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Supporting Information

Gold(I)-Catalyzed Intramolecular Tandem Cyclization Reaction of Alkylidenecyclopropane-Containing Alkynes

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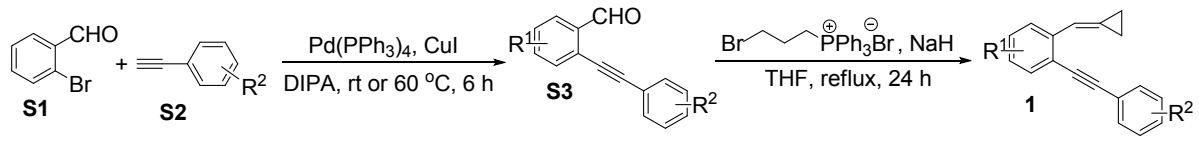
CONTENTS

1. General Remarks. MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. ^{1}H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. *J*-values are in Hz. HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. UV-visible spectra were obtained on a Hitachi U-3900 Spectrophotometer. Fluorescence spectra for emission and excitation were obtained on a Hitachi F-2700 FL Spectrophotometer.

Substrates **1a**,[1] **1b**,[1] **1h**,[1] **1j**,[1] **1k**,[1] **1aa**,[1] **1bb**,[1] **1dd**,[1] **1ee**,[1] **1jj**,[1] **8**,[2] and product **2a**[3] were synthesized by the procedure reported in the previous literature.

2. General procedure for the synthesis of methylenecyclopropanes **1**.



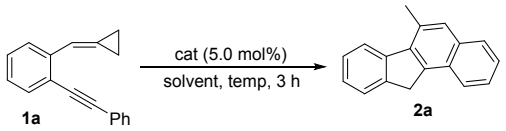
Scheme S1

The substrate **1** was synthesized according to Scheme S1. The compound **S3** was synthesized according to the previously reported procedure.[4]

Synthesis of substrate **1**: to a suspension of sodium hydride (15.0 mmol, 3.0 equiv) in THF (30 mL) was added (3-bromopropyl)triphenylphosphonium bromide (7.5 mmol, 1.5 equiv) and the reaction mixture was stirred for 12 hours under reflux. Then, a solution of aldehyde **S3** (5.0 mmol, 1.0 equiv) in THF (20 mL) was added to the mixture and the resulting mixture was stirred for another 12 hours. The reaction was quenched with water and extracted with petroleum ether. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure and the residue was purified by a silica gel chromatography (PE) to give methylenecyclopropanes **1** in 20-70% yields.[5]

3. Discussion on the ligand effect.

1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazole (IPr), as a carbene ligand, is unsuitable for the reaction (entries 1 and 12). Kinds of substituted triphenylphosphines as ligands are similarly ineffective in the reaction (entries 2, 11 and 13). To a very small extent, tricyclohexylphosphine as a ligand can promote the reaction (entry 4). Biphenyl phosphine ligands have good performances in the reaction compared to the three above (entries 3 and 5-10). Biphenyl phosphine ligands bearing electron-donating and sterically hindered group are in favor of the reaction.



entry	catalyst	solvent	temp (^{o}C)	yield[a] (%)
1	IPrAu(MeCN)NTf$_2$	toluene	100	NR
2	(2,4-*t*-Bu$C_6H_3O)_3$PAu(MeCN)OTf	toluene	100	NR
3	Me_4-*t*-BuXphosAuCl/$AgSbF_6$	toluene	100	42
4	Cy_3PAuCl/$AgSbF_6$	toluene	100	14
5	*t*-BuXphosAuCl/$AgSbF_6$	toluene	100	32
6	JackiephosAuCl/$AgSbF_6$	toluene	100	42
7	XphosAuCl/$AgSbF_6$	toluene	100	52
8	SphosAuCl/$AgSbF_6$	toluene	100	34
9	*t*-BuBrettphosAuCl/$AgSbF_6$	toluene	100	89
10	JohnphosAuCl/$AgSbF_6$	toluene	100	50
11	(*p*-$CF_3Ph)_3$P$AuSbF_6$	toluene	100	NR
12	IPrAu(MeCN)SbF_6	toluene	100	NR
13	Ph_3PAu(MeCN)SbF_6	toluene	100	NR
14	$AgSbF_6$	toluene	100	NR
15	*t*-BuBrettphosAuCl/$AgSbF_6$	DCE	100	21
16	*t*-BuBrettphosAuCl/$AgSbF_6$	dioxane	100	55
17	*t*-BuBrettphosAuCl/$AgSbF_6$	MeCN	100	20
18	*t*-BuBrettphosAuCl/$AgSbF_6$	PhCl	100	16
19	*t*-BuBrettphosAuCl/$AgSbF_6$	PhOMe	100	NR
20	*t*-BuBrettphosAuCl/$AgSbF_6$	toluene	90	42
21	*t*-BuBrettphosAuCl/$AgSbF_6$	toluene	110	75
22	*t*-BuBrettphosAu(MeCN)SbF_6	toluene	100	90 (83[b])

Reaction conditions: 1a (0.1 mmol), catalyst (5.0 mol%), solvent (0.5 mL). a Yields were determined by 1H NMR spectroscopy. b The isolated yield within 2 hours. NR is no reaction.

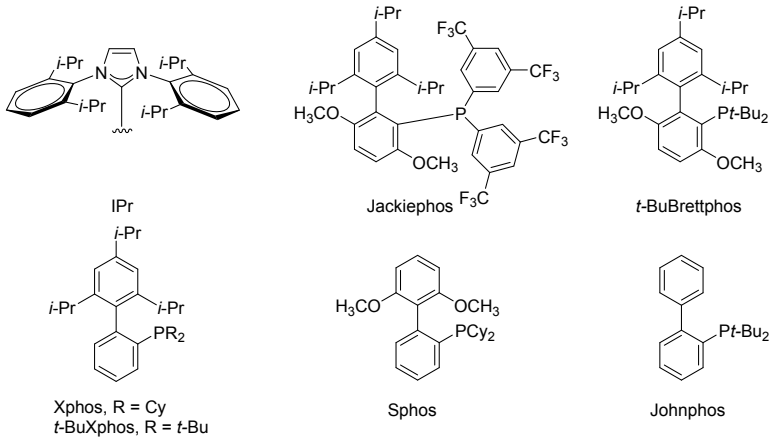
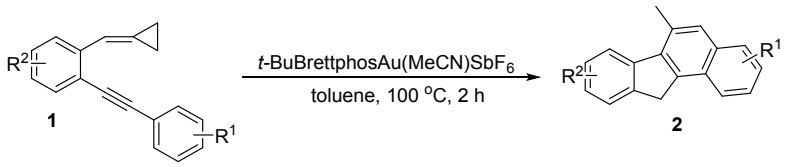


Table S1

4. General procedure for the synthesis of 2.

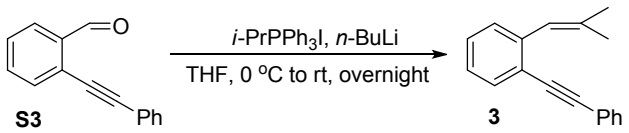


Scheme S2

Synthesis of products **2**: To a flame-dried flask were added the methylenecyclopropanes **1** (0.20 mmol, 1.0 equiv) and *t*-BuBrettphosAu(MeCN)SbF_6 (0.01 mmol, 0.05 equiv), and the flask was evacuated and backfilled with Ar for 3 times. Toluene (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 2 hours at 100 ^{o}C. Appropriate amount of

silica gel was added to the reaction mixture and the solvent was removed under vacuum pump at low temperature. Then, the crude product was purified by a silica gel chromatography (PE) to get the desired products **2** in 20-93% yields.

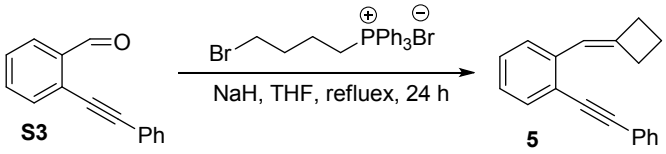
5. General procedure for the synthesis of 3.



Scheme S3

Synthesis of substrate **3**: To a 500 mL flame and vacuum dried three-neck flask was added (isopropyl)triphenylphosphonium iodide (15.0 mmol, 1.5 equiv) and 50 mL THF under Ar, then n-BuLi (2.4 M, 6.7 mL, 16 mmol, 1.6 equiv) was added slowly at 0 °C. After the addition was complete, the reaction mixture was allowed to stir at 0 °C for 2 h. Aldehyde **S3** (10 mmol, 1.0 equiv) was added to the flask slowly at 0 °C. The reaction mixture was warmed up to room temperature gradually and was stirred overnight. The reaction was quenched with water. The reaction mixture was extracted with Et_2O, and the combined organic phase was dried over anhydrous sodium sulfate. Then, the solvent was removed under reduced pressure and the residue was purified by a silica gel chromatography (PE) to give styrene **3** in 24% yield.

6. General procedure for the synthesis of 5.

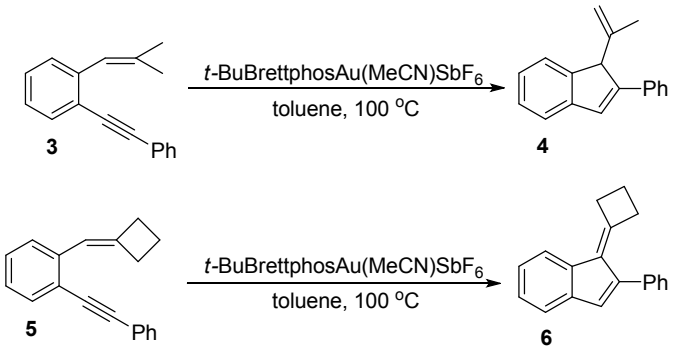


Scheme S4

Synthesis of substrate **5**: To a suspension of sodium hydride (15.0 mmol, 3.0 equiv) in THF (30 mL) was added (4-bromopropyl)triphenylphosphonium bromide (7.5 mmol, 1.5 equiv) and the mixture was stirred for 12 hours under reflux. Then, a solution of aldehyde **S3** (5.0 mmol, 1.0 equiv) in THF (20 mL) was added to the mixture and the resulting mixture was stirred for another 12 hours. The reaction was quenched with water and extracted with petroleum ether. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure and the residue was purified by a silica gel chromatography (PE) to give

methylenecyclobutane **5** in 46% yield.[5]

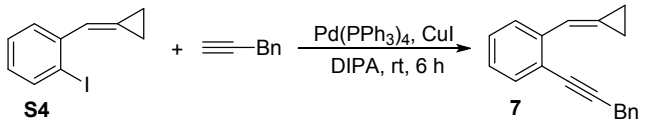
7. General procedure for the synthesis of 4 and 6.



Scheme S5

Synthesis of products **4** and **6**: To two flame-dried flasks were added substrates **3** and **5** (0.20 mmol, 1.0 equiv) and *t*-BuBrettphosAu(MeCN)SbF_6 (0.01 mmol, 0.05 equiv), respectively, and the flask was evacuated and backfilled with Ar for 3 times. Toluene (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 2 hours at 100 °C. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum pump at low temperature. Then, the crude product was purified by a silica gel chromatography (PE) to get the desired products **4** and **6** in 84% and 86% yields, respectively.

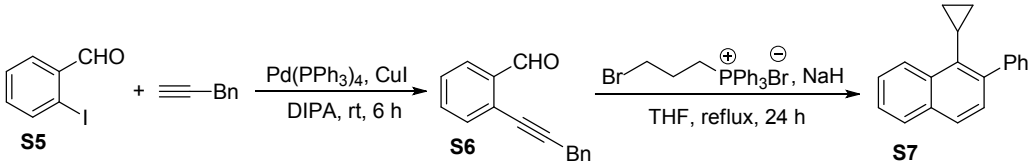
8. General procedure for the synthesis of 7.



Scheme S6

Synthesis of substrate **7**: the reaction was carried out in the same procedure as that for the synthesis of compound **S3**.

A failed pathway for the synthesis of substrate **7**.

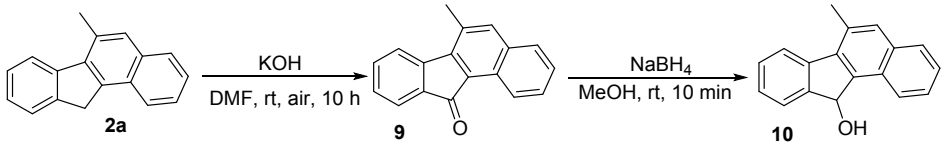


Scheme S7

Synthesis of substrate **S6**: the reaction was carried out in the same procedure as that for the synthesis of compound **S3**.

Synthesis of substrate **S7**: the reaction was carried out in the same procedure as that for the synthesis of compound **1**. The structure of **S7** was assigned by X-ray diffraction.

9. General procedure for the synthesis of products 9 and 10.

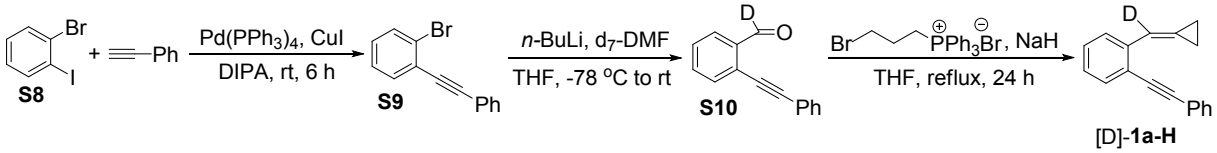


Scheme S8

Synthesis of product **9**: To a solution of 6-methyl-11*H*-benzo[a]fluorine **2a** (0.20 mmol, 1.0 equiv) in DMF (2.0 mL) in a flame-dried flask was added potassium hydroxide (0.20 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred at room temperature for 10 hours under air. Then the reaction mixture was added 10 mL of water and extracted with Et_2O. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure and the residue was purified by a silica gel chromatography (PE:EA = 20:1) to give product **9** in 99% yield.

Synthesis of product **10**: To a solution of **9** (0.20 mmol, 1.0 equiv) in methanol (2.0 mL) in a flame-dried flask was added sodium borohydride (0.24 mmol, 1.2 equiv) at room temperature. The reaction mixture was stirred at room temperature for 10 min. Then the reaction was quenched with water and extracted with Et_2O. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure and the residue was purified by a silica gel chromatography (PE:EA = 10:1) to give product **10** in 99% yield.

10. Procedures for the synthesis of the deuterated compounds.



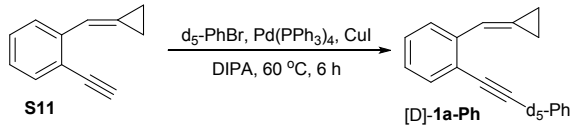
Scheme S9

The deuterated compound [D]-**1a-H** was synthesized according to Scheme S9.

Synthesis of deuterated aldehyde **S10**: To a 100 mL flame and vacuum dried three-neck flask was added 1-bromo-2-(phenylethynyl)benzene (15.0 mmol, 1.0 equiv) and 50 mL of THF under

Ar, then *n*-BuLi (2.4 M, 7.5 mL, 18 mmol, 1.2 equiv) was added slowly at -78 °C. After the addition was complete, the reaction mixture was allowed to stir at -78 °C for 2 h. Deuterated DMF (22.5 mmol, 1.5 equiv) was added to the flask slowly at -78 °C. The reaction mixture was warmed up to room temperature gradually and was stirred overnight. The reaction was quenched with water and was extracted with Et_2O, and the combined organic phase was dried over anhydrous sodium sulfate. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel chromatography (PE) to give the corresponding deuterated aldehyde **S10** in 60% yield.

Synthesis of deuterated substrate [D]-**1a-H**: the reaction was carried out in the same procedure as that for the synthesis of substrate **1**.



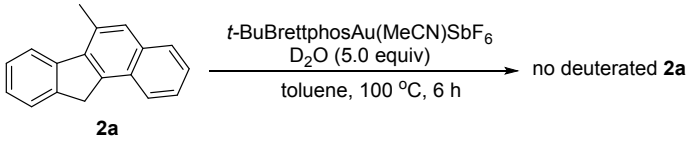
Scheme S10

The deuterated compound [D]-**1a-Ph** was synthesized according to Scheme S10.

The compound **S11** was synthesized according to the previously reported procedure.[6]

Synthesis of deuterated substrate [D]-**1a-Ph**: the reaction was carried out in the same procedure as that for the synthesis of substrate **S3**.

11. General procedure for H/D exchanging experiment of product 2a.



Scheme S11

To a flame-dried flask were added **2a** (0.20 mmol, 1.0 equiv) and *t*-BuBrettphosAu(MeCN)SbF_6 (0.01 mmol, 0.05 equiv), and the flask was evacuated and backfilled with Ar for 3 times. Toluene (2.0 mL) was added to this flask via a syringe under Ar. Then D_2O was added to this flask via a syringe. The reaction mixture was stirred for 6 hours at 100 °C. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum pump at low temperature. Then, the crude product was purified by a silica gel chromatography (PE) to get the corresponding no deuterated **2a** and 92% of **2a** was recovered.

12. UV/FL spectra and quantum yields of 2b and 2ii.

Sample preparation: To a 25 mL volumetric flask was added **2b** or **2ii** (0.01 mmol) and diluted with CH_2Cl_2 to 100 mL. The solution was shaken several times and then its 1.0 mL solution was moved to another 100 mL volumetric flask and diluted with CH_2Cl_2 to 100 mL. The solution was shaken several times for using.

Quantum yield determination: All the quantum yields of samples were determined based on 1.0 $*10^{-5}$ mol/L tryptophan in deionized water ($\Phi = 0.14$).

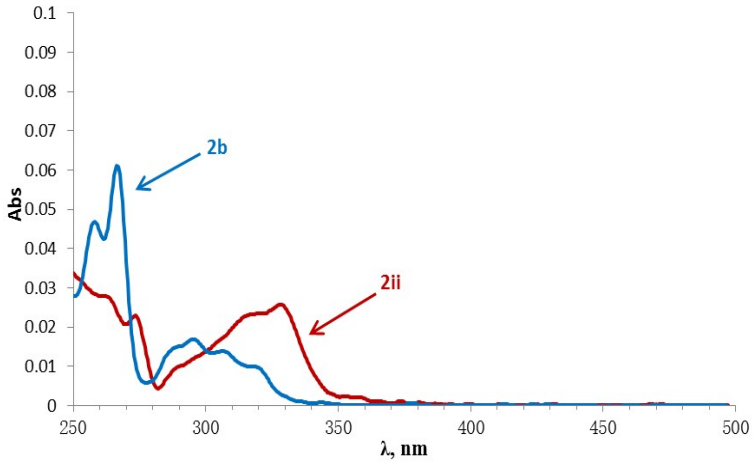


Figure S1. UV spectra: sample preparation: 1.0 * 10^{-5} mol/L in CH_2Cl_2 with 4.0 nm slit.

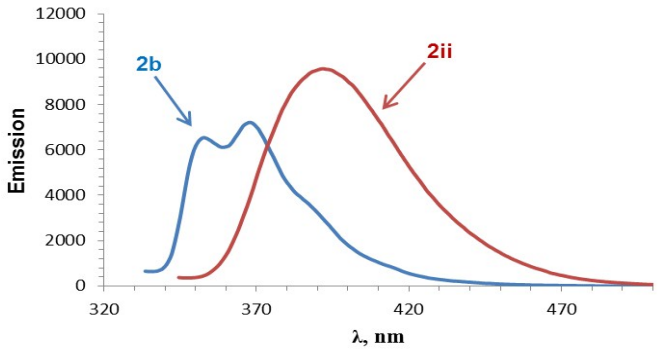
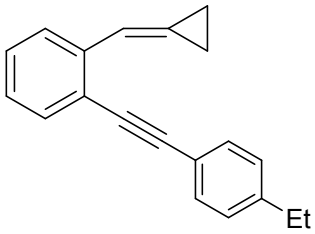
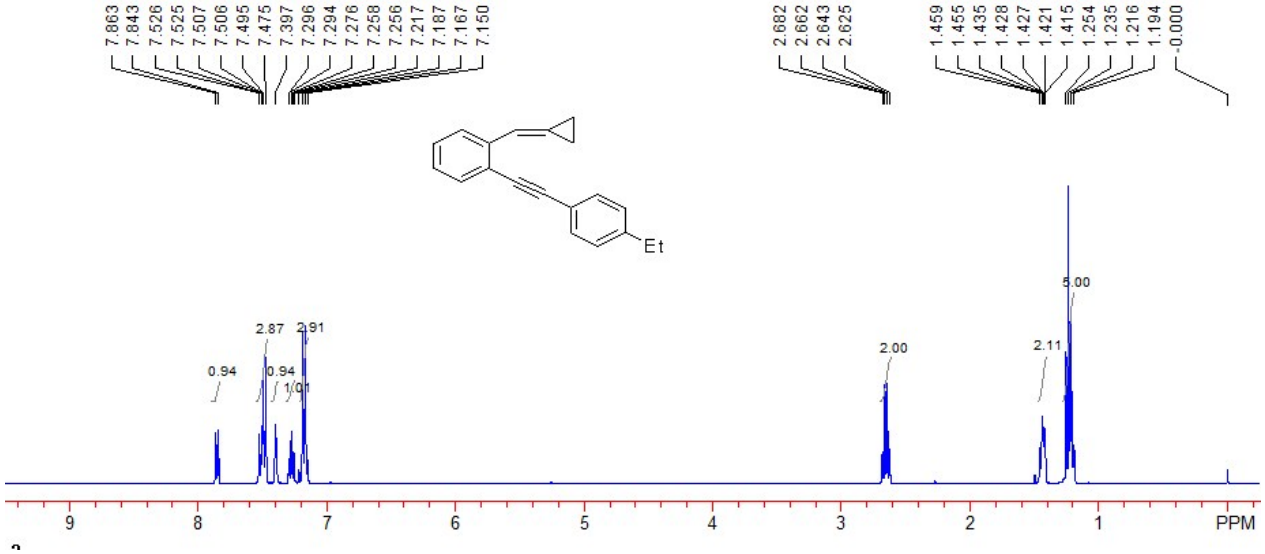


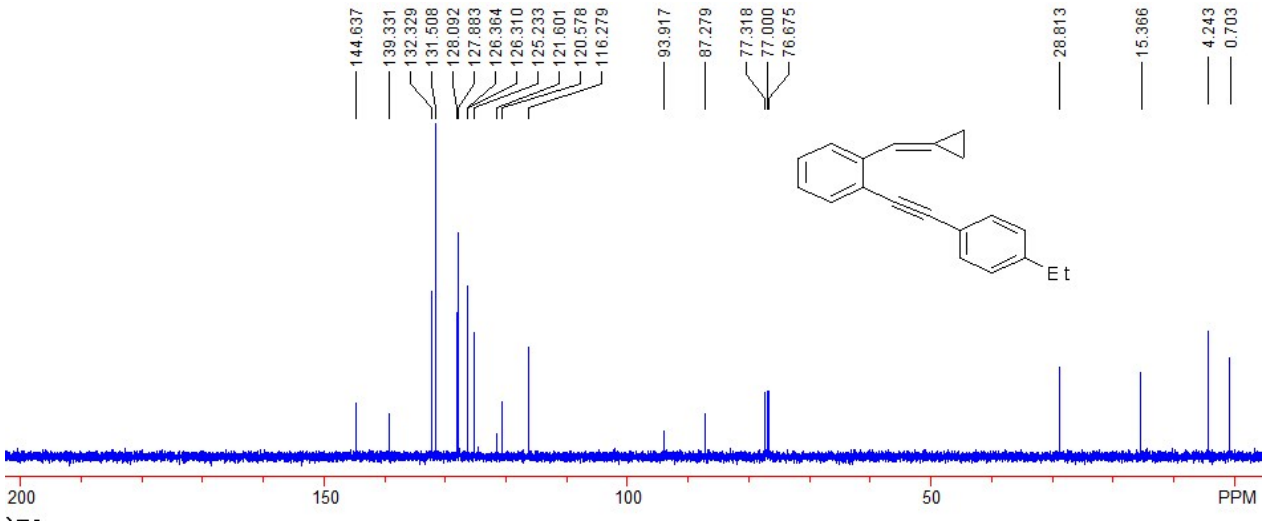
Figure S2. Fluorescence emission of **2b** and **2ii**: samples were measured in CH_2Cl_2, $c = 1.0\ \mu M$. Excitation at 271 nm with 2.5 nm EX slit and 10.0 EM slit. Quantum yield of **2b** ($\Phi = 0.25$), quantum yield of **2ii** ($\Phi = 0.59$).

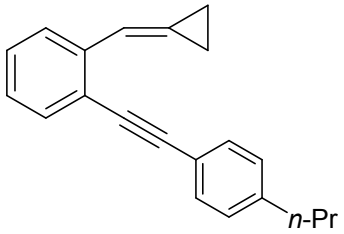
13. Characterization and spectra charts.



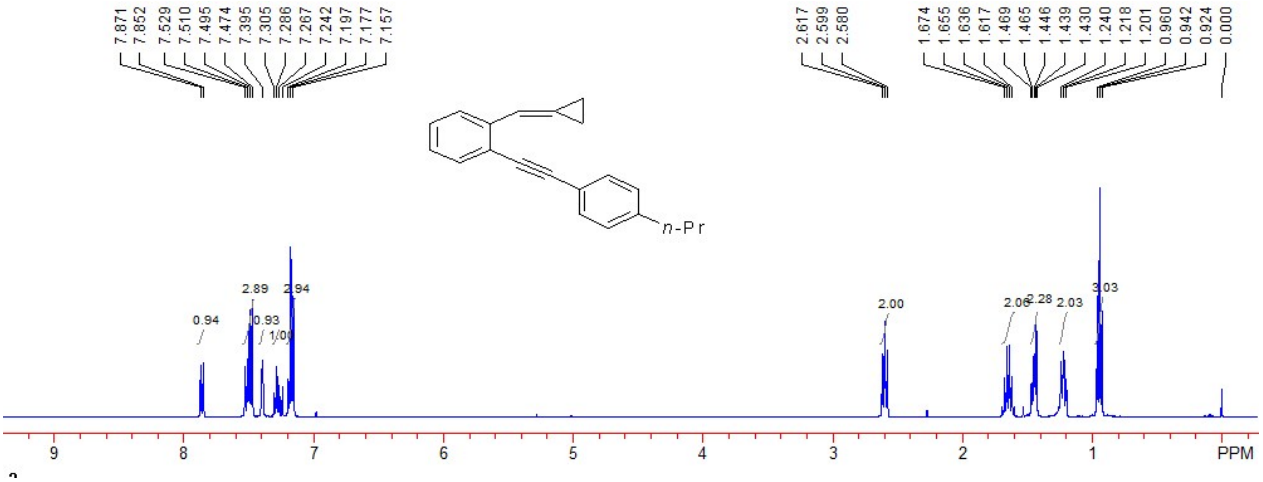
Compound **1c**. 585 mg, yield: 25%; white solid. MP: 55-57 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19-1.25 (m, 5H, CH_2, CH_3), 1.42-1.46 (m, 2H, CH_2), 2.65 (q, J = 8.0 Hz, 2H, CH_2), 7.15-7.22 (m, 3H, Ar), 7.26-7.30 (m, 1H, Ar), 7.40 (s, 1H, =CH), 7.48-7.53 (m, 3H, Ar), 7.85 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.2, 15.4, 28.8, 87.3, 93.9, 116.3, 120.6, 121.6, 125.2, 126.3, 126.4, 127.9, 128.1, 131.5, 132.3, 139.3, 144.6. IR (neat) ν 2970, 2933, 2204, 1952, 1592, 1509, 1457, 1303, 1039 cm^{-1}. MS (%) m/e 258 (M^+, 100.00), 229 (63.71), 202 (11.18), 152 (11.07), 128 (17.12), 114 (19.49), 91 (11.06). HRMS (EI) calcd.for $C_{20}H_{18}$: 258.1409, found: 258.1402.

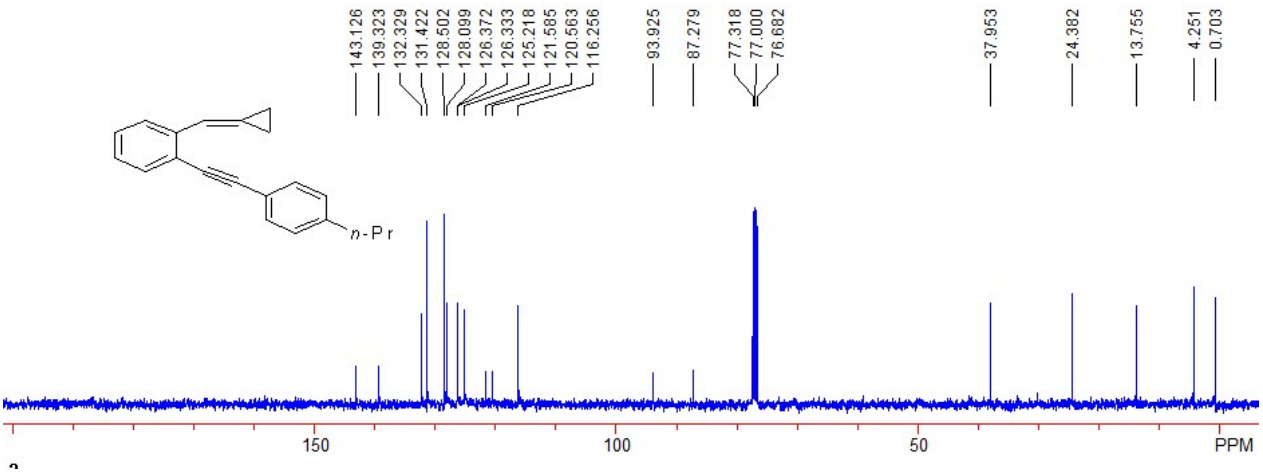


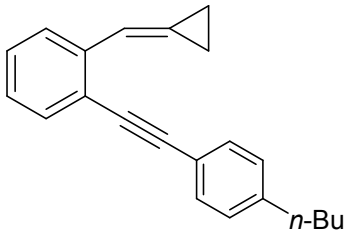




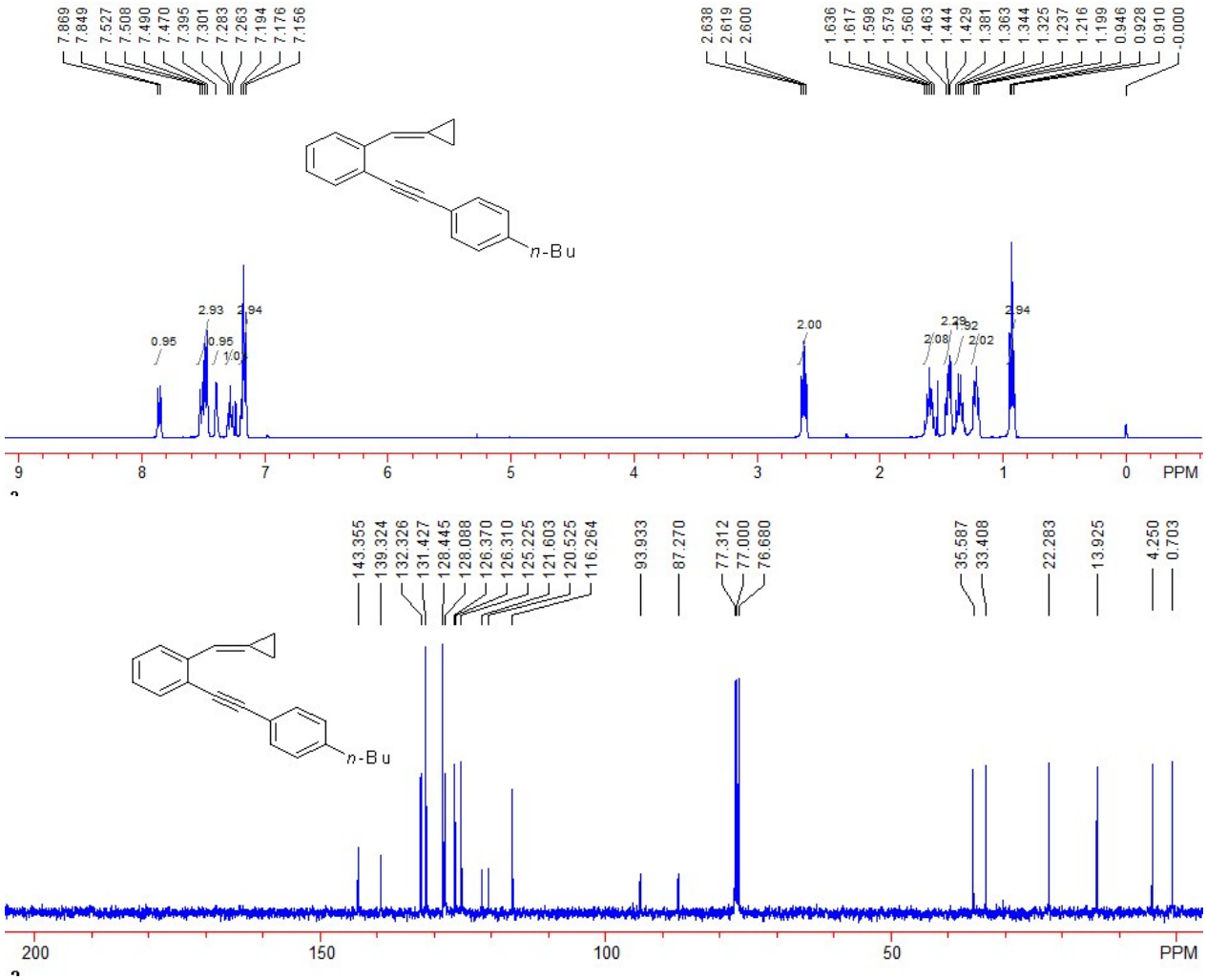
Compound **1d**. 809 mg, yield: 41%; white solid. MP: 56-57 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.94 (t, *J* = 7.2 Hz, 3H, CH_3), 1.20-1.24 (m, 2H, CH_2), 1.43-1.47 (m, 2H, CH_2), 1.62-1.67 (m, 2H, CH_2), 2.60 (t, *J* = 8.0 Hz, 2H, CH_2), 7.16-7.20 (m, 3H, Ar), 7.29 (t, *J* = 7.6 Hz,, 1H, Ar), 7.40 (s, 1H, =CH), 7.47-7.53 (m, 3H, Ar), 7.86 (d, *J* = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.3, 13.8, 24.4, 38.0, 87.3, 93.9, 116.3, 120.6, 121.6, 125.2, 126.3, 126.4, 128.1, 128.5, 131.4, 132.3, 139.3, 143.1. IR (neat) ν 2953, 2867, 1919, 1505, 1445, 1115, 1040, 936 cm^{-1}. MS (%) m/e 272 (M^+, 100.00), 229 (37.42), 202 (6.50), 152 (7.15), 115 (14.58), 91 (10.17). HRMS (EI) calcd.for $C_{21}H_{20}$: 272.1565, found: 272.1560.

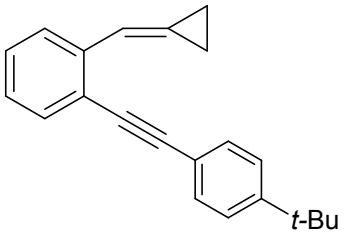




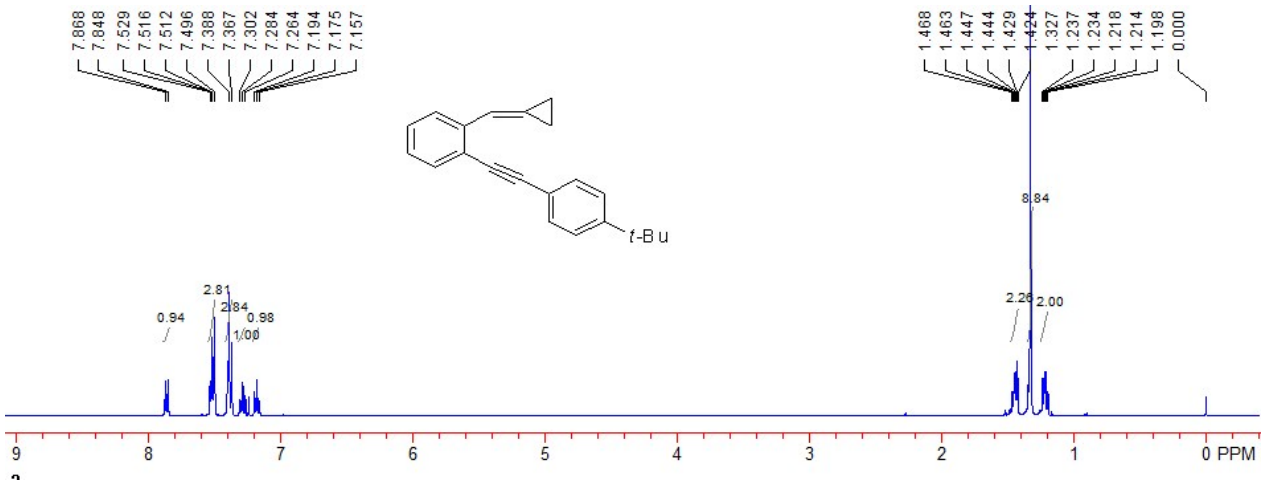


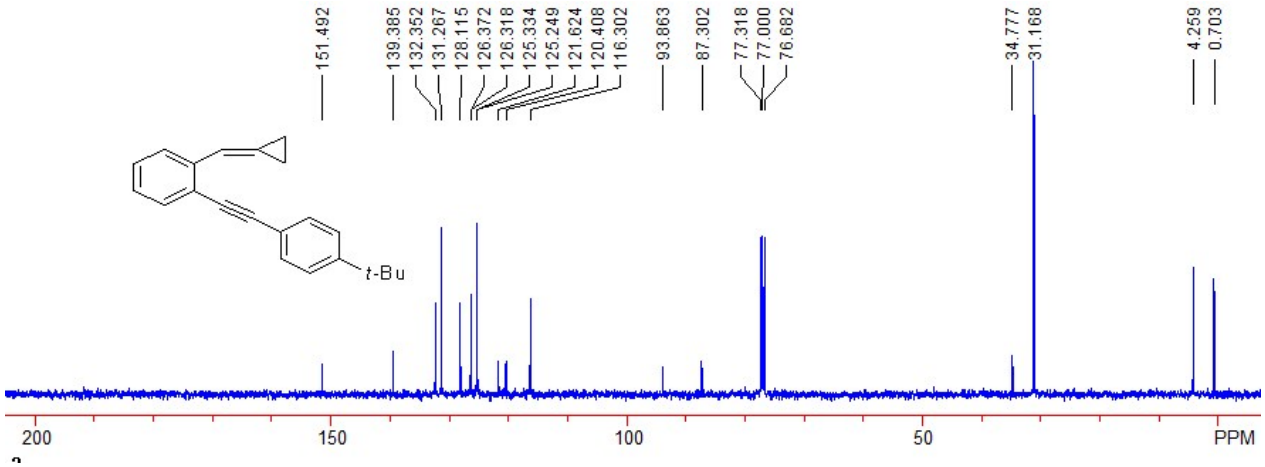
Compound **1e**. 737 mg, yield: 32%; colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.93 (t, *J* = 7.2 Hz, 3H, CH_3), 1.20-1.24 (m, 2H, CH_2), 1.33-1.38 (m, 2H, CH_2), 1.43-1.46 (m, 2H, CH_2), 1.56-1.64 (m, 2H, CH_2), 2.62 (t, *J* = 7.6 Hz, 2H, CH_2), 7.16-7.19 (m, 3H, Ar), 7.28 (t, *J* = 8.0 Hz, 1H, Ar), 7.40 (s, 1H, =CH), 7.47-7.53 (m, 3H, Ar), 7.86 (d, *J* = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.3, 13.9, 22.3, 33.4, 35.6, 87.3, 93.9, 116.3, 120.5, 121.6, 125.2, 126.3, 126.4, 128.1, 128.4, 131.4, 132.3, 139.3, 143.4. IR (neat) ν 2928, 2857, 1910, 1593, 1445, 1377, 1039 cm^{-1}. MS (%) m/e 286 (M^+, 100.00), 229 (37.34), 202 (6.85), 152 (6.46), 115 (11.47), 91 (11.65). HRMS (EI) calcd.for $C_{22}H_{22}$: 286.1722, found: 286.1718.

