

Electronic Supplementary Information

Enynone-enabled migratory insertion and Schmitt cyclization

cascade for the synthesis of furan-fused fluorenes

He Zhang, Tongxiang Cao, Hejiang Luo, Lianfen Chen, and Shifa Zhu*

Key Laboratory of Functional Molecular Engineering of Guangdong Province, Guangdong Engineering Research Center for Green Fine Chemicals and Chemical Engineering, School of Chemistry, South China University of Technology, Guangzhou, 510640, P. R. China

E-mail: zhusf@scut.edu.cn

Table of contents

1. Experimental procedures and spectroscopic data	2
1.1 General information.....	2
1.2 General procedure for the synthesis of enynones 1 and dialkynylbenzene 2	2
1.3 Optimization of the reaction conditions for Synthesis of 3aa	4
1.4 General procedure for the synthesis of 3am-3bm	4
1.5 Optimization of the reaction conditions for synthesis of 6a	12
1.6 General procedure for the synthesis of 6a-6j	13
1.7 General procedure for the synthesis of 8	15
2. References	15
3. X-Ray diffraction analysis.....	16
3.1 Crystal data and structure refinement for 3am	16
3.2 Crystal data and structure refinement for 6d	17
4. Copies of NMR spectra	18

1. Experimental procedures and spectroscopic data

1. 1 General information

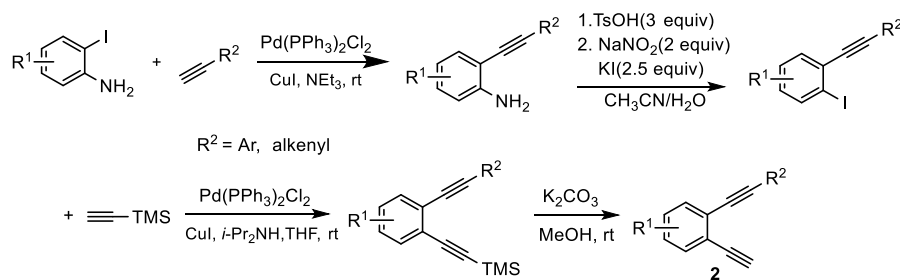
All reactions were carried out under an inert atmosphere of dry N₂ in Schlenk tube, solvents were purified by standard method. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F), ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using EI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

1.2 General procedure for the synthesis of enynes **1** and dialkynylbenzene **2**

1.2. 1 General procedure for preparation of enynes **1a–1o**

The typical procedure for the preparation of enynes **1a–1o** was according to literature.^[1] The characterization data of **1a–1o** was consistent with literature.^[1]

1.2.2 Typical experimental procedure for the synthesis of dialkynylbenzene **2**^[2]



To a solution of the corresponding 2-iodoaniline (1.0 eq.), Pd(PPh₃)₂Cl₂ (2.0 mol %), and CuI (1.0 mol %) in NEt₃ (0.25 M) was added the appropriate phenylacetylene (1.2 eq.). The resulting mixture was stirred under nitrogen atmosphere at room temperature overnight. After the reaction finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the 2-phenylaniline in 80-90% yield.

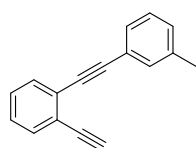
To a solution of *p*-TsOH H₂O (3.0 eq.) in MeCN (0.25 M) was added phenylaniline (1.0 eq.). The resulting suspension of ammonium salt was cooled to 0 °C and was added gradually a solution of NaNO₂ (2.0 eq.) and KI (2.5 eq.) in water (5 M). The reaction mixture was stirred for 10 min at 0 °C. Saturated NaHCO₃ solution and Na₂S₂O₃ solution was added to the reaction mixture successively. The reaction suspension was extracted with diethyl ether and purified on a silica-gel column chromatography (petroleum ether) to provide 1-iodo-2-(phenylethynyl)benzene in 71-76%.

To a solution of the corresponding 2-iodoaniline (1.0 eq.), Pd(PPh₃)₂Cl₂ (2.0 mol %), i-Pr₂NH (0.1 eq.) and CuI (1.0 mol %) in THF (0.25 M) was added the appropriate trimethylsilylacetylene (1.2 eq.). The resulting mixture was stirred under nitrogen atmosphere at room temperature overnight. After the reaction finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the trimethyl((2-(phenylethynyl)phenyl)ethynyl)silane in 78-92% yield.

To a solution of trimethyl((2-(phenylethynyl)phenyl)ethynyl)silane (1.0 eq.) in MeOH was added K₂CO₃ (2.0 eq.). The reaction mixture was stirred for 10 min at room temperature. The mixture was diluted with DCM, and the organic layer was washed with saturated NaCl solution, dried and concentrated to afford the desired product **2** in 90-96% yield.

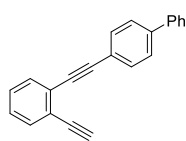
The characterization data of **2a–2h** and **2j** was consistent with literature. [3,4,5]

1-Ethynyl-2-(m-tolyethynyl)benzene (2i)



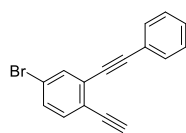
Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 3.36 (s, 1H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 138.1, 132.6, 132.4, 131.8, 129.5, 128.9, 128.6, 128.3, 127.9, 126.5, 124.7, 123.0, 93.8, 87.6, 82.3, 81.2, 21.3. IR (KBr, cm⁻¹) 3448, 3293, 2921, 2207, 1641, 1483, 1441, 1250, 1087, 843, 755, 685, 624. HRMS (ESI) Calcd for C₁₇H₁₂ (M+Na)⁺ 239.0831, found 239.0827.

4-((2-Ethynylphenyl)ethynyl)-1,1'-biphenyl (2k)



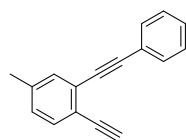
White solid, m. p. = 61-62 °C ¹H NMR (400 MHz, CDCl₃) δ 7.64 (ddd, *J* = 15.8, 11.9, 7.8 Hz, 8H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.32 (m, 3H), 3.43 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.3, 140.4, 132.7, 132.3, 131.8, 128.9, 128.6, 128.0, 127.7, 127.1, 126.4, 124.7, 122.1, 93.6, 88.6, 82.3, 81.2. IR (KBr, cm⁻¹) 3289, 3062, 2216, 1917, 1593, 1484, 1442, 1398, 1265, 1101, 1006, 954, 839, 760, 694, 657, 559. HRMS (ESI) Calcd for C₂₀H₁₂ (M+H)⁺ 253.1012, found 253.1019.

4-Bromo-1-ethynyl-2-(phenylethynyl)benzene (2l)



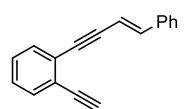
White solid, m. p. = 46-47 °C ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.61 (s, 2H), 7.44 – 7.37 (m, 5H), 3.45 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 134.5, 133.7, 131.9, 131.2, 128.9, 128.5, 128.1, 123.6, 122.7, 122.5, 94.9, 86.6, 82.3, 81.4. IR (KBr, cm⁻¹) 3745, 3521, 3496, 3464, 3442, 2959, 1539, 1491, 1071, 1023, 819, 754, 687. HRMS (ESI) Calcd for C₁₆H₉Br (M-H)⁻ 278.9815, found 278.9820.

1-Ethynyl-4-methyl-2-(phenylethynyl)benzene (2m)



White solid, m. p. = 56-57 °C ¹H NMR (400 MHz, CDCl₃) δ ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 3.3 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 4H), 7.14 (d, *J* = 7.8 Hz, 1H), 3.43 (s, 1H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 132.6, 132.4, 131.9, 129.1, 128.6, 128.5, 126.2, 123.4, 121.8, 93.3, 88.3, 82.5, 80.6, 21.3. IR (KBr, cm⁻¹) 3817, 3744, 3520, 3497, 3442, 3287, 3028, 2921, 2213, 2105, 1911, 1599, 1492, 1443, 1376, 1237, 1098, 1068, 1027, 915, 888, 821, 755, 689, 652, 619, 583, 544, 515. HRMS (ESI) Calcd for C₁₇H₁₂ (M+Na)⁺ 239.0831, found 239.0834.

(E)-1-Ethynyl-2-(4-phenylbut-3-en-1-yn-1-yl)benzene (2n)

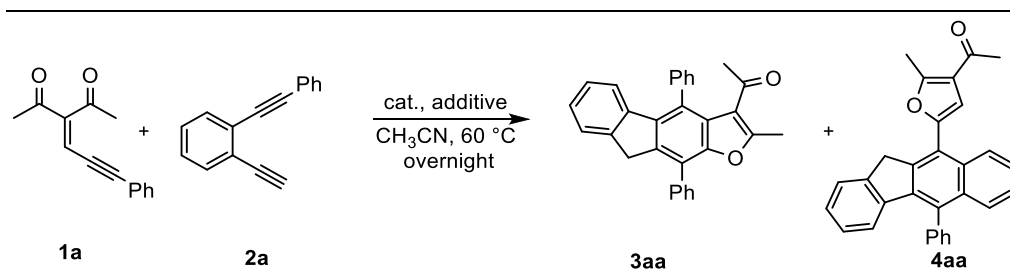


E/Z = 10:1, yellow oil, ¹H NMR (400 MHz, CDCl₃) δ Isomer E δ 7.41 (dd, *J* = 13.2, 7.5 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.28 – 7.15 (m, 5H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.35 (d, *J* = 16.2 Hz, 1H), 3.27 (s, 1H). Isomer Z δ 7.93 (d, *J* = 7.5 Hz, 2H), 6.62 (d, *J* = 12.0 Hz, 1H), 5.89 (d, *J* = 12.0 Hz, 1H), 3.22 (s, 1H) ppm (remaining peaks

could not be assigned) ^{13}C NMR (100 MHz, CDCl_3) Isomer E δ 142.0, 136.3, 132.7, 131.9, 128.8, 128.6, 127.9, 126.5, 126.4, 124.4, 108.1, 107.2, 93.2, 90.2, 82.3, 81.2. Isomer Z δ 139.2, 132.9, 132.2, 129.1, 128.6, 128.3 ppm (the remaining signals could not be assigned) IR (KBr, cm^{-1}) 3703, 3521, 3498, 2922, 1475, 1266, 953, 750, 519. HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{12}$ ($\text{M}+\text{H}$) $^+$ 229.1012, found 229.1020.

1.3 Optimization of the reaction conditions for Synthesis of **3aa**

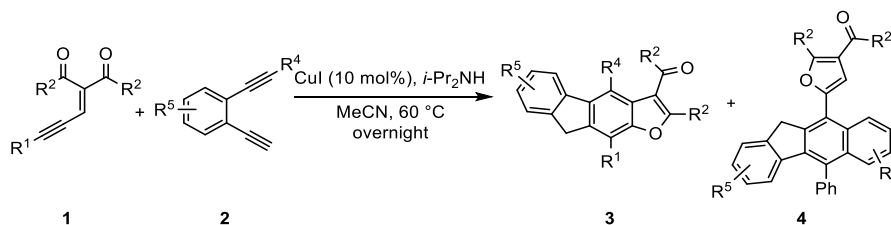
Table S1 Optimization of the Reaction Conditions for Synthesis of **3aa**^a



Entry	Cat.	Base	3aa/4aa ^b	3aa ^c (%)
1	CuI	-	6:1	58
2	CuBr	-	-	trace
3	CuCl	-	-	trace
4	$\text{Cu}(\text{MeCN})_4\text{PF}_4$	-	6:1	34
5	CuI	K_2CO_3	4:1	30
6	CuI	NaHCO_3	5:1	45
7	CuI	<i>i</i> - Pr_2NEt	8:1	69
8	CuI	<i>i</i>-Pr_2NH	8:1	75^d

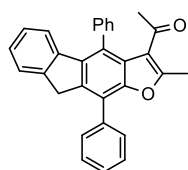
^aThe reaction was performed at 60 °C overnight. The molar ratio of **1a:2a** = 1:1. [**1a**] = 0.1 mmol, Cu(I) = 10 mol %, base (1.0 eq.) in MeCN (1 mL); ^bIsomeric ratio of **3aa** and **4aa** determined by ^1H NMR spectroscopy. ^cYield of **3aa** determined by ^1H NMR spectroscopy. ^dIsolated yield of **3aa**.

1.4 General procedure for the synthesis of **3am-3bm**



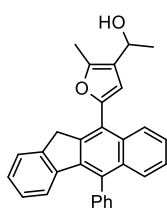
To an acetonitrile (MeCN, 1.0 mL) suspension of CuI (10 mol %) in Schlenk tube with a magnetic bar under nitrogen atmosphere, was added alkynyl (**2**, 0.1 mmol), *i*- Pr_2NH (1 eq.) and enynes (**1**, 0.1 mmol). The reaction mixture was then heated to a temperature of 60 °C and stirred. The reaction was monitored by TLC. The reaction mixture was purified by chromatography with petroleum/ethyl acetate, 20/1, and recrystallization to afford **3**. **4aa** was confirmed after further reduction with NaBH_4 to afford **7aa**.

1-(2-Methyl-4,10-diphenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3aa)



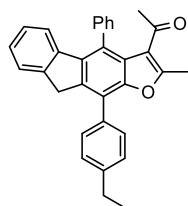
White solid, m. p. = 177-178 °C, yield: 75%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.7$ Hz, 2H), 7.63 – 7.50 (m, 8H), 7.47 (d, $J = 7.4$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.83 (d, $J = 7.9$ Hz, 1H), 4.01 (s, 2H), 2.46 (s, 3H), 1.59 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.2, 157.1, 150.5, 143.9, 141.5, 139.5, 139.2, 135.3, 135.0, 130.1, 129.6, 129.3, 128.6, 128.6, 128.4, 128.0, 126.3, 126.1, 125.5, 124.6, 122.8, 122.2, 121.1, 36.3, 30.7, 13.5. **IR** (KBr, cm^{-1}) 3689, 3057, 2922, 1957, 1893, 1681, 1587, 1446, 1384, 1332, 1273, 1218, 1161, 1118, 1028, 941, 625, 496. **HRMS** (ESI) Calcd for $\text{C}_{30}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 415.1693, found 415.1694.

1-(2-Methyl-5-(5-phenyl-11H-benzo[*b*]fluoren-10-yl)furan-3-yl)ethan-1-ol (7aa)



White solid, m. p. = 178-179 °C, yield: 7%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.4$ Hz, 1H), 7.59 (t, $J = 9.3$ Hz, 4H), 7.50 – 7.36 (m, 5H), 7.21 (d, $J = 7.4$ Hz, 1H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.72 (s, 1H), 6.44 (d, $J = 7.8$ Hz, 1H), 5.01 (d, $J = 6.2$ Hz, 1H), 4.18 (s, 2H), 2.48 (s, 3H), 1.75 (s, 1H), 1.61 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.2, 147.6, 144.2, 141.1, 140.9, 139.0, 137.3, 134.1, 133.2, 130.8, 130.1, 129.2, 127.9, 127.2, 126.7, 126.5, 125.7, 125.6, 125.3, 125.0, 124.7, 124.4, 123.7, 109.7, 63.0, 37.3, 24.2, 12.2. **IR** (KBr, cm^{-1}) 3744, 3521, 3497, 2922, 1540, 761, 700. **HRMS** (ESI) Calcd for $\text{C}_{30}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 439.1669, found. 439.1667.

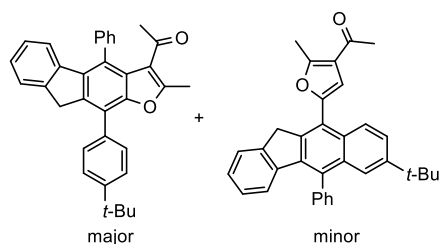
1-(10-(4-Ethylphenyl)-2-methyl-4-phenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3ab)



White solid, m. p. = 166-167 °C, yield: 70%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60 (dd, $J = 20.5, 7.9$ Hz, 7H), 7.45 (dd, $J = 12.3, 7.7$ Hz, 3H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.83 (d, $J = 7.9$ Hz, 1H), 4.02 (s, 2H), 2.82 (q, $J = 7.6$ Hz, 2H), 2.46 (s, 3H), 1.58 (s, 3H), 1.39 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.3, 157.1, 150.6, 145.1, 144.0, 143.9, 141.6, 139.6, 139.3, 135.3, 132.2, 130.2, 129.6, 129.3, 128.4, 128.2, 126.3, 126.1, 125.5, 124.6, 122.8, 122.2, 121.1, 36.4, 30.7, 28.8, 15.4, 13.5. **IR** (KBr, cm^{-1}) 3711, 3060, 2962, 2314, 1685, 1579, 1452, 1333, 1271, 1192, 1110, 1023, 940, 803, 756, 610, 518. **HRMS** (ESI) Calcd for $\text{C}_{32}\text{H}_{26}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 443.2006, found 443.2004.

