Hz, 1H), 7.73 (dd, $J = 17.6, 8.3$ Hz, 2H), 7.50 (t, $J = 7.0$ Hz, 1H), 7.43 (t, $J = 7.9$ Hz, 1H), 7.26-7.17 (m, 4H), 7.10 (d, $J = 7.0$ Hz, 2H), 6.99 (t, $J = 7.7$ Hz, 1H), 6.66 (s, 1H), 6.61-6.52 (m, 2H), 6.47 (d, $J = 7.2$ Hz, 1H), 3.45 (s, 1H), 2.76 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 150.4, 144.1, 140.9, 138.6, 133.9, 132.3, 129.0, 128.9, 128.7, 128.2, 127.2, 127.2, 126.5, 126.3, 125.7, 119.5, 113.8, 110.3, 35.8, 22.0$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NH}^+$ (M+H) $^+$ 362.1903, found 362.1901.

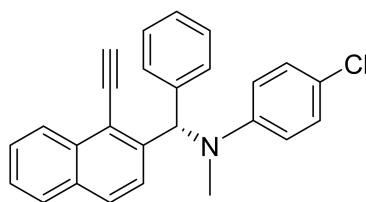


5e

(S)-N-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)-4-fluoro-N-methylaniline (5e).

Yellow solid (34.4 mg, 94% yield). Mp: 97.1-97.4 °C. HPLC: 88:12 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 5.62 min, tr (minor) = 6.20 min. $[\alpha]_{\text{D}}^{25} = 57.7$ (c = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.29$ (d, $J = 8.4$ Hz, 1H), 7.70 (dd, $J = 17.3, 8.4$ Hz, 2H), 7.51-7.46 (m, 1H), 7.43-7.39 (m, 1H), 7.26-7.20 (m, 3H), 7.19-7.15 (m, 3H), 6.82-6.77 (m, 2H), 6.70-6.66 (m, 2H), 6.50 (s, 1H), 3.47 (s, 1H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 147.4, 144.0, 141.1, 133.9, 132.3, 129.1, 128.6, 128.6, 128.2, 127.4, 126.6, 126.4, 125.7, 115.5, 115.3, 115.2, 88.6, 79.9, 66.8, 37.1$. ^{19}F NMR (376 MHz, CDCl_3) $\delta = -128.0$. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{20}\text{FNH}^+$ (M+H) $^+$ 366.1653, found

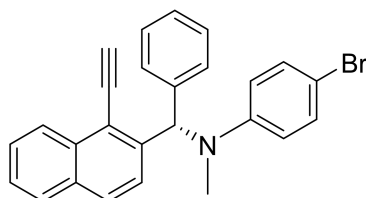
366.1650.



5f

(S)-4-chloro-N-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)-N-methylaniline (5f).

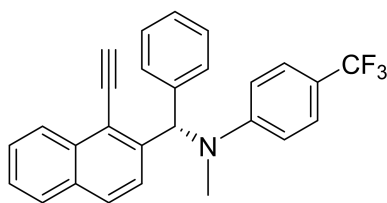
Yellow oil (31.7 mg, 83% yield). HPLC: 90:10 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 5.78 min, tr (minor) = 5.47 min. $[\alpha]_D^{25} = 100.5$ (c = 0.1, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) $\delta = 8.38$ (d, $J = 8.4$ Hz, 1H), 7.78 (dd, $J = 19.0, 8.3$ Hz, 2H), 7.60-7.55 (m, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.37-7.27 (m, 3H), 7.24-7.21 (m, 1H), 7.17 (d, $J = 7.5$ Hz, 2H), 7.13-7.11 (m, 2H), 6.71 (d, $J = 8.1$ Hz, 2H), 6.65 (s, 1H), 3.51 (s, 1H), 2.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 149.1, 143.6, 140.5, 133.9, 132.4, 129.1, 128.9, 128.7, 128.6, 128.3, 127.5, 126.7, 126.4, 125.7, 121.8, 119.9, 114.2, 88.8, 79.7, 66.0, 35.8$. HRMS (APCI) m/z calcd for C₂₆H₂₀ClNH⁺ (M+H)⁺ 382.1357, found 382.1351.



5g

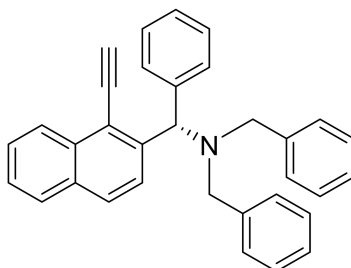
(S)-4-bromo-N-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)-N-methylaniline (5g).

Yellow oil (31.7 mg, 74% yield). HPLC: 88:12 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 0.7 mL/min, tr (major) = 8.74 min, tr (minor) = 8.18 min. $[\alpha]_D^{25} = -24.6$ (c = 0.1, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) $\delta = 8.30$ (d, $J = 8.4$ Hz, 1H), 7.72 (dd, $J = 20.1, 8.3$ Hz, 2H), 7.53-7.48 (m, 1H), 7.46-7.41 (m, 1H), 7.28-7.13 (m, 6H), 7.09 (d, $J = 7.1$ Hz, 2H), 6.63-6.53 (m, 3H), 3.44 (s, 1H), 2.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) $\delta = 149.5, 143.5, 140.4, 133.9, 132.4, 131.8, 129.1, 128.7, 128.6, 128.3, 127.5, 127.5, 126.7, 126.4, 125.7, 114.6, 108.9, 88.8, 79.6, 65.9, 35.6$. HRMS (APCI) m/z calcd for C₂₆H₂₀BrNH⁺ (M+H)⁺ 426.0852, found 426.0855.



5h

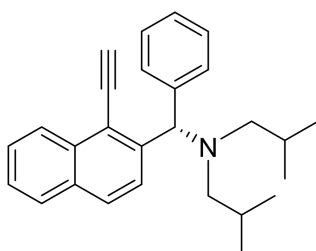
(S)-N-((1-ethynynaphthalen-2-yl)(phenyl)methyl)-N-methyl-4-(trifluoromethyl)aniline (5h). Yellow oil (34.1 mg, 82% yield). HPLC: 82:18 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 5.63 min, tr (minor) = 5.26 min. $[\alpha]_D^{25} = -34.3$ (c = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.31$ (d, $J = 8.4$ Hz, 1H), 7.72 (dd, $J = 18.1, 8.3$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.33 (d, $J = 8.8$ Hz, 2H), 7.27-7.19 (m, 3H), 7.14-7.05 (m, 3H), 6.75-6.66 (m, 3H), 3.41 (s, 1H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 152.4, 143.0, 139.9, 133.9, 132.5, 129.2, 128.9, 128.6, 128.3, 127.6, 126.9, 126.4, 125.7, 120.2, 111.8, 88.9, 79.5, 65.6, 35.2$. ^{19}F NMR (376 MHz, CDCl_3) $\delta = -60.8$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{20}\text{F}_3\text{NH}^+$ (M+H) $^+$ 416.1621, found 416.1624.



5i

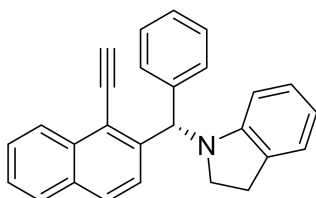
(S)-N,N-dibenzyl-1-(1-ethynynaphthalen-2-yl)-1-phenylmethanamine (5i). Yellow oil (26.7 mg, 61% yield). HPLC: 74:26 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 6.66 min, tr (minor) = 5.89 min. $[\alpha]_D^{25} = 29.7$ (c = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.29$ (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.72-7.66 (m, 2H), 7.61 (d, $J = 7.7$ Hz, 2H), 7.48-7.43 (m, 1H), 7.40-7.35 (m, 1H), 7.26-7.12 (m, 12H), 7.09-7.05 (m, 1H), 5.75 (s, 1H), 3.72-3.60 (m, 4H), 3.54 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 144.3, 142.9, 138.6, 133.9, 132.2, 129.3, 129.2, 128.6, 128.3, 128.2, 128.1, 127.2, 127.1, 126.8, 126.5, 126.4, 125.6, 118.9, 88.2, 80.2, 67.3, 53.4$. HRMS (APCI) m/z calcd for

$C_{33}H_{27}NH^+$ ($M+H$) $^+$ 438.2216, found 438.2214.



5j

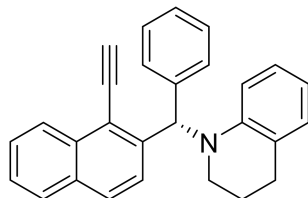
(S)-N-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)-N-isobutyl-2-methylpropan-1-amine (5j). Yellow oil (30.7 mg, 83% yield). HPLC: 90:10 er (Chiralpak IA column, 254 nm, hexane/isopropanol = 98:2, flow rate 0.5 mL/min, tr (major) = 6.75 min, tr (minor) = 7.08 min. $[\alpha]_D^{25} = 47.7$ (c = 0.1, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) δ = 8.39 (d, J = 8.3 Hz, 1H), 7.79 (dd, J = 8.2, 5.7 Hz, 2H), 7.71 (d, J = 8.7 Hz, 1H), 7.57-7.53 (m, 1H), 7.48 (t, J = 7.5 Hz, 3H), 7.23 (d, J = 9.0 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 5.79 (s, 1H), 3.73 (s, 1H), 2.31 (qd, J = 13.0, 7.1 Hz, 4H), 1.79 (dq, J = 14.0, 6.6 Hz, 2H), 0.91 (d, J = 6.6 Hz, 6H), 0.81 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.1, 132.0, 129.0, 128.2, 128.0, 127.9, 126.9, 126.8, 126.7, 126.5, 126.2, 87.2, 80.4, 69.1, 60.8, 26.9, 21.3. HRMS (APCI) m/z calcd for $C_{27}H_{31}NH^+$ ($M+H$) $^+$ 370.2529, found 370.2526.



5k

(S)-1-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)indoline (5k). Yellow oil (25.3 mg, 70% yield). HPLC: 85:15 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 6.00 min, tr (minor) = 7.29 min. $[\alpha]_D^{25} = 62.8$ (c = 0.1, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) δ = 8.31 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.43-7.36 (m, 3H), 7.21 (t, J = 7.2 Hz, 2H), 7.17-7.11 (m, 1H), 7.00 (d, J = 7.0 Hz, 1H), 6.77 (t, J = 7.5 Hz, 1H), 6.56 (t, J = 7.1 Hz, 1H), 6.12 (s, 1H), 6.01 (d, J =

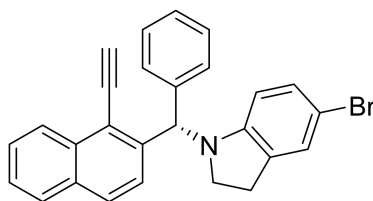
7.7 Hz, 1H), 3.66 (s, 1H), 3.13 (t, $J = 8.3$ Hz, 2H), 2.86 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 151.9, 140.7, 133.3, 131.7, 128.0, 128.0, 127.7, 126.8, 126.7, 126.6, 126.0, 125.9, 125.1, 123.7, 117.6, 108.7, 65.3, 52.6, 28.0$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{21}\text{NH}^+$ ($\text{M}+\text{H}$) $^+$ 360.1747, found 360.1742.



5l

(S)-1-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)-1,2,3,4-tetrahydroquinoline

(5l). Yellow oil (32.8 mg, 88% yield). HPLC: 90:10 er (Chiralpak OJH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, t_r (major) = 10.28 min, t_r (minor) = 8.71 min. $[\alpha]_{\text{D}}^{25} = 68.7$ ($c = 0.1, \text{CH}_2\text{Cl}_2$). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.32$ (d, $J = 8.4$ Hz, 1H), 7.72 (dd, $J = 21.0, 8.0$ Hz, 2H), 7.52-7.47 (m, 1H), 7.45-7.40 (m, 1H), 7.23-7.19 (m, 3H), 7.10 (d, $J = 7.1$ Hz, 2H), 6.92-6.82 (m, 2H), 6.61 (s, 1H), 6.48 (t, $J = 8.6$ Hz, 2H), 3.46 (s, 1H), 3.07-2.96 (m, 2H), 2.70 (t, $J = 6.2$ Hz, 2H), 1.82 (p, $J = 6.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 145.9, 144.0, 140.4, 134.0, 132.4, 129.1, 128.9, 128.5, 128.3, 127.3, 127.2, 126.6, 126.4, 126.0, 122.8, 119.9, 115.8, 111.5, 88.9, 79.6, 65.0, 46.4, 28.7, 22.7$. HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{22}\text{BrNH}^+$ ($\text{M}+\text{H}$) $^+$ 374.1903, found 374.1901.

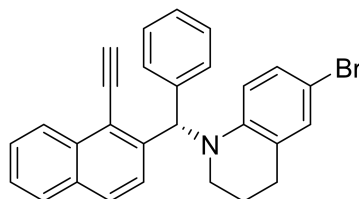


5m

(S)-5-bromo-1-((1-ethynyl-naphthalen-2-yl)(phenyl)methyl)indoline (5m).

Yellow oil (35.5 mg, 81% yield). HPLC: 85:15 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, t_r (major) = 6.99 min, t_r (minor) = 7.76 min. $[\alpha]_{\text{D}}^{25} = -34.3$ ($c = 0.1, \text{CH}_2\text{Cl}_2$). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.31$ (d, $J = 8.3$ Hz, 1H), 7.71 (dd, $J = 8.2, 3.4$ Hz, 2H), 7.56-7.47 (m, 2H), 7.42 (t, $J = 7.4$ Hz,

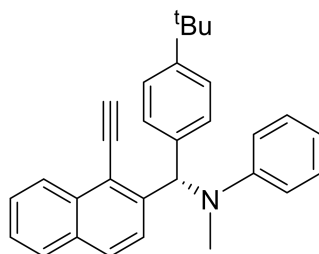
1H), 7.34 (d, $J = 7.5$ Hz, 2H), 7.24-7.14 (m, 3H), 7.06-7.06 (m, 1H), 6.85 (d, $J = 8.3$ Hz, 1H), 6.10 (s, 1H), 5.86 (d, $J = 8.3$ Hz, 1H), 3.66 (s, 1H), 3.13 (t, $J = 8.1$ Hz, 2H), 2.83 (t, $J = 8.1$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 150.9, 142.7, 140.2, 133.3, 132.6, 131.8, 129.2, 128.9, 128.1, 127.9, 127.7, 127.0, 126.9, 126.7, 126.2, 126.0, 125.0, 118.1, 109.6, 109.2, 88.4, 79.4, 65.0, 52.4, 27.8$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{20}\text{BrNH}^+$ ($\text{M}+\text{H}$) $^+$ 438.0852, found 438.0849.



5n

(S)-6-bromo-1-((1-ethynyl)naphthalen-2-yl)(phenyl)methyl-1,2,3,4

tetrahydroquinoline (5n). Yellow oil (41.2 mg, 91% yield). HPLC: 84:16 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, t_r (major) = 5.57 min, t_r (minor) = 5.20 min. $[\alpha]_{\text{D}}^{25} = 27.8$ ($c = 0.1, \text{CH}_2\text{Cl}_2$). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.32$ (d, $J = 8.0$ Hz, 1H), 7.72 (dd, $J = 25.0, 8.1$ Hz, 2H), 7.53-7.42 (m, 2H), 7.28-7.20 (m, 3H), 7.14-7.09 (m, 3H), 7.01-6.89 (m, 2H), 6.54 (s, 1H), 6.33 (d, $J = 8.2$ Hz, 1H), 3.46 (s, 1H), 3.07-2.89 (m, 2H), 2.66 (s, 2H), 1.84-1.75 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 144.10, 142.52, 139.11, 133.12, 131.61, 130.43, 128.93, 128.14, 128.02, 127.91, 127.49, 126.66, 125.96, 125.58, 125.26, 124.06, 119.39, 106.72, 64.24, 45.37, 27.66, 21.57$. HRMS (APCI) m/z calcd for $\text{C}_{28}\text{H}_{22}\text{BrNH}^+$ ($\text{M}+\text{H}$) $^+$ 452.1008, found 452.1004.

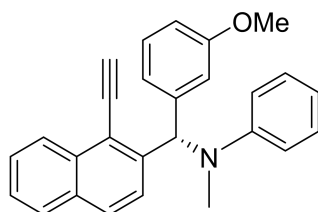


6a

(S)-N-((4-(tert-butyl)phenyl)(1-ethynyl)naphthalen-2-yl)methyl-N-methylaniline

(6a). Yellow oil (38.7 mg, 96% yield). HPLC: 78:22 er (Chiralpak OJH column, 254

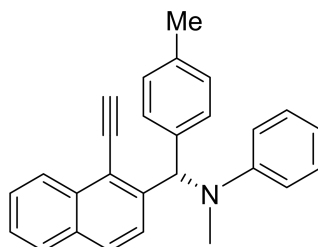
nm, hexane/isopropanol = 98:2, flow rate 0.5 mL/min, tr (major) = 11.24 min, tr (minor) = 9.69 min. $[\alpha]_{\text{D}}^{25} = 74.2$ (c = 0.1, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 8.38$ (d, $J = 8.4$ Hz, 1H), 7.77 (dd, $J = 17.7, 8.4$ Hz, 2H), 7.58-7.53 (m, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.33-7.29 (m, 3H), 7.21-7.16 (m, 2H), 7.11-7.06 (m, 2H), 6.86-6.80 (m, 2H), 6.73-6.67 (m, 2H), 3.50 (s, 1H), 2.83 (s, 3H), 1.30 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 150.5, 150.1, 144.4, 137.6, 133.9, 132.3, 129.1, 129.0, 128.4, 128.2, 127.3, 126.5, 126.4, 125.9, 125.4, 119.6, 116.9, 113.1, 88.6, 79.8, 65.4, 35.7, 34.6, 31.5$. HRMS (APCI) m/z calcd for $\text{C}_{30}\text{H}_{29}\text{NH}^+$ (M+H) $^+$ 404.2373, found 404.2374.



6b

(S)-N-((1-ethynyl-2-naphthyl)(3-methoxyphenyl)methyl)-N-methylaniline

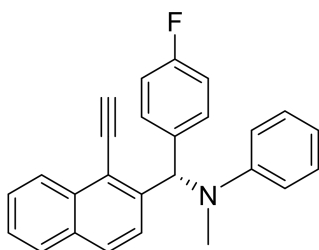
(6b). Yellow oil (27.6 mg, 73% yield). HPLC: 85:15 er (Chiralpak ODH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 6.19 min, tr (minor) = 7.39 min. $[\alpha]_{\text{D}}^{25} = 43.3$ (c = 0.1, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 8.38$ (d, $J = 8.4$ Hz, 1H), 7.78 (dd, $J = 18.9, 8.3$ Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.29 (dd, $J = 8.6, 2.5$ Hz, 1H), 7.24-7.16 (m, 3H), 6.83-6.75 (m, 5H), 6.72-6.68 (m, 2H), 3.73 (s, 3H), 3.51 (s, 1H), 2.84 (d, $J = 2.5$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 159.9, 150.5, 144.0, 142.7, 132.4, 129.6, 129.1, 129.0, 128.2, 127.3, 126.6, 126.4, 125.8, 121.2, 119.8, 117.0, 114.6, 113.2, 112.5, 88.7, 79.7, 65.9, 55.3, 35.8$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NOH}^+$ (M+H) $^+$ 378.1852, found 378.1848.



6c

(S)-N-((1-ethynyl-2-naphthyl)(p-tolyl)methyl)-N-methylaniline (6c). Yellow

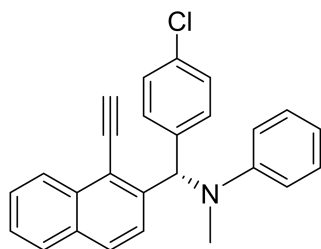
oil (29.6 mg, 82% yield). HPLC: 78:22 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 0.7 mL/min, tr (major) = 9.88 min, tr (minor) = 12.64 min. $[\alpha]_{\text{D}}^{25} = 16.2$ ($c = 0.1$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.38$ (d, $J = 8.3$ Hz, 1H), 7.79 (dd, $J = 18.1, 8.3$ Hz, 2H), 7.59-7.55 (m, 1H), 7.52-7.48 (m, 1H), 7.34-7.30 (m, 1H), 7.20-7.16 (m, 2H), 7.11 (d, $J = 8.2$ Hz, 2H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.80 (d, $J = 8.2$ Hz, 2H), 6.72-6.67 (m, 2H), 3.53 (s, 1H), 2.84 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 144.4, 137.8, 136.9, 129.3, 129.1, 129.0, 128.8, 127.3, 126.5, 126.4, 125.7, 116.9, 113.1, 88.7, 79.7, 65.6, 35.7, 21.3$. HRMS (APCI) m/z calcd for $\text{C}_{27}\text{H}_{23}\text{NH}^+$ ($\text{M}+\text{H}$) $^+$ 362.1903, found 362.1898.



6d

(S)-N-((1-ethynynaphthalen-2-yl)(4-fluorophenyl)methyl)-N-methylaniline (6d).

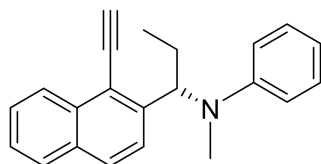
Yellow oil (35.1 mg, 96% yield). HPLC: 92:8 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 0.7 mL/min, tr (major) = 10.42 min, tr (minor) = 11.35 min. $[\alpha]_{\text{D}}^{25} = 30.8$ ($c = 0.1$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.39$ (d, $J = 8.2$ Hz, 1H), 7.80 (dd, $J = 14.6, 8.1$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.30 (d, $J = 8.6$ Hz, 1H), 7.21-7.13 (m, 4H), 7.00 (t, $J = 8.2$ Hz, 2H), 6.82-6.78 (m, 2H), 6.72 (t, $J = 7.2$ Hz, 1H), 6.68 (s, 1H), 3.87-3.24 (m, 1H), 2.84-2.81 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 143.9, 136.7, 134.0, 132.4, 130.3, 129.2, 129.2, 128.3, 127.4, 126.7, 126.4, 119.6, 117.3, 115.6, 115.4, 113.4, 88.9, 79.6, 65.4, 35.8$. ^{19}F NMR (376 MHz, CDCl_3) $\delta = -115.4$. HRMS (APCI) m/z calcd for $\text{C}_{26}\text{H}_{20}\text{FNH}^+$ ($\text{M}+\text{H}$) $^+$ 366.1653, found 366.1650.



6e

(S)-N-((4-chlorophenyl)(1-ethynynaphthalen-2-yl)methyl)-N-methylaniline (6e).

Yellow oil (34.9 mg, 84% yield). HPLC: 92:8 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 8.24 min, tr (minor) = 9.54 min. $[\alpha]_D^{25} = 42.3$ (c = 0.1, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ = 8.38 (d, *J* = 8.4 Hz, 1H), 7.80 (dd, *J* = 15.6, 8.4 Hz, 2H), 7.60-7.55 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.31-7.24 (m, 3H), 7.22-7.16 (m, 2H), 7.12 (d, *J* = 7.1 Hz, 2H), 6.81-6.78 (m, 2H), 6.75-6.70 (m, 1H), 6.67-6.66 (m, 1H), 3.52 (s, 1H), 2.85-2.76 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 150.3, 143.5, 139.6, 133.1, 130.1, 129.2, 129.2, 128.8, 128.3, 127.5, 126.7, 126.4, 125.5, 119.7, 117.4, 113.4, 88.9, 79.6, 65.5, 35.9. HRMS (APCI) m/z calcd for C₂₆H₂₀ClNH⁺ (M+H)⁺ 382.1357, found 382.1355.

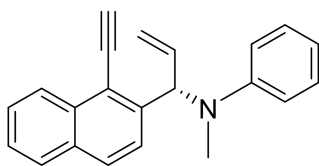


6f

(S)-N-(1-(1-ethynynaphthalen-2-yl)propyl)-N-methylaniline (6f).

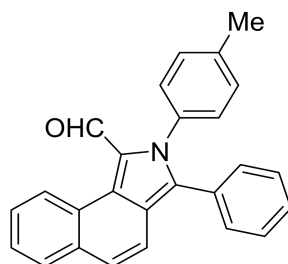
Yellow oil (26.0 mg, 87% yield). HPLC: 94:6 er (Chiralpak OJH column, 254 nm, hexane/isopropanol = 98:2, flow rate 0.7 mL/min, tr (major) = 11.69 min, tr (minor) = 12.53 min. $[\alpha]_D^{25} = -53.4$ (c = 0.1, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ = 8.40 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 9.1 Hz, 2H), 7.58-7.53 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 5.39-5.33 (m, 1H), 3.75 (s, 1H), 3.08 (s, 3H), 2.17-2.01 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 150.4, 146.1, 134.0, 132.1, 129.3, 129.1, 128.2, 127.2, 126.2, 123.7, 116.7, 113.2, 88.2, 80.0, 62.7, 33.2, 29.2, 27.1, 12.3, 9.9. HRMS

(APCI) m/z calcd for $C_{22}H_{21}NH^+$ ($M+H$)⁺ 300.1347, found 300.1344.



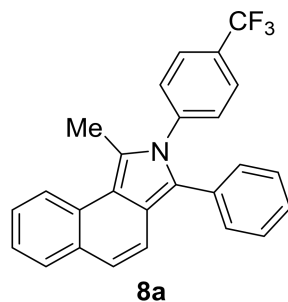
6g

(S)-N-(1-(1-ethynyl-2-allylnaphthalen-2-yl)allyl)-N-methylaniline (6g). Yellow oil (26.7 mg, 90% yield). HPLC: 86:14 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, tr (major) = 5.49 min, tr (minor) = 5.05 min. $[\alpha]_D^{25} = 27.3$ ($c = 0.1$, CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$) $\delta = 8.35$ (d, $J = 8.4$ Hz, 1H), 7.77-7.72 (m, 2H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.56-7.52 (m, 1H), 7.48-7.43 (m, 1H), 7.35-7.30 (m, 1H), 7.28-7.23 (m, 2H), 6.82 (d, $J = 8.1$ Hz, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.45-6.38 (m, 1H), 4.18 (dd, $J = 5.7, 1.3$ Hz, 2H), 3.71 (s, 1H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 149.6, 137.9, 134.0, 132.4, 130.3, 129.3, 129.0, 128.2, 127.4, 126.6, 126.4, 122.6, 117.5, 116.8, 112.9, 87.7, 80.0, 55.2, 38.2$. HRMS (APCI) m/z calcd for $C_{22}H_{19}NH^+$ ($M+H$)⁺ 298.1590, found 298.1593.



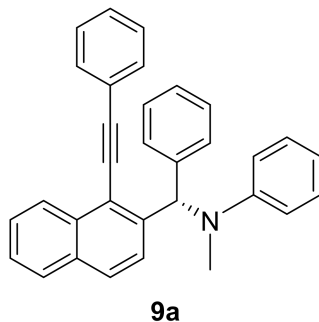
7a

3-phenyl-2-(p-tolyl)-2H-benzo[e]isoindole-1-carbaldehyde (7a). Yellow oil (27.1 mg, 75% yield). 1H NMR (400 MHz, $CDCl_3$) $\delta = 9.90$ (d, $J = 8.1$ Hz, 1H), 9.71 (s, 1H), 7.77 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.61-7.51 (m, 2H), 7.46 (d, $J = 3.4$ Hz, 2H), 7.27-7.22 (m, 4H), 7.18 (s, 1H), 7.13 (s, 4H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 179.5, 139.4, 136.5, 134.6, 133.7, 130.0, 129.8, 129.0, 128.7, 128.6, 128.4, 127.7, 127.4, 126.7, 126.4, 123.0, 118.8, 21.4$. HRMS (APCI) m/z calcd for $C_{26}H_{19}NOH^+$ ($M+H$)⁺ 362.1539, found 362.1537.



1-methyl-3-phenyl-2-(4-(trifluoromethyl)phenyl)-2H-benzo[e]isoindole (8a).

Yellow solid (33.7 mg, 84% yield). Mp: 121.2-121.6 °C. ¹H NMR (400 MHz, CDCl₃) δ = 8.29 (d, *J* = 8.01 Hz, 1H), 7.75-7.72 (m, 1H), 7.67 (d, *J* = 8.25 Hz, 2H), 7.53-7.48 (m, 2H), 7.42-7.38 (m, 1H), 7.33 (d, *J* = 8.16 Hz, 2H), 7.28-7.24 (m, 3H), 7.23-7.20 (m, 1H), 7.18-7.15 (m, 2H), 2.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.9, 132.0, 131.9, 130.1, 129.7, 128.5, 126.6, 126.4, 126.3, 126.2, 125.0, 124.6, 124.4, 123.4, 122.8, 120.9, 119.7, 117.4, 14.4. ¹⁹F NMR (376 MHz, CDCl₃) δ = -62.5. HRMS (APCI) *m/z* calcd for C₂₆H₁₈F₃NH⁺ (M+H)⁺ 402.1464, found 402.1465.



(S)-N-methyl-N-(phenyl(1-(phenylethynyl)naphthalen-2-yl)methyl)aniline (9a).

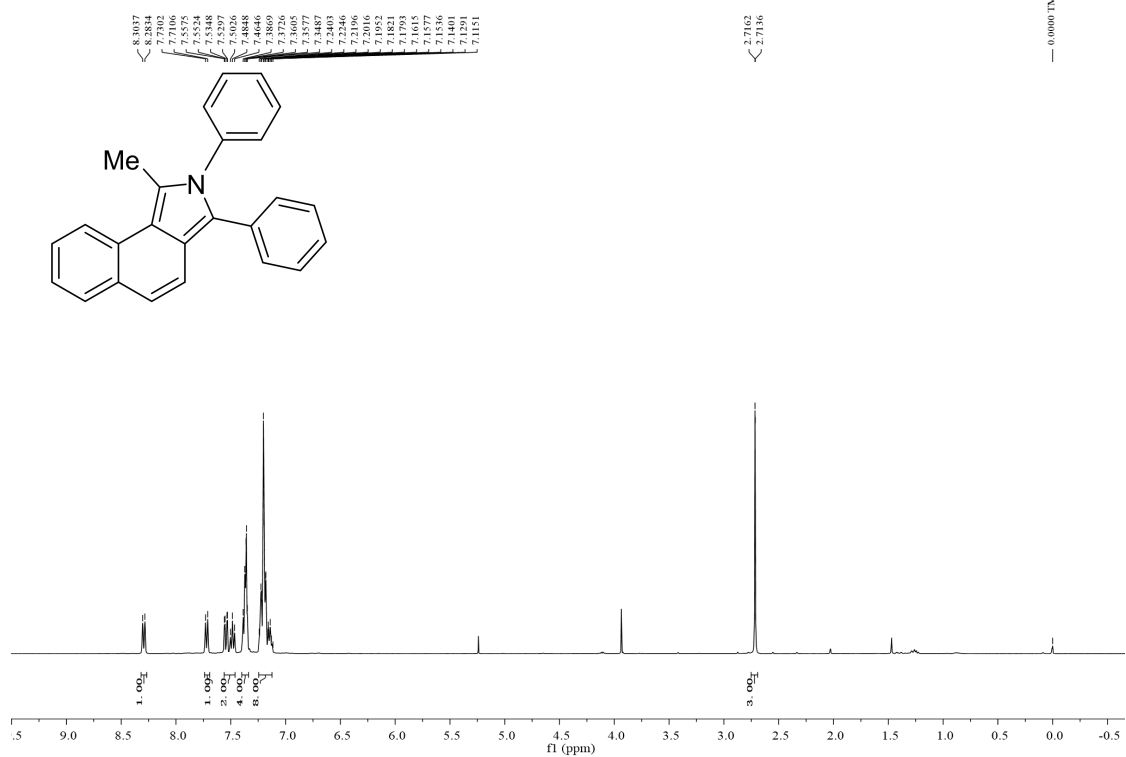
Yellow oil (35.2 mg, 83% yield). HPLC: 90:10 er (Chiralpak ADH column, 254 nm, hexane/isopropanol = 98:2, flow rate 1.0 mL/min, *t_r* (major) = 8.21 min, *t_r* (minor) = 6.13 min. [α]_D²⁵ = 22.3 (c = 0.1, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.55-7.50 (m, 1H), 7.46-7.42 (m, 1H), 7.29-7.24 (m, 2H), 7.22-7.08 (m, 9H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.68-6.62 (m, 2H), 2.77 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 150.5, 142.6, 141.1, 133.6, 132.5, 131.7, 129.3, 128.7, 128.6, 128.5, 128.3, 128.3, 127.3, 127.2, 126.6, 126.5, 126.4, 121.3, 116.7, 101.1, 66.2, 35.3. HRMS (APCI) *m/z* calcd for C₃₂H₂₅NH⁺ (M+H)⁺ 424.2060, found 424.2059.

IV References

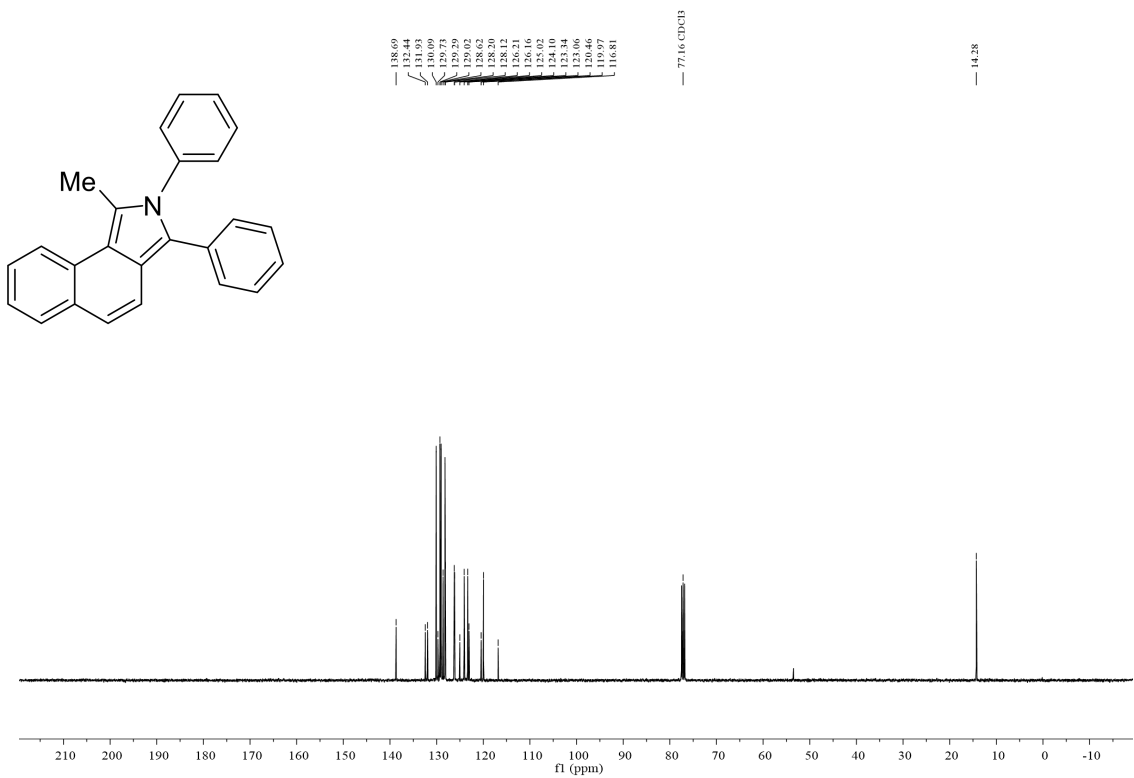
- [1] Sun, R.; Jiang, Y.; Tang, X. Y.; et al. Rh^{II}-Catalyzed Cyclization of Ester/Thioester-Containing N-Sulfonyl-1, 2, 3-triazoles: Facile Synthesis of Alkylidenephthalans and Alkylidenethiophthalans. *Asian Journal of Organic Chemistry*, **2017**, 6, 83–87.
- [2] Liao, M. Y.; Li J. X.; Zhu, H. H.; et al. Synthesis of Axially Chiral N-Arylpyrroles through the Enantioselective Annulation of Yne-Allylic Esters with a Cooperative Copper-Squaramide Catalysis. *Organic Letters*, **2025**, 27(19), 4836–4841.

V NMR Spectrum

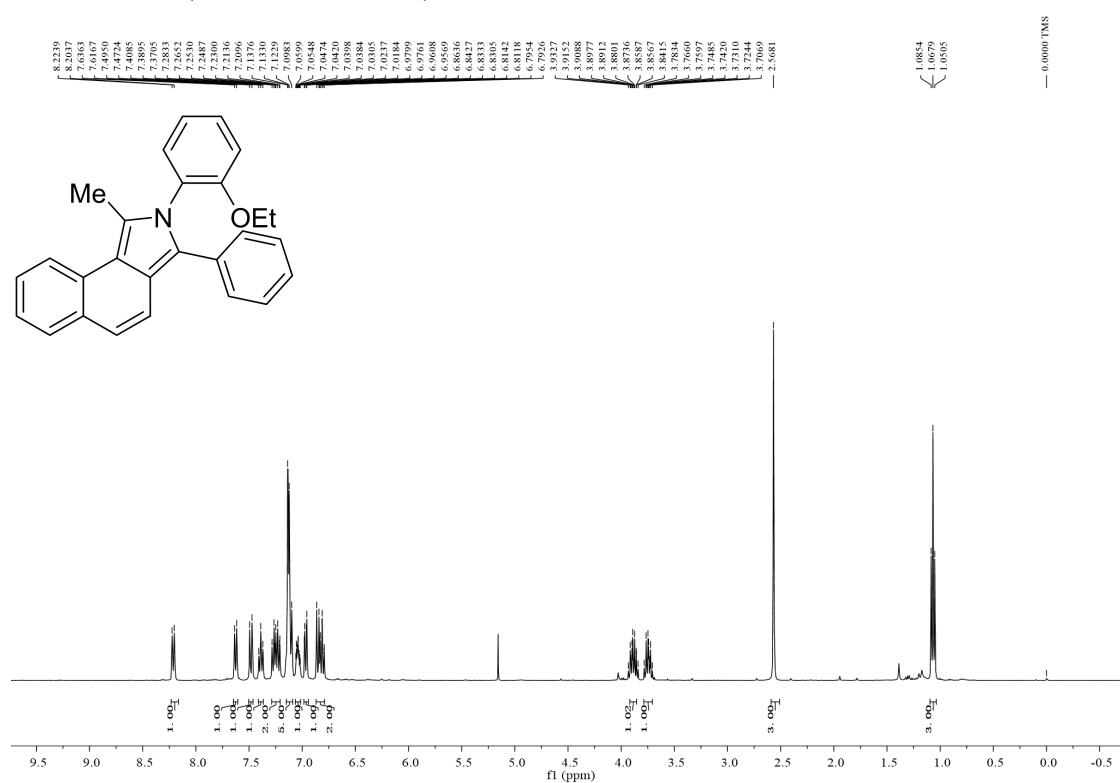
¹H NMR-3a (400 MHz, CDCl₃)



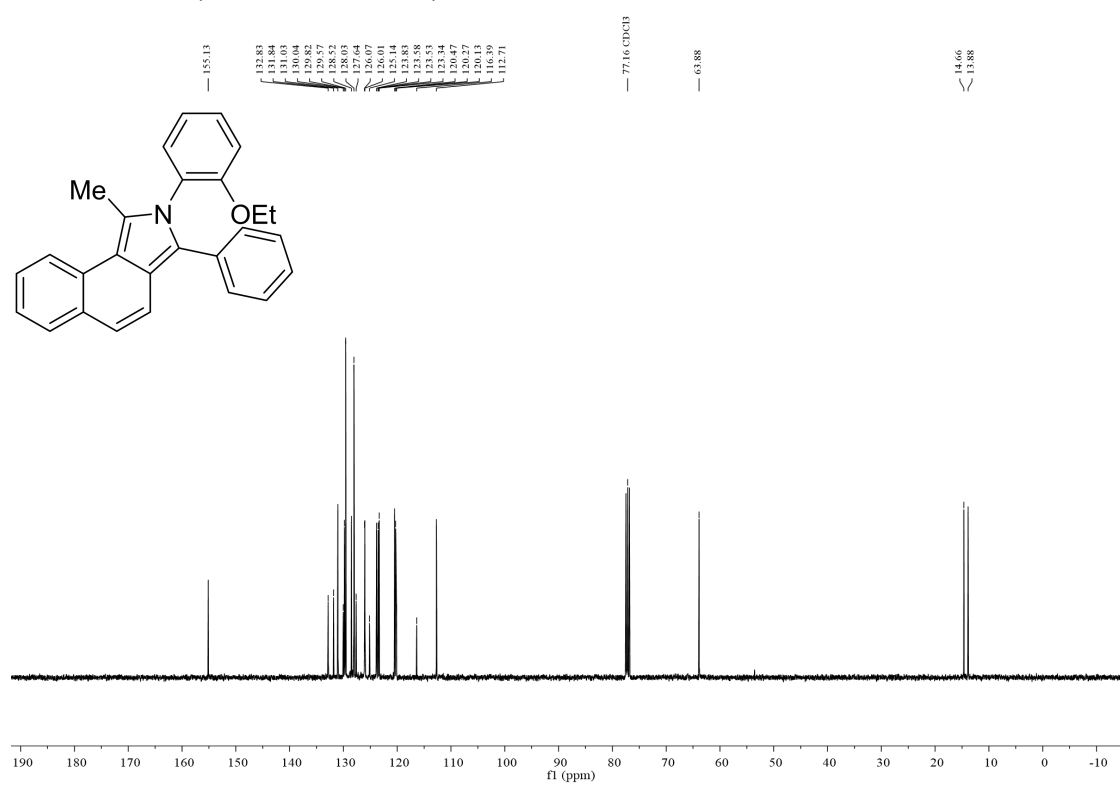
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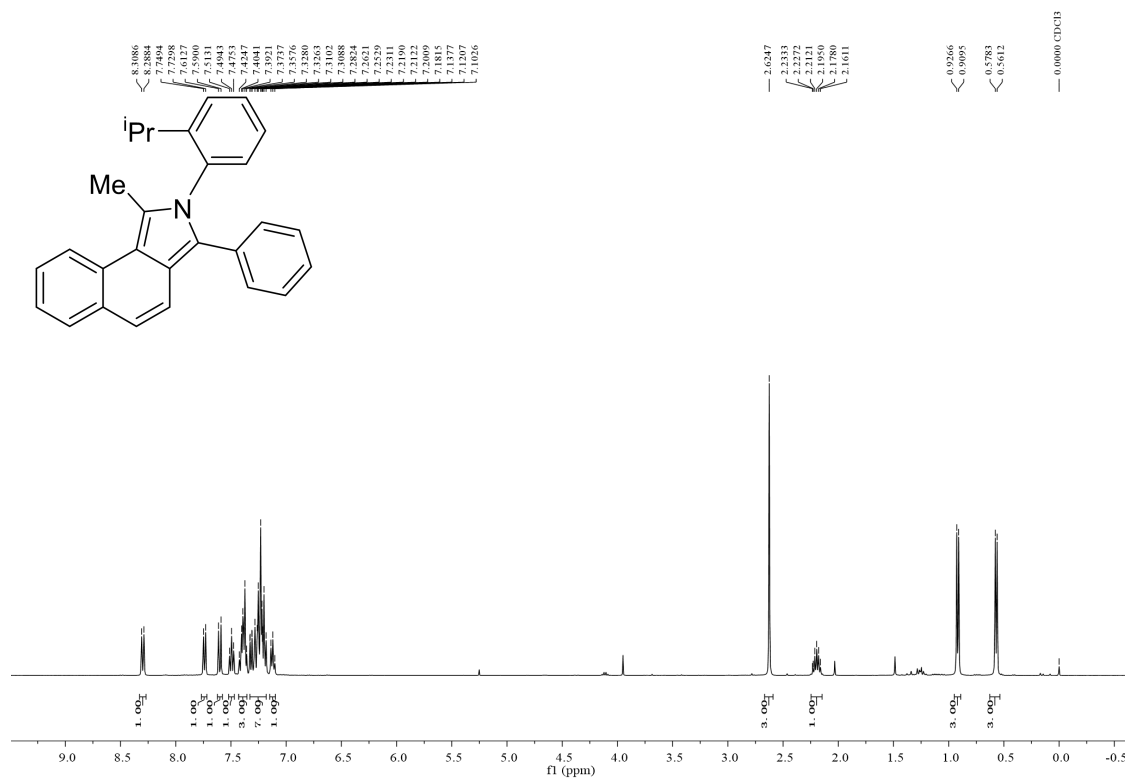
¹H NMR-3b (400 MHz, CDCl₃)



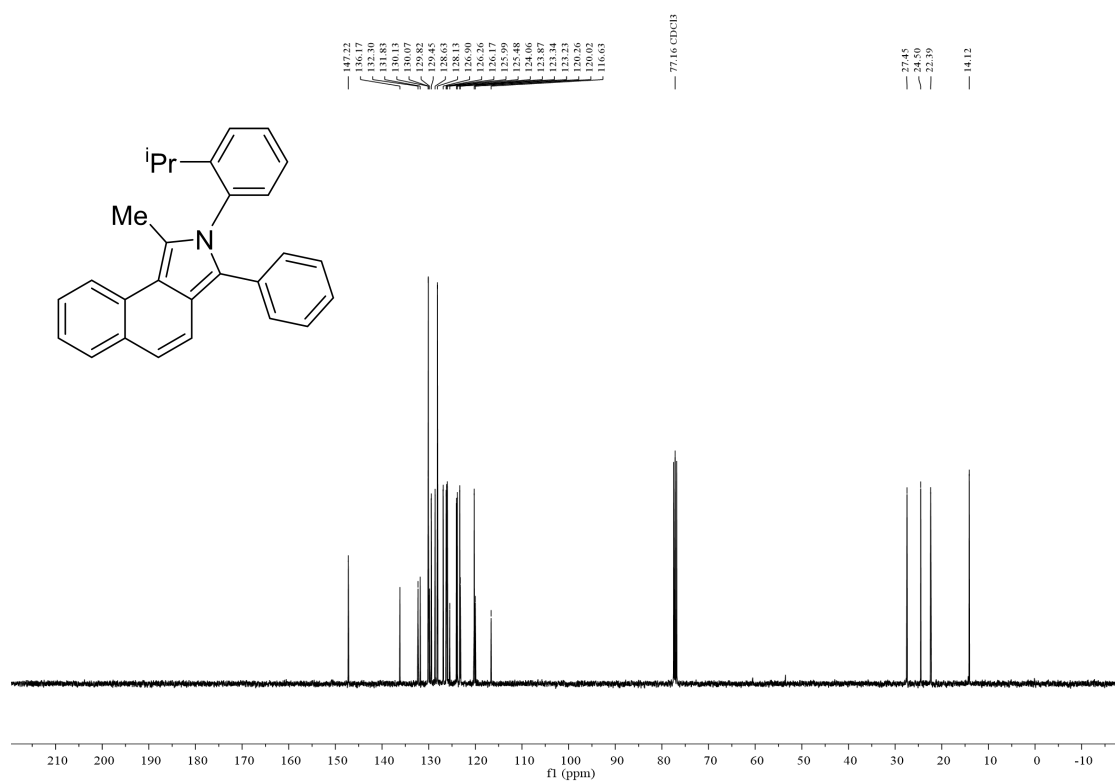
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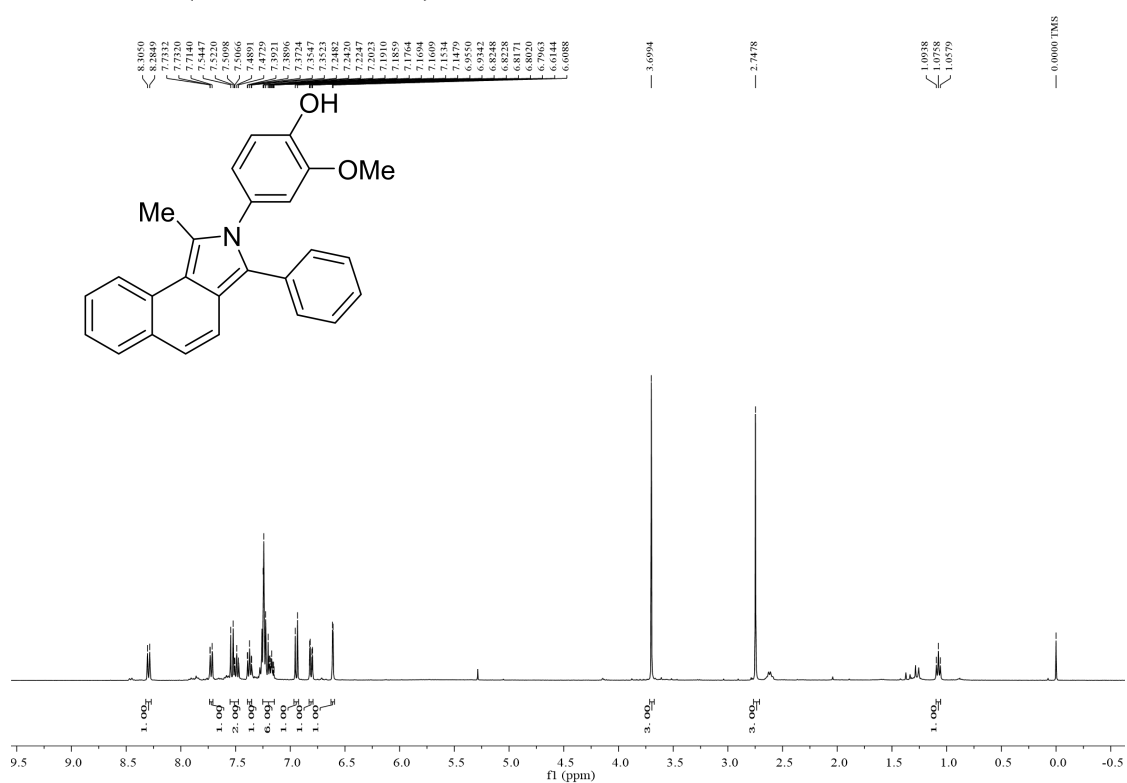
¹H NMR-3c (400 MHz, CDCl₃)