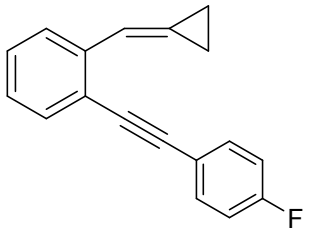




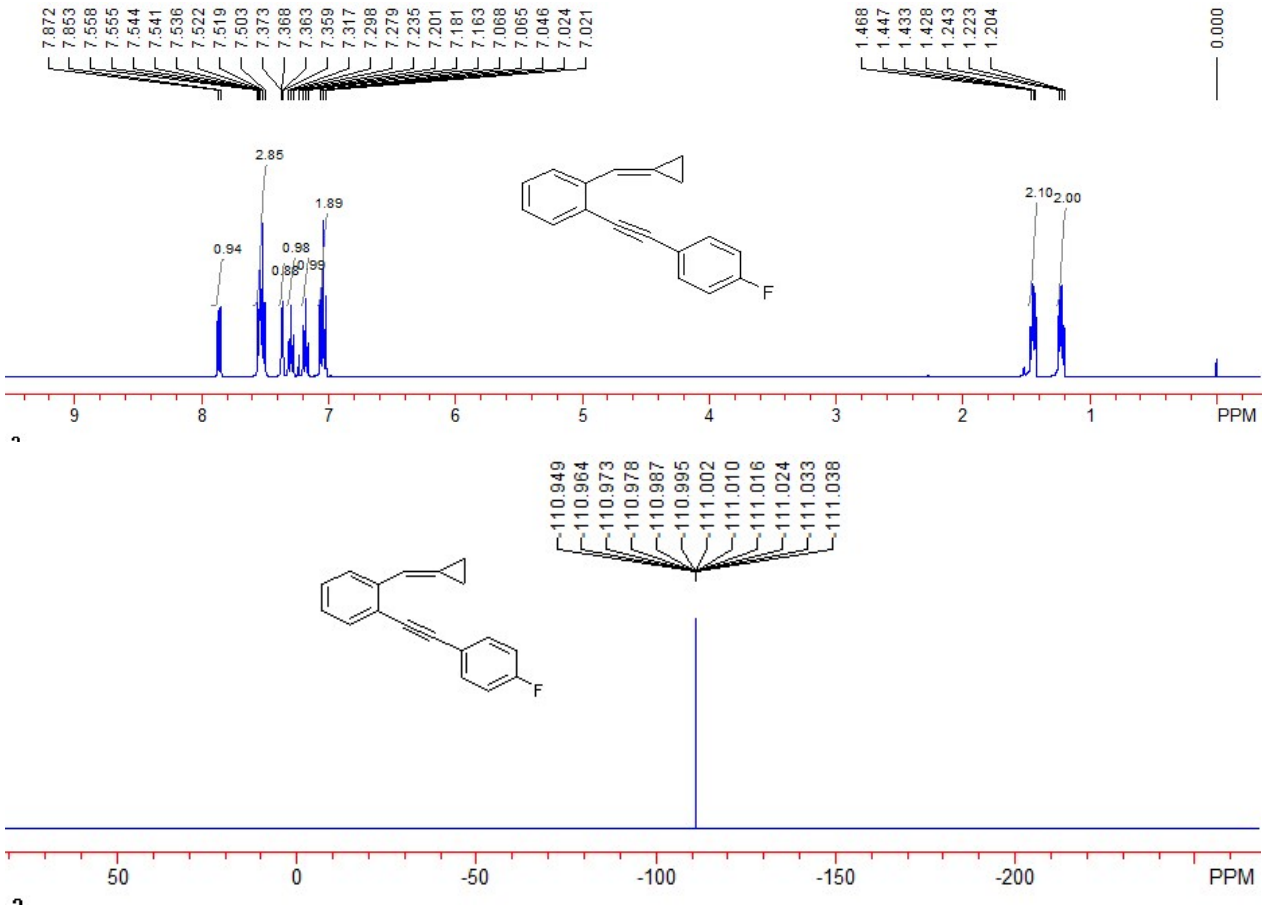
Compound **1f**. 645 mg, yield: 28%; white solid. MP: 86-88 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20-1.24 (m, 2H, CH_2), 1.33(s, 9H, $3CH_3$), 1.42-1.47 (m, 2H, CH_2), 7.16-7.19 (m, 1H, Ar), 7.26-7.30 (m, 1H, Ar), 7.37-7.39 (m, 3H, =CH, Ar), 7.50-7.53 (m, 3H, Ar), 7.86 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.3, 31.2, 34.8, 87.3, 93.9, 116.3, 120.4, 121.6, 125.2, 126.3, 126.4, 128.1, 131.3, 132.4, 139.4, 151.5. IR (neat) ν 2961, 2866, 1911, 1508, 1405, 1267, 1114 cm^{-1}. MS (%) m/e 286 (M^+, 100.00), 229 (29.36), 202 (6.56), 152 (6.46), 115 (11.19), 91 (7.07). HRMS (EI) calcd.for $C_{22}H_{22}$: 286.1722, found: 286.1725.

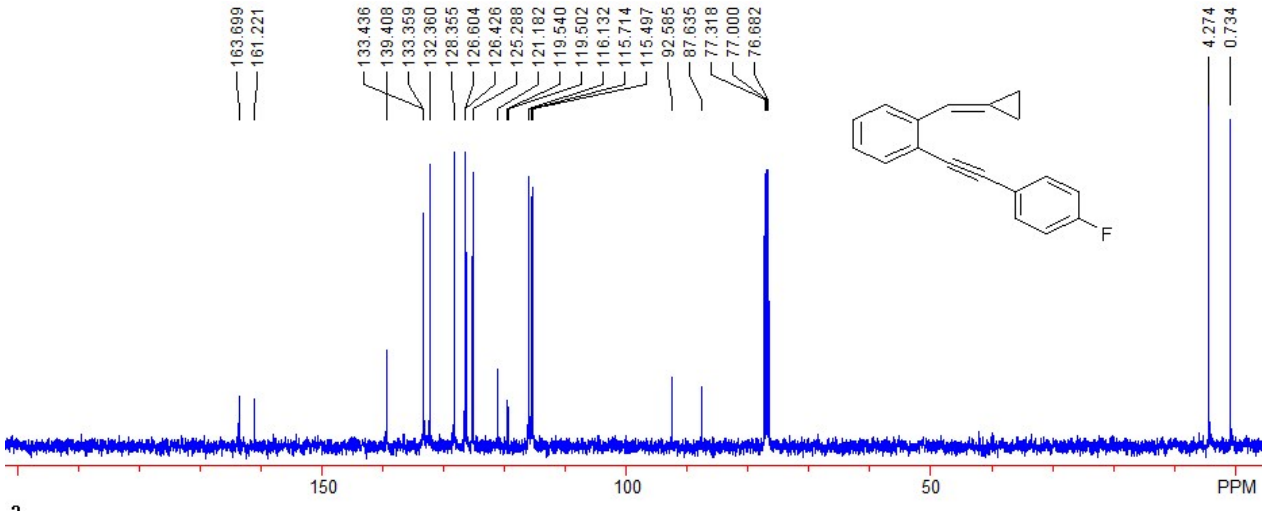


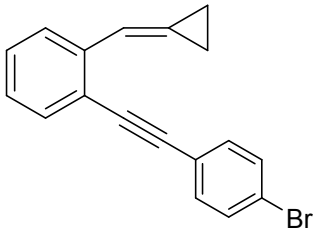




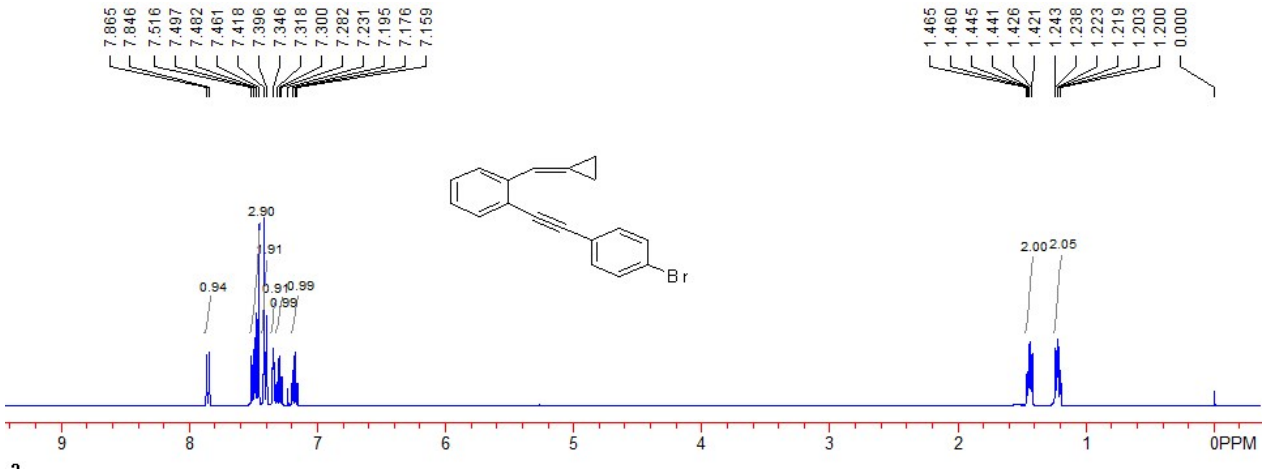
Compound **1g**. 1.070 g, yield: 53%; white solid. MP: 48-50 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20-1.24 (m, 2H, CH_2), 1.43-1.47 (m, 2H, CH_2), 7.02-7.07 (m, 2H, Ar), 7.16-7.20 (m, 1H, Ar), 7.28-7.32 (m, 1H, Ar), 7.36-7.37 (m, 1H, =CH), 7.50-7.56 (m, 3H, Ar), 7.86 (d, J = 7.6Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.3, 87.6, 92.6, 115.5, 115.7, 116.1, 119.5 (d, $J_{C\text{-}F}$ = 3.8 Hz), 121.2, 125.3, 126.5 (d, $J_{C\text{-}F}$ = 17.8 Hz), 128.4, 132.4, 133.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 139.4, 162.5 (d, $J_{C\text{-}F}$ = 247.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -110.95 ~ -111.04 (m, 1F). IR (neat) ν 2976, 1592, 1504, 1477, 1221, 1154, 1038 cm^{-1}. MS (%) m/e 248 (M^+, 100.00), 229 (1.63), 202 (0.97), 152 (11.66), 115 (7.97), 91 (0.41). HRMS (EI) calcd.for $C_{18}H_{13}F$: 248.1001, found: 248.0998.

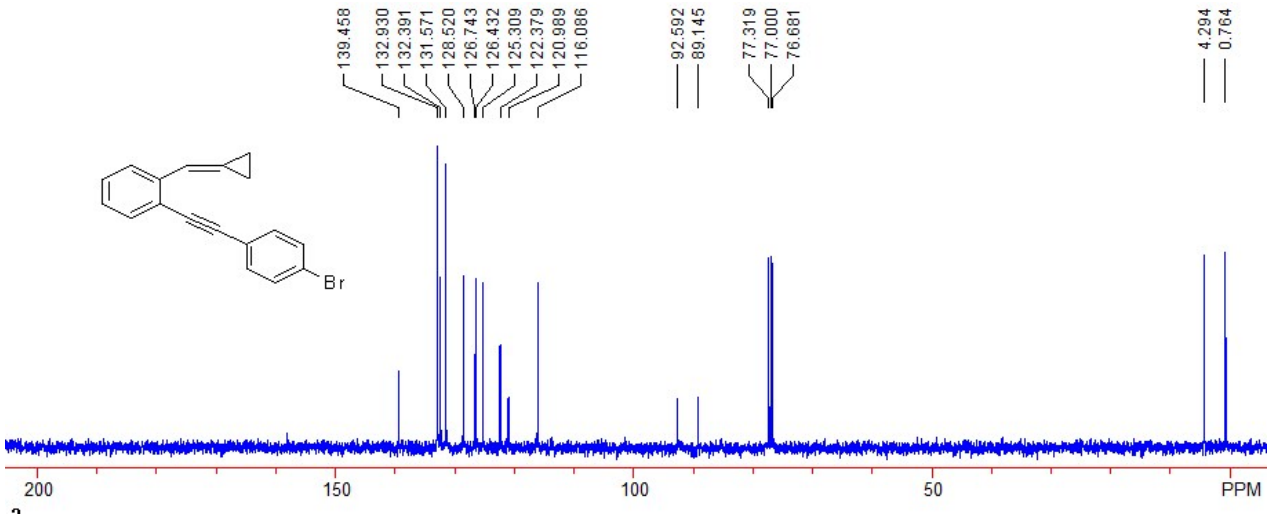


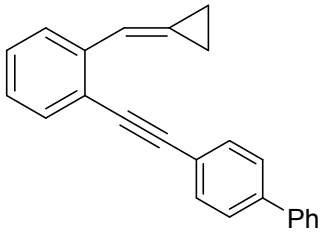




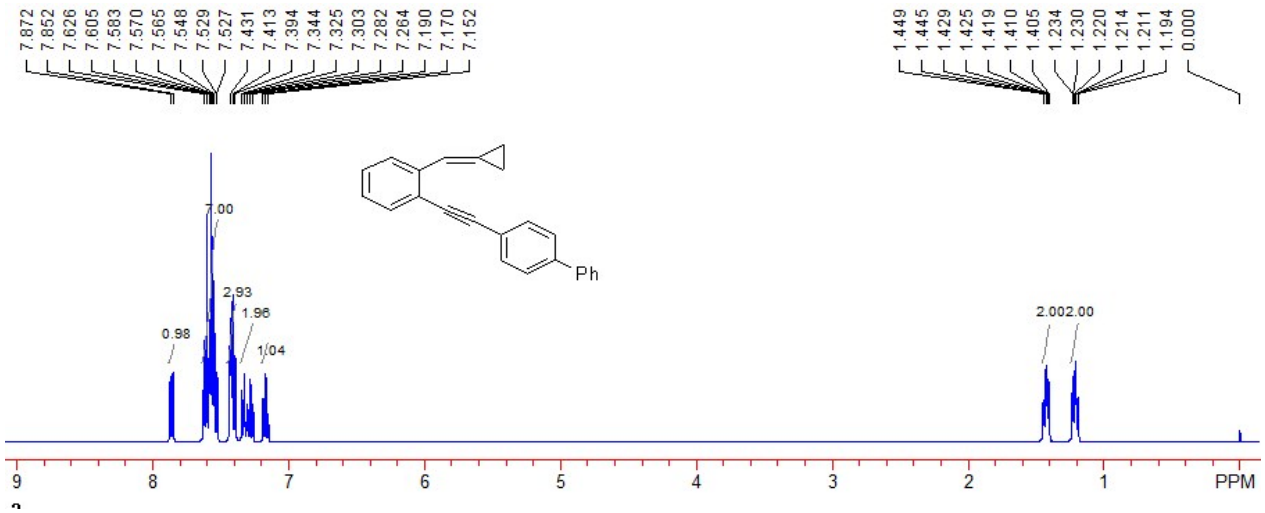
Compound **1i**. 737 mg, yield: 46%; white solid. MP: 55-57 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20-1.24 (m, 2H, CH_2), 1.42-1.47 (m, 2H, CH_2), 7.16-7.20 (m, 1H, Ar), 7.28-7.32 (m, 1H, Ar), 7.35 (s, 1H, =CH), 7.40-7.42 (m, 2H, Ar), 7.46-7.52 (m, 3H, Ar), 7.86 (d, *J* = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.8, 4.3, 89.1, 92.6, 116.1, 121.0, 122.4, 125.3, 126.4, 126.7, 128.5, 131.6, 132.4, 132.9, 139.5. IR (neat) ν 3070, 2920, 1899, 1593, 1474, 1314, 1009 cm^{-1}. MS (%) m/e 308 (82.25), 228 (M^+, 100.00), 202 (18.80), 152 (20.79), 115 (14.35), 91 (0.33). HRMS (EI) calcd.for $C_{18}H_{13}Br$: 308.0201, found: 308.0193.

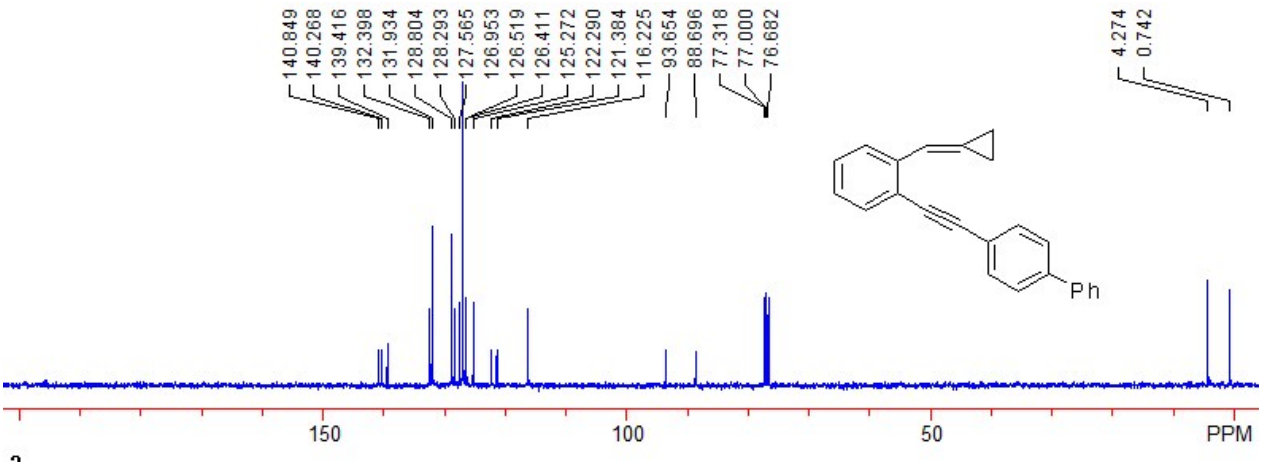


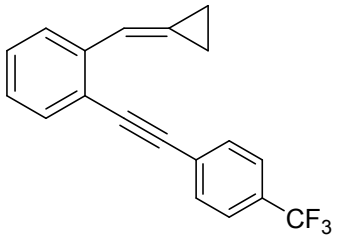




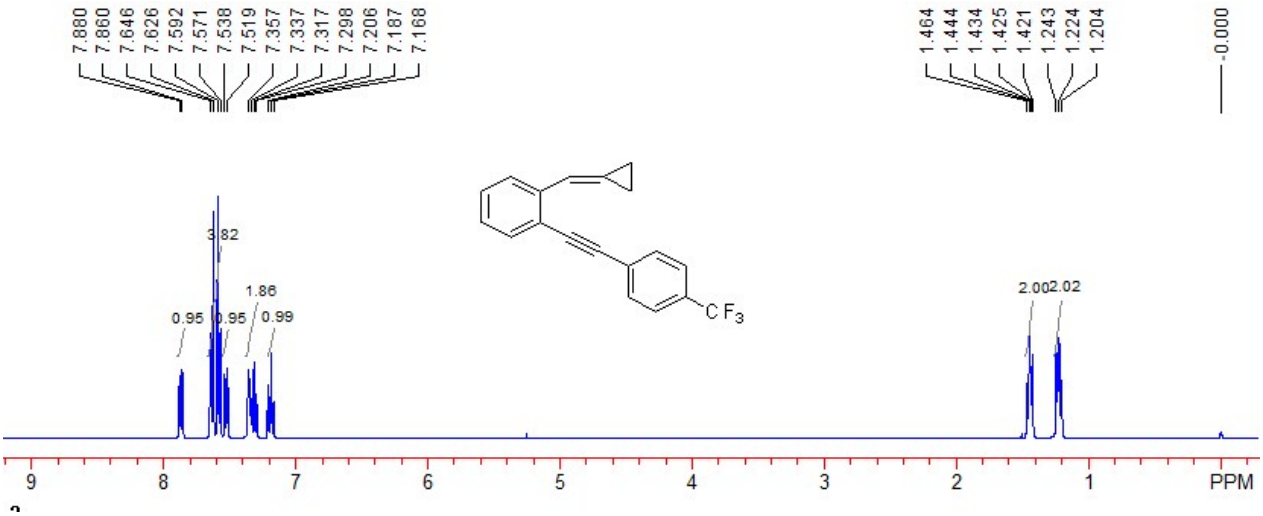
Compound **1k**. 346 mg, yield: 15%; white solid. MP: 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19-1.23 (m, 2H, CH_2), 1.41-1.45 (m, 2H, CH_2), 7.15-7.19 (m, 1H, Ar), 7.26-7.34 (m, 2H, Ar), 7.39-7.43 (m, 3H, =CH, Ar), 7.53-7.63 (m, 7H, Ar), 7.86 (d, J = 8.0Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.3, 88.7, 93.6, 116.2, 121.4, 122.3, 125.3, 126.4, 126.5, 127.0, 127.6, 128.3, 128.8, 131.9, 132.4, 139.4, 140.3, 140.8. IR (neat) ν 3031, 2970, 1522, 1485, 1445, 1113, 1038 cm^{-1}. MS (%) m/e 306 (M^+, 100.00), 229 (7.42), 202 (3.20), 152 (17.05), 115 (2.77), 91 (1.40). HRMS (EI) calcd.for $C_{24}H_{18}$: 306.1409, found: 306.1406.

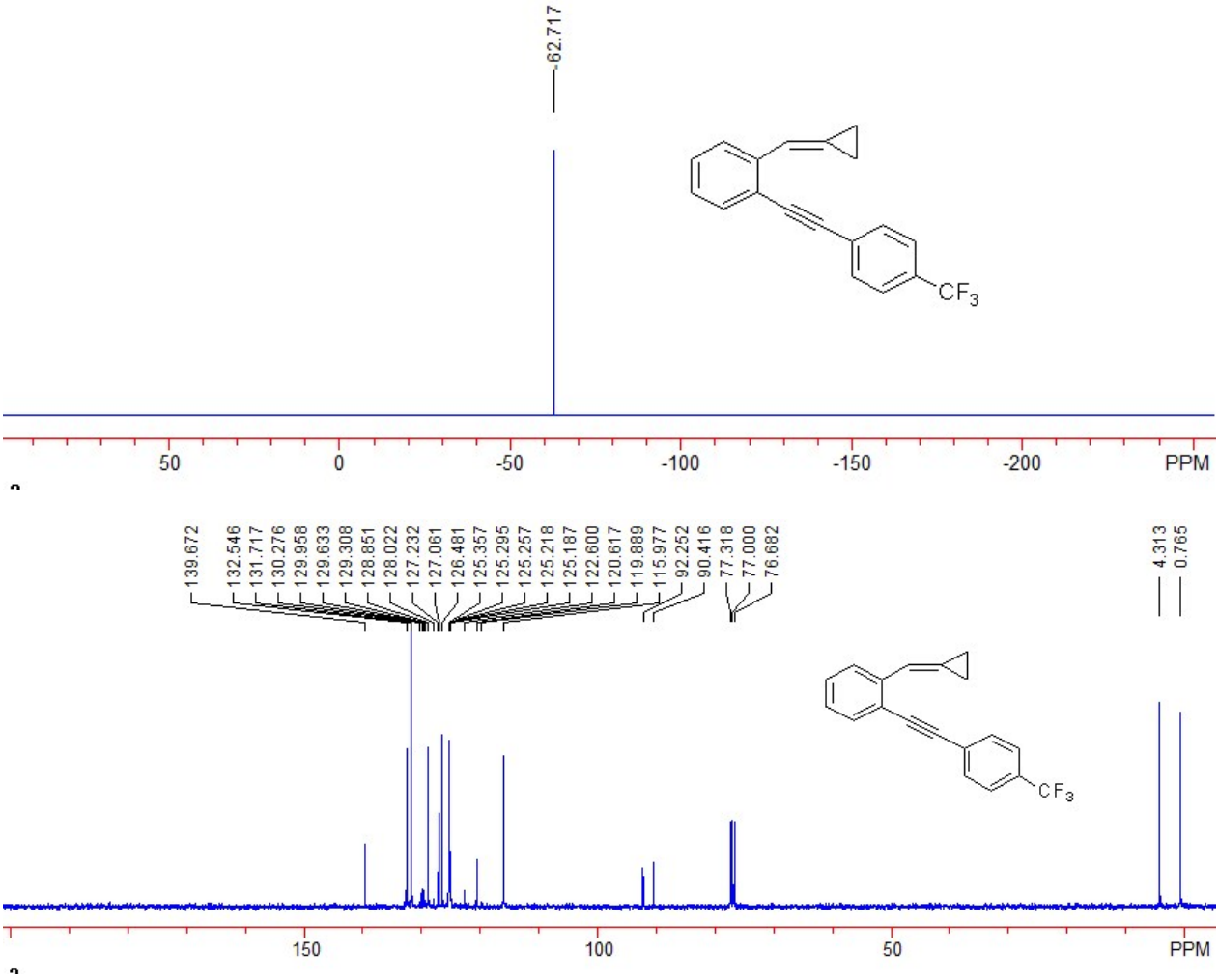


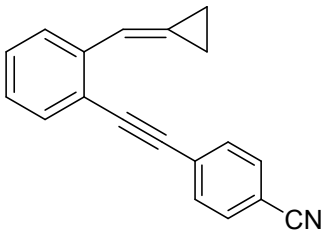




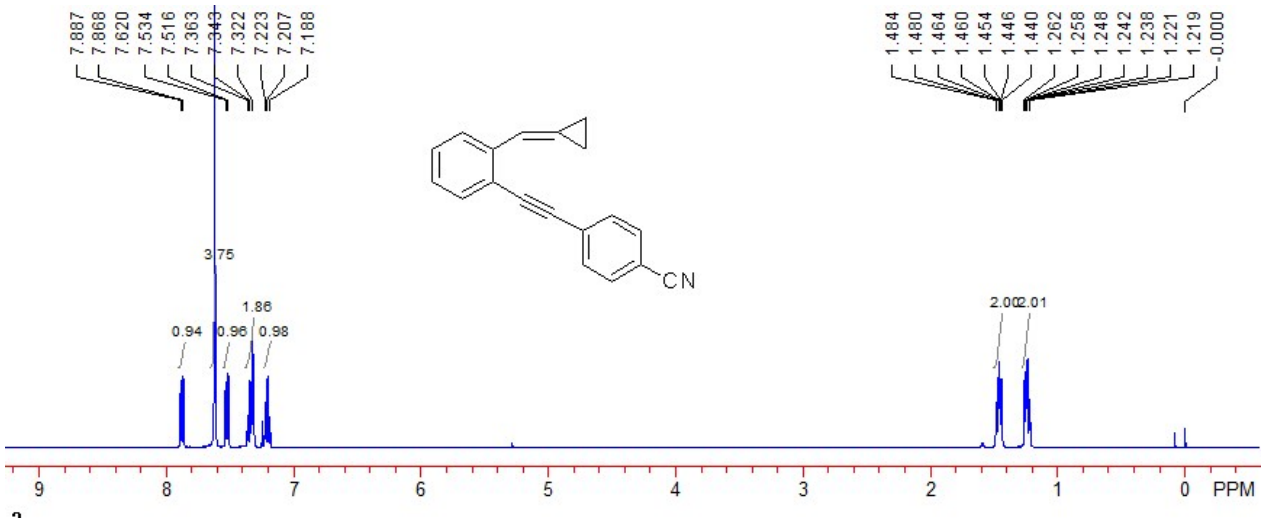
Compound **1l**. 450 mg, yield: 31%; white solid. MP: 99-101 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20-1.24 (m, 2H, CH_2), 1.42-1.46 (m, 2H, CH_2), 7.19 (t, J = 7.6 Hz, 1H, Ar), 7.30-7.36 (m, 2H, =CH, Ar), 7.53 (d, J = 7.6 Hz, 1H, Ar), 7.57-7.65 (m, 4H, Ar), 7.87 (d, J = 8.0Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.8, 4.3, 90.4, 92.3, 116.0, 120.6, 124.0 (q, $J_{C\text{-}F}$ = 271.1 Hz), 125.2 (q, $J_{C\text{-}F}$ = 3.9 Hz), 125.4, 126.5, 127.1, 127.2, 128.9, 129.8 (d, $J_{C\text{-}F}$ = 32.5 Hz), 131.7, 132.5, 139.7. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -62.72 (s, 3F). IR (neat) ν 2928, 2211, 1610, 1476, 1319, 1158 cm^{-1}. MS (%) m/e 298 (59.14), 228 (M^+, 100.00), 202 (20.62), 152 (30.94), 115 (16.88), 91 (2.03). HRMS (EI) calcd.for $C_{19}H_{13}F_3$: 298.0969, found: 298.0963.

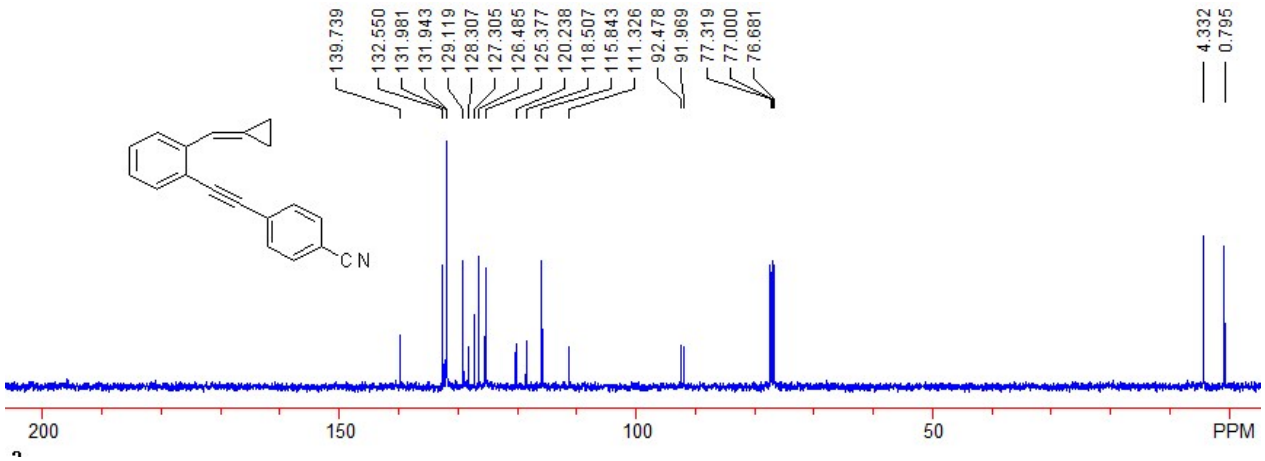


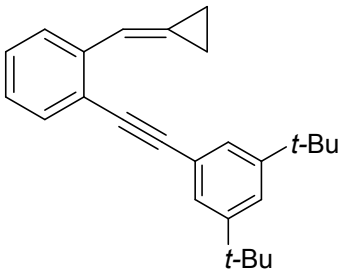




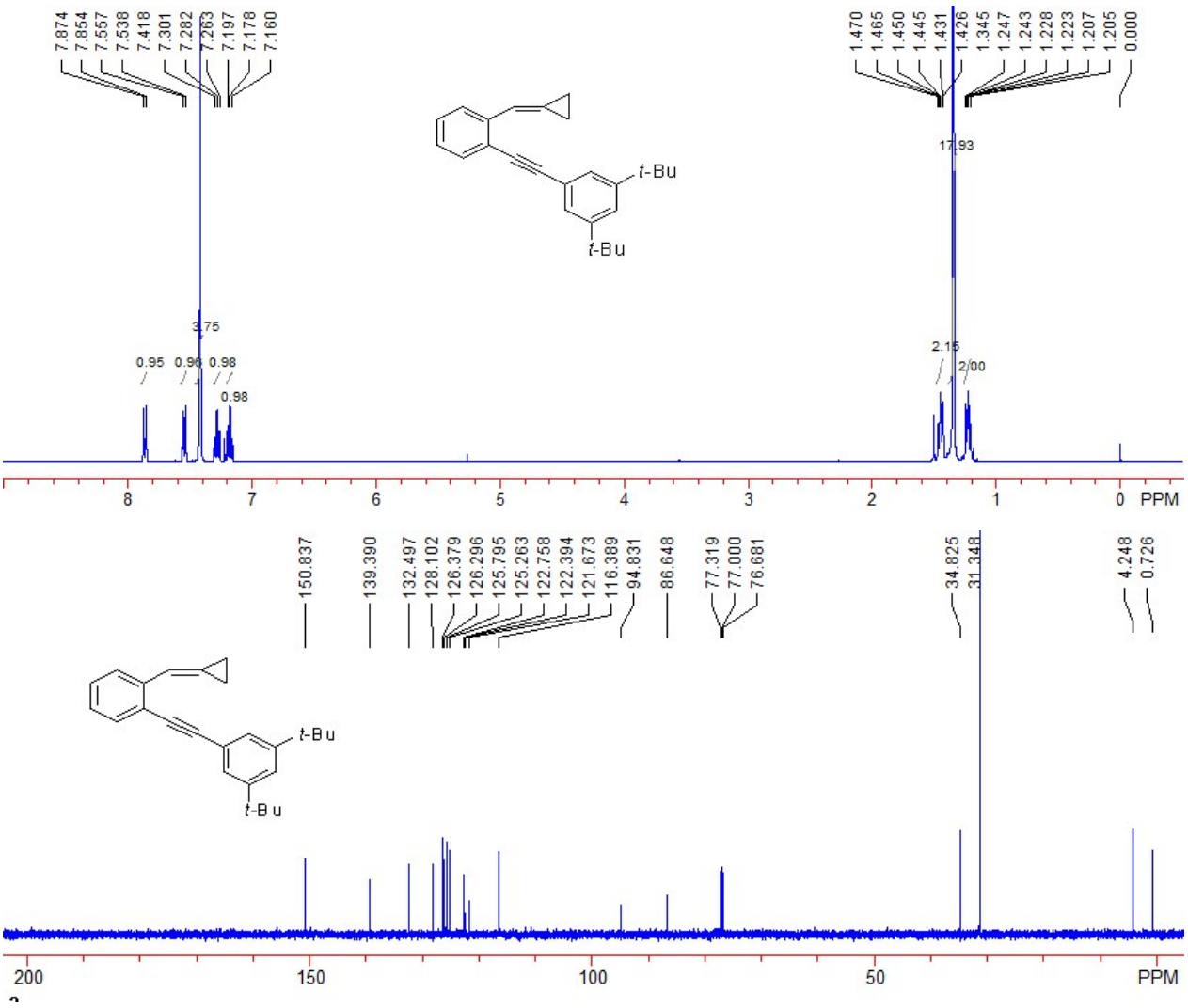
Compound **1m**. 320 mg, yield: 85%; white solid. MP: 88-90 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.22-1.26 (m, 2H, CH_2), 1.44-1.48 (m, 2H, CH_2), 7.19-7.22 (m, 1H, Ar), 7.32-7.36 (m, 2H, =CH, Ar), 7.53 (d, *J* = 7.2 Hz, 1H, Ar), 7.62 (br s, 4H, Ar), 7.88 (d, *J* = 7.2Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.8, 4.3, 92.0, 92.5, 111.3, 115.8, 118.5, 120.2, 125.4, 126.5, 127.3, 128.3, 129.1, 131.9, 132.0, 132.6, 139.7. IR (neat) ν 2974, 2231, 1602, 1501, 1445, 1175, 1037 cm^{-1}. MS (%) m/e 255 (M^+, 100.00), 228 (4.00), 202 (2.22), 152 (13.21), 115 (10.81), 91 (0.30). HRMS (EI) calcd.for $C_{19}H_{13}N$: 255.1048, found: 255.1049.

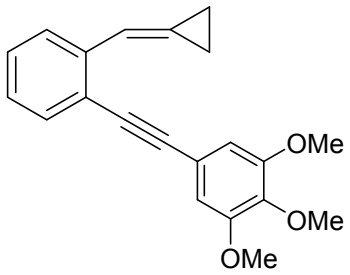






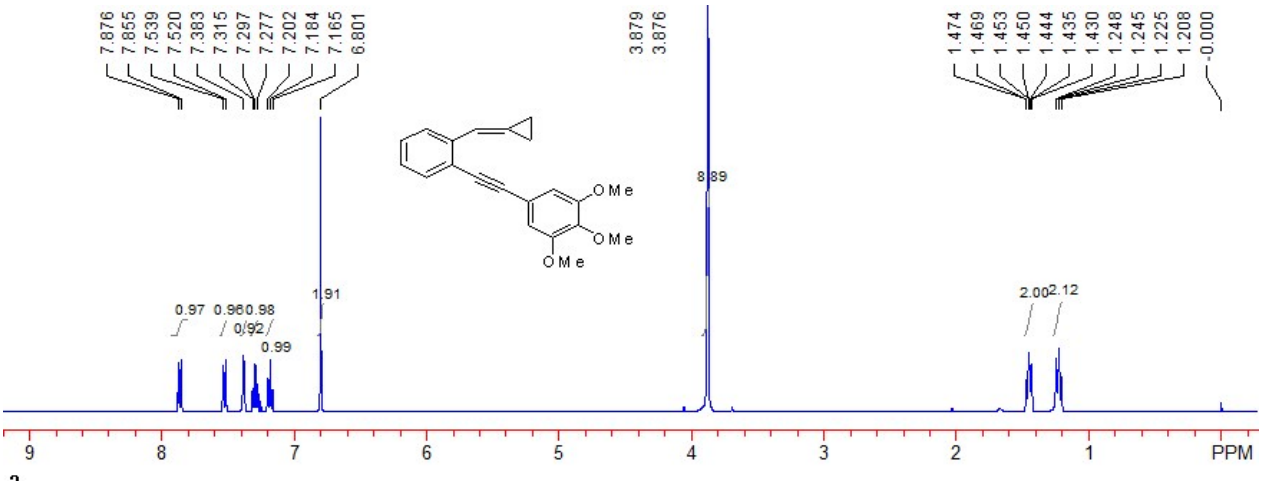
Compound **1n**. 766 mg, yield: 32%; white solid. MP: 85-88 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20-1.25 (m, 2H, CH_2), 1.35 (s, 18H, $6CH_3$), 1.43-1.47 (m, 2H, CH_2), 7.18 (t, J = 7.6Hz, 1H, Ar), 7.28 (t, J = 7.6 Hz, 1H, Ar), 7.42 (br s, 4H, =CH, Ar), 7.55 (d, J = 7.6Hz, 1H, Ar), 7.86 (d, J = 7.6Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.2, 31.3, 34.8, 86.6, 94.8, 116.4, 121.7, 122.4, 122.8, 125.3, 125.8, 126.3, 126.4, 128.1, 132.5, 150.8. IR (neat) ν 2960, 1587, 1447, 1395, 1271, 1106, 1039 cm^{-1}. MS (%) m/e 342 (M^+, 100.00), 228 (6.71), 202 (2.02), 152 (5.74), 115 (3.45), 91 (2.16). HRMS (EI) calcd.for $C_{26}H_{30}$: 342.2348, found: 342.2346.

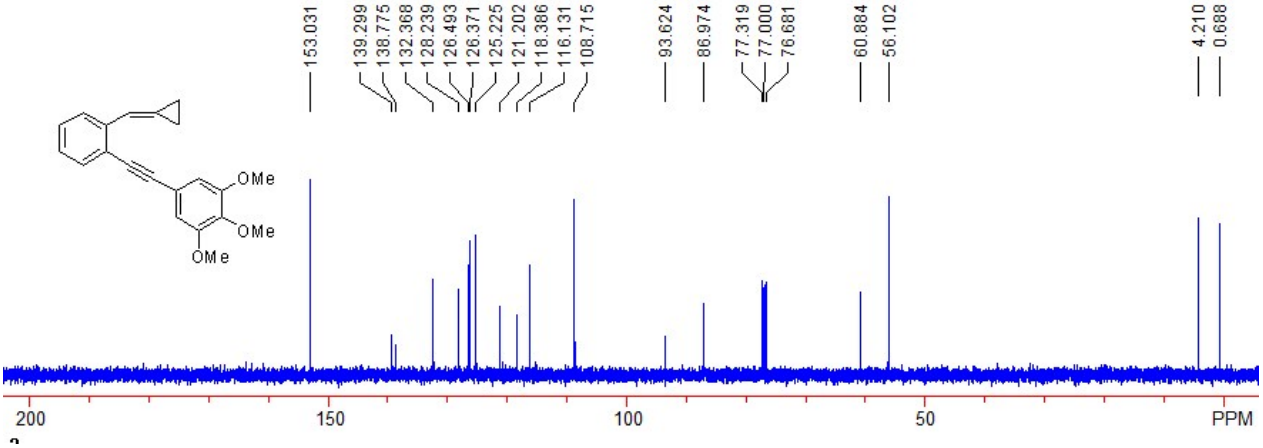


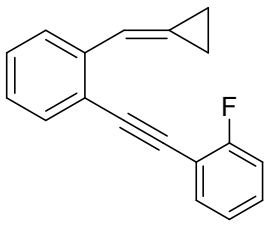


Compound **1o**. 538 mg, yield: 42%; white solid. MP: 79-82 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21-1.25 (m, 2H, CH_2), 1.43-1.47 (m, 2H, CH_2), 3.87 (s, 3H, CH_3), 3.88 (s, 6H, $2CH_3$), 6.80 (s, 2H, Ar), 7.18 (t, J = 7.6 Hz, 1H, Ar), 7.30 (t, J = 7.6 Hz, 1H, Ar), 7.38 (s, 1H, =CH), 7.53 (d, J = 7.6 Hz, 1H, Ar), 7.87 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.2, 56.1, 60.9, 87.0, 93.6, 108.7, 116.1, 118.4, 121.2, 125.2, 126.4, 126.5, 128.2, 132.4, 138.8, 139.3, 150.0. IR (neat) ν 2971, 2817, 1574, 1462, 1355, 1249, 1124 cm^{-1}. MS (%) m/e 320 (M^+, 100.00), 228 (2.33), 202 (9.87), 152 (7.88), 115 (3.36), 91 (0.57). HRMS (EI) calcd.for $C_{21}H_{20}O_3$:

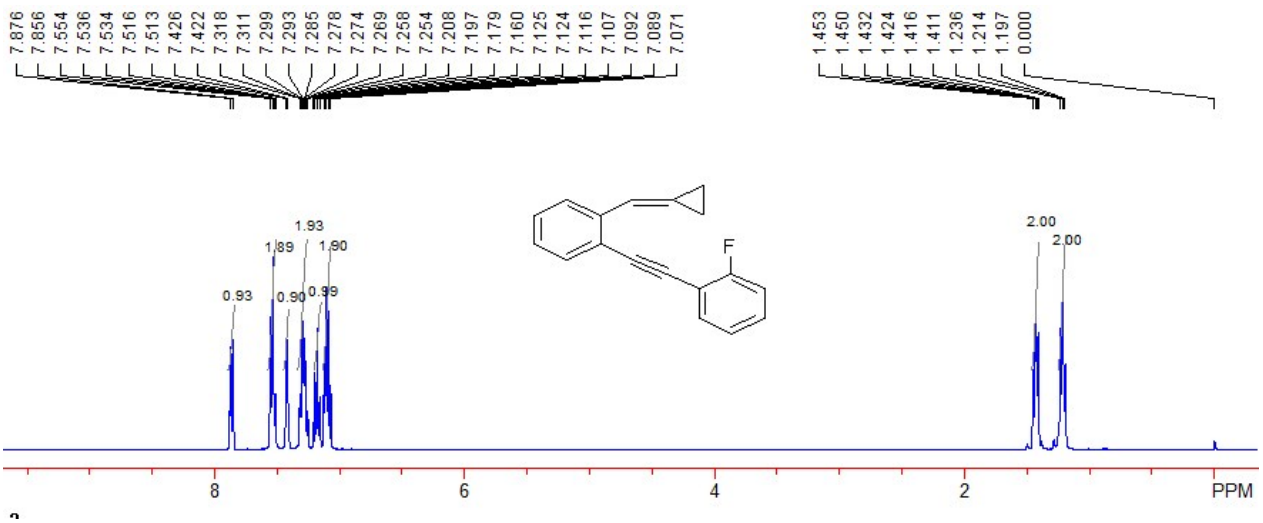
320.1412, found: 320.1409.