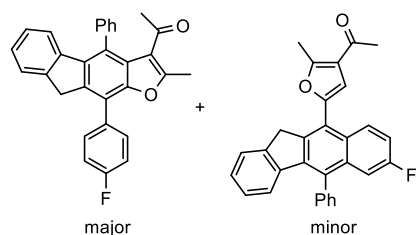
1-(10-(4-(Tert-Butyl)phenyl)-2-methyl-4-phenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3ac)

White solid, m. p. = 222-223 °C, yield: 65%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ Isomer **3ac** δ 7.67 – 7.47



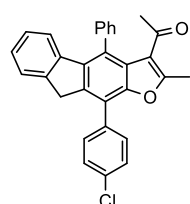
(m, 9H), 7.43 (d, $J = 7.2$ Hz, 1H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.78 (d, $J = 7.9$ Hz, 1H), 4.00 (s, 2H), 2.43 (s, 3H), 1.54 (s, 3H), 1.43 (s, 9H). Isomer **4ac** δ 8.08 (d, $J = 8.9$ Hz, 1H), 6.93 (s, 1H), 6.46 (d, $J = 7.9$ Hz, 1H), 4.14 (s, 2H), 2.78 (s, 3H), 2.55 (s, 3H), 1.27 (s, 9H) ppm (remaining peaks could not be assigned) $^{13}\text{C NMR}$ (100 MHz, CDCl_3) mixtures **3ac** and **4ac** δ 199.3, 194.2, 158.2, 157.0, 150.8, 150.6, 149.5, 148.1, 144.0, 141.6, 141.2, 139.59, 139.30, 138.95, 135.31, 134.91, 131.93, 130.17, 129.98, 129.27, 129.13, 128.37, 127.90, 127.2, 126.58, 126.28, 126.1, 125.6, 125.5, 124.9, 124.8, 124.6, 123.7, 122.9, 122.8, 122.1, 122.0, 121.1, 111.0, 36.5, 34.9, 34.8, 31.5, 31.1, 30.7, 29.7, 29.3, 14.7, 13.5. **IR** (KBr, cm^{-1}) 3703, 3057, 2958, 1680, 1580, 1455, 1270, 1227, 1122, 1024, 945, 811, 732, 616, 556. **HRMS** (ESI) Calcd for $\text{C}_{34}\text{H}_{30}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 493.2138, found 493.2135.

1-(10-(4-Fluorophenyl)-2-methyl-4-phenyl-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3ad)



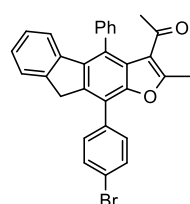
White solid, m. p. = 172-174 °C, yield: 82%. ¹H NMR (400 MHz, CDCl₃) Isomer **3ad** δ 7.66 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.56 (d, *J* = 7.0 Hz, 5H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.29 (s, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 3.97 (s, 2H), 2.46 (s, 3H), 1.58 (s, 3H). Isomer **4ad** δ 8.15 – 8.08 (m, 1H), 6.94 (s, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 4.13 (s, 2H), 2.78 (s, 3H), 2.55 (s, 3H) ppm (remaining peaks could not be assigned) ¹³C NMR (101 MHz, CDCl₃) mixtures **3ad** and **4ad** δ 199.1, 194.1, 161.3, 158.5, 157.0, 150.5, 148.9, 143.7, 141.4, 140.6, 139.5, 139.1, 138.4, 138.3, 135.4, 131.4, 131.3, 130.1, 129.9, 129.4, 129.3, 128.7, 128.5, 128.3, 127.7, 126.7, 126.4, 126.2, 125.6, 124.7, 123.9, 122.8, 121.2, 115.8, 115.6, 111.3, 37.0, 36.2, 30.7, 29.7, 14.7, 13.4. ¹⁹F NMR (376 MHz, CDCl₃) Isomer **3ad** δ -113.8 Isomer **4ad** δ -114.7 IR (KBr, cm⁻¹) 3711, 3062, 2922, 2855, 1680, 1510, 1453, 1226, 1157, 1110, 1022, 948, 808, 757, 613. HRMS (ESI) Calcd for C₃₀H₂₁FO₂ (M+H)⁺ 433.1598, found 443.1597.

1-(10-(4-Chlorophenyl)-2-methyl-4-phenyl-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3ae)



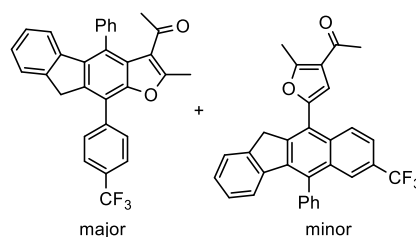
White solid, m. p. = 217-218 °C, yield: 62%. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 8.9, 3.2 Hz, 7H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 3.87 (s, 2H), 2.35 (s, 3H), 1.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 199.1, 157.1, 150.3, 143.7, 141.4, 139.4, 139.0, 135.4, 134.0, 133.4, 131.0, 130.1, 129.3, 128.9, 128.9, 128.5, 126.4, 126.2, 125.6, 124.7, 122.8, 121.2, 120.9, 36.2, 30.7, 13.4. IR (KBr, cm⁻¹) 3710, 3060, 2925, 1582, 1487, 1267, 1225, 1154, 1112, 1021, 934, 790, 754, 701, 480. HRMS (ESI) Calcd for C₃₀H₂₁ClO₂ (M+H)⁺ 449.1303, found 449.1302.

1-(10-(4-Bromophenyl)-2-methyl-4-phenyl-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3af)



White solid, m. p. = 135-136 °C, yield: 65%. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.51 (m, 7H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.96 (s, 2H), 2.42 (s, 3H), 1.55 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 199.2, 157.1, 150.5, 143.9, 141.5, 139.6, 139.2, 135.3, 135.0, 130.2, 129.7, 129.3, 128.7, 128.6, 128.4, 128.0, 126.4, 126.1, 125.5, 124.7, 122.8, 122.2, 121.2, 36.3, 30.7, 13.5. IR (KBr, cm⁻¹) 3711, 3058, 2922, 1679, 1582, 1445, 1385, 1335, 1272, 1224, 1159, 1116, 1025, 944, 802, 760, 704, 625, 497. HRMS (ESI) Calcd for C₃₀H₂₁BrO₂ (M+Na)⁺ 515.0617, found 515.0616.

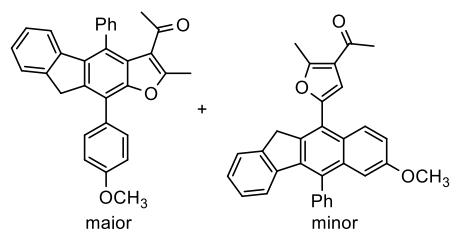
1-(2-Methyl-4-phenyl-10-(4-(trifluoromethyl)phenyl)-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3ag)



White solid, m. p. = 187-189 °C, yield: 66%. ¹H NMR (400 MHz, CDCl₃) Isomer **3ag** δ 7.80 (dd, *J* = 17.1, 8.1 Hz, 4H), 7.52 (dd, *J* = 17.4, 6.6 Hz, 5H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.94 (s, 2H), 2.42 (s, 3H), 1.56 (s, 3H). Isomer **4ag** δ 8.25 (d, *J* = 8.9 Hz, 1H), 7.89 (s, 1H), 7.63 (d, *J* = 4.5 Hz, 1H), 6.96 (s, 1H), 6.45 (d, *J* = 7.9 Hz, 1H), 4.17 (s, 1H), 2.79 (s, 1H), 2.56 (s, 1H) ppm (remaining peaks could not be assigned) ¹³C NMR (100 MHz, CDCl₃)

Isomer **3ag** δ 199.0, 157.1, 150.2, 143.6, 141.3, 139.4, 138.9, 135.6, 130.0, 130.0, 129.8, 129.5, 129.3, 128.6, 126.5, 126.3, 125.7, 125.7, 125.6, 124.7, 122.8, 121.2, 120.7, 36.2, 30.7, 13.4. Isomer **4ag** δ 194.0, 138.8, 29.73 ppm (the remaining signals could not be assigned) ^{19}F NMR (376 MHz, CDCl_3) Isomer **3ag** δ -62.5. IR (KBr, cm^{-1}) 3624, 3061, 2923, 2855, 1679, 1580, 1448, 1398, 1322, 1275, 1228, 1166, 1122, 1068, 1022, 946, 845, 758, 618. HRMS (ESI) Calcd for $\text{C}_{31}\text{H}_{21}\text{F}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 483.1566, found 483.1566.

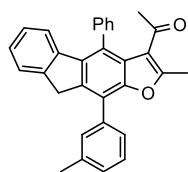
1-(10-(4-Methoxyphenyl)-2-methyl-4-phenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (**3ah**)



Colorless oil, yield: 46%. ^1H NMR (400 MHz, CDCl_3) Isomer **3ah** δ 7.60 (dd, $J = 7.1, 3.9$ Hz, 3H), 7.52 (d, $J = 2.8$ Hz, 4H), 7.42 (d, $J = 7.2$ Hz, 1H), 7.16 (dd, $J = 8.5, 5.2$ Hz, 1H), 7.10 (d, $J = 8.5$ Hz, 2H), 7.00 (dd, $J = 11.7, 7.3$ Hz, 1H), 6.79 (d, $J = 7.9$ Hz, 1H), 3.96 (s, 2H), 3.90 (s, 3H), 2.43 (s, 3H), 1.54 (s, 3H). Isomer **4ah** δ 8.05 (d, $J =$

9.2 Hz, 1H), 6.92 (s, 1H), 6.88 (s, 1H), 6.45 (d, $J = 7.9$ Hz, 1H), 4.11 (s, 1H), 3.69 (s, 3H), 2.78 (s, 2H), 2.56 (s, 2H) ppm (remaining peaks could not be assigned) ^{13}C NMR (100 MHz, CDCl_3) mixtures **3ah** and **4ah** δ 199.3, 194.2, 159.3, 158.3, 157.3, 157.0, 150.6, 149.3, 144.1, 143.9, 141.6, 141.1, 139.5, 139.3, 139.3, 139.0, 137.9, 135.3, 134.6, 133.7, 130.8, 130.1, 129.9, 129.5, 129.3, 129.3, 128.4, 128.2, 128.0, 127.3, 127.1, 126.7, 126.6, 126.3, 126.1, 125.5, 124.8, 124.6, 123.7, 123.1, 122.9, 122.8, 121.9, 121.1, 118.0, 114.1, 111.0, 105.7, 55.4, 55.1, 36.9, 36.4, 30.7, 29.7, 29.4, 14.7, 13.5. IR (KBr, cm^{-1}) 3057, 2922, 2846, 1676, 1611, 1508, 1455, 1349, 1283, 1235, 1177, 1121, 1032, 949, 832, 732, 620, 514. HRMS (ESI) Calcd for $\text{C}_{31}\text{H}_{24}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 445.1798, found 445.1797.

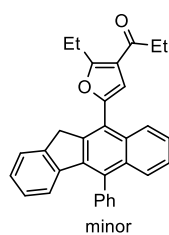
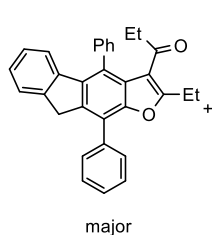
1-(2-Methyl-4-phenyl-10-(*m*-tolyl)-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (**3ai**)



White solid, m. p. = 131-132 $^{\circ}\text{C}$, yield: 65%. ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.49 (m, 5H), 7.44 (t, $J = 7.4$ Hz, 4H), 7.29 (d, $J = 4.0$ Hz, 1H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.79 (d, $J = 7.9$ Hz, 1H), 3.96 (s, 2H), 2.48 (s, 3H), 2.42 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.2, 157.1, 150.6, 144.0, 141.6, 139.6, 139.3, 138.3, 135.3, 135.0, 130.3, 130.2, 129.3, 128.8, 128.6,

128.5, 128.4, 126.8, 126.4, 126.1, 125.5, 124.7, 122.8, 122.4, 121.2, 36.3, 30.7, 21.7, 13.5. IR (KBr, cm^{-1}) 3690, 3052, 2921, 1680, 1587, 1447, 1382, 1336, 1276, 1233, 1161, 1115, 1031, 948, 903, 628. HRMS (ESI) Calcd for $\text{C}_{31}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 451.1669, found 451.1670.

1-(2-Ethyl-4,10-diphenyl-9H-fluoreno[2,3-*b*]furan-3-yl)propan-1-one (**3aj**)

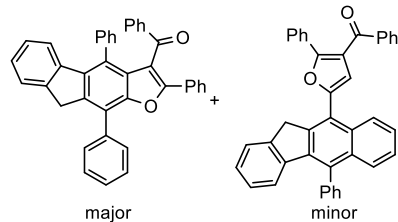


Colorless oil, yield: 84%. ^1H NMR (400 MHz, CDCl_3) Isomer **3aj** δ 7.56 (d, $J = 7.3$ Hz, 2H), 7.50 – 7.31 (m, 8H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.3$ Hz, 1H), 6.86 (dd, $J = 14.9, 7.4$ Hz, 1H), 6.63 (d, $J = 7.9$ Hz, 1H), 3.84 (s, 2H), 2.60 (q, $J = 7.5$ Hz, 2H), 1.78 (q, $J = 7.2$ Hz, 2H), 1.16 – 1.07 (m, 3H), 0.55 (t, $J = 7.2$ Hz, 3H). Isomer **4aj** δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.08 (s, 2H),

6.34 (d, $J = 7.9$ Hz, 1H), 4.03 (s, 2H), 3.11 (q, $J = 7.5$ Hz, 2H), 2.78 (q, $J = 7.2$ Hz, 2H), 1.28 (dd, $J = 15.5, 8.0$ Hz, 3H) ppm (remaining peaks could not be assigned) ^{13}C NMR (100 MHz, CDCl_3) mixtures **3aj** and **4aj** δ 203.2, 197.2, 163.1, 160.2, 150.5, 149.2, 143.9, 141.6, 141.0, 139.4, 138.8, 135.2, 135.2, 134.8, 133.3, 130.9, 130.0, 129.7, 129.3, 128.6, 128.6, 128.4, 128.0, 127.9, 127.4, 126.9, 126.7, 126.3, 126.1, 125.8, 125.6, 125.2, 124.8, 124.7, 123.8, 122.7, 122.2, 121.4, 119.5, 110.8, 37.8, 37.1, 36.4, 34.7, 29.8, 22.0, 20.9, 13.0, 12.3, 8.3, 8.1. IR (KBr, cm^{-1}) 3692, 3058, 2976, 2932, 1955, 1685, 1588, 1452,

1379, 1329, 1245, 1116, 1019, 919, 758, 706, 601, 496. **HRMS** (ESI) Calcd for $C_{32}H_{26}O_2$ (M+H)⁺ 443.2006, found 443.2008.

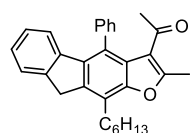
Phenyl(2,4,10-triphenyl-9H-fluoreno[2,3-*b*]furan-3-yl)methanone (3ak)



White solid, m. p. = 150-151 °C, yield: 63%. ¹H NMR (400 MHz, CDCl₃) Isomer **3ak** δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.44 (m, 5H), 7.44 – 7.34 (m, 4H), 7.34 – 7.27 (m, 2H), 7.21-7.16 (m, 1H), 7.13 – 7.05 (m, 5H), 6.93 (m, 4H), 6.78 (t, *J* = 7.6 Hz, 1H), 3.90 (s, 2H). Isomer **4ak** δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 6.35 (d,

J = 7.7 Hz, 3H), 4.14 (s, 2H) ppm (remaining peaks could not be assigned) ¹³C NMR (100 MHz, CDCl₃) mixtures **3ak** and **4ak** δ 193.9, 191.9, 155.6, 153.0, 150.6, 150.3, 143.9, 143.7, 141.8, 141.4, 141.0, 140.2, 138.9, 138.2, 137.6, 137.0, 135.8, 135.2, 135.1, 133.4, 133.3, 133.1, 130.8, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 128.8, 128.7, 128.6, 128.6, 128.2, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.0, 126.7, 126.4, 126.3, 126.2, 125.7, 125.2, 124.9, 124.6, 123.8, 123.1, 122.8, 122.3, 117.2, 114.7, 37.4, 36.5. **IR** (KBr, cm⁻¹) 3728, 3059, 2922, 1957, 1815, 1662, 1593, 1486, 1450, 1373, 1326, 1276, 1168, 1067, 1025, 891, 838, 755, 605, 508. **HRMS** (ESI) Calcd for $C_{40}H_{26}O_2$ (M+H)⁺ 539.2006, found 539.2009.