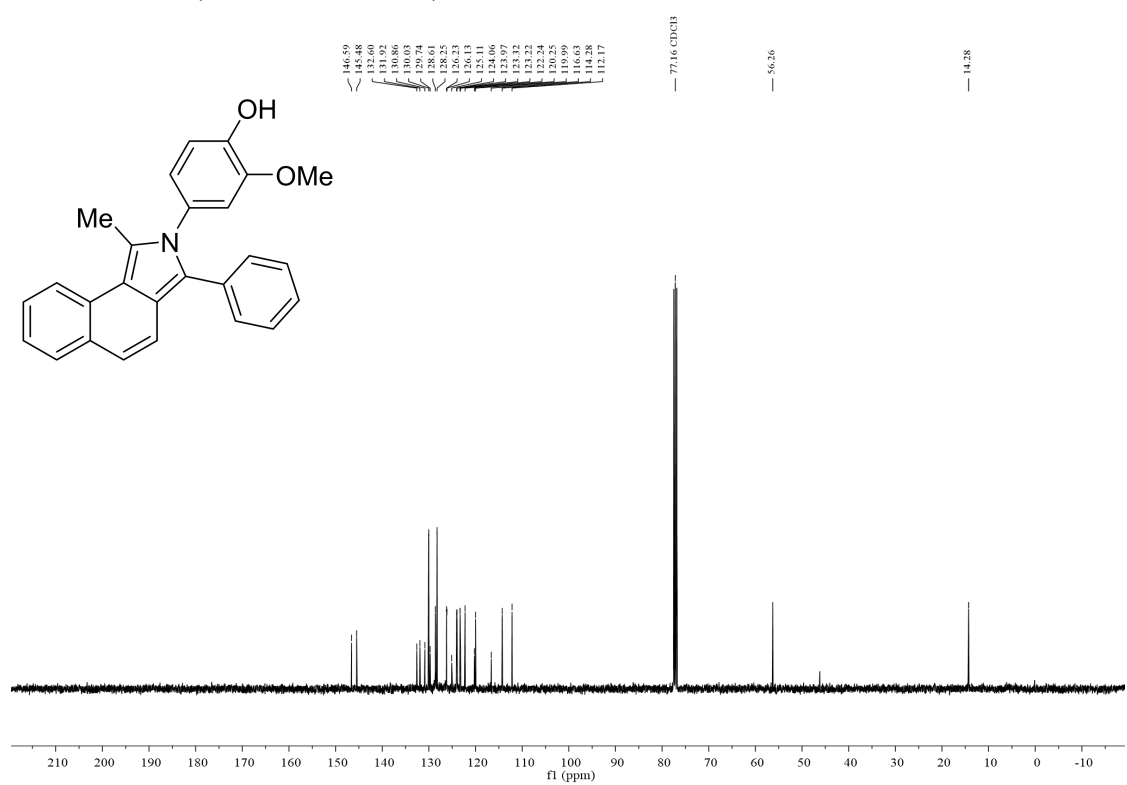
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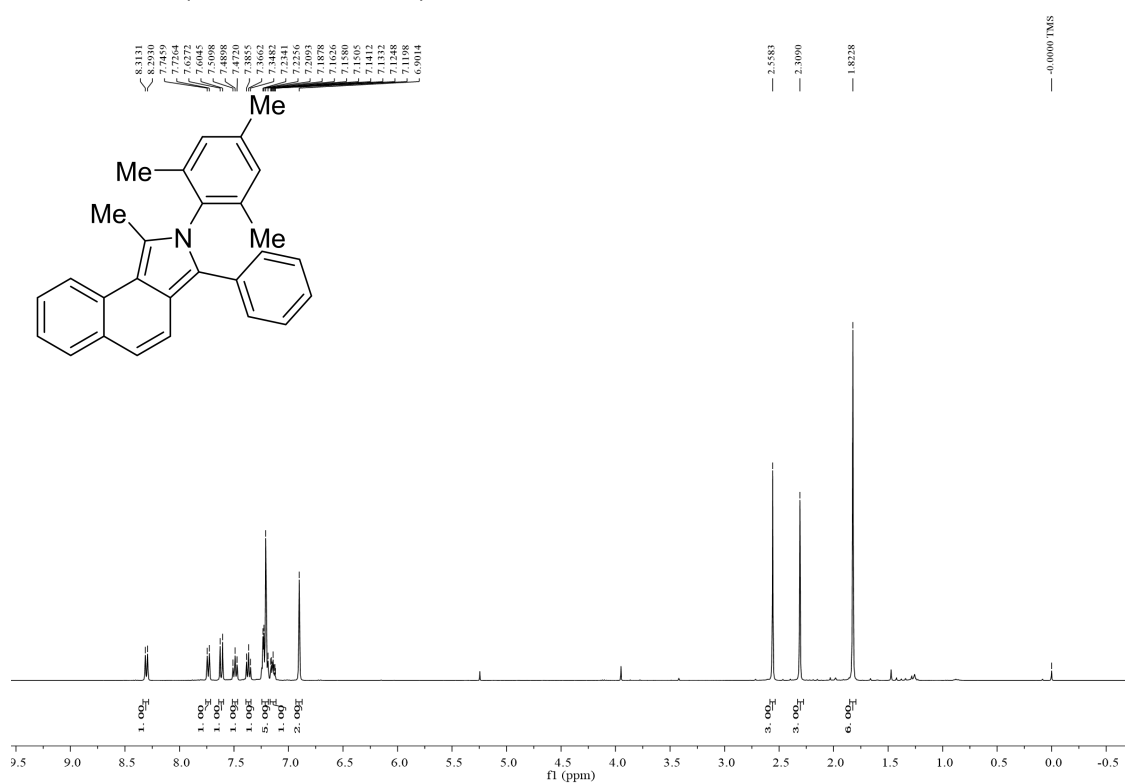
¹H NMR-3d (400 MHz, CDCl₃)



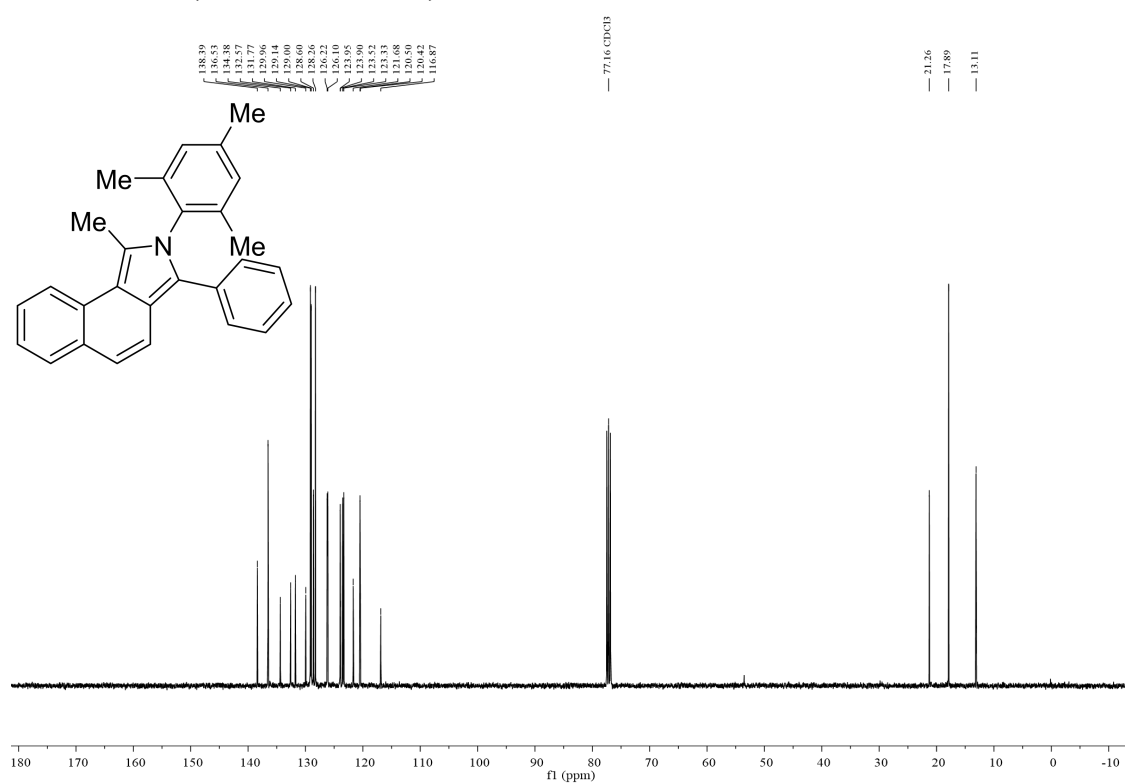
¹³C NMR-3d (100 MHz, CDCl₃)



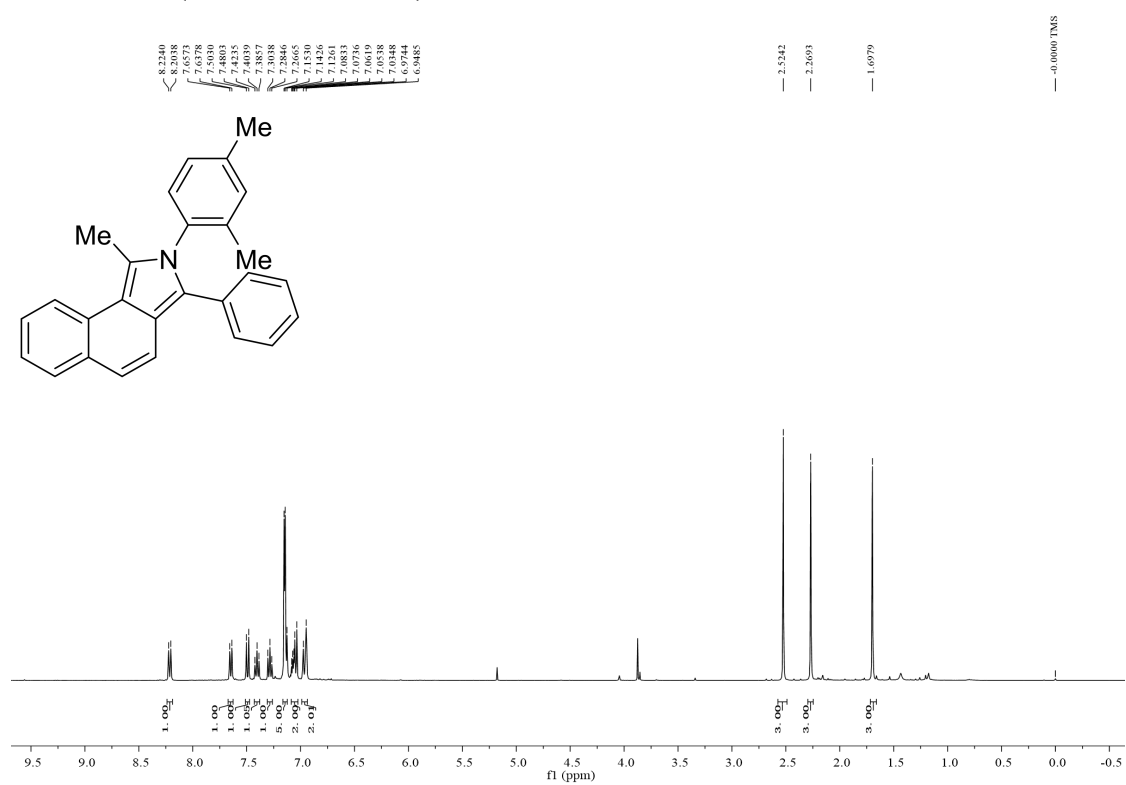
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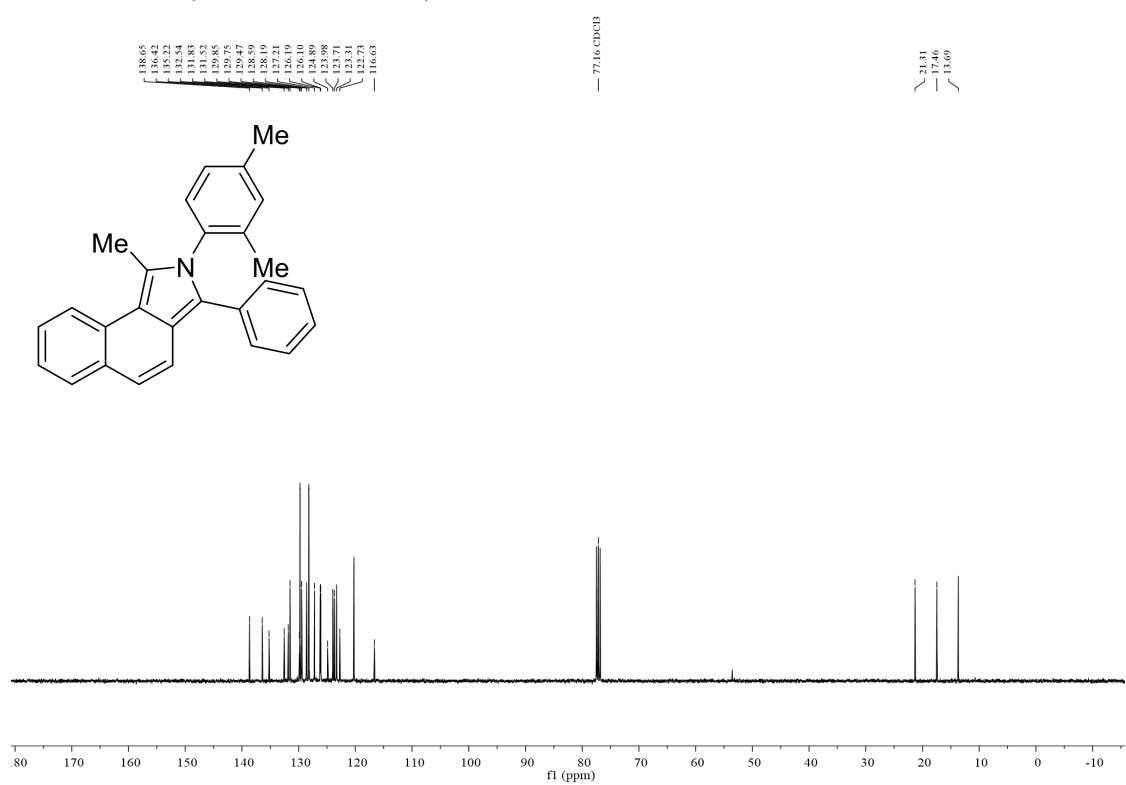
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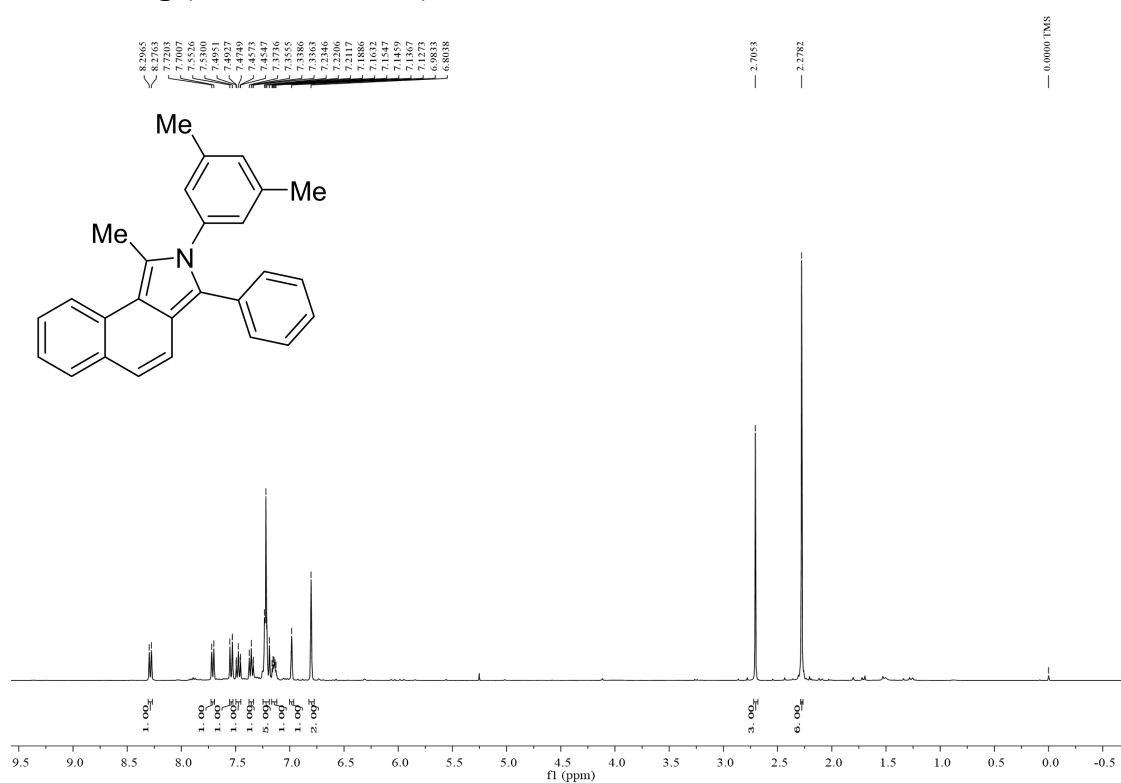
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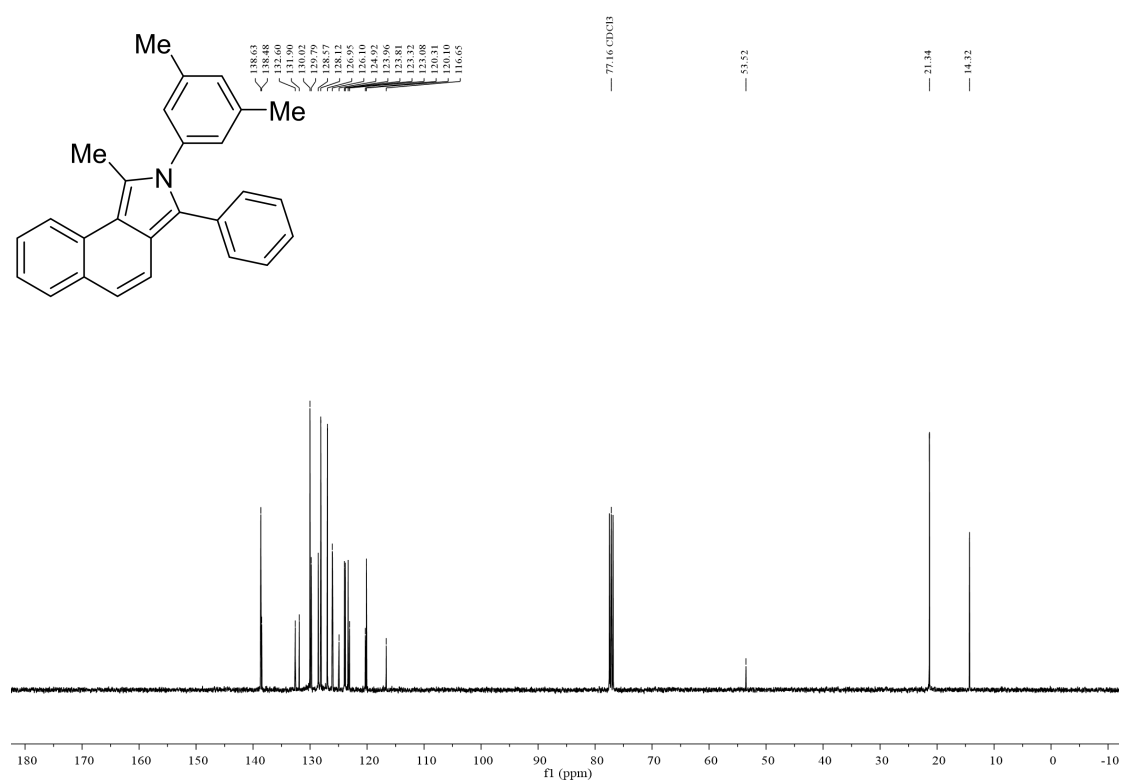
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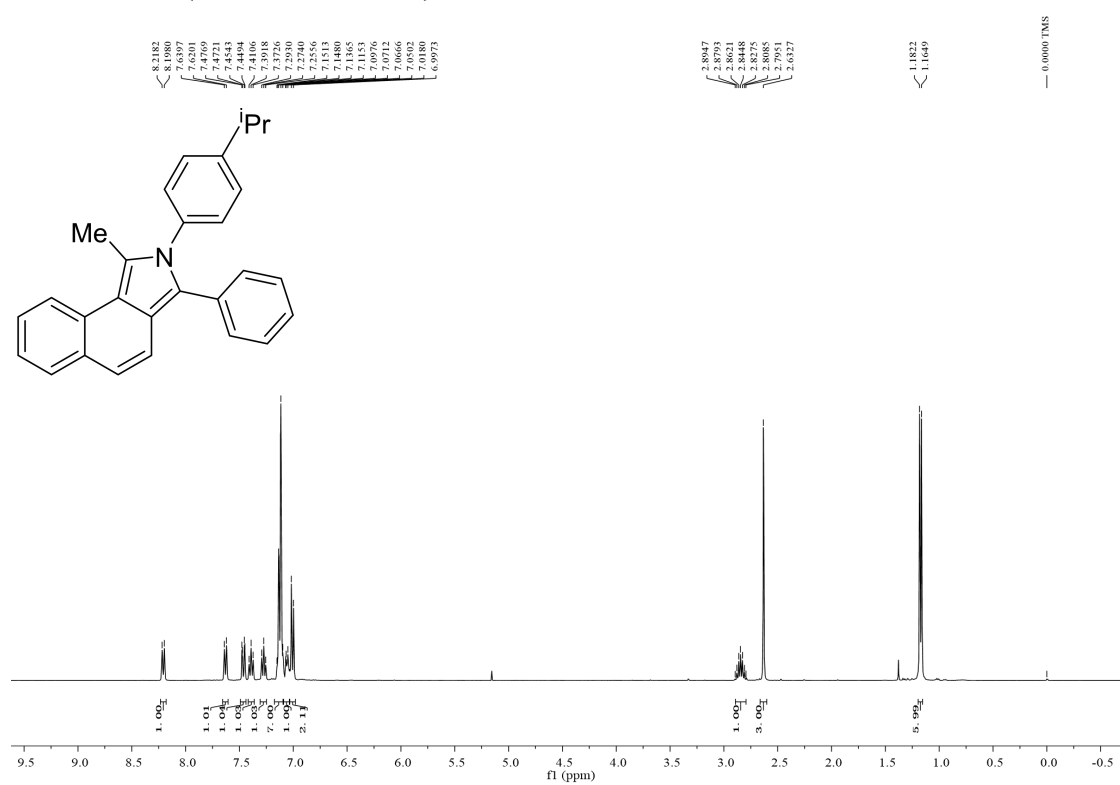
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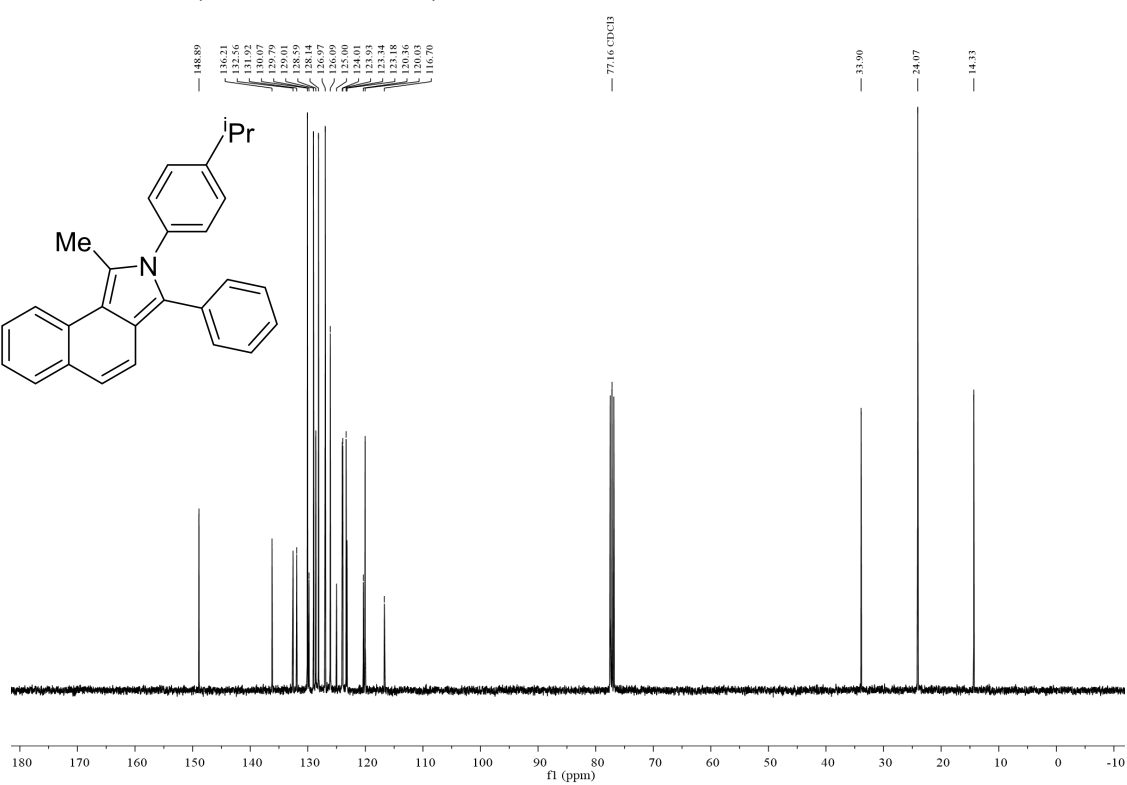
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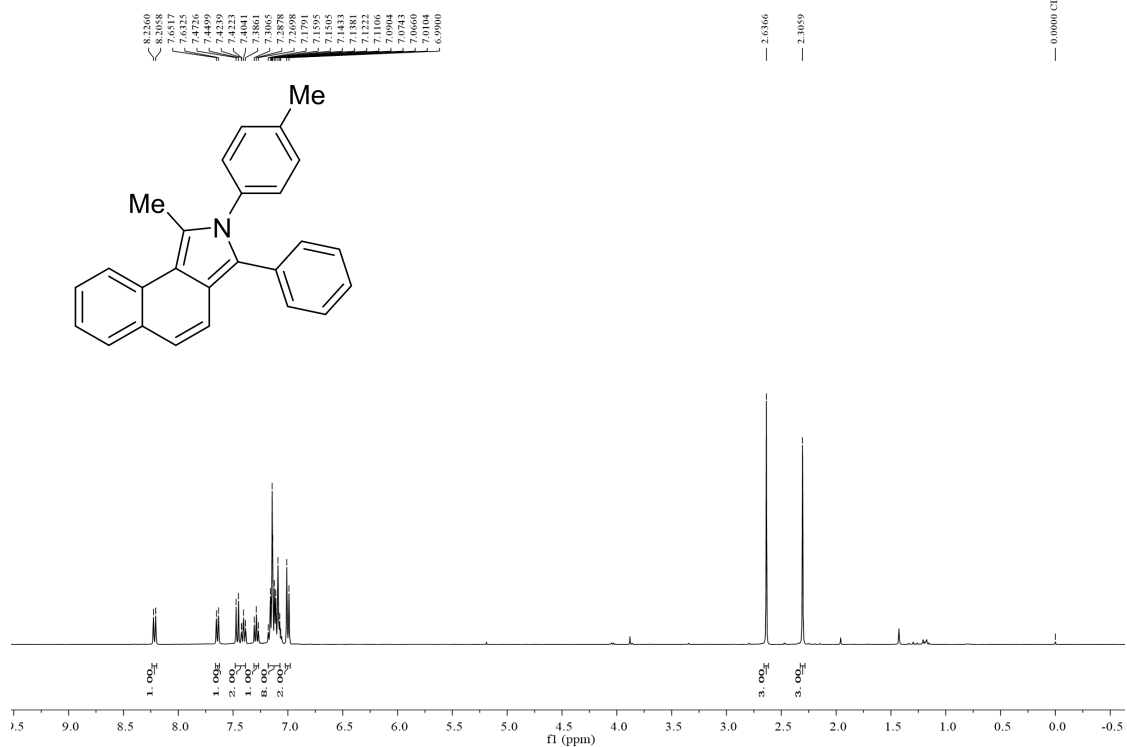
¹H NMR-3h (400 MHz, CDCl₃)