Compound **1p**. 630 mg, yield: 38%; white solid. MP: 65-68 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20-1.24 (m, 2H, CH_2), 1.42-1.45 (m, 2H, CH_2), 7.07-7.13 (m, 2H, Ar), 7.16-7.20 (m, 1H, Ar), 7.25-7.32 (m, 2H, Ar), 7.42-7.43 (m, 1H, =CH), 7.51-7.55 (m, 2H, Ar), 7.87 (d, J = 8.0Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.3, 87.0, 93.1 (d, $J_{C\text{-}F}$ = 3.1 Hz), 112.1 (d, $J_{C\text{-}F}$ = 15.4 Hz), 115.5 (d, $J_{C\text{-}F}$ = 20.9 Hz), 116.1, 121.0, 123.9(d, $J_{C\text{-}F}$ = 3.9 Hz), 125.3, 126.4, 126.8, 128.6, 129.9 (d, $J_{C\text{-}F}$ = 7.8 Hz), 132.4, 133.2, 139.6, 162.6(d, $J_{C\text{-}F}$ = 250.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -109.51 ~ -109.57 (m, 1F). IR (neat) ν 2970, 2215, 1568, 1494, 1262, 1103, 1064 cm^{-1}. MS (%) m/e 248 (M^+, 100.00), 229 (2.77), 202 (1.33), 152 (12.07), 115 (6.96), 91 (0.27). HRMS (EI) calcd.for $C_{18}H_{13}F$: 248.1001, found: 248.1000.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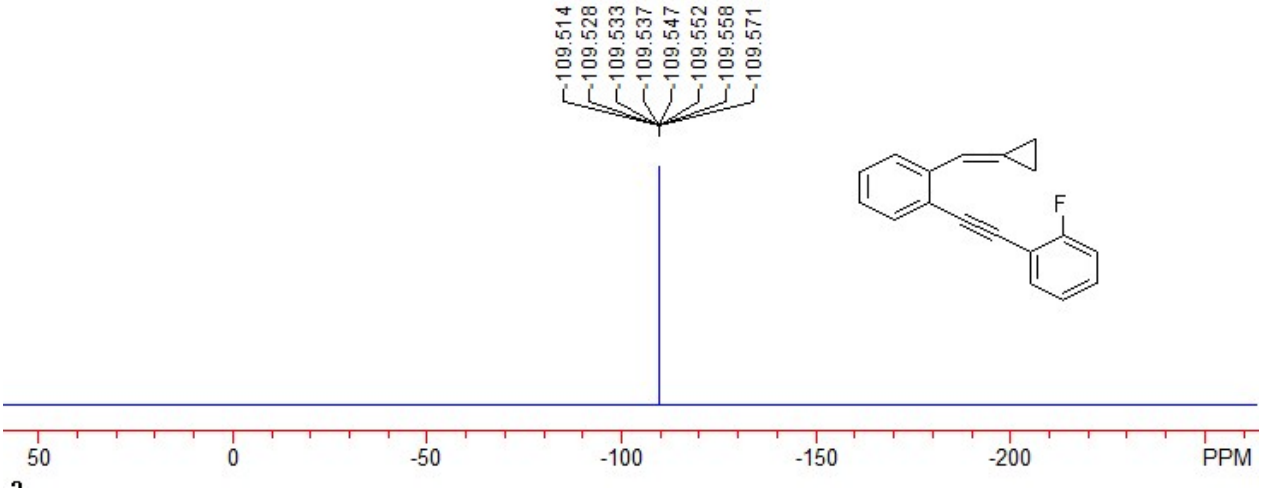
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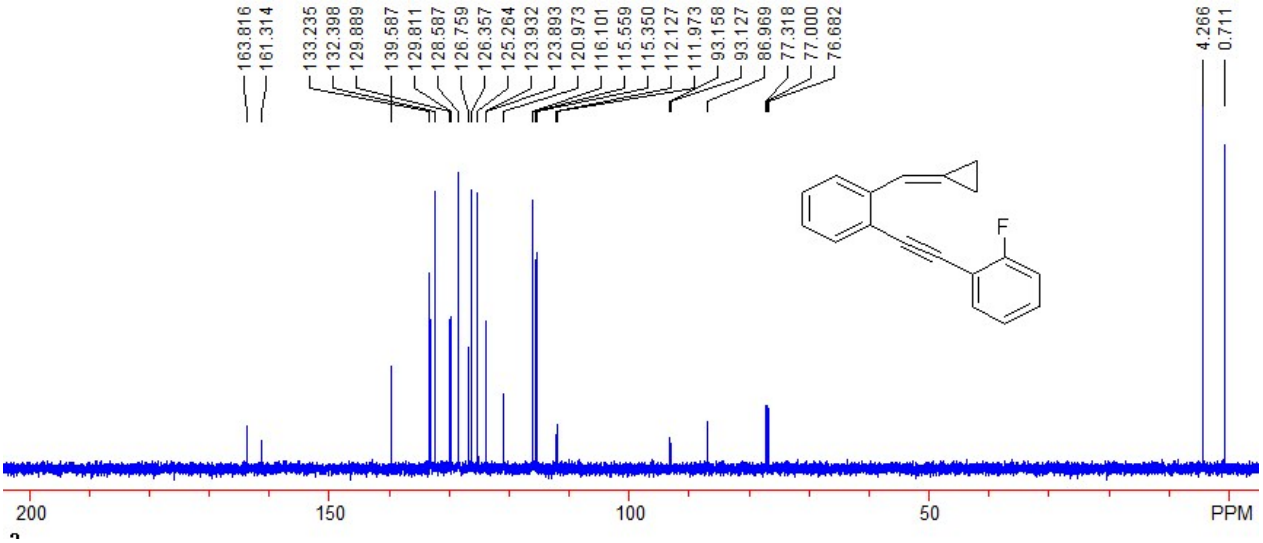
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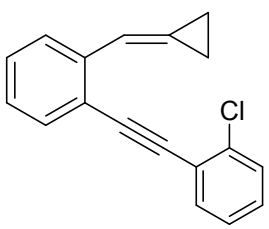
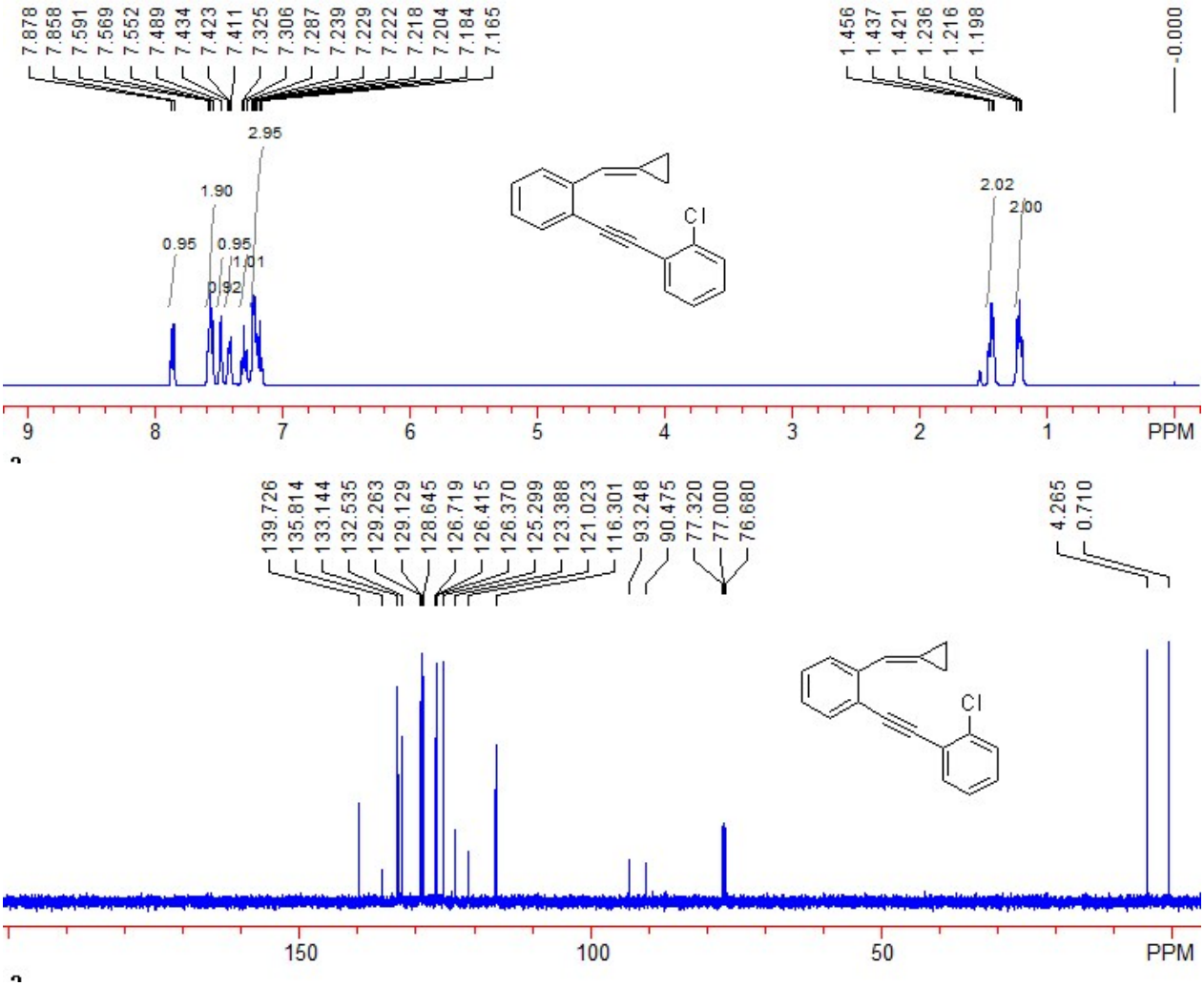
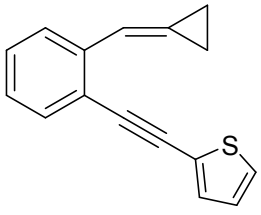

Cl

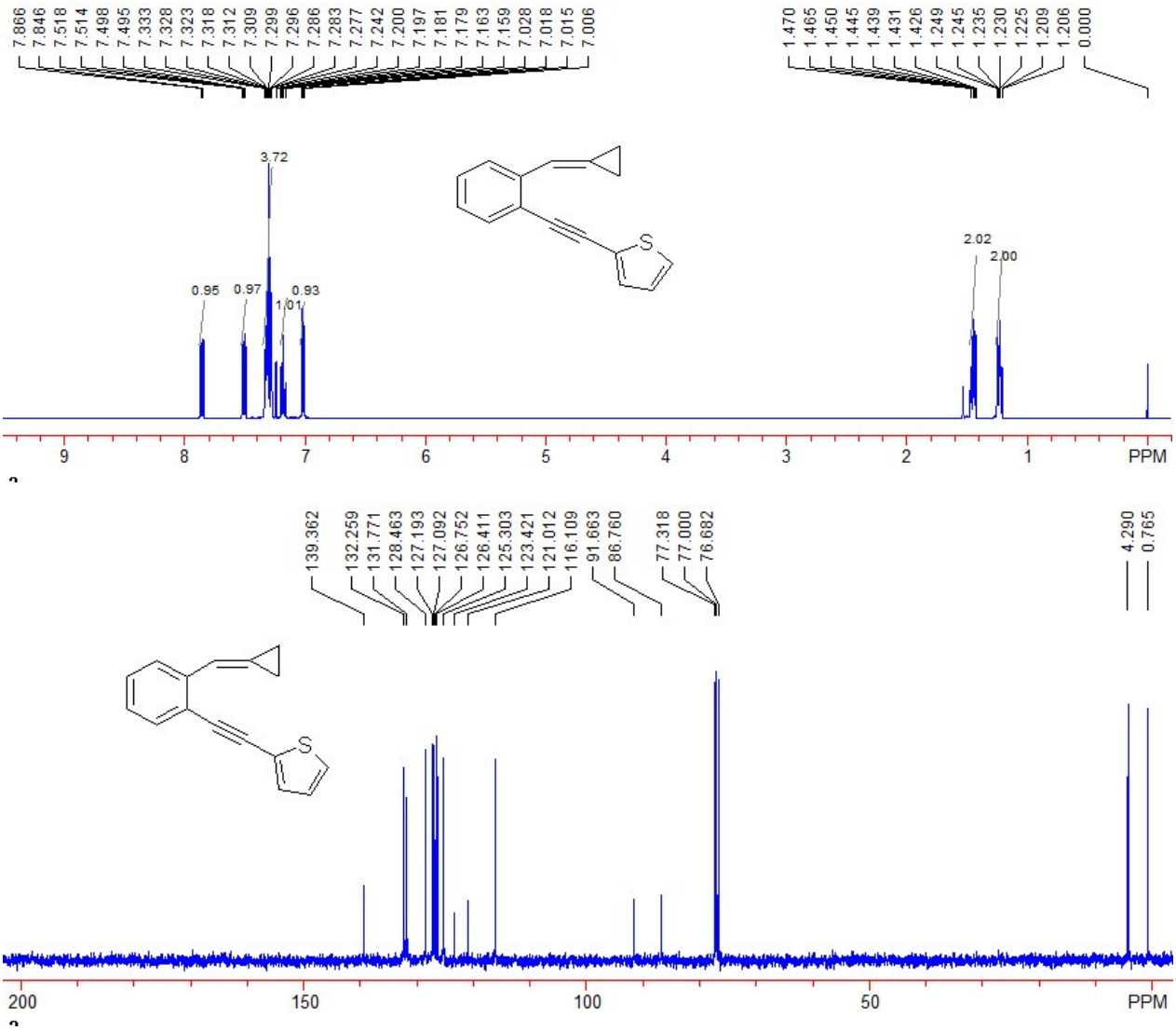
Compound **1q**. 1.260 g, yield: 59%; white solid. MP: 91-93 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20-1.24 (m, 2H, CH_2), 1.42-1.46 (m, 2H, CH_2), 7.17-7.24 (m, 3H, Ar), 7.29-7.33 (m, 1H, Ar), 7.41-7.43 (m, 1H, Ar), 7.49 (s, 1H, =CH), 7.55-7.59 (m, 2H, Ar), 7.87 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.7, 4.3, 90.5, 93.2, 116.3, 121.0, 123.4, 125.3, 126.3, 126.4, 126.7, 128.6, 129.1, 129.3, 132.5, 133.1135.8, 139.7. IR (neat) ν 2969, 2216, 1626, 1484, 1427, 1126, 1056 cm^{-1}. MS (%) m/e 264 (89.52), 229 (M^+, 100.00), 202 (14.13), 152 (14.67), 115 (15.45), 91 (1.15). HRMS (EI) calcd.for $C_{18}H_{13}Cl$: 264.0706, found: 264.0707.

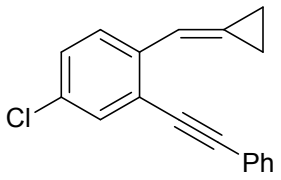




Compound **1s**. 800 mg, yield: 61%; white solid. MP: 108-110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21-1.25 (m, 2H, CH_2), 1.43-1.47 (m, 2H, CH_2), 7.01-7.03 (m, 1H, Ar), 7.16-7.20 (m,

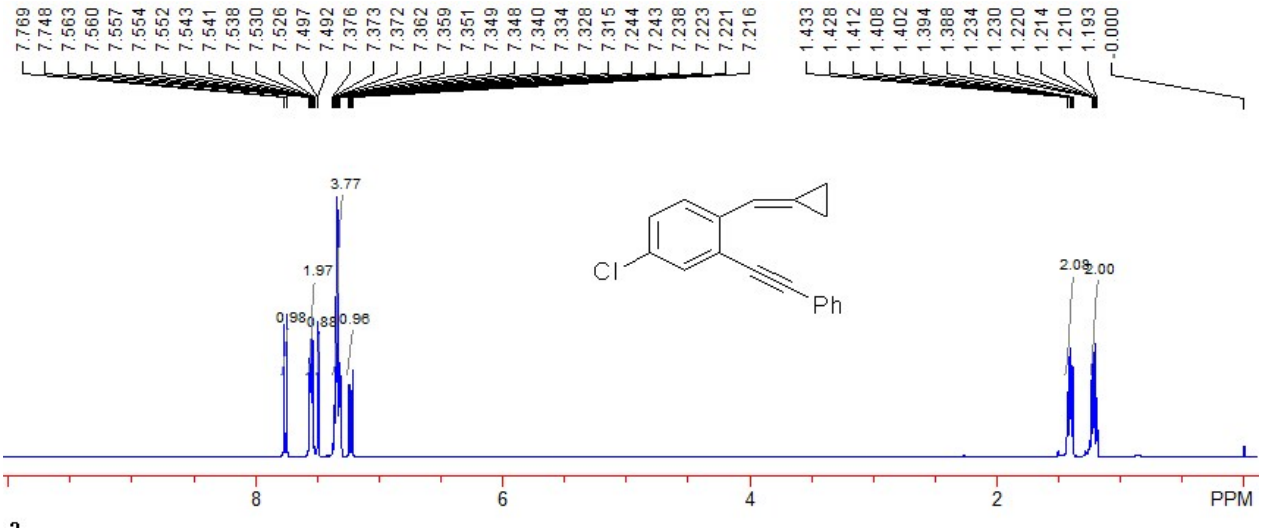
1H, Ar), 7.28-7.33 (m, 4H, =CH , Ar), 7.50-7.52 (m, 1H, Ar), 7.86 (d, *J* = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.8, 4.3, 86.8, 91.7, 116.1, 121.0, 123.4, 125.3, 126.4, 126.8, 127.1, 127.2, 128.5, 131.8, 132.3, 139.4. IR (neat) ν 2976, 2199, 1591, 1474, 1423, 1214, 1123 cm^{-1}. MS (%) m/e 236 (M^+, 100.00), 229 (2.98), 202 (32.73), 152 (11.44), 115 (5.02), 91 (2.20). HRMS (EI) calcd.for $C_{16}H_{12}S$: 236.0660, found: 236.0654.

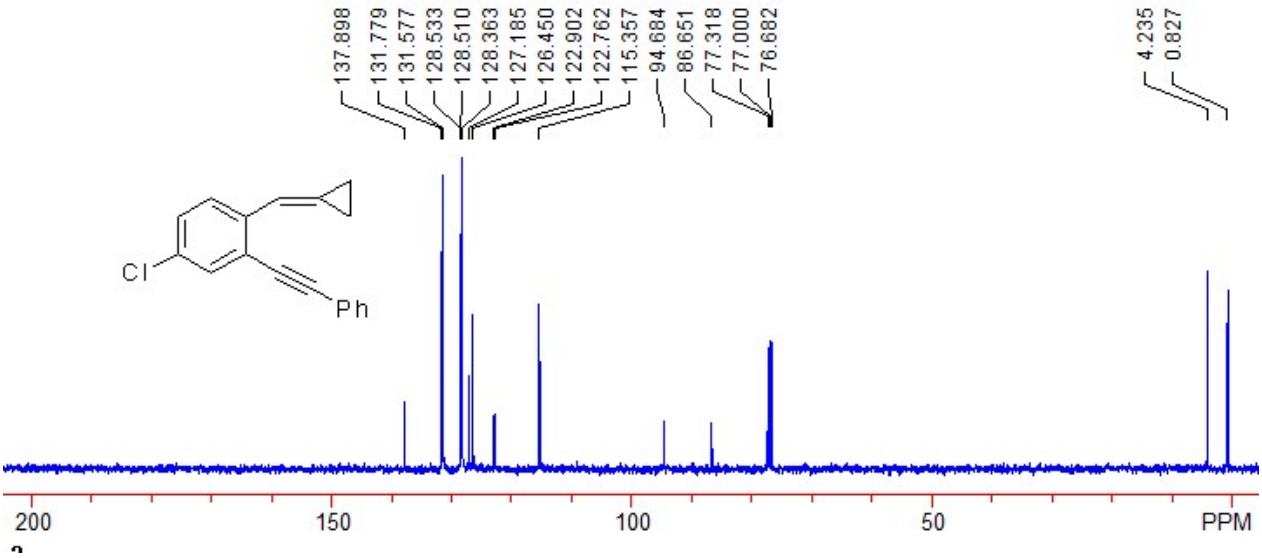


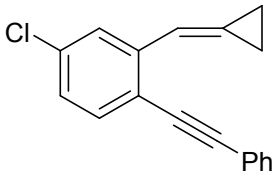


Compound **1cc**. 790 mg, yield: 38%; white solid. MP: 123-125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19-1.23 (m, 2H, CH_2), 1.39-1.43 (m, 2H, CH_2), 7.22-7.24 (m, 1H, Ar), 7.32-7.38 (m, 4H, Ar), 7.49 (d, *J* = 2.0 Hz, 1H, =CH), 7.53-7.56 (m, 2H, Ar), 7.76 (d, *J* = 8.4Hz, 1H, Ar). ^{13}C

NMR ($CDCl_3$, 100 MHz, TMS) δ 0.8, 4.2, 86.7, 94.7, 115.4, 122.8, 122.9, 126.5, 127.2, 128.4, 128.5, 128.6, 131.6, 131.8, 137.9. IR (neat) ν 3068, 2977, 1956, 1583, 1477, 1397, 1114 cm^{-1}. MS (%) m/e 264 (13.79), 238 (M^+, 100.00), 202 (73.00), 152 (3.31), 115 (5.89), 91 (1.37). HRMS (EI) calcd.for $C_{18}H_{13}Cl$: 264.0706, found: 264.0701.

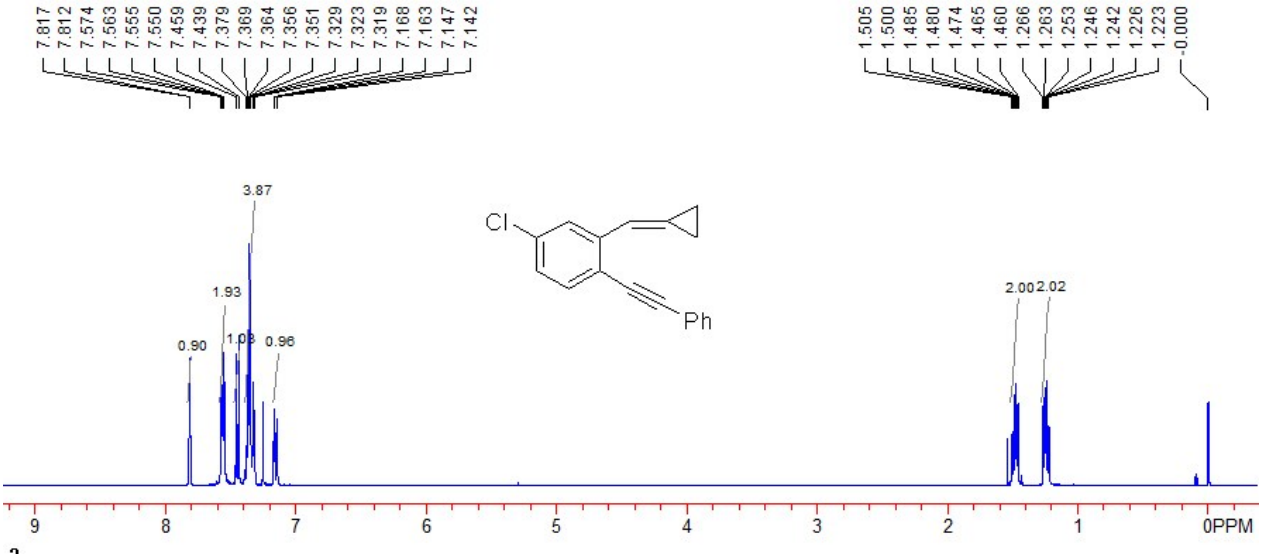


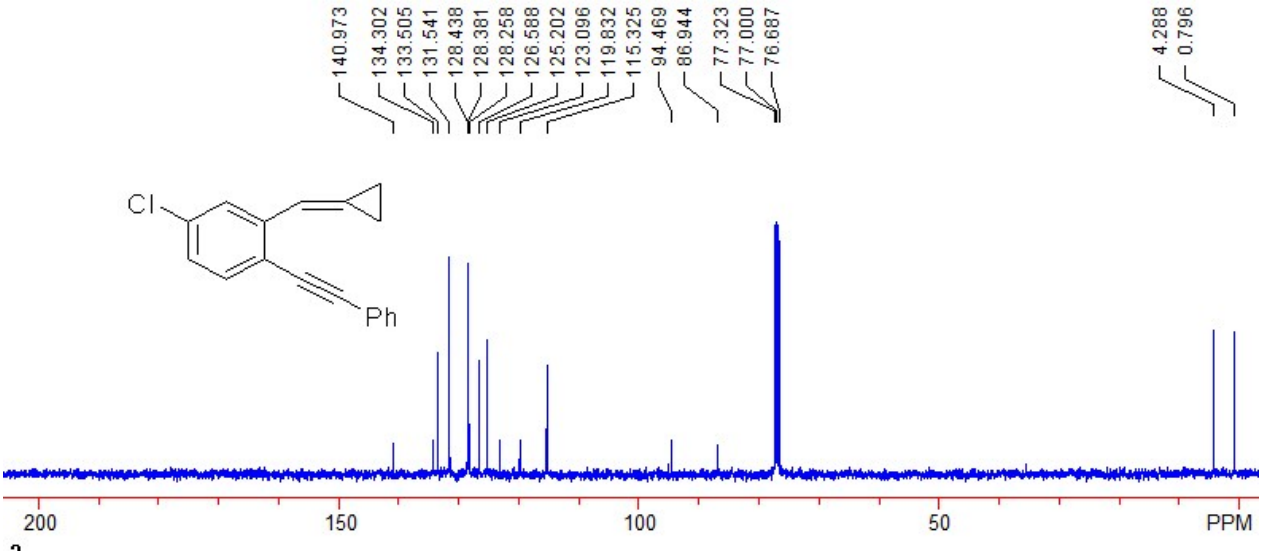


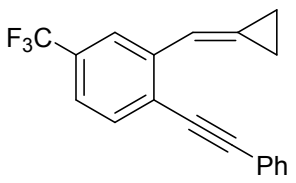


Compound **1ff**. 270 mg, yield: 15%; white solid.^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.22-1.27 (m, 2H, CH_2), 1.46-1.51 (m, 2H, CH_2), 7.14-7.17 (m, 1H, Ar), 7.32-7.38 (m, 4H, =CH, Ar), 7.45 (d, J = 8.0 Hz, 1H, Ar), 7.55-7.57 (m, 2H, Ar), 7.81 (d, J = 2.0Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.8, 4.3, 86.9, 94.5, 115.3, 119.8, 123.1, 125.2, 126.6, 128.2, 128.3, 128.4,

131.5, 133.5, 134.3, 141.0. IR (neat) ν 3046, 2978, 1732, 1580, 1490, 1267, 1109 cm^{-1}. MS (%) m/e 264 (9.37), 238 (M^+, 100.00), 202 (92.04), 152 (3.40), 115 (8.57), 91 (3.36). HRMS (EI) calcd.for $C_{18}H_{13}Cl$: 264.0706, found: 264.0695.

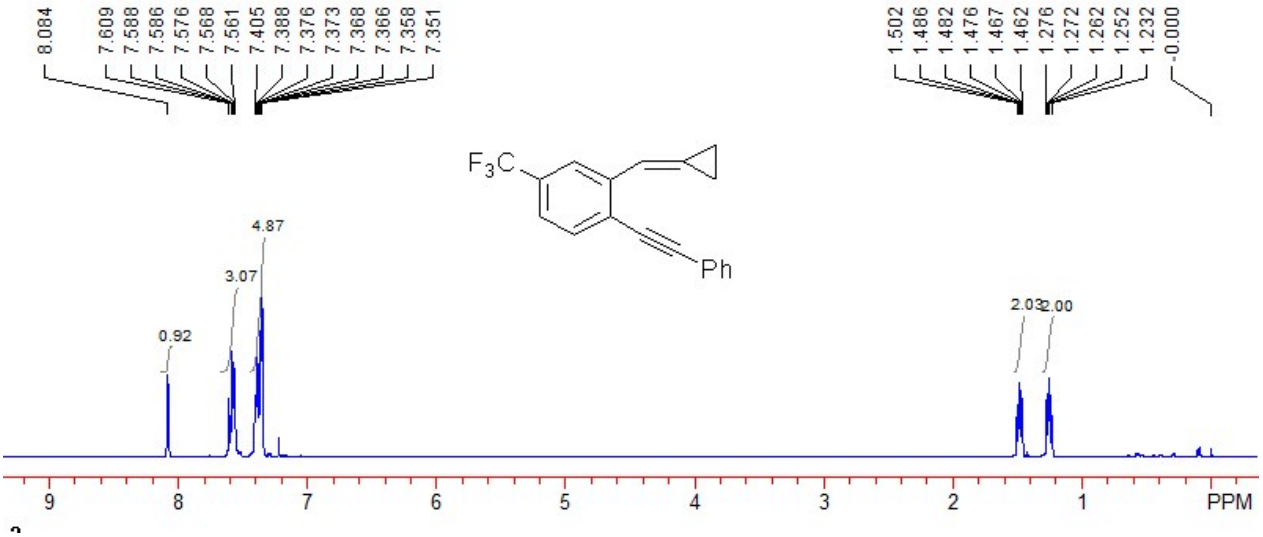


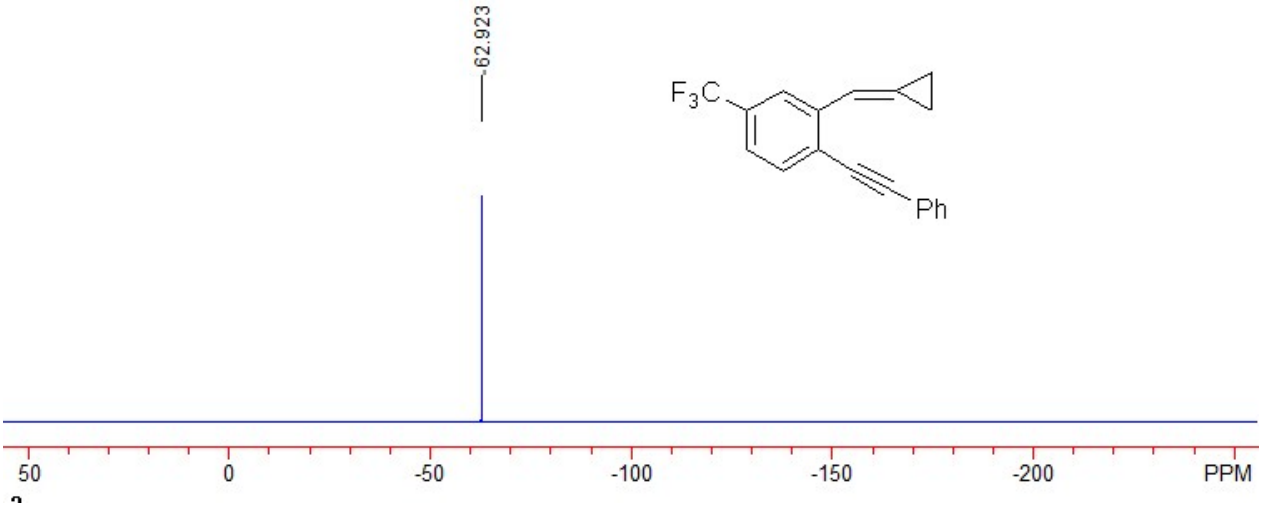


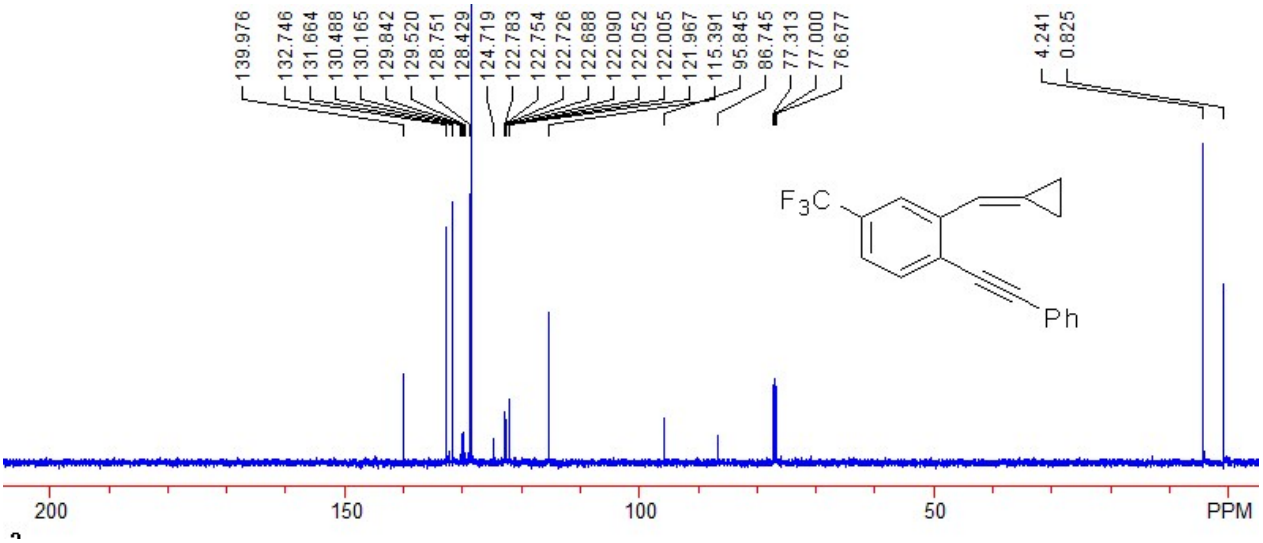


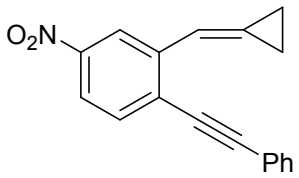
Compound **1gg**. 1.020 g, yield: 45%; white solid. MP: 131-134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23-1.28 (m, 2H, CH_2), 1.46-1.50 (m, 2H, CH_2), 7.35-7.41 (m, 5H, =CH, Ar), 7.56-7.61 (m, 3H, Ar), 8.08 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.8, 4.2, 86.7, 95.8, 115.4, 122.0 (q, $J_{C\text{-}F}$ = 4.7 Hz), 122.7 (q, $J_{C\text{-}F}$ = 2.8 Hz), 123.4 (d, $J_{C\text{-}F}$ = 266.7 Hz), 128.4, 128.8, 130.0

(q, $J_{C\text{-}F}$ = 32.3 Hz), 131.7, 132.7, 140.0. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -62.92 (s, 3F). IR (neat) ν 2976, 2209, 1610, 1441, 1324, 1228, 1106 cm^{-1}. MS (%) m/e 298 (M^+, 100.00), 228 (79.32), 202 (17.93), 152 (10.38), 115 (29.55), 91 (5.63). HRMS (EI) calcd.for $C_{19}H_{13}F_3$: 298.0969, found: 298.0962.