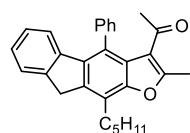
1-(10-Hexyl-2-methyl-4-phenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3al)



White solid, m. p. = 100-101 °C, yield: 95%. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 6.6 Hz, 4H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 3.95 (s, 2H), 3.02 (t, *J* = 7.7 Hz, 2H), 2.48 (s, 3H), 1.82 – 1.76 (m, 2H), 1.51 (s, 3H), 1.47 (s, 2H), 1.36 (s, 4H), 0.91 (t, *J* = 6.4

Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 199.4, 156.5, 151.7, 143.6, 142.0, 139.5, 134.7, 130.2, 129.1, 128.2, 127.1, 126.3, 125.9, 124.9, 124.7, 122.7, 121.9, 121.2, 35.2, 31.8, 30.6, 29.6, 29.2, 27.6, 22.7, 14.2, 13.5. **IR** (KBr, cm⁻¹) 3058, 2926, 2859, 1682, 1584, 1452, 1387, 1342, 1265, 1160, 1032, 953, 730, 622. **HRMS** (ESI) Calcd for $C_{30}H_{30}O_2$ (M+H)⁺ 423.2319, found 423.2318.

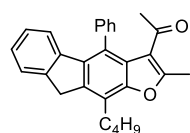
1-(2-Methyl-10-pentyl-4-phenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3am)



White solid, m. p. = 118-119 °C, yield: 88%. ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.41 (m, 6H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 2H), 3.04 – 2.94 (m, 2H), 2.48 (s, 3H), 1.86 – 1.76 (m, 2H), 1.51 (s, 3H), 1.44 (dd, *J* = 8.3, 4.9 Hz, 4H), 0.93 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz,

CDCl₃) δ 199.4, 156.5, 151.7, 143.6, 142.0, 139.5, 134.8, 130.2, 129.2, 128.2, 127.1, 126.3, 125.9, 124.9, 124.7, 123.3, 122.7, 121.9, 121.2, 35.2, 32.0, 30.6, 29.0, 27.6, 22.6, 14.1, 13.5. **IR** (KBr, cm⁻¹) 3718, 3059, 2928, 2861, 2315, 1681, 1582, 1452, 1388, 1339, 1263, 1157, 1092, 1023, 952, 802, 756, 624. **HRMS** (ESI) Calcd for $C_{29}H_{28}O_2$ (M+H)⁺ 409.2162, found 409.2161.

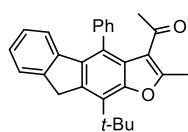
1-(10-Butyl-2-methyl-4-phenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3an)



White solid, m. p. = 139-149 °C, yield: 86%. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 5.6 Hz, 4H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 3.99 (s, 2H), 3.06 (t, *J* = 7.7 Hz, 2H), 2.52 (s, 3H), 1.86 – 1.78 (m, 2H), 1.55 (s, 3H), 1.54 – 1.47 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

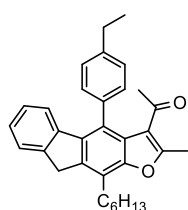
¹³C NMR (100 MHz, CDCl₃) δ 199.4, 156.5, 151.7, 143.6, 142.0, 139.5, 134.8, 130.2, 129.3, 129.2, 128.2, 127.1, 126.3, 125.9, 124.9, 124.7, 122.7, 121.8, 121.2, 35.2, 31.5, 30.6, 27.3, 23.0, 14.1, 13.5. **IR** (KBr, cm⁻¹) 3728, 3058, 2939, 2865, 1681, 1584, 1452, 1386, 1267, 1159, 1069, 1023, 953, 755, 626. **HRMS** (ESI) Calcd for $C_{28}H_{26}O_2$ (M+Na)⁺ 417.1825, found 417.1830.

1-(10-(Tert-butyl)-2-methyl-4-phenyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3ao)



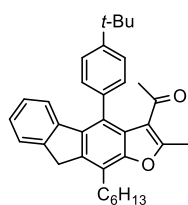
White solid, m. p. = 177-178 °C, yield: 94%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (dt, $J = 8.5, 3.9$ Hz, 6H), 7.14 (t, $J = 7.4$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.62 (d, $J = 7.9$ Hz, 1H), 4.26 (s, 2H), 2.47 (s, 3H), 1.73 (s, 9H), 1.52 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.7, 155.2, 151.8, 143.9, 140.7, 139.5, 137.6, 136.1, 130.2, 130.0, 129.2, 128.3, 127.6, 126.2, 126.1, 125.9, 124.1, 122.7, 120.6, 39.0, 37.3, 31.7, 30.7, 13.4. **IR** (KBr, cm^{-1}) 3713, 3046, 2920, 2851, 1680, 1591, 1451, 1369, 1232, 1139, 1027, 953, 807, 757, 696, 626. **HRMS** (ESI) Calcd for $\text{C}_{28}\text{H}_{26}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 395.2006, found 395.2005.

1-(4-(4-Ethylphenyl)-10-hexyl-2-methyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3ba)



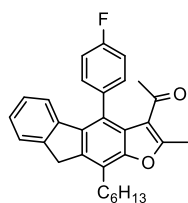
Colorless oil, yield: 56%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.4$ Hz, 1H), 7.35 (q, $J = 8.0$ Hz, 4H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 7.9$ Hz, 1H), 3.94 (s, 2H), 3.01 (t, $J = 7.7$ Hz, 2H), 2.77 (q, $J = 7.6$ Hz, 2H), 2.47 (s, 3H), 1.83 – 1.74 (m, 2H), 1.47 (s, 5H), 1.34 (dd, $J = 13.6, 5.9$ Hz, 7H), 0.91 (t, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.8, 156.5, 151.7, 144.4, 143.6, 142.1, 139.5, 136.7, 134.7, 130.1, 128.6, 127.2, 126.3, 125.8, 125.1, 124.7, 122.7, 121.7, 121.3, 35.2, 31.8, 30.5, 29.6, 29.3, 28.8, 27.6, 22.7, 15.8, 14.2, 13.4. **IR** (KBr, cm^{-1}) 3729, 2927, 2861, 1680, 1583, 1454, 1388, 1264, 1157, 1025, 953, 836, 625. **HRMS** (ESI) Calcd for $\text{C}_{32}\text{H}_{34}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 473.2451, found 473.2449.

1-(4-(4-(Tert-butyl)phenyl)-10-hexyl-2-methyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3bb)

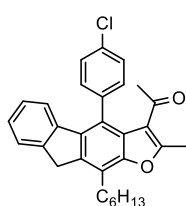


Colorless oil, yield: 60%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (t, $J = 8.3$ Hz, 3H), 7.29 (d, $J = 7.9$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 6.93 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 7.9$ Hz, 1H), 3.85 (s, 2H), 2.92 (t, $J = 7.7$ Hz, 2H), 2.39 (s, 3H), 1.71 (dd, $J = 14.9, 7.4$ Hz, 2H), 1.38 (d, $J = 8.5$ Hz, 2H), 1.34 (s, 12H), 1.31 – 1.24 (m, 4H), 0.83 (t, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 199.6, 156.6, 151.7, 151.4, 143.6, 142.2, 139.5, 136.5, 134.8, 129.9, 127.1, 126.3, 126.0, 125.8, 125.1, 124.7, 122.8, 121.7, 121.4, 35.2, 34.8, 31.8, 31.5, 30.4, 29.6, 29.3, 27.6, 22.7, 14.2, 13.4. **IR** (KBr, cm^{-1}) 3710, 3051, 2955, 2862, 1681, 1582, 1456, 1389, 1268, 1194, 1159, 1109, 1023, 952, 837, 758, 622, 561. **HRMS** (ESI) Calcd for $\text{C}_{34}\text{H}_{38}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 479.2945, found 479.2946.

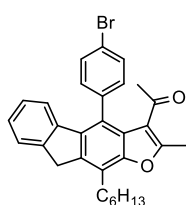
1-(4-(4-Fluorophenyl)-10-hexyl-2-methyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3bc)



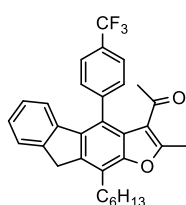
White solid, m. p. = 130-131 °C, yield: 74%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.4$ Hz, 1H), 7.45 – 7.37 (m, 2H), 7.21 (dd, $J = 15.4, 7.8$ Hz, 3H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.72 (d, $J = 7.9$ Hz, 1H), 3.94 (s, 2H), 3.01 (t, $J = 7.7$ Hz, 2H), 2.49 (s, 3H), 1.83 – 1.75 (m, 2H), 1.63 (s, 3H), 1.50 – 1.42 (m, 2H), 1.40 – 1.28 (m, 4H), 0.91 (t, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.0, 162.7 (d, $J = 247.9$ Hz), 156.5, 151.7, 143.7, 141.9, 139.5, 135.5 (d, $J = 3.3$ Hz), 135.0, 131.9, 131.8, 131.3, 128.3, 126.4, 126.0, 125.8, 125.0, 124.8, 122.5, 122.1, 121.0, 116.16 (d, $J = 21.3$ Hz), 35.2, 31.8, 30.9, 29.6, 29.2, 27.6, 22.7, 14.2, 13.5. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -113.4. **IR** (KBr, cm^{-1}) 3713, 3063, 2929, 2860, 2315, 1682, 1589, 1508, 1455, 1389, 1340, 1226, 1155, 1088, 1022, 951, 839, 728, 626, 517. **HRMS** (ESI) Calcd for $\text{C}_{30}\text{H}_{29}\text{FO}_2$ ($\text{M}+\text{H}$) $^+$ 441.2224, found 441.2230.

1-(4-(4-Chlorophenyl)-10-hexyl-2-methyl-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3bd)

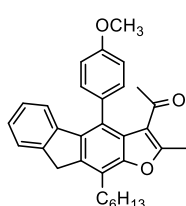
White solid, m. p. = 103-104 °C, yield: 98%. $^1\text{H NMR}$ (400 MHz, DMSO) δ 7.49 (d, $J = 7.8$ Hz, 3H), 7.38 (d, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 7.9$ Hz, 1H), 3.92 (s, 2H), 3.00 (t, $J = 7.6$ Hz, 2H), 2.49 (s, 3H), 1.82 – 1.74 (m, 2H), 1.63 (s, 3H), 1.45 (d, $J = 7.3$ Hz, 2H), 1.36 (s, 4H), 0.91 (t, $J = 6.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, DMSO) δ 198.9, 156.6, 151.7, 143.7, 141.8, 139.6, 137.9, 134.8, 134.2, 131.6, 129.4, 126.4, 126.1, 125.6, 124.9, 124.8, 122.5, 122.3, 121.0, 35.2, 31.8, 30.9, 29.6, 29.2, 27.6, 22.7, 14.2, 13.6. **IR** (KBr, cm^{-1}) 3710, 2926, 2859, 1682, 1583, 1453, 1389, 1342, 1262, 1160, 1090, 1019, 952, 830, 727, 625, 502. **HRMS** (ESI) Calcd for $\text{C}_{30}\text{H}_{29}\text{ClO}_2$ ($\text{M}+\text{H}$) $^+$ 457.1929, found 457.1930.

1-(4-(4-Bromophenyl)-10-hexyl-2-methyl-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3be)

White solid, m. p. = 109-110 °C, yield: 78%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 7.4$ Hz, 1H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 7.9$ Hz, 1H), 3.92 (s, 2H), 3.06 – 2.92 (m, 2H), 2.49 (s, 3H), 1.82 – 1.73 (m, 2H), 1.62 (s, 3H), 1.49 – 1.42 (m, 2H), 1.35 (dd, $J = 9.2, 5.9$ Hz, 4H), 0.91 (t, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 198.9, 156.6, 151.7, 143.7, 141.7, 139.6, 138.4, 134.7, 132.3, 131.9, 131.0, 126.4, 126.1, 125.5, 124.9, 124.7, 122.5, 122.3, 121.0, 35.2, 31.8, 30.9, 29.6, 29.2, 27.6, 22.7, 14.2, 13.6. **IR** (KBr, cm^{-1}) 2926, 2860, 1680, 1583, 1453, 1391, 1230, 1071, 1014, 956, 896, 827, 726, 627, 498. **HRMS** (ESI) Calcd for $\text{C}_{30}\text{H}_{29}\text{BrO}_2$ ($\text{M}+\text{H}$) $^+$ 501.1424, found 501.1425.

1-(10-Hexyl-2-methyl-4-(4-(trifluoromethyl)phenyl)-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3bf)

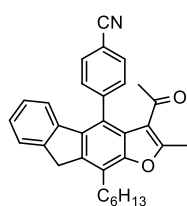
White solid, m. p. = 145-146 °C, yield: 75%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.8$ Hz, 2H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.45 (d, $J = 7.4$ Hz, 1H), 7.12 (t, $J = 7.4$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.58 (d, $J = 7.9$ Hz, 1H), 3.88 (s, 2H), 2.95 (t, $J = 7.7$ Hz, 2H), 2.43 (s, 3H), 1.76 – 1.68 (m, 2H), 1.50 (s, 3H), 1.39 (d, $J = 7.4$ Hz, 2H), 1.28 (d, $J = 11.8$ Hz, 4H), 0.84 (t, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 198.5, 156.8, 151.7, 143.7, 143.4, 141.5, 139.7, 134.7, 130.7, 130.4 (q, $J = 32.6$ Hz), 126.5, 126.2, 126.0 (q, $J = 3.6$ Hz), 125.3, 124.9, 124.6, 122.9, 122.6, 122.4, 120.9, 117.7, 35.2, 31.8, 30.7, 29.6, 29.2, 27.6, 22.7, 14.1, 13.6. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.3. **IR** (KBr, cm^{-1}) 3711, 2929, 2861, 1685, 1580, 1456, 1395, 1323, 1264, 1165, 1125, 1067, 1020, 952, 846, 759, 725, 619. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{29}\text{F}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 491.2192, found 491.2193.

1-(10-Hexyl-4-(4-methoxyphenyl)-2-methyl-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3bg)

White solid, m. p. = 117-118 °C, yield: 61%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (d, $J = 7.4$ Hz, 1H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.07 (t, $J = 9.0$ Hz, 3H), 6.89 (d, $J = 7.8$ Hz, 1H), 3.96 (d, $J = 7.5$ Hz, 5H), 3.04 (t, $J = 7.7$ Hz, 2H), 2.52 (s, 3H), 1.87 – 1.79 (m, 2H), 1.62 (s, 3H), 1.50 (d, $J = 7.3$ Hz, 2H), 1.44 – 1.35 (m, 4H), 0.96 (t, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.6, 159.5, 156.3, 151.7, 143.6, 142.2, 139.5, 135.1, 131.8, 131.3, 126.8, 126.3, 125.8,

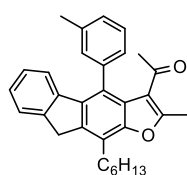
125.3, 124.7, 122.7, 121.7, 121.3, 114.5, 55.4, 35.2, 31.8, 30.8, 29.6, 29.3, 27.6, 22.7, 14.2, 13.4. **IR** (KBr, cm^{-1}) 3714, 2929, 2859, 2314, 1682, 1597, 1513, 1454, 1389, 1342, 1284, 1246, 1173, 1105, 1031, 951, 834, 758, 728, 624. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{32}\text{O}_3$ ($\text{M}+\text{H}$)⁺ 453.2424, found 453.2426.

4-(3-Acetyl-10-hexyl-2-methyl-9H-fluoreno[2,3-*b*]furan-4-yl)benzonitrile (3bh)



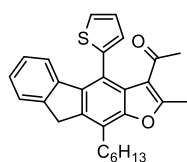
White solid, m. p. = 133-134 °C, yield: 58%. **¹H NMR** (400 MHz, CDCl_3) δ 7.85 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 7.4 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 7.9 Hz, 1H), 3.98 (s, 2H), 3.05 (t, J = 7.7 Hz, 2H), 2.57 (s, 3H), 1.85 – 1.80 (m, 2H), 1.79 (s, 3H), 1.53 – 1.46 (m, 2H), 1.43 – 1.35 (m, 4H), 0.95 (t, J = 6.7 Hz, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 197.6, 157.2, 151.7, 144.6, 143.7, 141.4, 139.7, 134.7, 132.7, 131.1, 126.5, 126.3, 125.0, 125.0, 124.2, 122.8, 122.3, 120.6, 118.8, 111.9, 35.2, 31.8, 31.0, 29.5, 29.2, 27.6, 22.7, 14.2, 14.0. **IR** (KBr, cm^{-1}) 3714, 3060, 2928, 2860, 2314, 2227, 1686, 1593, 1454, 1394, 1340, 1265, 1193, 1103, 1023, 952, 841, 758, 613, 553. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{29}\text{NO}_2$ ($\text{M}+\text{H}$)⁺ 448.2271, found 448.2276.