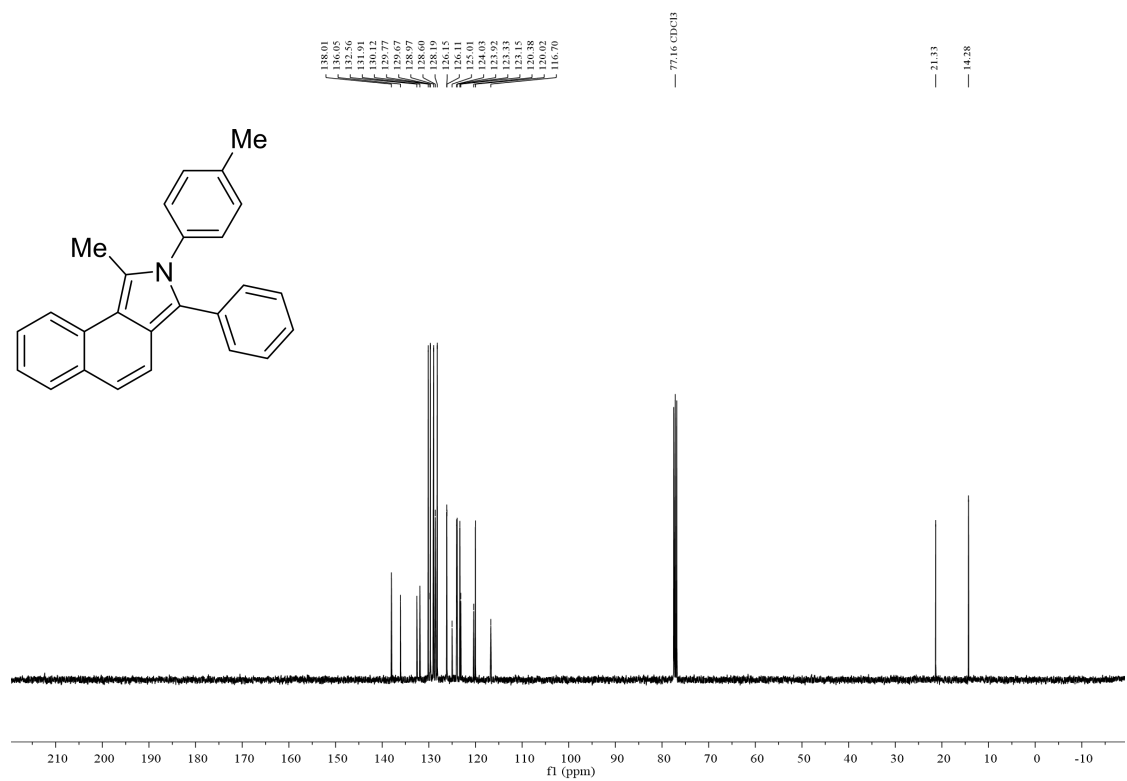
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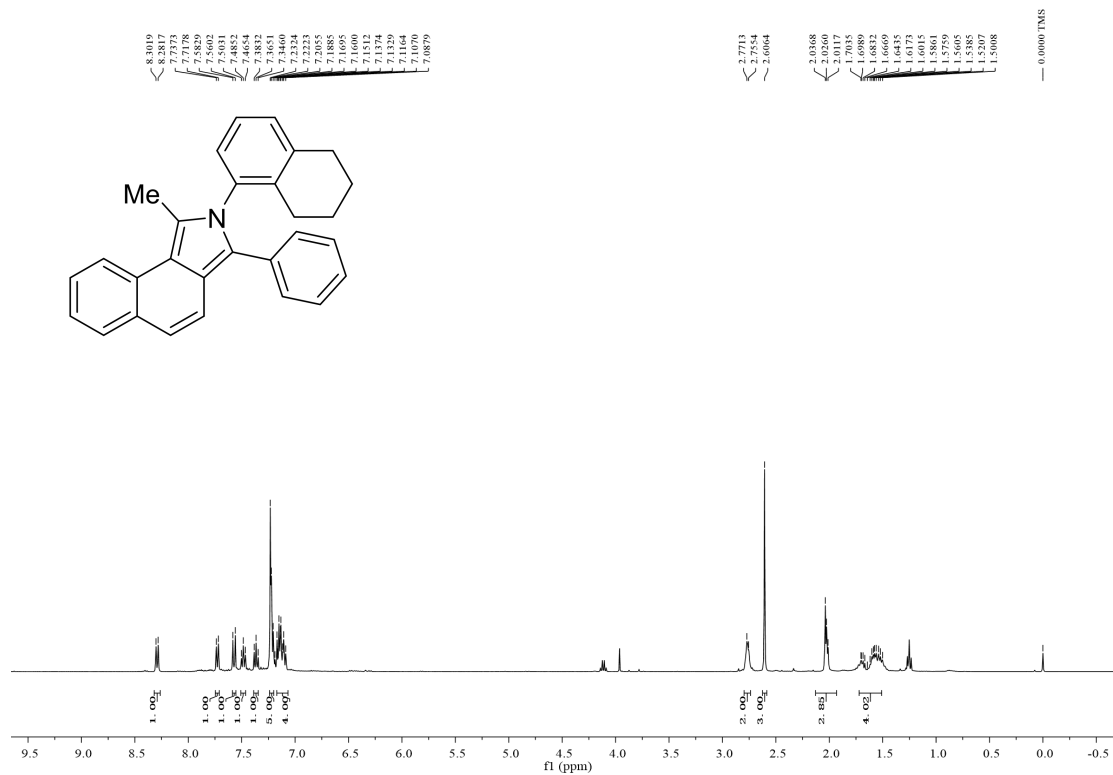
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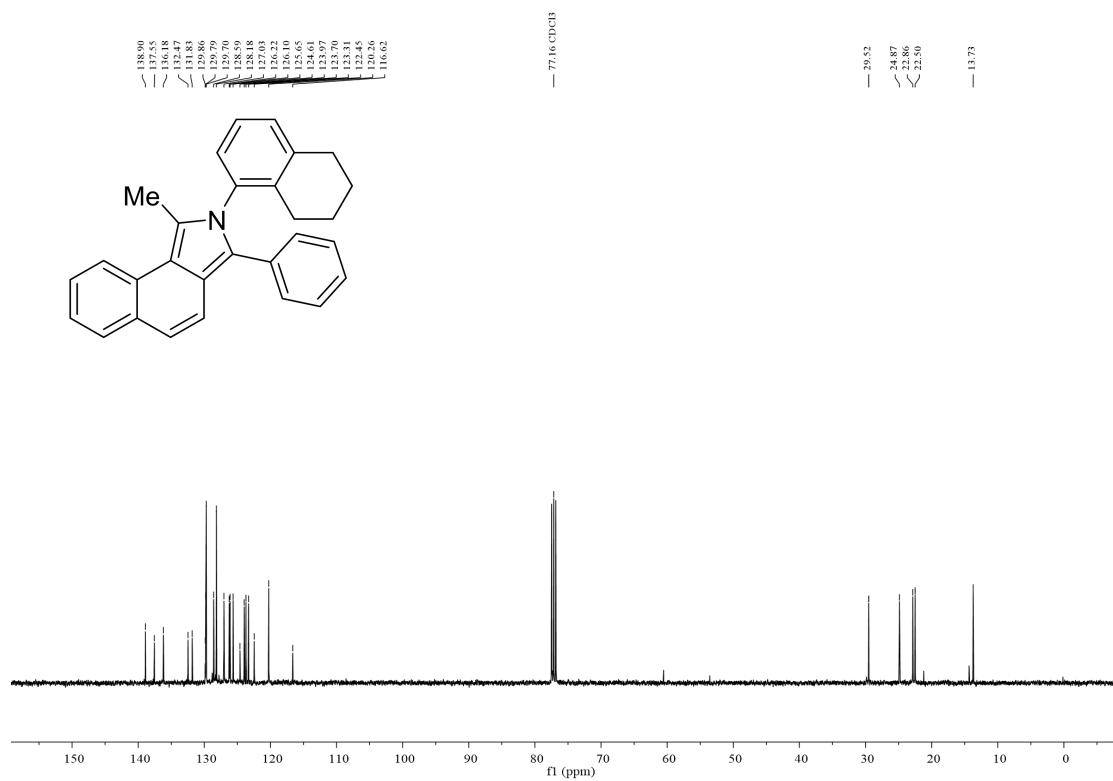
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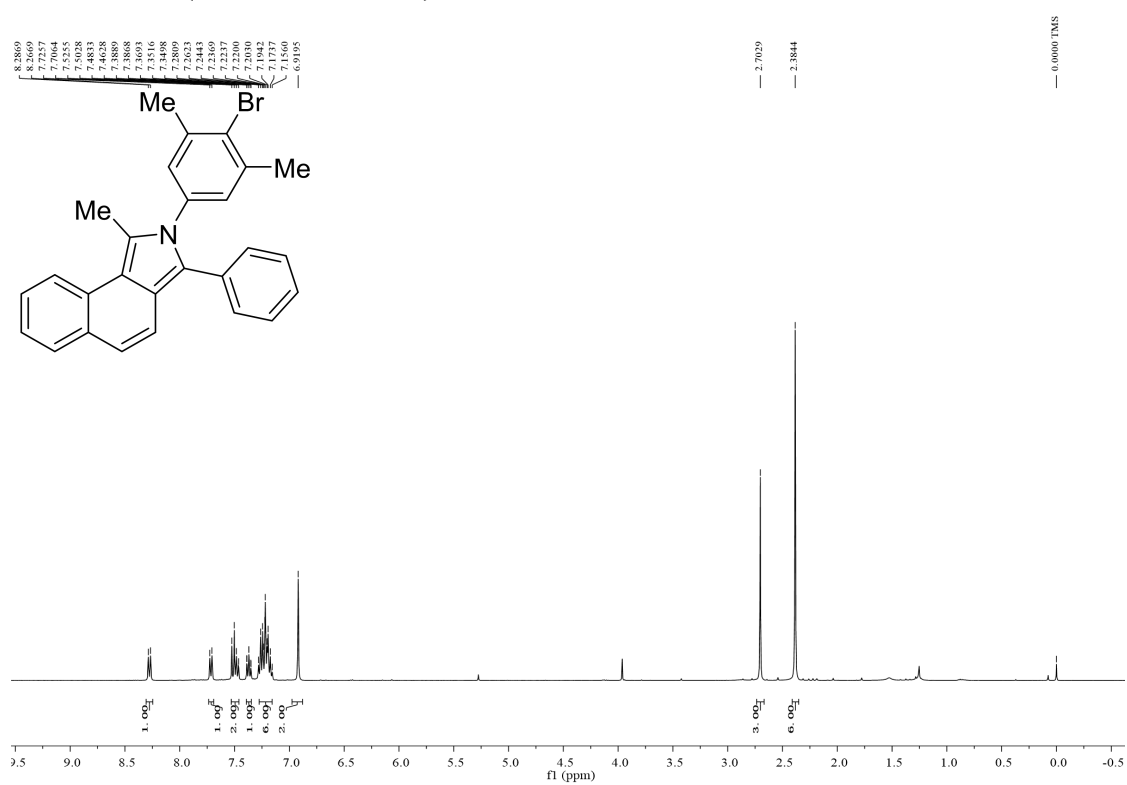
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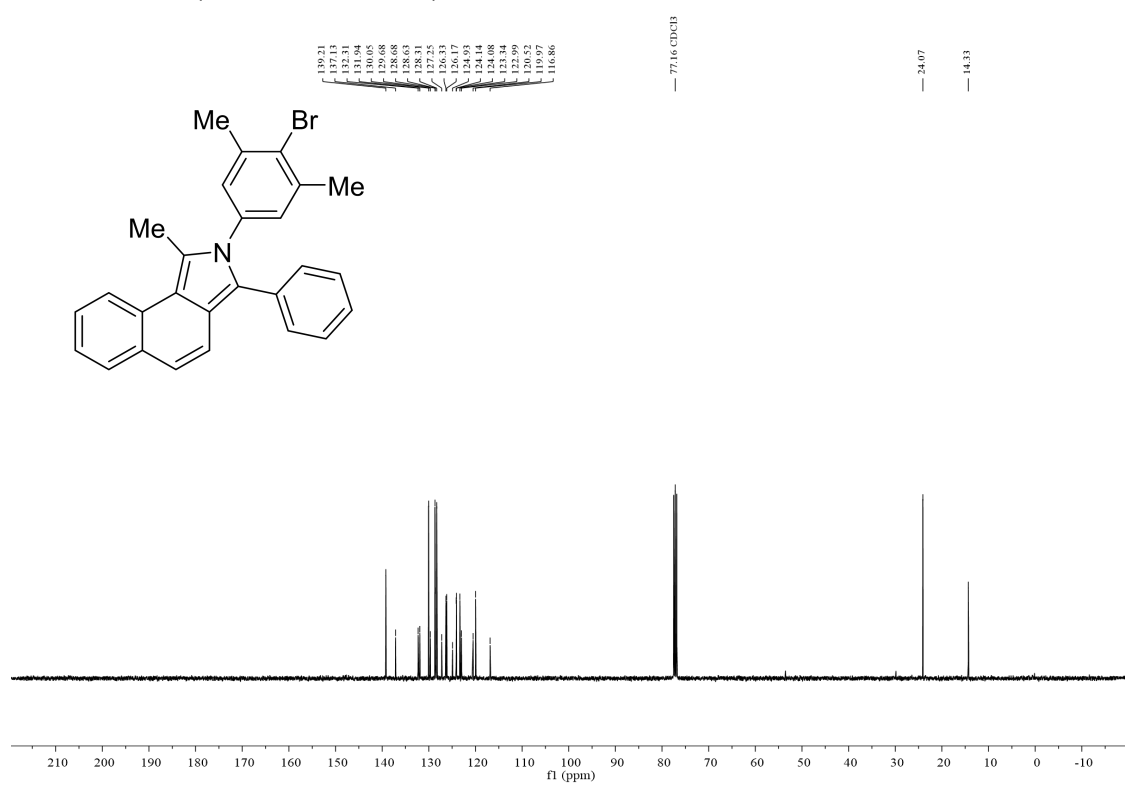
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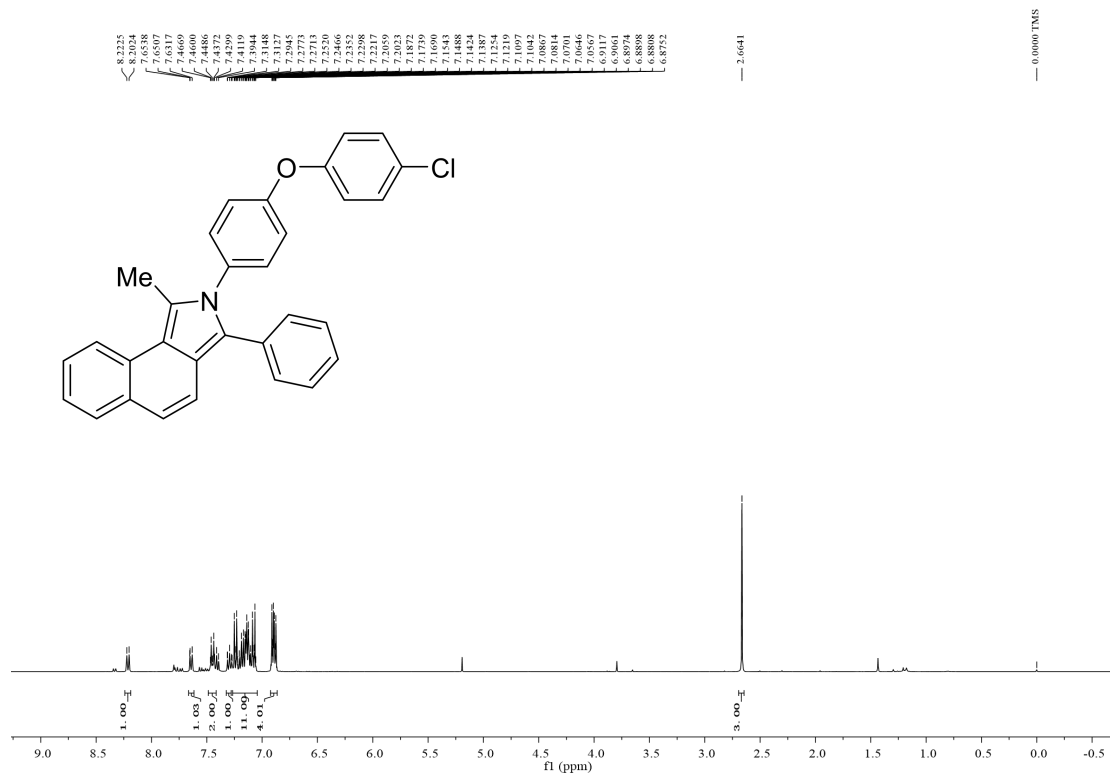
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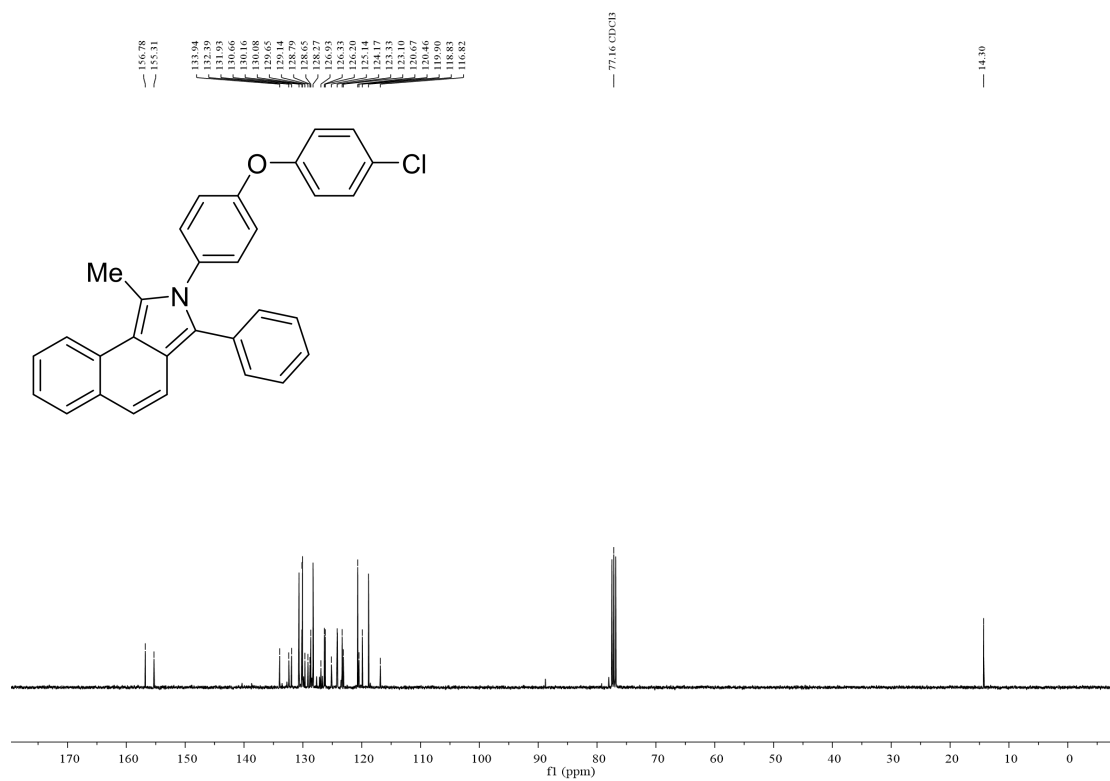
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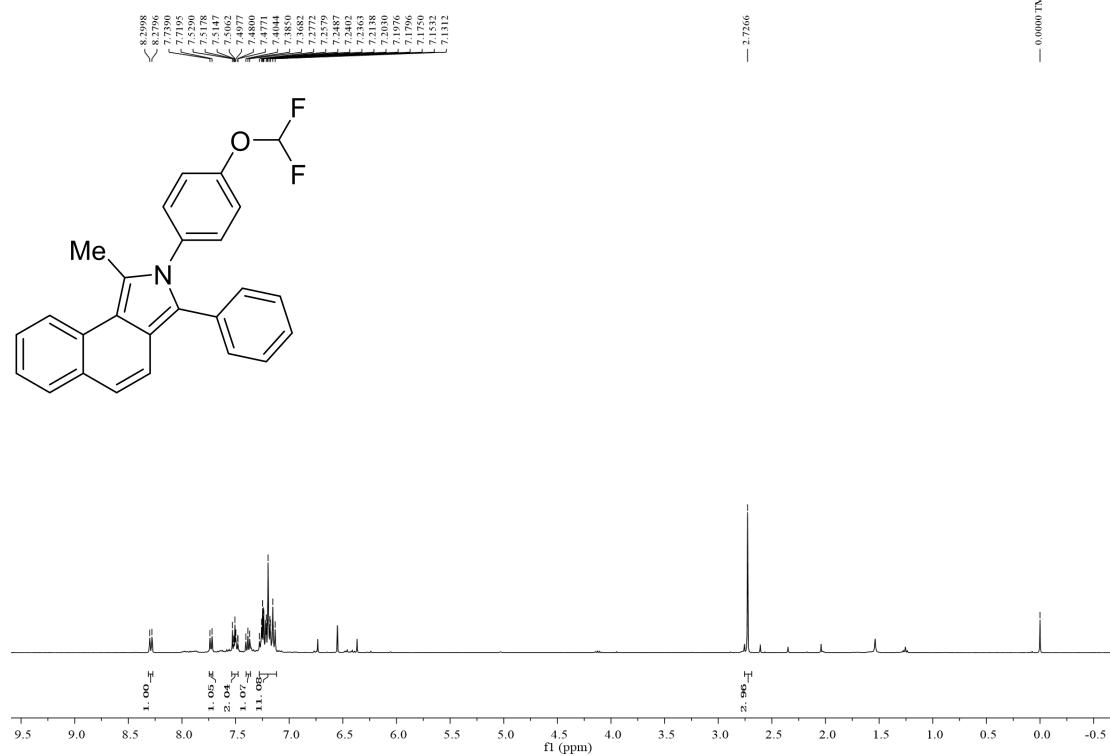
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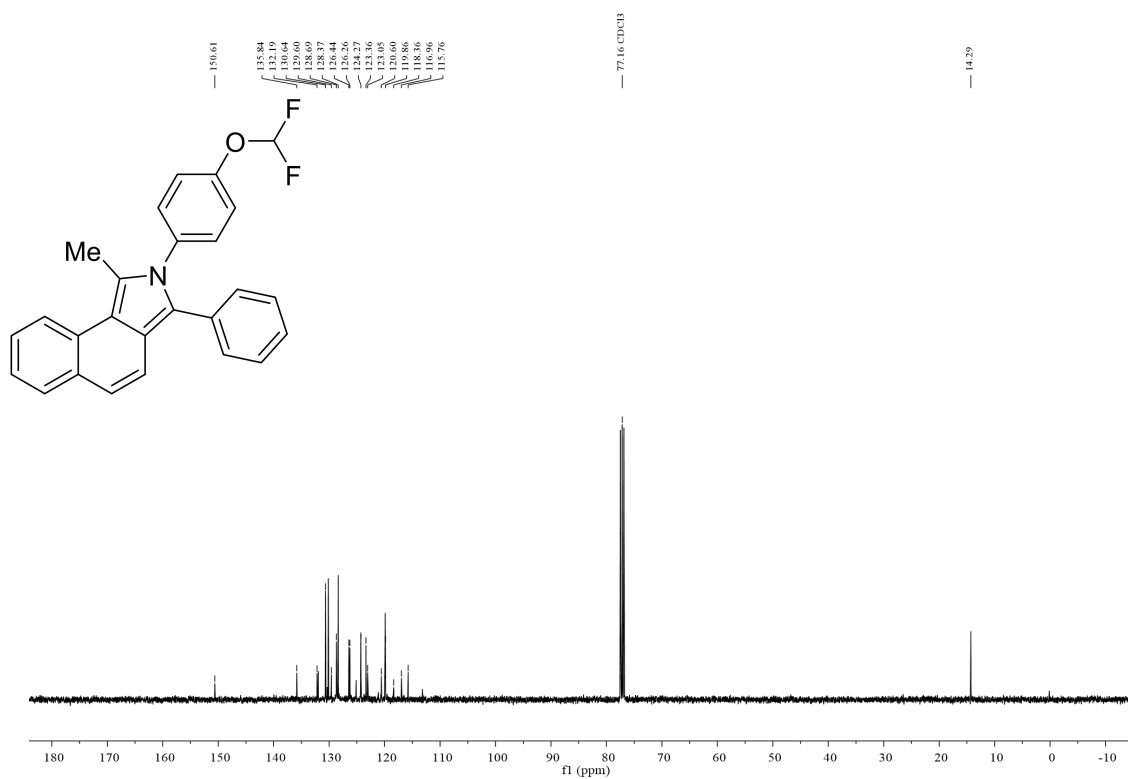
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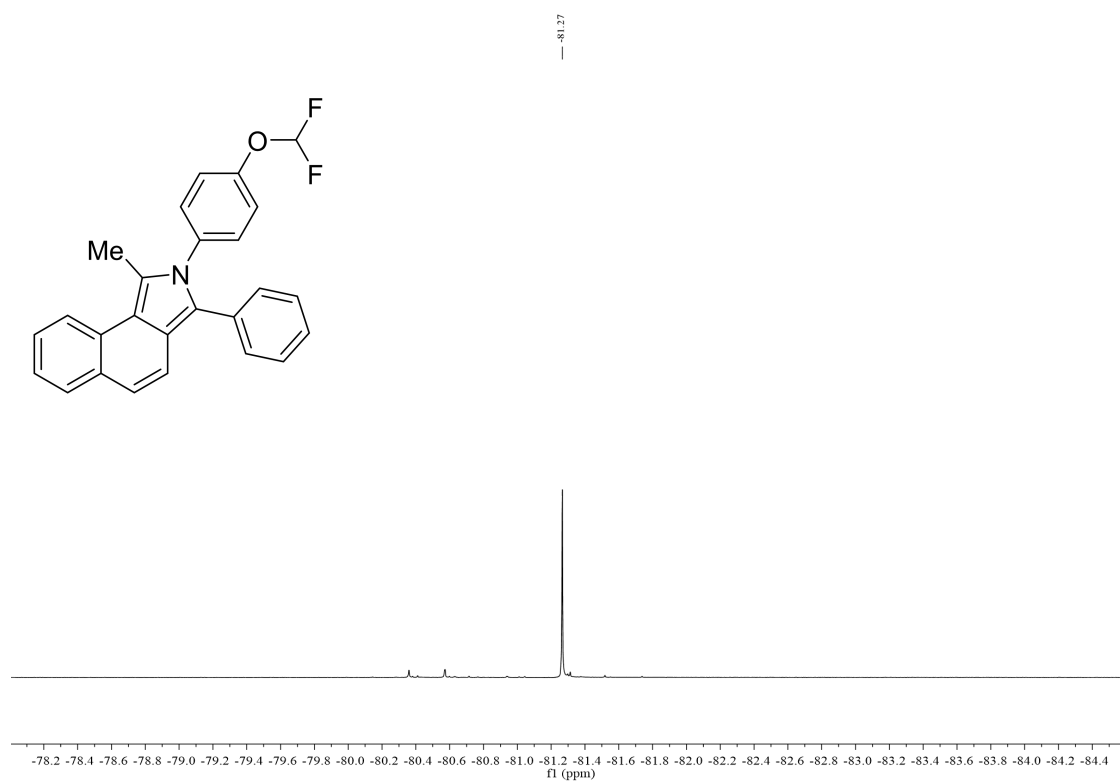
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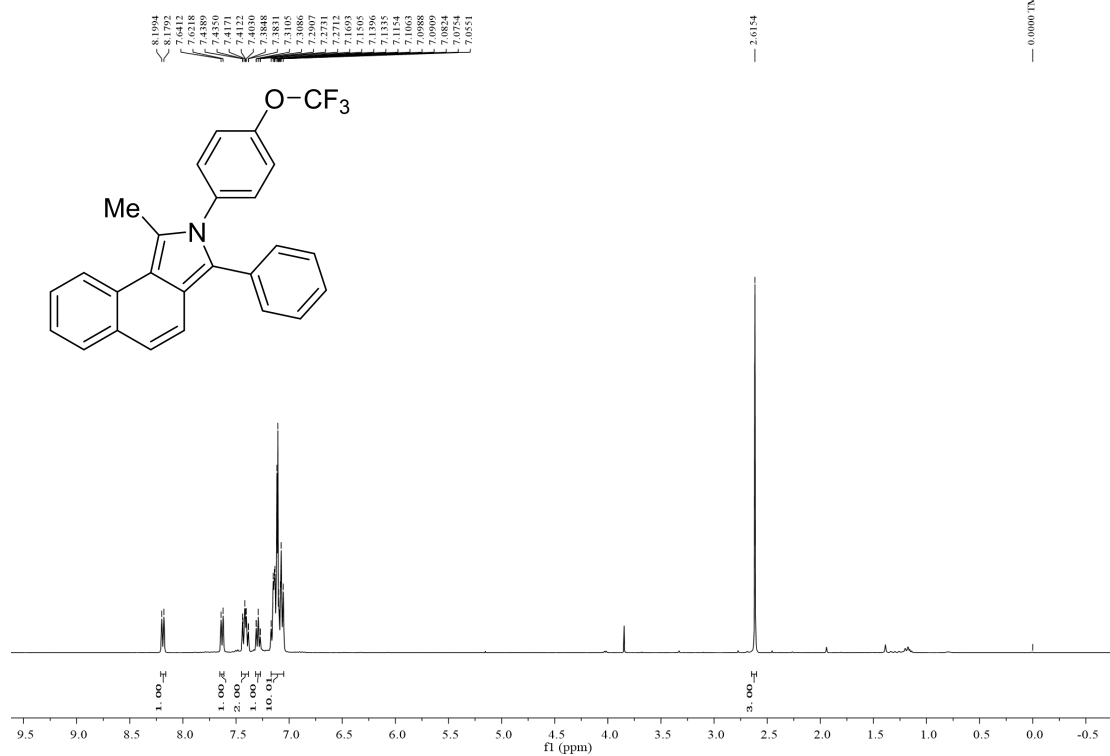
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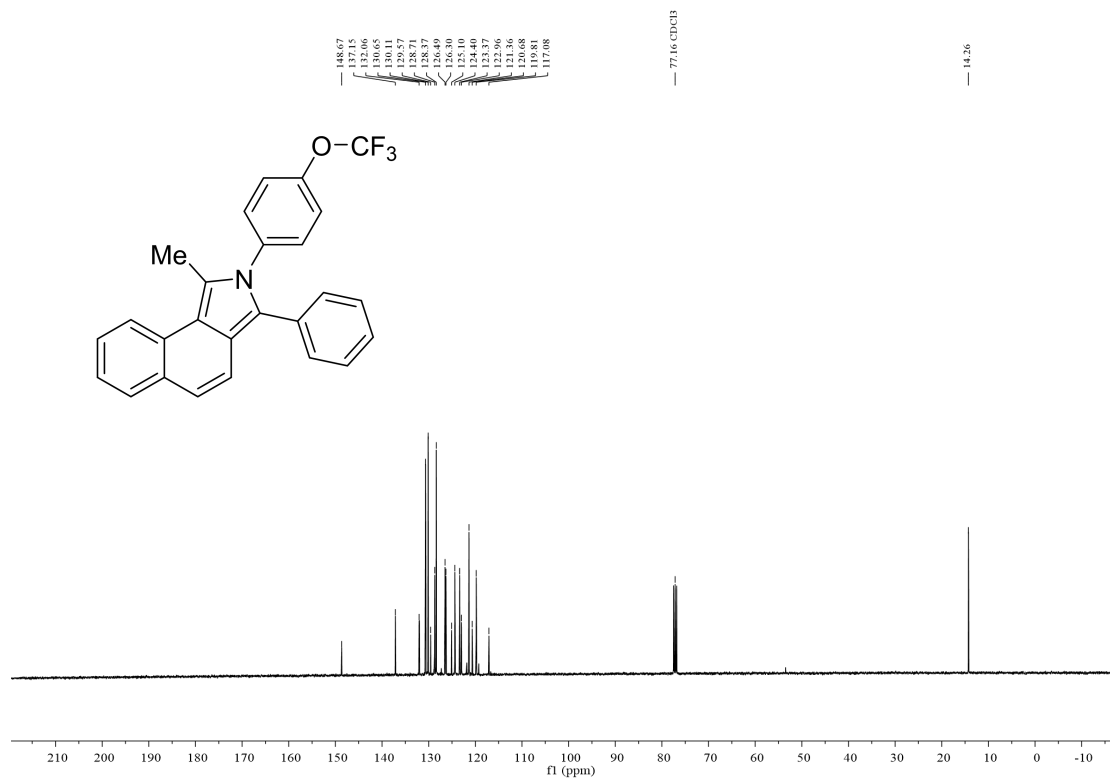
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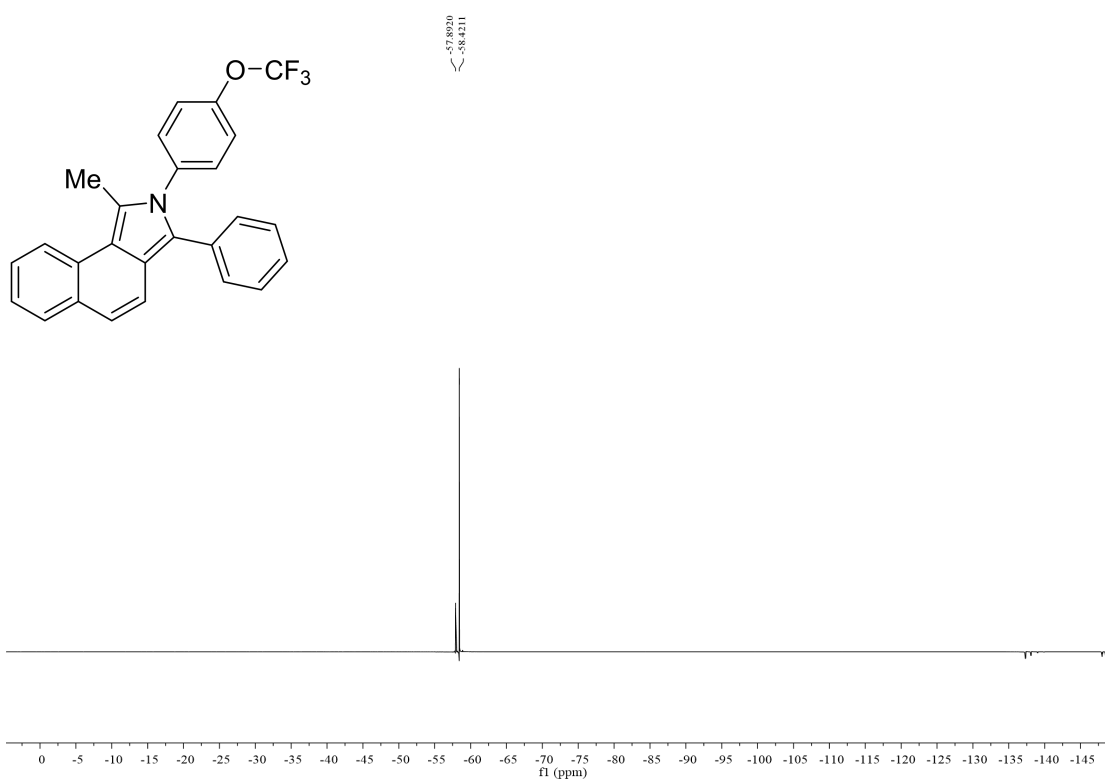
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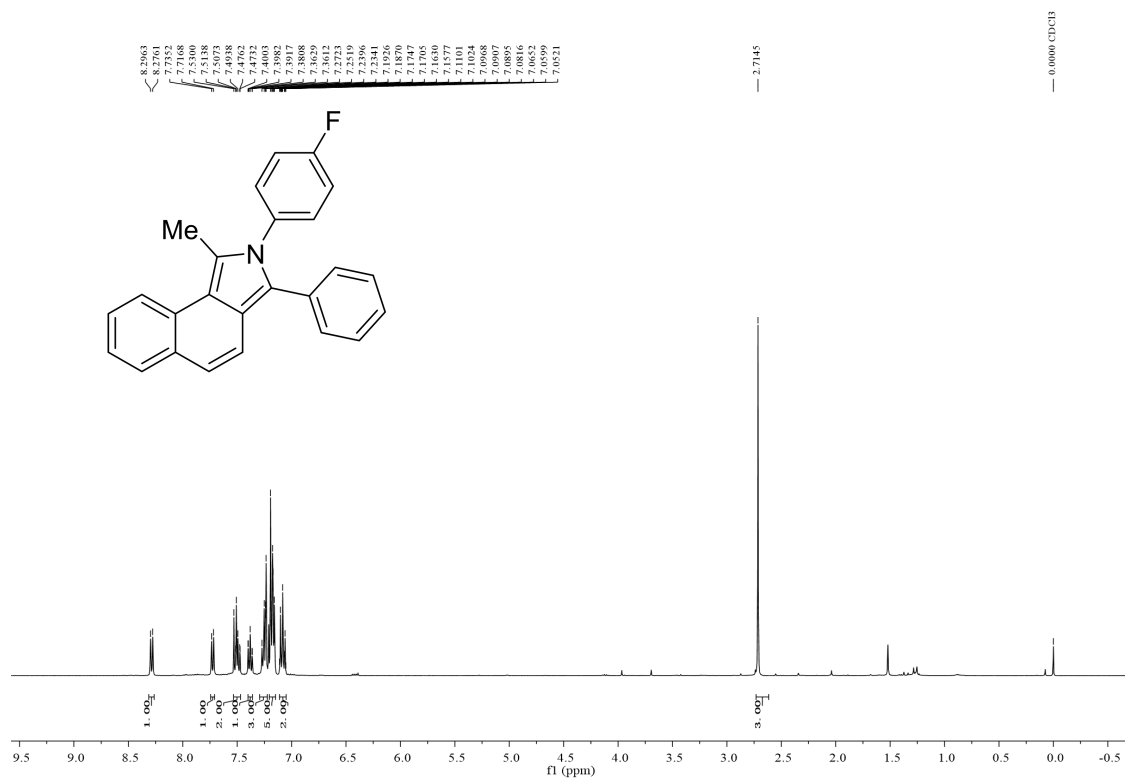
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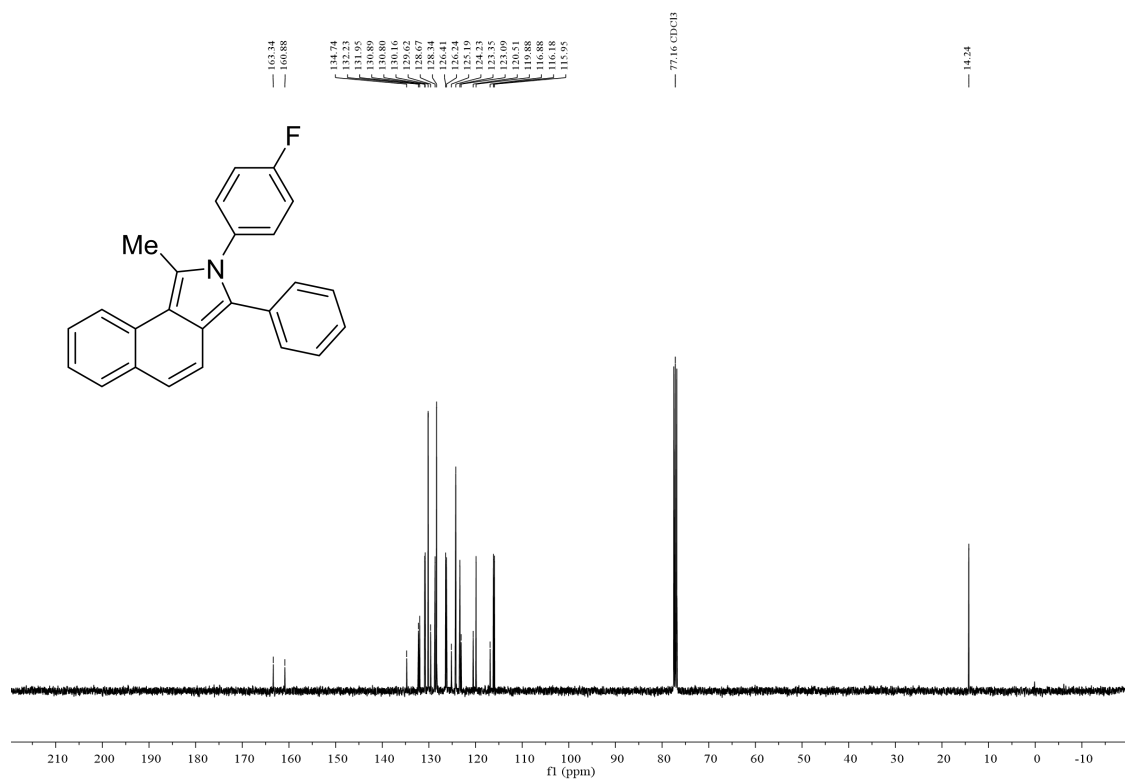
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¹H NMR-3o (400 MHz, CDCl₃)



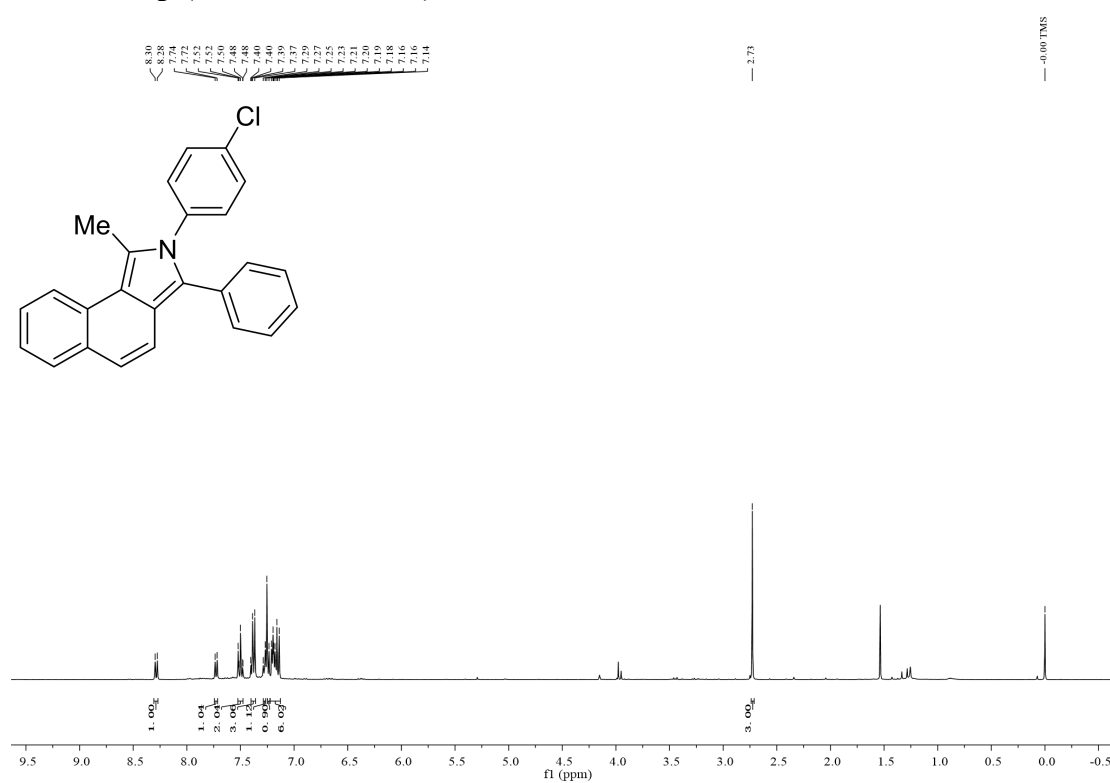
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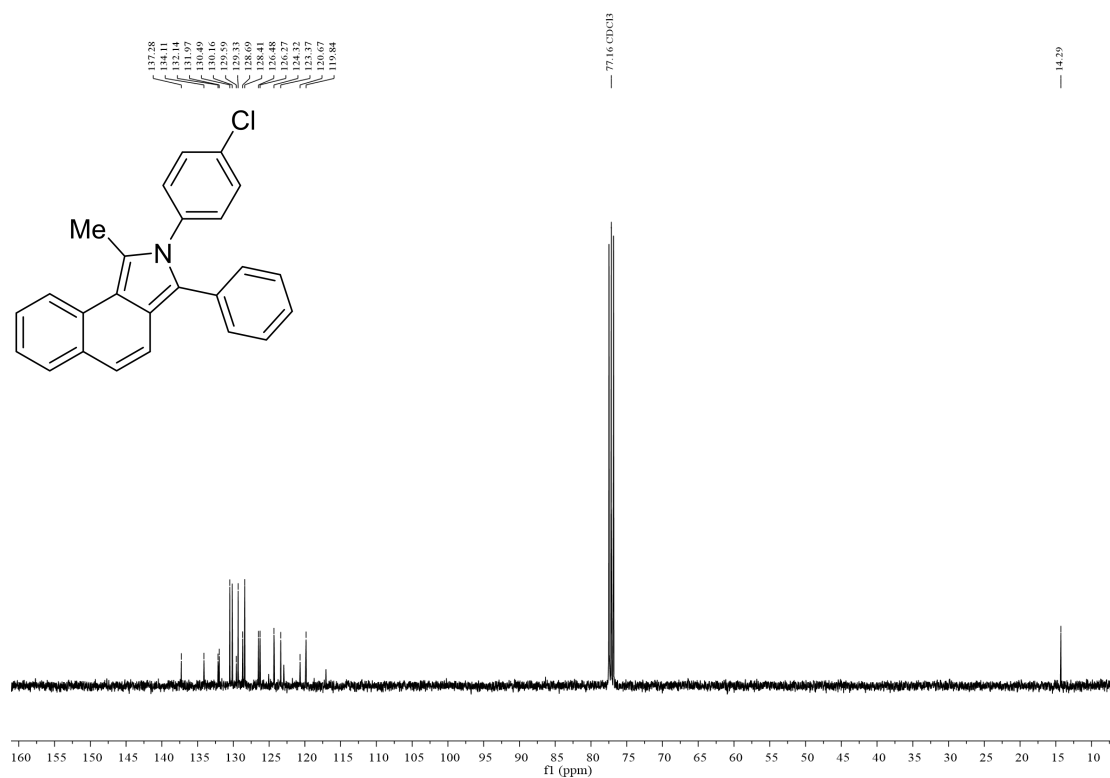
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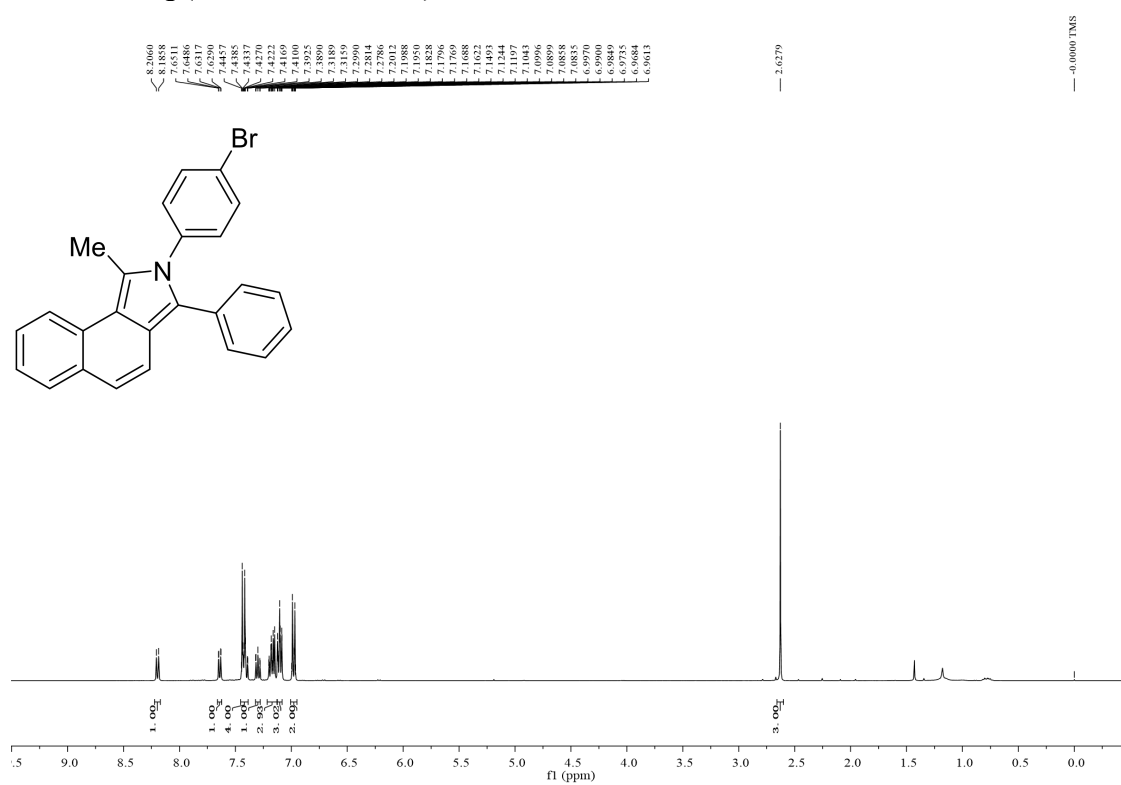
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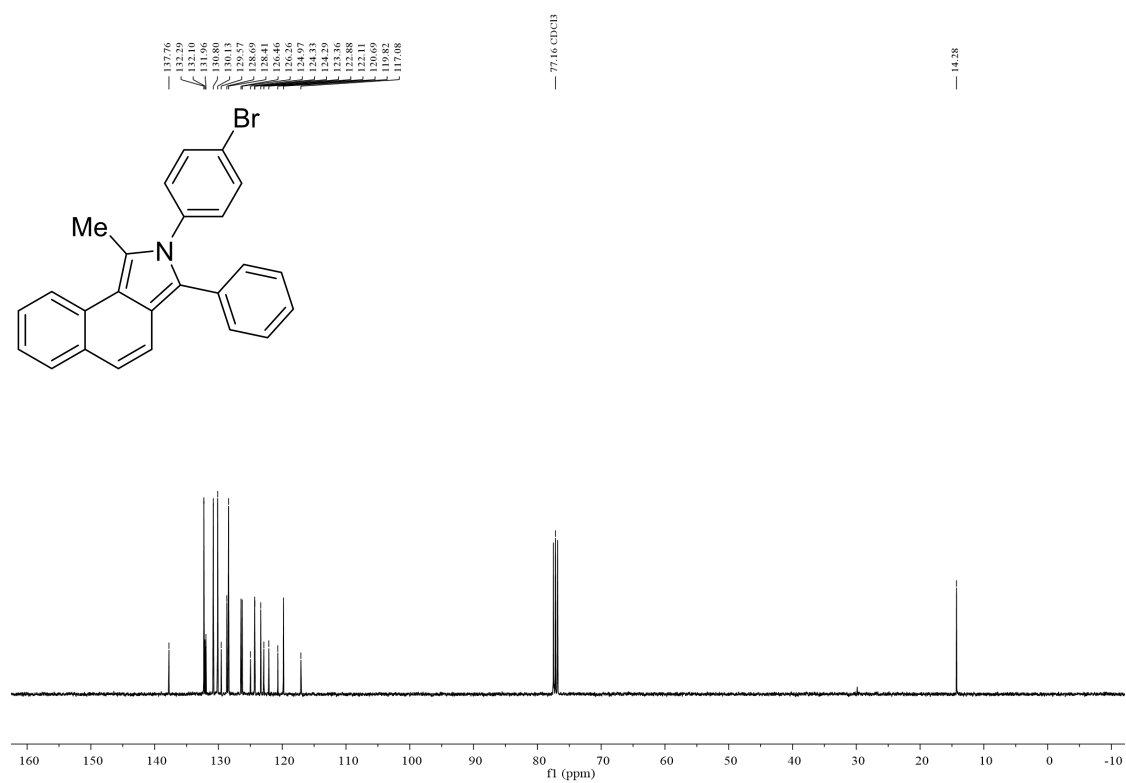
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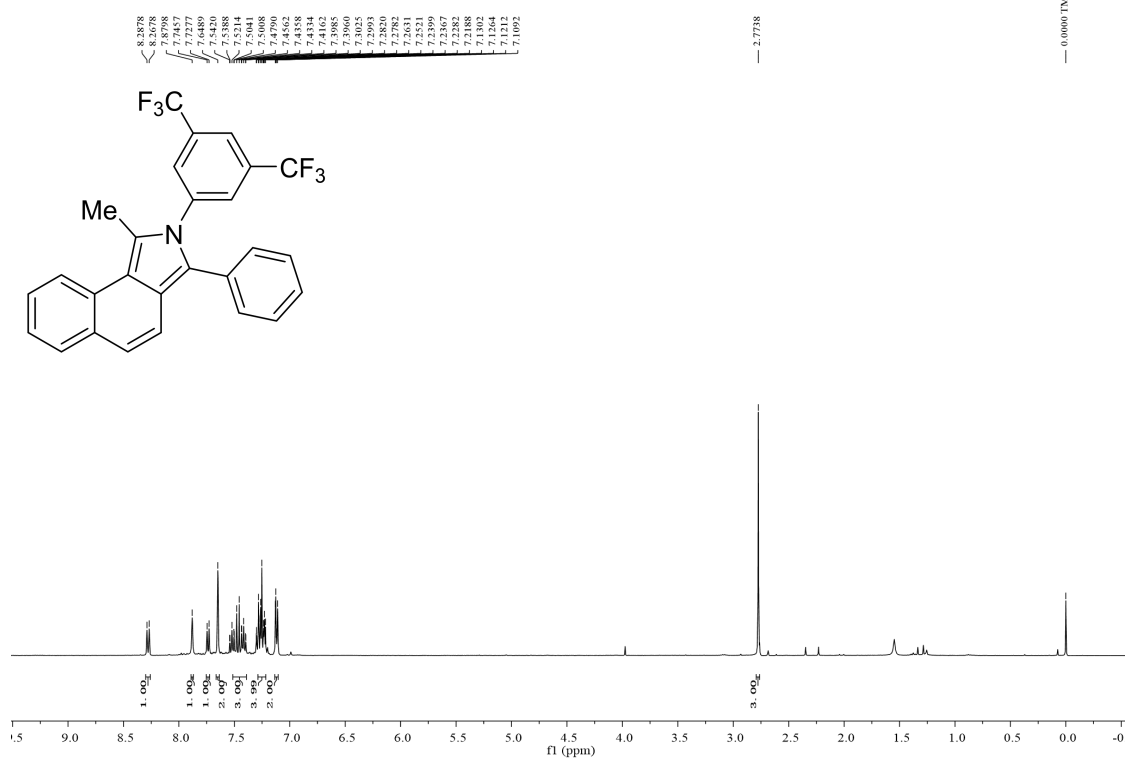
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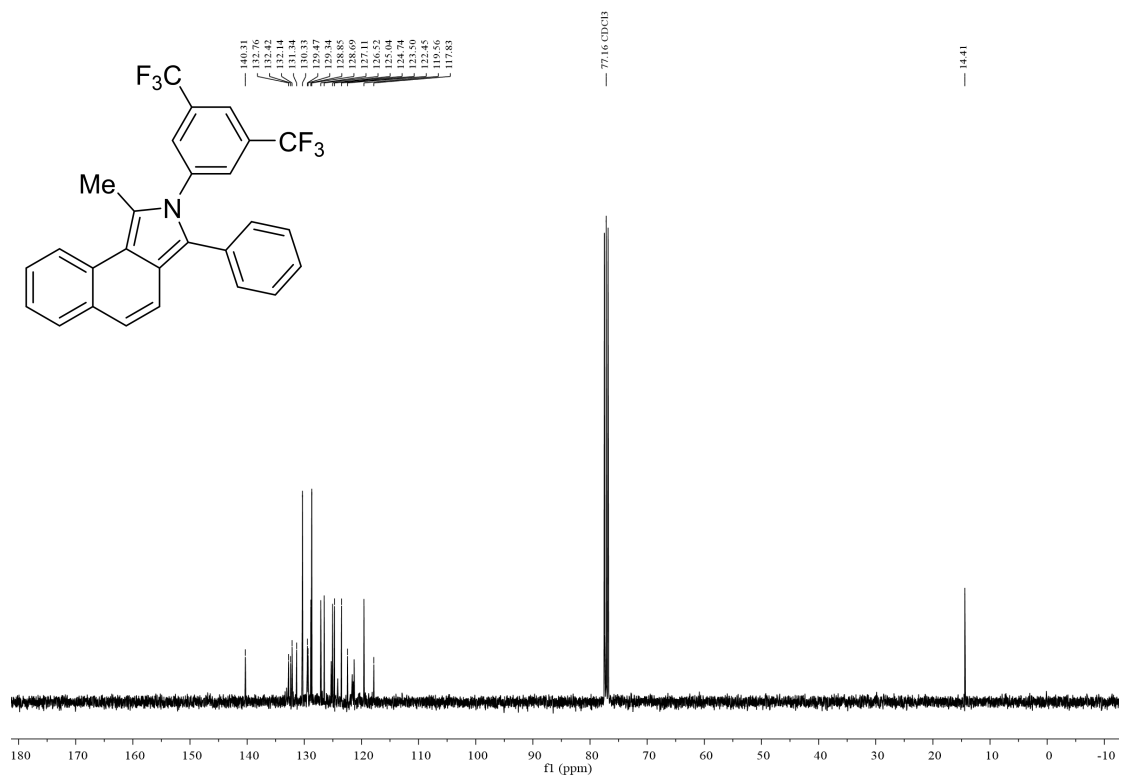
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¹H NMR-3r (400 MHz, CDCl₃)