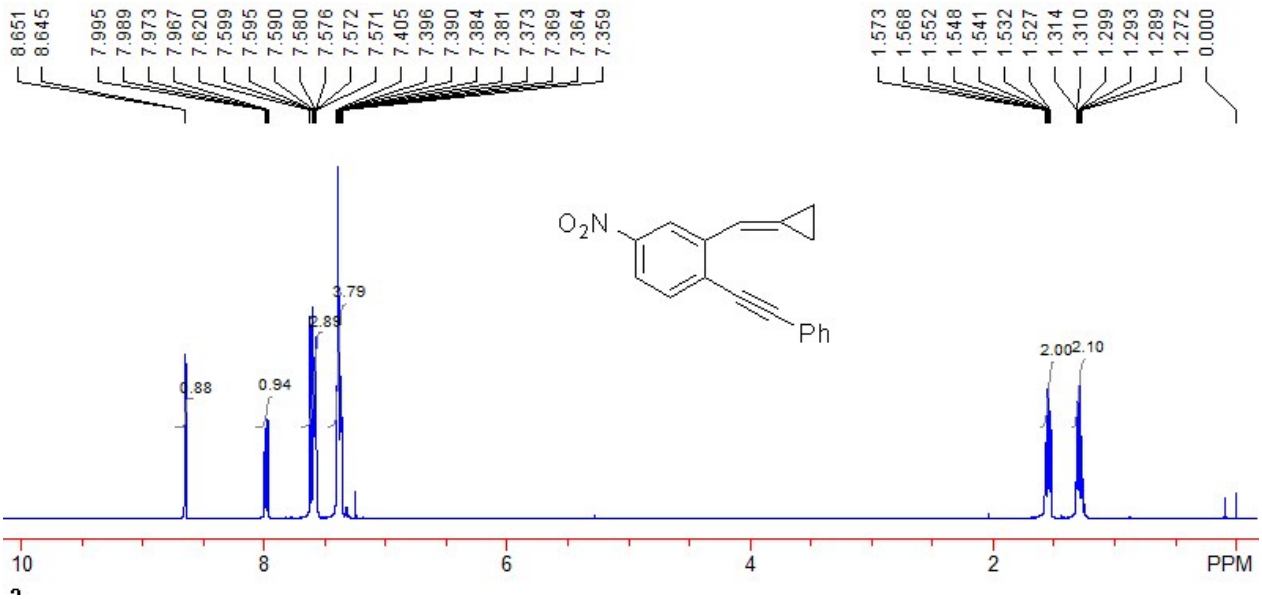


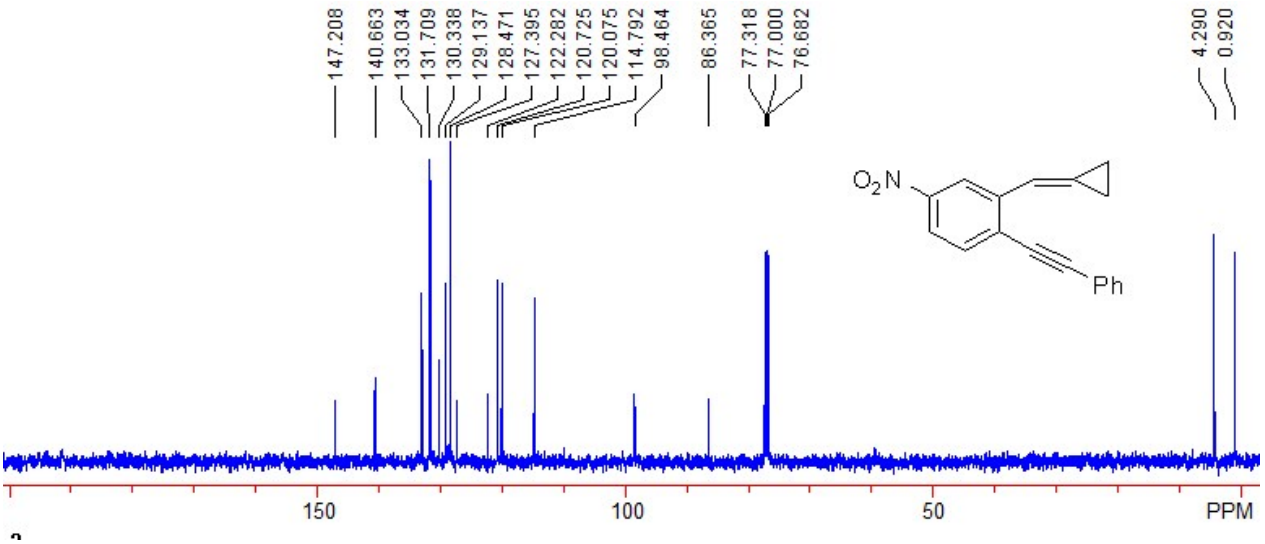


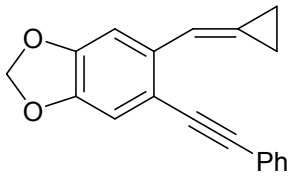




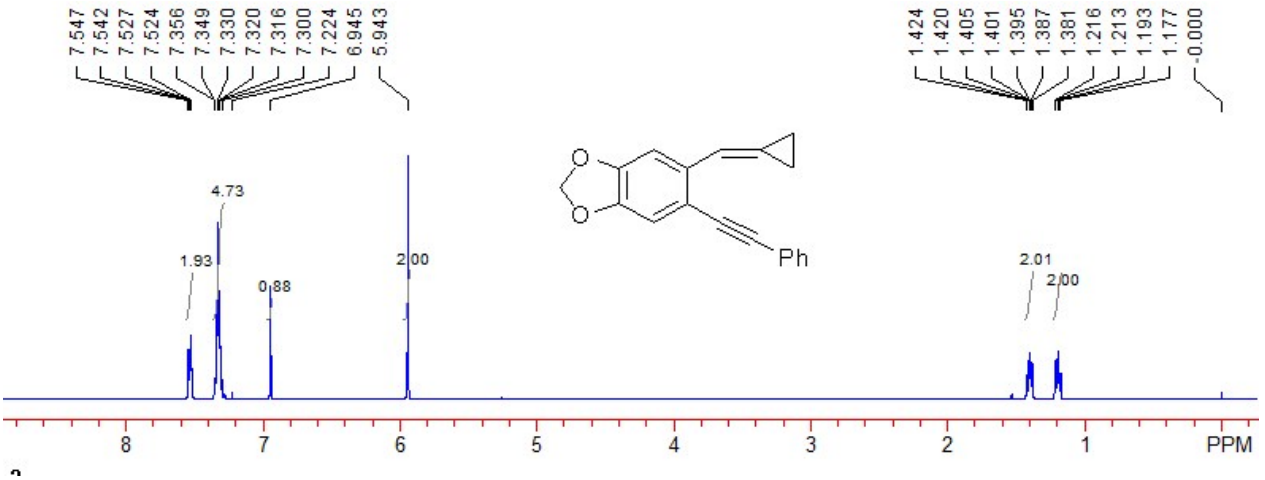
Compound **1hh**. 650 mg, yield: 29%; white solid. MP: 162-164 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.27-1.31 (m, 2H, CH_2), 1.53-1.57 (m, 2H, CH_2), 7.36-7.41 (m, 4H, =CH, Ar), 7.57-7.62 (m, 3H, Ar), 7.98 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, Ar), 8.65 (d, J = 2.4 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.9, 4.3, 86.4, 98.5, 114.8, 120.1, 120.7, 122.3, 127.4, 128.5, 129.1, 130.3, 131.7, 133.0, 140.7, 147.2. IR (neat) ν 2974, 2217, 1596, 1442, 1359, 1279, 1080 cm^{-1}. MS (%) m/e 275 (M^+, 100.00), 228 (67.20), 202 (25.09), 152 (5.04), 115 (11.02), 91 (2.79). HRMS (EI) calcd.for $C_{18}H_{13}NO_2$: 275.0946, found: 279.0956.

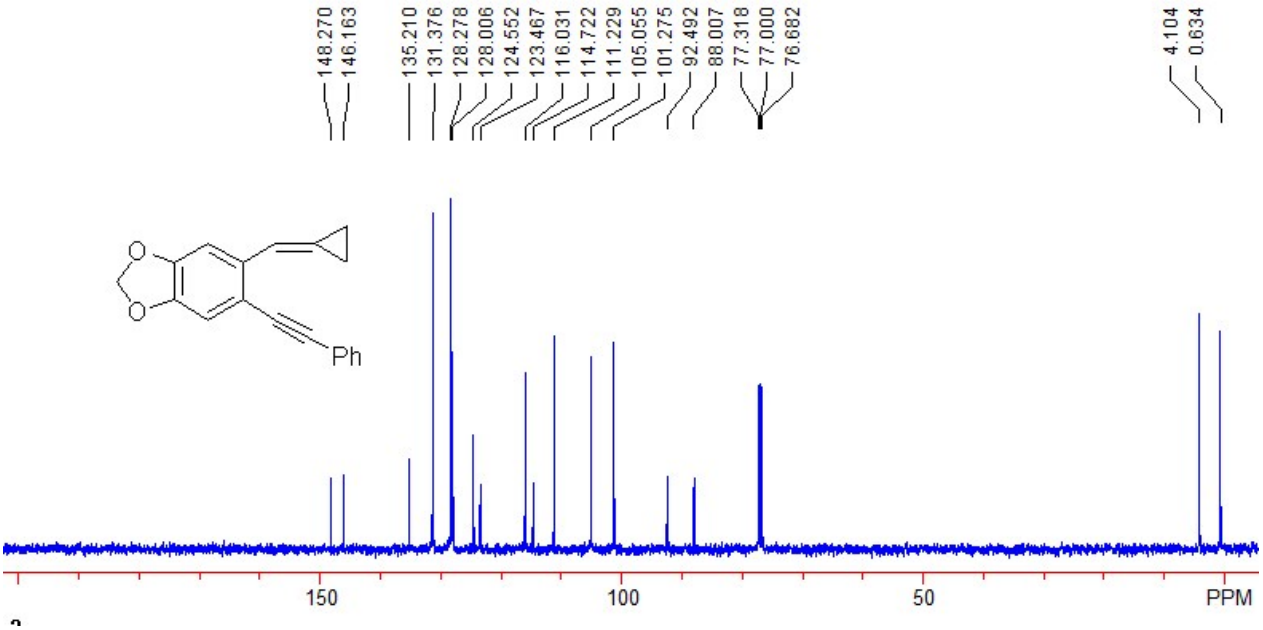


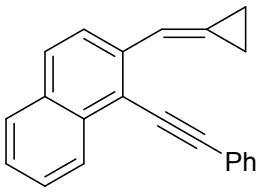




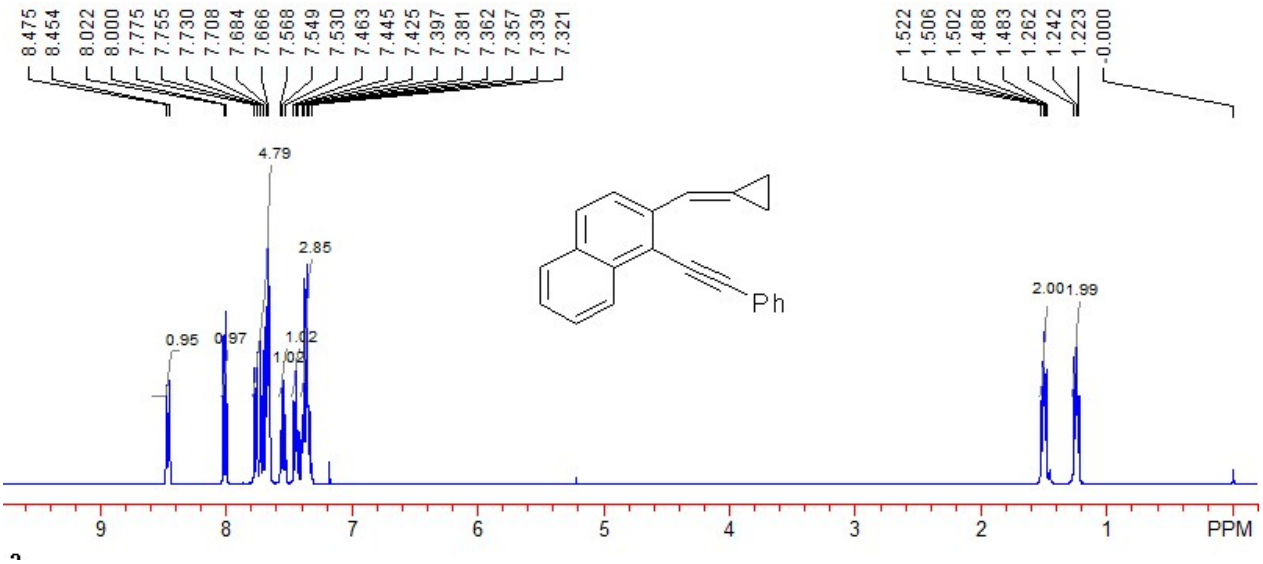
Compound **1ii**. 625 mg, yield: 42%; white solid. MP: 118-120 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.18-1.22 (m, 2H, CH_2), 1.38-1.42 (m, 2H, CH_2), 5.94 (s, 2H, CH_2), 6.95 (s, 1H, Ar), 7.30-7.36 (m, 5H, =CH, Ar), 7.53 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.6, 4.1, 88.0, 92.5, 102.3, 105.1, 111.2, 114.7, 116.0, 123.5, 124.6, 128.0, 128.3, 131.4, 135.2, 146.2, 148.3. IR (neat) ν 2910, 2196, 1615, 1500, 1441, 1241, 1137 cm^{-1}. MS (%) m/e 274 (M^+, 100.00), 228 (0.88), 202 (6.92), 152 (1.32), 115 (5.49), 91 (1.95). HRMS (EI) calcd.for $C_{19}H_{14}O_2$: 274.0994, found: 274.0988.

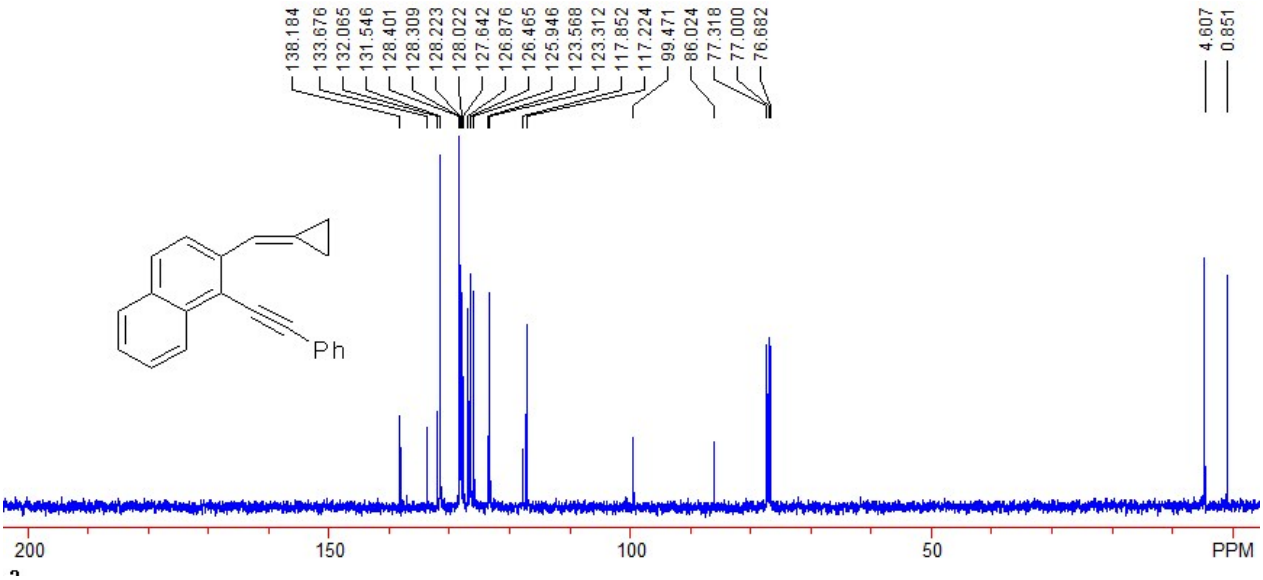


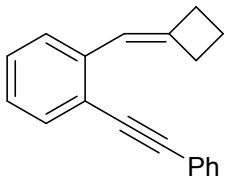




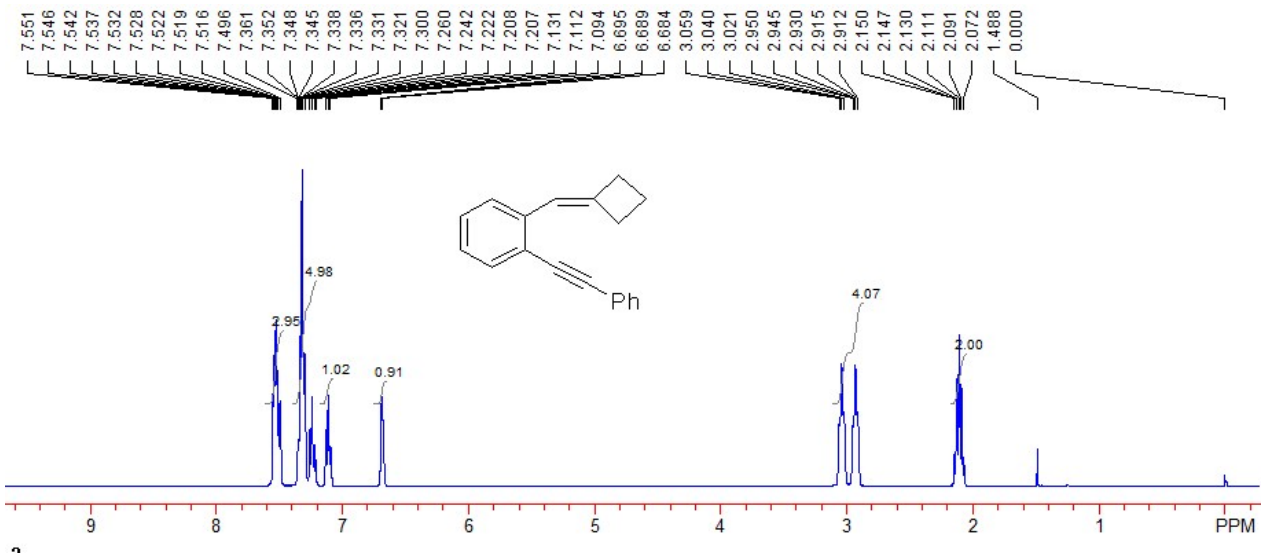
Compound **1kk**. 961 mg, yield: 42%; white solid. MP: 135-138 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.22-1.26 (m, 2H, CH_2), 1.48-1.52 (m, 2H, CH_2), 7.32-7.40 (m, 3H, =CH, Ar), 7.44 (t, *J* = 7.6 Hz, 1H, Ar), 7.55 (t, *J* = 7.6 Hz, 1H, Ar), 7.67-7.78 (m, 5H, Ar), 8.01 (d, *J* = 8.8 Hz, 1H, Ar), 8.46 (d, *J* = 8.8 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.9, 4.6, 86.0, 99.5, 117.2, 117.9, 123.3, 125.9, 126.5, 126.9, 127.6, 128.0, 128.2, 128.3, 128.4, 131.5, 132.1, 133.7, 138.2. IR (neat) ν 2970, 1979, 1594, 1488, 1260, 1071, 972 cm^{-1}. MS (%) m/e 280 (M^+, 100.00), 228 (0.31), 202 (16.13), 152 (1.32), 115 (1.86), 91 (1.29). HRMS (EI) calcd.for $C_{22}H_{16}$: 280.1252, found: 280.1254.

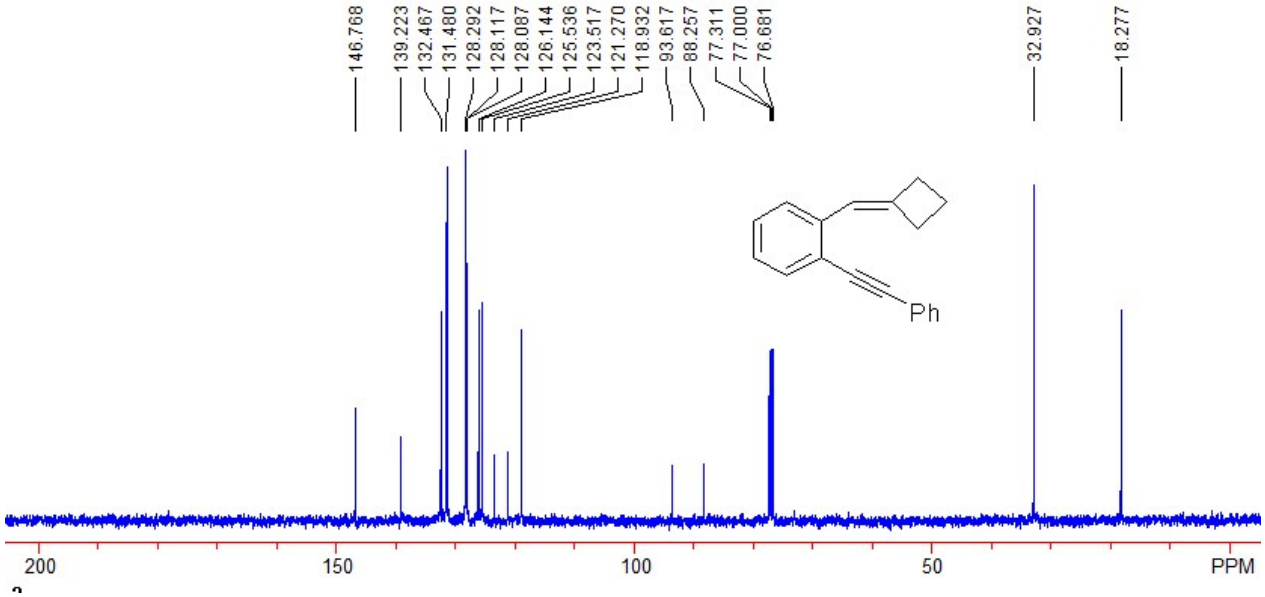


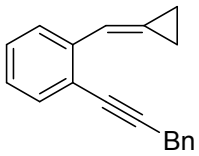




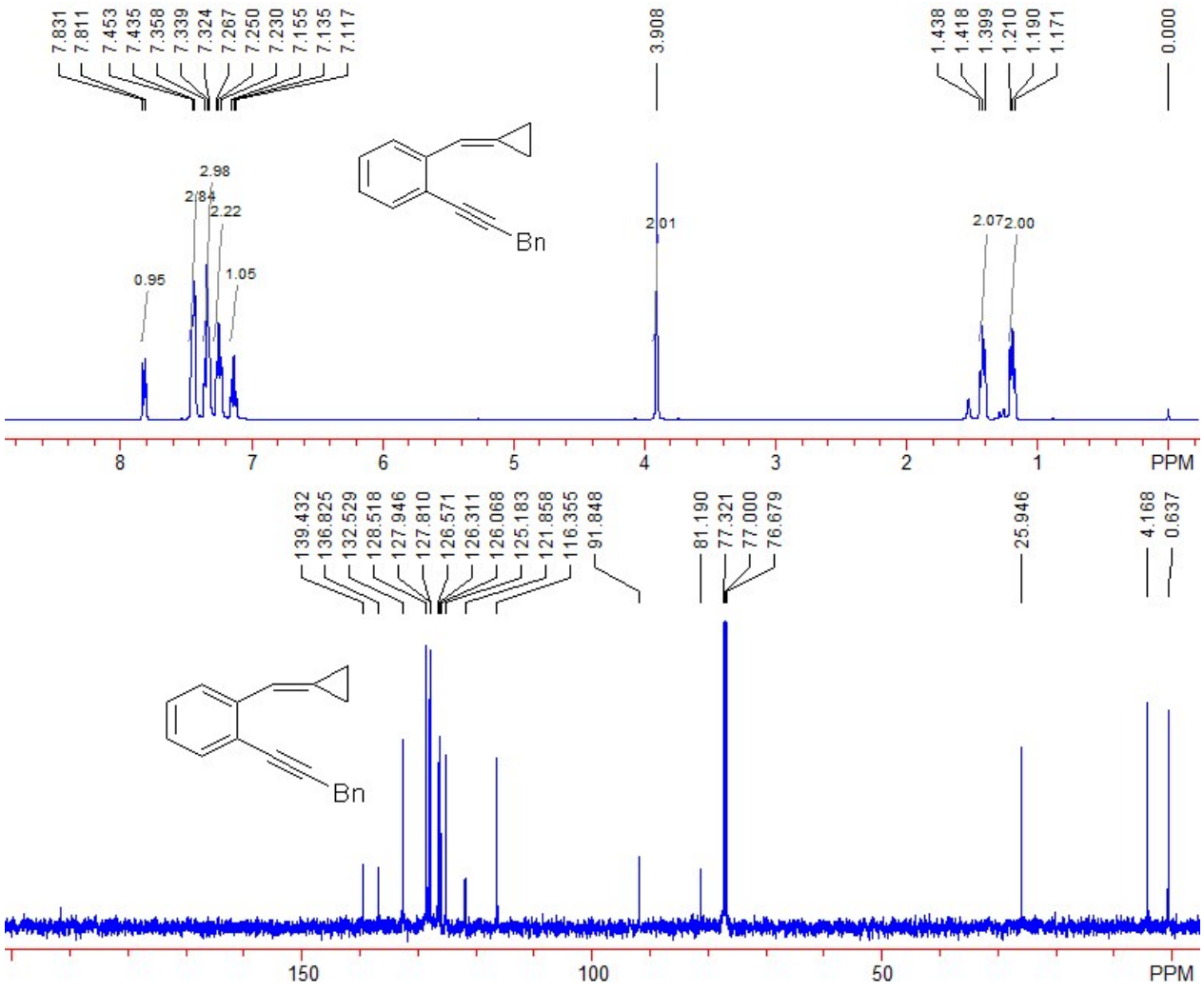
Compound **5**. 583 mg, yield: 47%; white solid. MP: 60-62 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.07-2.15 (m, 2H, CH_2), 2.91-2.95 (m, 2H, CH_2), 3.02-3.06 (m, 2H, CH_2), 6.69 (t, J = 2.0 Hz, 1H, =CH), 7.11 (t, J = 7.6 Hz, 1H, Ar), 7.22-7.36 (m, 5H, Ar), 7.50-7.55 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.3, 32.9, 88.3, 93.6, 118.9, 121.3, 123.5, 125.5, 126.1, 128.0, 128.1, 128.3, 131.5, 132.5, 139.2, 146.8. IR (neat) ν 2953, 1660, 1595, 1444, 1356, 1238, 1069 cm^{-1}. MS (%) m/e 244 (M^+, 100.00), 228 (91.01), 202 (26.95), 152 (20.04), 115 (28.76), 91 (39.62). HRMS (EI) calcd.for $C_{19}H_{16}$: 244.1252, found: 244.1251.

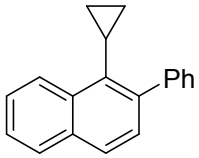




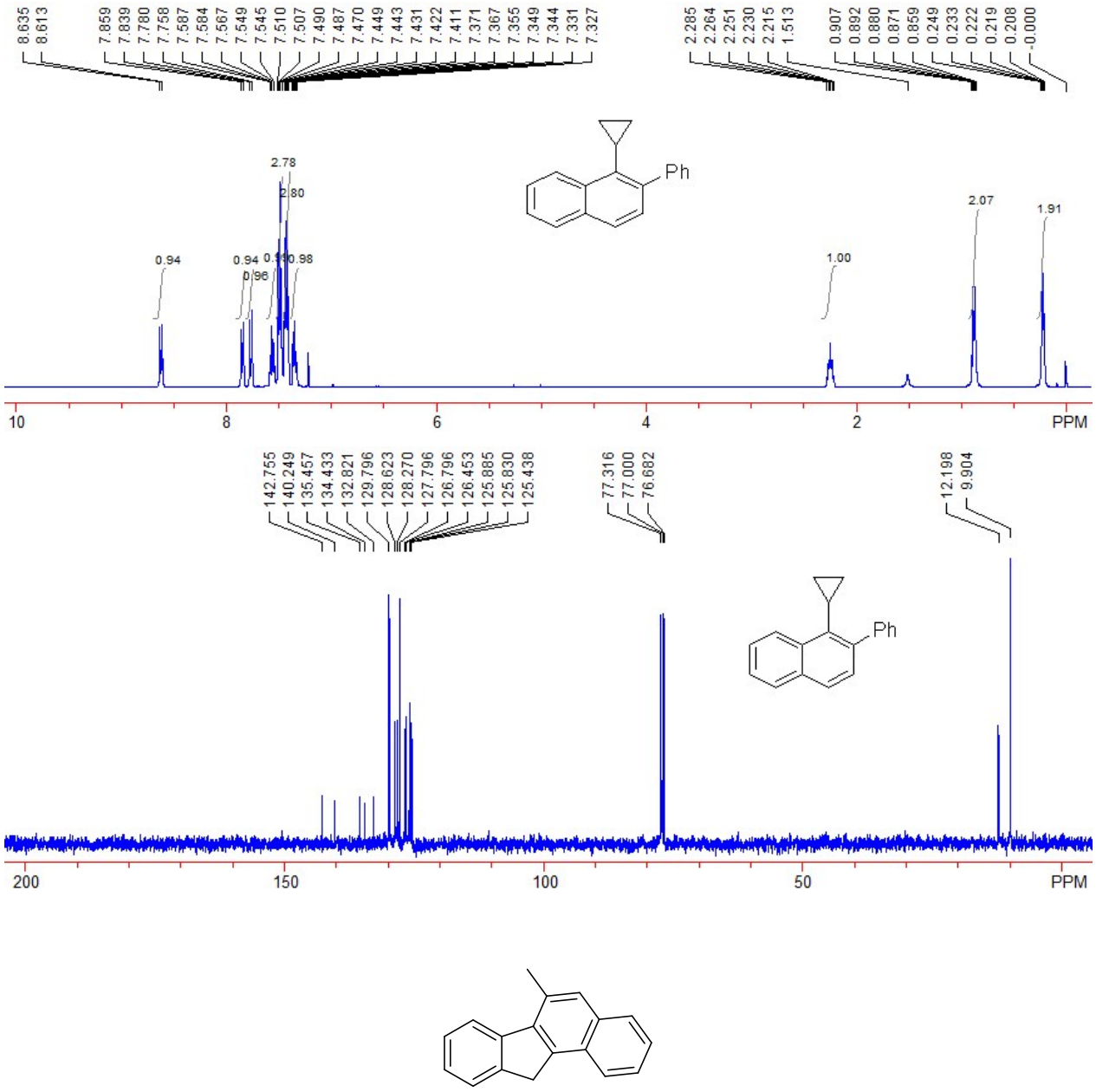


Compound **7**. 829 mg, yield: 68%; colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.17-1.21 (m, 2H, CH_2), 1.40-1.44 (m, 2H, CH_2), 3.91 (s, 2H, CH_2), 7.14 (t, J = 8.0 Hz, 1H, Ar), 7.25 (t, J = 8.0 Hz, 2H, Ar), 7.32-7.36 (m, 3H, =CH, Ar), 7.44-7.45 (m, 3H, Ar), 7.82 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.6, 4.2, 25.9, 81.2, 91.8, 116.4, 121.9, 125.2, 126.1, 126.3, 126.6, 127.8, 127.9, 128.5, 132.5, 136.8, 139.4. IR (neat) ν 3029, 2850, 1705, 1621, 1520, 1358, 1129 cm^{-1}. MS (%) m/e 244 (38.26), 229 (M^+, 100.00), 202 (24.79), 152 (30.36), 115 (63.38), 91 (57.26). HRMS (EI) calcd.for $C_{19}H_{16}$: 244.1252, found: 244.1253.

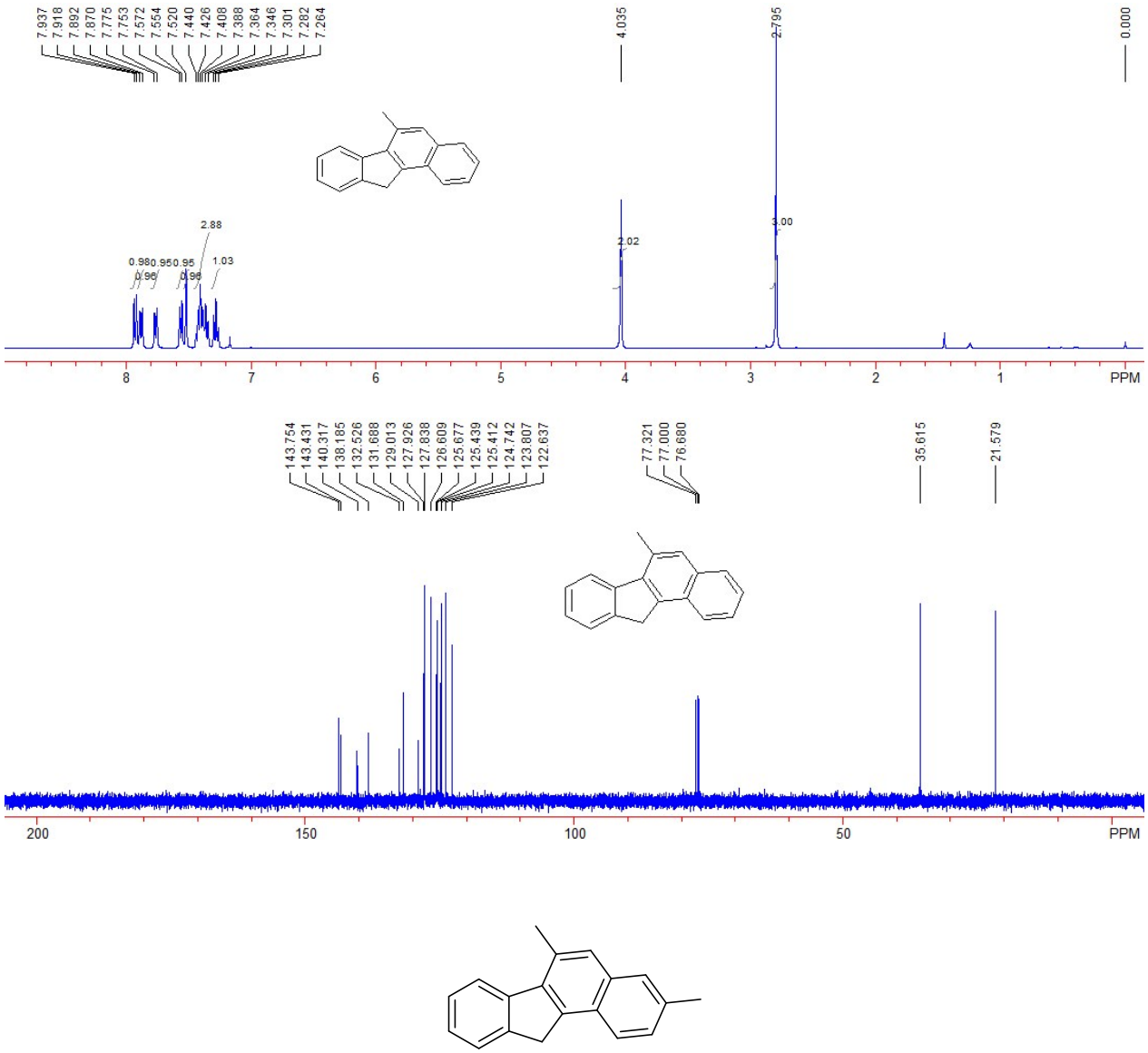




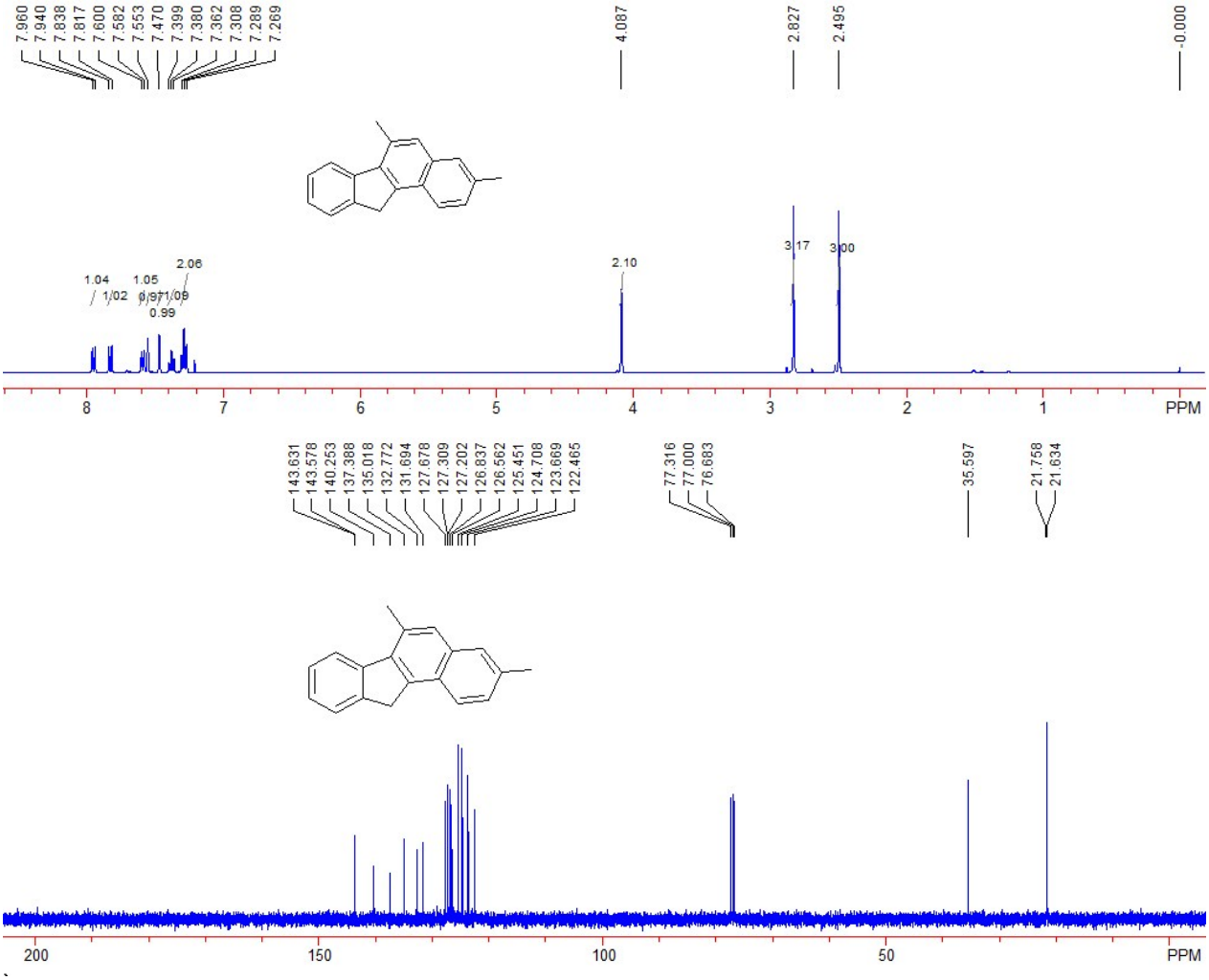
Compound **S7**. 322 mg, yield: 22%; white solid. MP: 148-150 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.21-0.25 (m, 2H, CH_2), 0.86-0.91 (m, 2H, CH_2), 2.22-2.29 (m, 1H, CH), 7.33-7.37 (m, 1H, Ar), 7.41-7.45 (m, 3H, Ar), 7.47-7.51 (m, 3H, Ar), 7.55-7.59 (m, 1H, Ar), 7.77 (d, J = 8.8 Hz, 1H, Ar), 7.85 (d, J = 8.8 Hz, 1H, Ar), 8.62 (d, J = 8.8 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 9.9, 12.2, 125.4, 125.8, 125.9, 126.5, 126.8, 127.8, 128.3, 128.6, 129.8, 132.8, 134.4, 135.5, 140.2, 142.8. IR (neat) ν 2985, 2823, 1650, 1532, 1460, 1259, 1026 cm^{-1}. MS (%) m/e 244 (M^+, 100.00), 229 (74.21), 202 (12.87), 152 (5.92), 115 (11.53), 91 (11.56). HRMS (EI) calcd.for $C_{19}H_{16}$: 244.1252, found: 244.1256.

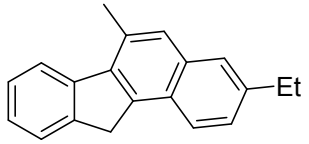


Compound **2a**. 38 mg, yield: 83%; white solid. MP: 105-107 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.80 (s, 3H, CH_3), 4.04 (s, 2H, CH_2), 7.28 (t, J = 7.2 Hz, 1H, Ar), 7.35-7.44 (m, 3H, Ar), 7.52 (s, 1H, Ar), 7.56 (d, J = 7.2 Hz, 1H, Ar), 7.76 (d, J = 8.8 Hz,1H, Ar), 7.88 (d, J = 8.8 Hz, 1H, Ar), 7.93 (d, J = 8.8 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.6, 122.6, 123.8, 124.7, 125.4, 125.5, 125.7, 126.6, 127.8, 127.9, 129.0, 131.7, 132.5, 138.2, 140.3, 143.4, 143.8. IR (neat) ν 2970, 1942, 1590, 1455, 1375, 1174, 1022 cm^{-1}. MS (%) m/e 230 (M^+, 100.00), 215 (90.77), 202 (6.64), 189 (3.58), 115 (19.78), 108 (34.70), 75 (4.98). HRMS (EI) calcd. for $C_{18}H_{14}$: 230.1096, found: 230.1098.

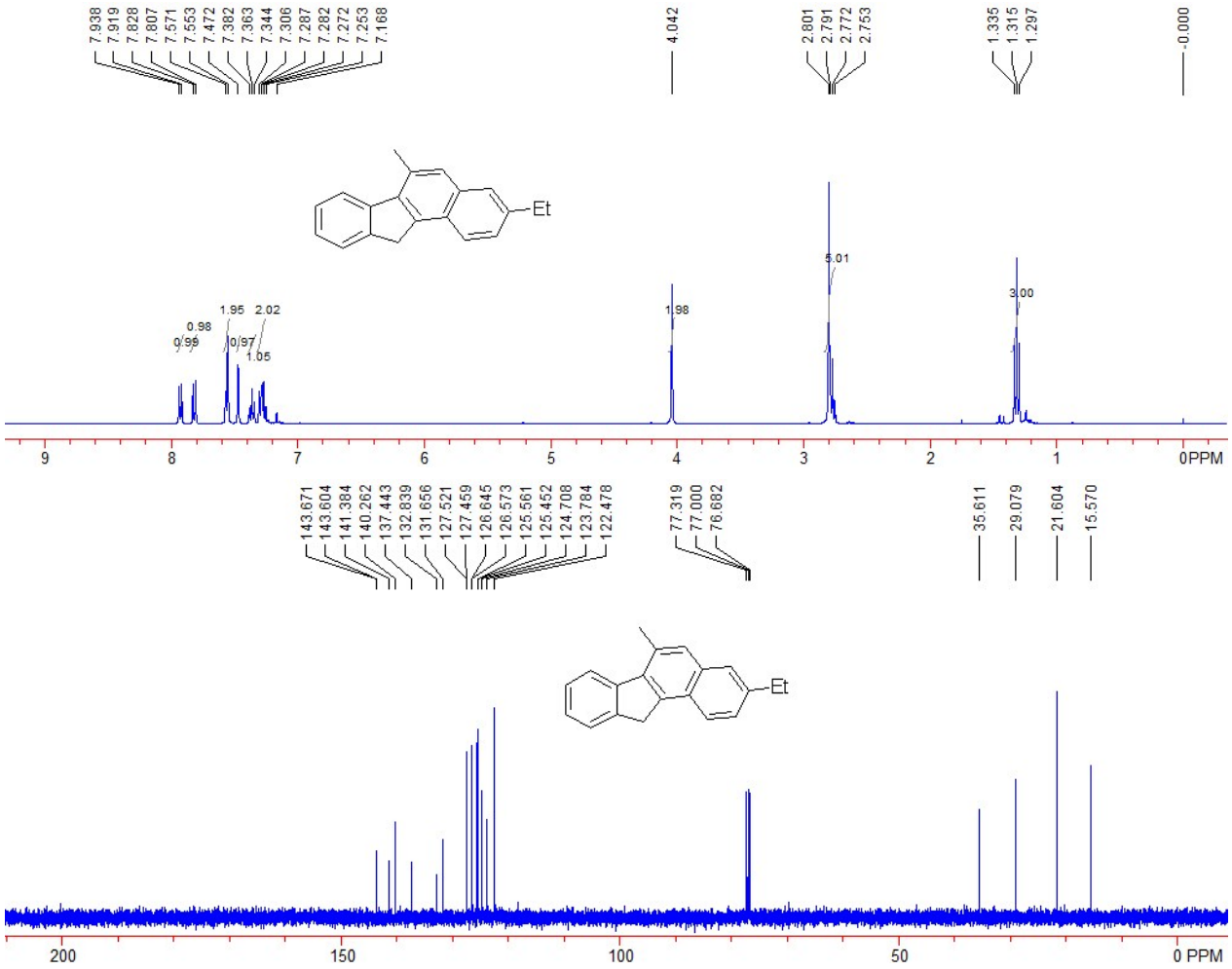


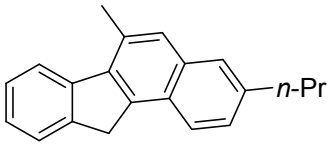
Compound **2b**. 42 mg, yield: 86%; white solid. MP: 126-128 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.50 (s, 3H, CH_3), 2.83 (s, 3H, CH_3), 4.09 (s, 2H, CH_2), 7.29 (t, J = 8.0 Hz, 2H, Ar), 7.38 (t, J = 7.2 Hz, 1H, Ar), 7.47 (s, 1H, Ar), 7.55 (s, 1H, Ar), 7.59 (d, J = 7.2 Hz, 1H, Ar), 7.83 (d, J = 8.0 Hz, 1H, Ar), 7.95 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.8, 35.6, 122.5, 123.7, 124.7, 125.5, 126.6, 126.8, 127.2, 127.3, 127.7, 131.7, 132.8, 135.0, 137.4, 140.3, 143.5, 143.6. IR (neat) ν 2918, 1936, 1629, 1455, 1358, 1257, 1178 cm^{-1}. MS (%) m/e 244 (M^+, 100.00), 229 (92.07), 207 (9.22), 189 (3.22), 114 (37.89), 108 (3.07), 75 (3.50). HRMS (EI) calcd.for $C_{19}H_{16}$: 244.1252, found: 244.1261.