1-(10-Hexyl-2-methyl-4-(*m*-tolyl)-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3bi)



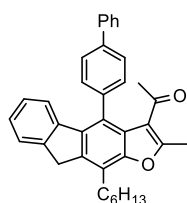
Colorless oil, m. p. = 177-178 °C, yield: 67%. **¹H NMR** (400 MHz, CDCl_3) δ 7.42 (d, J = 7.4 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.20 – 7.16 (m, 3H), 7.09 (t, J = 7.3 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 3.86 (s, 2H), 2.93 (t, J = 7.7 Hz, 2H), 2.40 (s, 3H), 2.32 (s, 3H), 1.74 – 1.67 (m, 2H), 1.43 (s, 3H), 1.37 (d, J = 7.2 Hz, 2H), 1.28 (d, J = 3.1 Hz, 4H), 0.83 (t, J = 6.7 Hz, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 199.5, 156.3, 151.7, 143.6, 142.1, 139.5, 139.3, 138.9, 134.6, 130.8, 129.0, 128.8, 127.3, 126.3, 125.8, 124.9, 124.7, 123.3, 122.8, 121.7, 121.3, 35.2, 31.8, 30.6, 29.6, 29.3, 27.6, 22.7, 21.5, 14.2, 13.5. **IR** (KBr, cm^{-1}) 3692, 3045, 2926, 2860, 1683, 1588, 1453, 1386, 1343, 1271, 1207, 1155, 1034, 954, 882, 625. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{32}\text{O}_2$ ($\text{M}+\text{Na}$)⁺ 459.2295, found 459.2297.

1-(10-Hexyl-2-methyl-4-(thiophen-2-yl)-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3bj)



White solid, m. p. = 105-106 °C, yield: 63%. **¹H NMR** (400 MHz, CDCl_3) δ 7.56 – 7.46 (m, 2H), 7.27 (d, J = 2.0 Hz, 1H), 7.19 (dd, J = 13.3, 6.1 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.93 (s, 2H), 3.00 (t, J = 7.7 Hz, 2H), 2.48 (s, 3H), 1.83 – 1.74 (m, 2H), 1.68 (s, 3H), 1.49 – 1.42 (m, 2H), 1.40 – 1.30 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 199.4, 156.4, 151.7, 143.6, 141.9, 139.7, 139.4, 135.6, 129.9, 126.6, 126.5, 126.0, 125.6, 124.7, 124.3, 122.5, 122.2, 121.4, 121.2, 35.2, 31.8, 30.2, 29.6, 29.2, 27.6, 22.7, 14.2, 13.5. **IR** (KBr, cm^{-1}) 3443, 3101, 2925, 2859, 1680, 1585, 1454, 1385, 1260, 1201, 1154, 1038, 955, 841, 758, 726, 640. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{32}\text{O}_2$ ($\text{M}+\text{Na}$)⁺ 459.2295, found 459.2297.

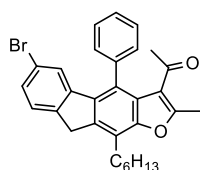
1-(4-([1,1'-Biphenyl]-4-yl)-10-hexyl-2-methyl-9H-fluoreno[2,3-*b*]furan-3-yl)ethan-1-one (3bk)



White solid, m. p. = 148-149 °C, yield: 83%. **¹H NMR** (400 MHz, CDCl_3) δ 7.83 (dd, J = 11.4, 7.8 Hz, 4H), 7.64 – 7.54 (m, 5H), 7.46 (t, J = 7.3 Hz, 1H), 7.25 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 4.02 (s, 2H), 3.09 (t, J = 7.6 Hz, 2H), 2.57 (s, 3H), 1.94 – 1.82 (m, 2H), 1.63 (s, 3H), 1.56 (s, 2H), 1.45 (d, J = 3.1 Hz, 4H), 1.01 (d, J = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 199.4, 156.6, 151.8, 143.7, 142.0, 140.8, 140.4, 139.6, 138.5, 134.8, 130.7, 129.0, 127.7,

127.1, 126.7, 126.4, 126.0, 125.0, 124.8, 122.8, 122.0, 121.3, 35.2, 31.8, 30.8, 29.6, 29.3, 27.7, 22.8, 14.2, 13.5. **IR** (KBr, cm^{-1}) 3714, 3054, 2926, 2859, 2315, 1683, 1585, 1456, 1342, 1265, 1018, 952, 842, 755, 624. **HRMS** (ESI) Calcd for $\text{C}_{34}\text{H}_{32}\text{O}_2$ ($\text{M}+\text{Na}$)⁺ 495.2295, found 495.2283.

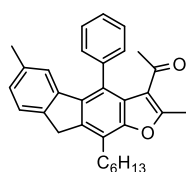
1-(10-Hexyl-2-methyl-4-(naphthalen-2-yl)-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3bl)



White solid, m. p. = 117-118 °C, yield: 68%. **¹H NMR** (400 MHz, CDCl_3) δ 7.56 (s, 3H), 7.46 (s, 2H), 7.36 (s, 1H), 7.31 (s, 1H), 6.85 (s, 1H), 3.91 (s, 2H), 3.02 (s, 2H), 2.52 (s, 3H), 1.80 (d, $J = 6.7$ Hz, 2H), 1.55 (s, 3H), 1.49 (s, 2H), 1.38 (s, 4H), 0.94 (s, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 199.2, 156.9, 151.9, 144.1, 142.2, 139.7, 138.8, 133.6, 129.9, 129.3, 128.5, 127.5, 125.9, 125.8, 124.9, 122.0, 121.1, 120.3,

34.8, 31.8, 30.7, 29.6, 29.2, 27.6, 22.7, 14.2, 13.5. **IR** (KBr, cm^{-1}). 3849, 3704, 3522, 3498, 2925, 1682, 1588, 1448, 655. **HRMS** (ESI) Calcd for $\text{C}_{30}\text{H}_{29}\text{BrO}_2$ ($\text{M}+\text{H}$)⁺ 501.1424, found 501.1421.

1-(10-Hexyl-2,6-dimethyl-4-phenyl-9H-fluoreno[2,3-b]furan-3-yl)ethan-1-one (3bm)

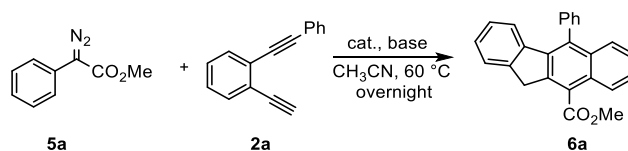


White solid, m. p. = 116-117 °C, yield: 63%. **¹H NMR** (400 MHz, CDCl_3) δ 7.51 (d, $J = 14.1$ Hz, 5H), 7.41 (d, $J = 7.1$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.58 (s, 1H), 3.93 (s, 2H), 3.03 (s, 2H), 2.51 (s, 3H), 2.15 (s, 3H), 1.81 (s, 2H), 1.55 (s, 3H), 1.49 (s, 2H), 1.39 (s, 4H), 0.94 (s, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 199.5, 156.5, 151.6, 142.1, 140.7, 139.9, 139.5, 135.7, 134.8, 130.2, 129.1, 128.1, 127.0, 126.8,

124.7, 124.4, 123.5, 121.8, 121.2, 34.8, 31.8, 30.7, 29.6, 29.26, 27.6, 22.7, 21.7, 14.2, 13.5. **IR** (KBr, cm^{-1}) 3925, 3817, 3742, 3565, 3524, 3481, 3456, 3425, 2927, 1680, 1581, 1460, 1387, 1284, 1264, 1208, 1111, 1072, 1029, 952, 805, 724, 702, 627. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{32}\text{O}_2$ ($\text{M}+\text{Na}$)⁺ 459.2295, found 459.2290.

1.5 Optimization of the reaction conditions for synthesis of 6a

Table S2. Optimization of the reaction conditions for synthesis of **6a**^a

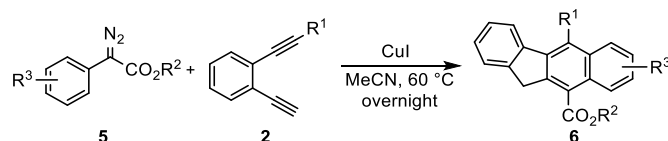


Entry	Cat. (5 mol %)	Base	Yield (%) ^b
1	CuBr	-	12
2	CuCl	-	41
3	$\text{Cu}(\text{MeCN})_4\text{PF}_4$	-	45
4	CuI	-	68^c
5	CuI	i-Pr ₂ NH	59
6 ^d	CuI	-	51

^aThe reaction was performed at 60 °C overnight. The molar ratio of **5a:2a** = 1.5:1. [**2a**] = 0.1M.

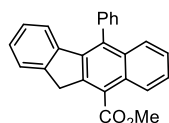
^bYield of **6a** determined by ¹H NMR spectroscopy. ^cIsolated yield of **6a**. ^d**5a:2a** = 1:1.

1.6 General procedure for the synthesis of 6a-6j



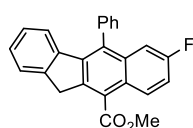
To an acetonitrile (MeCN, 1.0 mL) suspension of CuI (10 mol %) in Schlenk tube with a magnetic bar under nitrogen atmosphere, was added alkyne (**2**, 0.1 mmol) and diazonium (**5**, 0.15 mmol). The reaction was stirred at 60 °C unless being noted and monitored by TLC. After accomplished, the reaction mixture was purified by chromatography with petroleum/ethyl acetate(v/v: 20/1) to obtain **6**.

Methyl 5-phenyl-11H-benzo[*b*]fluorene-10-carboxylate (**6a**)



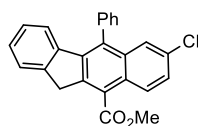
White solid, m. p. = 145-146 °C, yield = 68%; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 8.5 Hz, 1H), 7.54 (dt, *J* = 16.7, 7.3 Hz, 6H), 7.38 (t, *J* = 8.0 Hz, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 4.01 (s, 2H), 4.29 (s, 2H), 4.11 (s, 3H). ¹³C NMR (100MHz, CDCl₃) δ 168.9, 143.9, 142.8, 140.4, 138.6, 137.4, 136.8, 133.2, 129.8, 129.7, 129.3, 128.1, 127.5, 126.8, 126.6, 126.6, 125.7, 125.3, 124.9, 124.7, 123.7, 52.2, 37.5. IR (KBr, cm⁻¹) 3777, 3437, 3061, 2955, 1719, 1633, 1441, 1392, 1254, 1210, 1037, 969, 752, 598. HRMS (ESI) Calcd for C₂₅H₁₈O₂ (M+H)⁺ 351.1380, found 351.1381.

Methyl 7-fluoro-5-phenyl-11H-benzo[*b*]fluorene-10-carboxylate (**6b**)



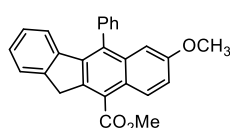
White solid, m. p. = 126-127 °C, yield = 56%; ¹H NMR (400 MHz, CDCl₃) δ 8.42 – 8.29 (m, 1H), 7.47 (d, *J* = 3.8 Hz, 3H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 11.0 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 7.9 Hz, 1H), 4.15 (s, 2H), 3.99 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 160.6 (d, *J* = 245.9 Hz), 144.1, 142.4, 140.1, 138.5, 138.1, 136.2, 136.2, 134.6, 134.6, 129.6, 129.4, 128.4, 127.9, 126.7, 124.8, 123.8, 116.7, 116.4, 110.4, 110.2, 52.2, 37.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.2. IR (KBr, cm⁻¹) 3714, 3061, 2952, 1719, 1619, 1508, 1437, 1210, 1124, 1038, 966, 864, 825, 751, 587, 453. HRMS (ESI) Calcd for C₂₅H₁₇FO₂ (M+H)⁺ 369.1285, found 369.1289.

Methyl 7-chloro-5-phenyl-11H-benzo[*b*]fluorene-10-carboxylate (**6c**)

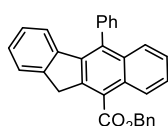


White solid, m. p. = 173-174 °C, yield = 55%; ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 5.6 Hz, 3H), 7.51 (d, *J* = 6.2 Hz, 2H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.25 (s, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.9 Hz, 1H), 4.29 (s, 2H), 4.13 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 144.0, 143.3, 140.0, 138.6, 137.8, 136.0, 134.2, 131.9, 129.7, 129.4, 128.4, 128.1, 127.9, 127.3, 127.1, 126.7, 125.5, 124.7, 123.8, 52.3, 37.7. IR (KBr, cm⁻¹) 3731, 3061, 2952, 1720, 1600, 1489, 1443, 1396, 1247, 1148, 1090, 1039, 969, 883, 821, 756, 711, 599. HRMS (ESI) Calcd for C₂₅H₁₇ClO₂ (M+H)⁺ 385.0990, found 385.0983.

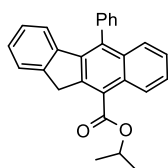
Methyl 7-methoxy-5-phenyl-11H-benzo[*b*]fluorene-10-carboxylate (**6d**)



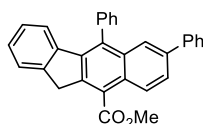
White solid, m. p. = 192-193 °C, yield = 46%; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.49 (m, 7H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 3.94 (s, 2H), 2.42 (s, 3H), 1.55 (s, 3H). ¹³C NMR (100MHz, CDCl₃) δ 169.0, 157.2, 144.2, 140.6, 140.5, 138.8, 137.9, 135.8, 134.6, 129.7, 129.3, 128.1, 127.4, 126.9, 126.5, 125.3, 124.7, 124.6, 123.6, 118.5, 105.8, 55.1, 52.1, 37.5. IR (KBr, cm⁻¹) 3460, 2918, 1733, 1624, 1509, 1428, 1242, 1149, 1030, 813. HRMS (ESI) Calcd for C₂₆H₂₀O₃ (M+H)⁺ 381.1485, found 381.1485.

Benzyl 5-phenyl-11H-benzo[*b*]fluorene-10-carboxylate (6e)

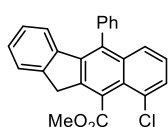
White solid, m. p. = 118-119 °C, yield = 61%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.41 (d, $J = 8.6$ Hz, 1H), 7.58 (dd, $J = 15.0, 6.9$ Hz, 6H), 7.42 (ddd, $J = 19.9, 15.1, 7.4$ Hz, 8H), 7.21 (d, $J = 7.4$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.39 (d, $J = 7.9$ Hz, 1H), 5.60 (s, 2H), 4.24 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.4, 143.9, 142.7, 140.4, 138.6, 137.4, 136.9, 135.9, 133.2, 129.8, 129.8, 129.3, 128.8, 128.7, 128.5, 128.1, 127.5, 126.9, 126.7, 126.6, 125.7, 125.3, 124.9, 124.8, 123.7, 67.2, 37.5. **IR** (KBr, cm^{-1}) 3458, 3063, 2955, 1454, 1393, 1248, 1207, 1137, 1036, 967, 756, 697, 594. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 449.1512, found 449.1516.

Isopropyl 5-phenyl-11H-benzo[*b*]fluorene-10-carboxylate (6f)

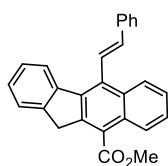
White solid, m. p. = 160-161 °C, yield = 85%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.39 (d, $J = 8.5$ Hz, 1H), 7.62 – 7.49 (m, 6H), 7.38 (t, $J = 7.0$ Hz, 3H), 7.21 (d, $J = 6.5$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.41 (d, $J = 7.8$ Hz, 1H), 5.60 – 5.47 (m, 1H), 4.29 (s, 2H), 1.53 (d, $J = 6.1$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.1, 143.9, 141.9, 140.5, 138.7, 137.4, 136.5, 133.2, 129.8, 129.7, 129.3, 128.1, 127.5, 126.9, 126.7, 126.5, 125.8, 125.7, 125.2, 124.8, 123.7, 69.1, 37.3, 22.3. **IR** (KBr, cm^{-1}) 3716, 3062, 2975, 2314, 1716, 1596, 1456, 1383, 1251, 1213, 1103, 1035, 963, 757, 700. **HRMS** (ESI) Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 379.1693, found 379.1696.