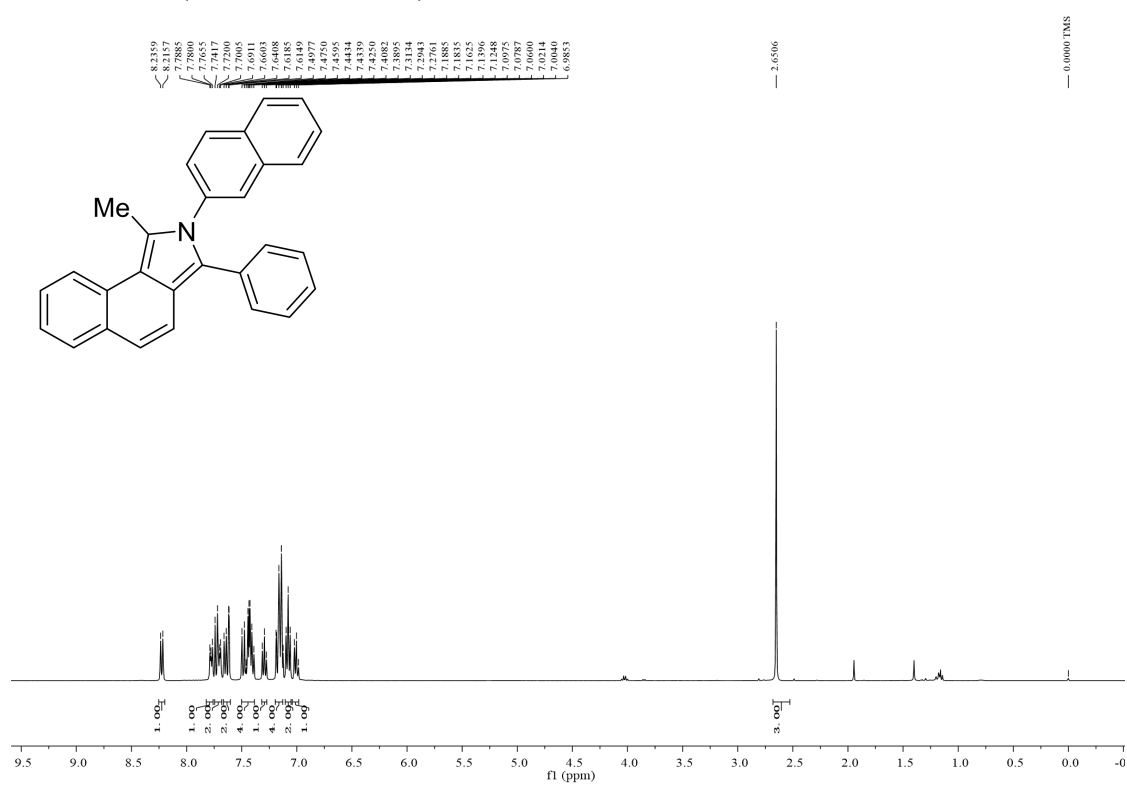
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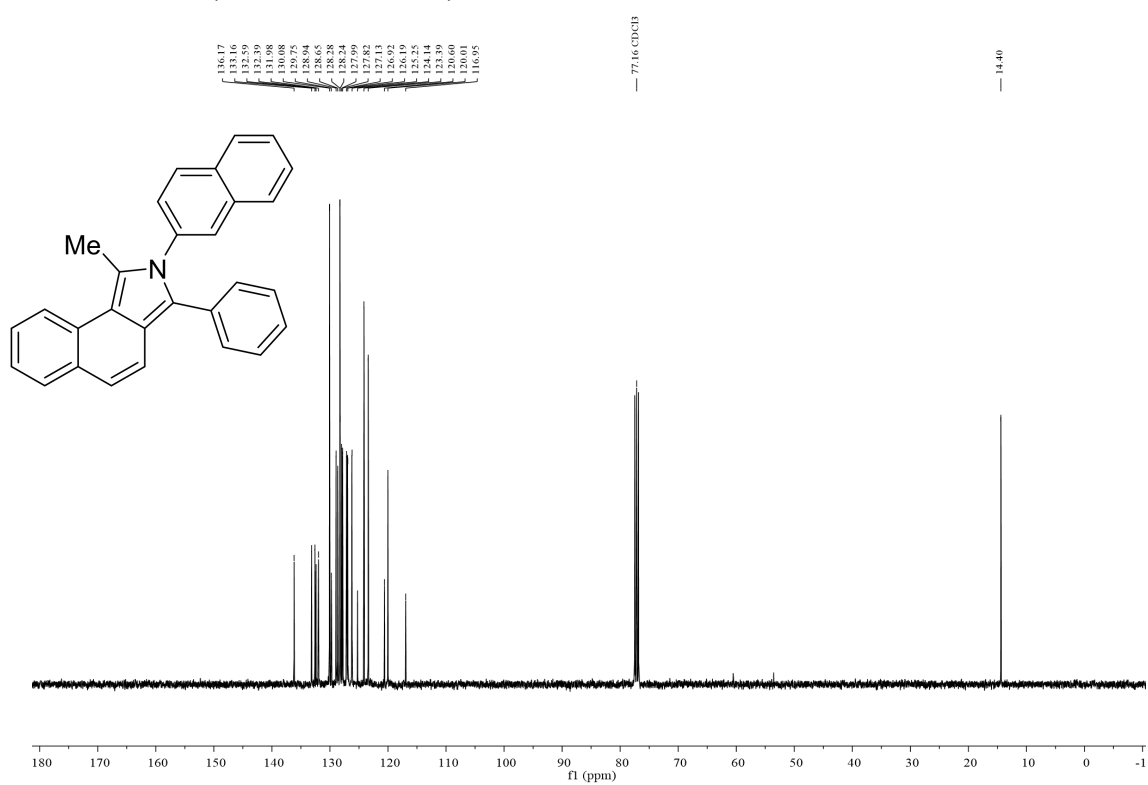
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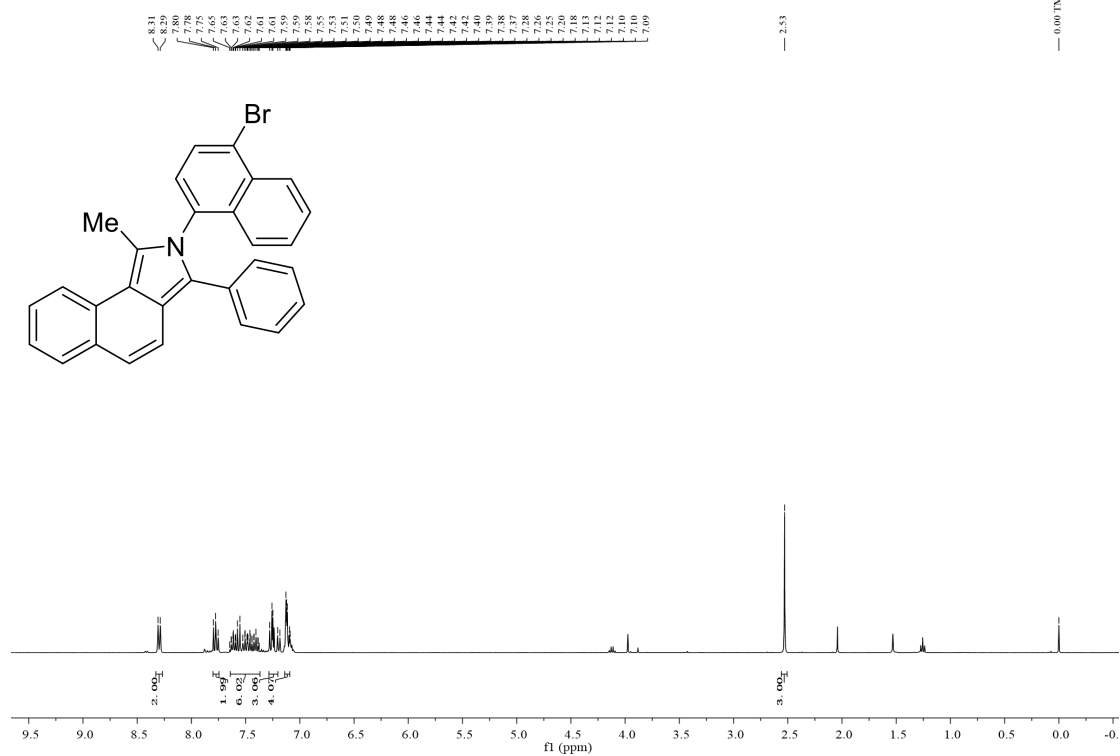
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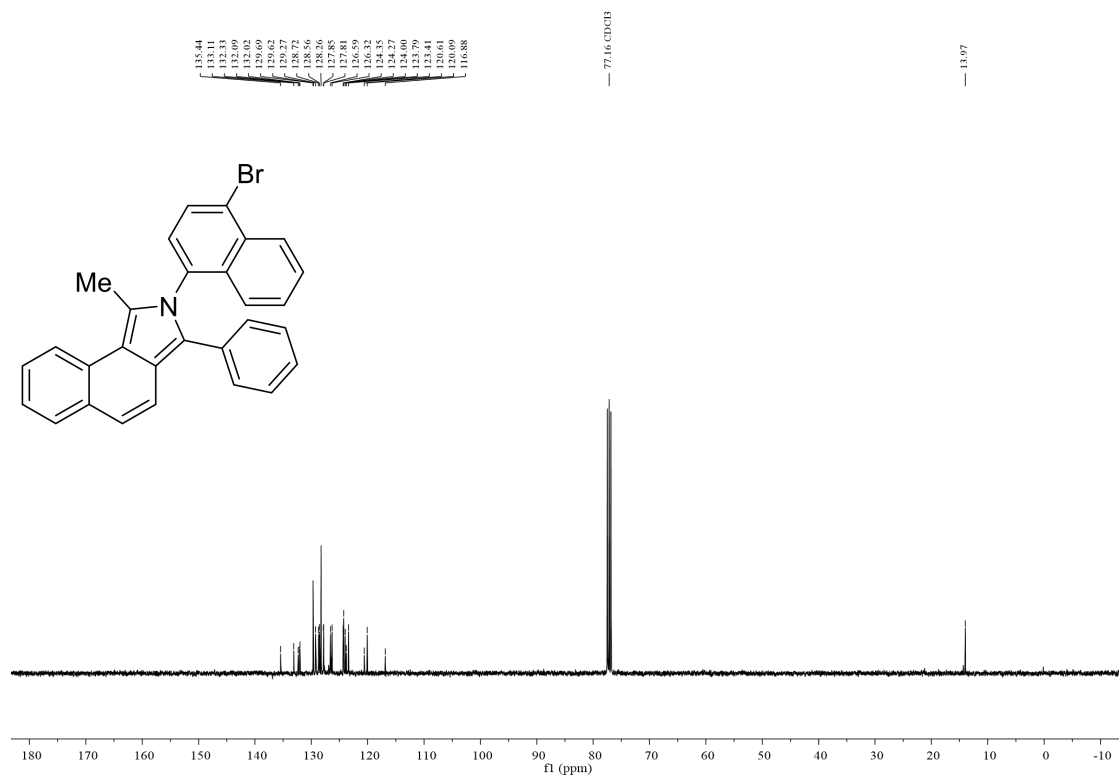
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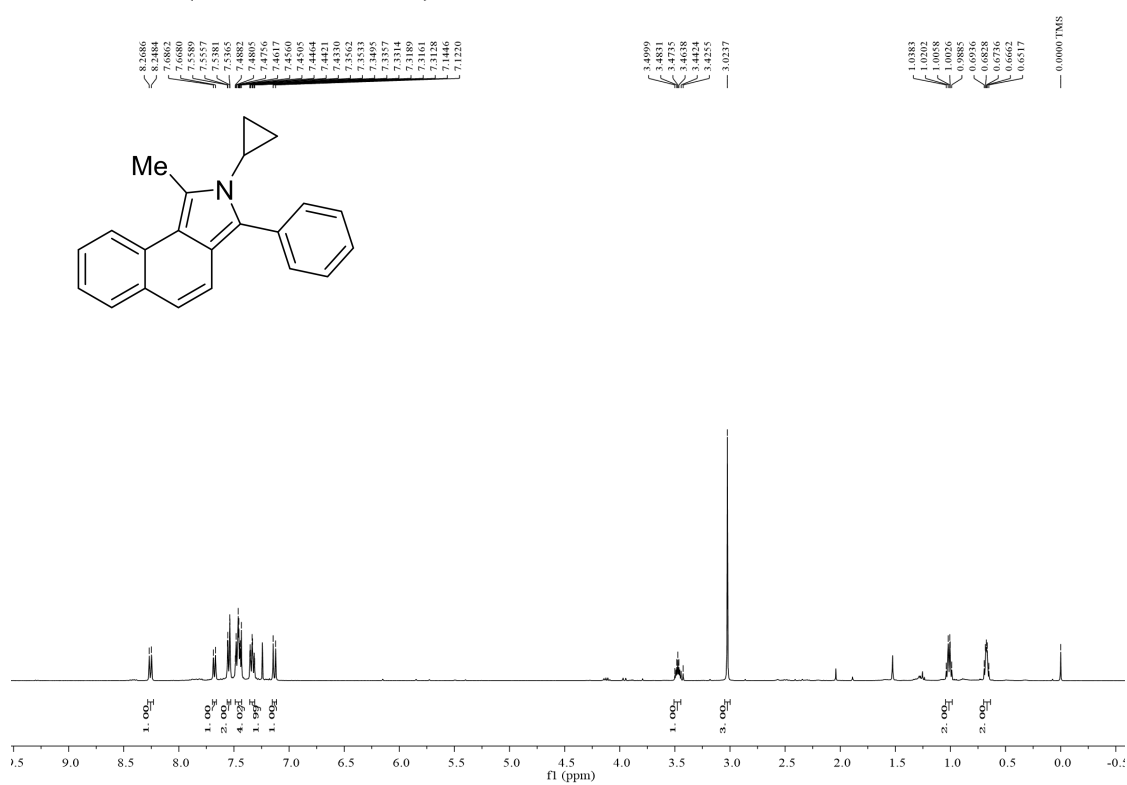
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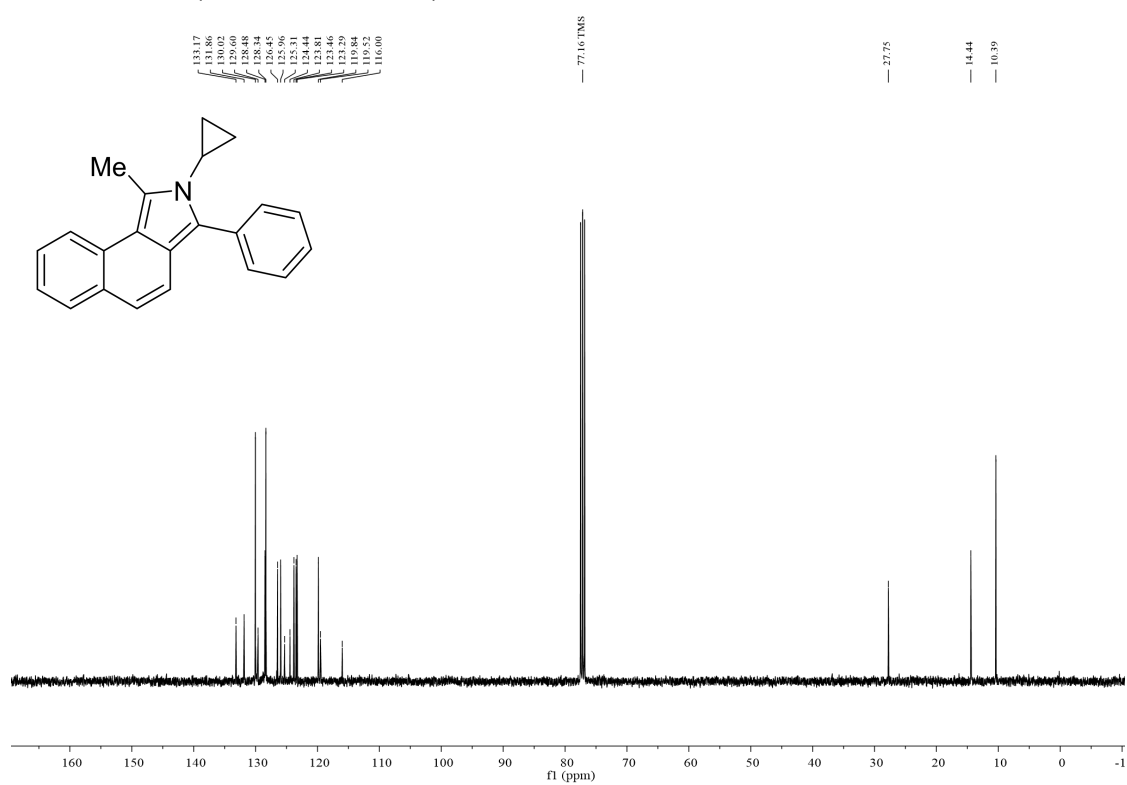
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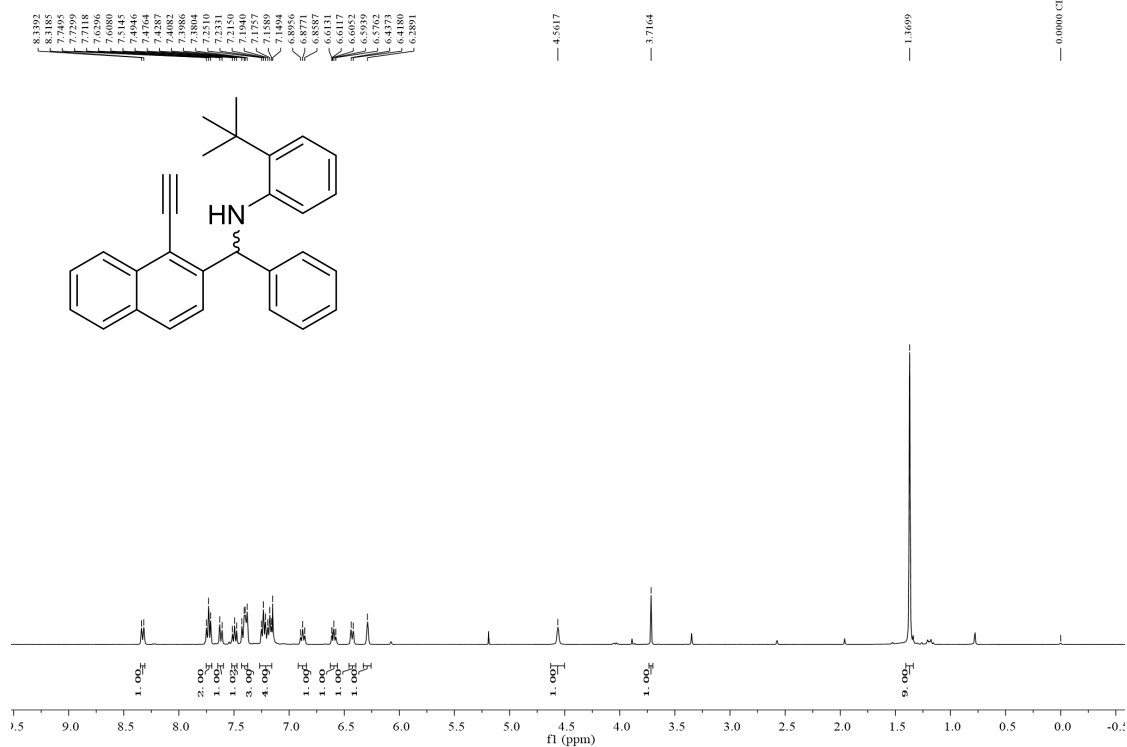
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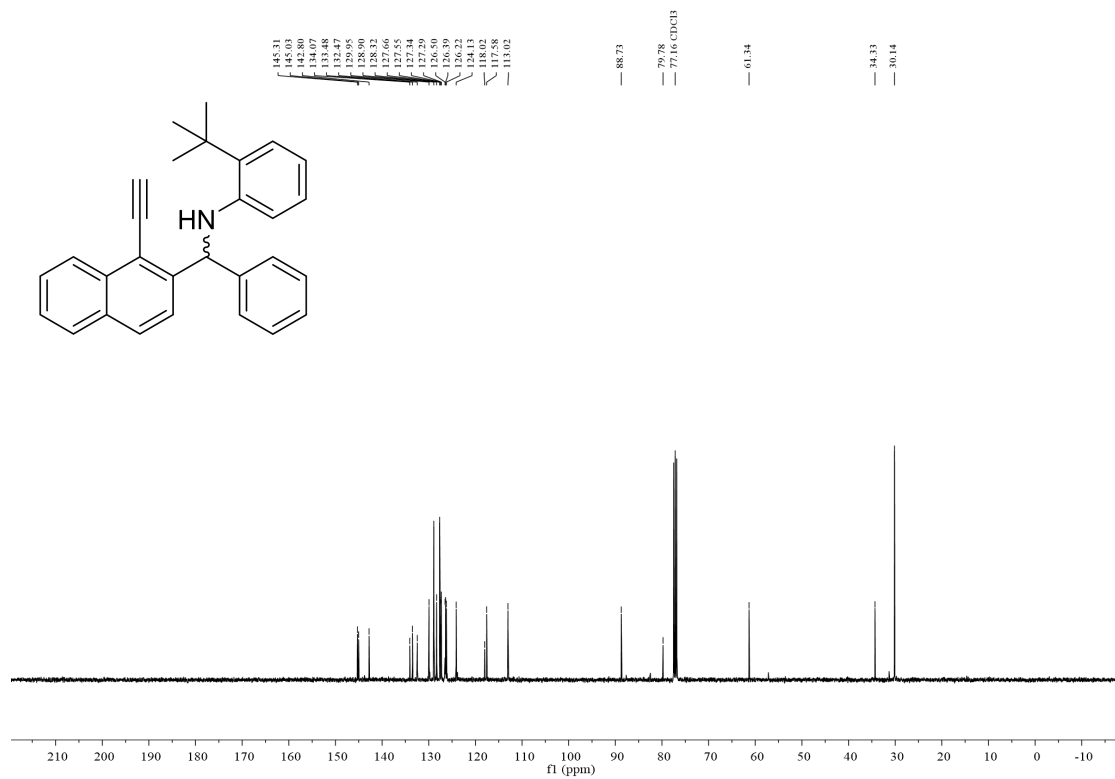
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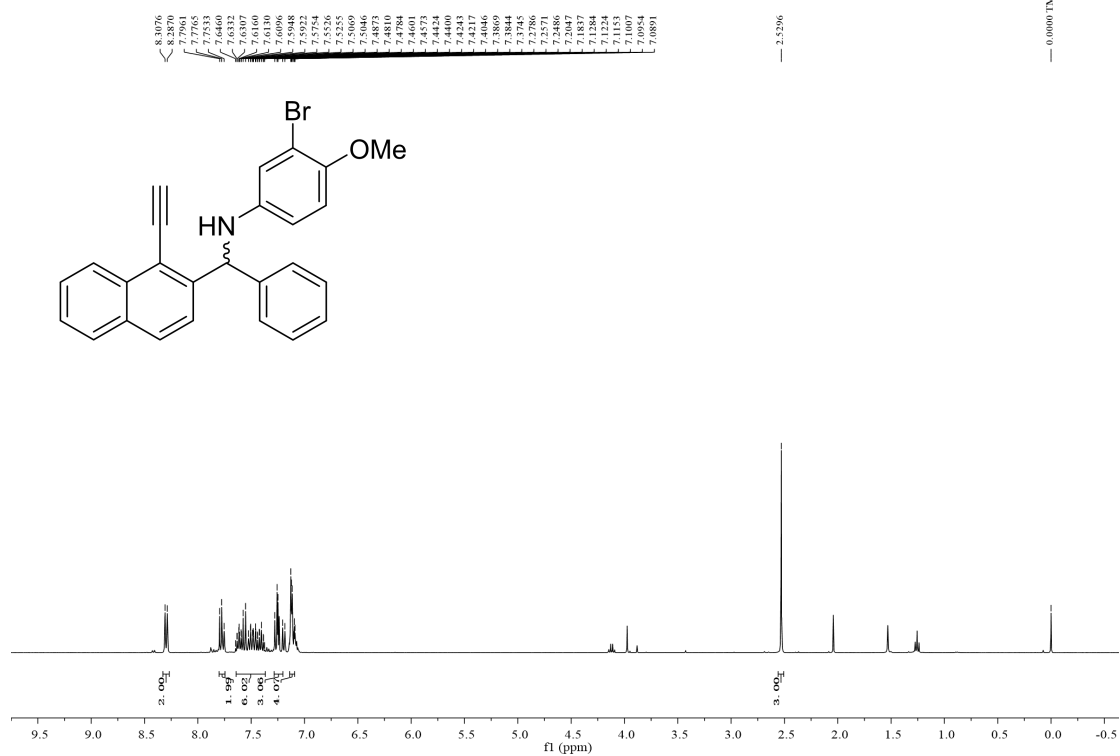
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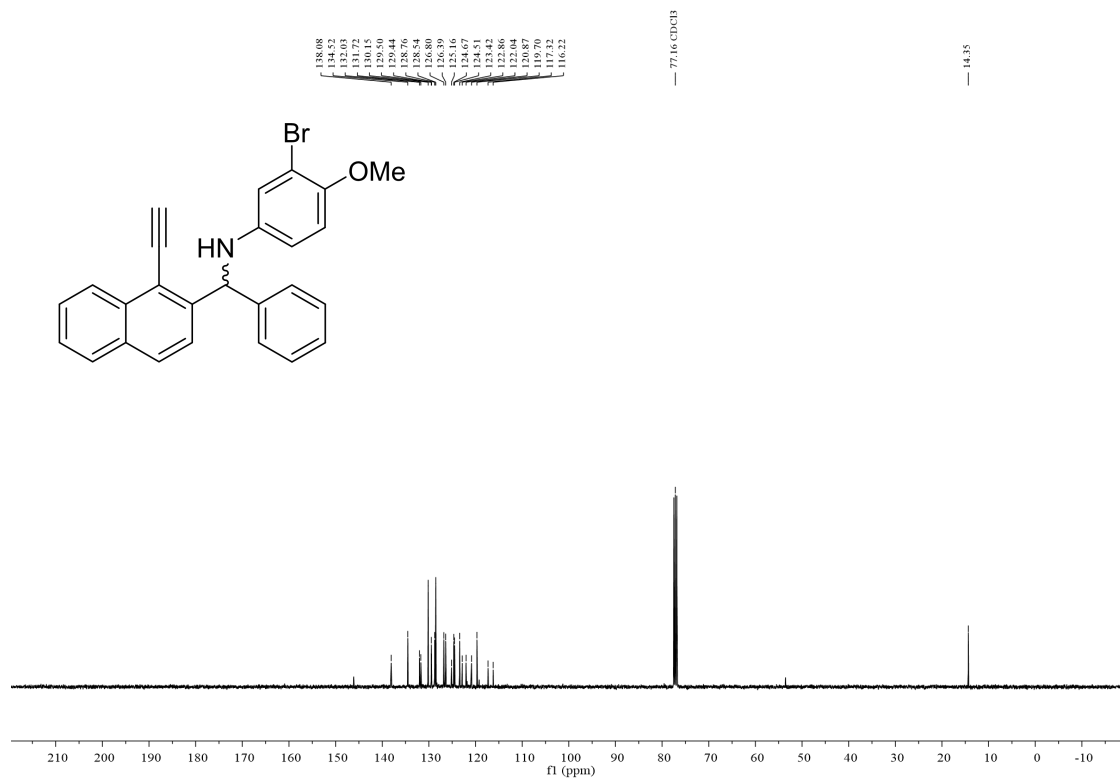
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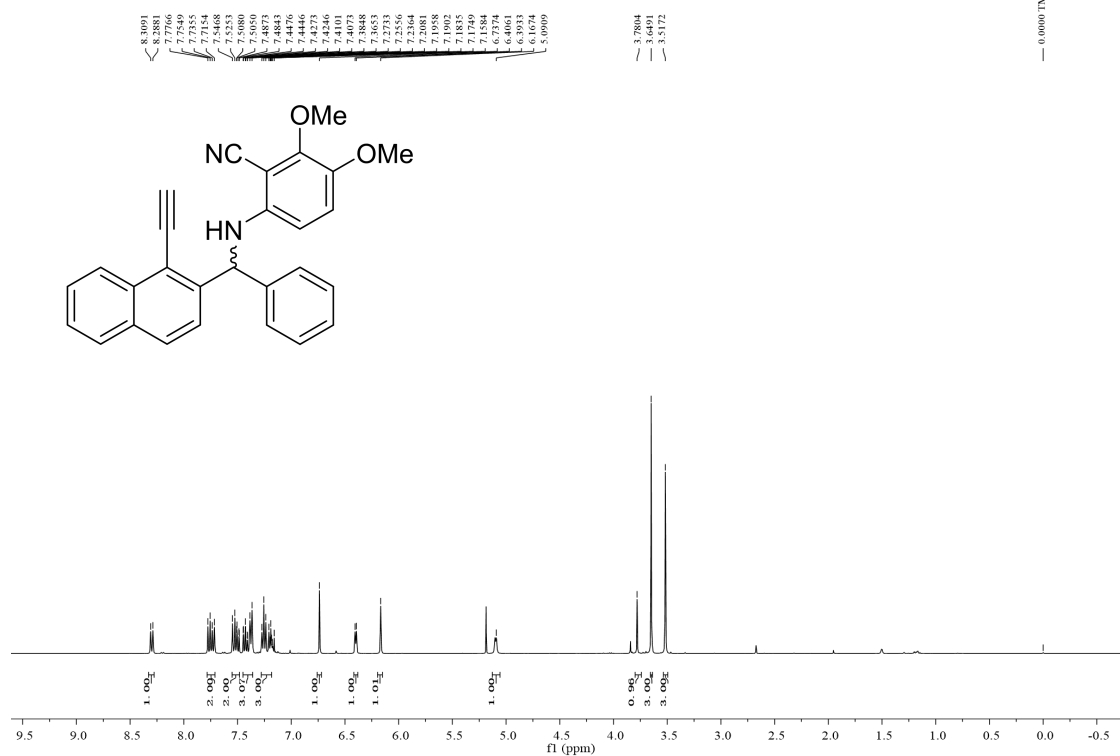
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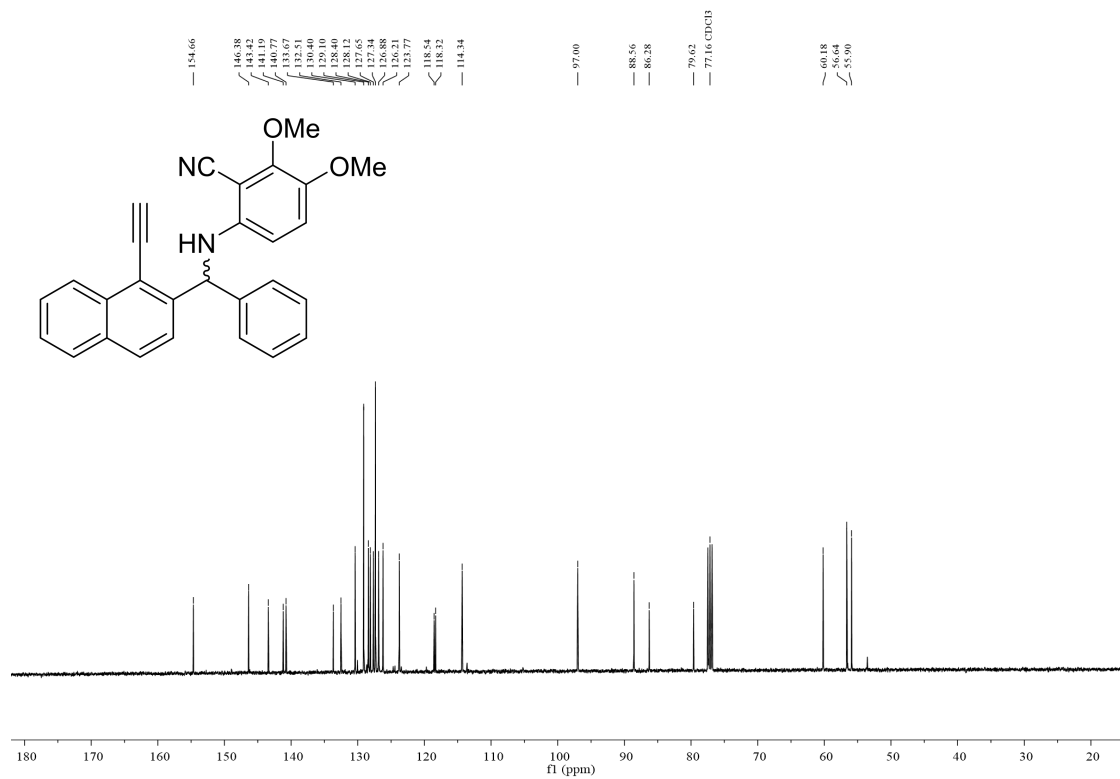
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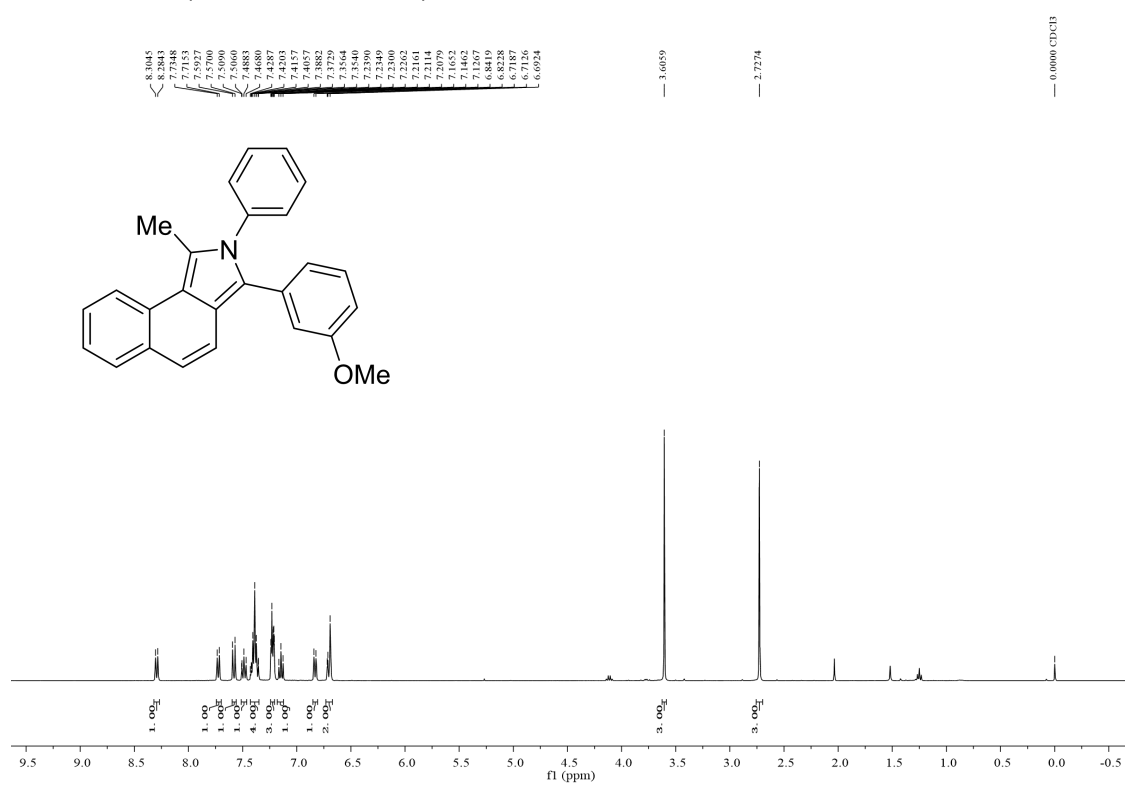
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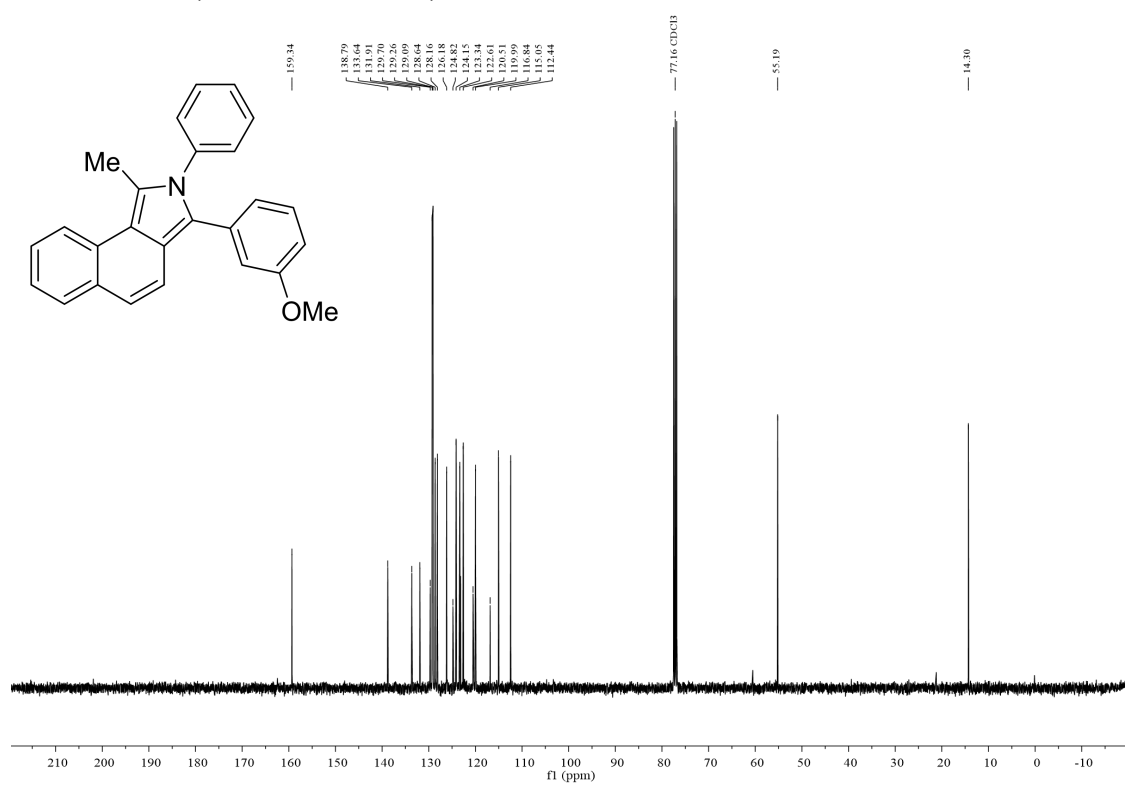
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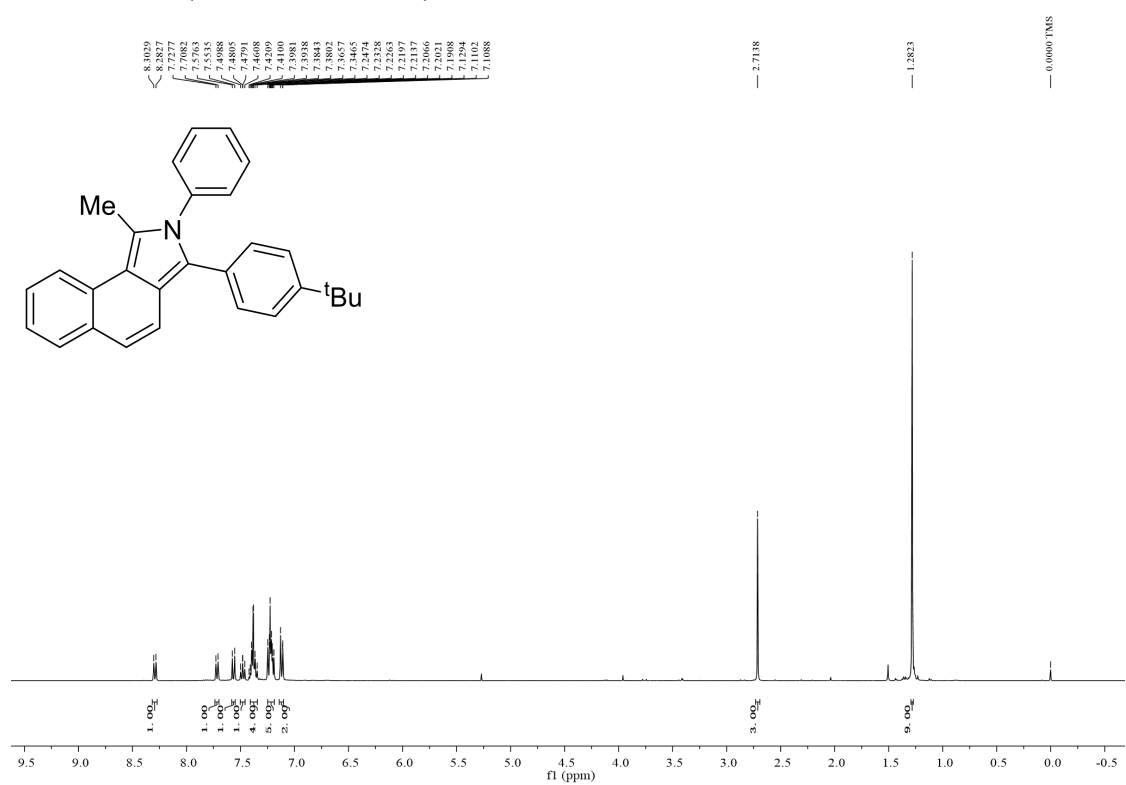
¹H NMR-4a (400 MHz, CDCl₃)



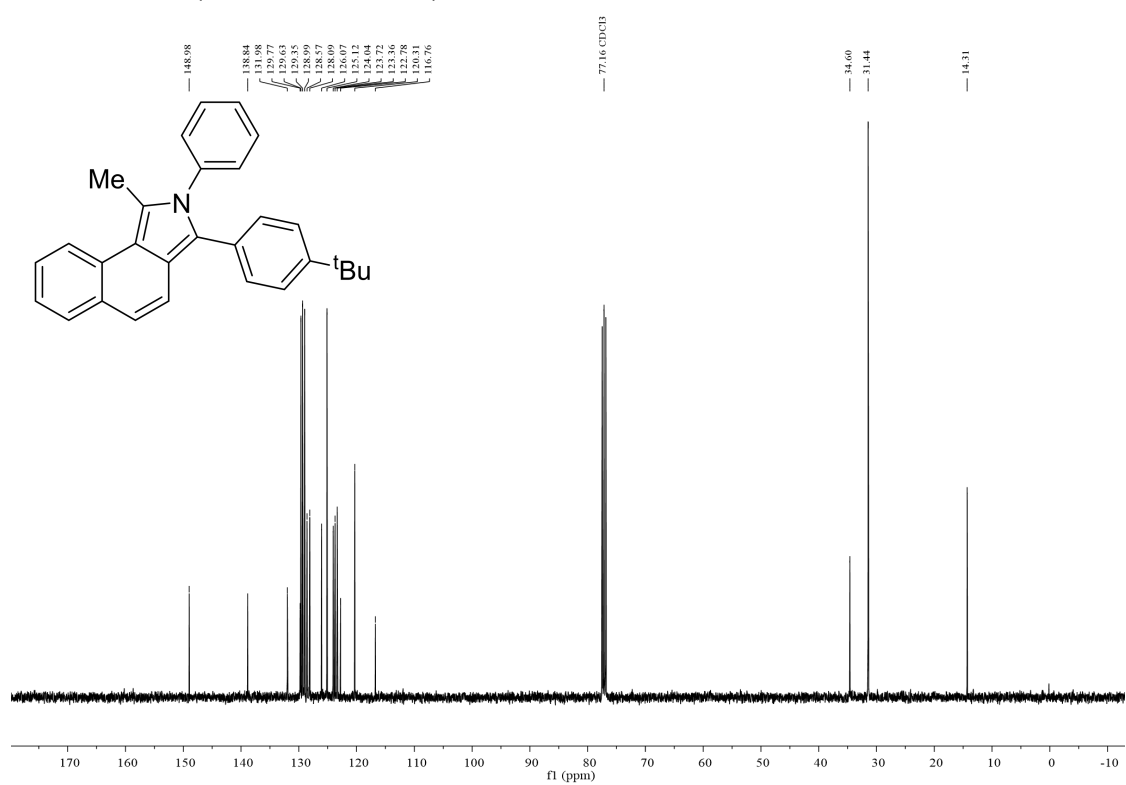
¹³C NMR-4a (100 MHz, CDCl₃)



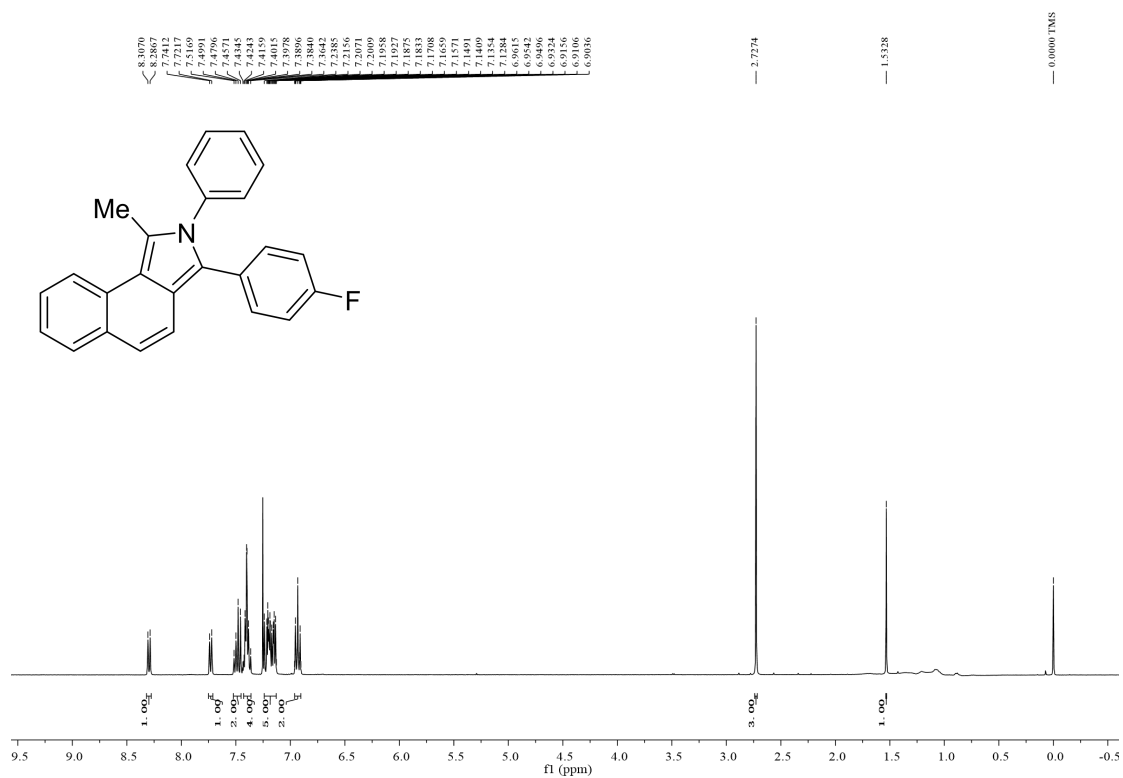
¹H NMR-4b (400 MHz, CDCl₃)



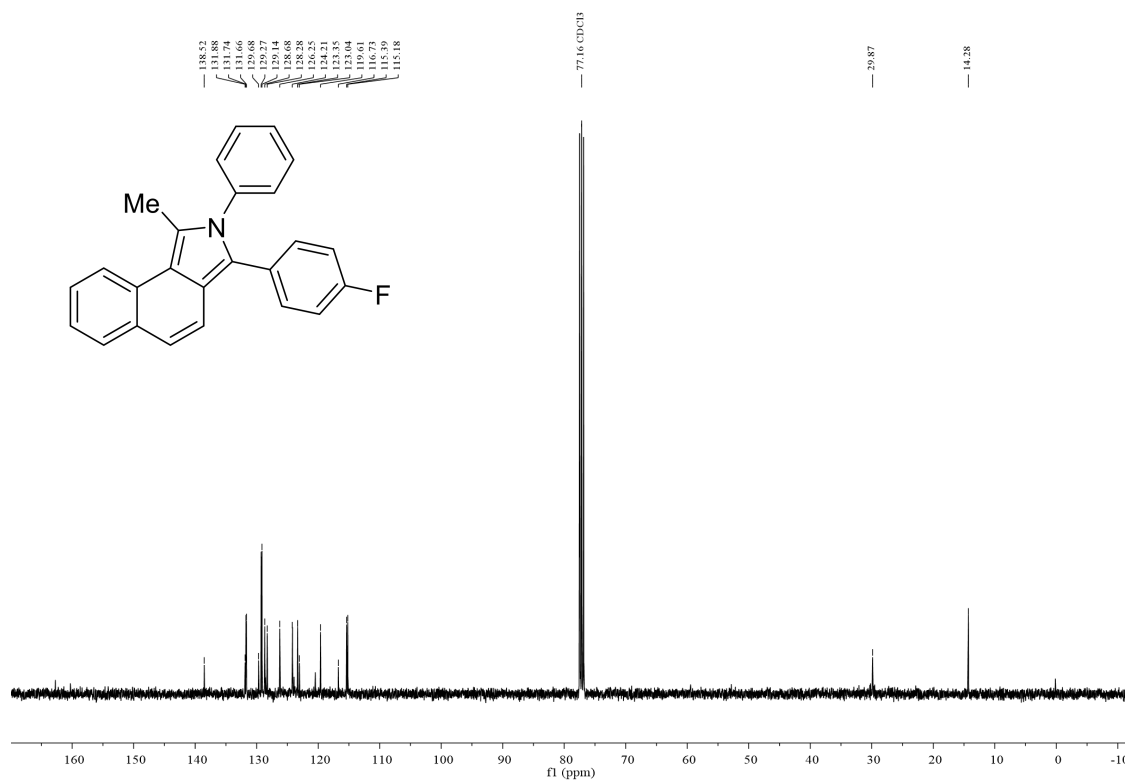
¹³C NMR-4b (100 MHz, CDCl₃)



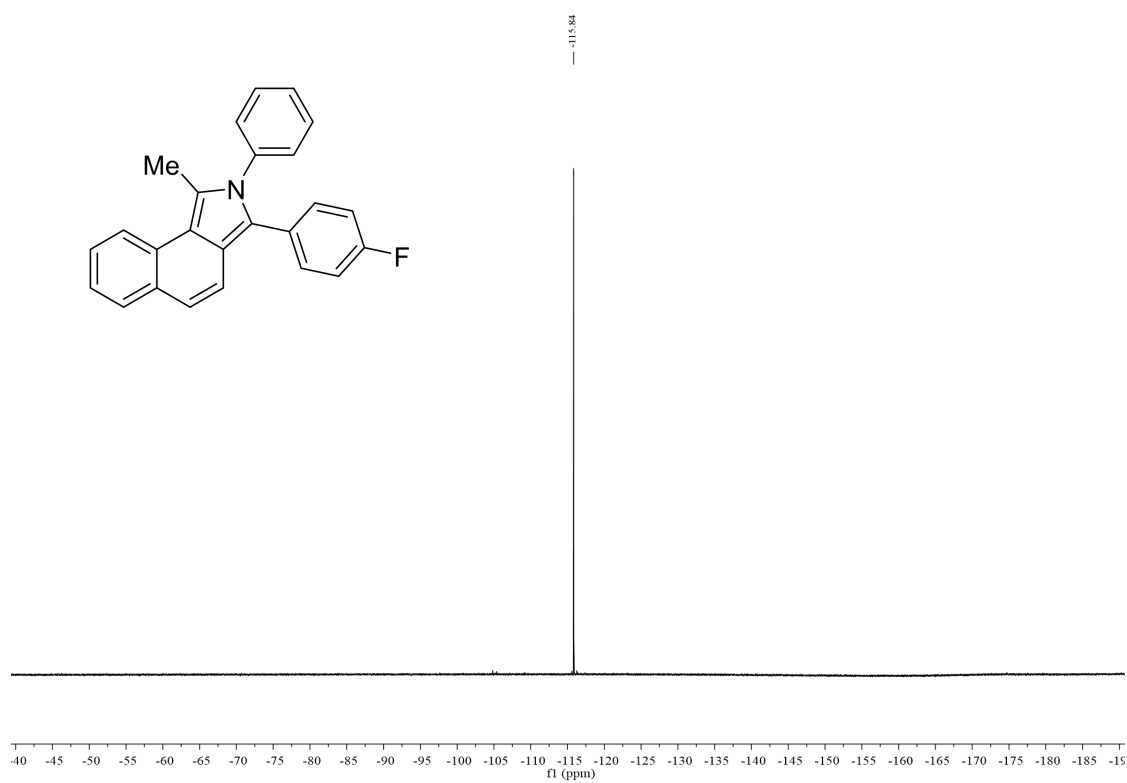
¹H NMR-4d (400 MHz, CDCl₃)



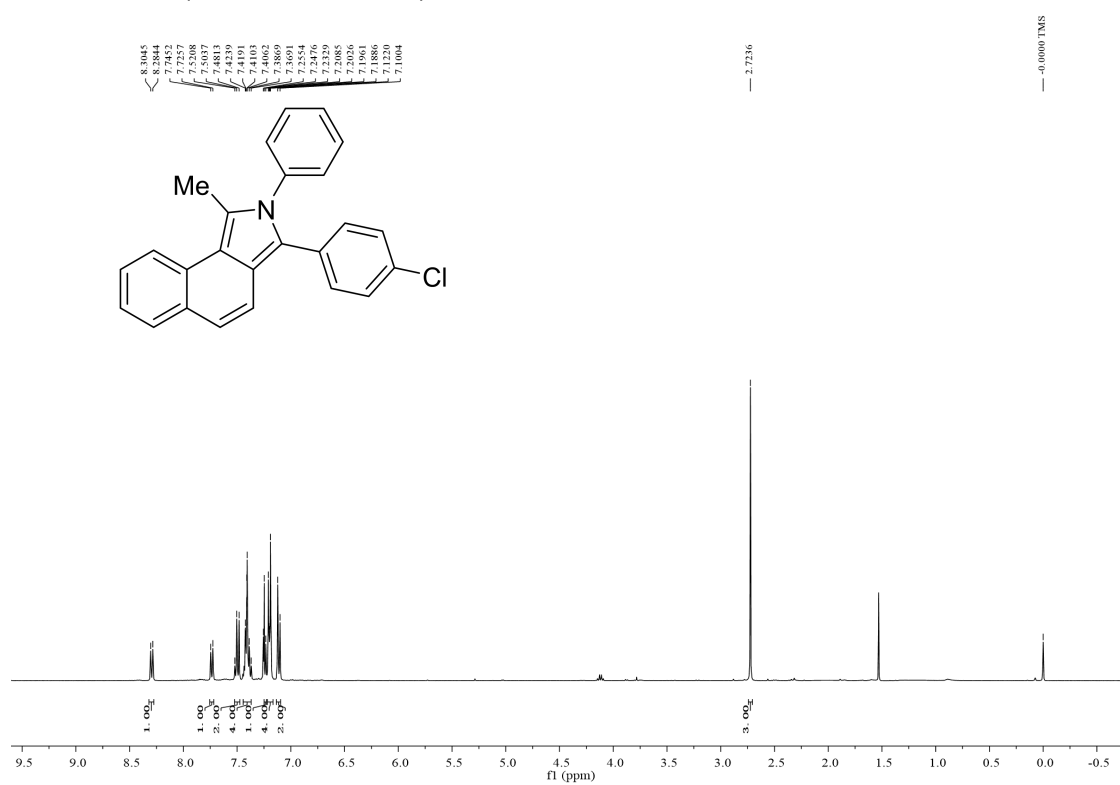
¹³C NMR-4d (100 MHz, CDCl₃)



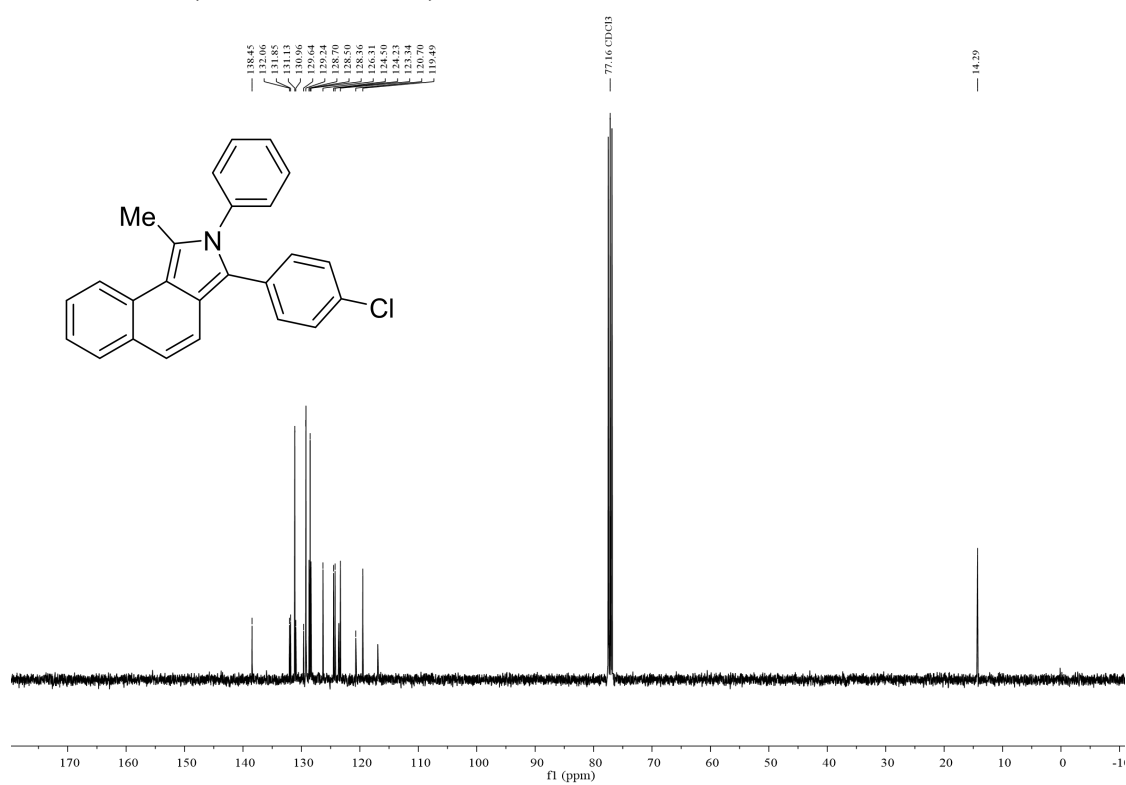
¹⁹F NMR-4d (376 MHz, CDCl₃)