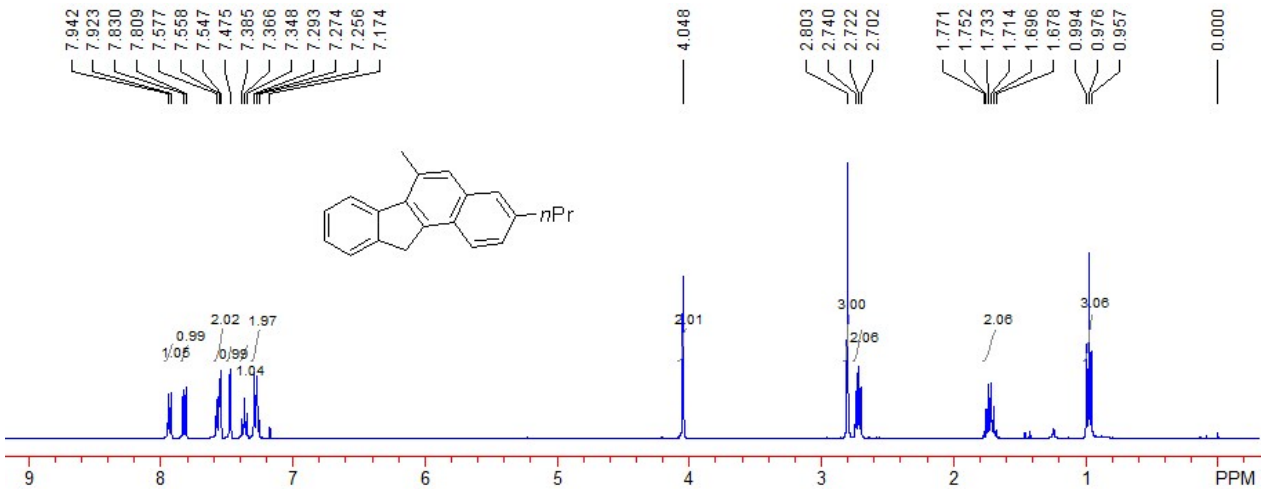


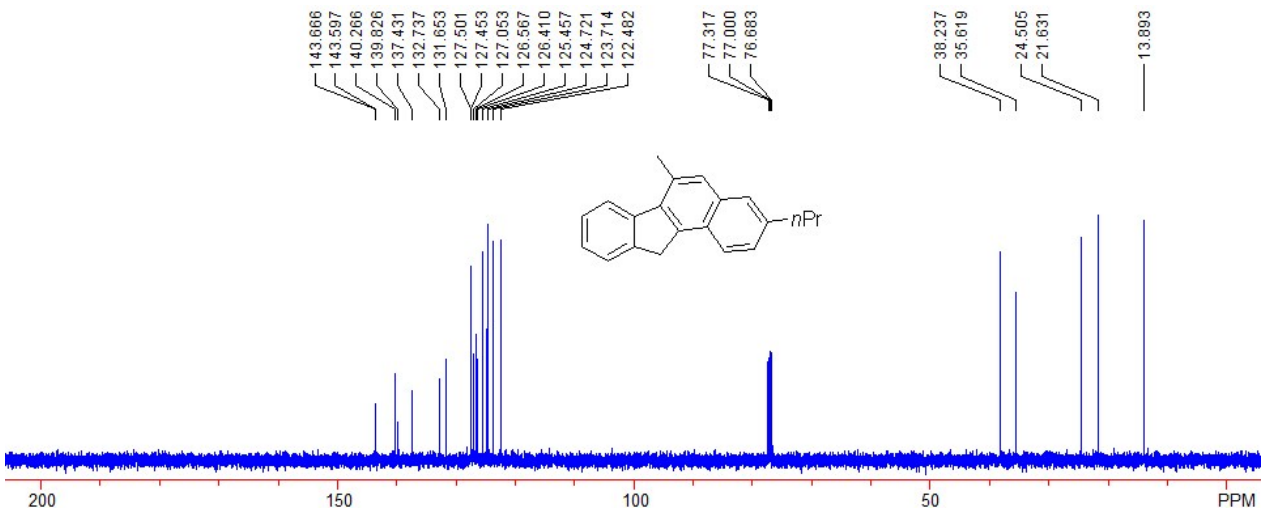
Compound **2c**. 44 mg, yield: 85%; white solid. MP: 127-130 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.32 (t, J = 7.2 Hz, 3H, CH_3), 2.75-2.80 (m, 5H, CH_2, CH_3), 4.04 (s, 2H, CH_2), 7.25-7.31 (m, 2H, Ar), 7.36 (t, J = 7.6 Hz, 1H, Ar), 7.47 (s, 1H, Ar), 7.55-7.57 (m, 2H, Ar), 7.82 (d, J = 8.4 Hz, 1H, Ar), 7.93 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.6, 21.6, 29.1, 35.6, 122.5, 123.8, 124.7, 125.5, 126.5, 126.6, 127.4, 127.5, 127.7, 131.7, 132.8, 137.4, 140.3, 141.4, 143.6, 143.7. IR (neat) ν 2962, 2860, 1937, 1630, 1456, 1359, 1178 cm^{-1}. MS (%) m/e 258 (M^+, 100.00), 243 (56.78), 229 (44.09), 189 (1.79), 114 (28.81), 108 (12.34), 75 (1.38). HRMS (EI) calcd. for $C_{20}H_{18}$: 258.1409, found: 258.1415.

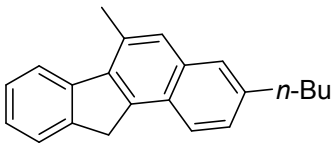




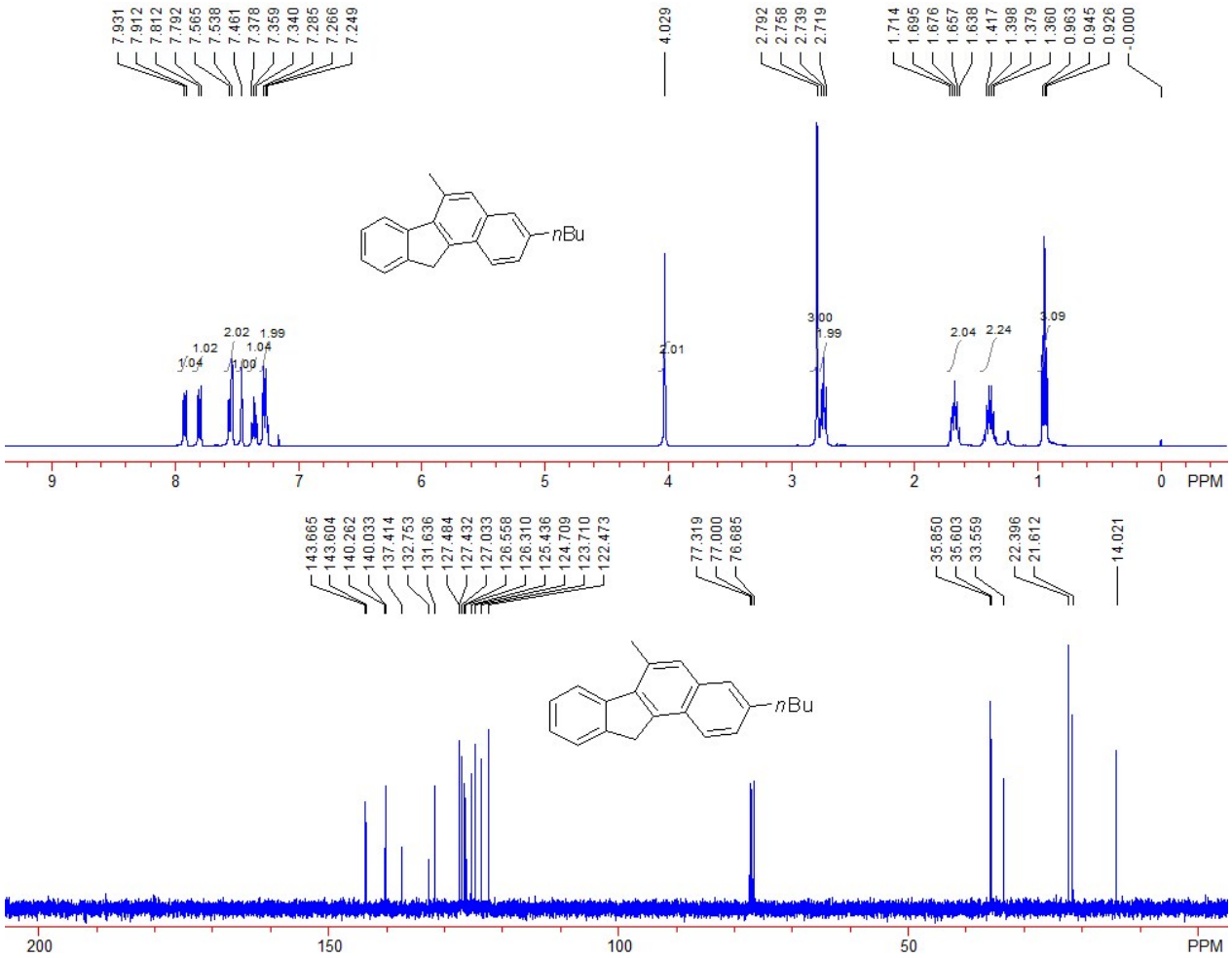
Compound **2d**. 44 mg, yield: 80%; white solid. MP: 136-138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.98 (t, *J* = 7.6 Hz, 3H, CH_3), 1.68-1.77 (m, 2H, CH_2), 2.72 (t, *J* = 8.0 Hz, 2H, CH_2), 2.80 (s, 3H, CH_3), 4.05 (s, 2H, CH_2), 7.26-7.29 (m, 2H, Ar), 7.37 (t, *J* = 7.2 Hz, 1H, Ar), 7.48 (s, 1H, Ar), 7.55-7.58 (m, 2H, Ar), 7.82 (d, *J* = 7.6 Hz, 1H, Ar), 7.93 (d, *J* = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 21.6, 24.5, 35.6, 38.2, 122.5, 123.7, 124.7, 125.5, 126.4, 126.6, 127.1, 127.4, 127.5, 131.7, 132.7, 137.4, 139.8, 140.3, 143.6, 143.7. IR (neat) ν 2959, 2865, 1943, 1597, 1455, 1396, 1178 cm^{-1}. MS (%) m/e 272 (M^+, 82.34), 243 (100.00), 228 (33.54), 215 (6.70), 114 (18.15), 101 (10.32), 75 (0.96). HRMS (EI) calcd. for $C_{21}H_{20}$: 272.1565, found: 272.1571.

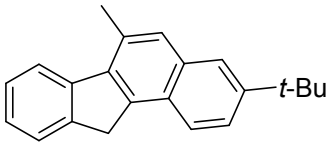




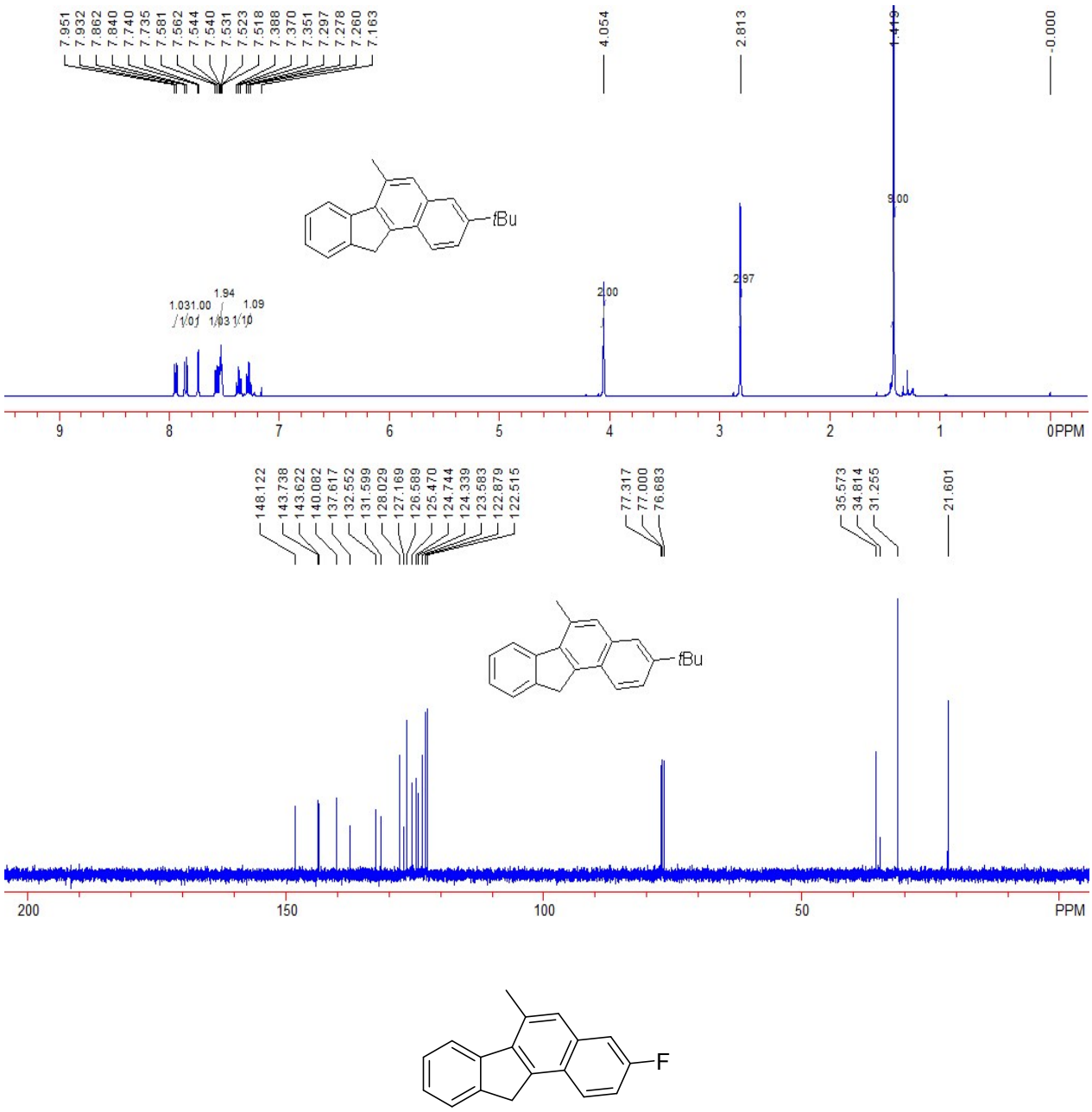


Compound **2e**. 50 mg, yield: 88%; white solid. MP: 125-128 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.95 (t, J = 7.6 Hz, 3H, CH_3), 1.36-1.42 (m, 2H, CH_2), 1.64-1.71 (m, 2H, CH_2), 2.74 (t, J = 8.0 Hz, 2H, CH_2), 2.79 (s, 3H, CH_3), 4.03 (s, 2H, CH_2), 7.25-7.29 (m, 2H, Ar), 7.36 (t, J = 7.6 Hz, 1H, Ar), 7.46 (s, 1H, Ar), 7.54-7.57 (m, 2H, Ar), 7.80 (d, J = 8.0 Hz, 1H, Ar), 7.92 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 21.6, 22.4, 33.6, 35.6, 35.9, 122.5, 123.7, 124.7, 125.4, 126.3, 126.6, 127.0, 127.4, 127.5, 131.6, 132.8, 137.4, 140.0, 140.3, 143.6, 143.7. IR (neat) ν 2925, 2851, 1604, 1456, 1396, 1178, 1033 cm^{-1}. MS (%) m/e 286 (M^+, 94.11), 243 (100.00), 228 (32.48), 215 (5.86), 114 (10.20), 101 (6.37), 75 (0.46). HRMS (EI) calcd.for $C_{22}H_{22}$: 286.1722, found: 286.1729.



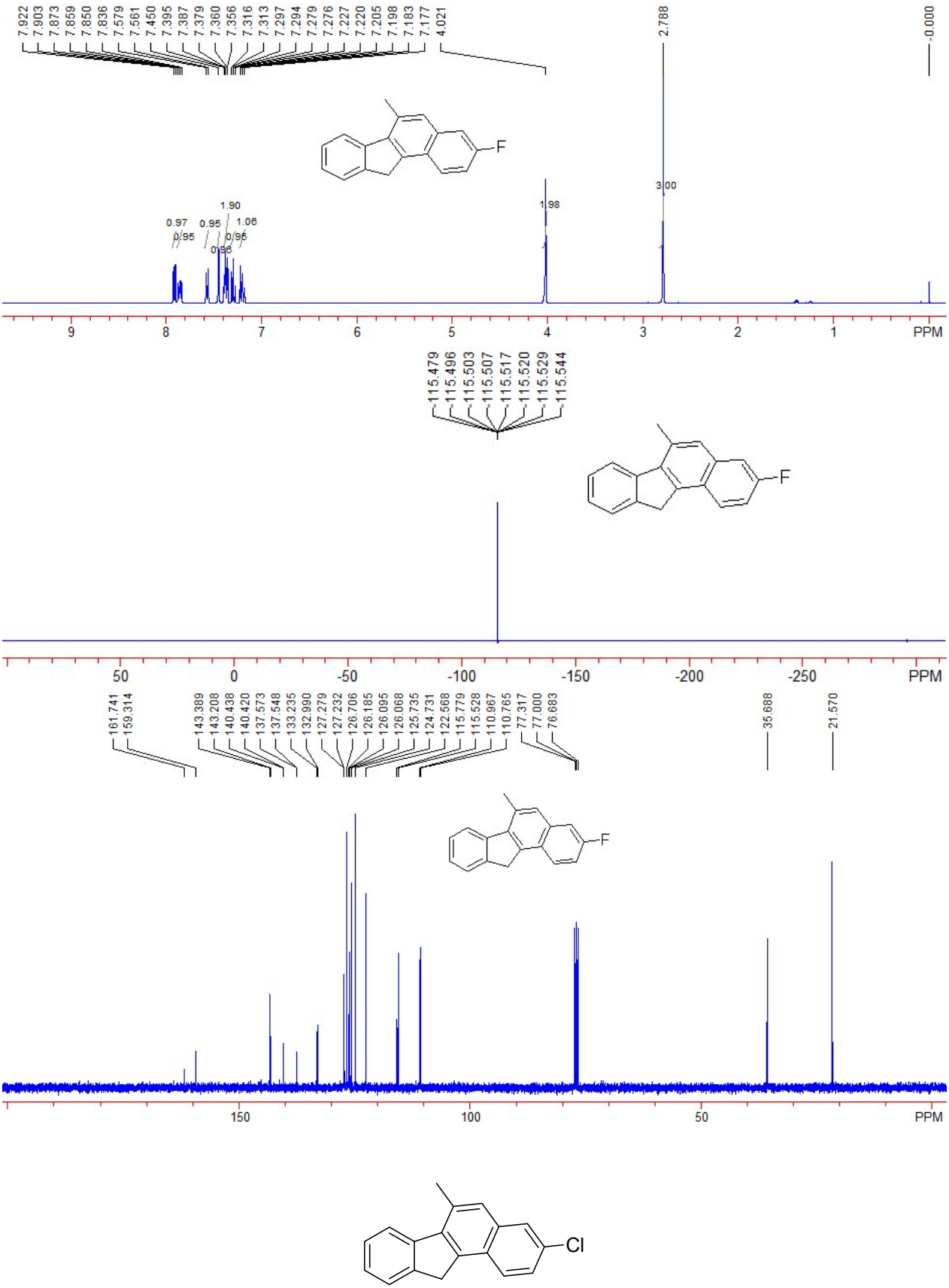


Compound **2f**. 53 mg, yield: 93%; white solid. MP: 141-143 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.42 (s, 9H, $3CH_3$), 2.81 (s, 3H, CH_3), 4.05 (s, 2H, CH_2), 7.28 (t, J = 7.2 Hz, 1H, Ar), 7.37 (t, J = 7.2 Hz, 1H, Ar), 7.52-7.54 (m, 2H, Ar), 7.57 (d, J = 7.6 Hz, 1H, Ar), 7.74 (d, J = 2.0 Hz, 1H, Ar), 7.85 (d, J = 8.8 Hz, 1H, Ar), 7.94 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 31.3, 34.8, 35.6, 122.5, 122.9, 123.6, 124.3, 124.7, 125.5, 126.6, 127.2, 128.0, 131.6, 132.6, 137.6, 140.1, 143.6, 143.7, 148.1. IR (neat) ν 2949, 2863, 1594, 1455, 1393, 1259, 1183 cm^{-1}. MS (%) m/e 286 (M^+, 66.92), 271 (100.00), 228 (9.98), 215 (16.67), 114 (41.27), 101 (10.08), 75 (0.67). HRMS (EI) calcd. for $C_{22}H_{22}$: 286.1722, found: 286.1729.



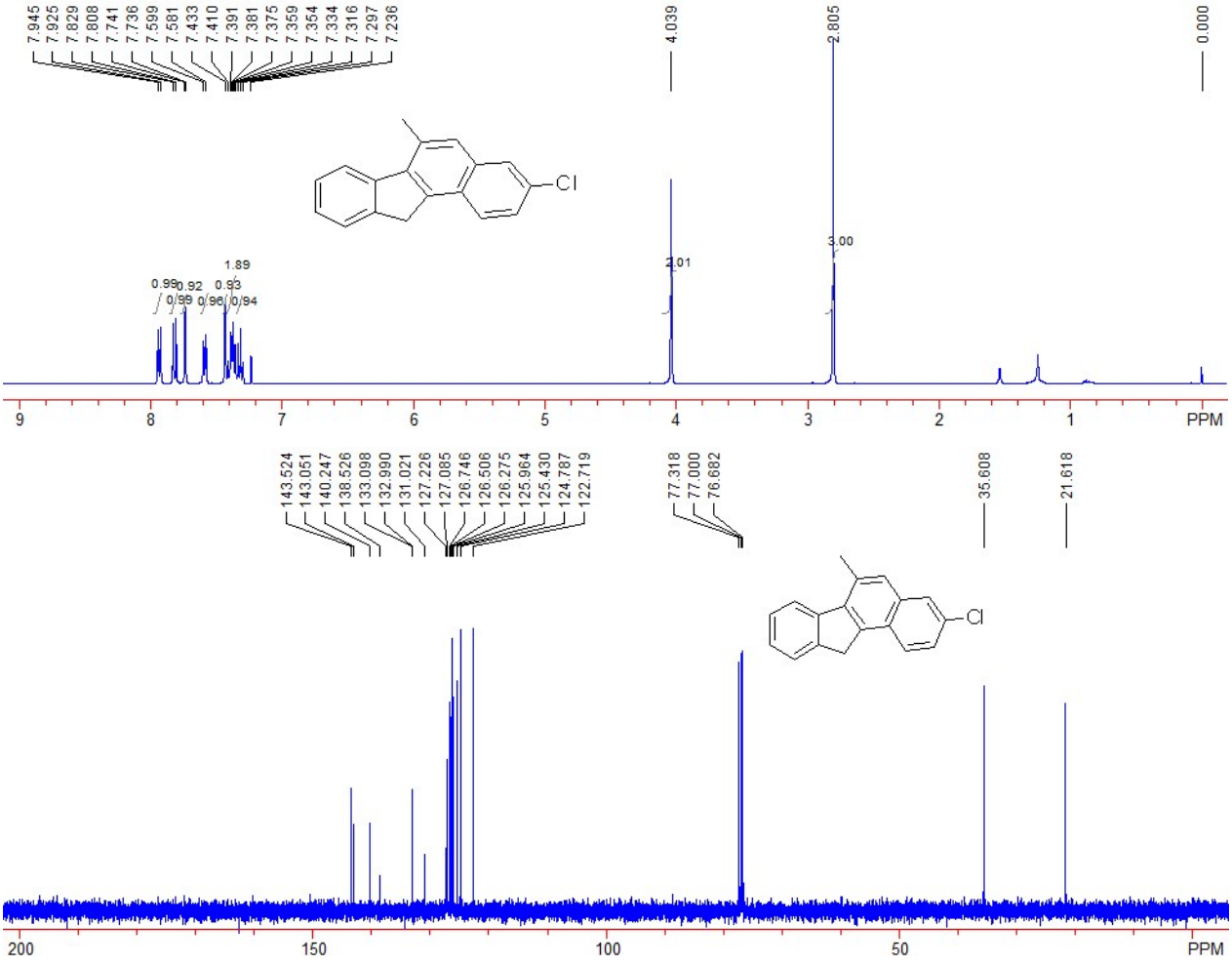
Compound **2g**. 38 mg, yield: 76%; white solid. MP: 110-112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.79 (s, 3H, CH_3), 4.02 (s, 2H, CH_2), 7.17-7.23 (m, 1H, Ar), 7.28-7.32 (m, 1H, Ar), 7.36 (d, J = 1.6 Hz, 1H, Ar), 7.38-7.40 (m, 2H, Ar), 7.45 (s, 1H, Ar), 7.57 (d, J = 7.2 Hz, 1H, Ar), 7.85 (dd, J_1 = 9.2 Hz, J_2 = 5.6 Hz, 1H, Ar), 7.91 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.7, 110.9 (d, $J_{C\text{-}F}$ = 20.2 Hz), 115.6 (d, $J_{C\text{-}F}$ = 25.1 Hz), 122.6, 124.7, 125.7, 126.0, 126.1, 126.2, 126.7, 127.2, 127.3, 133.0, 133.2, 137.5 (d, $J_{C\text{-}F}$ = 2.5 Hz), 140.4 (d, $J_{C\text{-}F}$ = 1.8 Hz), 143.3 (d, $J_{C\text{-}F}$ = 18.1 Hz), 160.5 (d, $J_{C\text{-}F}$ = 242.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -115.48 ~ -115.54 (m, 1F). IR (neat) ν 2922, 1633, 1520, 1459, 1359, 1226, 1141 cm^{-1}. MS (%) m/e 248 (M^+, 100.00), 233 (93.08), 207 (13.40), 122 (12.77), 97 (9.39), 75 (5.24). HRMS (EI)

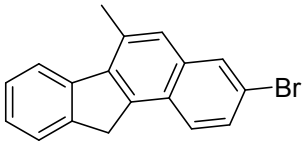
calcd. for $C_{18}H_{13}F$: 248.1001, found: 248.0998.



Compound **2h**. 38 mg, yield: 72%; white solid. MP: 129-131 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.81 (s, 3H, CH_3), 4.04 (s, 2H, CH_2), 7.32 (t, J = 7.6 Hz, 1H, Ar), 7.35-7.41 (m, 2H, Ar),

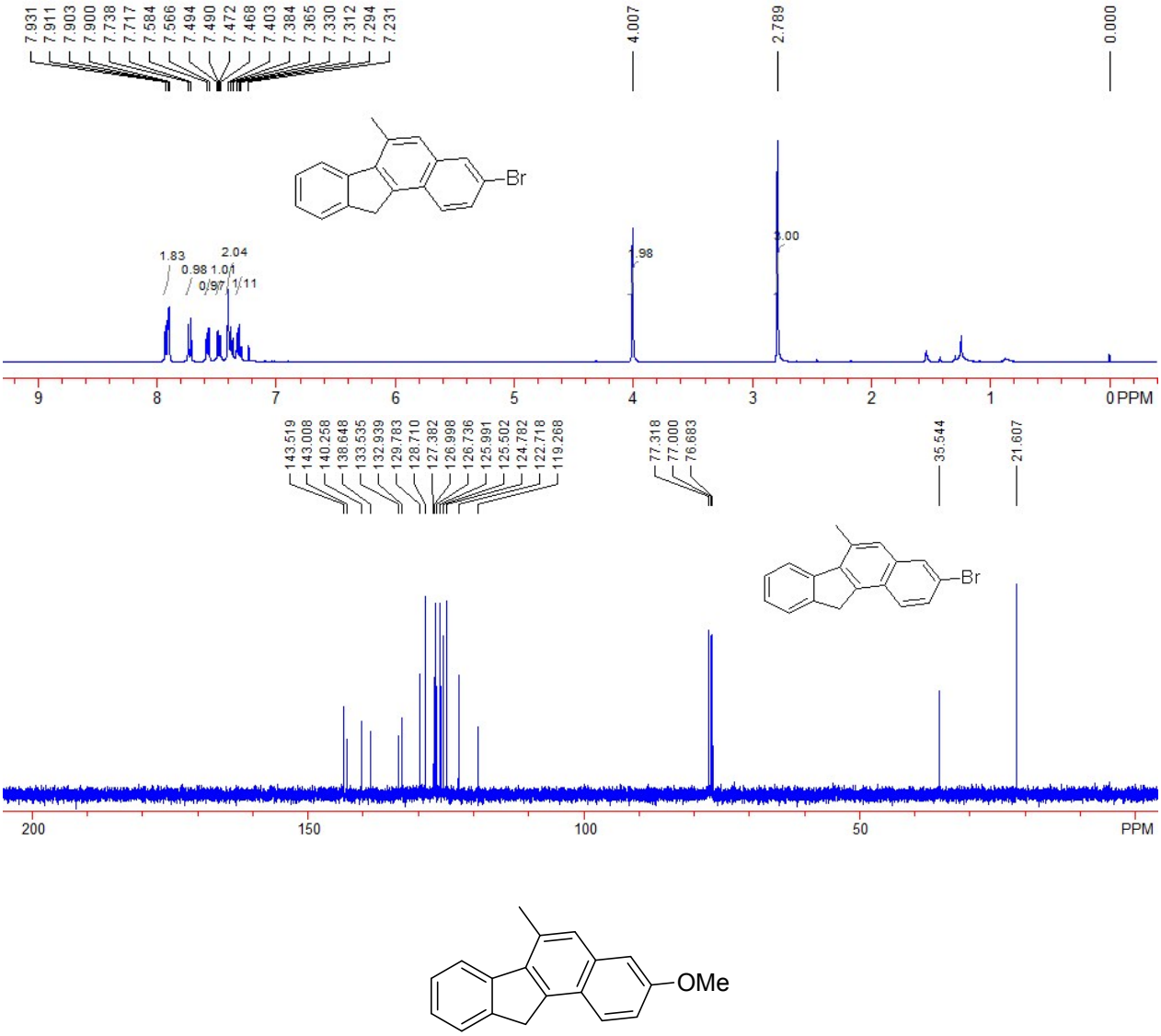
7.43 (s, 1H, Ar), 7.59 (d, J = 7.6 Hz, 2H, Ar), 7.74 (d, J = 2.0 Hz, 1H, Ar), 7.82 (d, J = 8.0 Hz, 1H, Ar), 7.94 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.6, 122.7, 124.8, 125.4, 126.0, 126.3, 126.5, 126.7, 127.1, 127.2, 131.0, 133.0, 133.1, 138.5, 140.2, 143.1, 143.5. IR (neat) ν 2920, 1950, 1586, 1490, 1372, 1174, 1091 cm^{-1}. MS (%) m/e 264 (80.40), 229 (M^+, 100.00), 202 (7.39), 132 (9.74), 115 (10.73), 75 (7.65). HRMS (EI) calcd. for $C_{18}H_{13}Cl$: 264.0706, found: 264.0707.



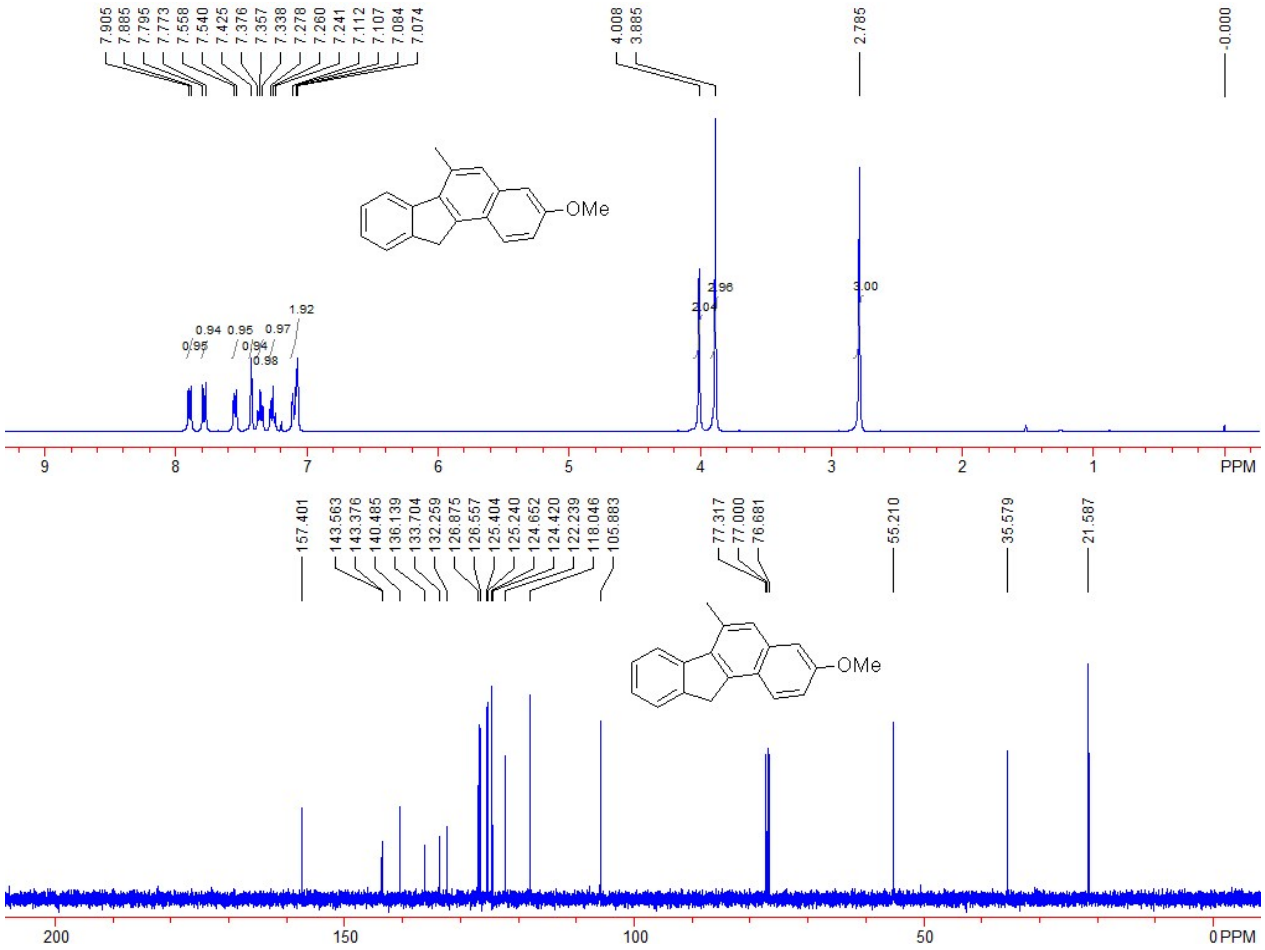


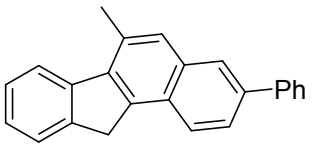
Compound **2i**. 40 mg, yield: 65%; white solid. MP: 148-150 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.79 (s, 3H, CH_3), 4.01 (s, 2H, CH_2), 7.29 (t, J = 7.2 Hz, 1H, Ar), 7.37-7.40 (m, 2H, Ar), 7.48 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H, Ar), 7.58 (d, J = 7.2 Hz, 1H, Ar), 7.73 (d, J = 8.8 Hz, 1H, Ar), 7.90-7.93 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.5, 119.3, 122.7, 124.8, 125.5, 126.0, 126.7, 127.0, 127.4, 128.7, 129.8, 132.9, 133.5, 138.6, 140.3, 143.0, 143.5. IR (neat)

ν 2921, 1606, 1574, 1457, 1394, 1186, 1063 cm^{-1}. MS (%) m/e 308 (45.25), 229 (M^+, 100.00), 202 (8.50), 155 (2.44), 115 (5.43), 75 (6.04). HRMS (EI) calcd. for $C_{18}H_{13}Br$: 308.0201, found: 308.0204.

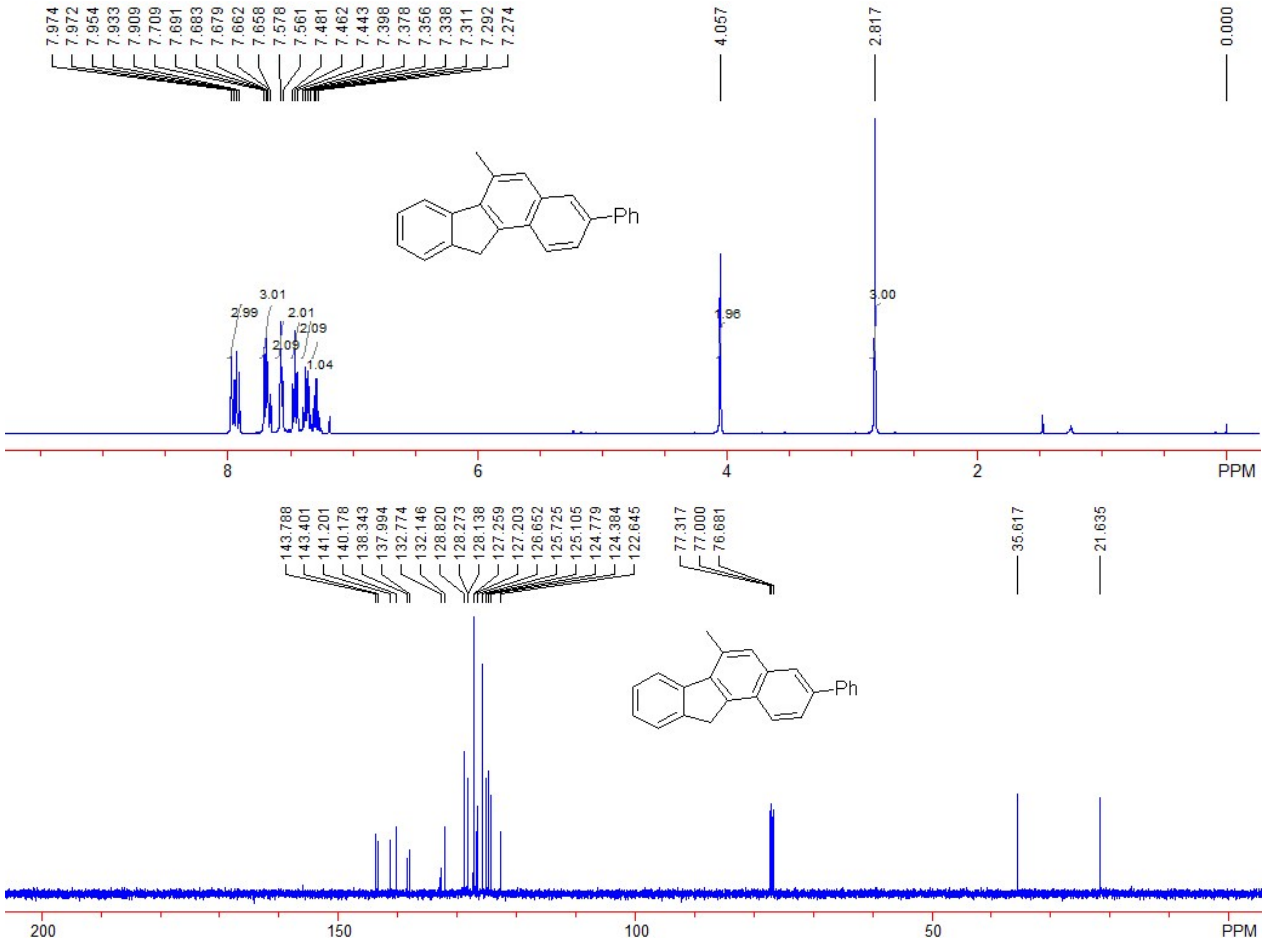


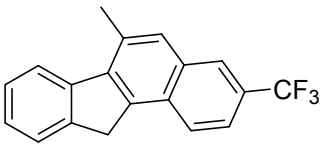
Compound **2j**. 49 mg, yield: 92%; white solid. MP: 148-150 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.79 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 4.01 (s, 2H, CH_2), 7.07-7.11 (m, 2H, Ar), 7.24-7.28 (m, 1H, Ar), 7.36 (t, *J* = 8.0 Hz, 1H, Ar), 7.43 (s, 1H, Ar), 7.55 (d, *J* = 8.0 Hz, 1H, Ar), 7.78 (d, *J* = 8.0 Hz, 1H, Ar), 7.89 (d, *J* = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.6, 55.2, 105.9, 118.0, 122.2, 124.4, 124.7, 125.2, 125.4, 126.6, 126.9, 132.3, 133.7, 136.1, 140.5, 143.4, 143.6, 157.4. IR (neat) ν 2959, 1624, 1577, 1472, 1363, 1234, 1186 cm^{-1}. MS (%) m/e 260 (M^+, 100.00), 229 (4.89), 202 (36.42), 130 (17.20), 115 (2.70), 75 (4.31). HRMS (EI) calcd. for $C_{19}H_{16}O$: 260.1201, found: 260.1208.