Methyl 5,7-diphenyl-11H-benzo[*b*]fluorene-10-carboxylate (6g)

White solid, m. p. = 163-164 °C, yield = 64%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.53 (d, $J = 8.8$ Hz, 1H), 7.81 – 7.75 (m, 2H), 7.58 (q, $J = 5.7$ Hz, 3H), 7.51 (t, $J = 8.6$ Hz, 3H), 7.41 – 7.34 (m, 4H), 7.29 (t, $J = 7.3$ Hz, 1H), 7.23 – 7.17 (m, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.39 (d, $J = 7.9$ Hz, 1H), 4.30 (s, 2H), 4.12 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.86, 144.04, 143.11, 140.97, 140.43, 138.49, 138.28, 137.92, 137.22, 133.55, 129.80, 129.38, 129.14, 128.88, 128.25, 127.62, 127.43, 126.70, 126.28, 125.99, 124.77, 124.67, 123.76, 52.22, 37.73. **IR** (KBr, cm^{-1}) 3713, 3047, 2926, 2858, 2314, 1734, 1594, 1482, 1445, 1251, 1164, 1089, 1013, 958, 832, 755, 696, 617, 501. **HRMS** (ESI) Calcd for $\text{C}_{31}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 449.1512, found 449.1512.

Methyl 9-chloro-5-phenyl-11H-benzo[*b*]fluorene-10-carboxylate (6h)

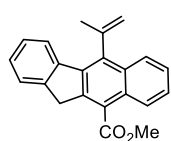
Yellow oil, yield = 66%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 (t, $J = 6.6$ Hz, 4H), 7.55 (t, $J = 6.9$ Hz, 2H), 7.39 (d, $J = 6.9$ Hz, 2H), 7.30 (d, $J = 7.6$ Hz, 2H), 7.06 (t, $J = 7.6$ Hz, 1H), 6.41 (d, $J = 7.9$ Hz, 1H), 4.15 (d, $J = 31.8$ Hz, 5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.5, 143.7, 141.8, 140.1, 138.2, 137.9, 135.4, 135.0, 129.9, 129.8, 129.3, 128.3, 128.2, 128.0, 126.8, 126.4, 126.1, 125.9, 125.5, 124.9, 123.9, 52.8, 36.0. **IR** (KBr, cm^{-1}) 3726, 3062, 2937, 2314, 1730, 1446, 1251, 1183, 1144, 880, 814, 733, 513. **HRMS** (ESI) Calcd for $\text{C}_{25}\text{H}_{17}\text{ClO}_2$ ($\text{M}+\text{H}$) $^+$ 385.0990, found 385.0989.

Methyl (E)-5-styryl-11H-benzo[*b*]fluorene-10-carboxylate (6i)

Yellow oil, yield = 70%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.44 (d, $J = 8.3$ Hz, 1H), 8.36 (d, $J = 8.3$ Hz, 1H), 8.09 (d, $J = 7.4$ Hz, 1H), 7.76 – 7.68 (m, 3H), 7.59 (d, $J = 6.6$ Hz, 2H), 7.53 (dd, $J = 14.6, 7.4$ Hz, 3H), 7.43 (t, $J = 6.9$ Hz, 1H), 7.36 (dd, $J = 14.2, 6.9$ Hz, 2H), 6.93 (d, $J = 16.7$ Hz, 1H), 4.30 (s, 2H), 4.15 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.9, 144.0, 142.8, 140.9, 137.1, 136.9, 136.8, 133.7, 132.4,

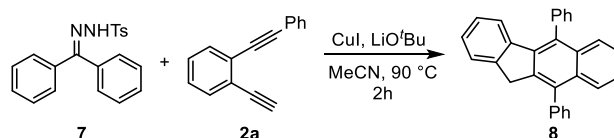
130.0, 129.0, 128.7, 128.3, 128.2, 127.5, 126.9, 126.7, 126.2, 125.7, 125.6, 125.0, 124.9, 124.5, 52.1, 37.6. **IR** (KBr, cm^{-1}) 3441, 2919, 1713, 1643, 1441, 1391, 1213, 1043, 974, 798, 753. **HRMS** (ESI) Calcd for $\text{C}_{27}\text{H}_{20}\text{O}_2$ ($\text{M}+\text{H}$)⁺ 377.1536, found 377.1543.

Methyl 5-(2-methylprop-1-en-1-yl)-11H-benzo[*b*]fluorene-10-carboxylate (6j)



Yellow solid, yield = 70%; **¹H NMR** (400 MHz, CDCl_3) δ 8.43 (d, J = 8.2 Hz, 1H), 8.19 (t, J = 6.7 Hz, 2H), 7.59 (dd, J = 15.3, 7.3 Hz, 3H), 7.40 (d, J = 4.1 Hz, 2H), 5.76 (s, 1H), 5.22 (s, 1H), 4.30 (s, 2H), 4.14 (s, 3H), 2.30 (s, 3H). **¹³C NMR** (100 MHz, CDCl_3) δ 168.9, 143.9, 143.1, 142.6, 140.1, 138.6, 135.0, 131.4, 129.9, 129.3, 127.5, 126.9, 126.6, 125.9, 125.8, 125.5, 124.8, 123.9, 117.5, 52.1, 37.4, 24.1. **IR** (KBr, cm^{-1}) 3443, 2954, 1714, 1639, 1438, 1212, 1042, 759. **HRMS** (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{H}$)⁺ 315.1380, found 315.1376.

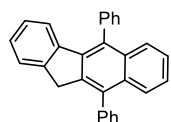
1.7 General procedure for the synthesis of 8



To an acetonitrile (MeCN, 1.0 mL) suspension of CuI (10 mol %) and LiO^tBu (2eq.) in Schlenk tube with a magnetic bar under nitrogen atmosphere, was added alkyne (**2a**, 0.1 mmol) and N-tosylhydrazones (**7**, 0.15 mmol). The reaction was stirred at 90 °C unless being noted and monitored by TLC. After accomplished, the reaction mixture was purified by chromatography with petroleum/ethyl acetate(v/v: 20/1) to obtain **8**.

The characterization data of **8** was consistent with literature.^[6]

5,10-Diphenyl-11H-benzo[*b*]fluorene (8)



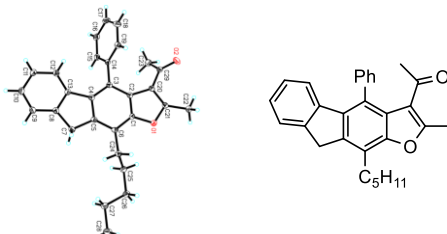
White solid, yield = 53%; **¹H NMR** (400 MHz, CDCl_3) δ 7.68 – 7.54 (m, 7H), 7.50 (d, J = 9.2 Hz, 5H), 7.42 – 7.33 (m, 3H), 7.19 (s, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.50 (d, J = 7.9 Hz, 1H), 3.87 (s, 2H). **¹³C NMR** (100 MHz, CDCl_3) δ 144.3, 141.5, 139.5, 139.3, 139.2, 137.0, 135.3, 133.2, 133.0, 131.6, 130.2, 130.0, 129.2, 128.7, 127.8, 127.4, 127.1, 126.5, 126.5, 125.8, 125.3, 125.1, 124.8, 123.8, 36.6.

2. References

- [1] H. Luo, K. Chen, H. Jiang and S. Zhu, *Org. Lett.*, 2016, **18**, 5208.
- [2] Y. Yang, J.-X. Yu, X.-H. Ouyang, and J.-H. Li, *Org. Lett.*, 2017, **19**, 3982.
- [3] E. Rettenmeier, M. M. Hansmann, A. Ahrens, K. R benacker, T. Saboo, J. Massholder, C. Meier, M. Rudolph, F. Rominger and A. Stephen K. Hashmi, *Chem. Eur.J.*, 2015, **21**, 14401.
- [4] A. Stephen K. Hashmi, M. Wietek, I. Braun, P. N çsel, L. Jongbloed and M. Rudolph, F. Romingera, *Adv. Synth. Catal.*, 2012, **354**, 555.
- [5] D. Li, Y. Wei and M. Shi, *Chem. Eur. J.*, 2013, **19**, 15682.
- [6] K. Wang, H. Zhang and J. L. Petersen, *J. Org. Chem.*, 1999, **64**, 1650.

3. X-Ray diffraction analysis

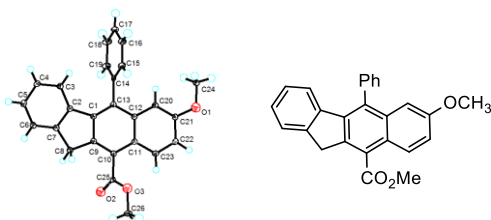
3.1 Crystal data and structure refinement for 3am



CCDC number	1888277
Identification code	3am
Empirical formula	C ₂₉ H ₂₈ O ₂
Formula weight	408.51
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.2239(5)
b/Å	11.0090(6)
c/Å	11.0538(6)
α/°	73.729(5)
β/°	86.050(5)
γ/°	65.798(5)
Volume/Å ³	1087.85(11)
Z	2
ρ _{calc} /g/cm ³	1.247
μ/mm ⁻¹	0.076
F(000)	436.0
Crystal size/mm ³	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.222 to 49.99
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 12, -13 ≤ l ≤ 12
Reflections collected	11241
Independent reflections	3818 [R _{int} = 0.0404, R _{sigma} = 0.0473]
Data/restraints/parameters	3818/0/292
Goodness-of-fit on F ²	1.043
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0458, wR ₂ = 0.1096
Final R indexes [all data]	R ₁ = 0.0577, wR ₂ = 0.1198

Largest diff. peak/hole / e Å⁻³ 0.23/-0.18

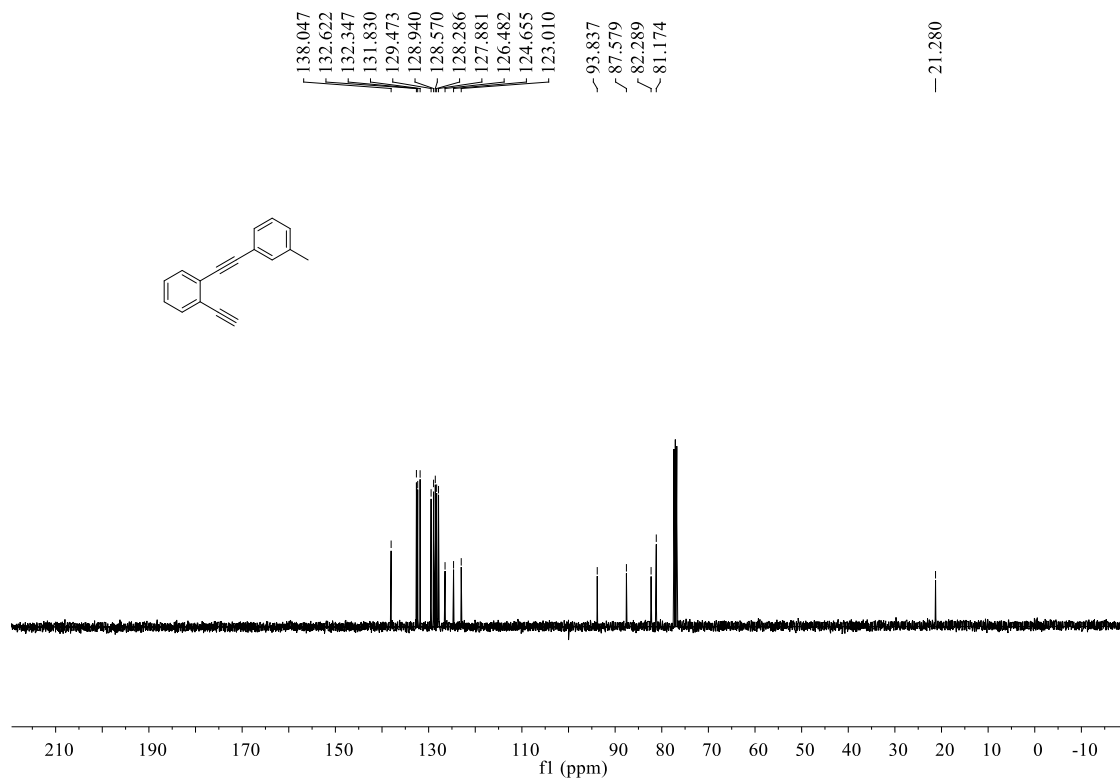
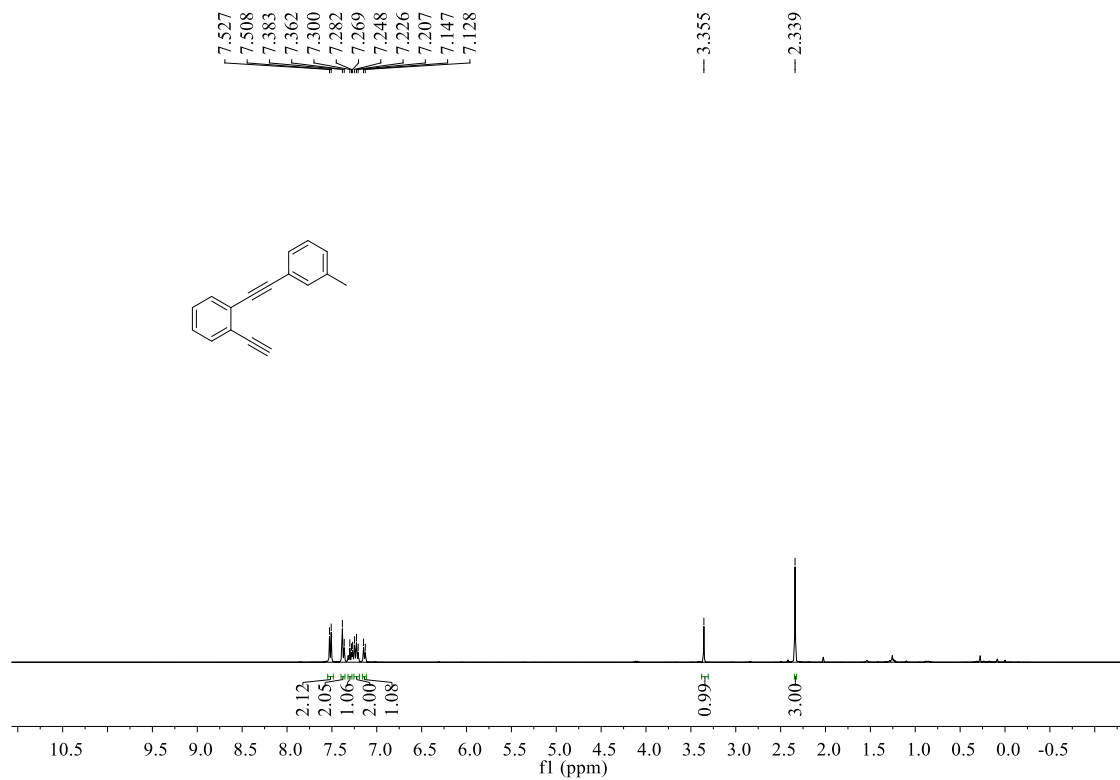
3.2 Crystal data and structure refinement for 6d