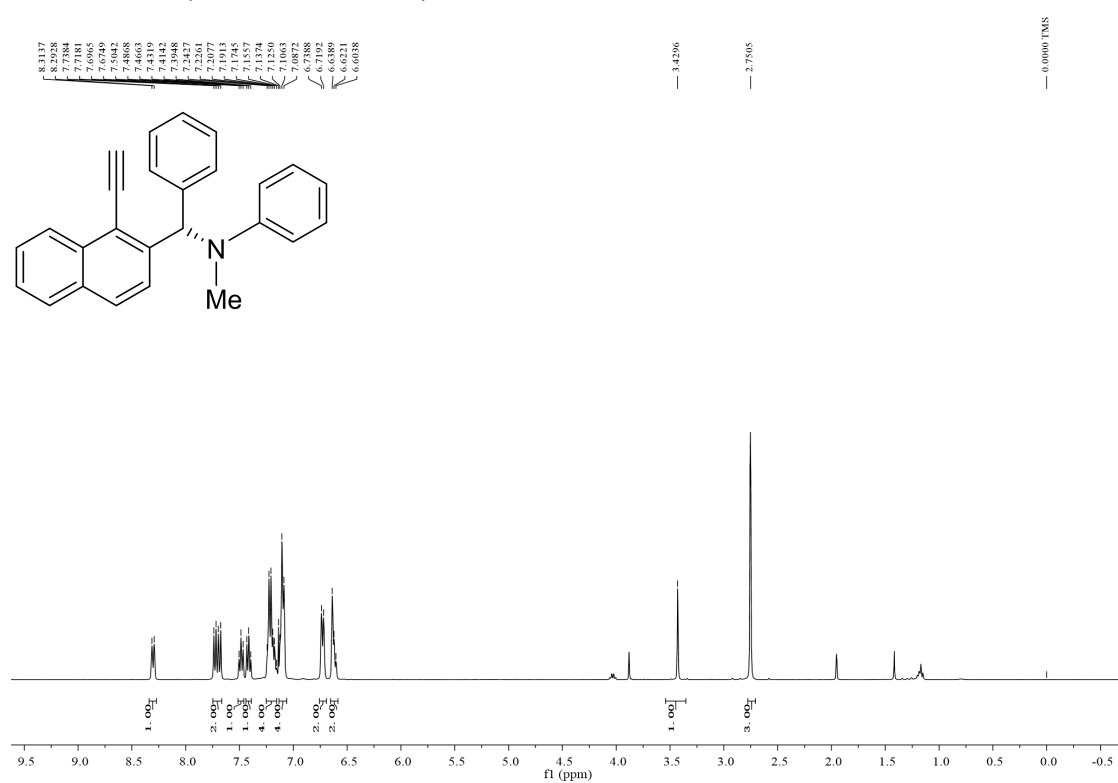
¹H NMR-4e (400 MHz, CDCl₃)



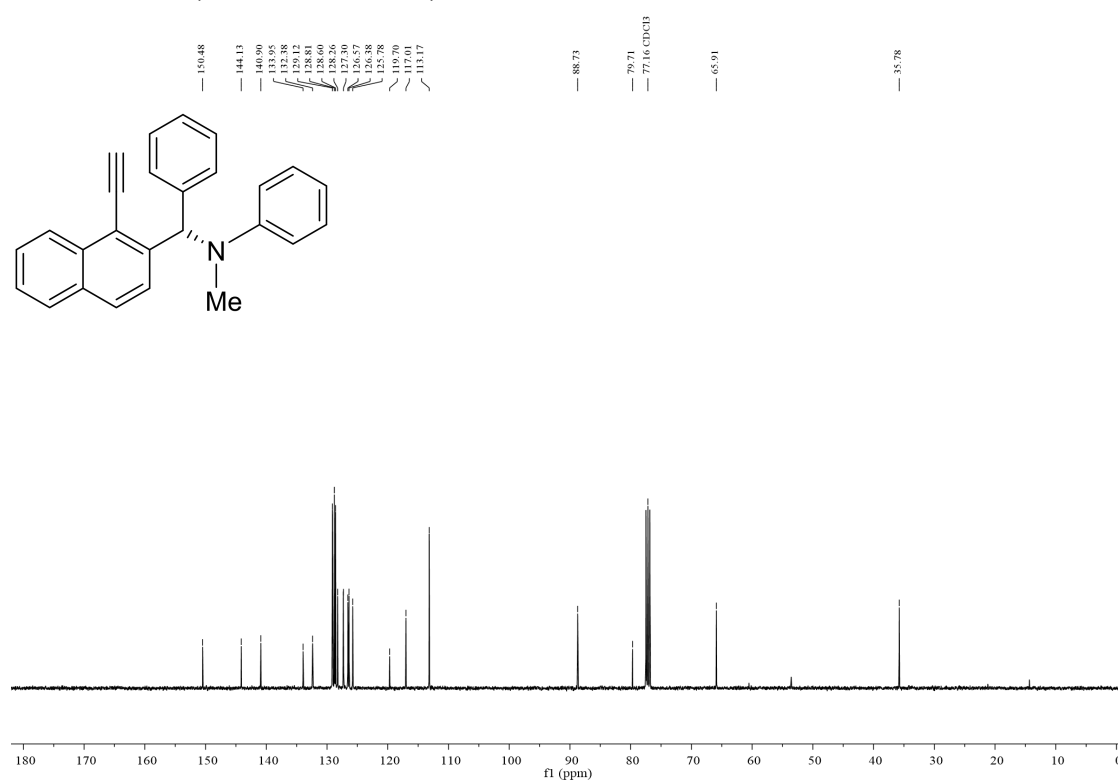
¹³C NMR-4e (100 MHz, CDCl₃)



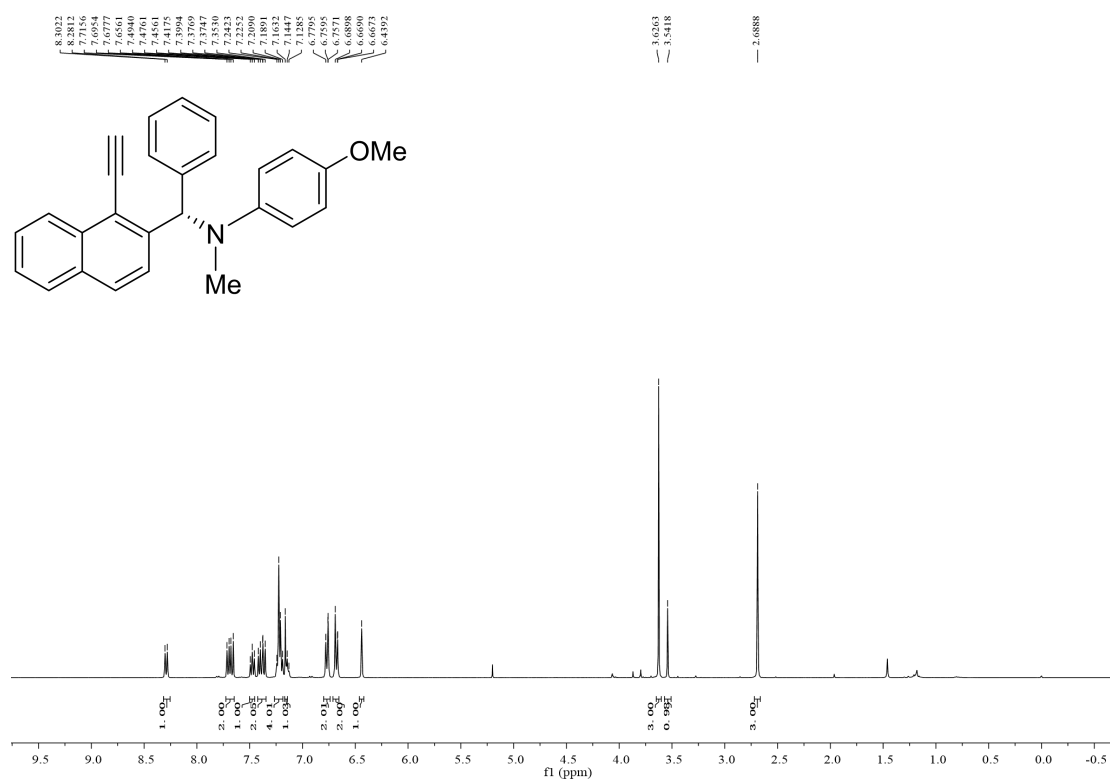
¹H NMR-5a (400 MHz, CDCl₃)



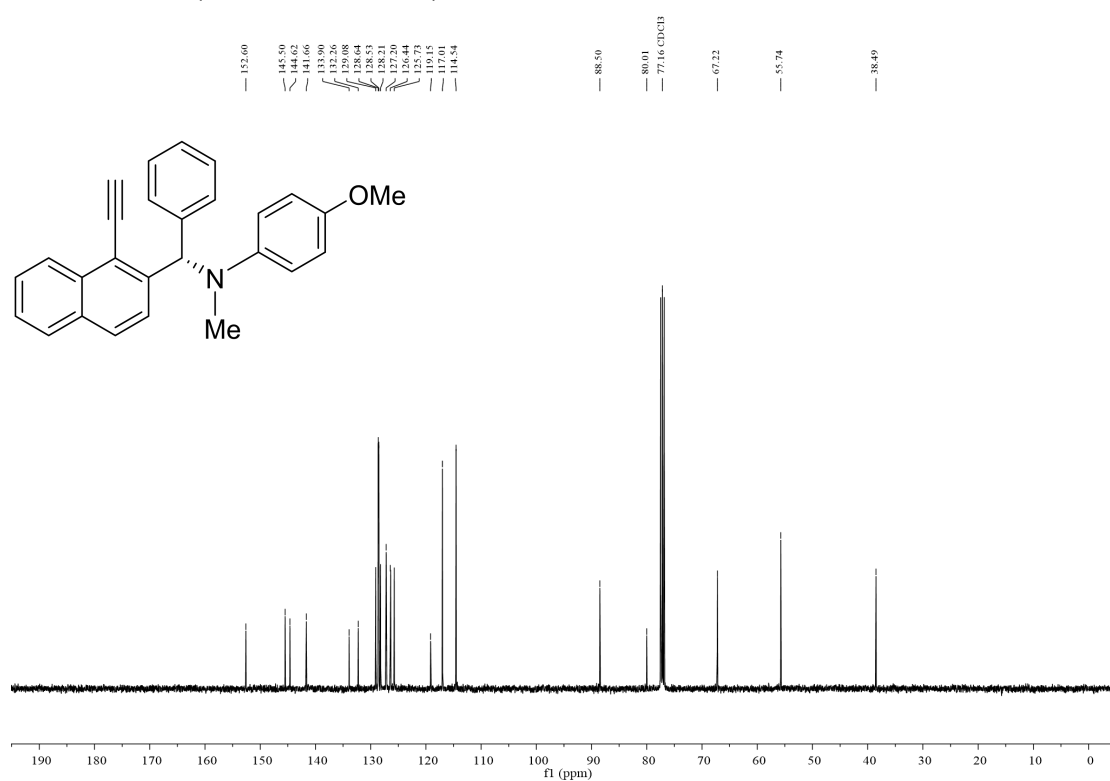
¹³C NMR-5a (100 MHz, CDCl₃)



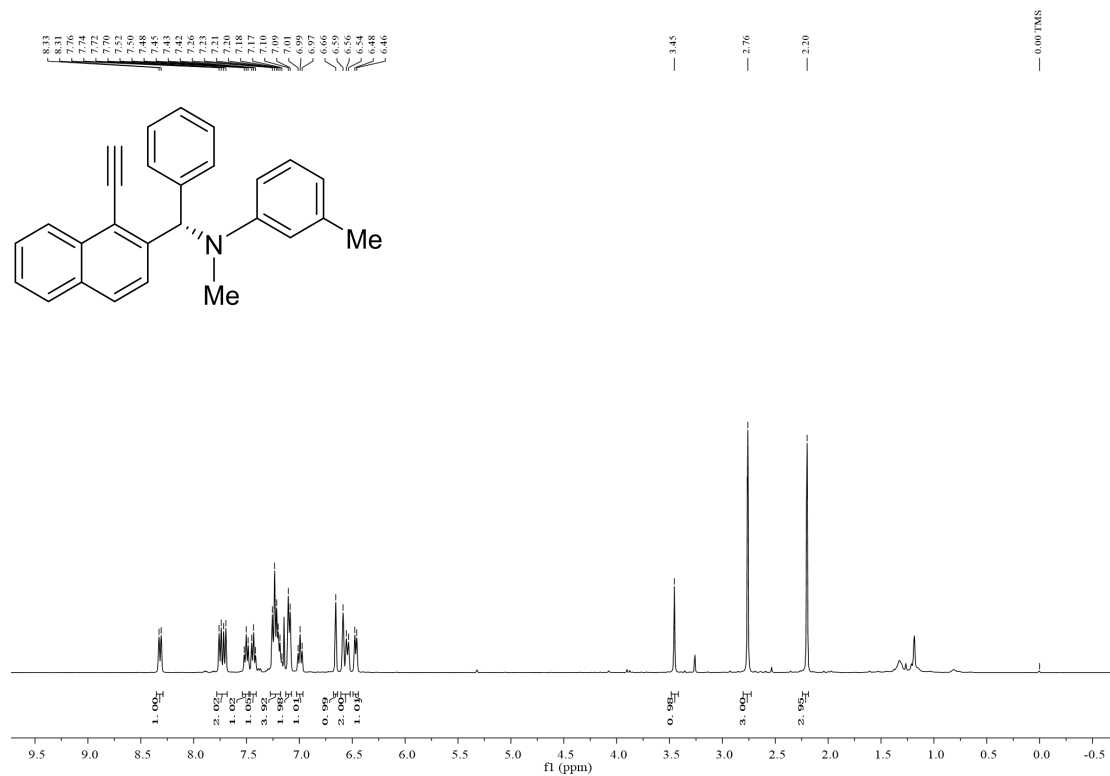
¹H NMR-5b (400 MHz, CDCl₃)



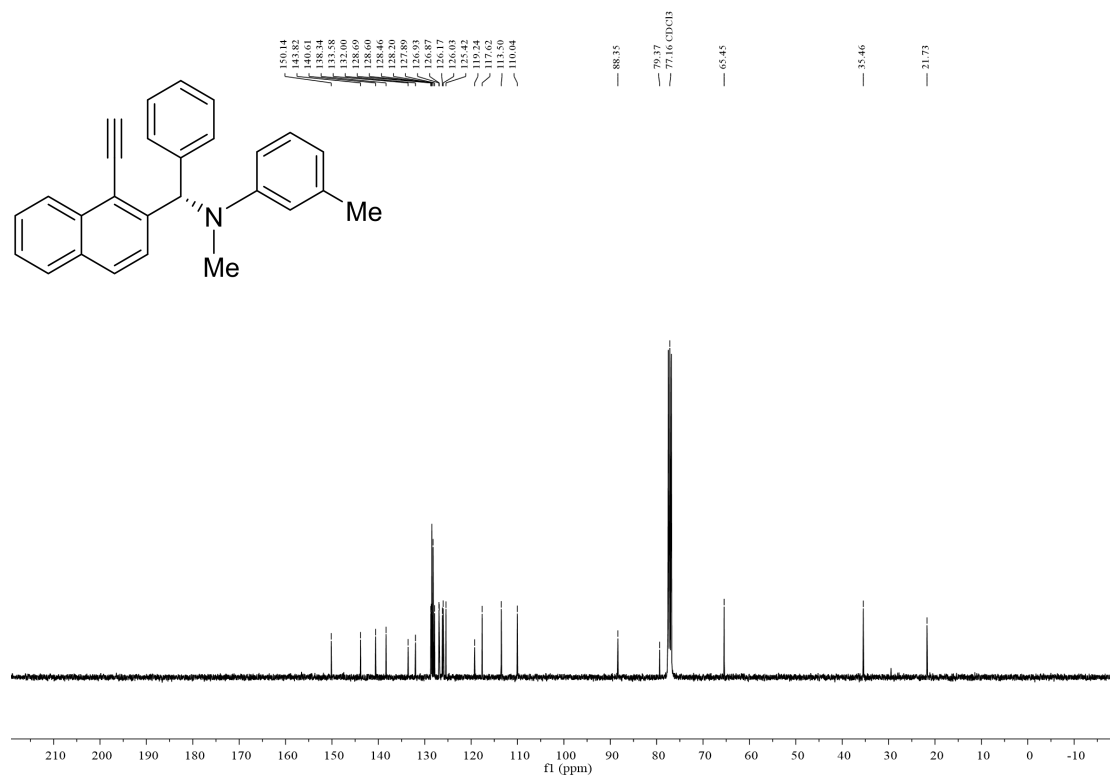
¹³C NMR-5b (100 MHz, CDCl₃)



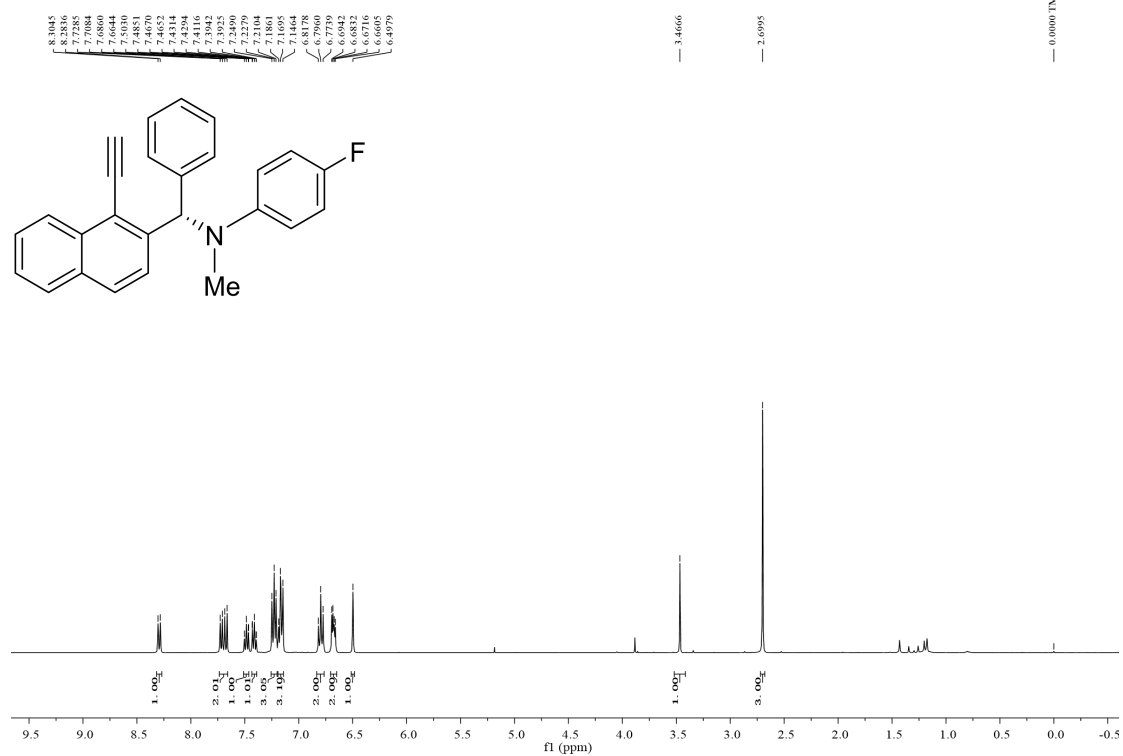
¹H NMR-5d (400 MHz, CDCl₃)



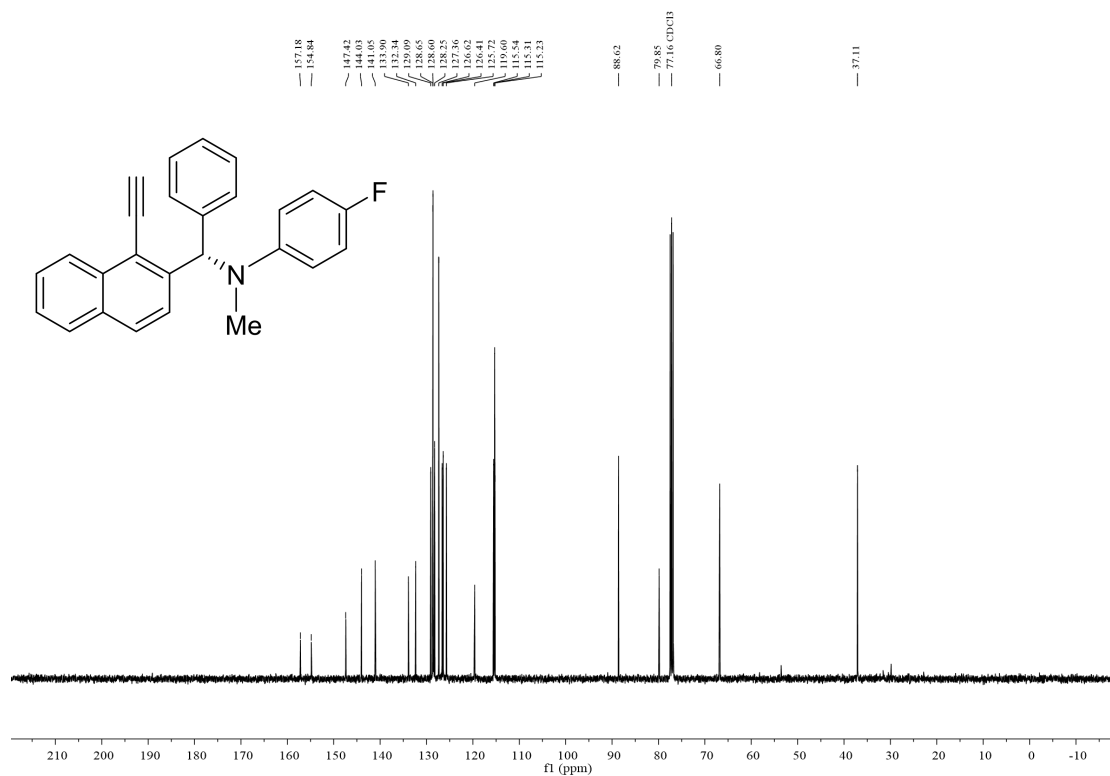
¹³C NMR-5d (100 MHz, CDCl₃)



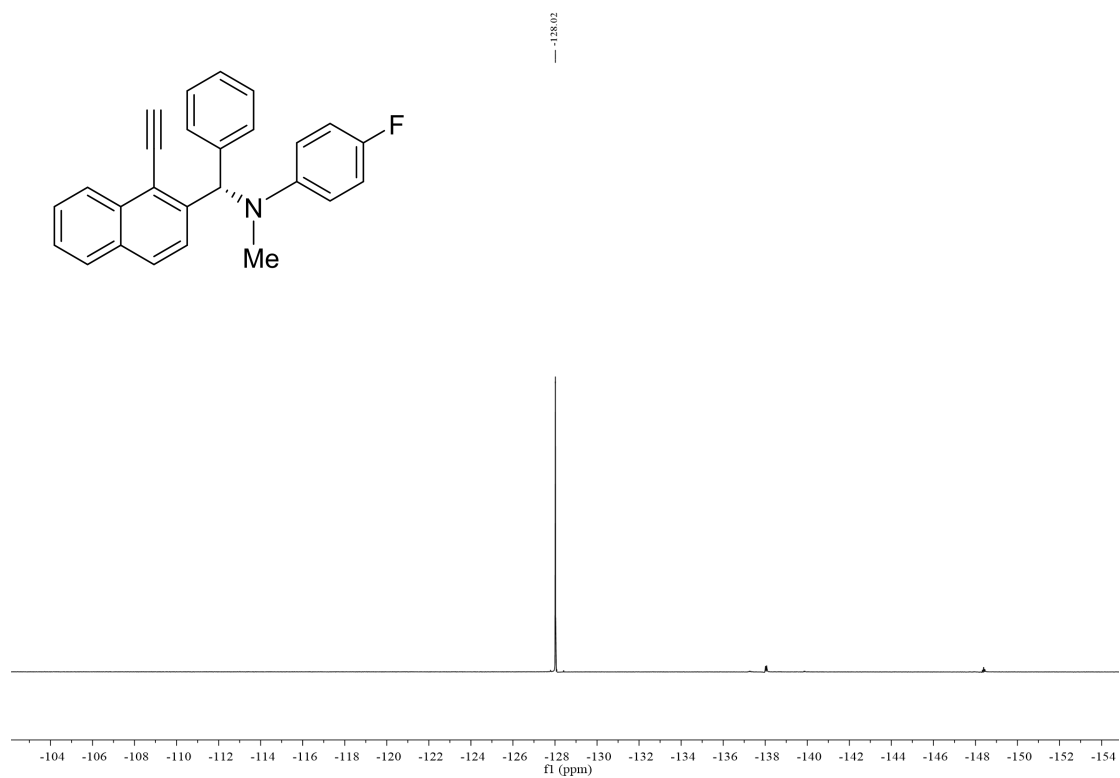
¹H NMR-5e (400 MHz, CDCl₃)



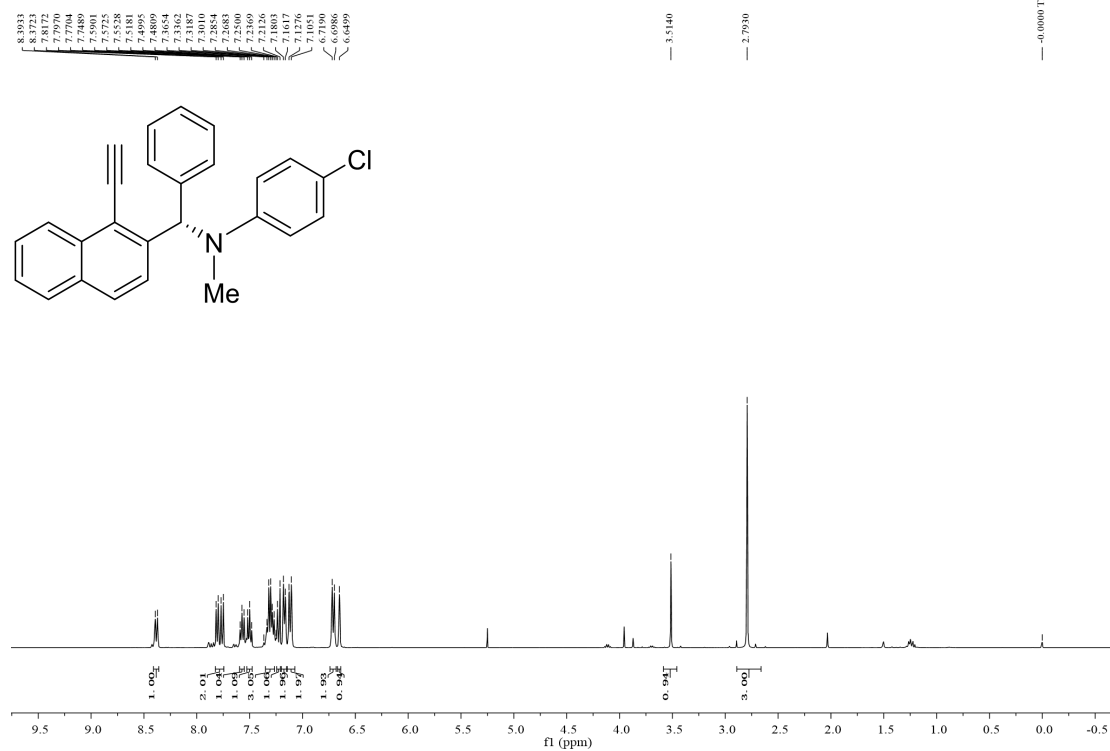
¹³C NMR-5e (100 MHz, CDCl₃)



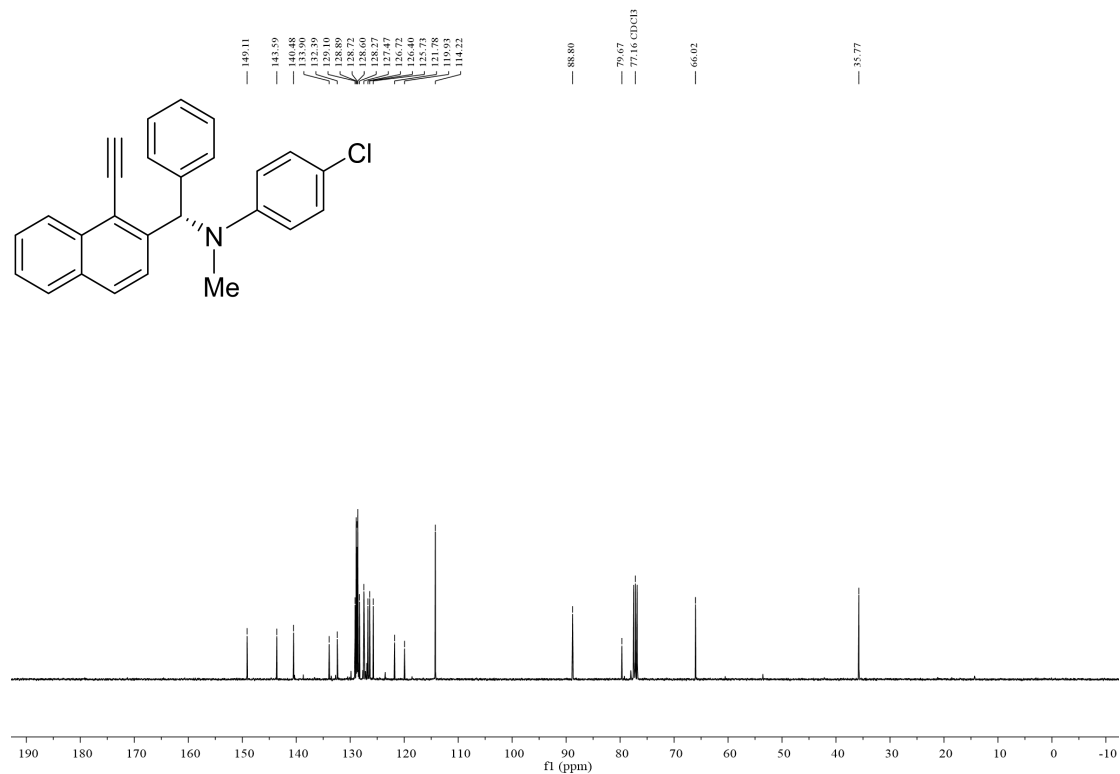
¹⁹F NMR-5e (376 MHz, CDCl₃)



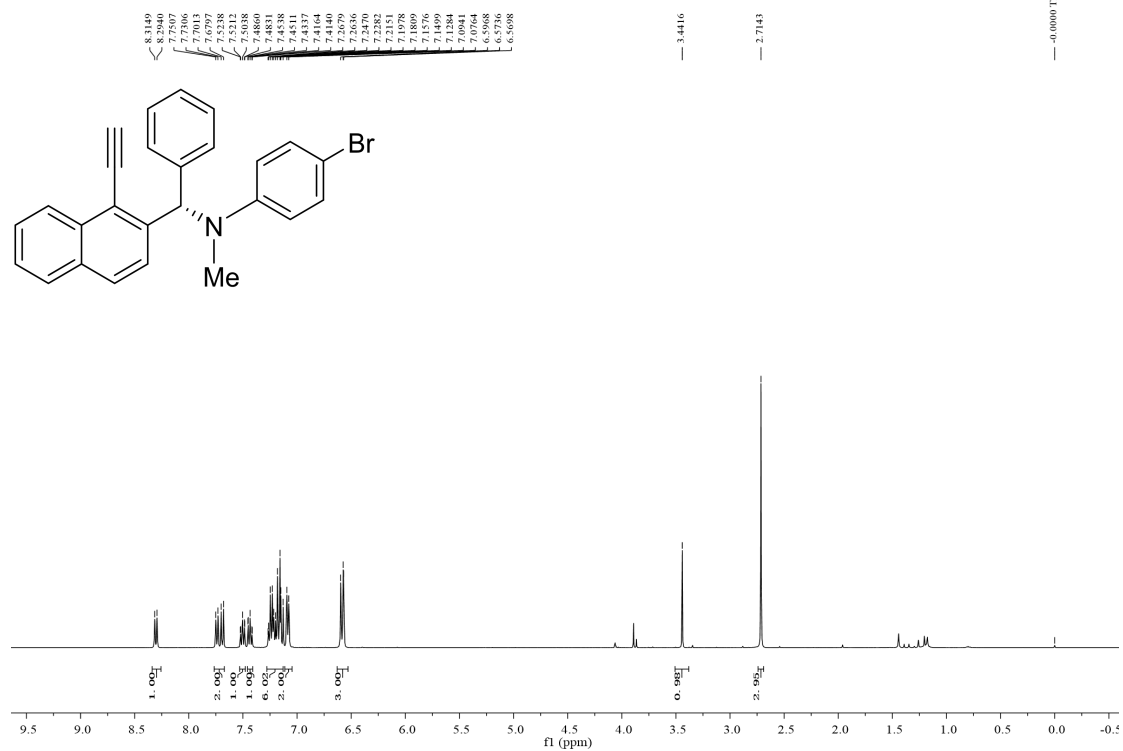
¹H NMR-5f (400 MHz, CDCl₃)



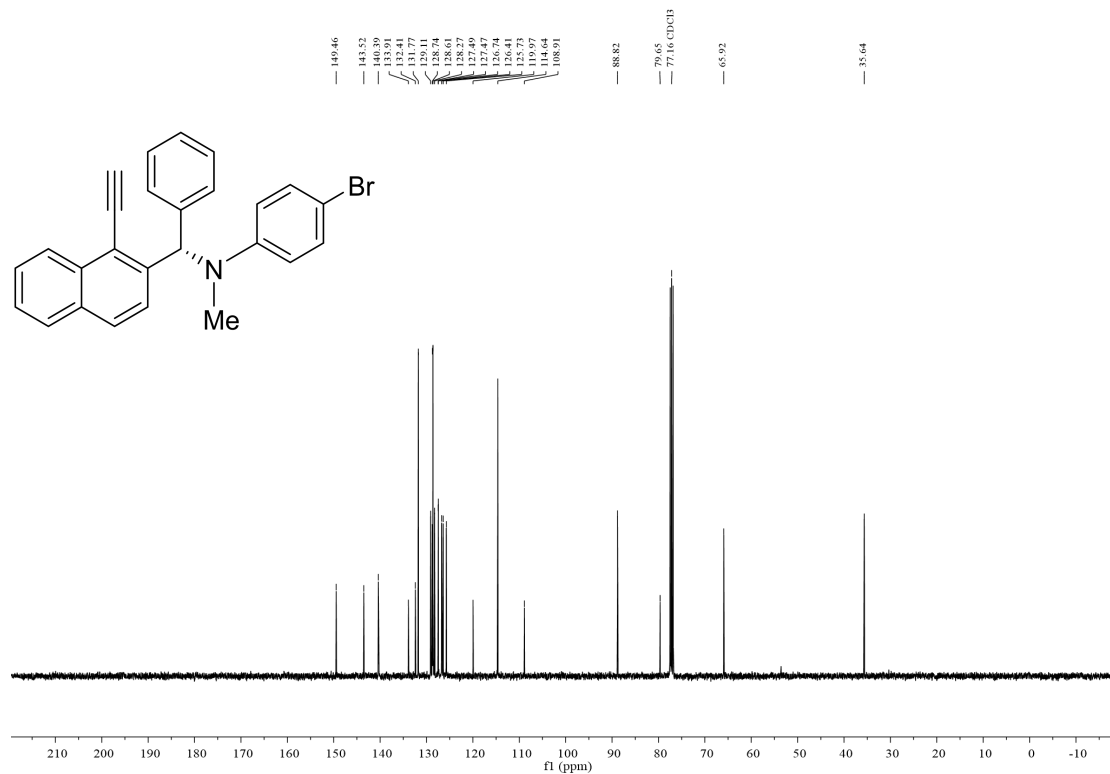
¹³C NMR-5f (100 MHz, CDCl₃)



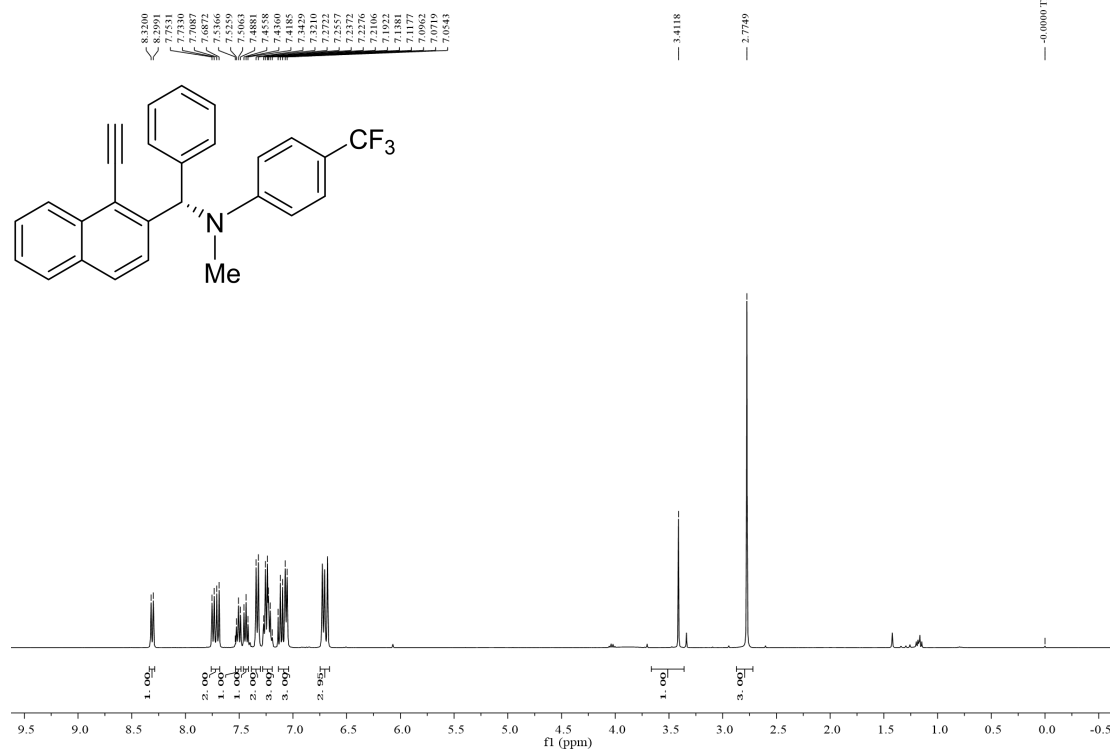
¹H NMR-5g (400 MHz, CDCl₃)



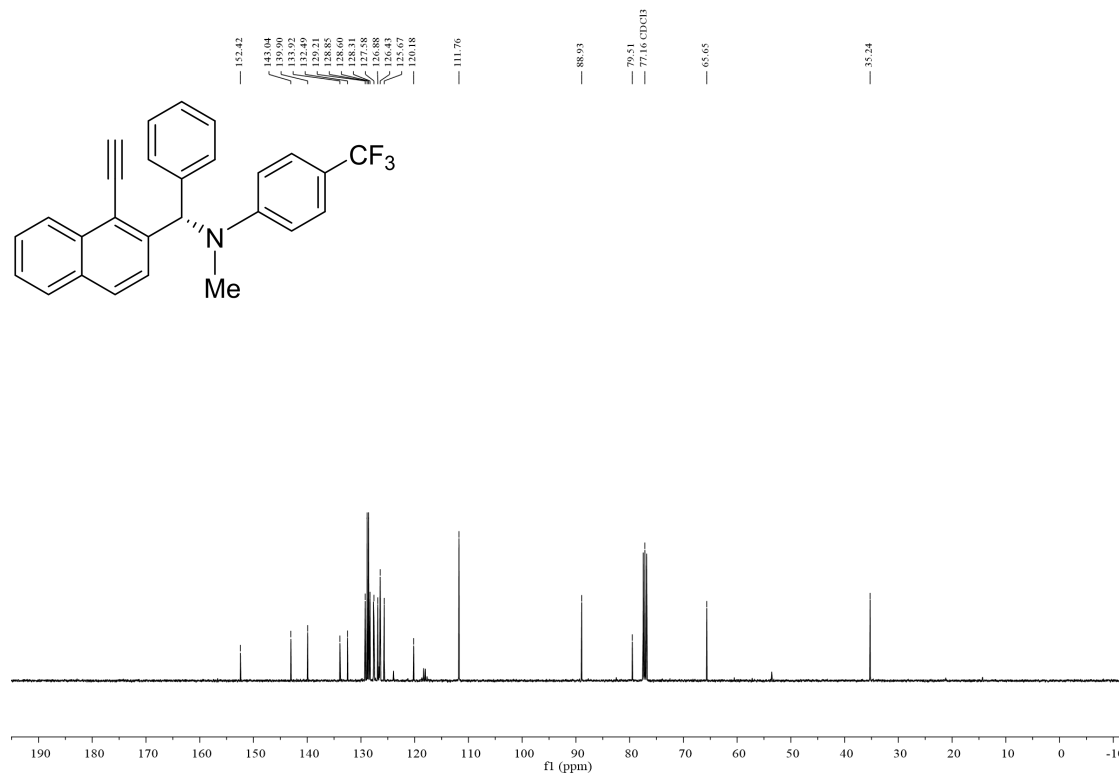
¹³C NMR-5g (100 MHz, CDCl₃)



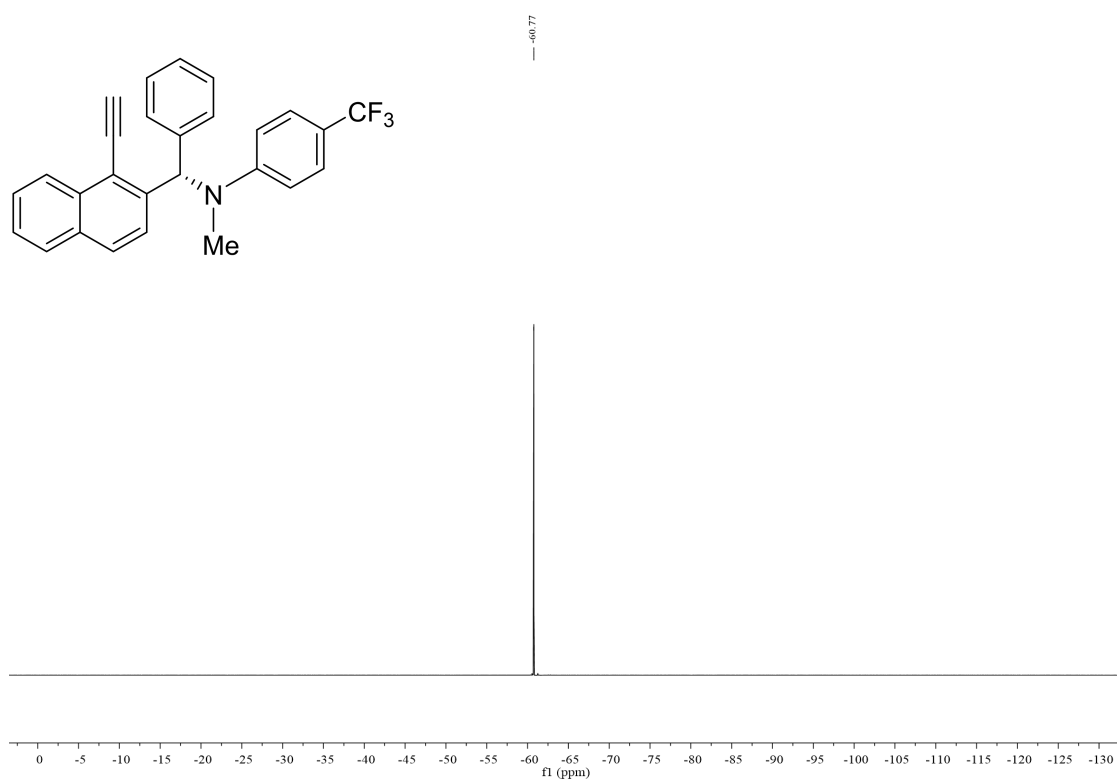
¹H NMR-5h (400 MHz, CDCl₃)



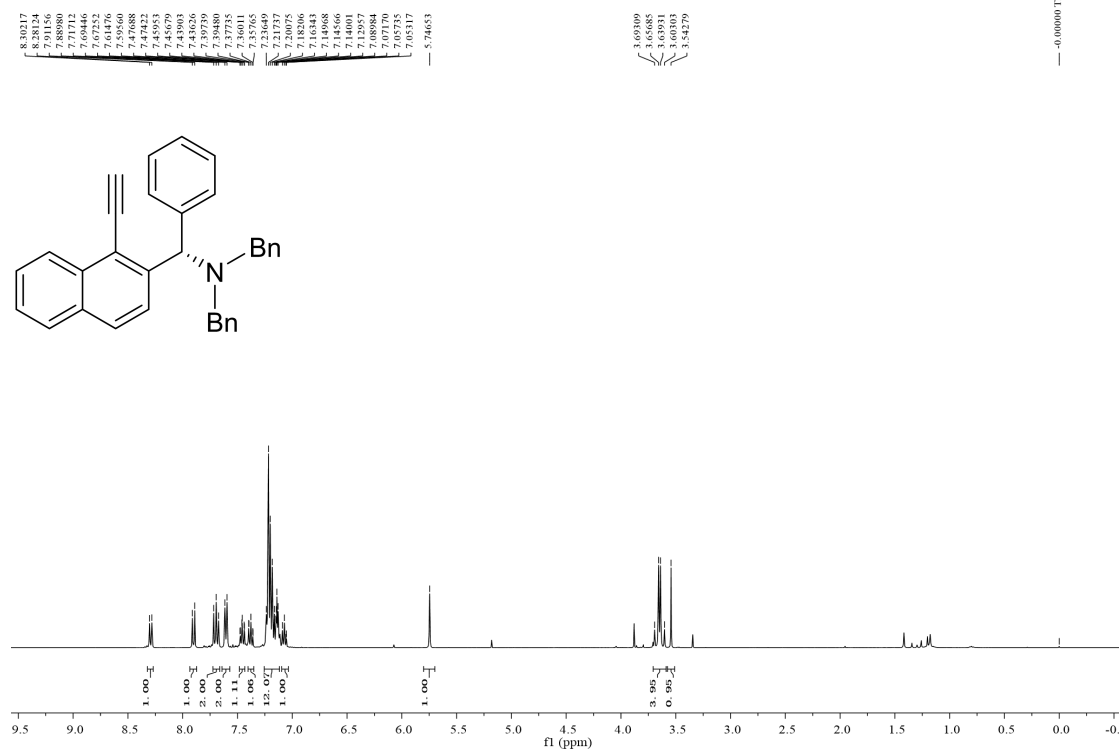
¹³C NMR-5h (100 MHz, CDCl₃)