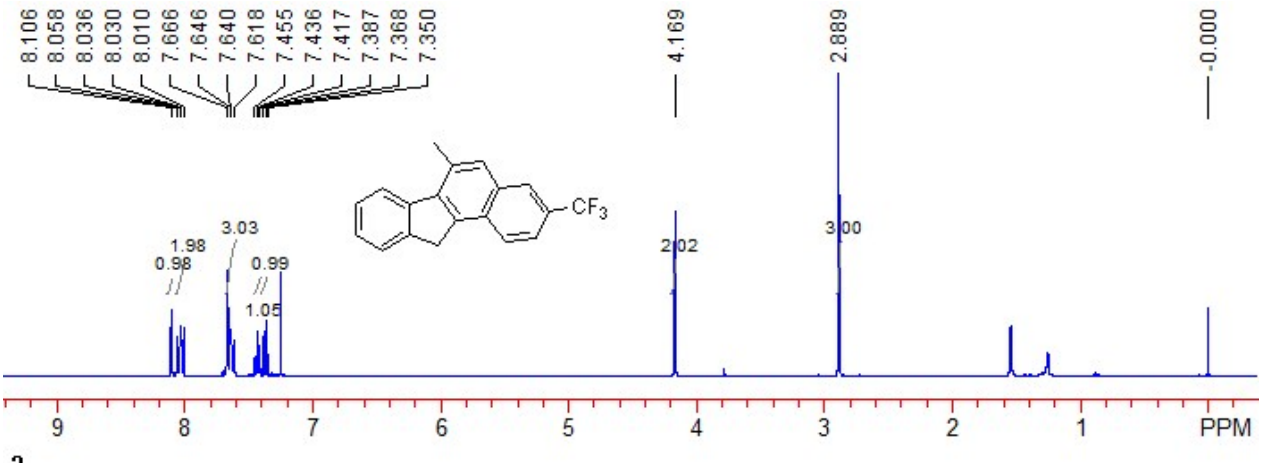


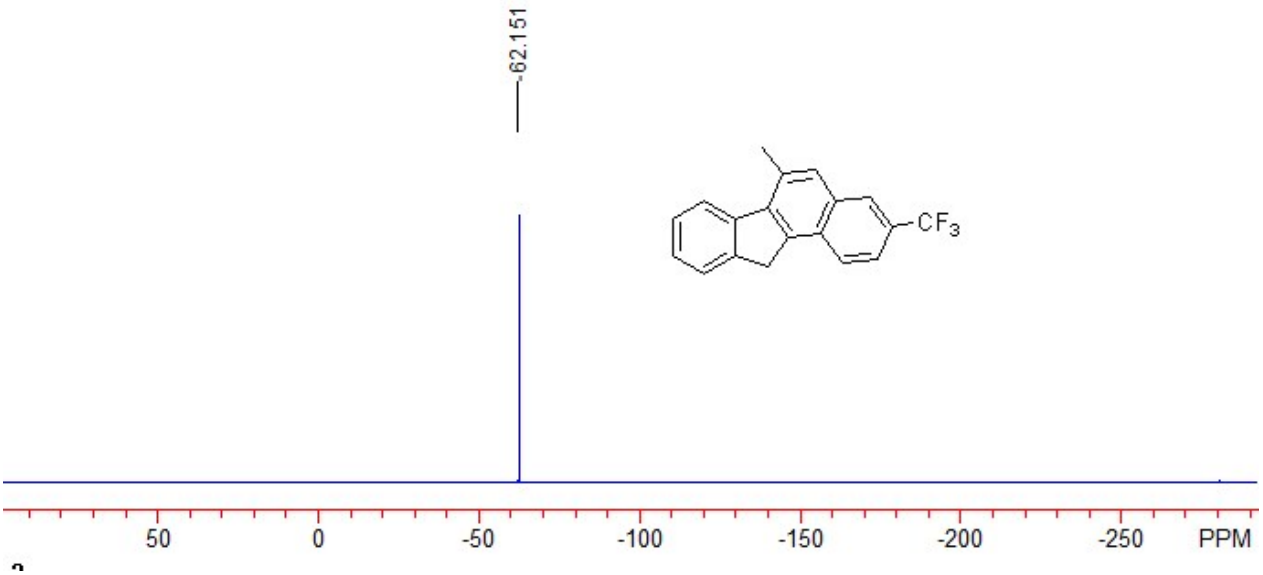
Compound **2k**. 42 mg, yield: 68%; white solid. MP: 172-174 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.82 (s, 3H, CH_3), 4.06 (s, 2H, CH_2), 7.29 (t, J = 7.6 Hz, 1H, Ar), 7.34-7.40 (m, 2H, Ar), 7.46 (t, J = 7.6 Hz, 2H, Ar), 7.56-7.58 (m, 2H, Ar), 7.66-7.71 (m, 3H, Ar), 7.91-7.97 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 35.6, 122.6, 124.4, 124.8, 125.1, 125.7, 126.7, 127.2, 127.3, 128.1, 128.3, 128.8, 132.1, 132.8, 138.0, 138.3, 140.2, 141.2, 143.4, 143.8. IR (neat) ν 2920, 1592, 1458, 1392, 1257, 1188, 1034 cm^{-1}. MS (%) m/e 306 (M^+, 100.00), 229 (10.45), 202 (3.08), 152 (4.33), 115 (3.19), 91 (5.38). HRMS (EI) calcd.for $C_{24}H_{18}$: 306.1409, found: 306.1398.

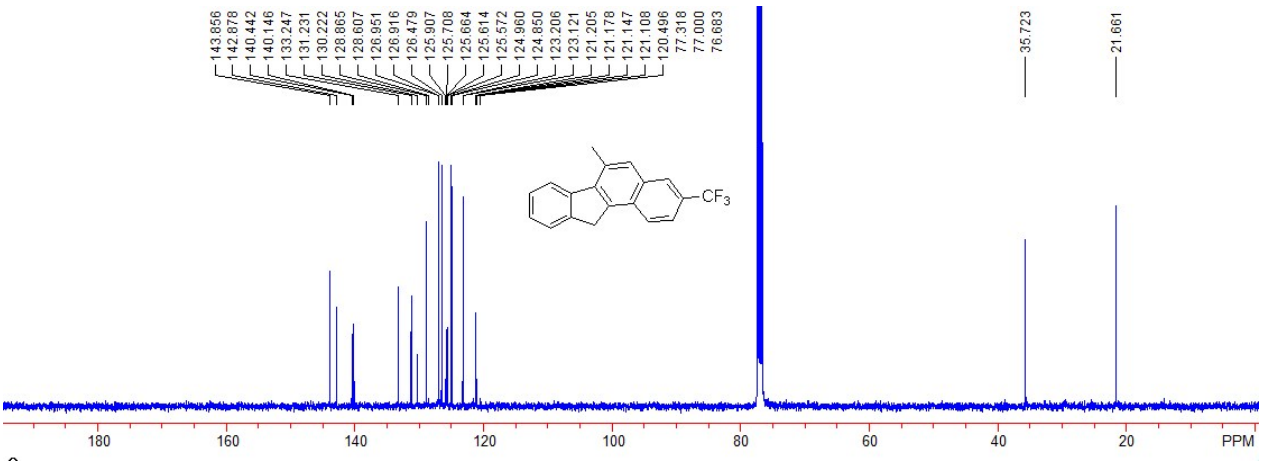


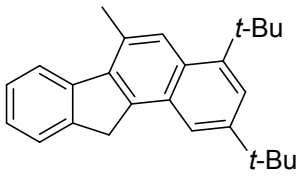


Compound **2l**. 12 mg, yield: 20%; white solid. MP: 156-158 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.89 (s, 3H, CH_3), 4.17 (s, 2H, CH_2), 7.37 (t, J = 7.6 Hz, 1H, Ar), 7.44 (t, J = 7.6 Hz, 1H, Ar), 7.62-7.67 (m, 3H, Ar), 8.01-8.06 (m, 2H, Ar), 8.11 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 35.7, 121.1 (q, $J_{C\text{-}F}$ = 3.1 Hz), 123.1, 124.5 (q, $J_{C\text{-}F}$ = 270.1 Hz), 124.9, 125.0, 125.6 (q, $J_{C\text{-}F}$ = 5.0 Hz), 126.5, 126.9, 127.1 (q, $J_{C\text{-}F}$ = 31.9 Hz), 128.9, 130.2, 131.2, 133.2, 140.1, 140.4, 142.9, 143.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -62.15 (s, 3F). IR (neat) ν 2921, 1634, 1455, 1352, 1216, 1189, 1067 cm^{-1}. MS (%) m/e 298 (M^+, 100.00), 229 (34.78), 202 (4.68), 149 (5.57), 114 (18.17), 91 (1.06). HRMS (EI) calcd.for $C_{19}H_{13}F_3$: 298.0969, found: 298.0972.



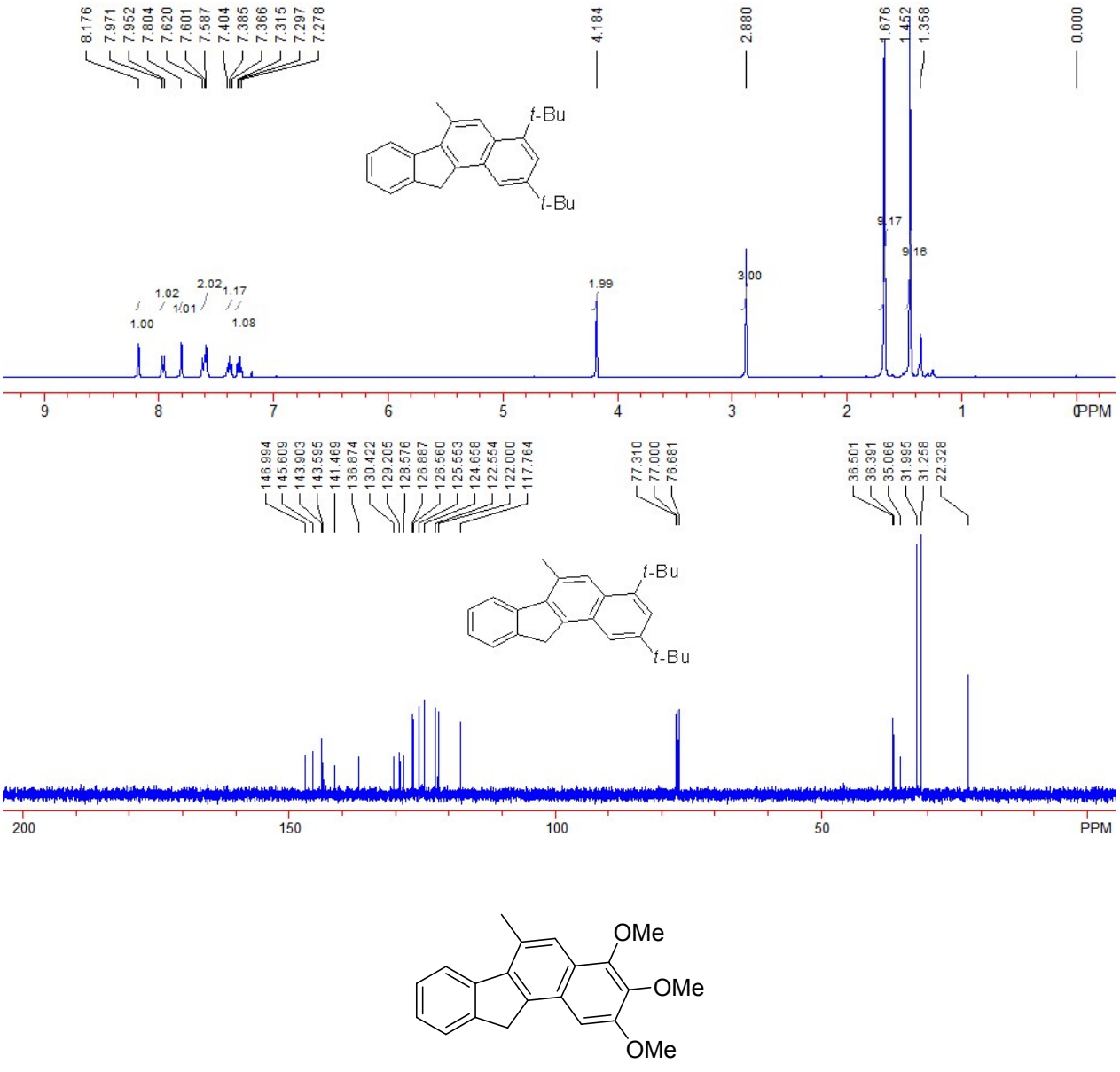






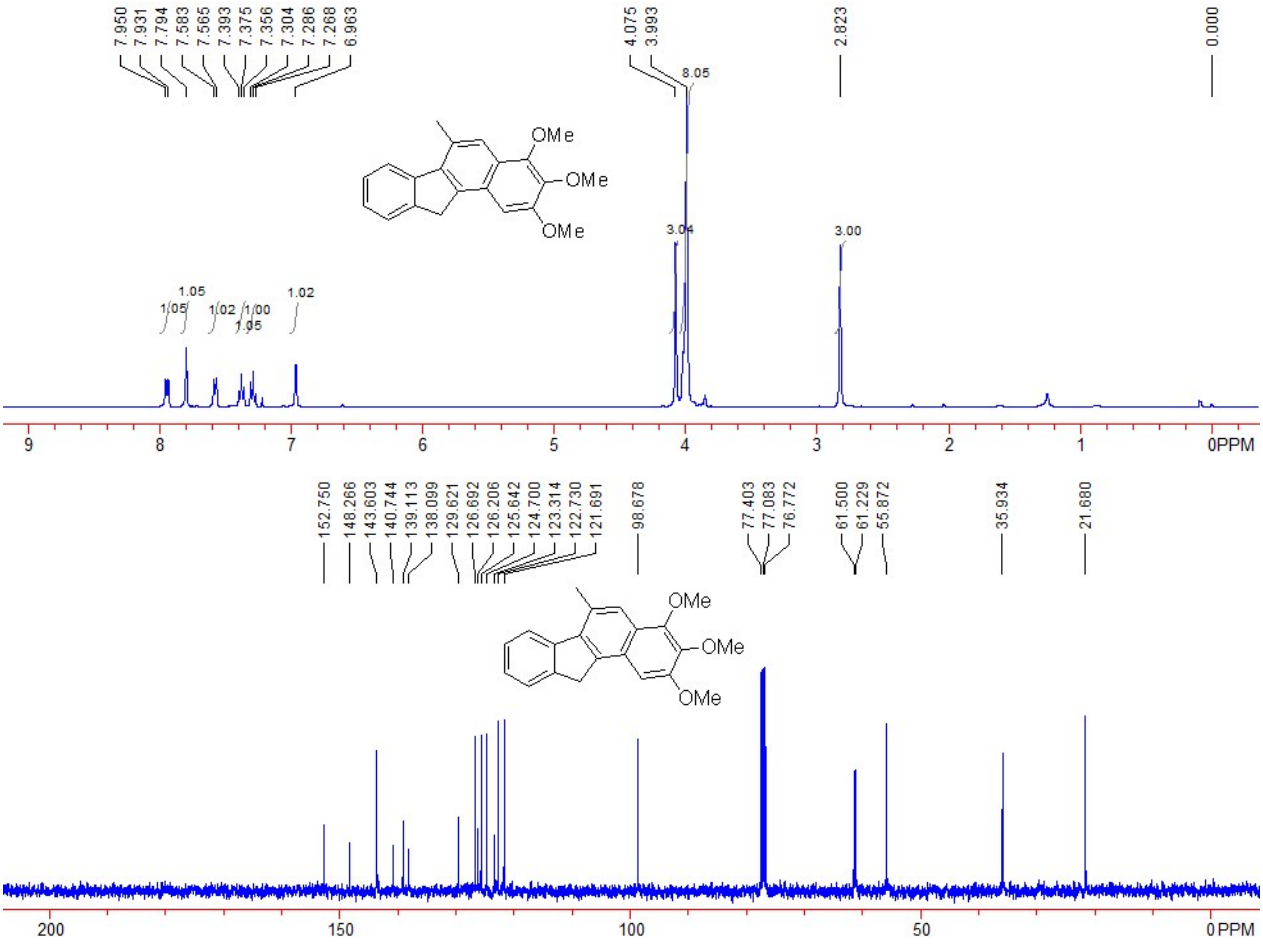
Compound **2n**. 41 mg, yield: 60%; white solid. MP: 183-185 °C. ^{1}H NMR ($CDCl_3$, 400 MHz,

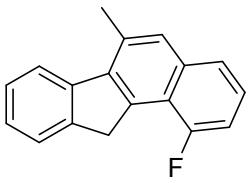
TMS) δ 1.45 (s, 9H, $3CH_3$), 1.68 (s, 9H, $3CH_3$), 2.88 (s, 3H, CH_3), 4.18 (s, 2H, CH_2), 7.30 (t, J = 7.6 Hz, 1H, Ar), 7.38 (t, J = 7.6 Hz, 1H, Ar), 7.59-7.62 (m, 2H, Ar), 7.80 (s, 1H, Ar), 7.96 (d, J = 7.6 Hz, 1H, Ar), 8.18 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 22.3, 31.3, 32.0, 35.1, 36.4, 36.5, 117.8, 122.0, 122.6, 124.7, 125.6, 126.6, 126.9, 128.6, 129.2, 130.4, 136.9, 141.5, 143.6, 143.9, 145.6, 147.0. IR (neat) ν 2952, 2867, 1621, 1457, 1362, 1266, 1155 cm^{-1}. MS (%) m/e 342 (60.13), 229 (6.51), 202 (1.34), 142 (8.13), 115 (1.98), 57 (M^+, 100.00). HRMS (EI) calcd.for $C_{26}H_{30}$: 342.2348, found: 342.2352.



Compound **2o**. 48 mg, yield: 75%; white solid. MP: 110-113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.82 (s, 3H, CH_3), 3.99 (brs, 8H, CH_2, $2CH_3$), 4.08 (s, 3H, CH_3), 6.96 (s, 1H, Ar), 7.29 (t, J = 7.2 Hz, 1H, Ar), 7.38 (t, J = 7.2 Hz, 1H, Ar), 7.57 (d, J = 7.2 Hz, 1H, Ar), 7.79 (s, 1H, Ar), 7.94 (d, J = 7.2 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 35.9, 55.9, 61.2, 61.5,

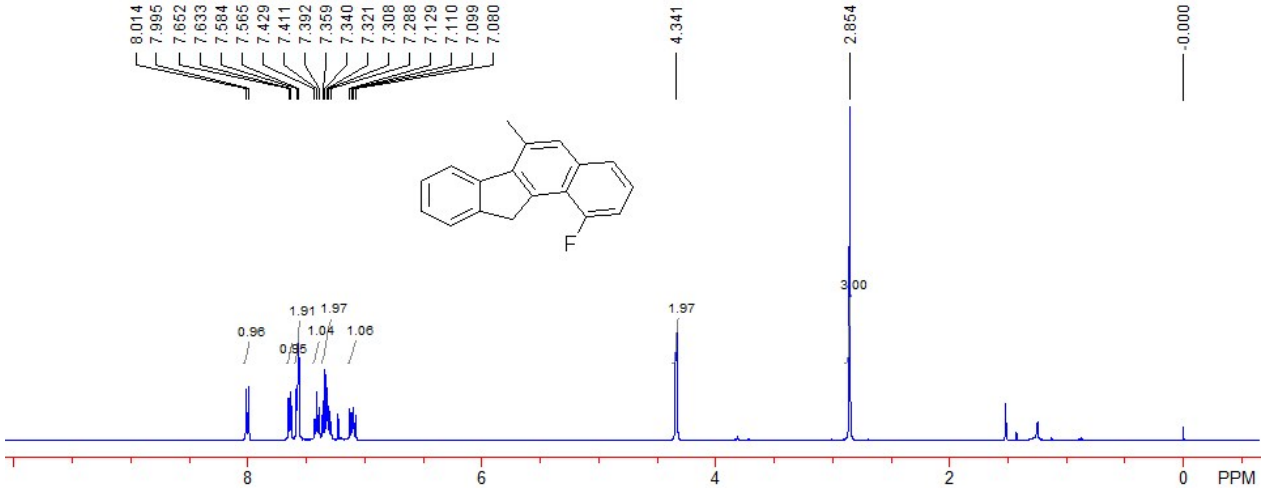
98.7, 121.7, 122.7, 123.3, 124.7, 125.6, 126.2, 126.7, 129.6, 138.1, 139.1, 140.7, 143.6, 148.3, 152.8. IR (neat) ν 2934, 2822, 1622, 1599, 1467, 1371, 1240 cm^{-1}. MS (%) m/e 320 (M^+, 100.00), 229 (1.64), 202 (7.51), 152 (0.95), 115 (4.18), 95 (21.96). HRMS (EI) calcd.for $C_{21}H_{20}O_3$: 320.1412, found: 320.1423.

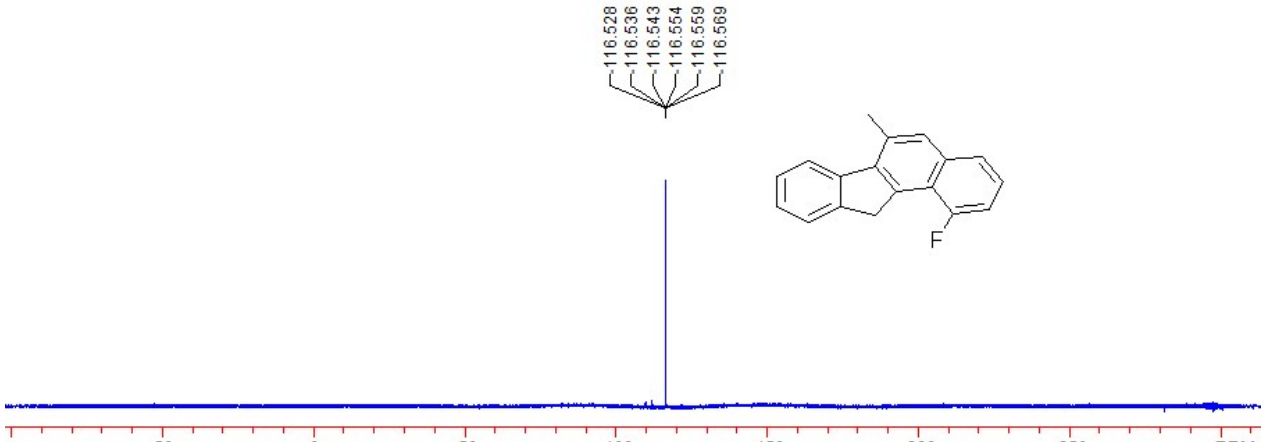


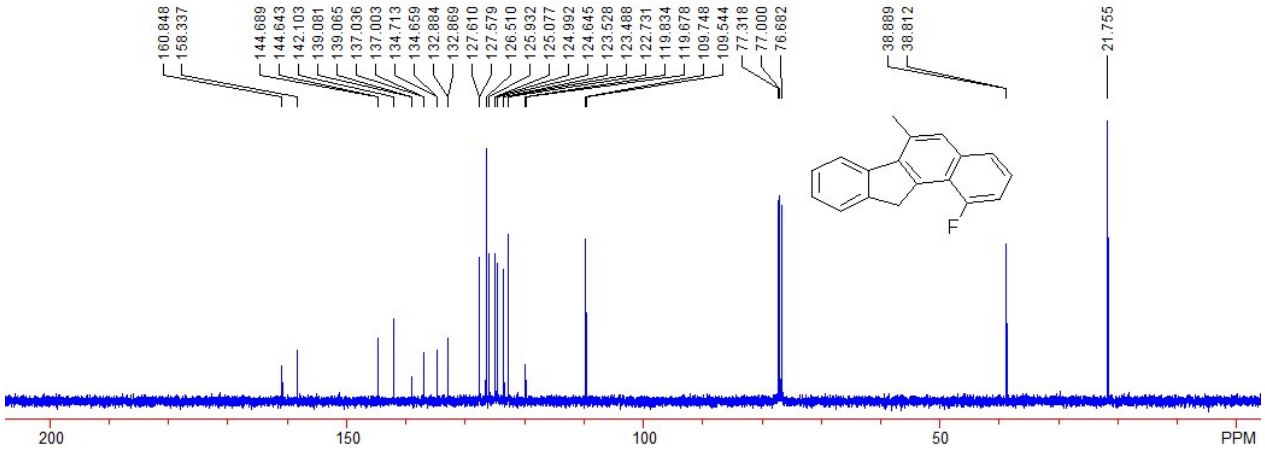


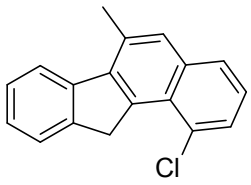
Compound **2p**. 15 mg, yield: 29%; white solid. MP: 116-119 ^oC.^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.85 (s, 3H, CH_3), 4.34 (s, 2H, CH_2), 7.08-7.13 (m, 1H, Ar), 7.29-7.36 (m, 2H, Ar), 7.41 (t, J = 7.6 Hz, 1H, Ar), 7.57-7.58 (m, 2H, Ar), 7.64 (d, J = 7.6 Hz, 1H, Ar), 8.01 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 38.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 109.6 (d, $J_{C\text{-}F}$ = 20.4 Hz), 119.8 (d, $J_{C\text{-}F}$ = 15.6 Hz), 122.7, 123.5 (d, $J_{C\text{-}F}$ = 4.0 Hz), 124.6, 125.0 (d, $J_{C\text{-}F}$ = 8.5 Hz), 125.9, 126.5, 127.6 (d, $J_{C\text{-}F}$ = 3.1 Hz), 132.8 (d, $J_{C\text{-}F}$ = 1.5 Hz), 134.7 (d, $J_{C\text{-}F}$ = 5.4 Hz), 137.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 139.0 (d, $J_{C\text{-}F}$ = 1.6 Hz), 142.1, 144.6 (d, $J_{C\text{-}F}$ = 4.6 Hz), 140.4 (d, $J_{C\text{-}F}$ = 1.8 Hz),

143.3 (d, $J_{C\text{-}F}$ = 18.1 Hz), 159.6 (d, $J_{C\text{-}F}$ = 251.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -116.53 ~ -116.57 (m, 1F). IR (neat) ν 2943, 1632, 1567, 1439, 1348, 1235, 1186 cm^{-1}. MS (%) m/e 248 (97.22), 233 (M^+, 100.00), 202 (0.74), 152 (0.50), 115 (4.55), 97 (7.28). HRMS (EI) calcd. for $C_{18}H_{13}F$: 248.1001, found: 248.1004.

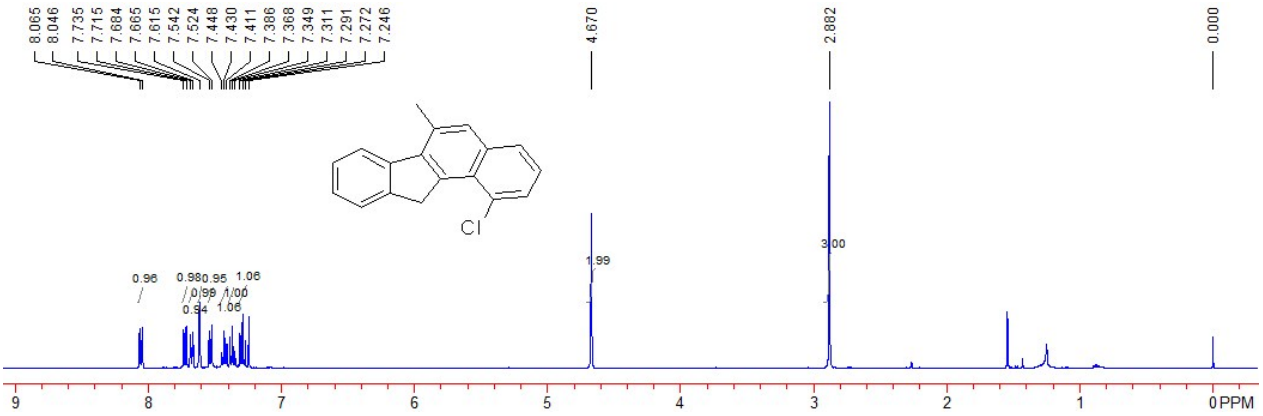


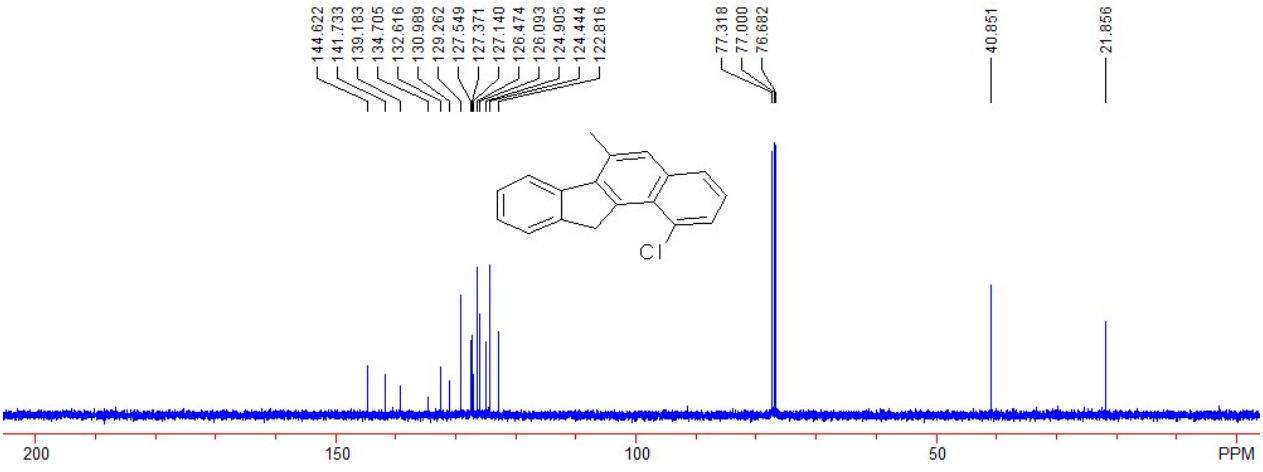


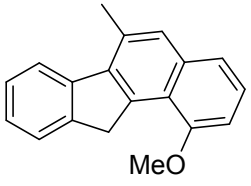




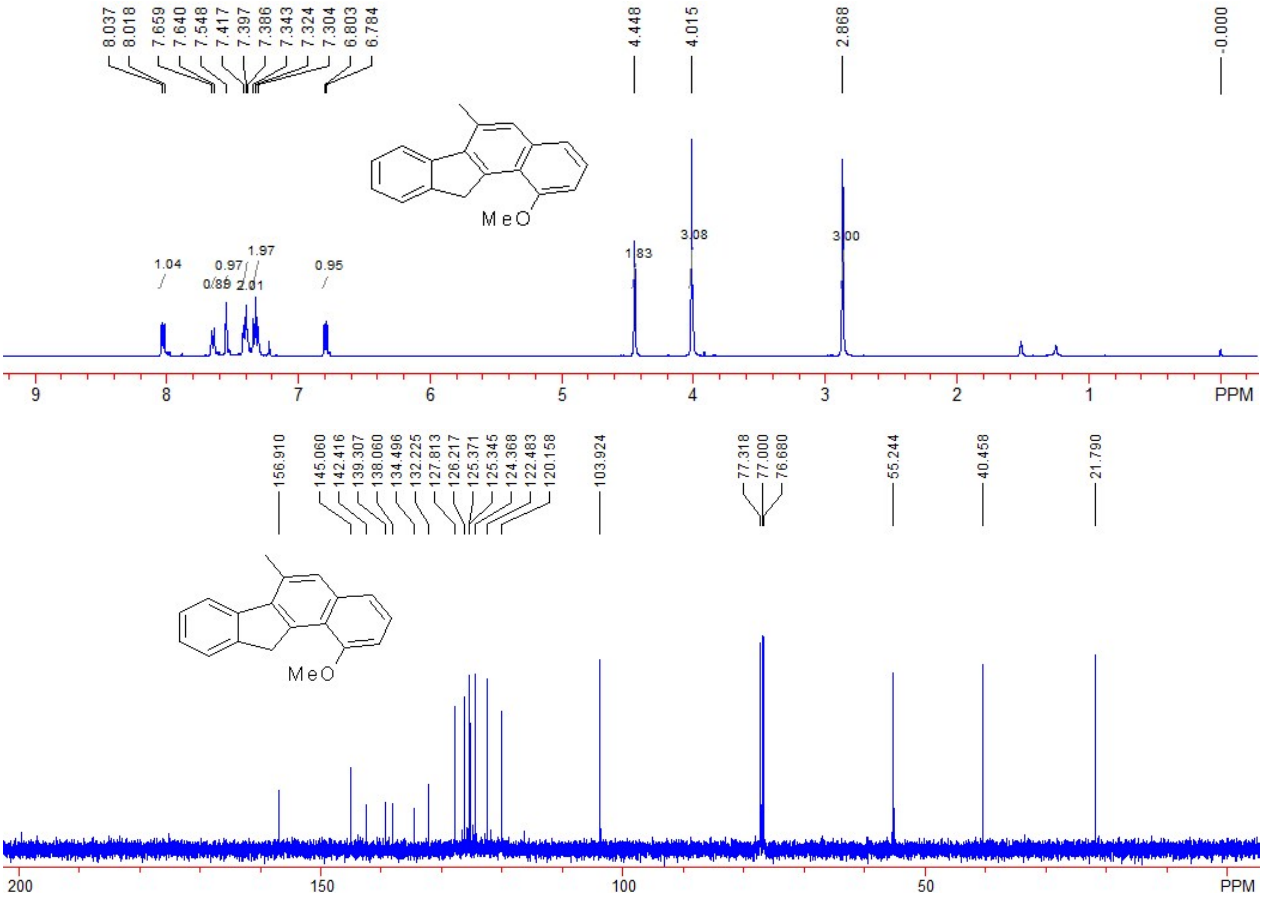
Compound **2q**. 18 mg, yield: 34%; white solid. MP: 125-127 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.88 (s, 3H, CH_3), 4.67 (s, 2H, CH_2), 7.29 (t, *J* = 7.6 Hz, 1H, Ar), 7.37 (t, *J* = 7.6 Hz, 1H, Ar), 7.43 (t, *J* = 7.6 Hz, 1H, Ar), 7.53 (d, *J* = 7.6 Hz, 1H, Ar), 7.62 (s, 1H, Ar), 7.67 (d, *J* = 7.6 Hz, 1H, Ar), 7.73 (d, *J* = 7.6 Hz, 1H, Ar), 8.06 (d, *J* = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.9, 40.9, 122.8, 124.4, 124.9, 126.1, 126.5, 127.1, 127.4, 127.5, 129.3, 131.0, 132.6, 134.7, 139.2, 141.7, 144.6. IR (neat) ν 2919, 2850, 1632, 1552, 1453, 1391, 1156 cm^{-1}. MS (%) m/e 264 (85.01), 229 (M^+, 100.00), 202 (7.37), 133 (7.99), 115 (7.58), 96 (7.57). HRMS (EI) calcd.for $C_{18}H_{13}Cl$: 264.0706, found: 264.0714.

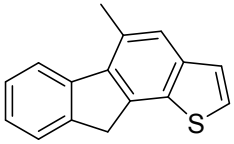






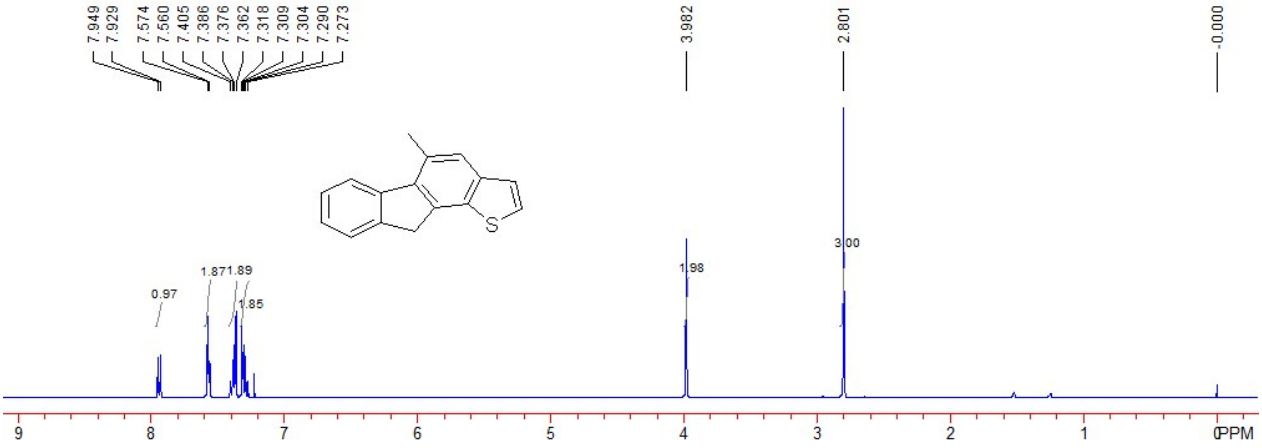
Compound **2r**. 13 mg, yield: 25%; white solid. MP: 110-112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.87 (s, 3H, CH_3), 4.02 (s, 3H, CH_3), 4.45 (s, 2H, CH_2), 6.79 (d, *J* = 7.6 Hz, 1H, Ar), 7.32 (t, *J* = 7.6 Hz, 2H, Ar), 7.39-7.42 (m, 2H, Ar), 7.55 (s, 1H, Ar), 7.65 (d, *J* = 7.6 Hz, 1H, Ar), 8.03 (d, *J* = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 40.5, 55.2, 103.9, 120.2, 122.5, 124.4, 125.3, 125.4, 126.2, 127.8, 132.2, 134.5, 138.1, 139.3, 142.4, 145.1, 156.9. IR (neat) ν 2921, 1644, 1567, 1448, 1362, 1273, 1120 cm^{-1}. MS (%) m/e 260 (M^+, 100.00), 245 (67.69), 202 (18.75), 130 (15.33), 115 (3.18), 95 (11.72). HRMS (EI) calcd. for $C_{19}H_{16}O$: 260.1201, found: 260.1203.