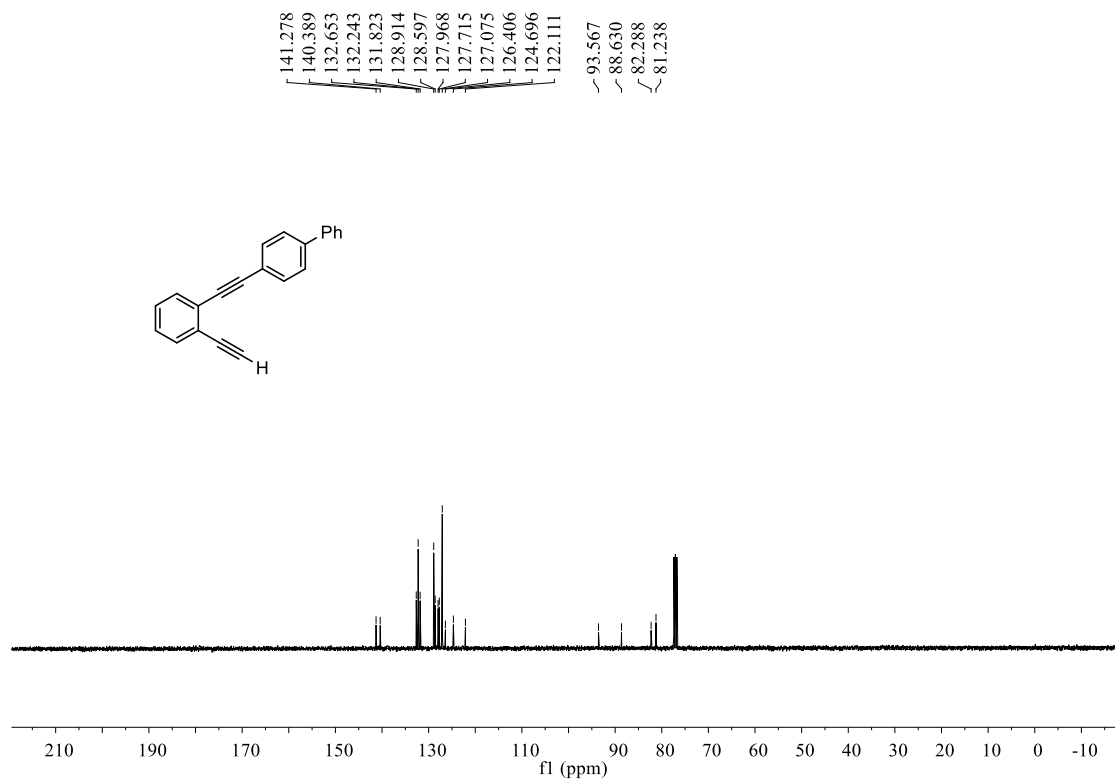
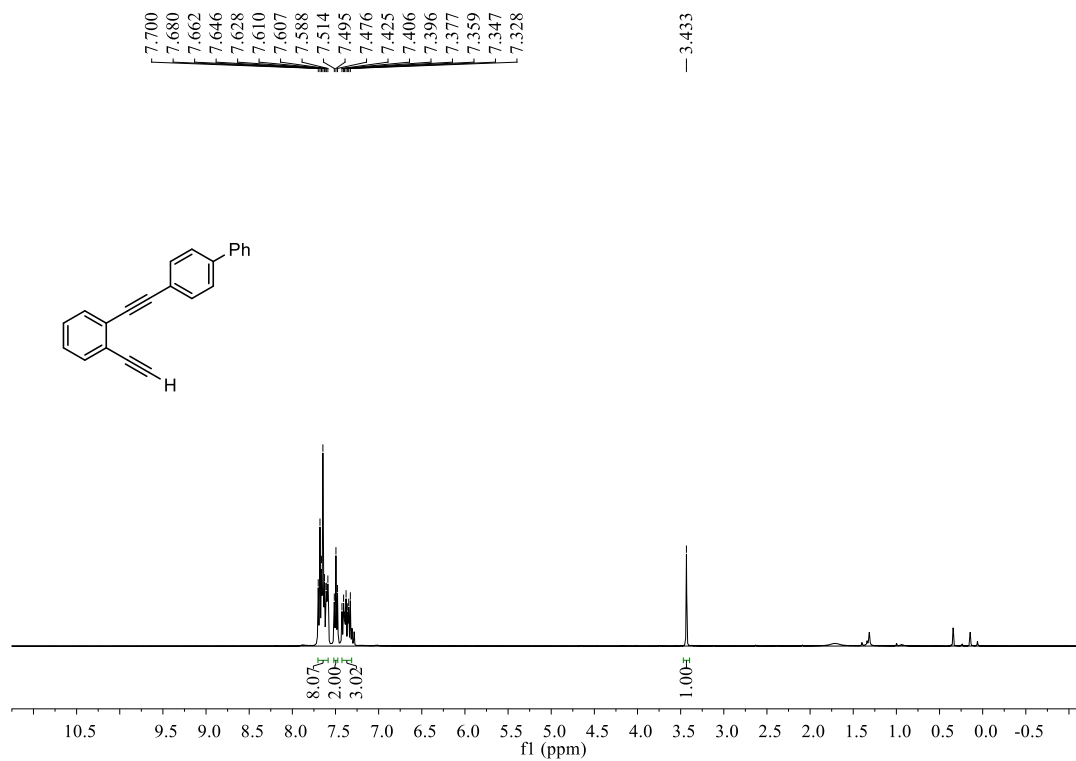
CCDC number	1888278
Identification code	6d
Empirical formula	C ₂₆ H ₂₀ O ₃
Formula weight	380.42
Temperature/K	100.01(10)
Crystal system	Monoclinic
Space group	P2 ₁ /n
a/Å	11.5269(6)
b/Å	6.9766(4)
c/Å	23.8120(12)
α/°	90
β/°	98.369(5)
γ/°	90
Volume/Å ³	1894.54(18)
Z	4
ρ _{calc} /g/cm ³	1.334
μ/mm ⁻¹	0.086
F(000)	800.0
Crystal size/mm ³	0.13 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.188 to 50
Index ranges	-13 ≤ h ≤ 13, -6 ≤ k ≤ 8, -26 ≤ l ≤ 28
Reflections collected	11699
Independent reflections	3333 [R _{int} = 0.0287, R _{sigma} = 0.0290]
Data/restraints/parameters	3333/0/273
Goodness-of-fit on F ²	1.084
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0398, wR ₂ = 0.0945
Final R indexes [all data]	R ₁ = 0.0474, wR ₂ = 0.0991
Largest diff. peak/hole / e Å ⁻³	0.20/-0.17

4. Copies of NMR spectra

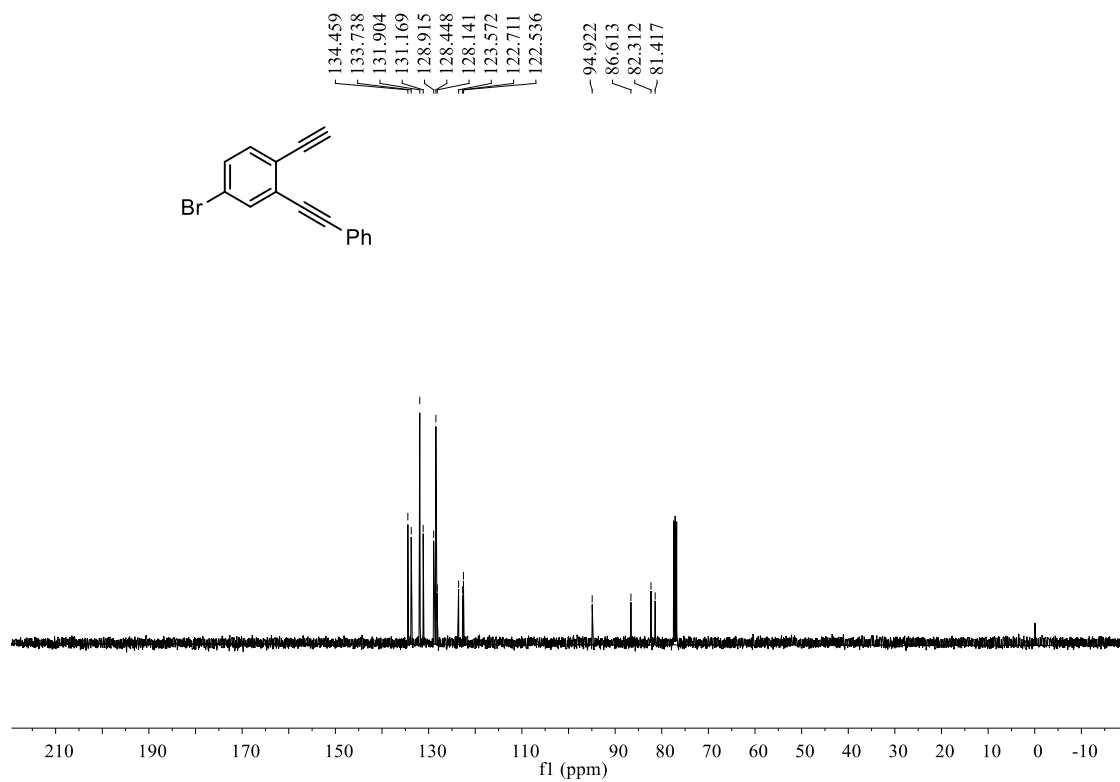
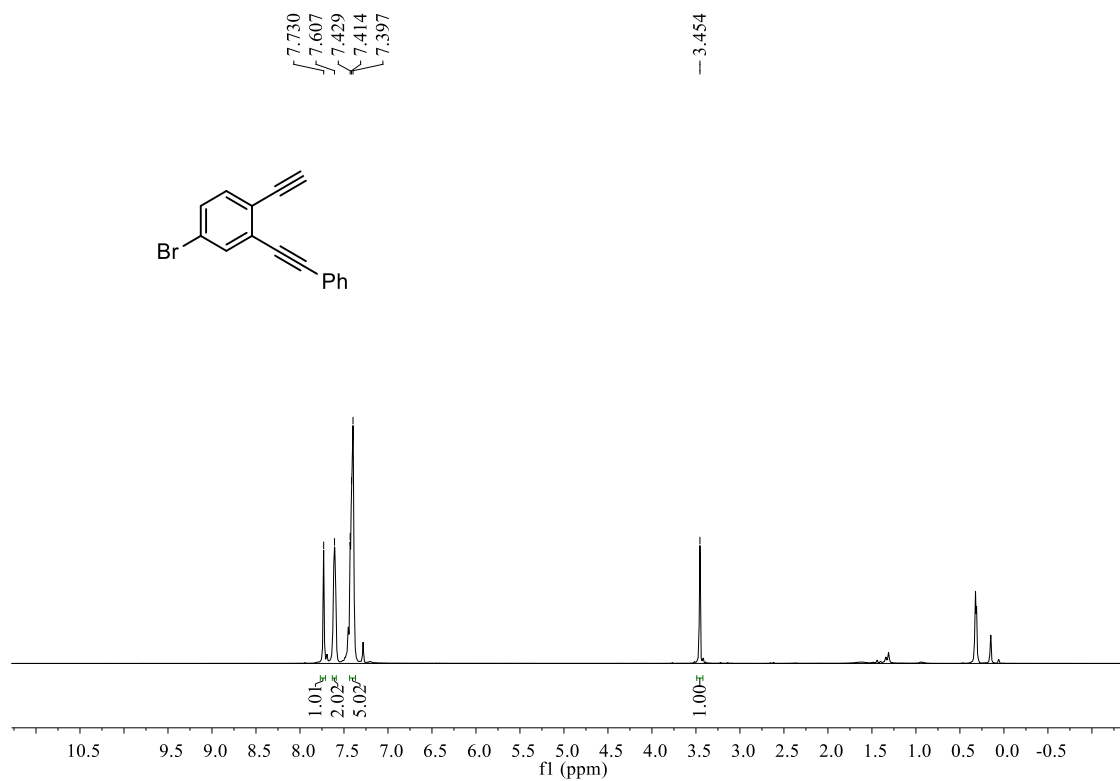
2i



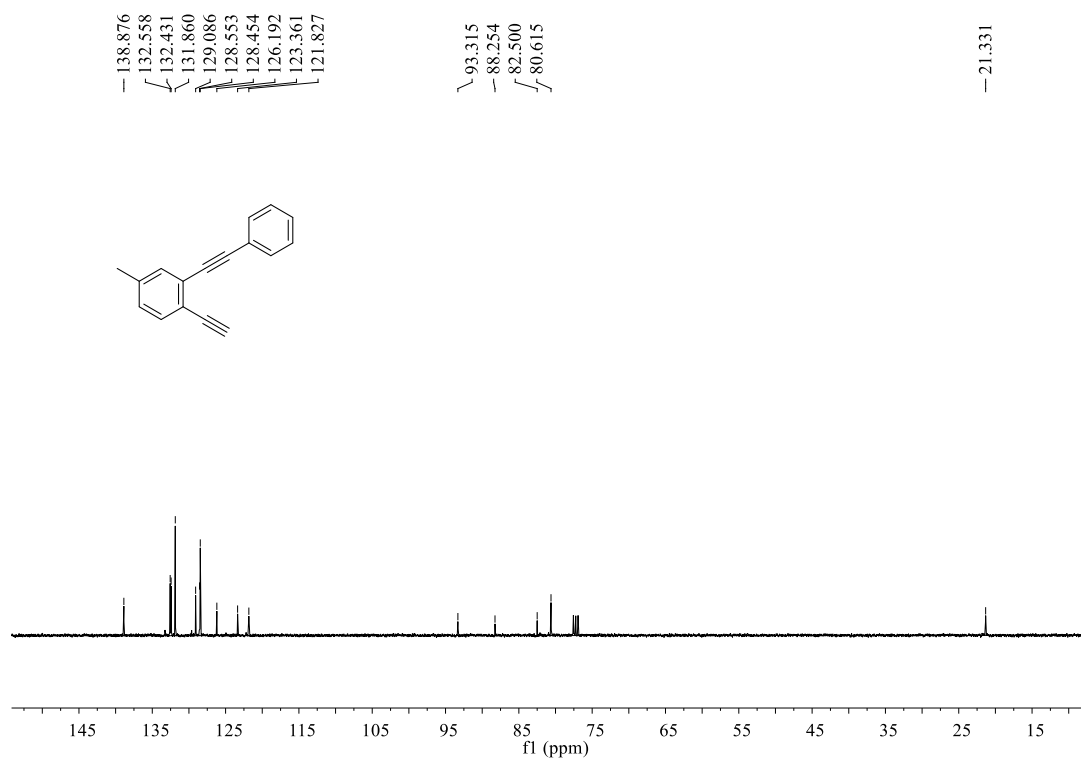
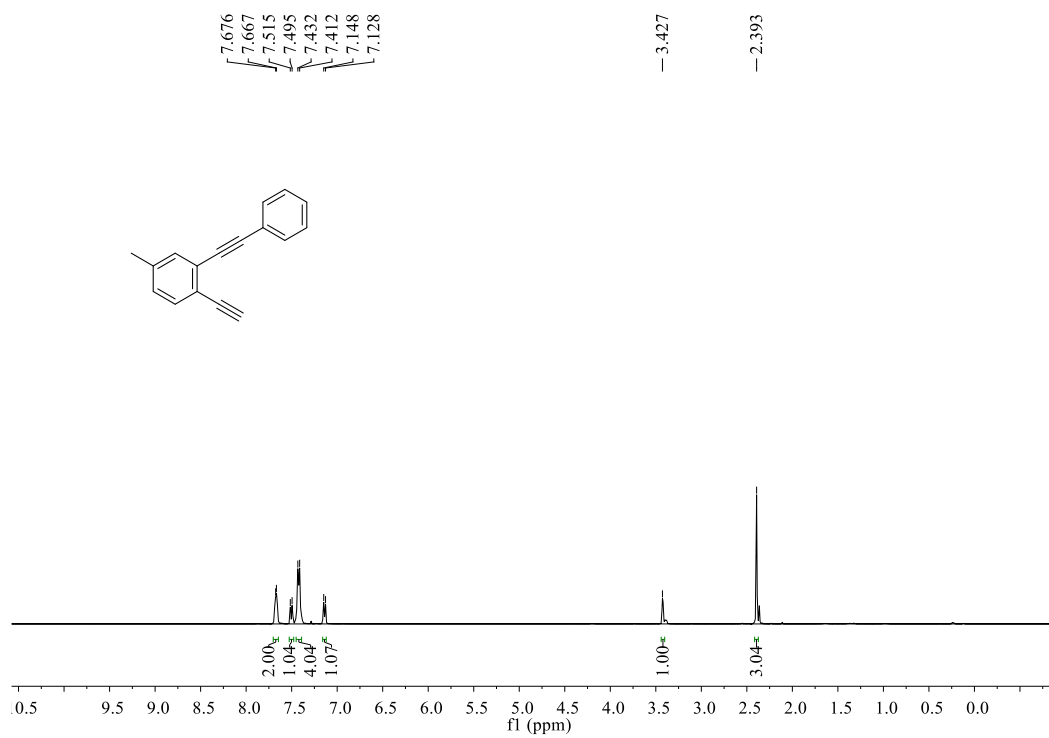
2k



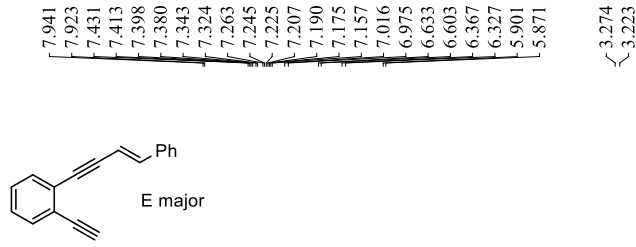
2l



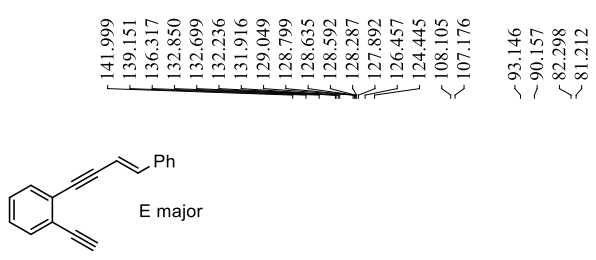
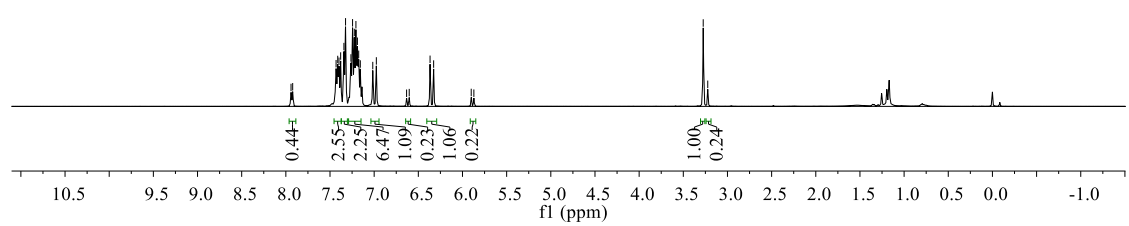
2m