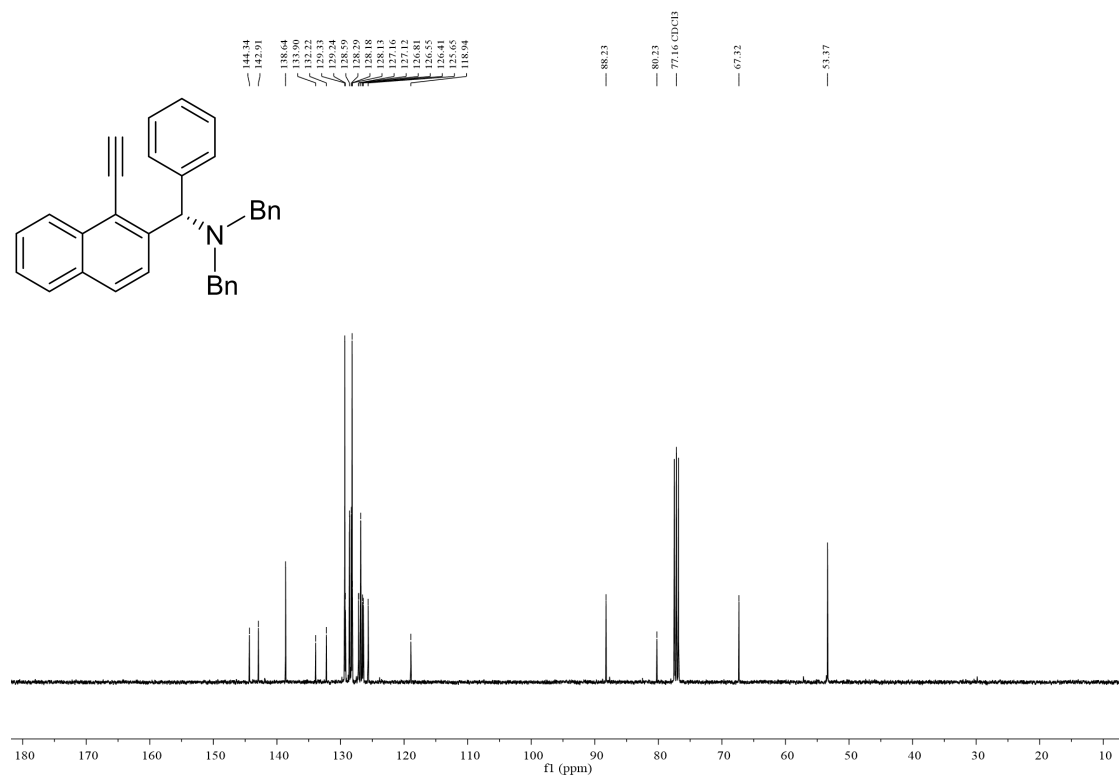
¹⁹F NMR-5h (376 MHz, CDCl₃)



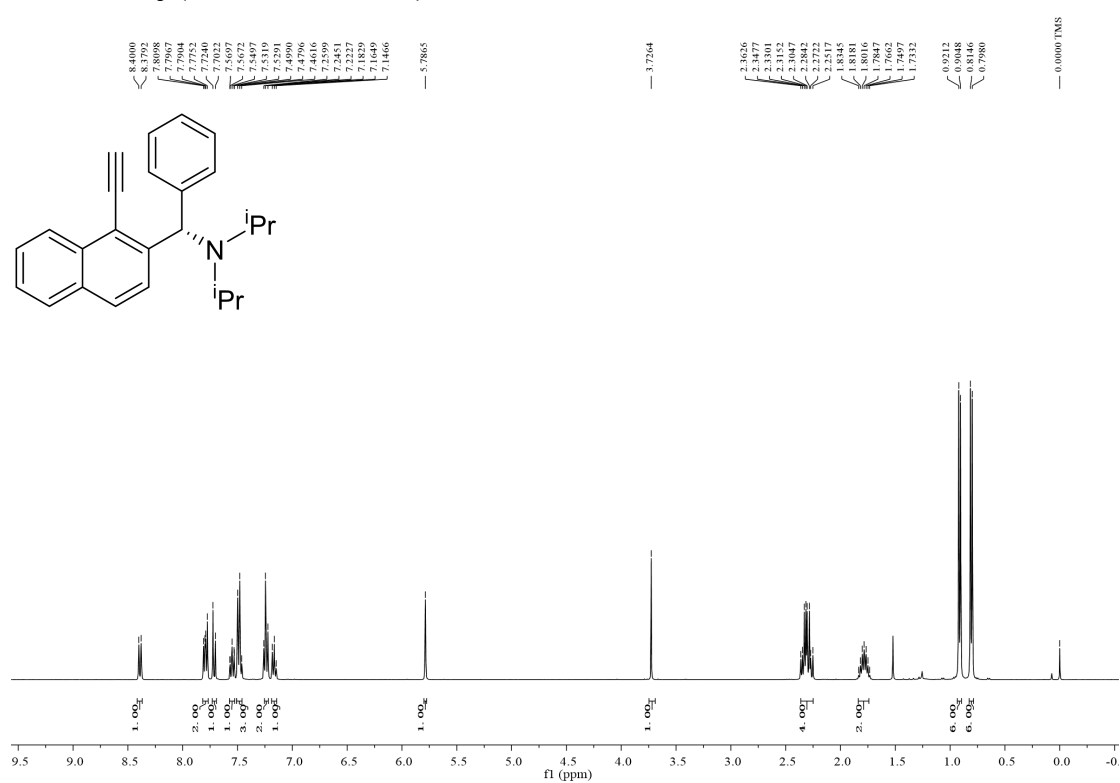
¹H NMR-5i (400 MHz, CDCl₃)



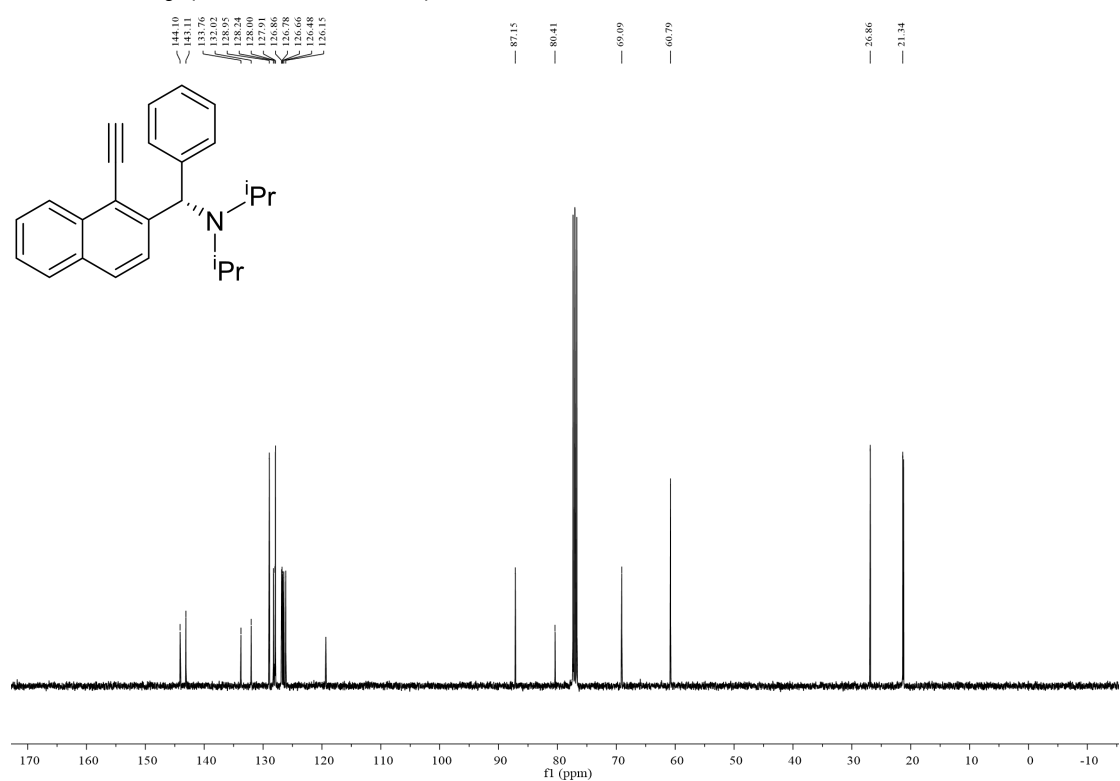
¹³C NMR-5i (100 MHz, CDCl₃)



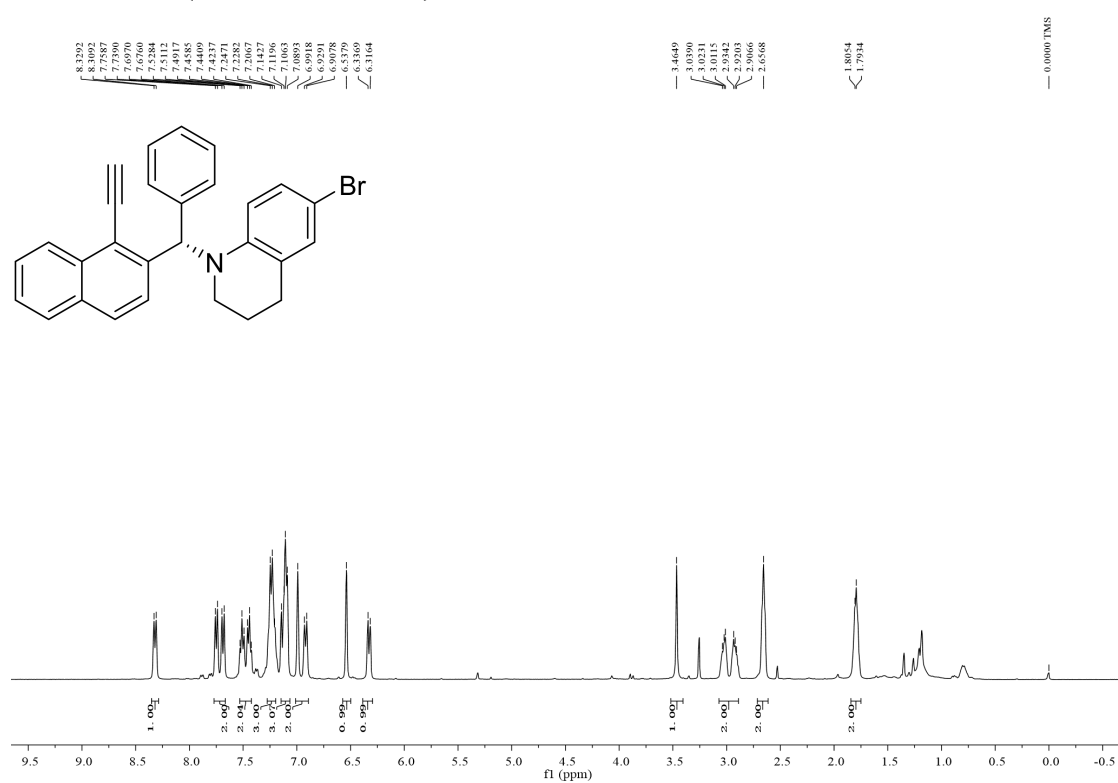
¹H NMR-5j (400 MHz, CDCl₃)



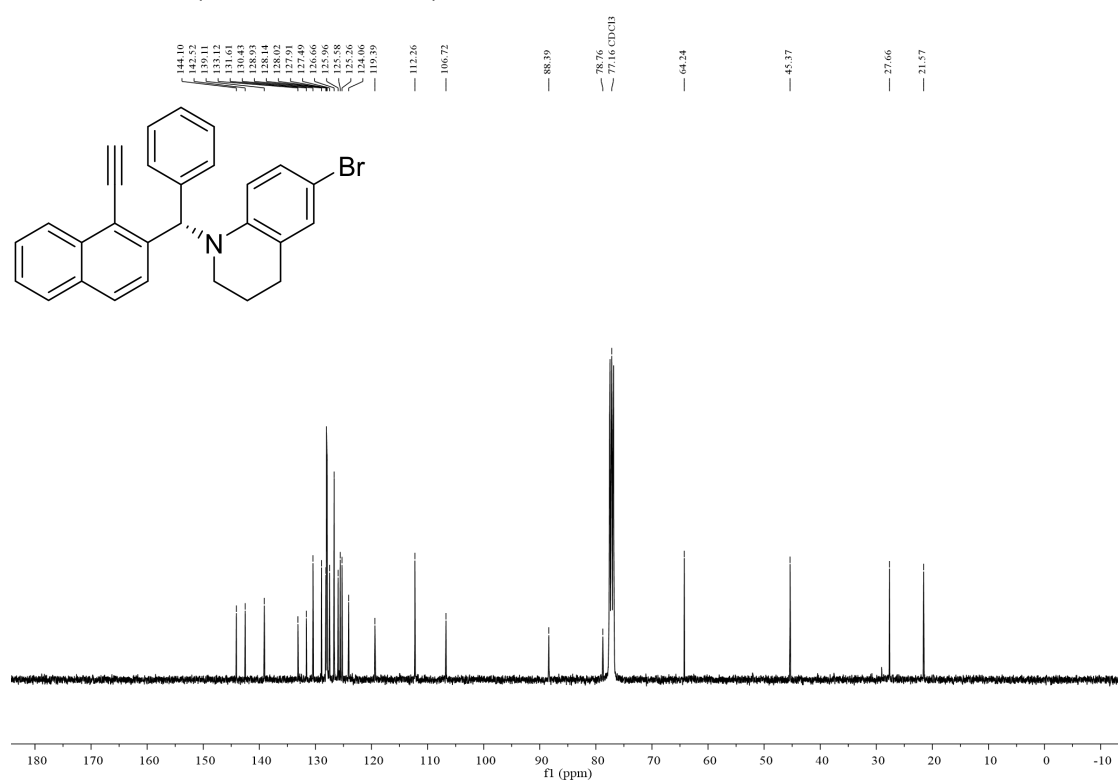
¹³C NMR-5j (100 MHz, CDCl₃)



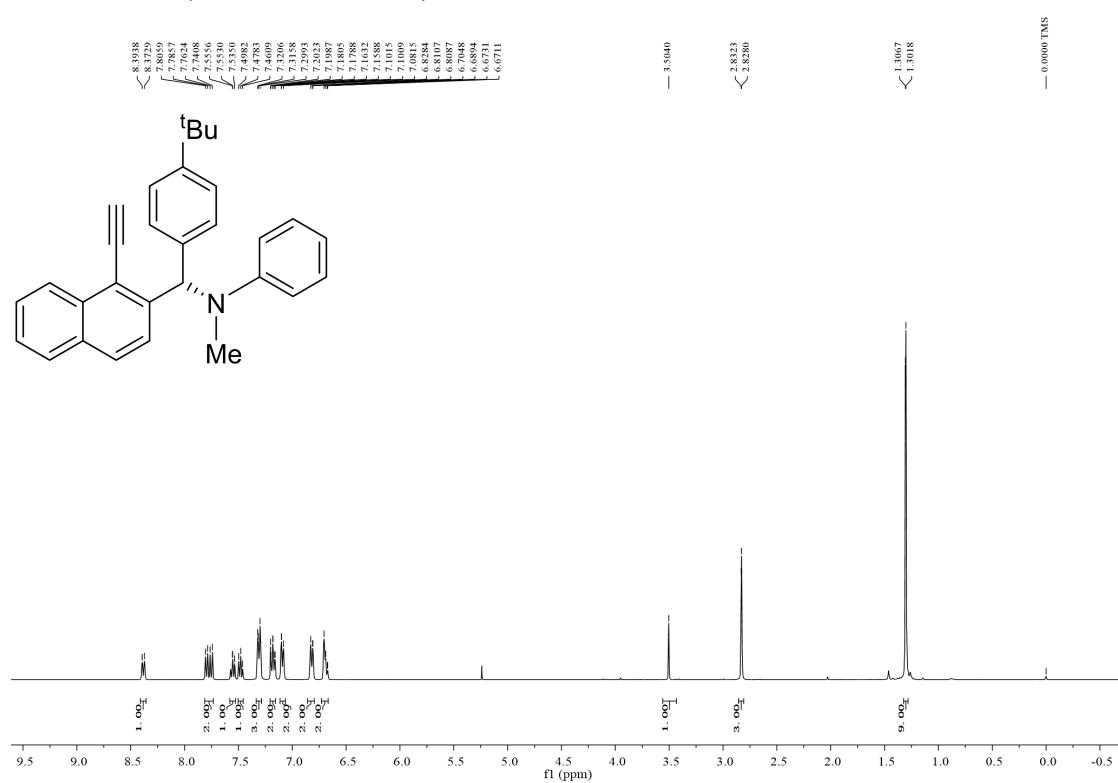
¹H NMR-5n (400 MHz, CDCl₃)



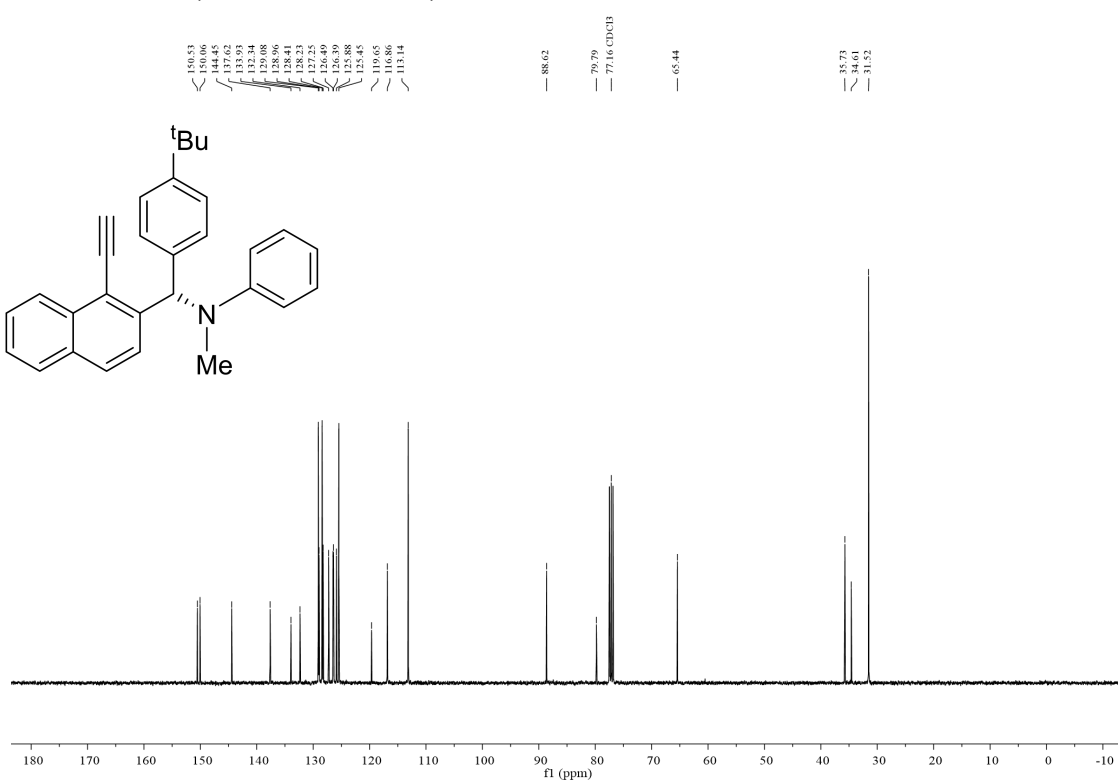
¹³C NMR-5n (100 MHz, CDCl₃)



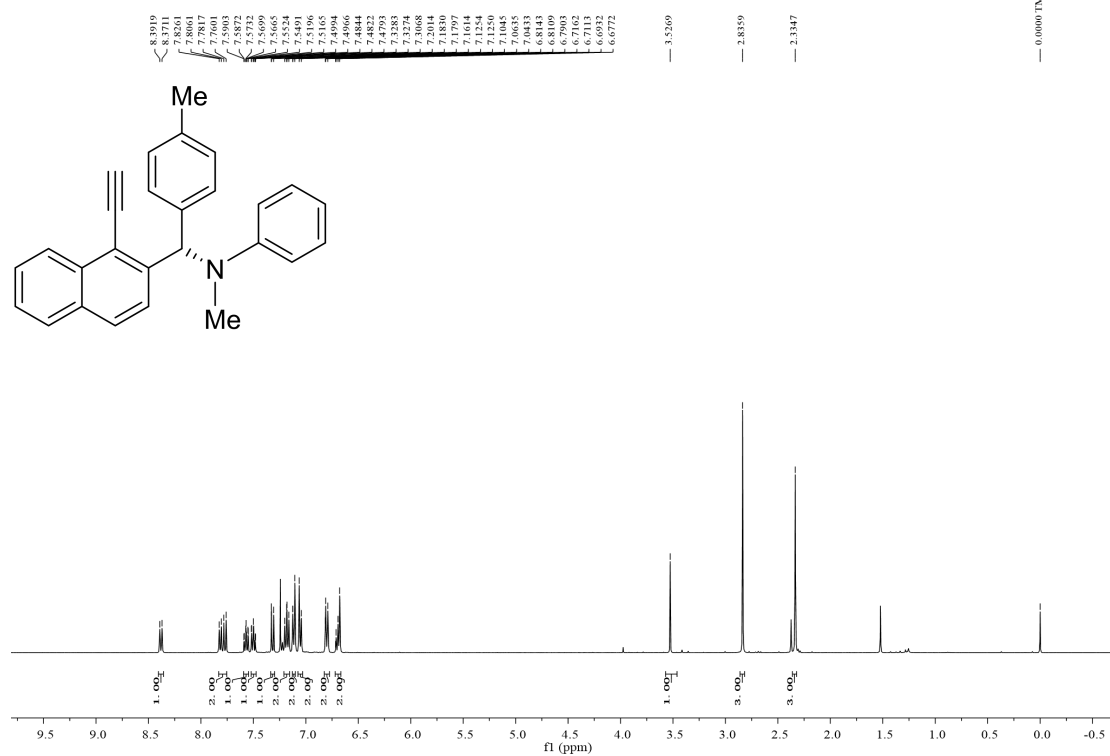
¹H NMR-6a (400 MHz, CDCl₃)



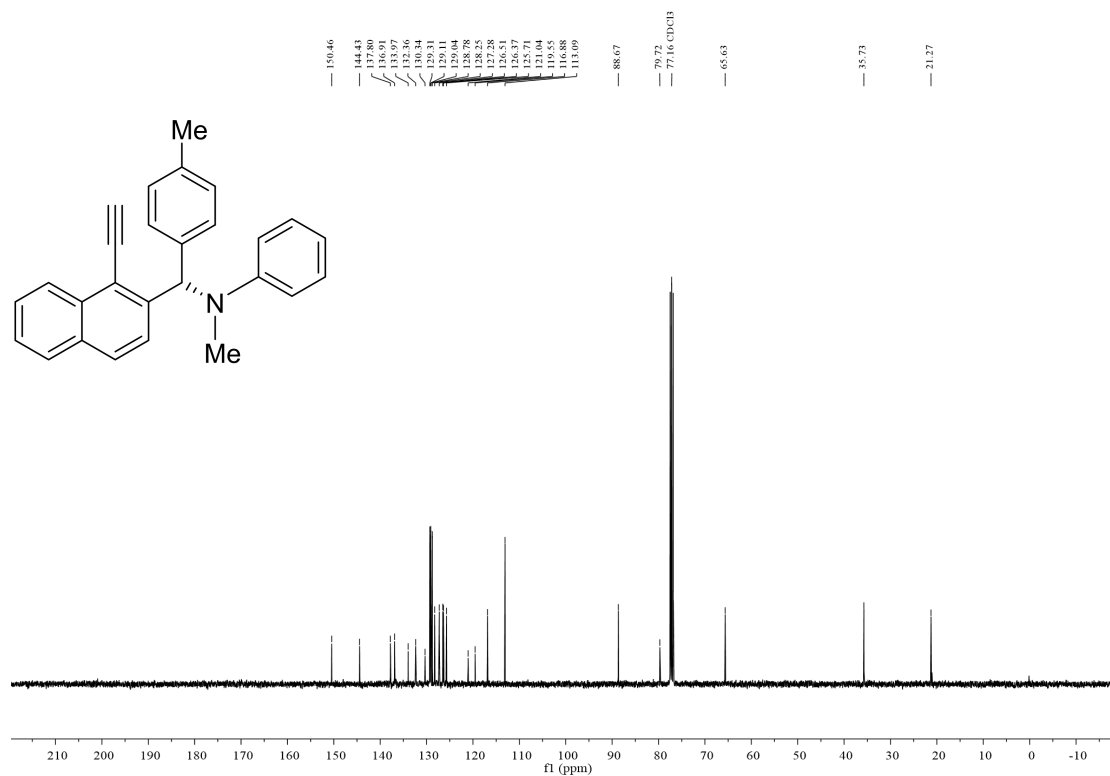
¹³C NMR-6a (100 MHz, CDCl₃)



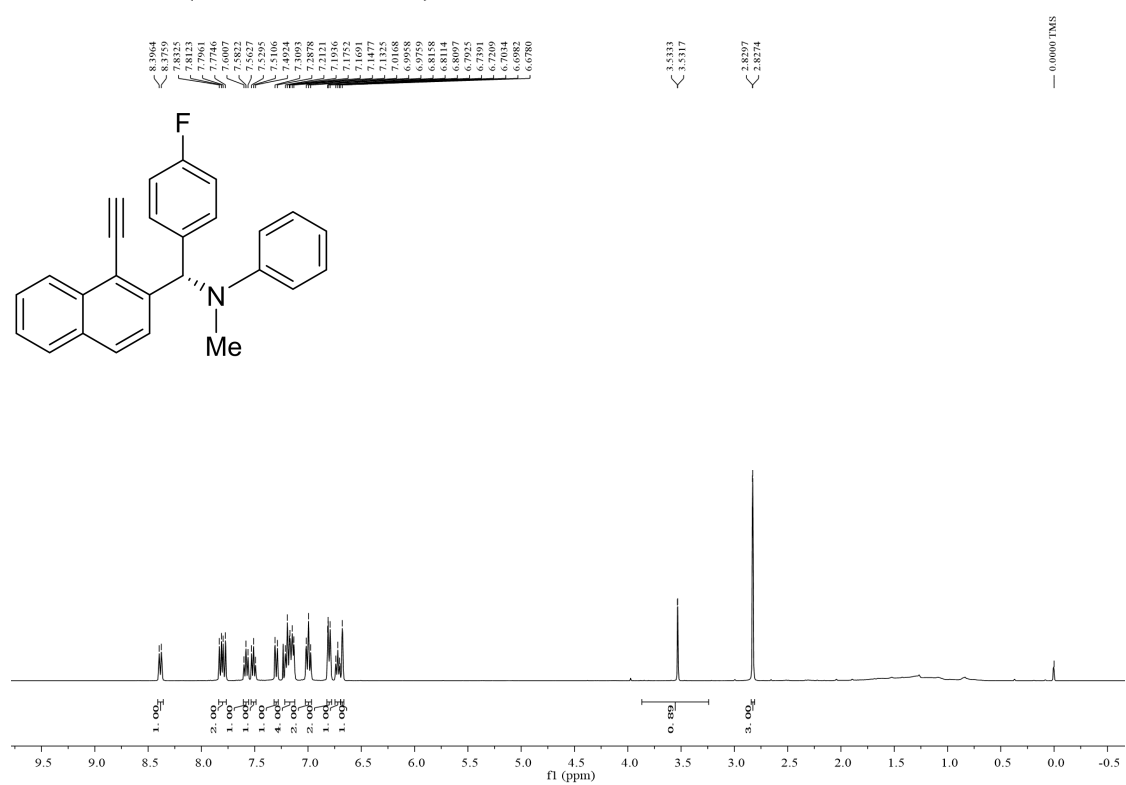
¹H NMR-6c (400 MHz, CDCl₃)



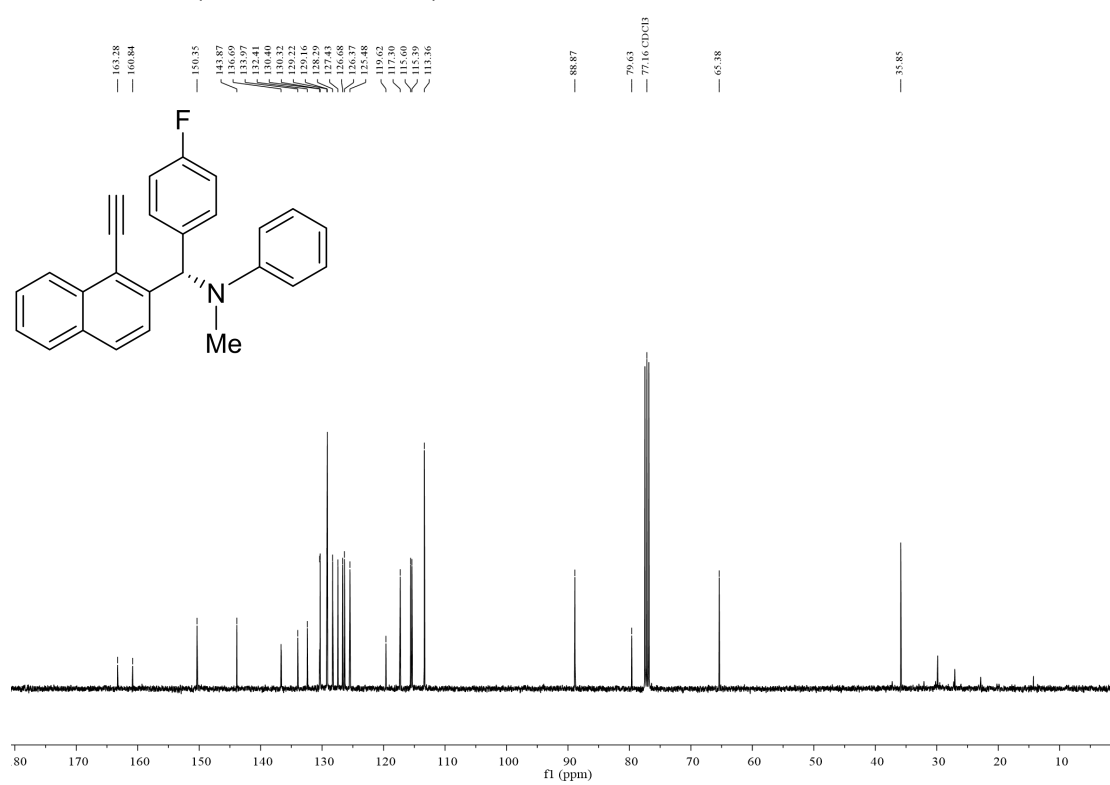
¹³C NMR-6c (100 MHz, CDCl₃)



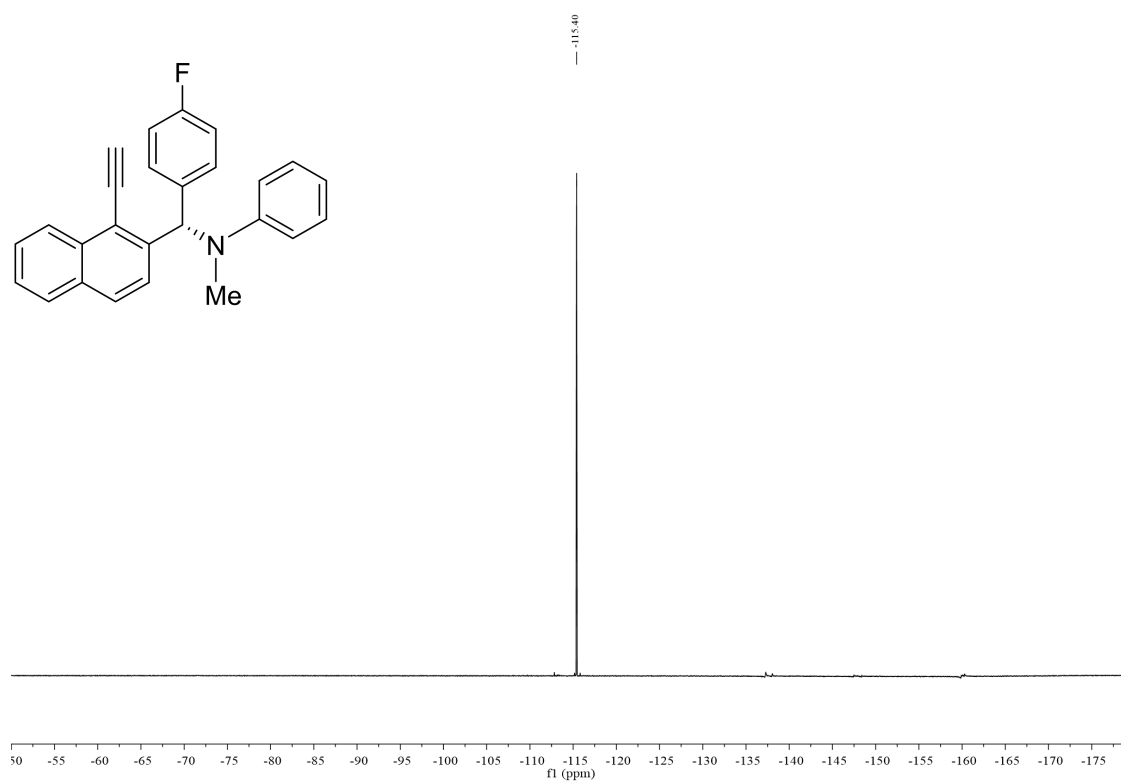
¹H NMR-6d (400 MHz, CDCl₃)



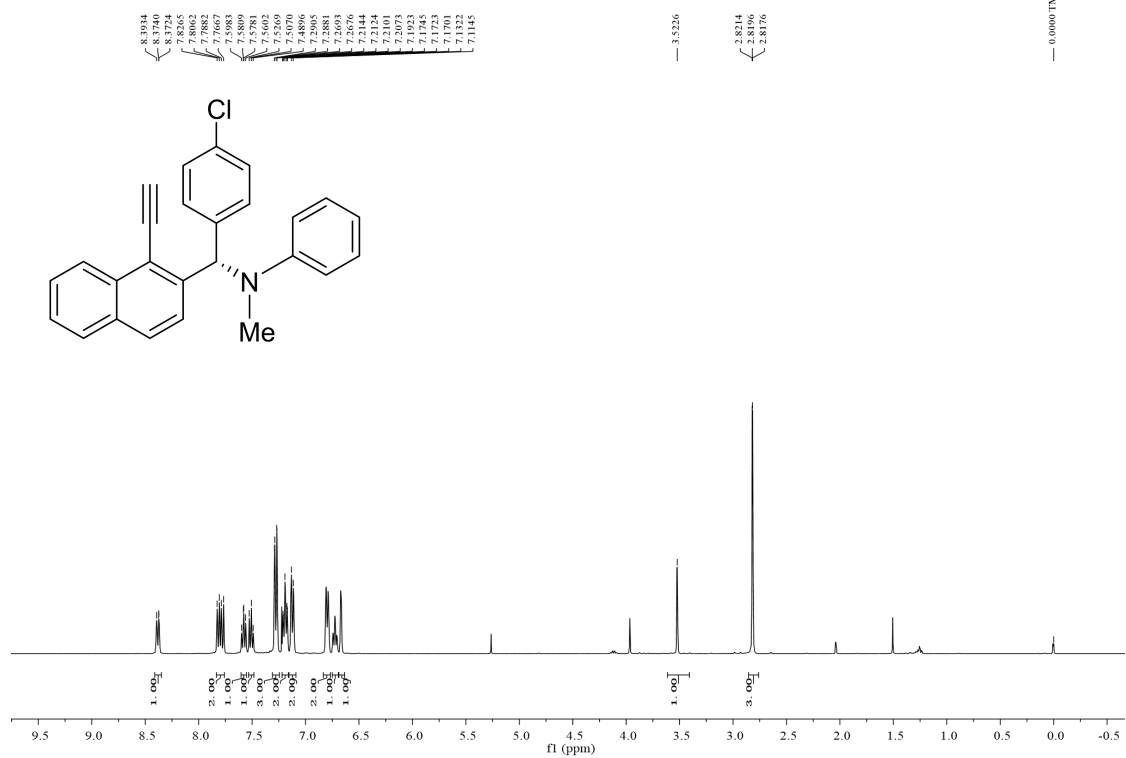
¹³C NMR-6d (100 MHz, CDCl₃)



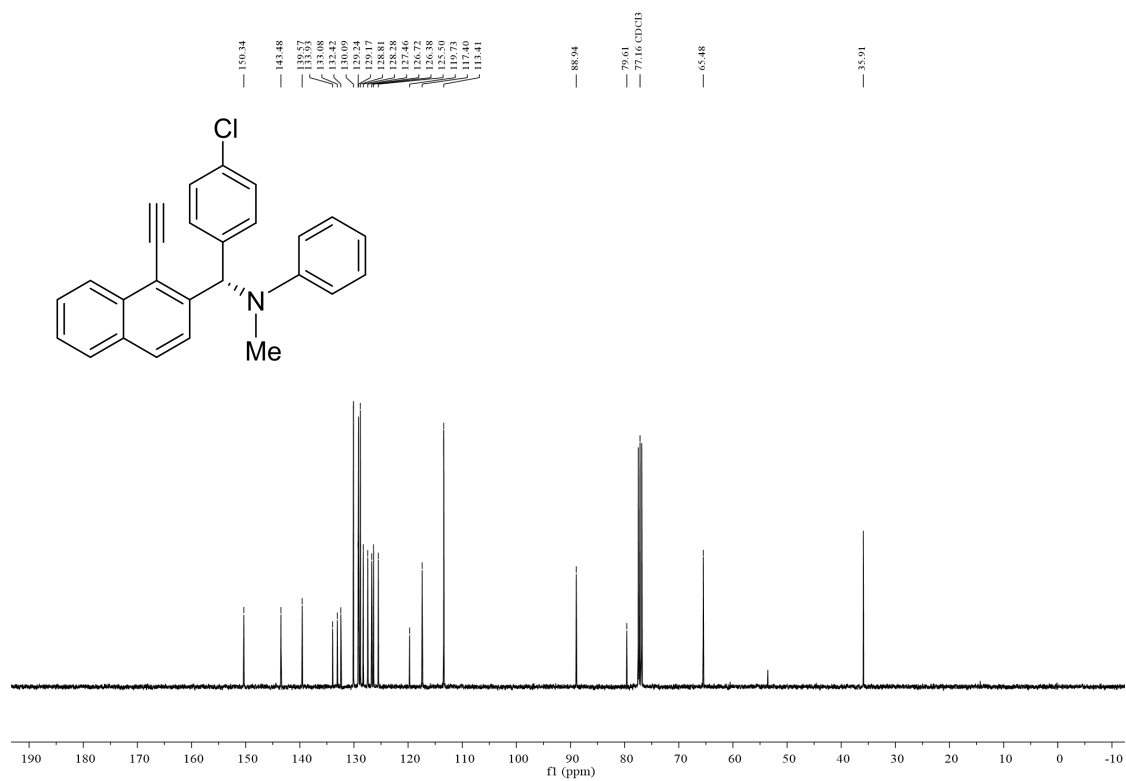
¹⁹F NMR-6d (376 MHz, CDCl₃)



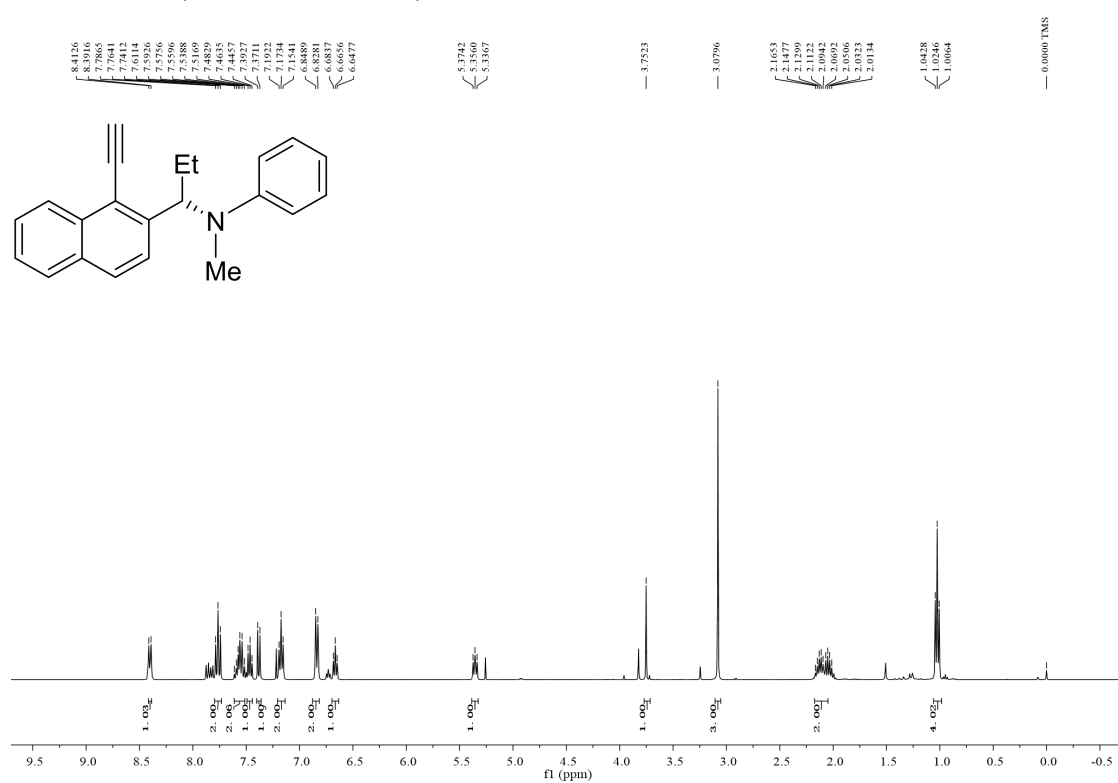
¹H NMR-6e (400 MHz, CDCl₃)



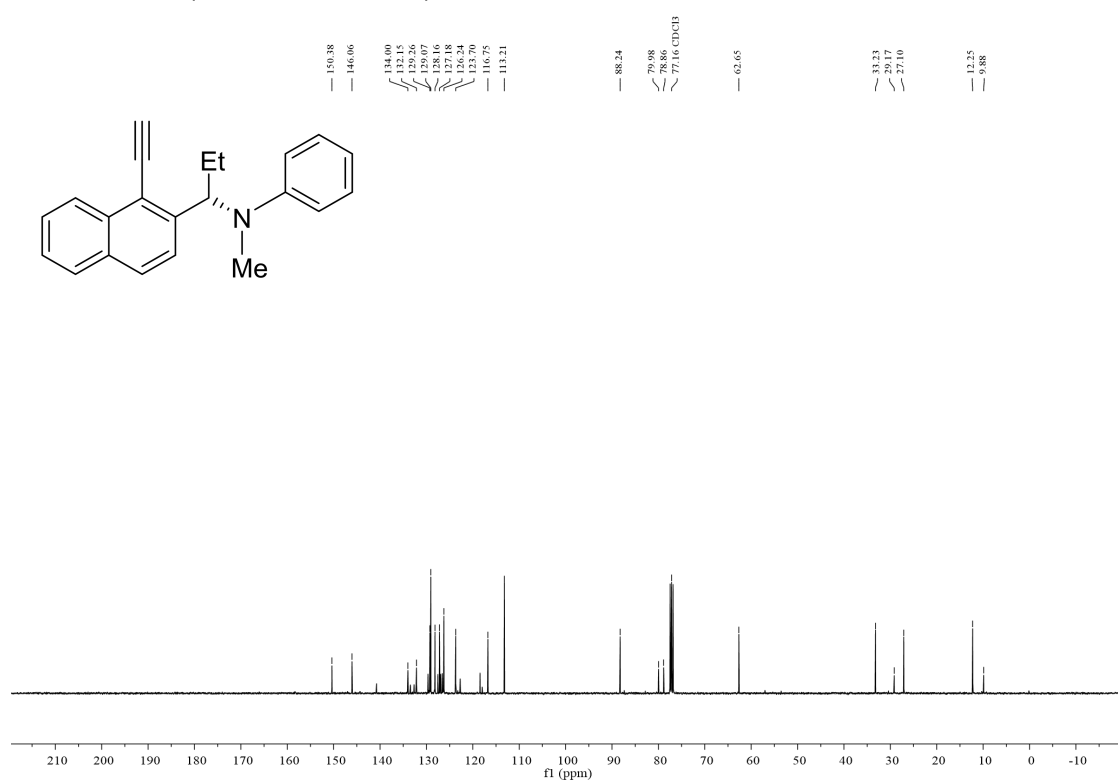
¹³C NMR-6e (100 MHz, CDCl₃)



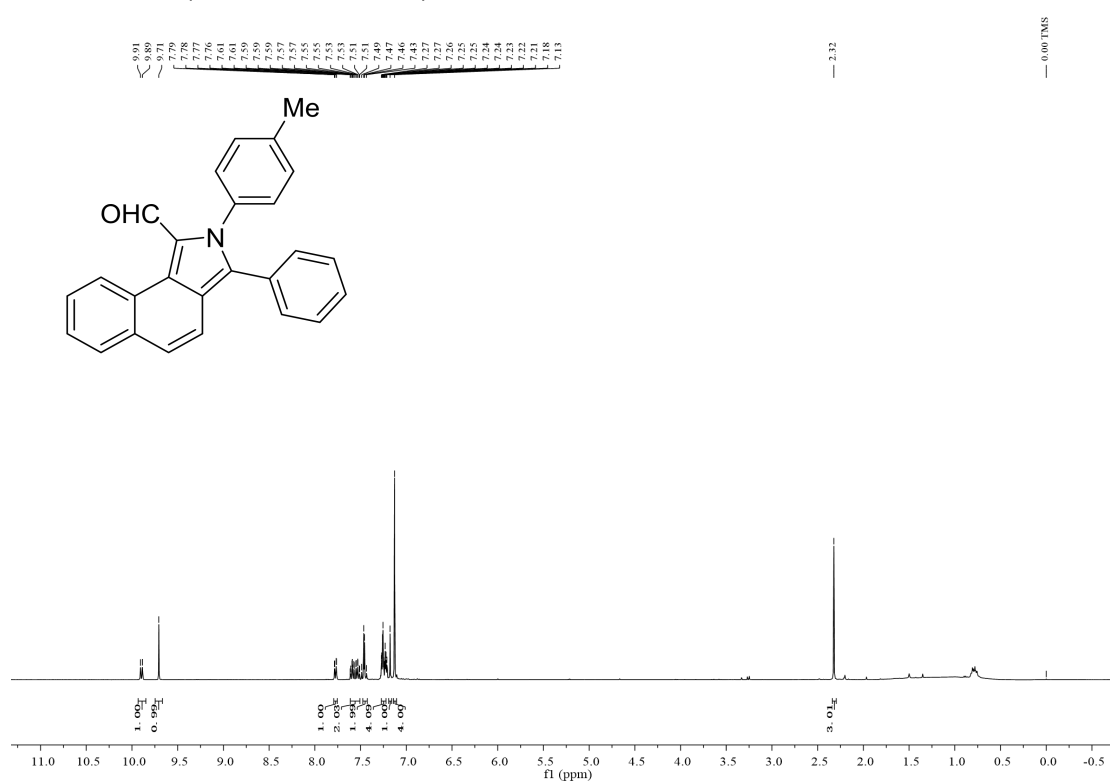
¹H NMR-6f (400 MHz, CDCl₃)



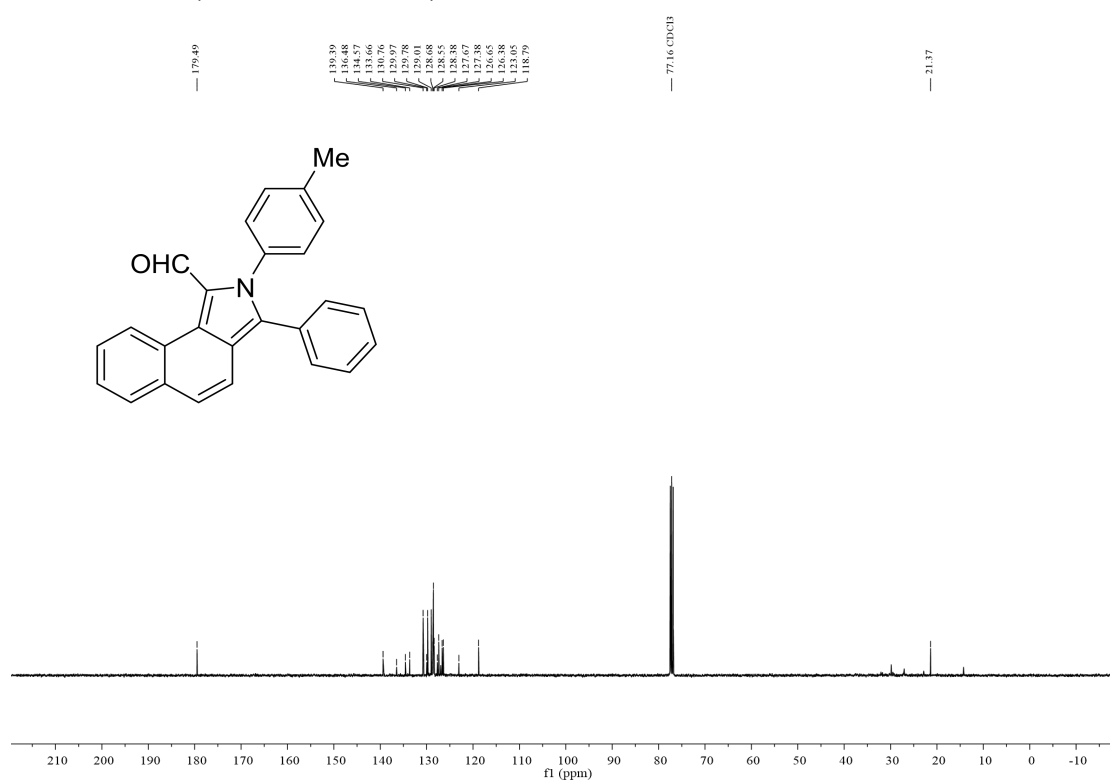
¹³C NMR-6f (100 MHz, CDCl₃)