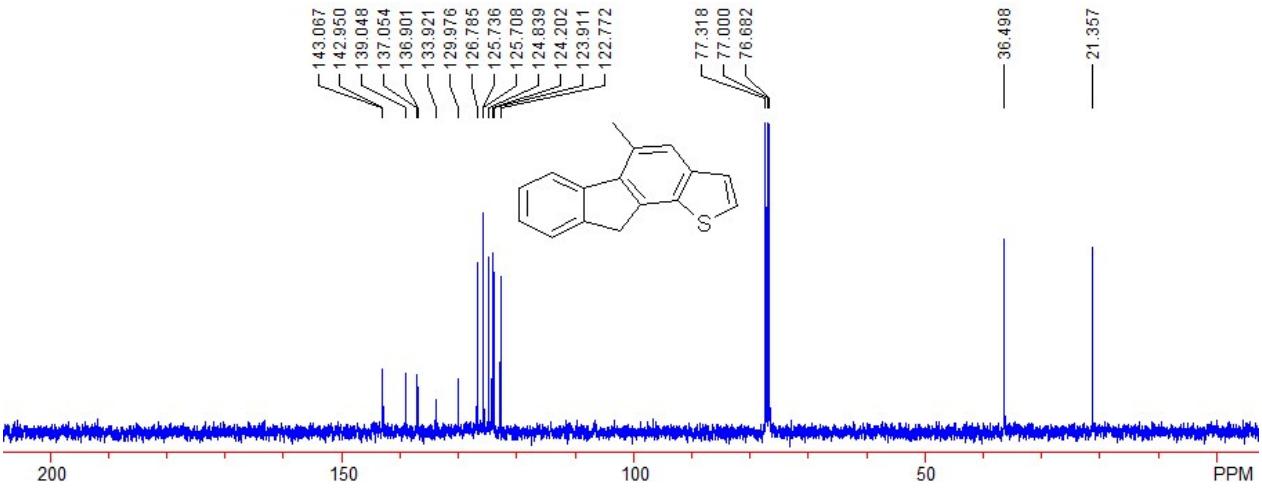


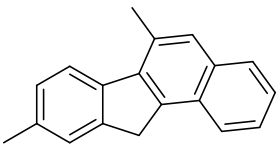


Compound **2s**. 35 mg, yield: 74%; white solid. MP: 126-129 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.80 (s, 3H, CH_3), 3.98 (s, 2H, CH_2), 7.27-7.32 (m, 2H, Ar), 7.36-7.41 (m, 2H, Ar), 7.56-7.57 (m, 2H, Ar), 7.94 (d, *J* = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 36.5, 122.8, 123.9, 124.2, 124.8, 125.7, 125.8, 126.8, 130.0, 133.9, 136.9, 137.1, 139.0, 143.0, 143.1.

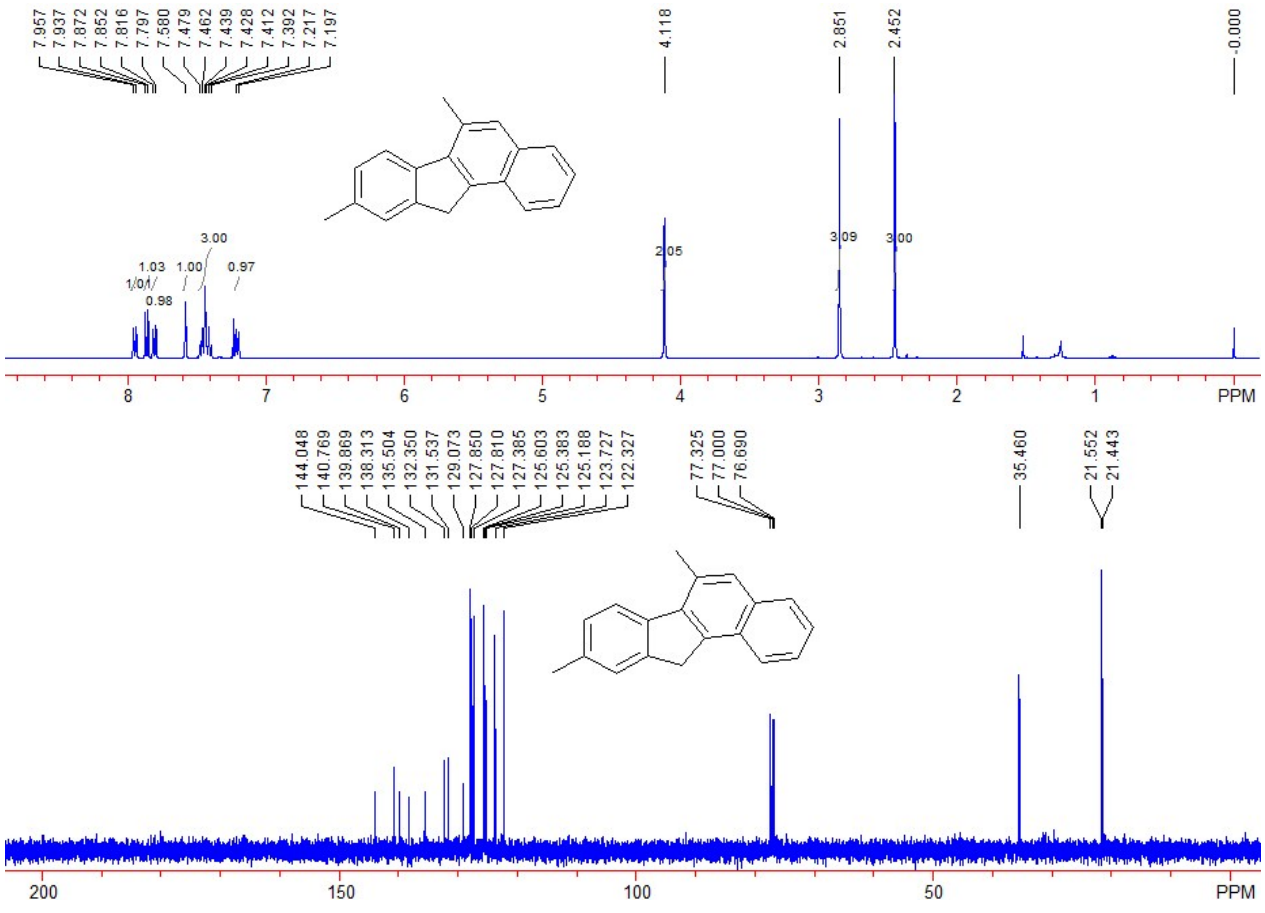
IR (neat) ν 3093, 2969, 1603, 1453, 1394, 1247, 1174 cm^{-1}. MS (%) m/e 236 (M^+, 100.00), 221 (89.55), 202 (7.79), 152 (2.30), 115 (3.46), 91 (5.15). HRMS (EI) calcd. for $C_{16}H_{12}S$: 236.0660, found: 236.0665.

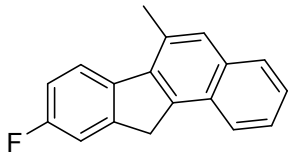




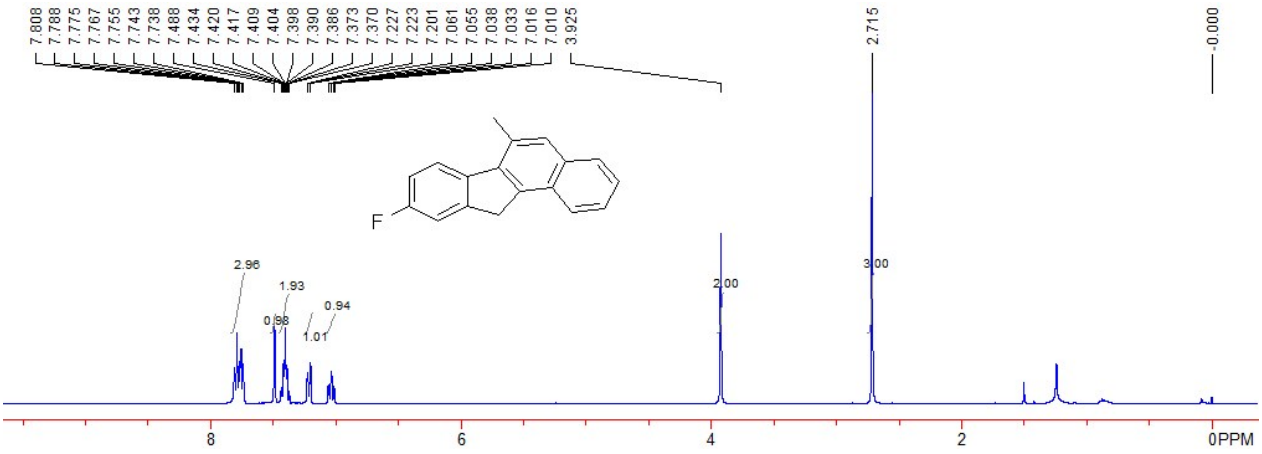


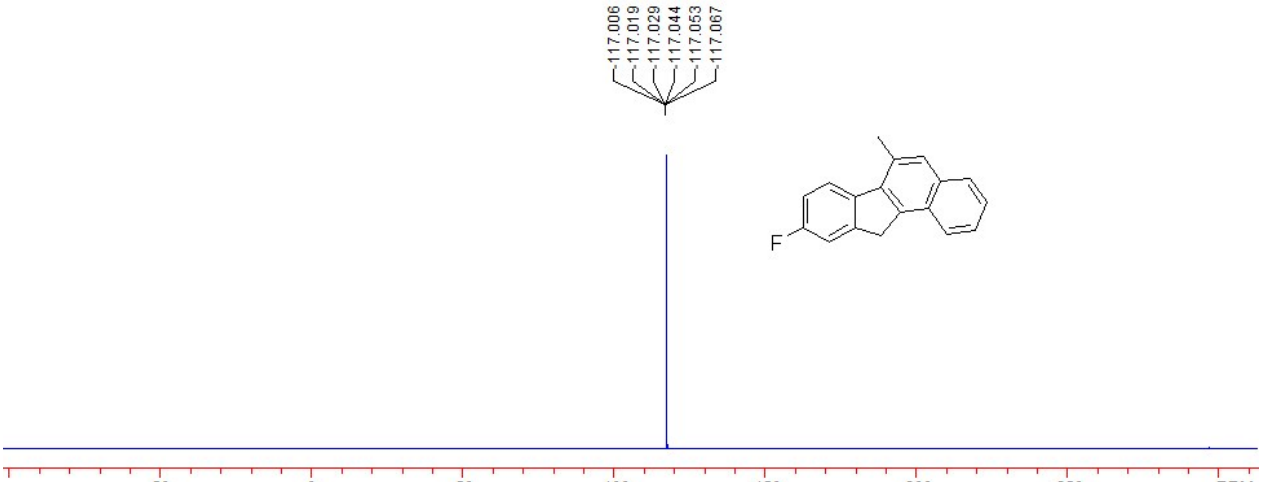
Compound **2aa**. 40 mg, yield: 82%; white solid. MP: 172-175 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H, CH_3), 2.85 (s, 3H, CH_3), 4.12 (s, 2H, CH_2), 7.21 (d, J = 8.0 Hz, 1H, Ar), 7.39-7.48 (m, 3H, Ar), 7.58 (s, 1H, Ar), 7.81 (d, J = 8.0 Hz, 1H, Ar), 7.86 (d, J = 8.0 Hz, 1H, Ar), 7.95 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 21.6, 35.5, 122.3, 123.7, 125.2, 125.4, 125.6, 127.4, 127.8, 127.9, 129.1, 131.5, 132.4, 135.5, 138.3, 139.9, 140.8, 144.0. IR (neat) ν 2919, 1936, 1589, 1473, 1375, 1202, 1137 cm^{-1}. MS (%) m/e 244 (M^+, 100.00), 229 (89.15), 202 (10.37), 122 (14.34), 114 (45.83), 88 (8.81). HRMS (EI) calcd. for $C_{19}H_{16}$: 244.1252, found: 244.1250.

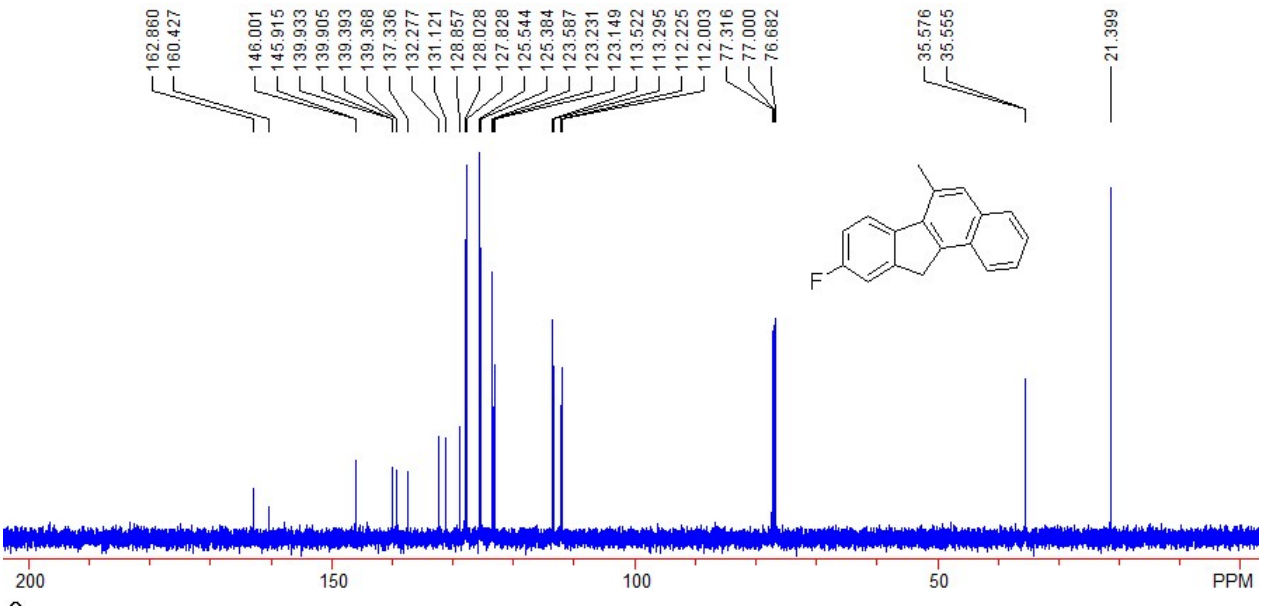


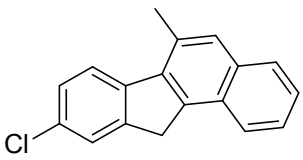


Compound **2bb**. 45 mg, yield: 88%; white solid. MP: 136-138 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.72 (s, 3H, CH_3), 3.93 (s, 2H, CH_2), 7.01-7.06 (m, 1H, Ar), 7.20-7.23 (m, 1H, Ar), 7.37-7.43 (m, 2H, Ar), 7.49 (s, 1H, Ar), 7.74-7.81 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 35.5 (d, $J_{C\text{-}F}$ = 2.1 Hz), 112.1 (d, $J_{C\text{-}F}$ = 22.2 Hz), 113.4 (d, $J_{C\text{-}F}$ = 22.7 Hz), 123.2 (d, $J_{C\text{-}F}$ = 8.2 Hz), 123.6, 125.5 (d, $J_{C\text{-}F}$ = 16.0 Hz), 127.9 (d, $J_{C\text{-}F}$ = 20.0 Hz), 128.9, 131.1, 132.3, 137.3, 139.3 (d, $J_{C\text{-}F}$ = 2.5 Hz), 139.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 146.0 (d, $J_{C\text{-}F}$ = 8.6 Hz), 161.2 (d, $J_{C\text{-}F}$ = 243.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -117.01 ~ -117.07 (m, 1F). IR (neat) ν 2920, 1608, 1495, 1356, 1274, 1180, 1090 cm^{-1}. MS (%) m/e 248 (M^+, 100.00), 233 (88.31), 220 (5.19), 157 (0.46), 115 (4.32), 97 (4.36). HRMS (EI) calcd.for $C_{18}H_{13}F$: 248.1001, found: 248.0995.



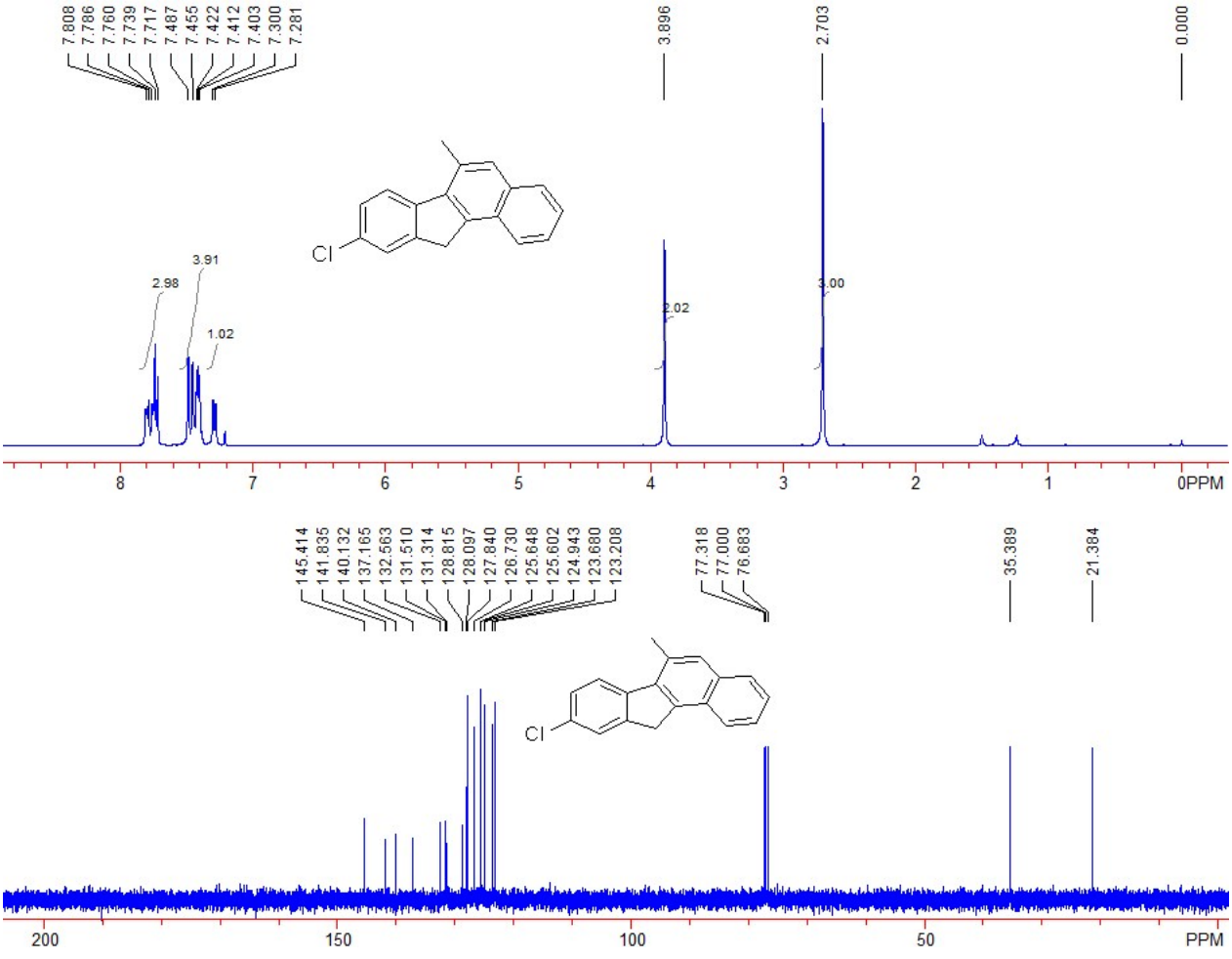


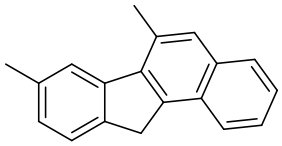




Compound **2cc**. 46 mg, yield: 85%; white solid. MP: 170-173 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz,

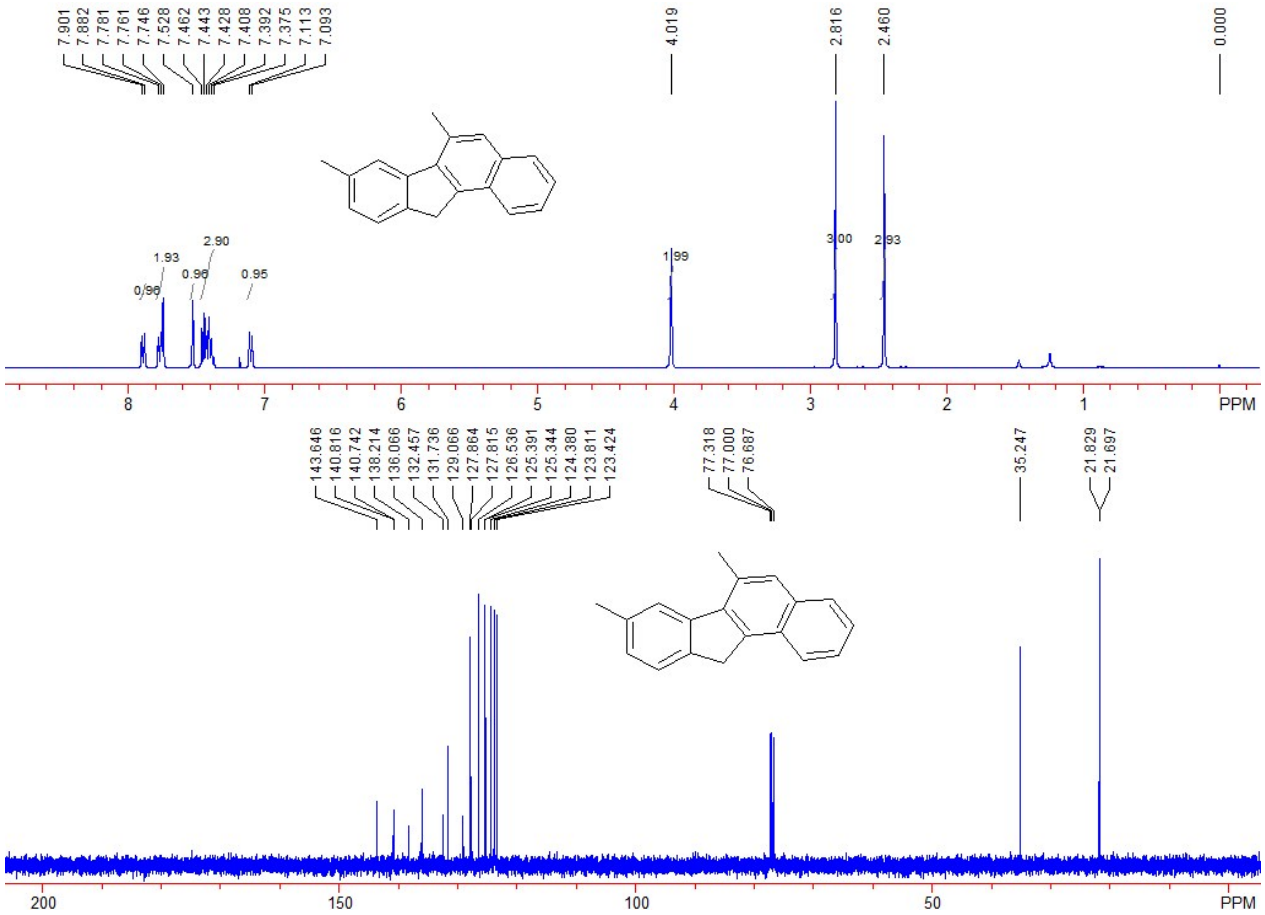
TMS) δ 2.70 (s, 3H, CH_3), 3.90 (s, 2H, CH_2), 7.29 (d, *J* = 7.6 Hz, 1H, Ar), 7.40-7.49 (m, 4H, Ar), 7.72-7.81 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 35.4, 123.2, 123.7, 124.9, 125.6, 125.7, 126.7, 127.8, 128.1, 128.8, 131.3, 131.5, 137.2, 140.1, 141.8, 145.4. IR (neat) ν 2923, 1631, 1569, 1445, 1356, 1270, 1152 cm^{-1}. MS (%) m/e 264 (47.50), 229 (M^+, 100.00), 202 (7.09), 132 (9.70), 115 (9.18), 101 (38.31). HRMS (EI) calcd.for $C_{18}H_{13}Cl$: 264.0706, found: 264.0710.

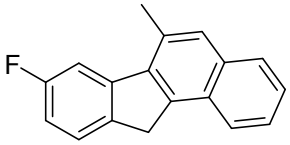




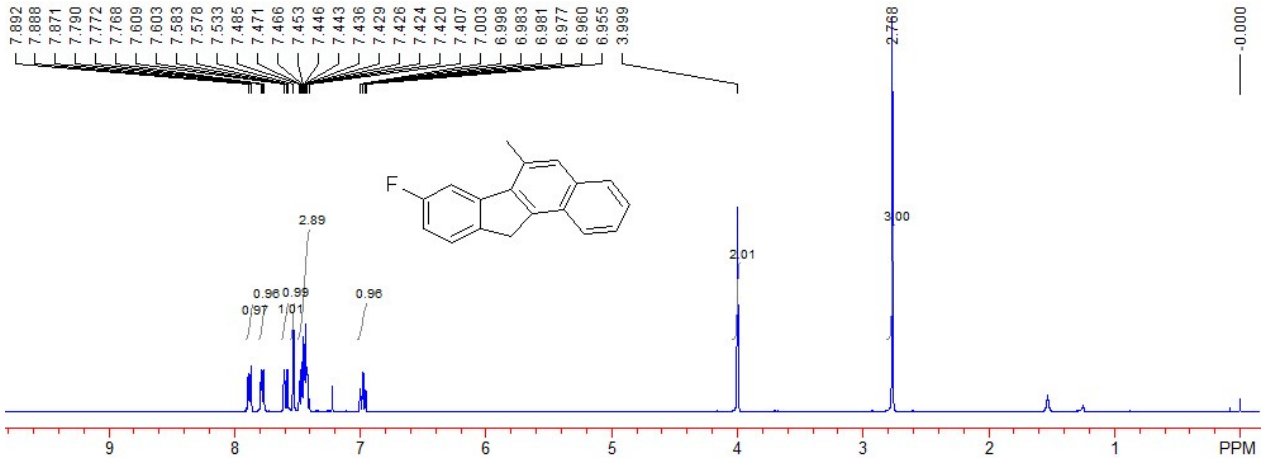
Compound **2dd**. 39 mg, yield: 78%; white solid. MP: 148-150 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 2.82 (s, 3H, CH_3), 4.02 (s, 2H, CH_2), 7.10 (d, *J* = 8.0 Hz, 1H, Ar), 7.38-7.46 (m, 3H, Ar), 7.53 (s, 1H, Ar), 7.75-7.78 (m, 2H, Ar), 7.89 (d, *J* = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 21.8, 35.2, 123.4, 123.8, 124.4, 125.3, 125.4, 126.5, 127.8, 127.9, 129.1, 131.7, 132.5, 136.1, 138.2, 140.7, 140.8, 143.6. IR (neat) ν 2920, 1612, 1515,

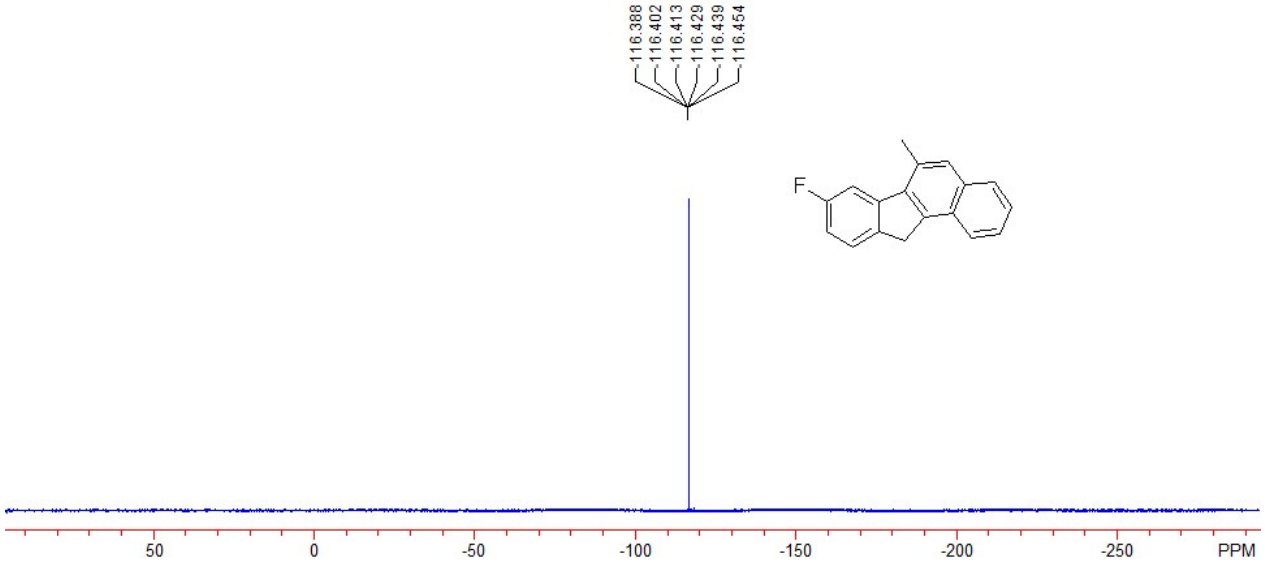
1440, 1351, 1168, 1039 cm^{-1}. MS (%) m/e 244 (M^+, 100.00), 229 (76.19), 202 (5.52), 122 (14.72), 114 (34.45), 88 (3.00). HRMS (EI) calcd. for $C_{19}H_{16}$: 244.1252, found: 244.1245.

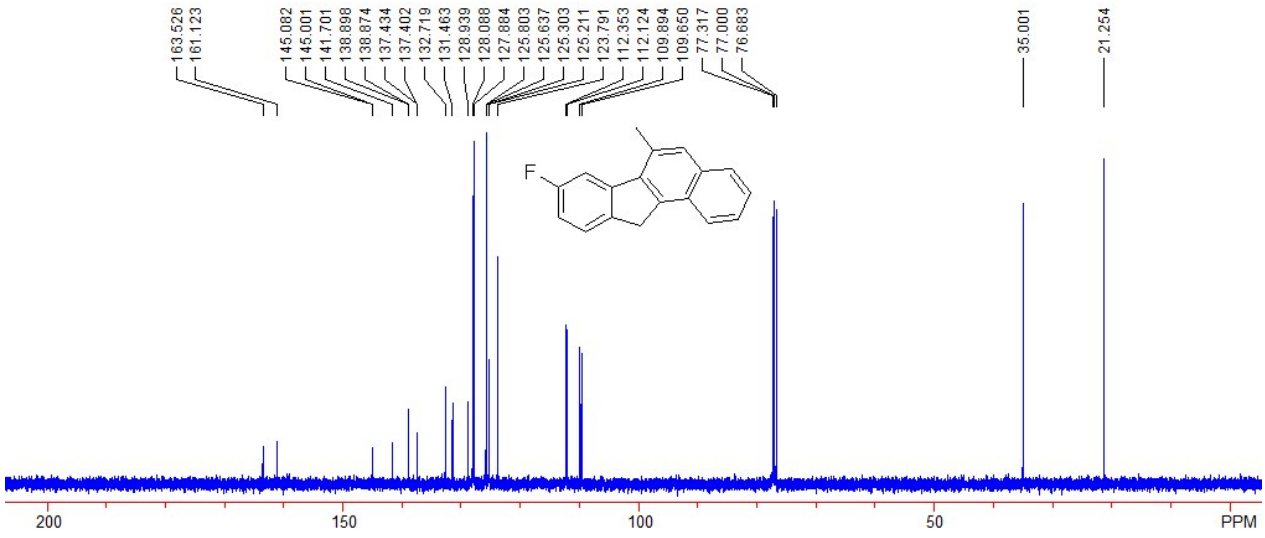


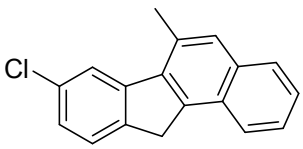


Compound **2ee**. 39 mg, yield: 76%; white solid. MP: 123-125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.77 (s, 3H, CH_3), 4.00 (s, 2H, CH_2), 6.96-7.00 (m, 1H, Ar), 7.41-7.49 (m, 3H, Ar), 7.53 (s, 1H, Ar), 7.58-7.61 (m, 1H, Ar), 7.77-7.79 (m, 1H, Ar), 7.87-7.89 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 35.0, 109.8 (d, $J_{C\text{-}F}$ = 24.4 Hz), 112.3 (d, $J_{C\text{-}F}$ = 22.9 Hz), 123.8, 125.3 (d, $J_{C\text{-}F}$ = 9.2 Hz), 125.6, 125.8, 127.9, 128.1, 128.9, 131.5, 132.7, 137.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 138.9 (d, $J_{C\text{-}F}$ = 2.4 Hz), 141.7, 145.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 162.3 (d, $J_{C\text{-}F}$ = 240.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -116.39 ~ -116.45 (m, 1F). IR (neat) ν 2921, 1607, 1581, 1471, 1327, 1166, 1016 cm^{-1}. MS (%) m/e 248 (98.98), 233 (M^+, 100.00), 220 (5.99), 125 (2.08), 115 (1.51), 97 (6.46). HRMS (EI) calcd. for $C_{18}H_{13}F$: 248.1001, found: 248.0996.



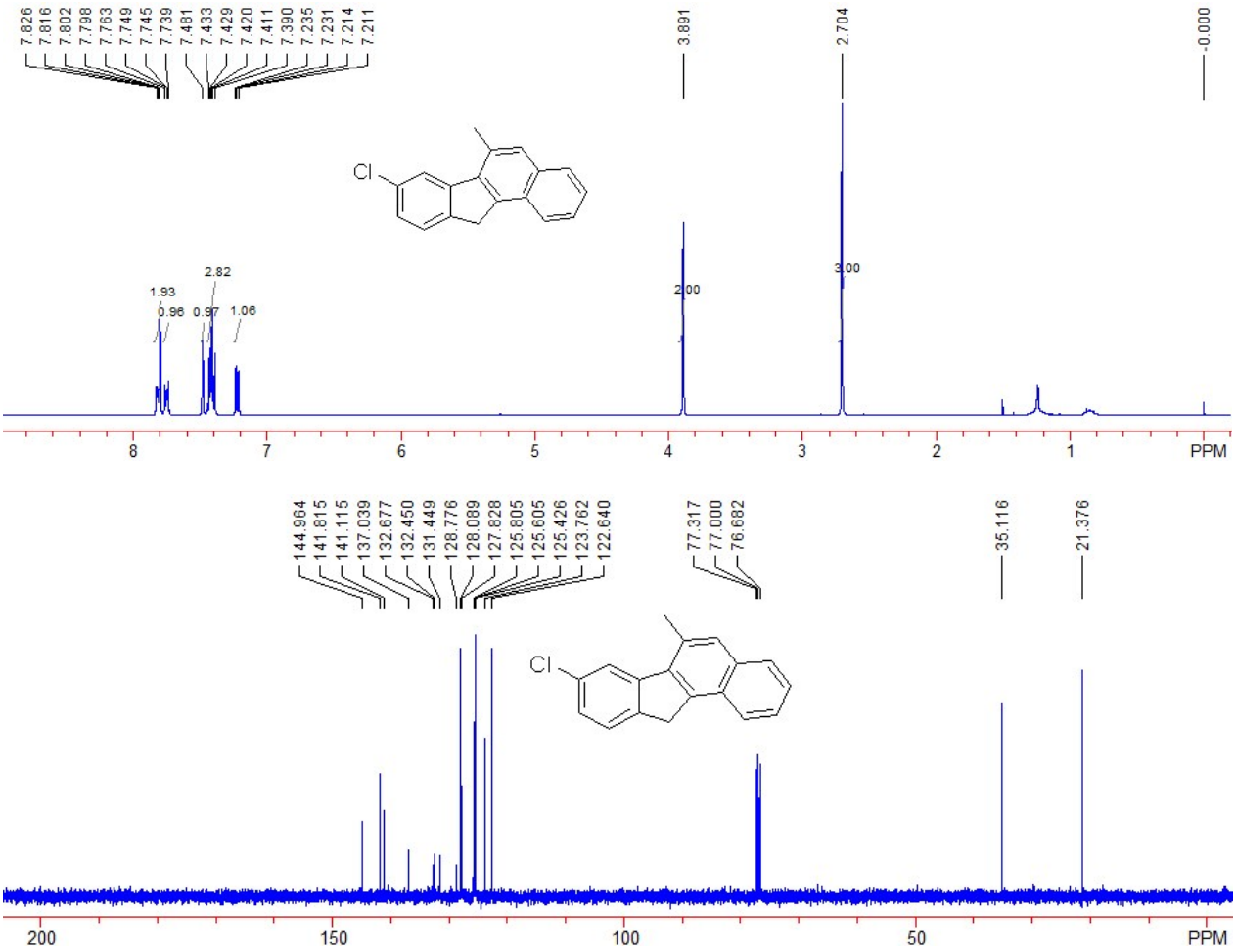


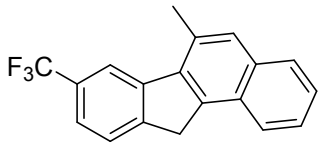




Compound **2ff**. 60 mg, yield: 80%; white solid. MP: 185-187 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz,

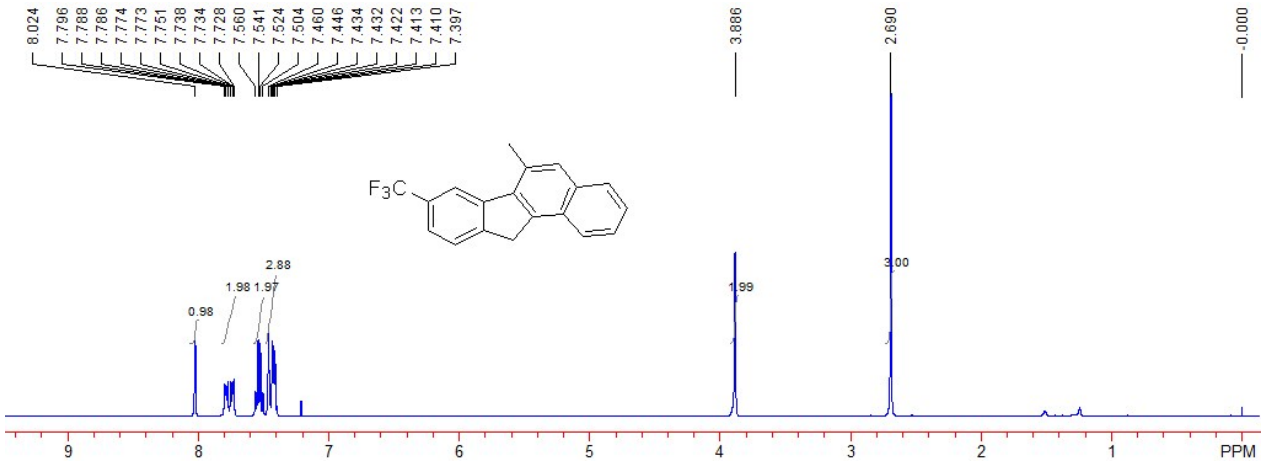
TMS) δ 2.70 (s, 3H, CH_3), 3.89 (s, 2H, CH_2), 7.22 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H, Ar), 7.39-7.43 (m, 3H, Ar), 7.48 (s, 1H, Ar), 7.74-7.76 (m, 1H, Ar), 7.80-7.83 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 35.1, 122.6, 123.8, 125.4, 125.6, 125.8, 127.8, 128.1, 128.8, 131.4, 132.5, 132.7, 137.0, 141.1, 141.8, 145.0. IR (neat) ν 2920, 2850, 1597, 1435, 1317, 1178, 1078 cm^{-1}. MS (%) m/e 264 (48.06), 229 (M^+, 100.00), 202 (4.60), 132 (8.34), 115 (6.97), 101 (20.37). HRMS (EI) calcd.for $C_{18}H_{13}Cl$: 264.0706, found: 264.0707.