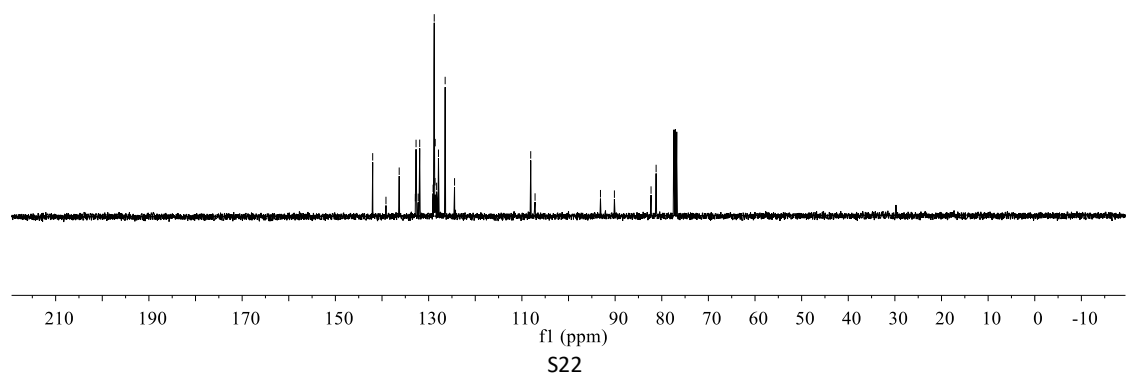
2n(E/Z = 5:1)



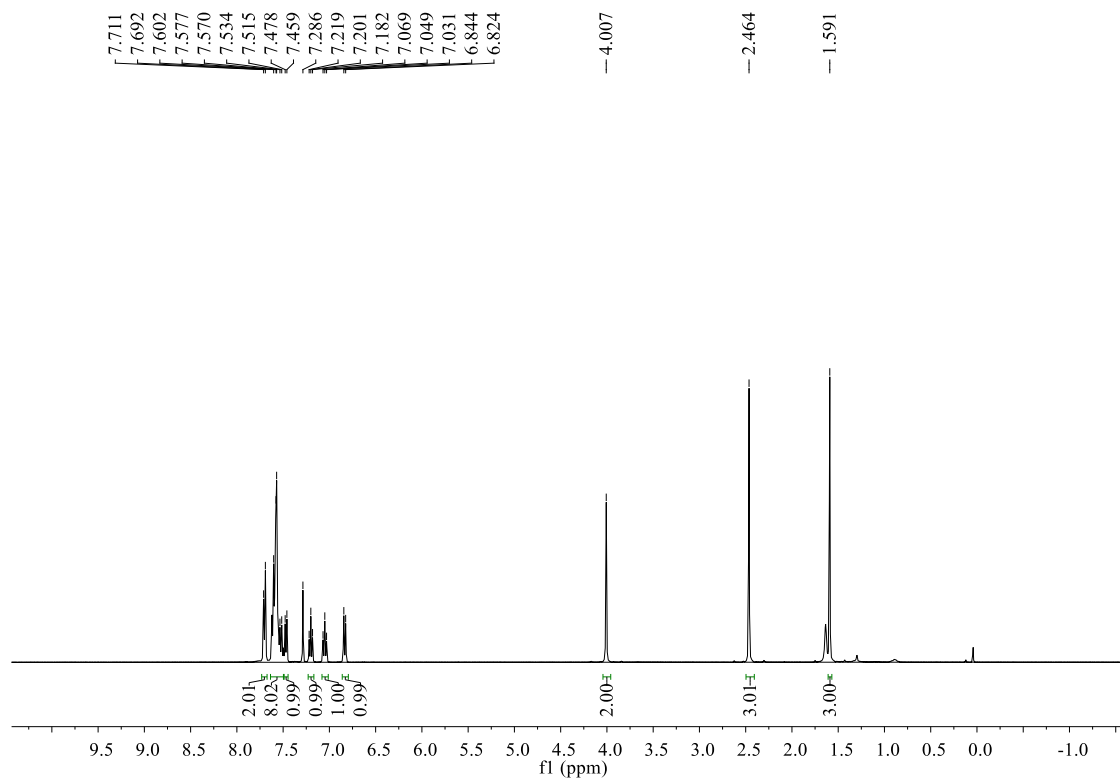
7.941
7.923
7.431
7.413
7.398
7.380
7.343
7.324
7.263
7.245
7.225
7.207
7.190
7.175
7.157
7.016
6.975
6.633
6.603
6.367
6.327
5.901
5.871
3.274
3.223

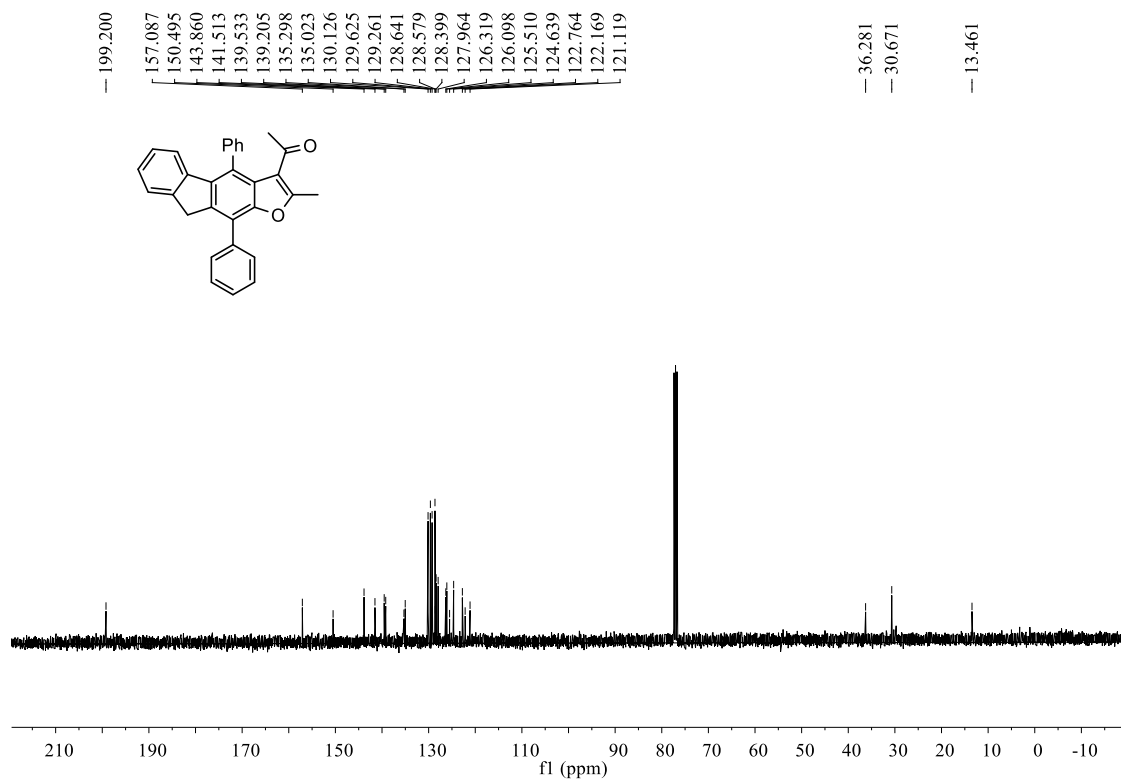


141.999
139.151
136.317
132.850
132.699
132.236
131.916
129.049
128.799
128.635
128.592
128.287
127.892
126.457
124.445
108.105
107.176
93.146
90.157
82.298
81.212

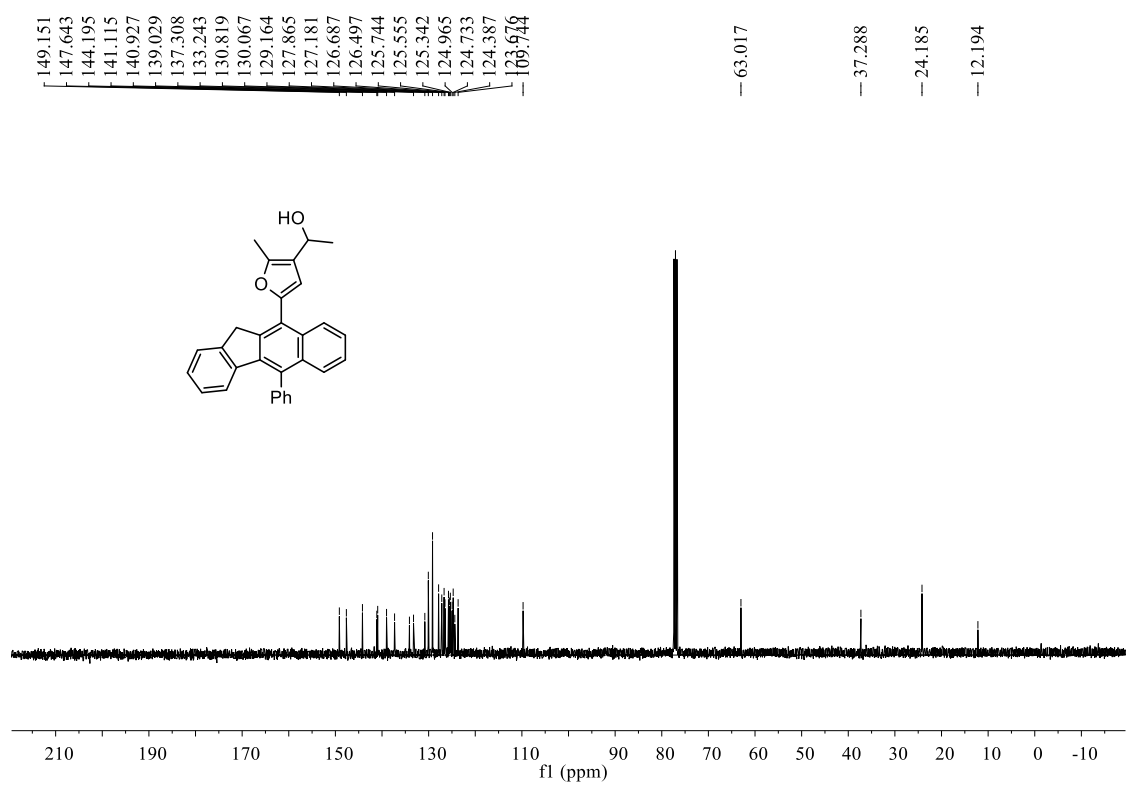
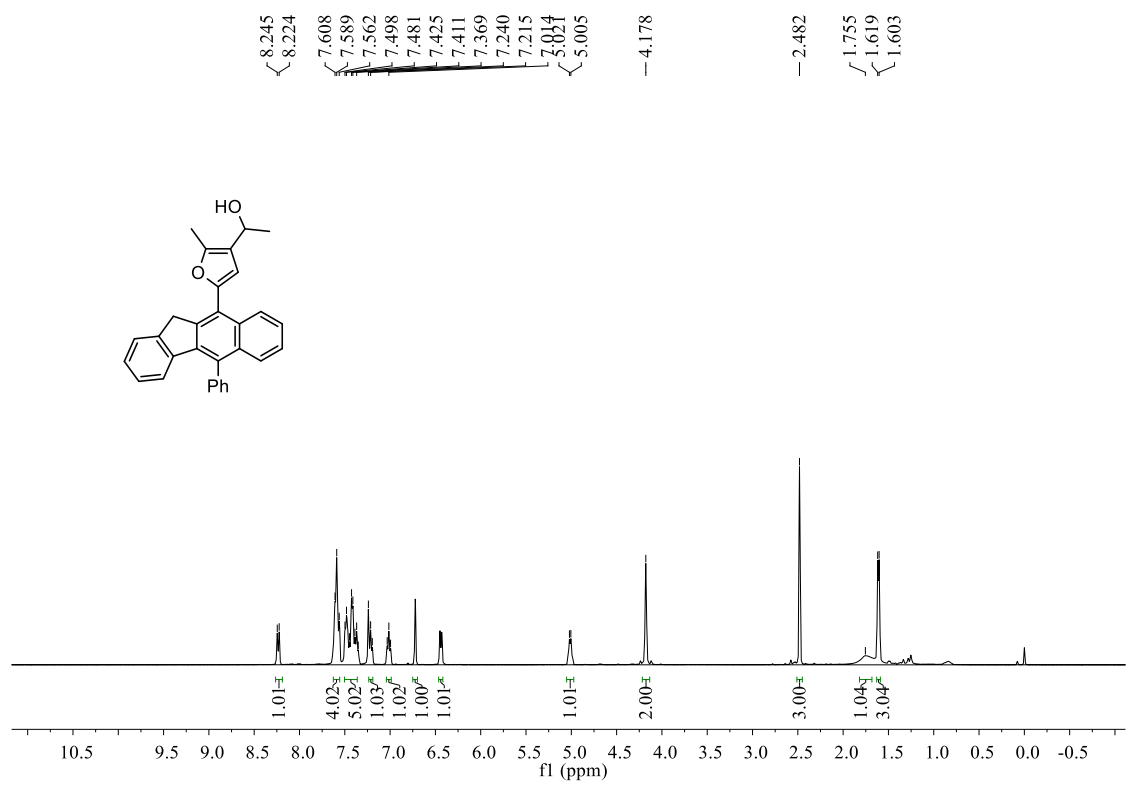