¹H NMR-7a (400 MHz, CDCl₃)



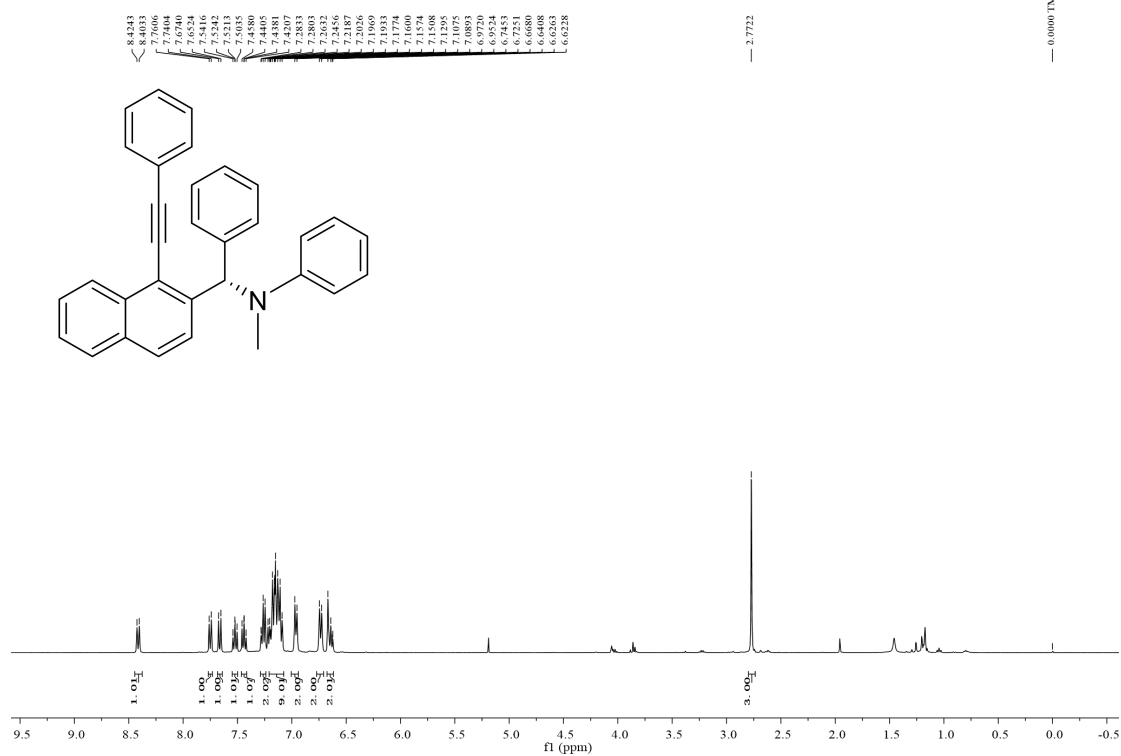
¹³C NMR-7a (100 MHz, CDCl₃)



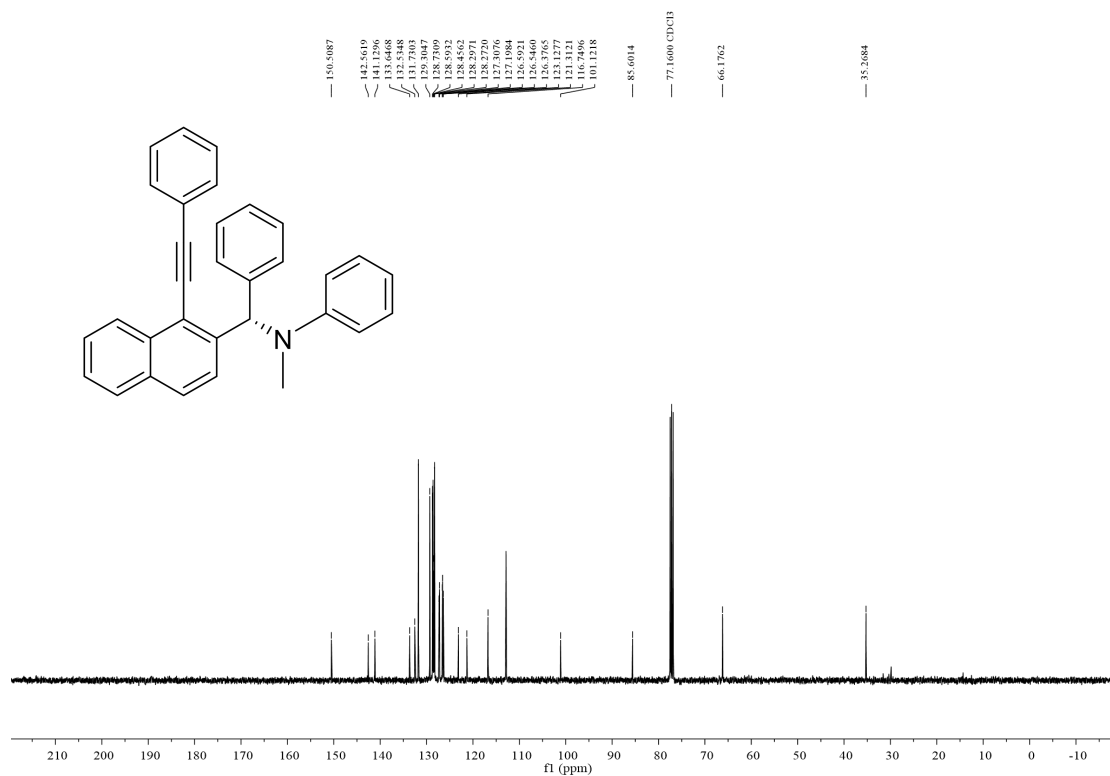
¹⁹F NMR-8a (376 MHz, CDCl₃)



¹H NMR-9a (400 MHz, CDCl₃)

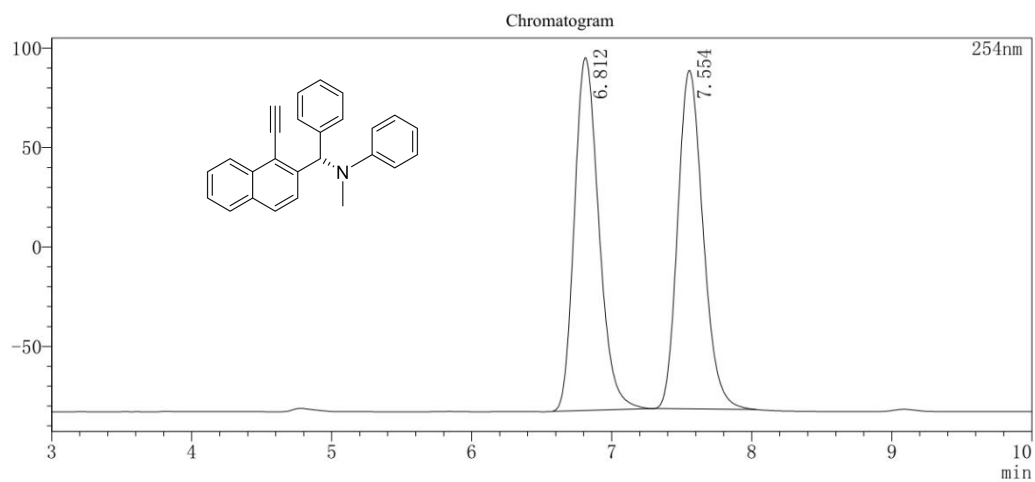


¹³C NMR-9a (100 MHz, CDCl₃)



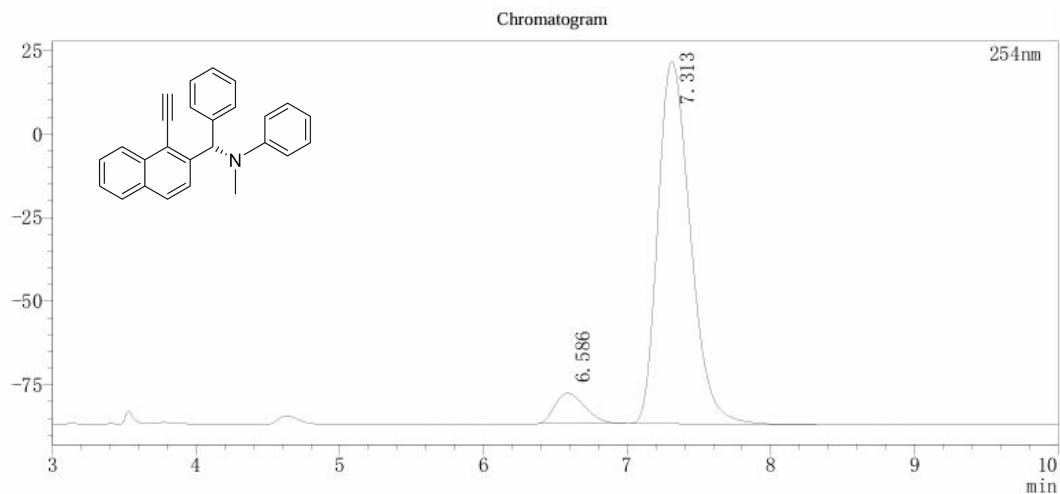
VI Chiral HPLC analysis trace

racemic-5a



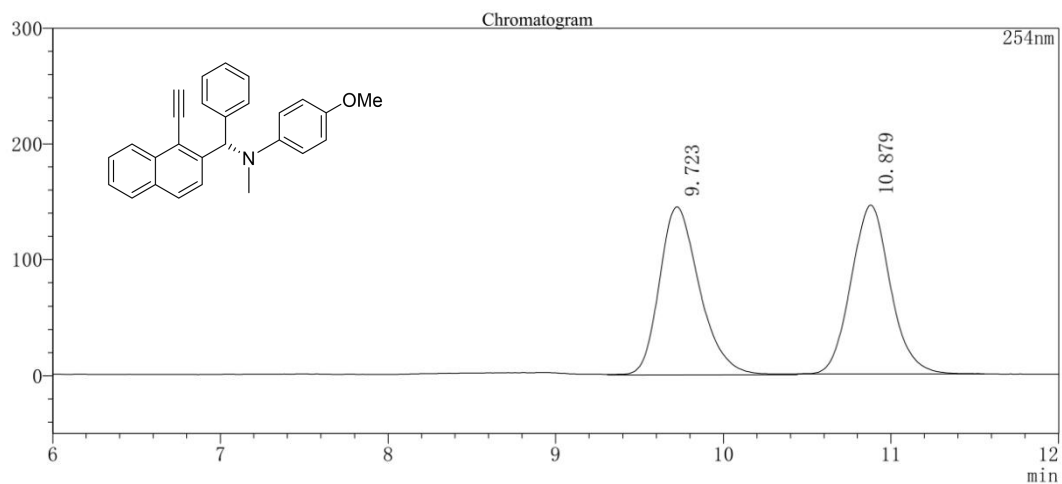
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	6.812	2151871	177358	50.139
2	7.554	2139922	170228	49.861
Total		4291792	347586	100.000

chiral-5a



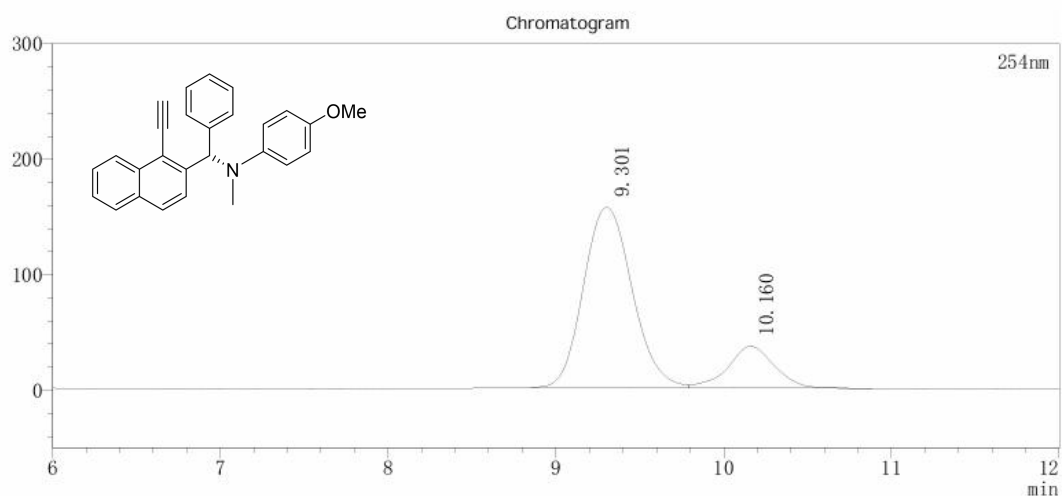
A 254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	6.586	131773	8995	7.218
2	7.313	1693931	108155	92.782
Total		1825704	117149	100.000

racemic-5b



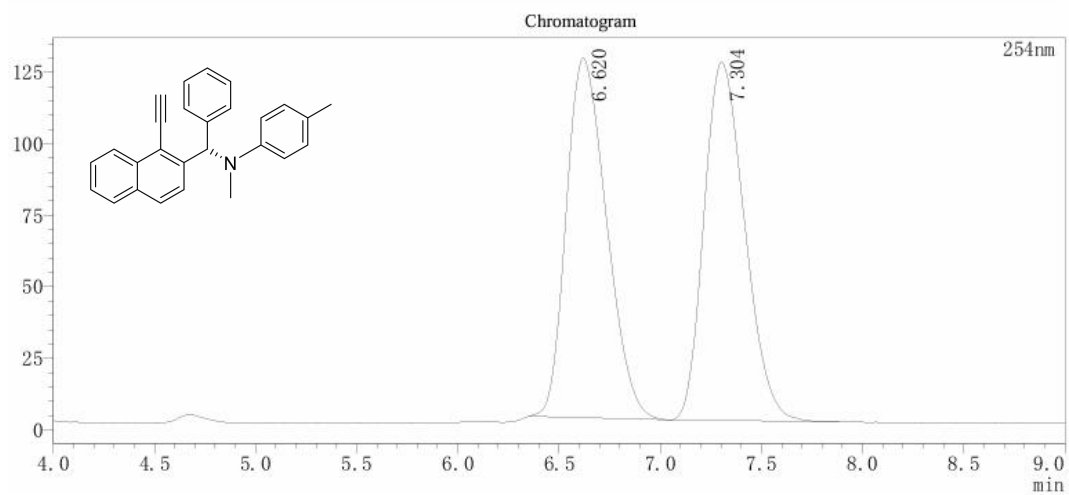
Peak#	Ret. Time	Area	Height	Area%
1	9.723	2417536	144749	50.386
2	10.879	2380472	145410	49.614
Total		4798008	290159	100.000

chiral-5b



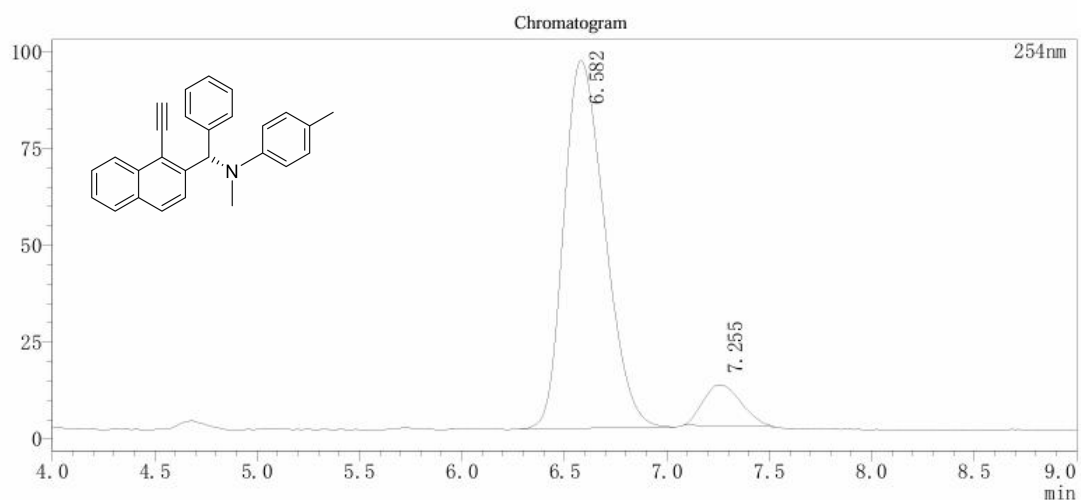
Peak#	Ret. Time	Area	Height	Area%
1	9.301	3142669	156033	81.793
2	10.160	699565	36302	18.207
Total		3842234	192334	100.000

racemic-5c



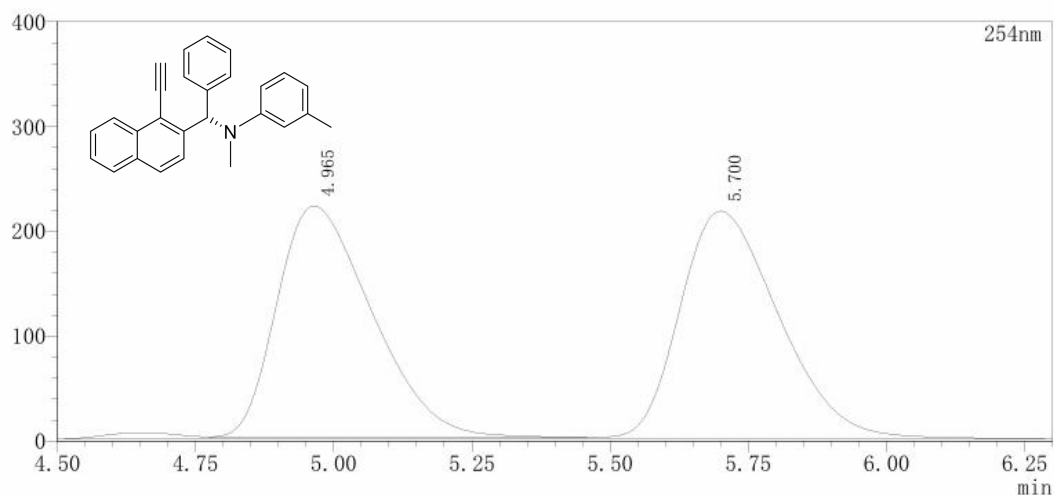
Peak#	Ret. Time	Area	Height	Area%
1	6.620	1747409	125726	49.856
2	7.304	1757527	125329	50.144
Total		3504936	251055	100.000

chiral-5c



Peak#	Ret. Time	Area	Height	Area%
1	6.582	1321078	94875	90.589
2	7.255	137239	10586	9.411
Total		1458316	105461	100.000

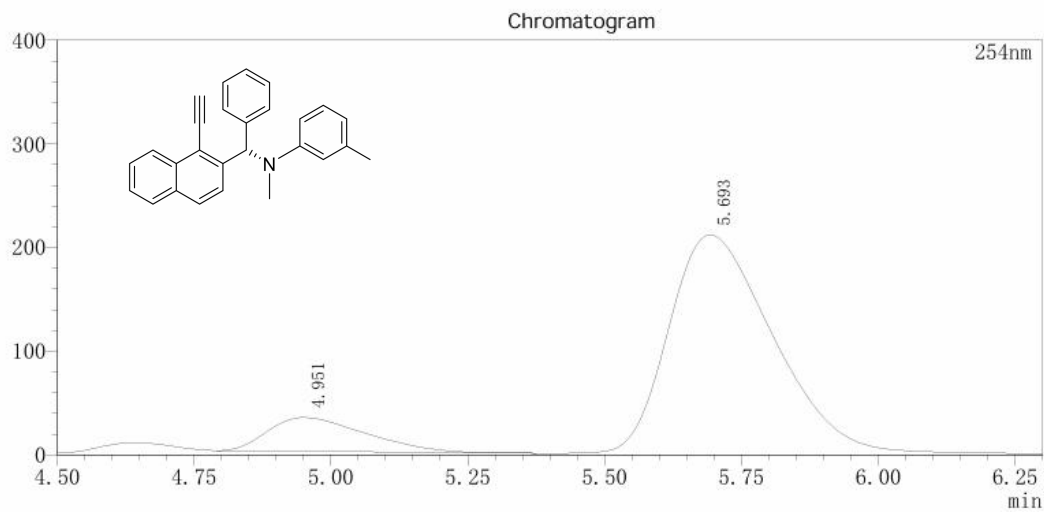
racemic-5d



254nm Peak table

Peak#	Ret. Time	Area	Height	Area%
1	4.965	2626773	220547	49.431
2	5.700	2687243	216473	50.569
Total		5314016	437019	100.000

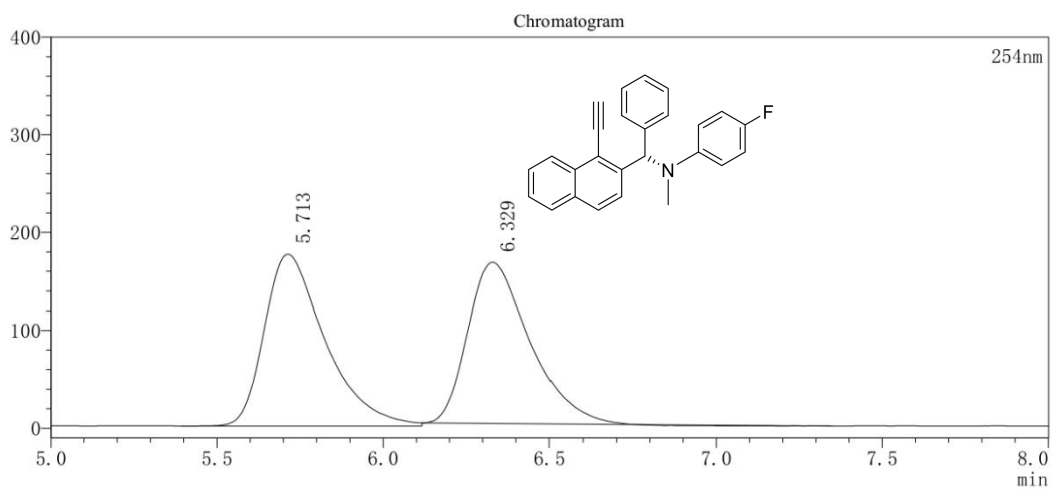
chiral-5d



254nm Peak Table

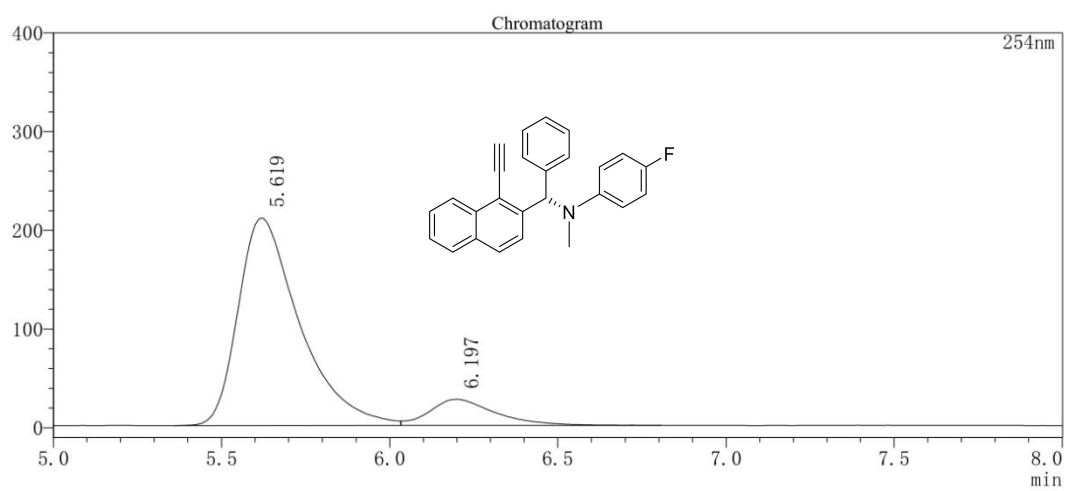
Peak#	Ret. Time	Area	Height	Area%
1	4.951	402191	32601	12.512
2	5.693	2812131	211344	87.488
Total		3214322	243946	100.000

racemic-5e



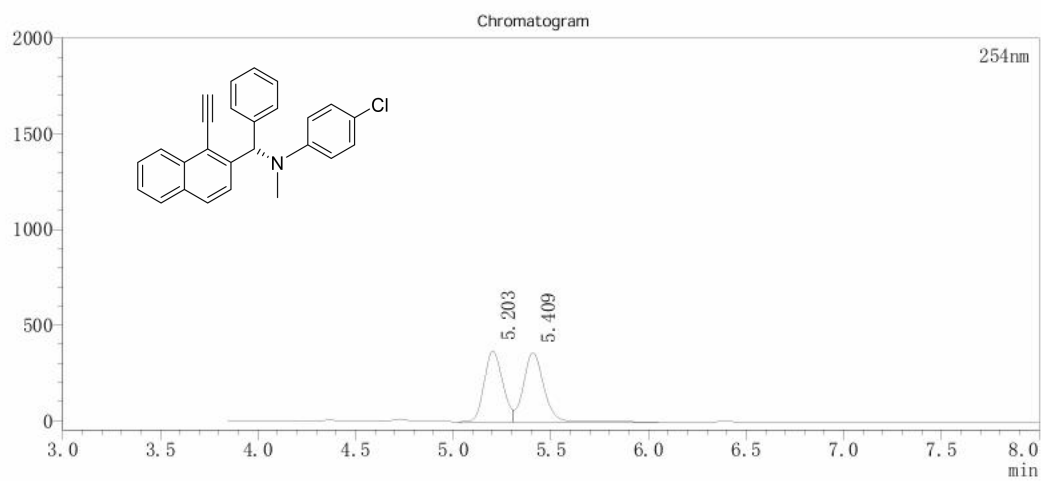
254nm		Peak Table			
Peak#	Ret. Time	Area	Height	Area%	
1	5.713	2242830	175565	51.342	
2	6.329	2125571	164474	48.658	
Total		4368402	340039	100.000	

chiral-5e



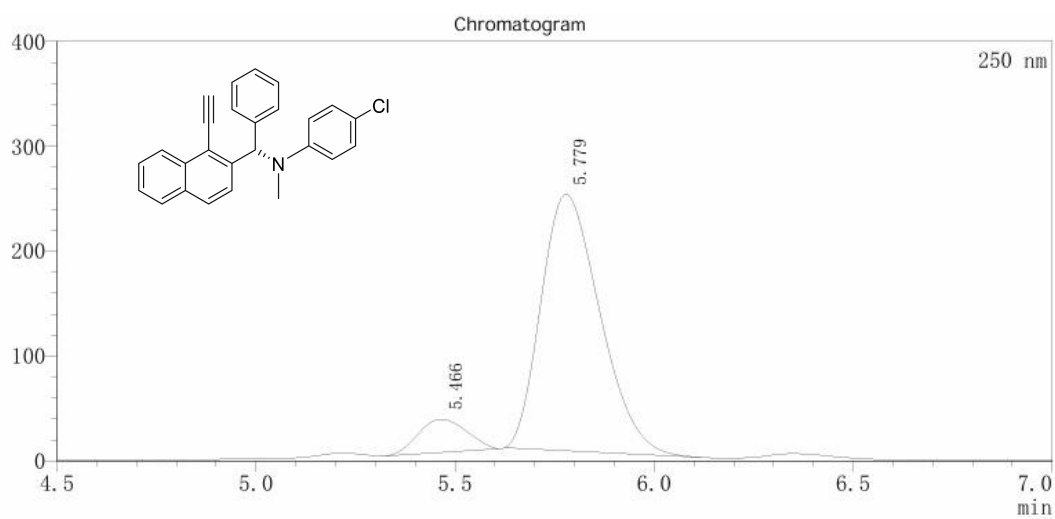
254nm		Peak Table			
Peak#	Ret. Time	Area	Height	Area%	
1	5.619	2682623	210398	88.154	
2	6.197	360501	26549	11.846	
Total		3043124	236946	100.000	

racemic-5f



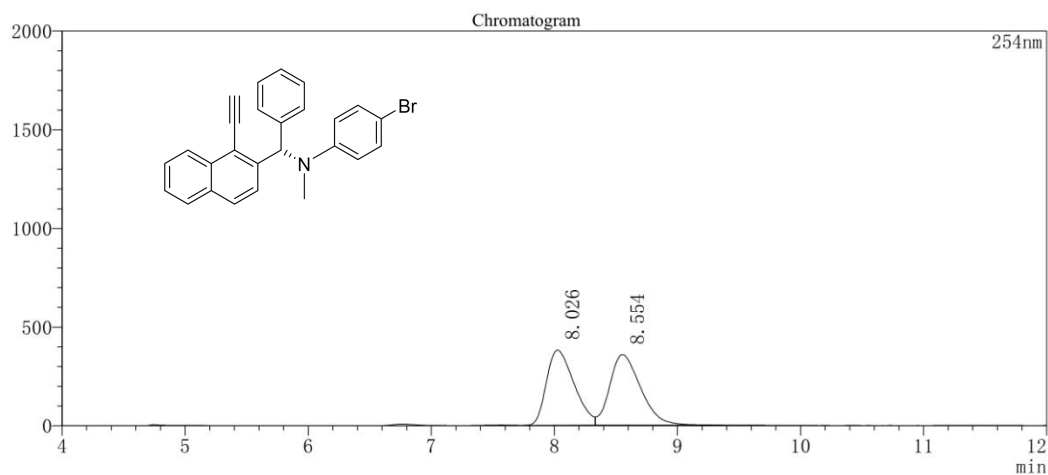
Peak#	Ret. Time	Area	Height	Area%
1	5.203	2422334	369580	48.658
2	5.409	2555982	360326	51.342
Total		4978316	729906	100.000

chiral-5f



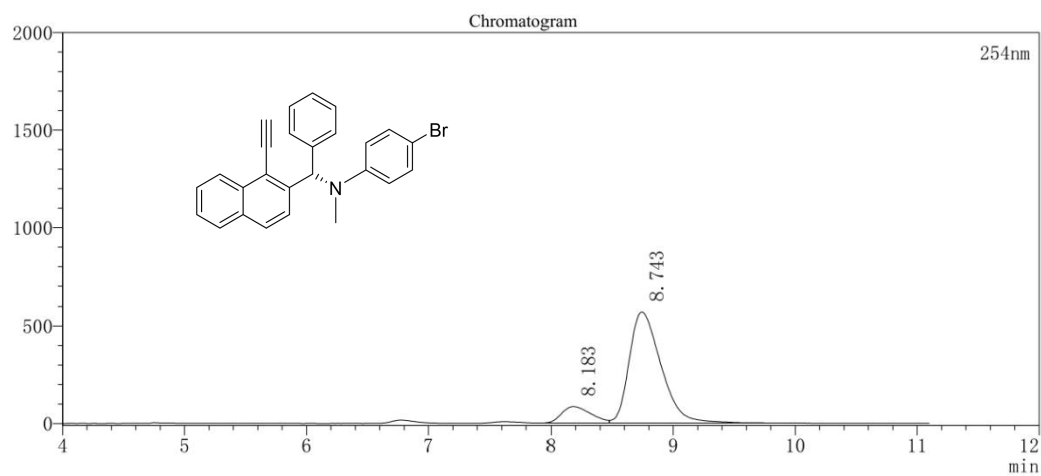
Peak#	Ret. Time	Area	Height	Area%
1	5.466	267579	31802	9.616
2	5.779	2514964	244322	90.384
Total		2782543	276124	100.000

racemic-5g



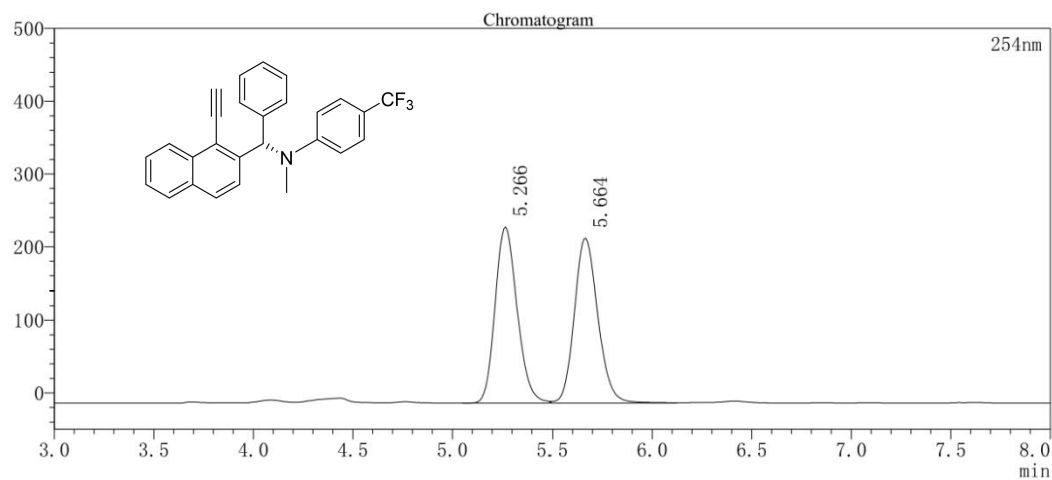
Peak#	Ret. Time	Area	Height	Area%
1	8.026	5952711	380803	48.786
2	8.554	6248915	358014	51.214
Total		12201626	738817	100.000

chiral-5g



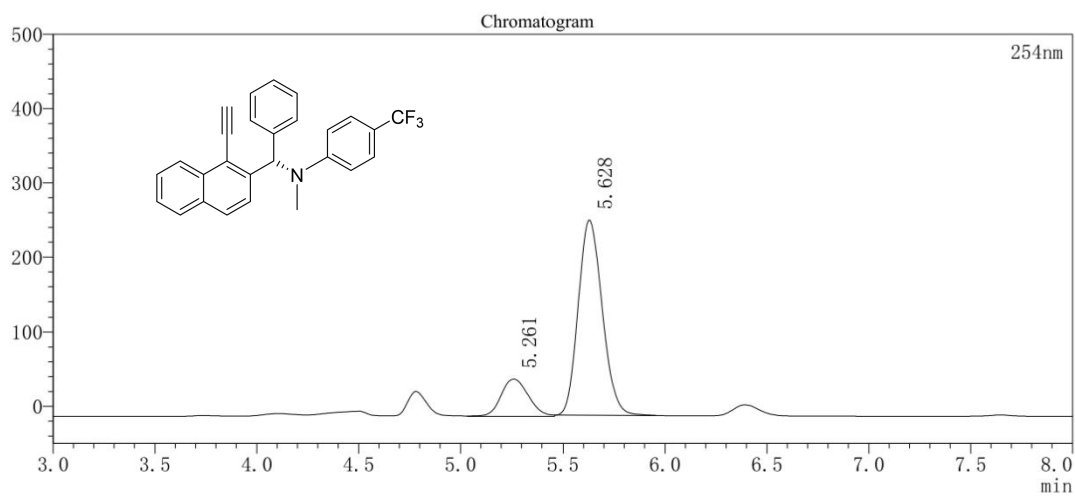
Peak#	Ret. Time	Area	Height	Area%
1	8.183	1417432	84923	12.067
2	8.743	10328476	570207	87.933
Total		11745907	655131	100.000

racemic-5h



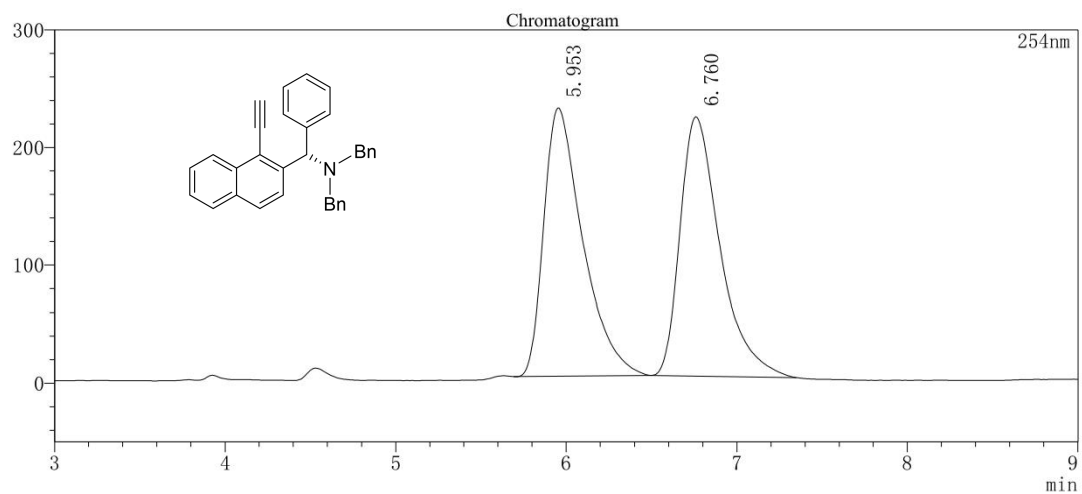
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	5.266	1859570	241168	49.997
2	5.664	1859794	225125	50.003
Total		3719363	466293	100.000

chiral-5h



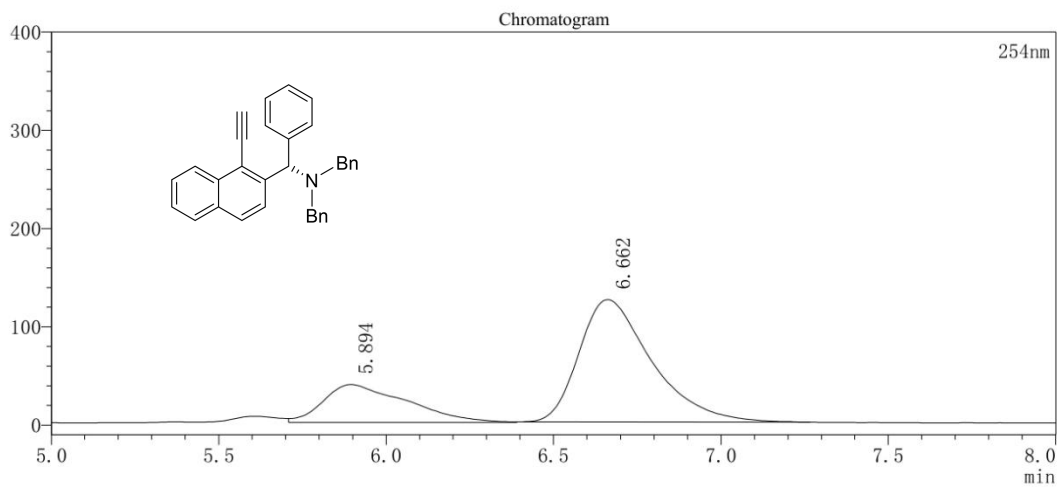
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	5.261	470121	50174	17.933
2	5.628	2151371	261694	82.067
Total		2621492	311868	100.000

racemic-5i



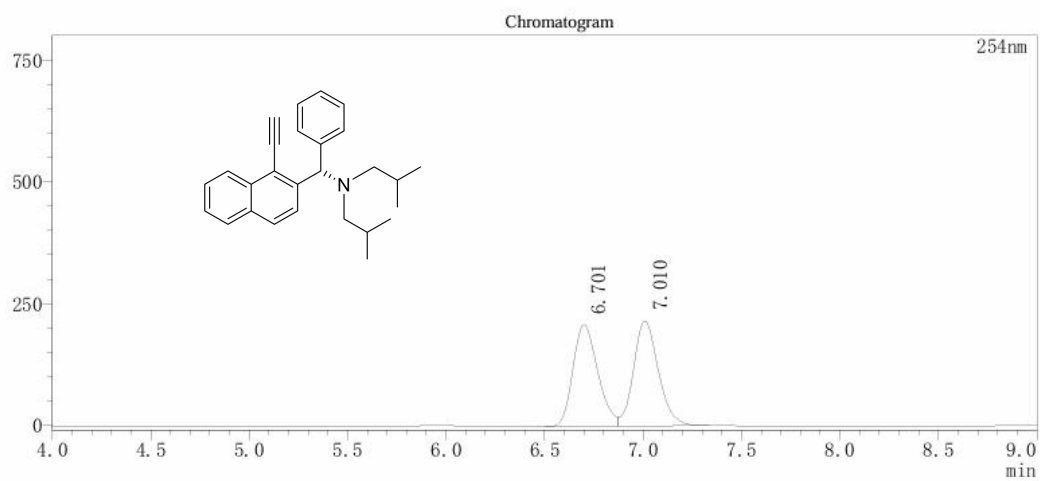
Peak#	Ret. Time	Area	Height	Area%
1	5.953	3610835	227617	50.194
2	6.760	3582903	220029	49.806
Total		7193738	447646	100.000

chiral-5i



Peak#	Ret. Time	Area	Height	Area%
1	5.894	672057	38610	26.395
2	6.662	1874077	124521	73.605
Total		2546135	163132	100.000

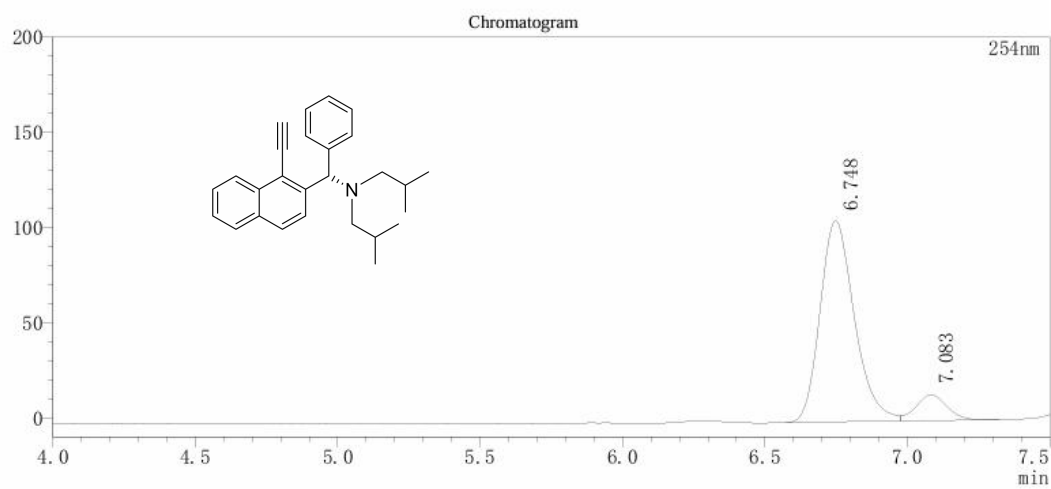
racemic-5j



254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.701	1826196	208742	49.312
2	7.010	1877137	215836	50.688
Total		3703333	424578	100.000