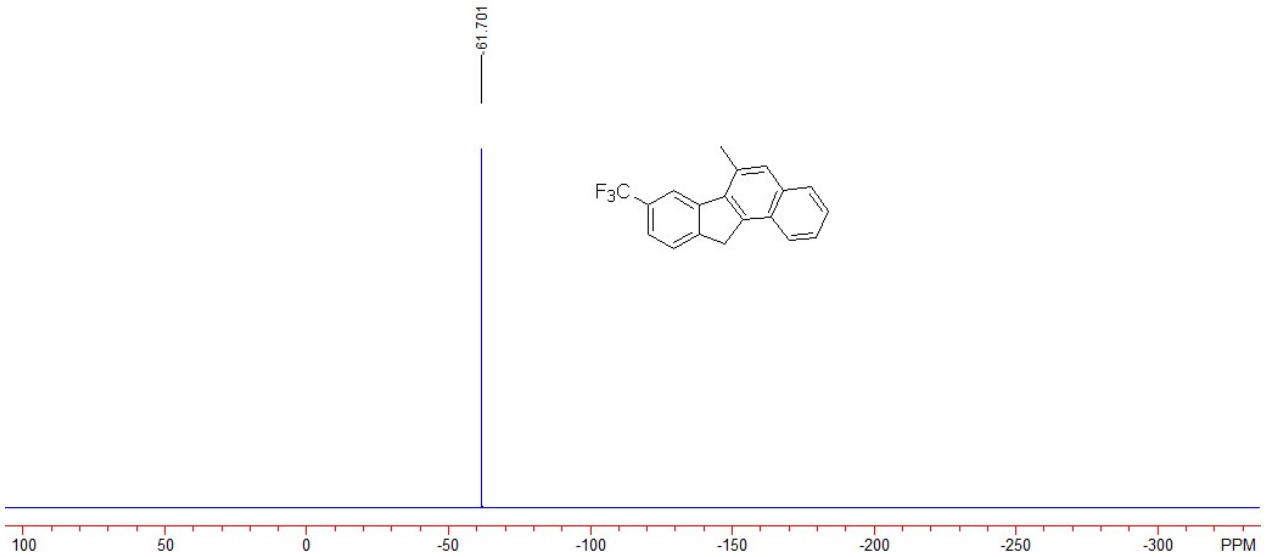


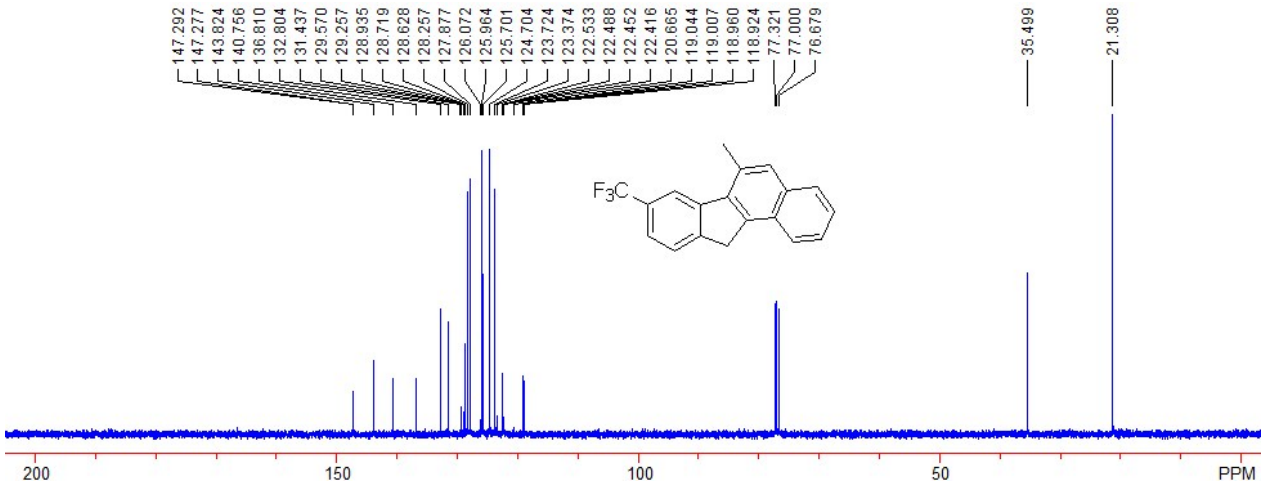


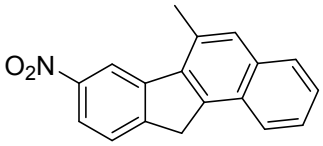
Compound **2gg**. 43 mg, yield: 72%; white solid. MP: 170-172 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.69 (s, 3H, CH_3), 3.89 (s, 2H, CH_2), 7.40-7.46 (m, 3H, Ar), 7.50-7.56 (m, 2H, Ar), 7.73-7.80 (m, 2H, Ar), 8.02 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 35.5, 119.0 (q, J_{C-F} = 4.7 Hz), 122.5 (q, J_{C-F} = 3.6 Hz), 123.7, 124.7, 124.8 (q, J_{C-F} = 269.8 Hz), 125.7, 126.0, 127.9, 128.3, 128.7, 129.1 (q, J_{C-F} = 32.2 Hz), 131.4, 132.8, 136.8, 140.8, 143.8, 147.3 (d, J_{C-F} = 1.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -61.70 (s, 3F). IR (neat) ν 2921, 1592, 1439, 1341, 1271, 1150, 1065 cm^{-1}. MS (%) m/e 298 (M^+, 100.00), 283 (75.66), 229 (56.71), 126 (5.77), 115 (8.96), 75 (6.31). HRMS (EI) calcd.for $C_{19}H_{13}F_3$: 298.0969, found: 298.0964.

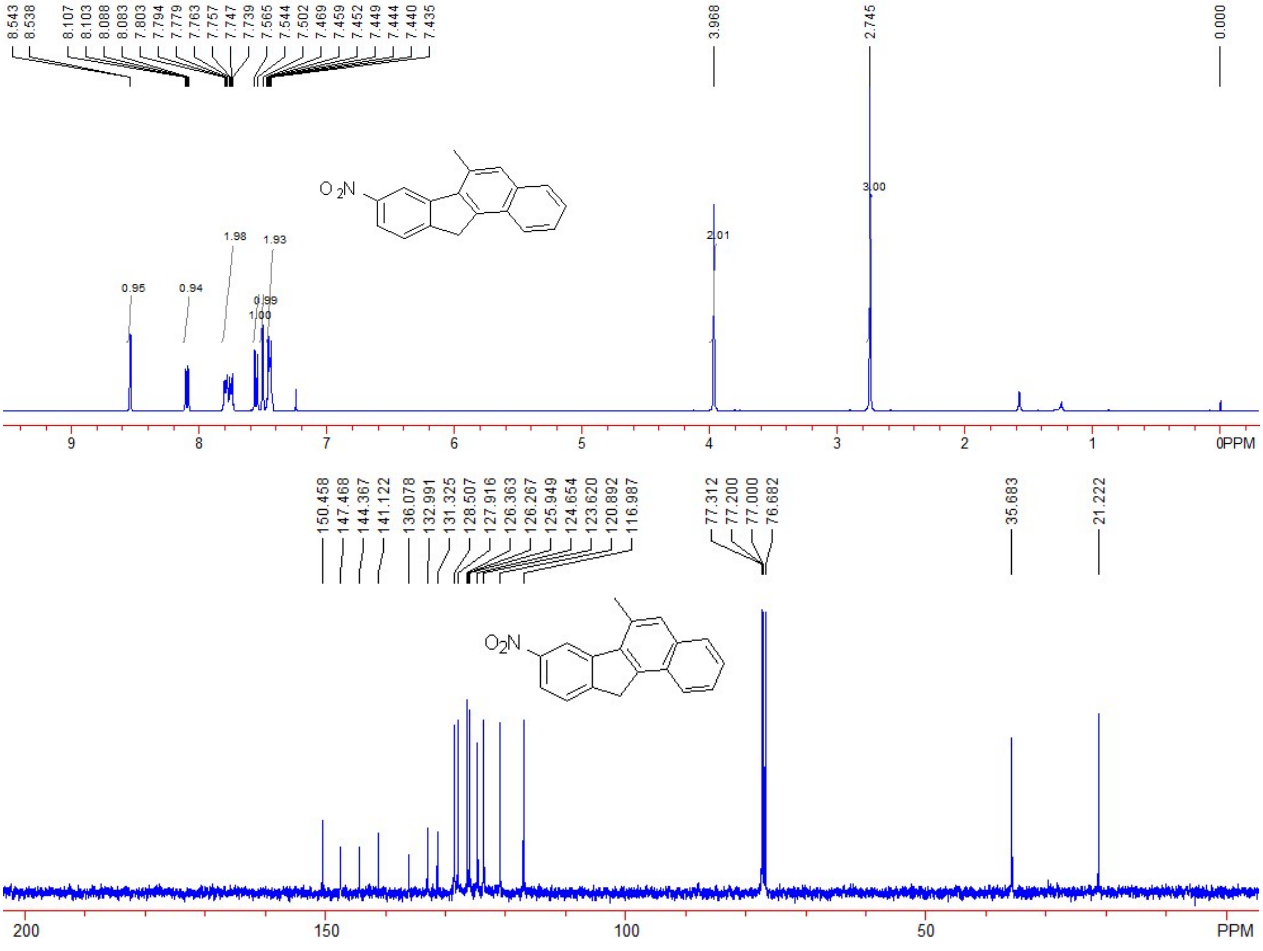


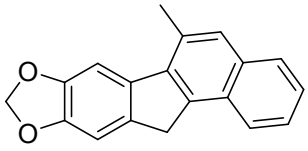






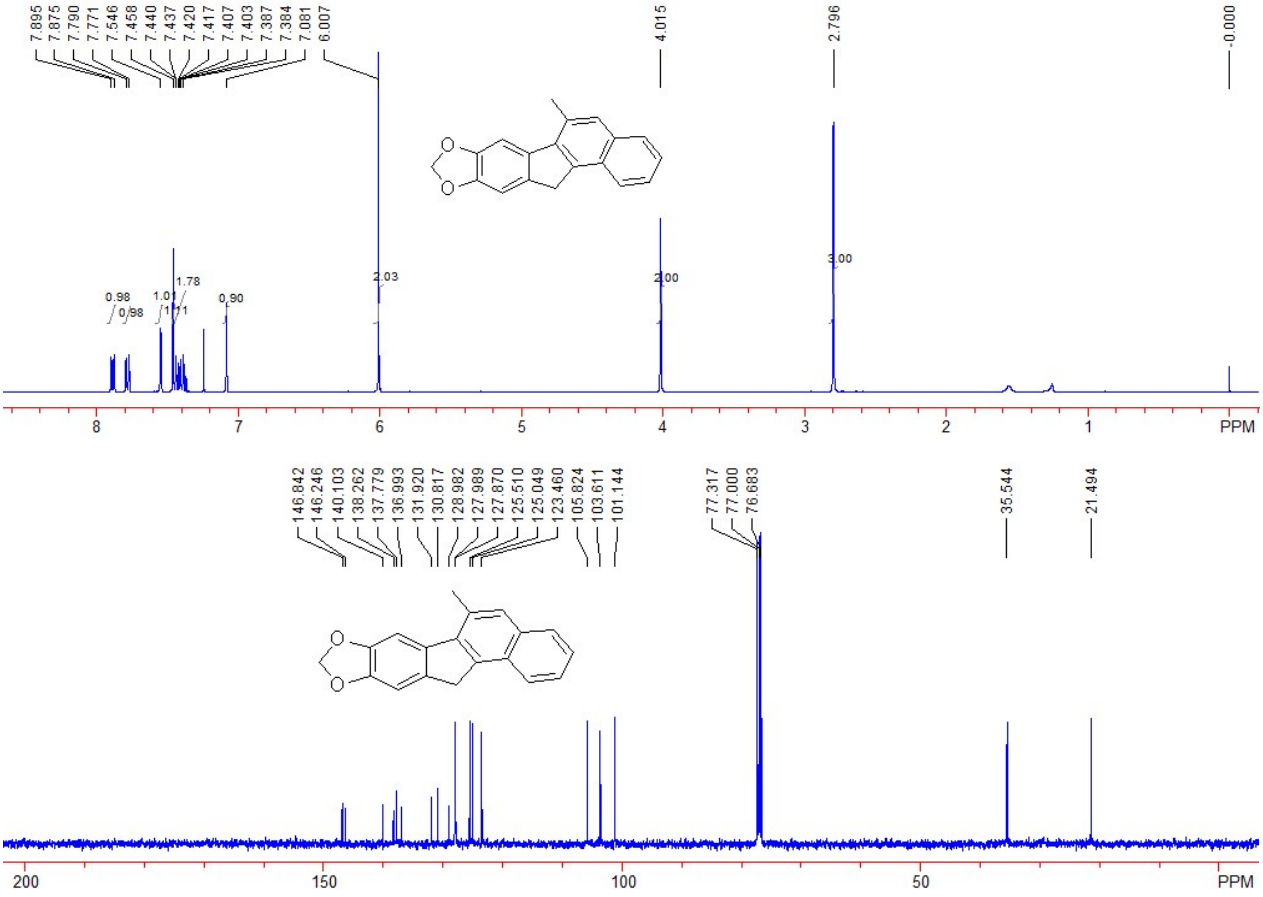
Compound **2hh**. 25 mg, yield: 46%; white solid. MP: 202-204 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.75 (s, 3H, CH_3), 3.97 (s, 2H, CH_2), 7.44-7.47 (m, 2H, Ar), 7.50 (s, 1H, Ar), 7.55 (d, J = 8.4 Hz, 1H, Ar), 7.74-7.80 (m, 2H, Ar), 8.10 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, Ar), 8.54 (d, J = 2.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 35.7, 117.0, 120.9, 123.6, 124.7, 125.9, 126.3, 126.4, 127.9, 128.5, 131.3, 133.0, 136.1, 141.1, 144.4, 147.5, 150.0. IR (neat) ν 2920, 2849, 1580, 1463, 1377, 1187, 1085 cm^{-1}. MS (%) m/e 275 (M^+, 100.00), 229 (91.81), 202 (27.44), 152 (3.32), 115 (12.70), 101 (54.26). HRMS (EI) calcd.for $C_{18}H_{13}NO_2$: 275.0946, found: 275.0954.

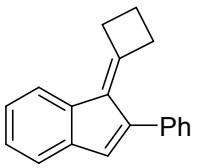




Compound **2ii**. 14 mg, yield: 25%; white solid. MP: 142-144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz,

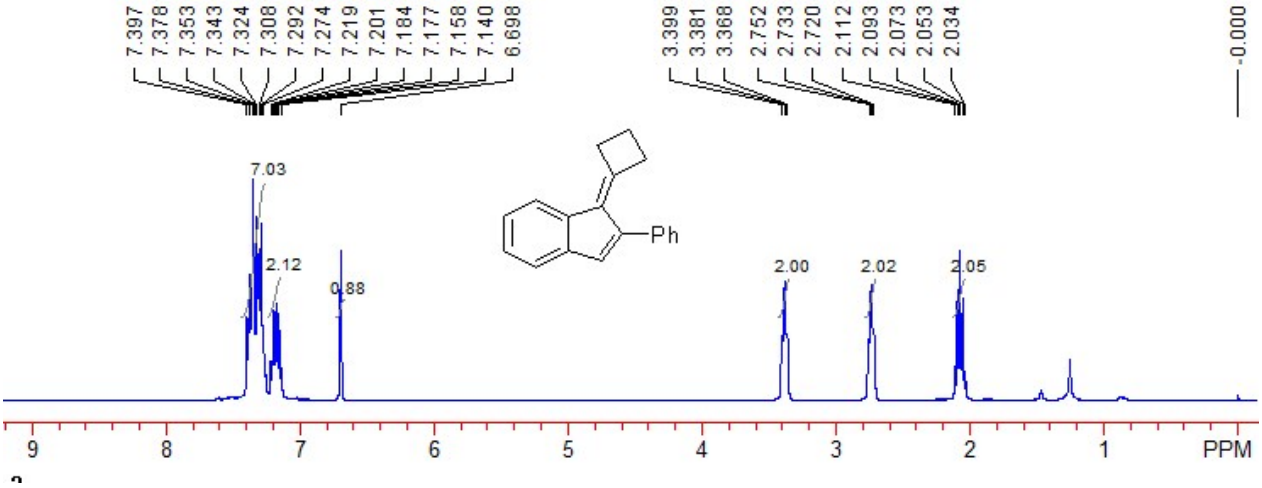
TMS) δ 2.80 (s, 3H, CH_3), 4.02 (s, 2H, CH_2), 6.01 (s, 2H, CH_2), 7.08 (s, 1H, Ar), 7.38-7.44 (m, 2H, Ar), 7.46 (s, 1H, Ar), 7.55 (s, 1H, Ar), 7.78 (d, *J* = 8.0 Hz, Ar), 7.89 (d, *J* = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 35.5, 101.1, 103.6, 105.8, 123.5, 125.0, 125.5, 127.9, 128.0, 129.0, 130.8, 131.9, 137.0, 137.8, 138.3, 140.1, 146.2, 146.8. IR (neat) ν 2922, 2853, 1610, 1466, 1308, 1227, 1156 cm^{-1}. MS (%) m/e 274 (M^+, 100.00), 244 (32.83), 202 (14.18), 122 (9.76), 94 (50.29), 75 (8.18). HRMS (EI) calcd. for $C_{19}H_{14}O_2$: 274.0994, found: 274.0992.

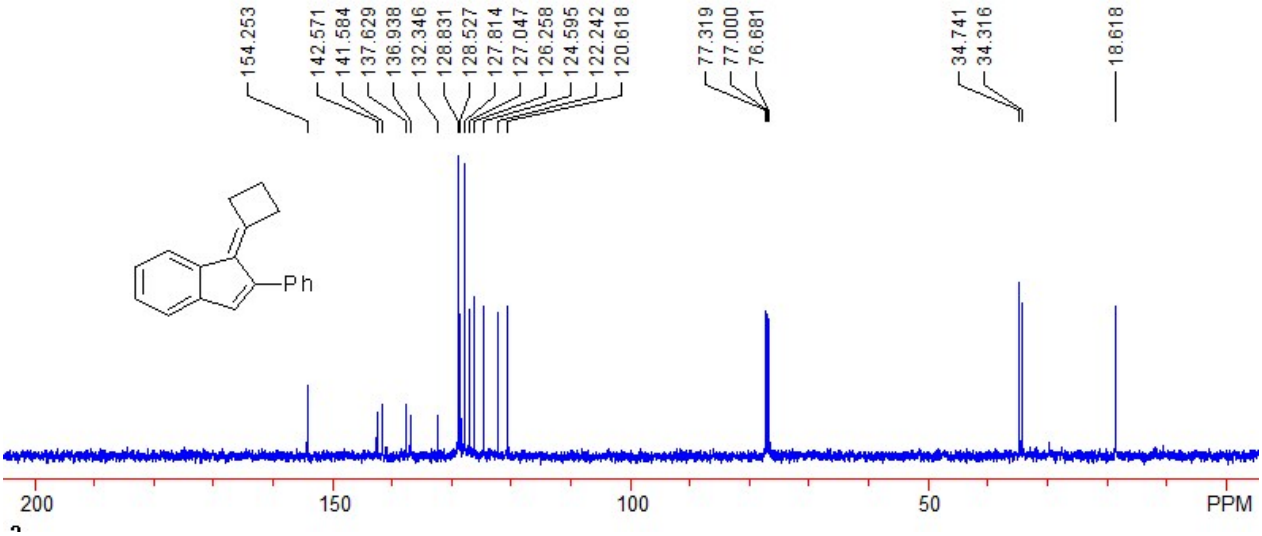


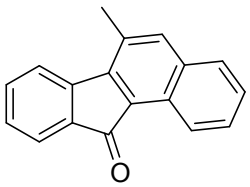


Compound **6**. 44 mg, yield: 88%; yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.03-2.11 (m, 2H, CH_2), 2.72-2.75 (m, 2H, CH_2), 3.37-3.40 (m, 2H, CH_2), 6.70 (s, 1H, =CH), 7.14-7.22 (m, 2H, Ar), 7.27-7.40 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.6, 34.3, 34.7, 120.6, 122.2, 124.6, 126.3, 127.8, 128.5, 128.8, 132.3, 136.9, 137.6, 141.6, 142.6, 154.3. IR (neat) ν 2953, 1660, 1595, 1444, 1356, 1238, 1069 cm^{-1}. MS (%) m/e 244 (80.88), 215 (M^+, 100.00), 202

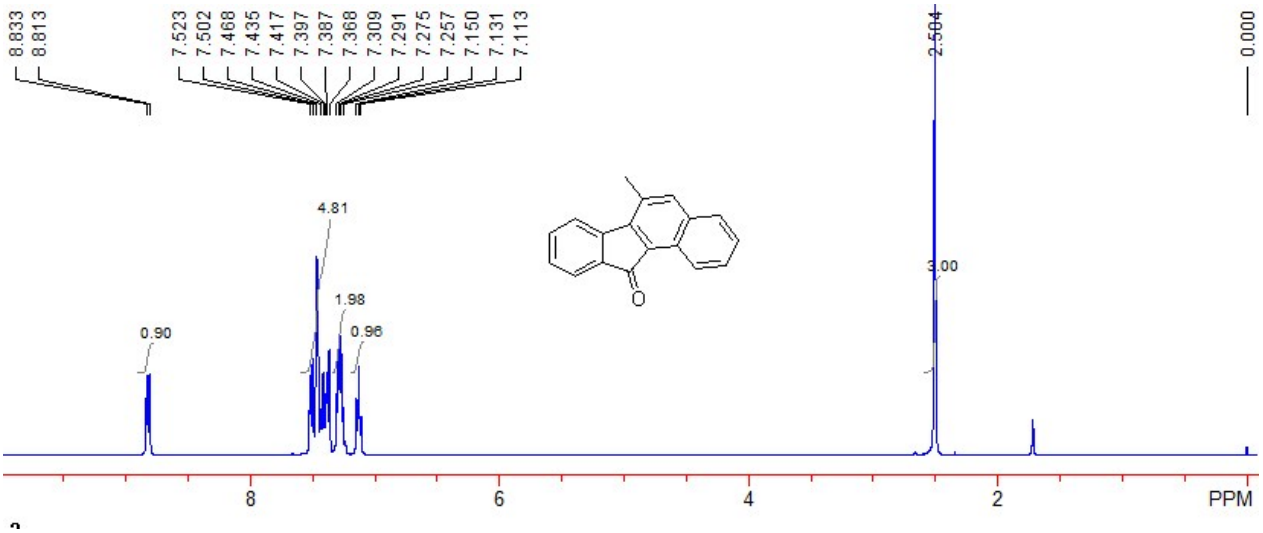
(14.64), 152 (4.25), 115 (9.46), 91 (4.90). HRMS (EI) calcd. for $C_{19}H_{16}$: 244.1252, found: 244.1258.

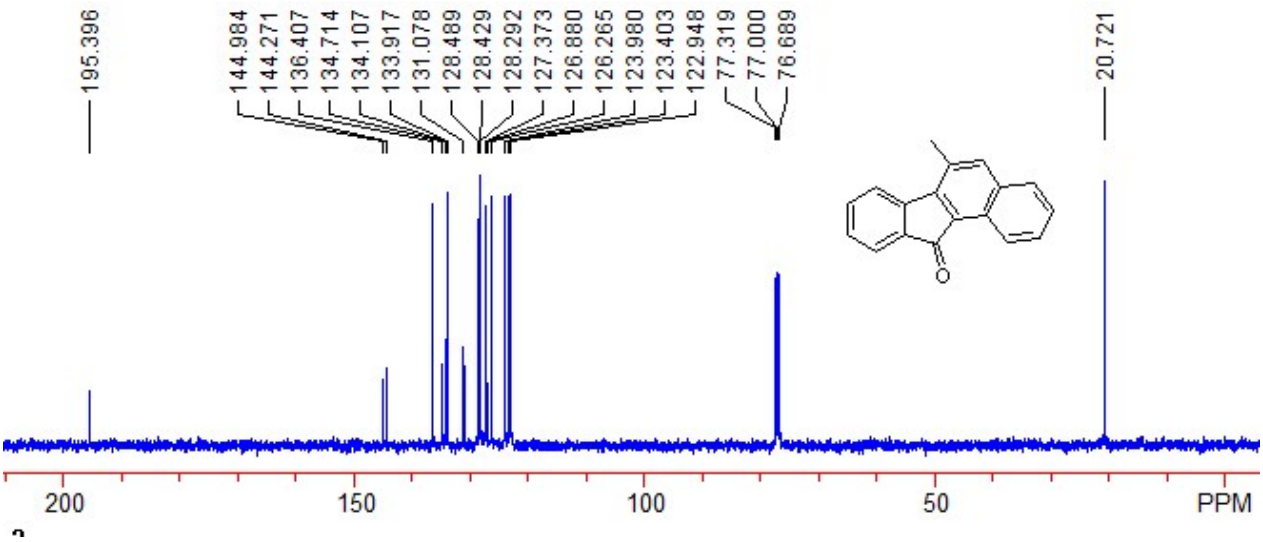


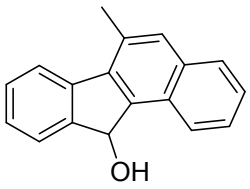




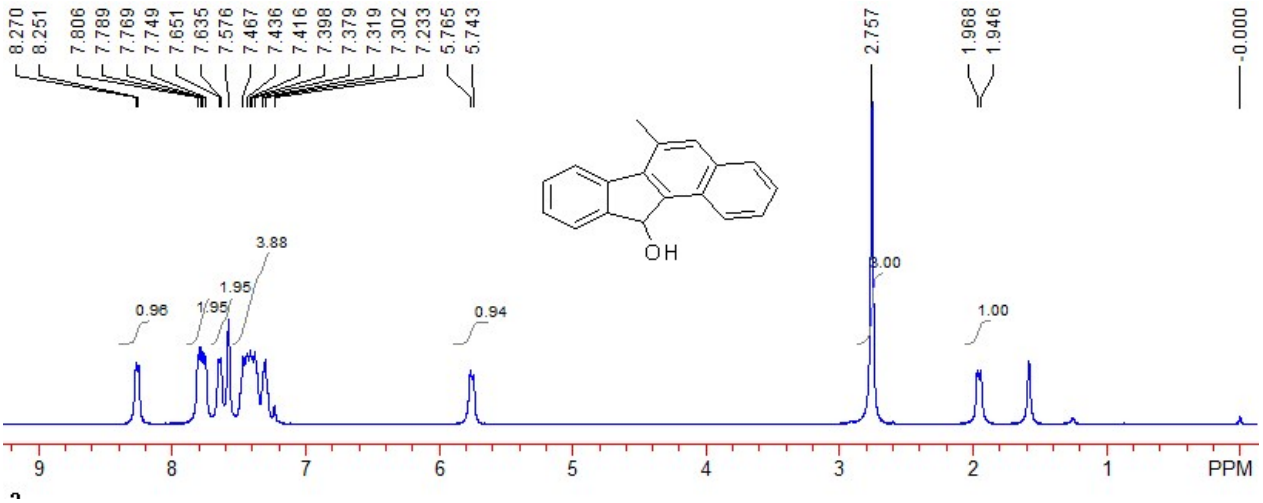
Compound **9**. 49 mg, yield: 100%; red solid. MP: 132-135 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.50 (s, 3H, CH_3), 7.13 (t, J = 7.6 Hz, 1H, Ar), 7.26-7.31 (m, 2H, Ar), 7.37-7.52 (m, 5H, Ar), 8.82 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.7, 122.9, 123.4, 124.0, 126.3, 126.9, 127.4, 128.3, 128.4, 128.5, 131.1, 133.9, 134.1, 134.7, 136.4, 144.3, 145.0, 195.4. IR (neat) ν 2921, 2160, 1932, 1690, 1591, 1339, 1202 cm^{-1}. MS (%) m/e 244 (M^+, 100.00), 215 (71.31), 207 (1.84), 189 (8.89), 115 (1.58), 75 (4.76). HRMS (EI) calcd.for $C_{18}H_{12}O$: 244.0888, found: 244.0880.

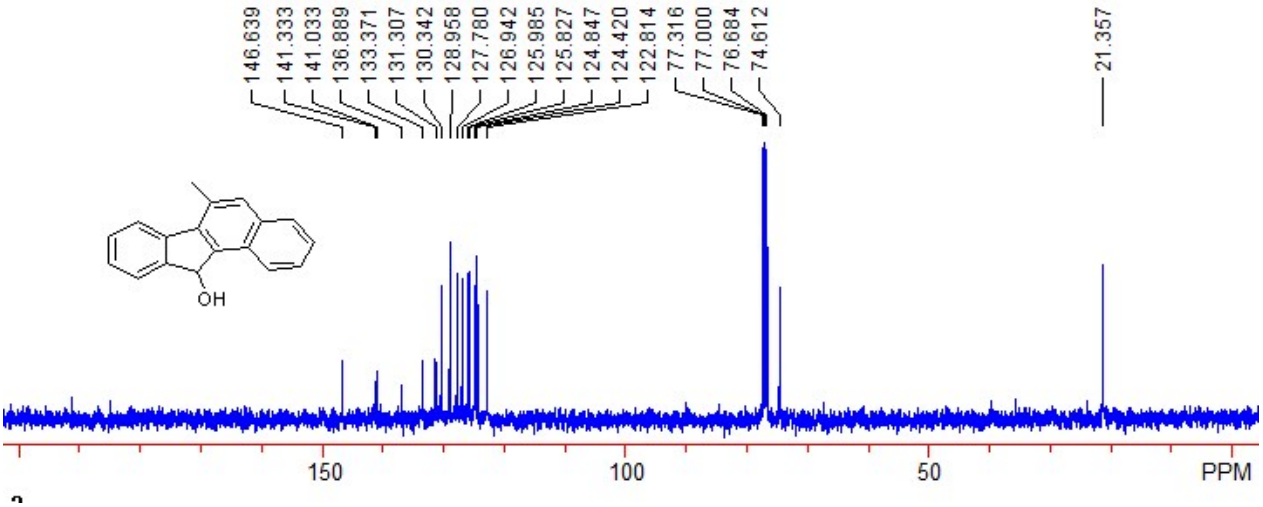






Compound **10**. 49 mg, yield: 100%; white solid. MP: 158-160 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.96 (d, *J* = 8.8 Hz, 1H, OH), 2.76 (s, 3H, CH_3), 5.75 (d, *J* = 8.8 Hz, 1H, CH), 7.30-7.47 (m, 4H, Ar), 7.58-7.65 (m, 2H, Ar), 7.75-7.81 (m, 2H, Ar), 8.26 (d, *J* = 7.6 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 74.6, 122.8, 124.4, 124.8, 125.8, 126.0, 126.9, 127.8, 129.0, 130.3, 131.3, 133.4, 136.9, 141.0, 141.3, 146.6. IR (neat) ν 2922, 2853, 1592, 1440, 1309, 1178, 1069 cm^{-1}. MS (%) m/e 246 (63.66), 231 (M^+, 100.00), 202 (42.28), 189 (7.65), 115 (8.08), 71 (30.67). HRMS (EI) calcd.for $C_{18}H_{14}O$: 246.1045, found: 246.1055.



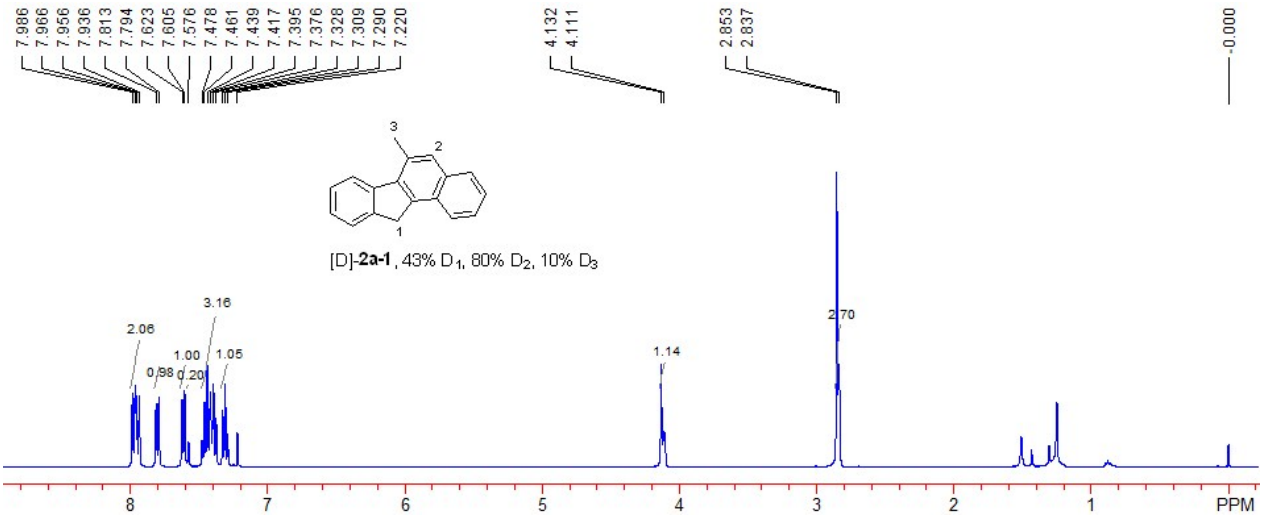


[D]-**2a-1**

4.11-4.13 (m, 1.14H, CH_2), D_1% = (2.00-1.14)/2.00*100% = 43%

7.58 (s, 0.20H, Ar), D_2% = (1.00-0.20)/1.00*100% = 80%

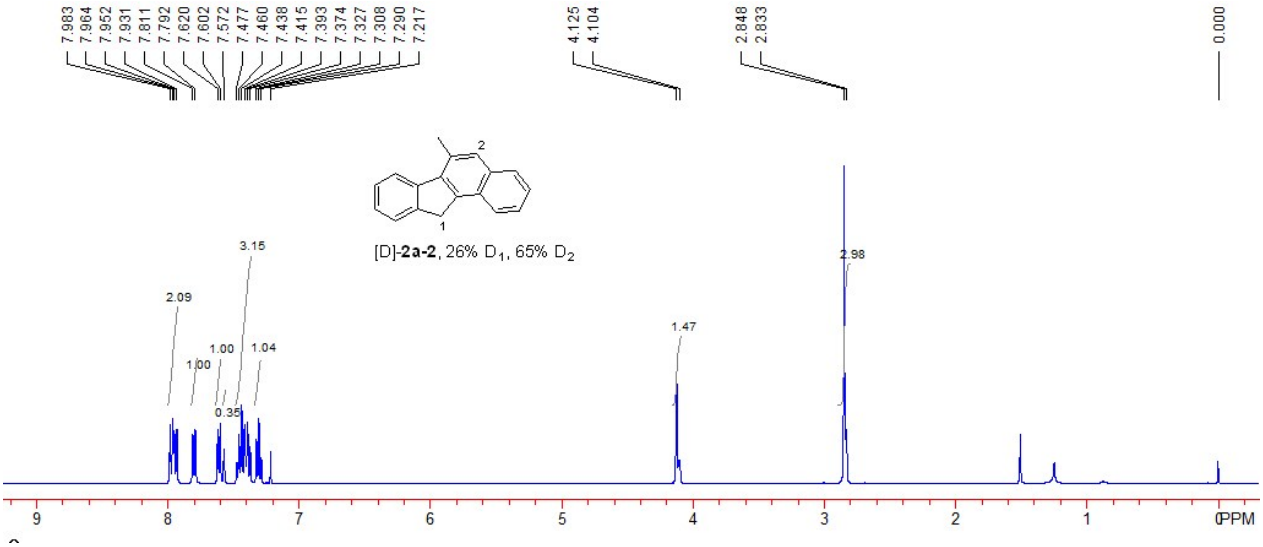
2.84-2.85 (m, 2.70H, CH_3), D_3% = (3.00-2.70)/3.00*100% = 10%



[D]-**2a-2**

4.10-4.13 (m, 1.47H, CH_2), D_1% = (2.00-1.47)/2.00*100% = 26%

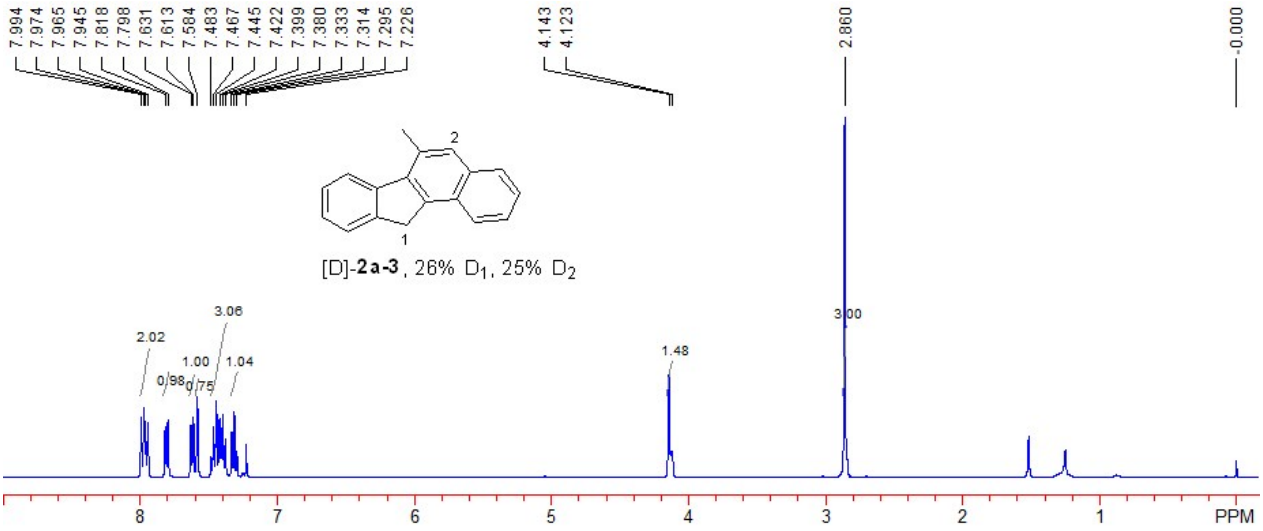
7.57 (s, 0.35H, Ar), D_2% = (1.00-0.35)/1.00*100% = 65%



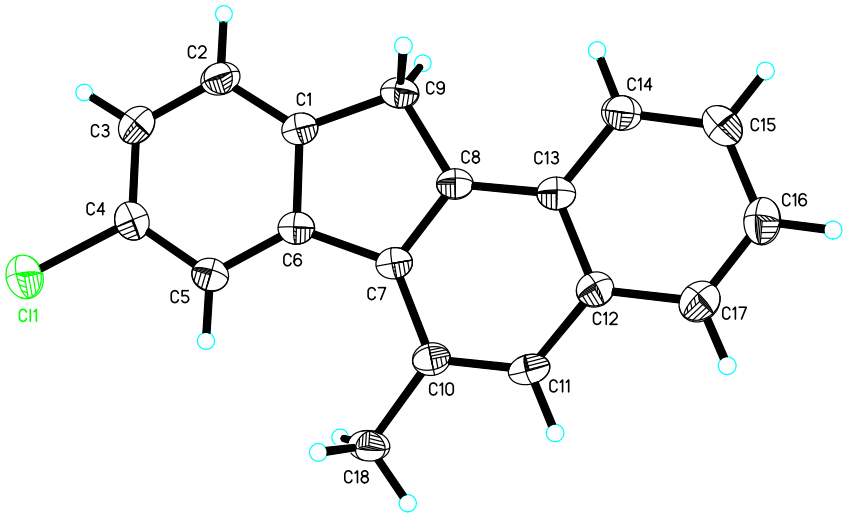
[D]-**2a-3**

4.12-4.14 (m, 1.48H, CH_2), D_1% = (2.00-1.48)/2.00*100% = 26%

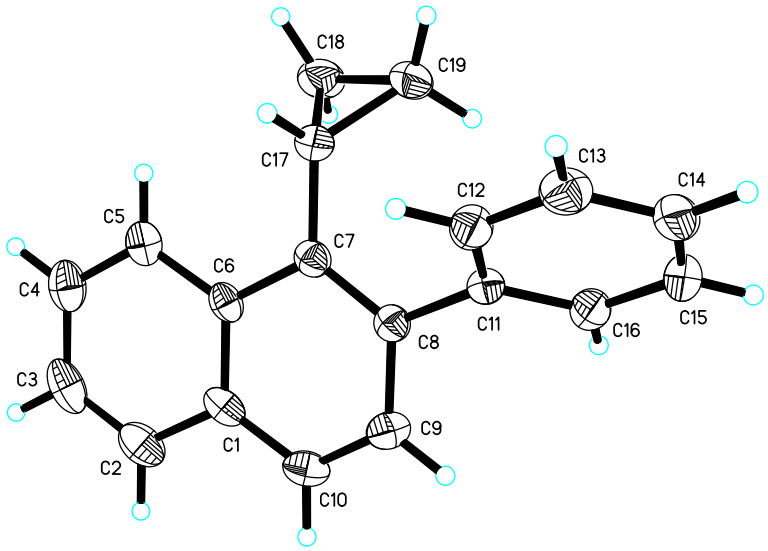
7.58 (s, 0.75H, Ar), D_2% = (1.00-0.75)/1.00*100% = 25%



14. X-ray Crystal Data of Compounds 2ff and S7.



The crystal data of **2ff** have been deposited in CCDC with number 1539942. Empirical formula: $C_{18}H_{13}Cl$, Formula weight: 264.73, Temperature: 293(2) K, Crystal system: Monoclinic, Space group: P 21/c, Unit cell dimensions: a = 20.610(3) Å, α = 90°; b = 5.5852(7) Å, β = 106.224(3)°; c = 23.364(3) Å, γ = 90°. Volume: 2582.3(6) $Å^3$, Z = 8, Density (calculated): 1.362 Mg/m^3, F(000): 1104, Crystal size: 0.200 x 0.170 x 0.100 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0539, wR2 = 0.1199.



The crystal data of **S7** have been deposited in CCDC with number 1559789. Empirical formula: $C_{19}H_{16}$, Formula weight: 244.32, Temperature: 293(2) K, Crystal system: Orthorhombic, Space group: P b c a, Unit cell dimensions: a = 10.220(7) Å, α = 90°; b = 14.584(10) Å, β = 90°; c = 17.645(12) Å, γ = 90°. Volume: 2630(3) $Å^3$, Z = 8, Density (calculated): 1.234 Mg/m^3, F(000): 1040, Crystal size: 0.200 x 0.170 x 0.130 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0661, wR2 = 0.1530.

15. References

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