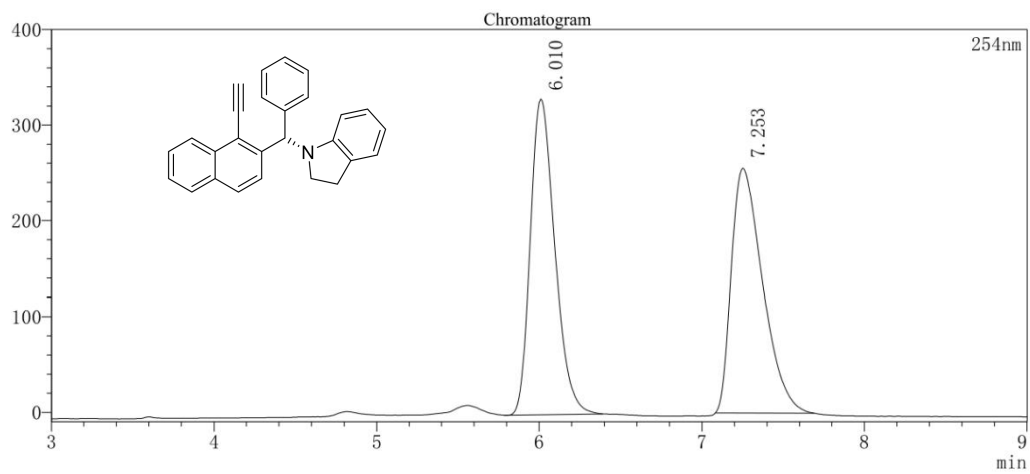
chiral-5j



254nm

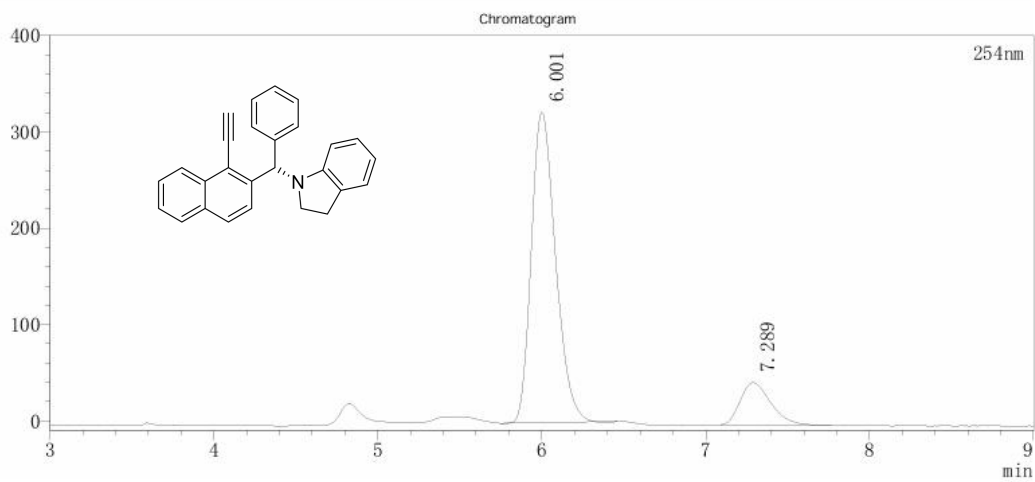
Peak#	Ret. Time	Area	Height	Area%
1	6.748	884644	105873	89.572
2	7.083	102988	13716	10.428
Total		987632	119589	100.000

racemic-5k



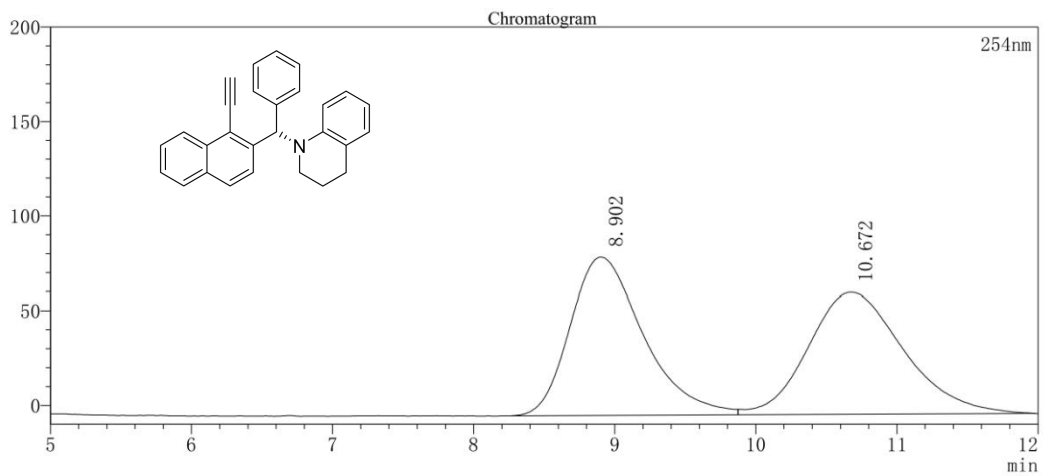
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	6.010	3455371	329781	50.263
2	7.253	3419229	255539	49.737
Total		6874599	585320	100.000

chiral-5k



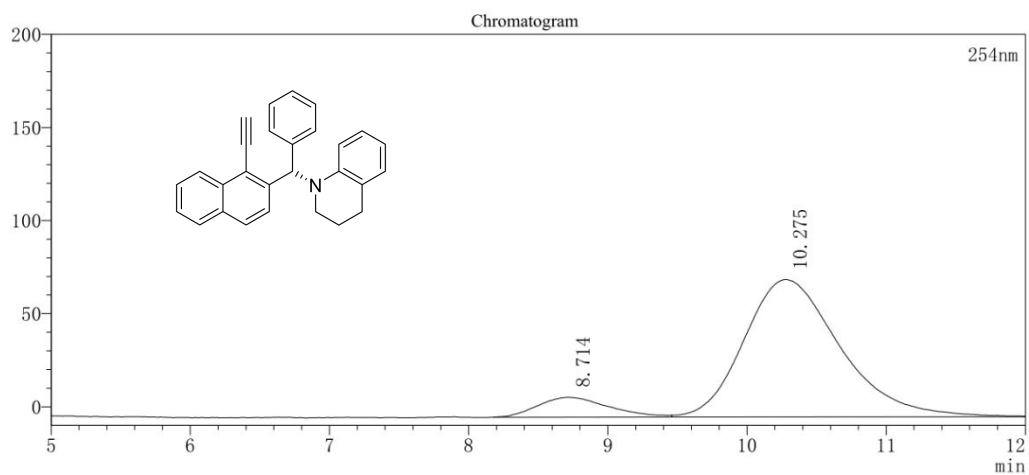
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	6.001	3312739	322352	85.251
2	7.289	573105	43969	14.749
Total		3885844	366321	100.000

racemic-5l



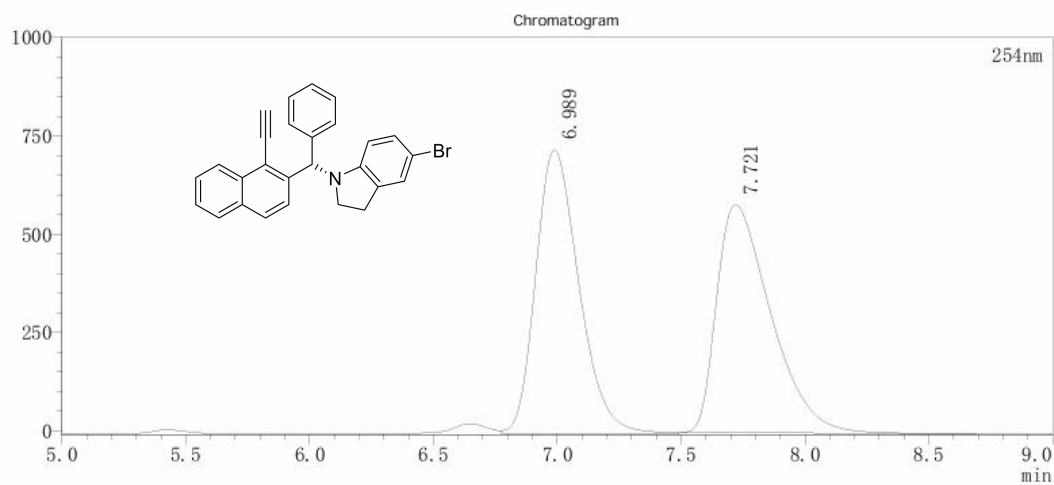
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	8.902	3018611	83491	49.918
2	10.672	3028588	64386	50.082
Total		6047199	147877	100.000

chiral-5l



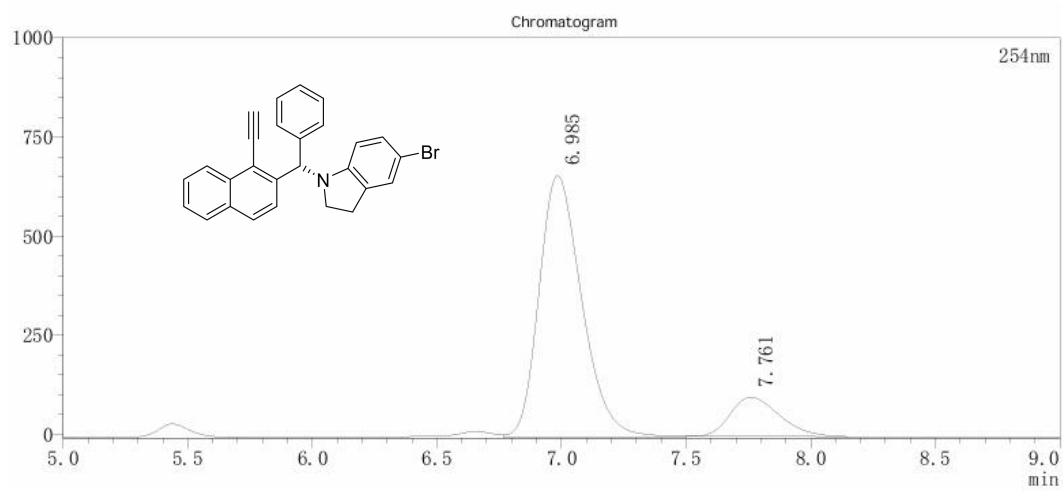
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	8.714	374164	10610	9.571
2	10.275	3535336	73765	90.429
Total		3909500	84376	100.000

racemic-5m



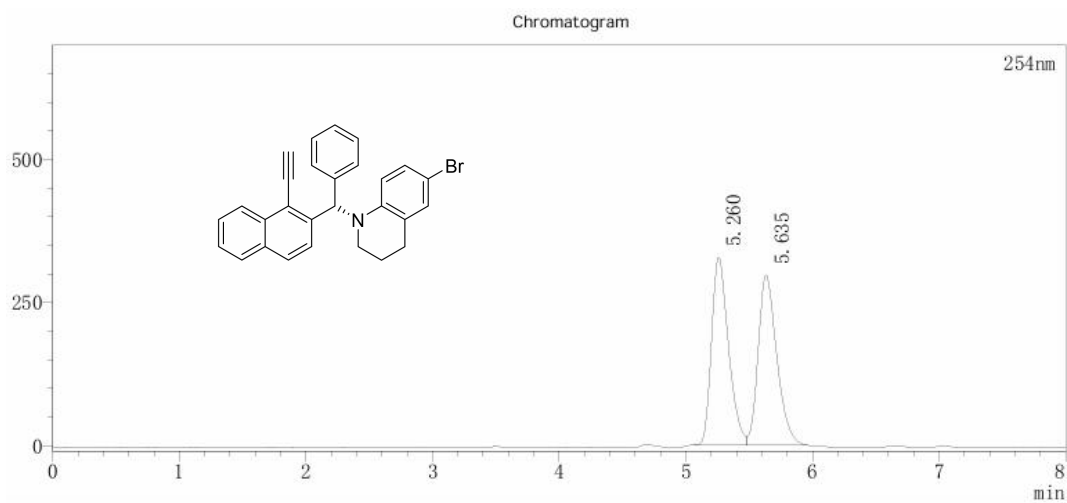
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	6.989	8794203	722461	49.987
2	7.721	8798606	579554	50.013
Total		17592810	1302015	100.000

chiral-5m



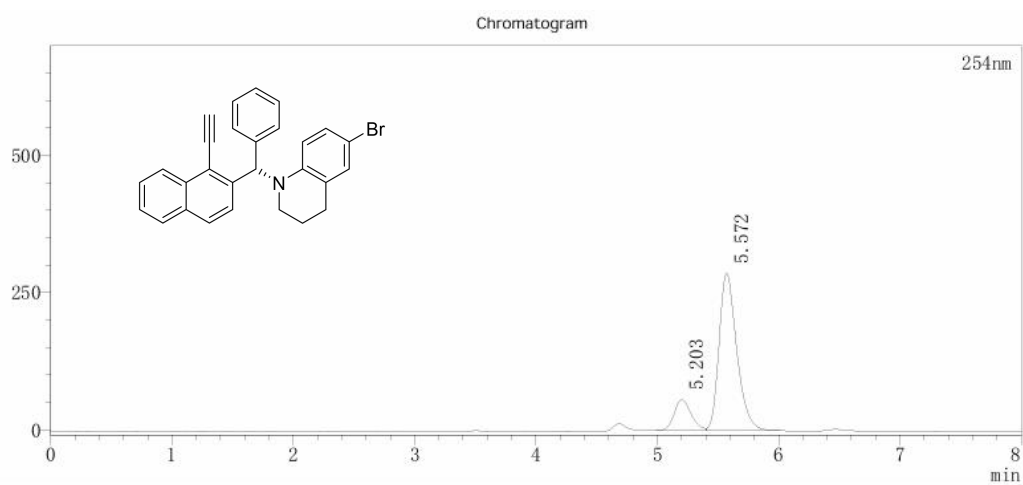
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	6.985	7887021	661323	85.349
2	7.761	1353834	98828	14.651
Total		9240855	760151	100.000

racemic-5n



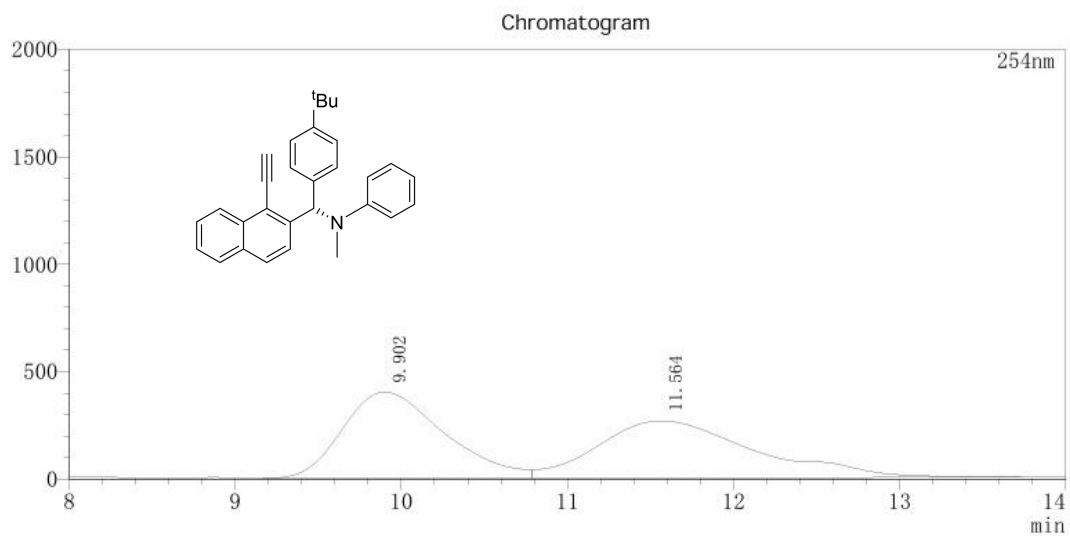
254nm		Peak Table			
Peak#	Ret. Time	Area	Height	Area%	
1	5.260	3070868	328753	50.228	
2	5.635	3042939	297370	49.772	
Total		6113807	626123	100.000	

chiral-5n



254nm		Peak Table			
Peak#	Ret. Time	Area	Height	Area%	
1	5.203	535446	56133	15.581	
2	5.572	2901030	286275	84.419	
Total		3436476	342408	100.000	

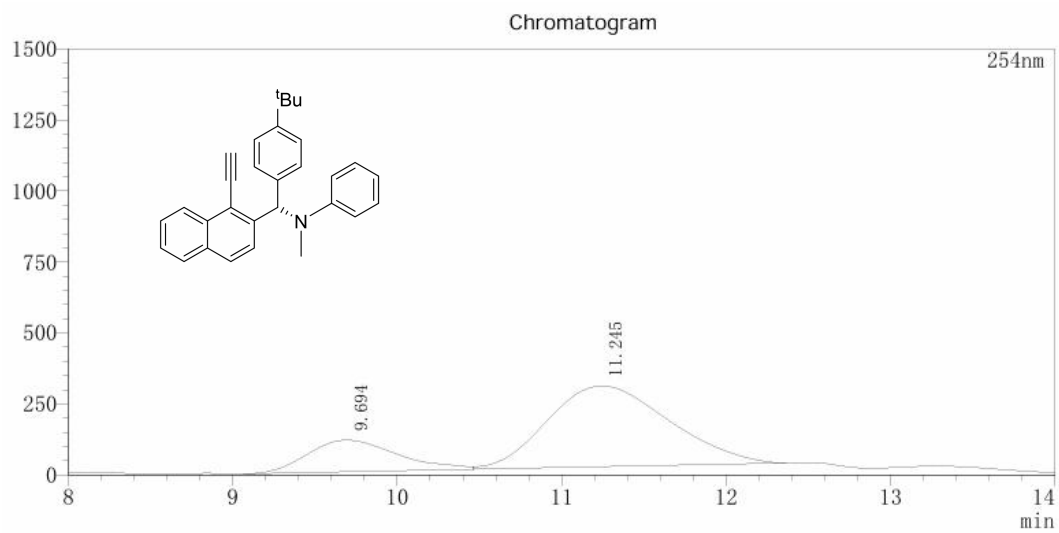
racemic-6a



254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.902	16925760	400108	49.461
2	11.564	17294332	264853	50.539
Total		34220093	664961	100.000

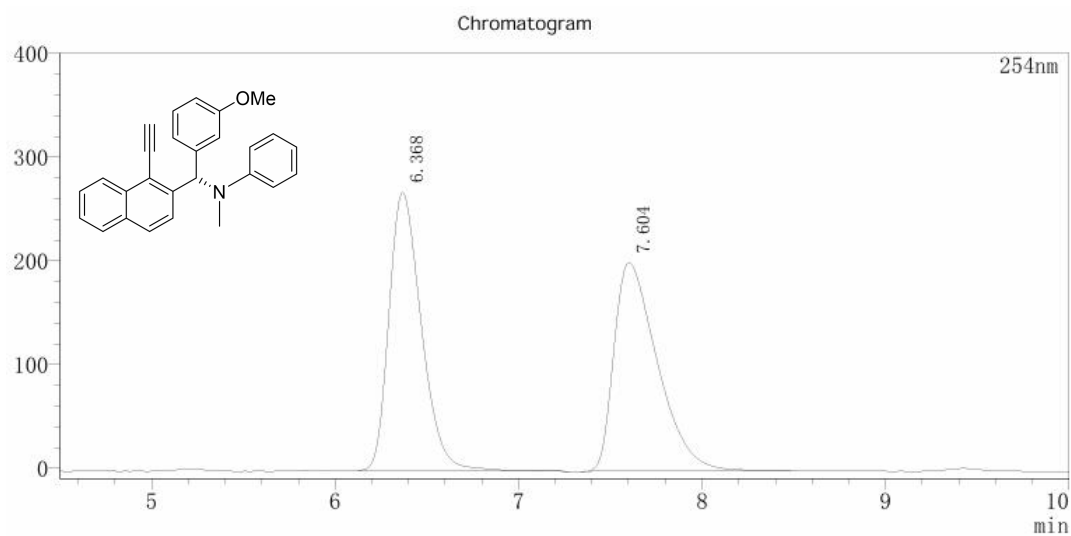
chiral-6a



254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.694	4223817	111490	22.427
2	11.245	14609814	283631	77.573
Total		18833631	395121	100.000

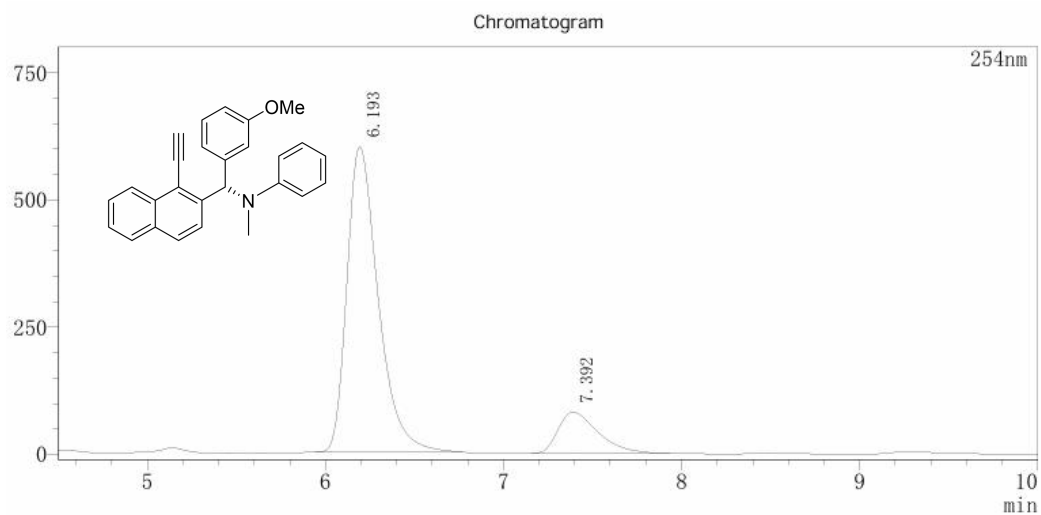
racemic-6b



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	6.368	3278014	268424	49.823
2	7.604	3301252	201051	50.177
Total		6579266	469475	100.000

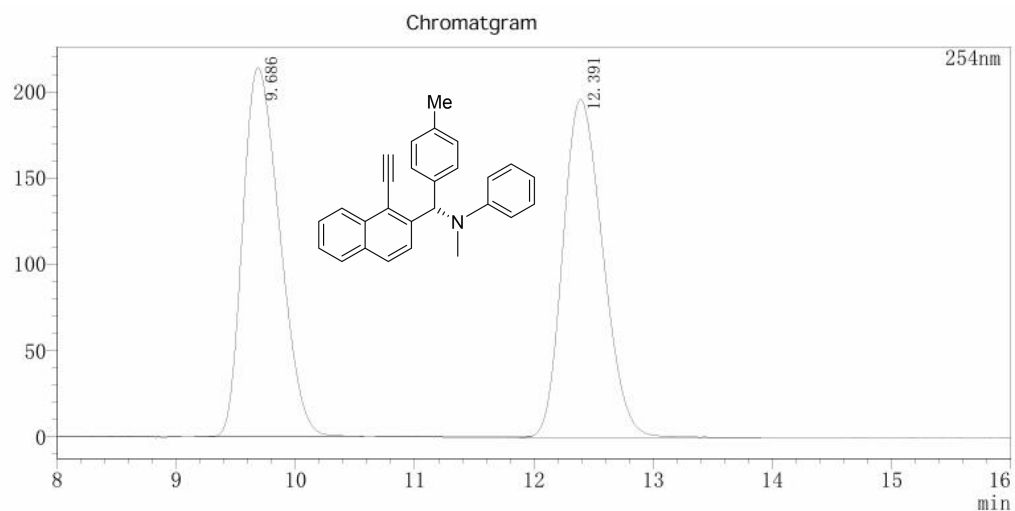
chiral-6b



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	6.193	7318231	600217	85.327
2	7.392	1258469	81064	14.673
Total		8576700	681281	100.000

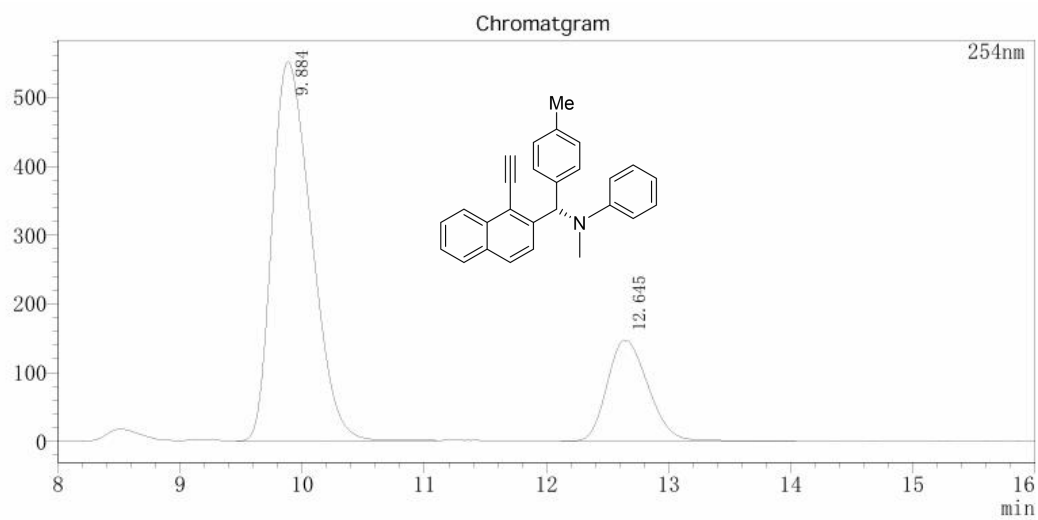
racemic-6c



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	9.686	4594987	213738	50.224
2	12.391	4554022	196010	49.776
Total		9149009	409748	100.000

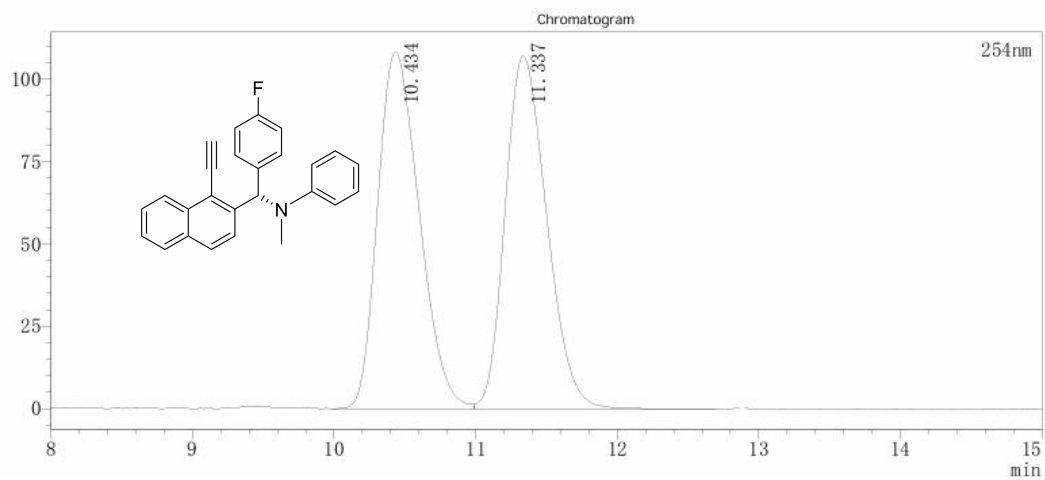
chiral-6c



254nm Peak Table

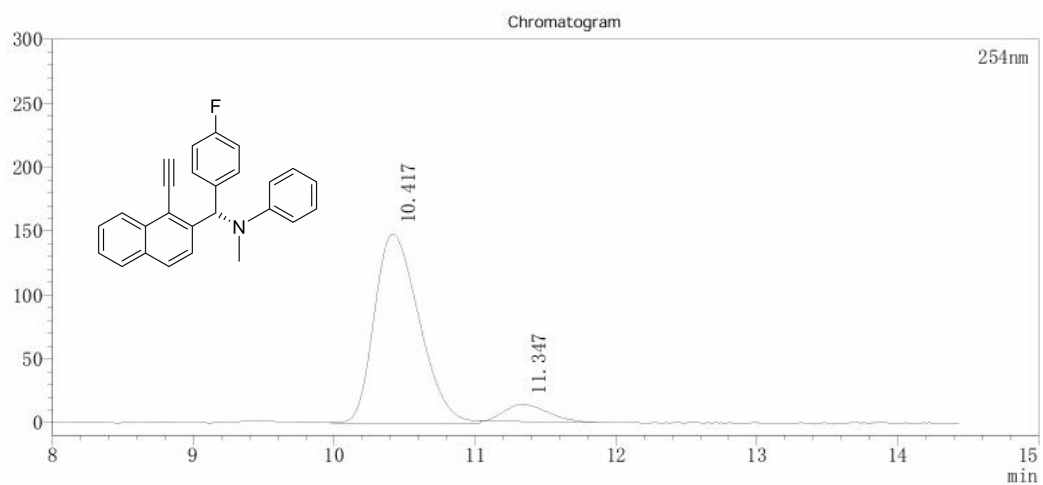
Peak#	Ret. Time	Area	Height	Area%
1	9.884	12294029	551332	78.304
2	12.645	3406402	146794	21.696
Total		15700431	698126	100.000

racemic-6d



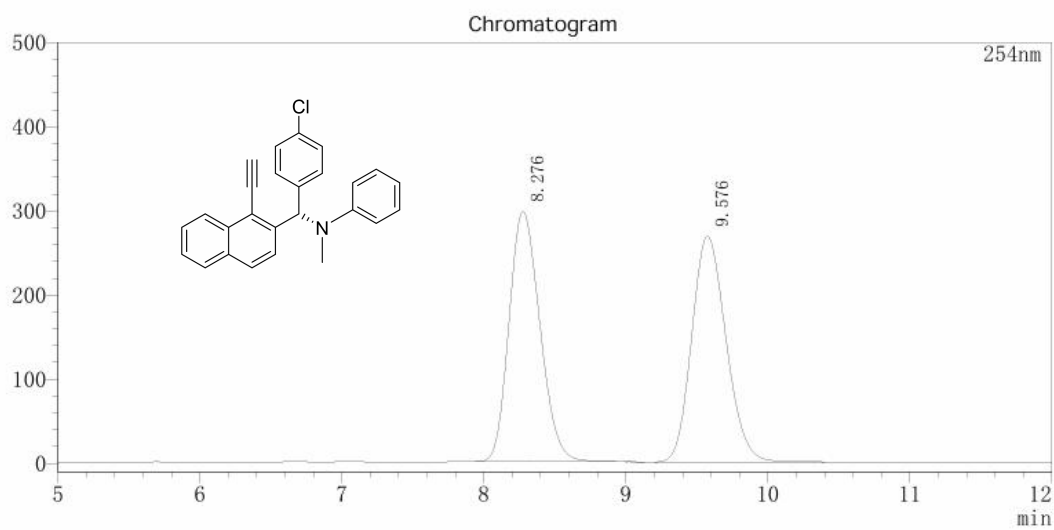
254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	10.434	2216058	108360	50.256
2	11.337	2193524	107176	49.744
Total		4409582	215536	100.000

chiral-6d



254nm		Peak Table		
Peak#	Ret. Time	Area	Height	Area%
1	10.417	3259677	147988	92.053
2	11.347	281425	13120	7.947
Total		3541102	161108	100.000

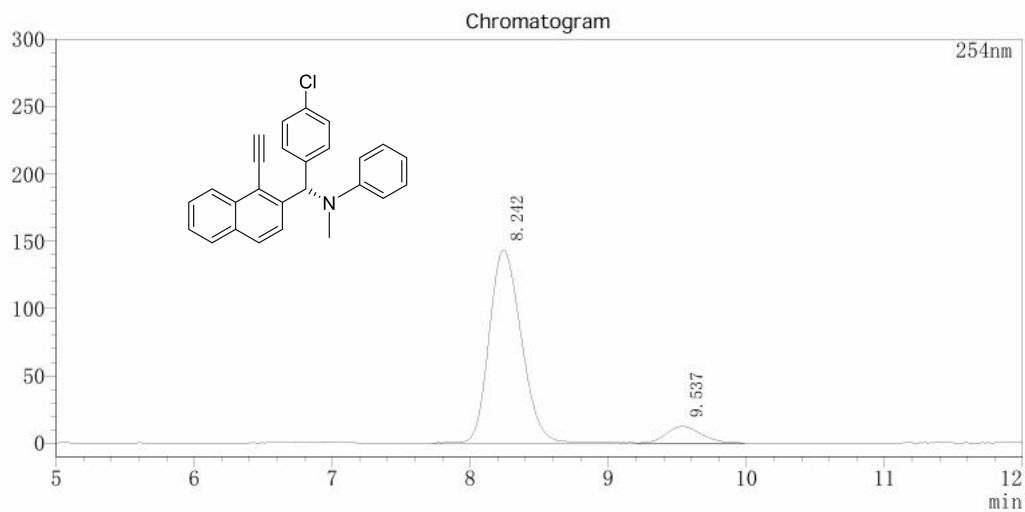
racemic-6e



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	8.276	4485411	297361	49.970
2	9.576	4490773	268196	50.030
总计		8976184	565558	100.000

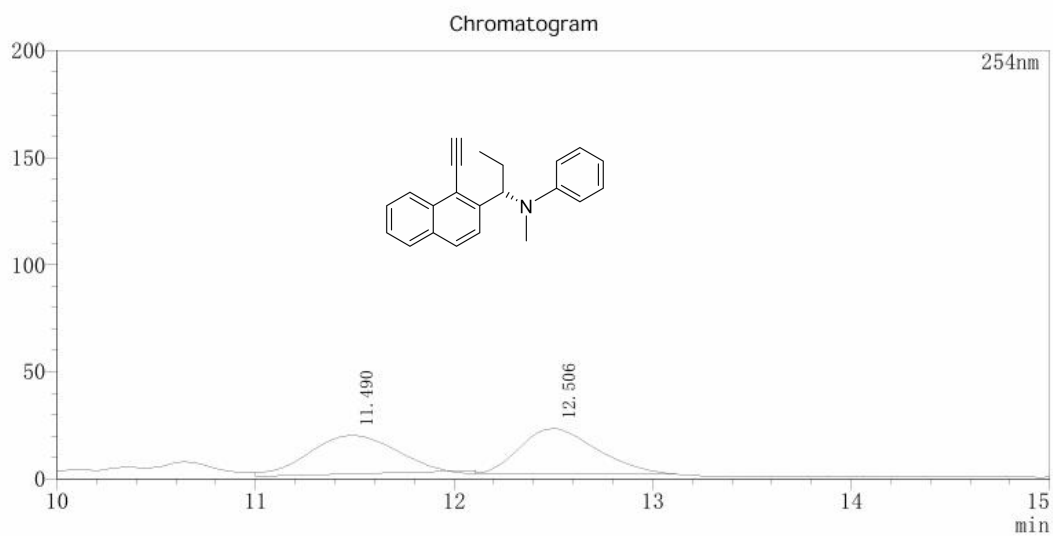
chiral-6e



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	8.242	2315330	143518	91.715
2	9.537	209157	12145	8.285
Total		2524487	155662	100.000

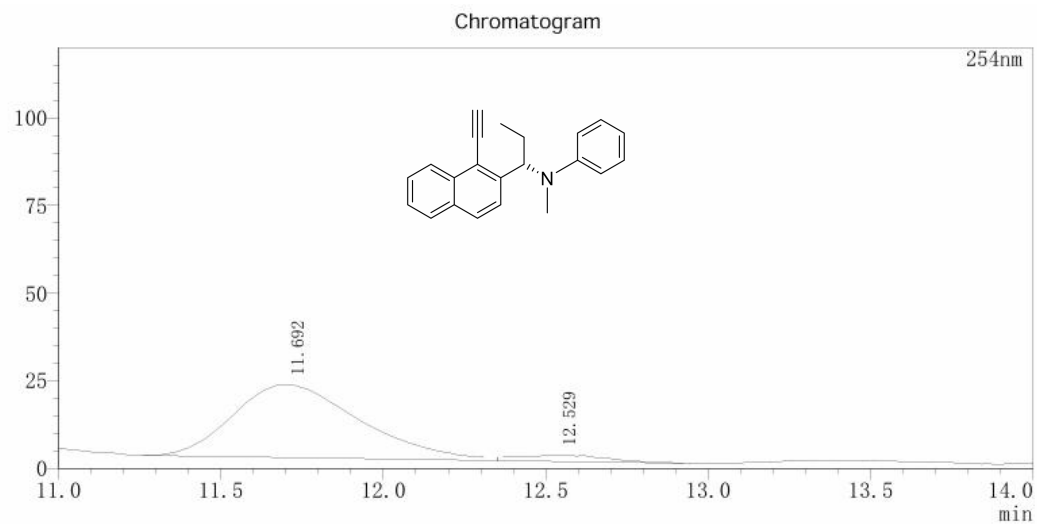
racemic-6f



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	11.490	539490	17927	49.056
2	12.506	560243	20986	50.944
Total		1099733	38912	100.000

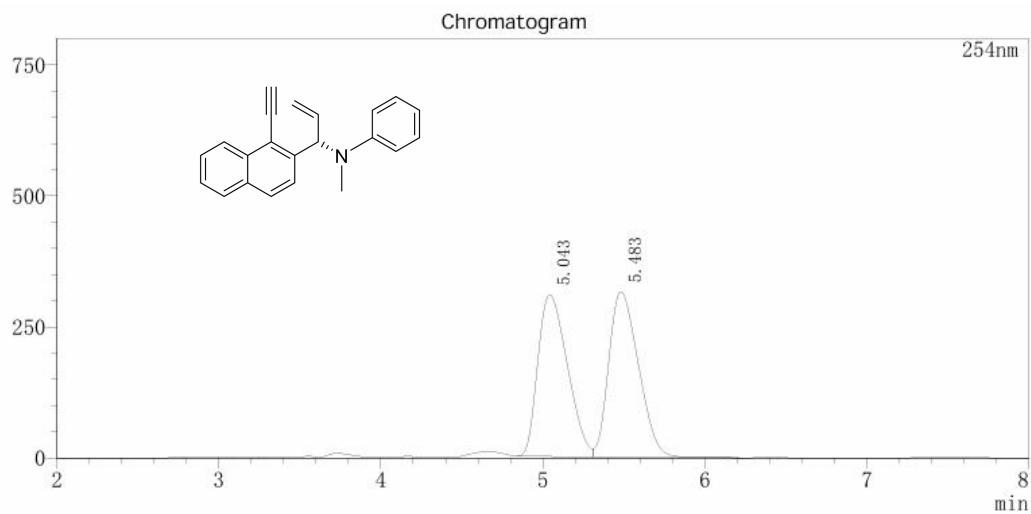
chiral-6f



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	11.692	562949	20836	94.251
2	12.529	34341	1750	5.749
Total		597290	22586	100.000

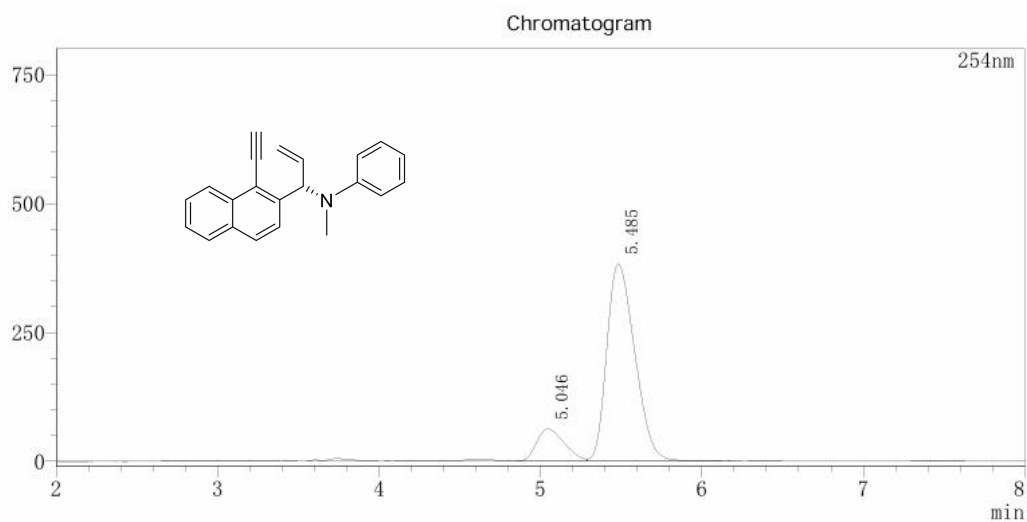
racemic-6g



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	5.043	3908239	308690	49.452
2	5.483	3994826	315117	50.548
Total		7903066	623807	100.000

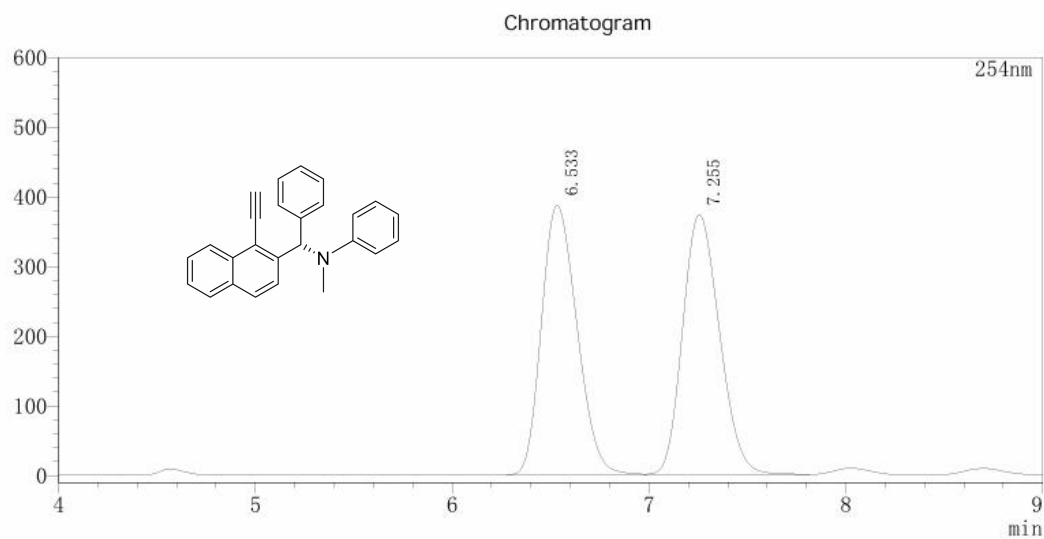
chiral-6g



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	5.046	732744	61946	13.751
2	5.485	4595745	382672	86.249
Total		5328488	444618	100.000

racemic-scale-up

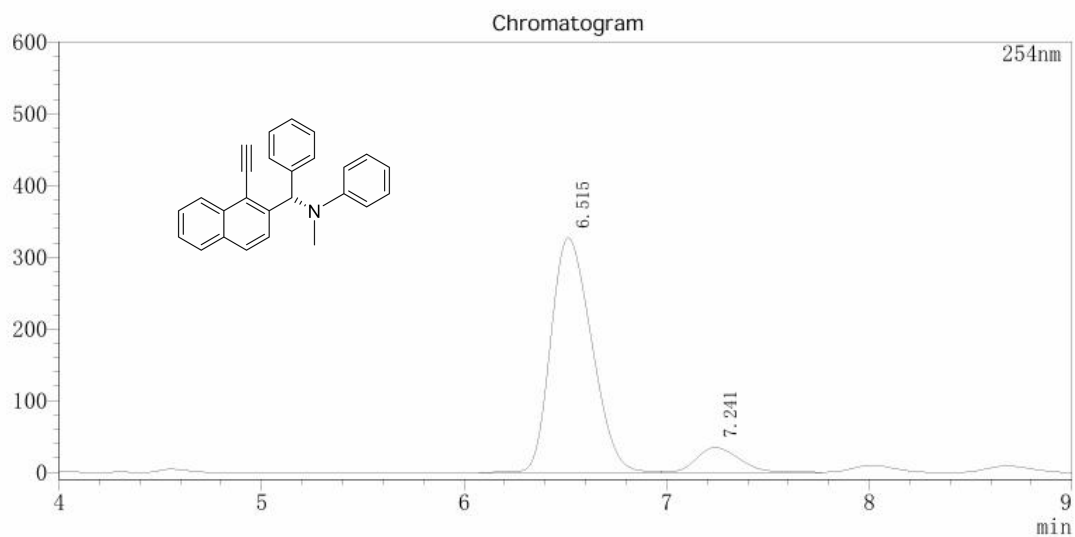


254nm

Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	6.533	4851710	387383	49.935
2	7.255	4864377	373191	50.065
Total		9716088	760574	100.000

chiral-scale-up

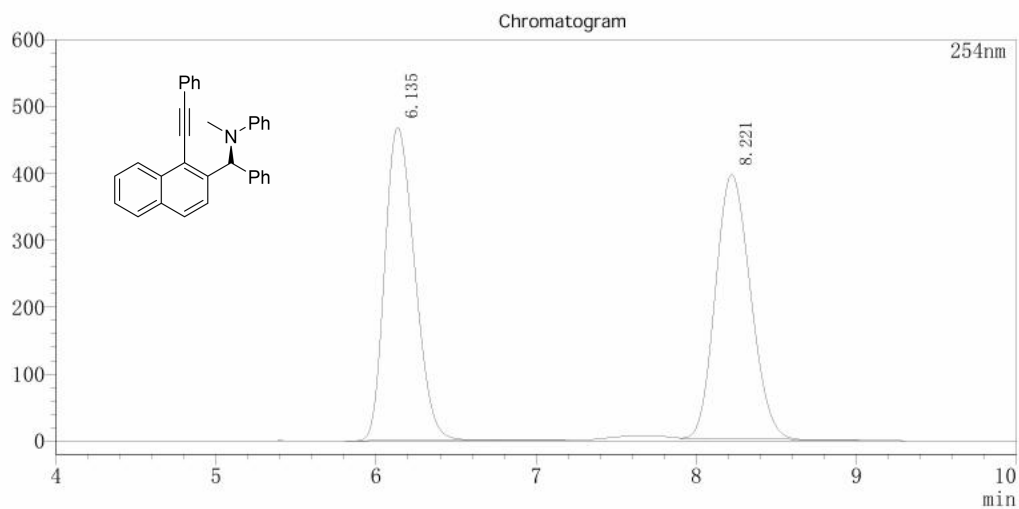


254nm

Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	6.515	4574586	327008	90.188
2	7.241	497683	34460	9.812
Total		5072268	361469	100.000

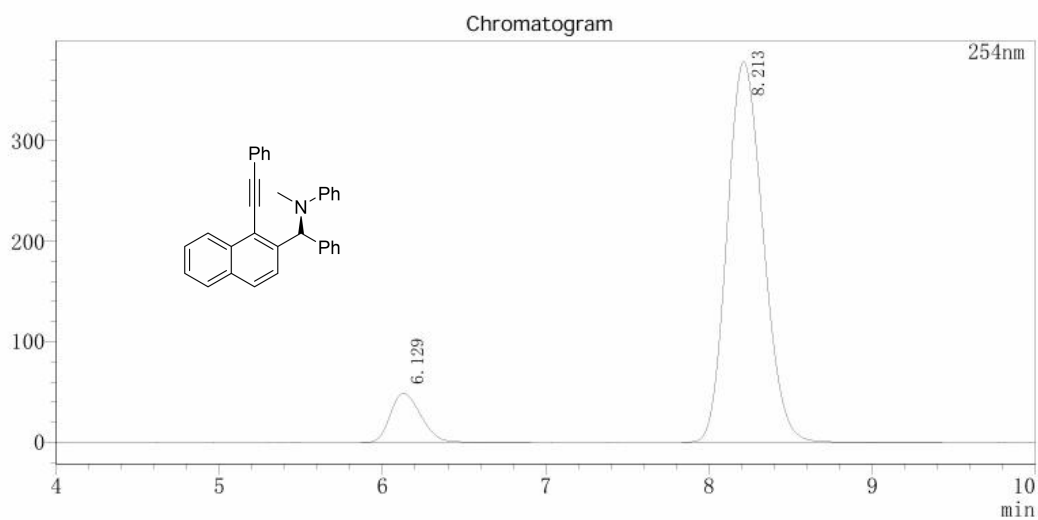
racemic-9a



254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	6.135	6092039	468879	50.435
2	8.221	5986952	394714	49.565
Total		12078991	863594	100.000

chiral-9a

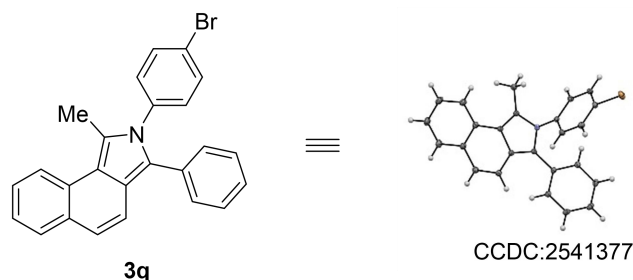


254nm Peak Table

Peak#	Ret. Time	Area	Height	Area%
1	6.129	634889	48748	9.842
2	8.213	5815686	378268	90.158
Total		6450575	427016	100.000

VII. Single Crystal X-Ray Diffraction of 3q, 5a and 7a.

Crystal data and structure refinement for **3q**. The method for crystal growth: mixture of dichloromethane and methanol, at room temperature. X-ray derived ORTEP of **3q** with thermal ellipsoids shown at the 50% probability level.

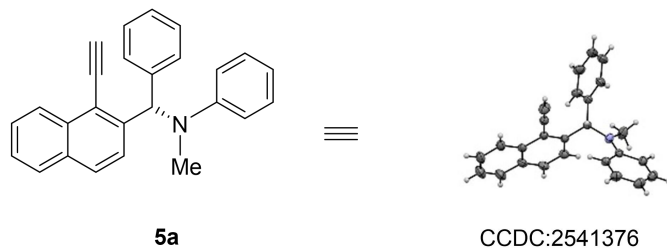


CCDC :2541377

Identification code	3q	
Empirical formula	C ₂₅ H ₁₈ BrN	
Formula weight	412.31	
Temperature	173.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.1703(6) Å	a = 90°
	b = 6.4509(3) Å	b = 100.878(3)°
	c = 26.2834(15) Å	g = 90°
Volume	1859.91(17) Å ³	
Z	4	
Density (calculated)	1.472 Mg/m ³	
Absorption coefficient	3.061 mm ⁻¹	
F(000)	840	
Crystal size	0.24 x 0.22 x 0.19 mm ³	
Theta range for data collection	3.424 to 71.998°	
Index ranges	-13 ≤ h ≤ 13, -7 ≤ k ≤ 7, -32 ≤ l ≤ 22	
Reflections collected	13857	
Independent reflections	3633 [R(int) = 0.0640]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7536 and 0.4499
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3633 / 0 / 245
Goodness-of-fit on F ²	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.1077
R indices (all data)	R1 = 0.0583, wR2 = 0.1173
Extinction coefficient	n/a
Largest diff. peak and hole	0.581 and -0.507 e.Å ⁻³

Crystal data and structure refinement for **5a**. The method for crystal growth: mixture of ethanol, at room temperature. X-ray derived ORTEP of **5a** with thermal ellipsoids shown at the 50% probability level.

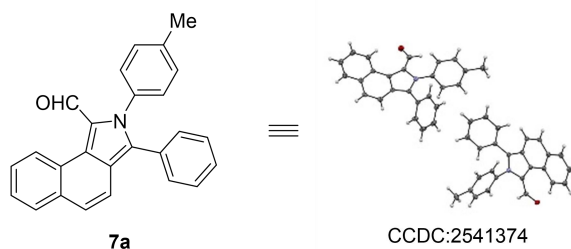


CCDC :2541376

Identification code	5a	
Empirical formula	C ₂₆ H ₂₁ N	
Formula weight	347.44	
Temperature	296.15 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 8.5087(14) Å	a = 90°
	b = 9.0486(15) Å	b = 105.010(8)°
	c = 13.346(2) Å	g = 90°
Volume	992.5(3) Å ³	
Z	2	
Density (calculated)	1.163 Mg/m ³	
Absorption coefficient	0.509 mm ⁻¹	
F(000)	368	
Crystal size	0.22 x 0.2 x 0.17 mm ³	
Theta range for data collection	3.428 to 74.873°	
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 11, -16 ≤ l ≤ 16	
Reflections collected	14515	
Independent reflections	3959 [R(int) = 0.0480]	
Completeness to theta = 67.679°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6650	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3959 / 1 / 246
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0423, wR2 = 0.0969
R indices (all data)	R1 = 0.0589, wR2 = 0.1102
Absolute structure parameter	0.4(5)
Extinction coefficient	0.032(3)
Largest diff. peak and hole	0.096 and -0.109 e.Å ⁻³

Crystal data and structure refinement for **7a**. The method for crystal growth: mixture of dichloromethane and methanol, at room temperature. X-ray derived ORTEP of **7a** with thermal ellipsoids shown at the 50% probability level.



CCDC :2541374

Identification code	7a	
Empirical formula	C ₂₆ H ₁₉ NO	
Formula weight	361.42	
Temperature	173.0 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2110(9) Å	a = 87.203(4)°
	b = 9.3934(9) Å	b = 80.528(4)°
	c = 22.180(2) Å	g = 84.782(4)°
Volume	1884.0(3) Å ³	
Z	4	
Density (calculated)	1.274 Mg/m ³	
Absorption coefficient	0.600 mm ⁻¹	
F(000)	760	
Crystal size	0.14 x 0.12 x 0.08 mm ³	
Theta range for data collection	2.021 to 68.320°	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 9, -24 ≤ l ≤ 26	
Reflections collected	18311	
Independent reflections	6773 [R(int) = 0.0486]	
Completeness to theta = 67.679°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6540	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6773 / 0 / 506
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0496, wR2 = 0.1221
R indices (all data)	R1 = 0.0652, wR2 = 0.1343
Extinction coefficient	n/a
Largest diff. peak and hole	0.267 and -0.241 e.Å ⁻³