3aa

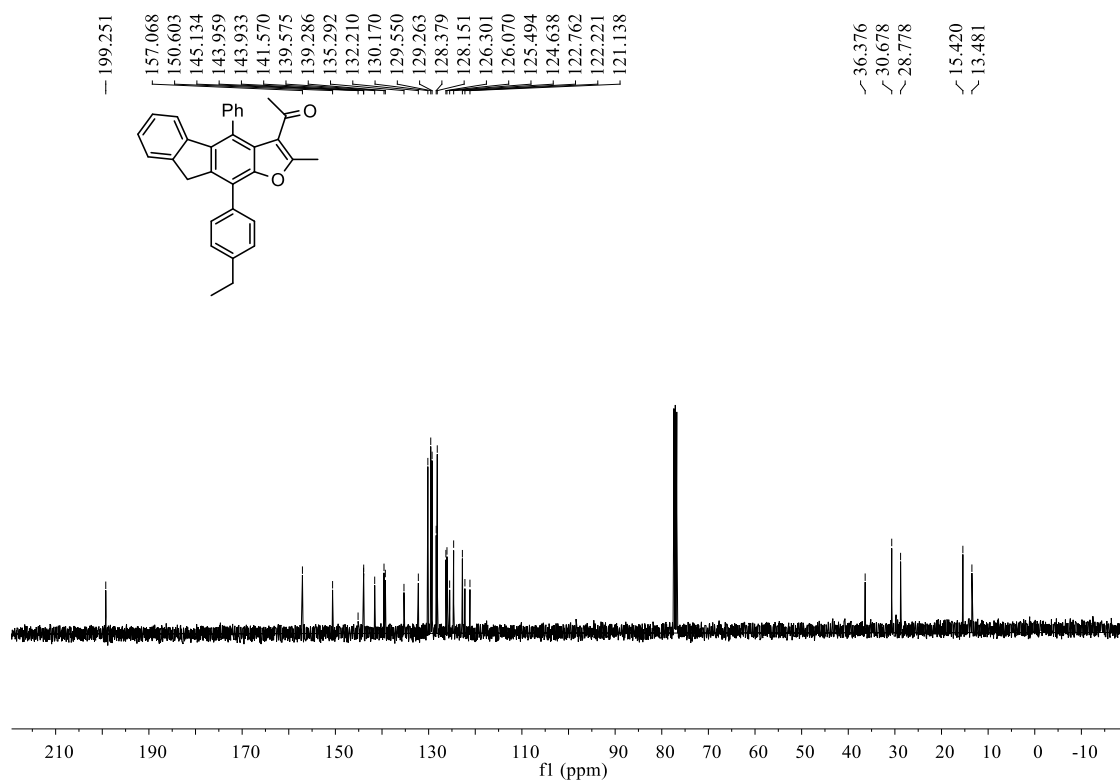
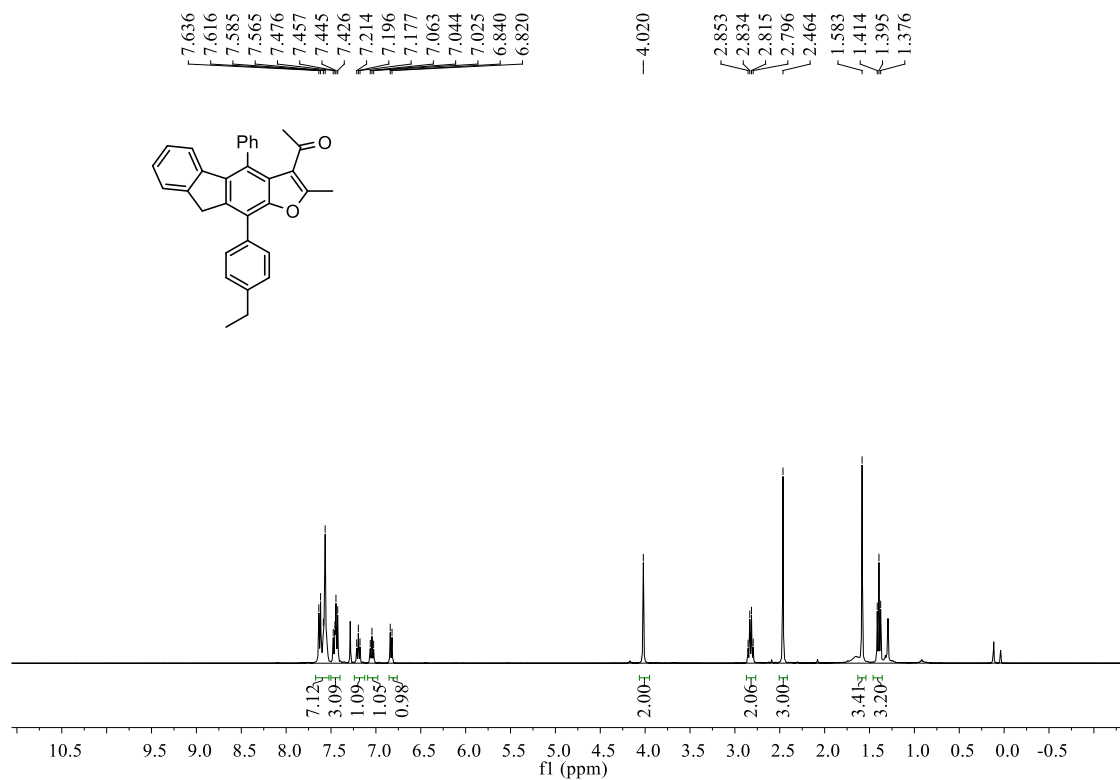




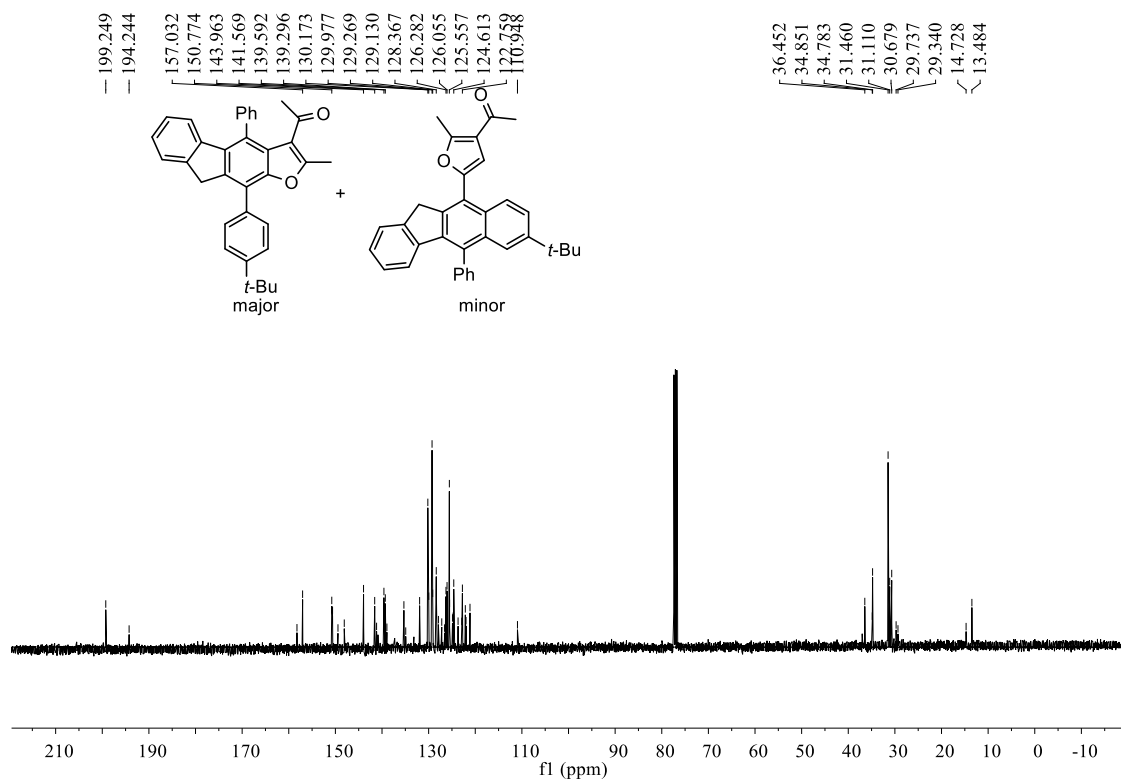
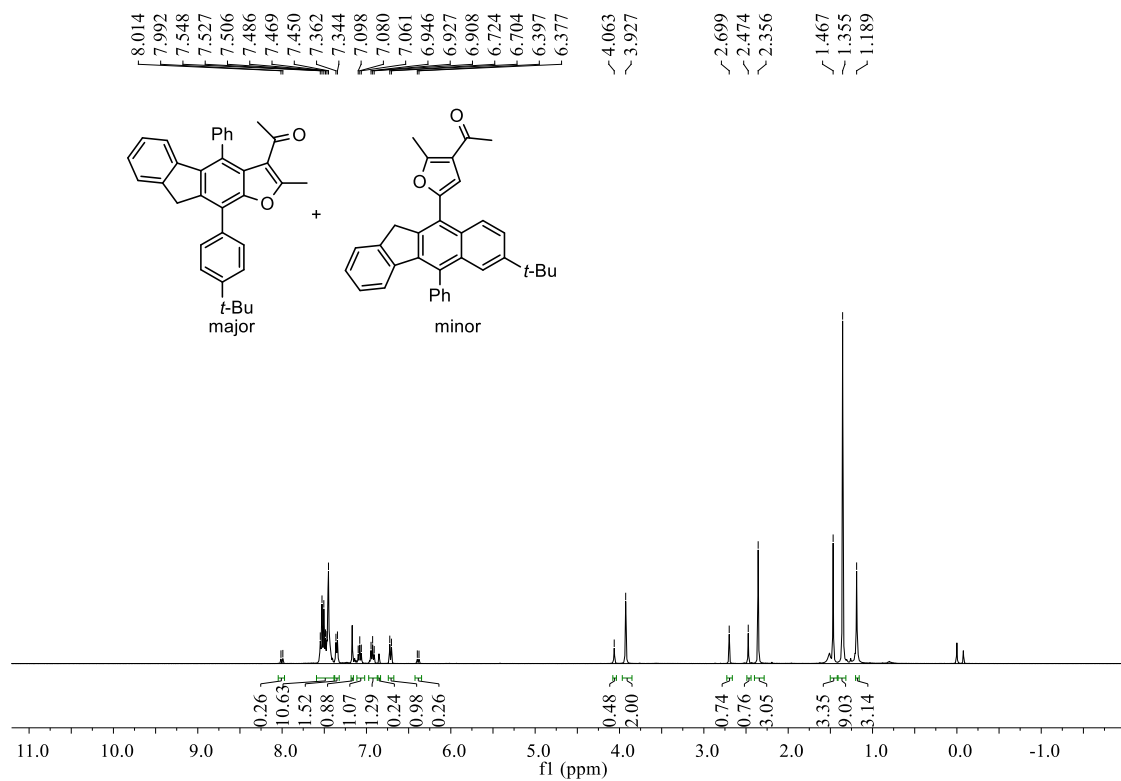
7aa



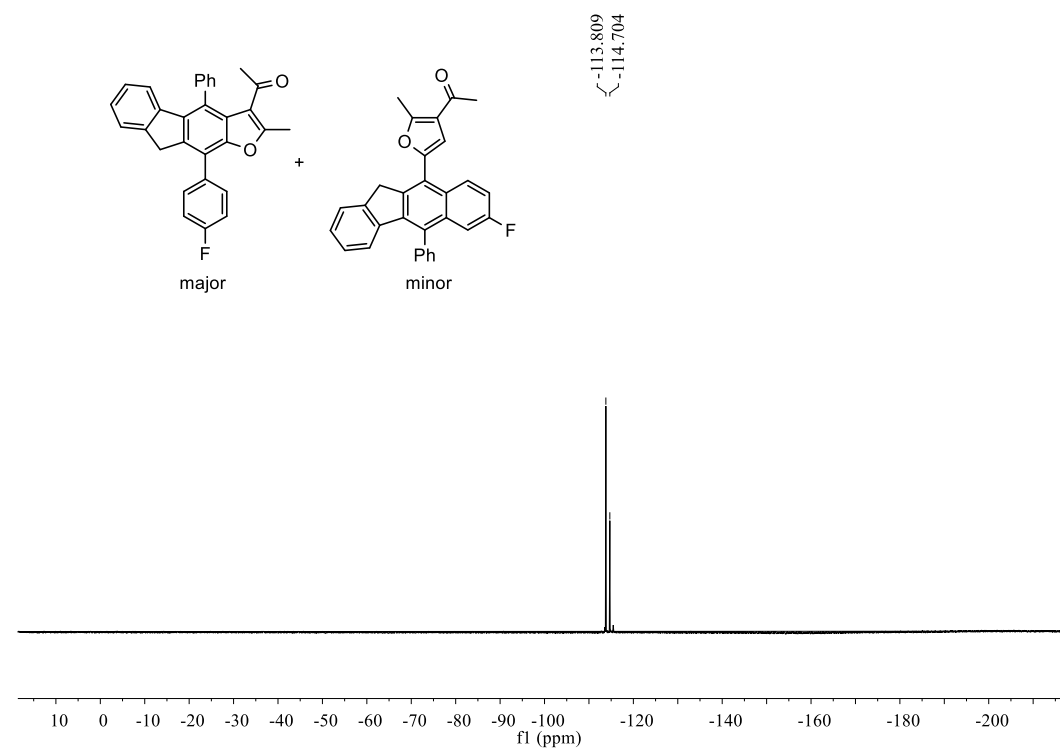
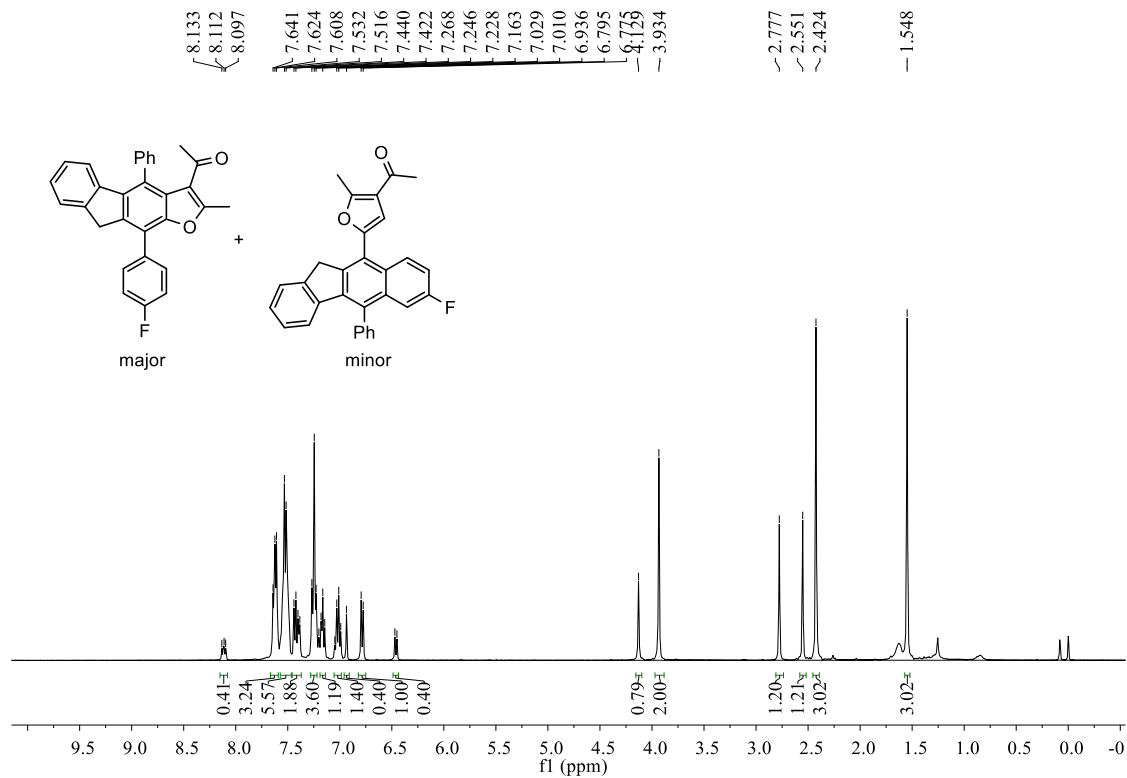
3ab

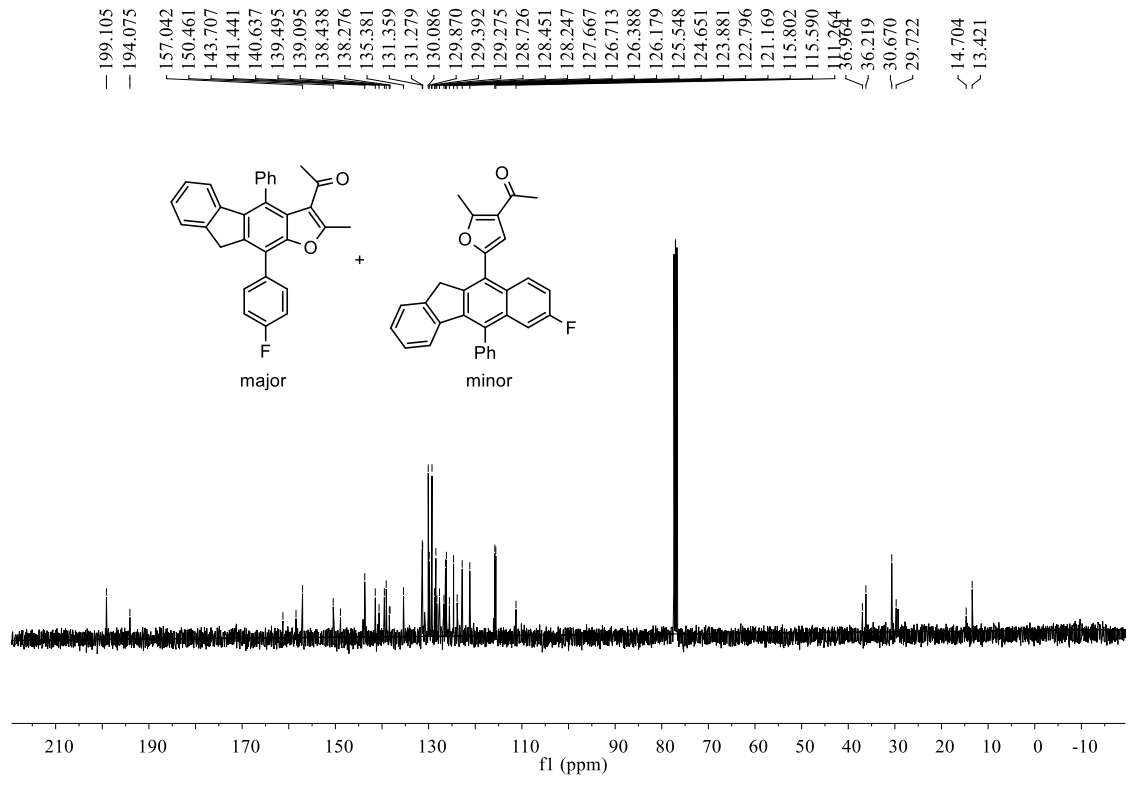


3ac

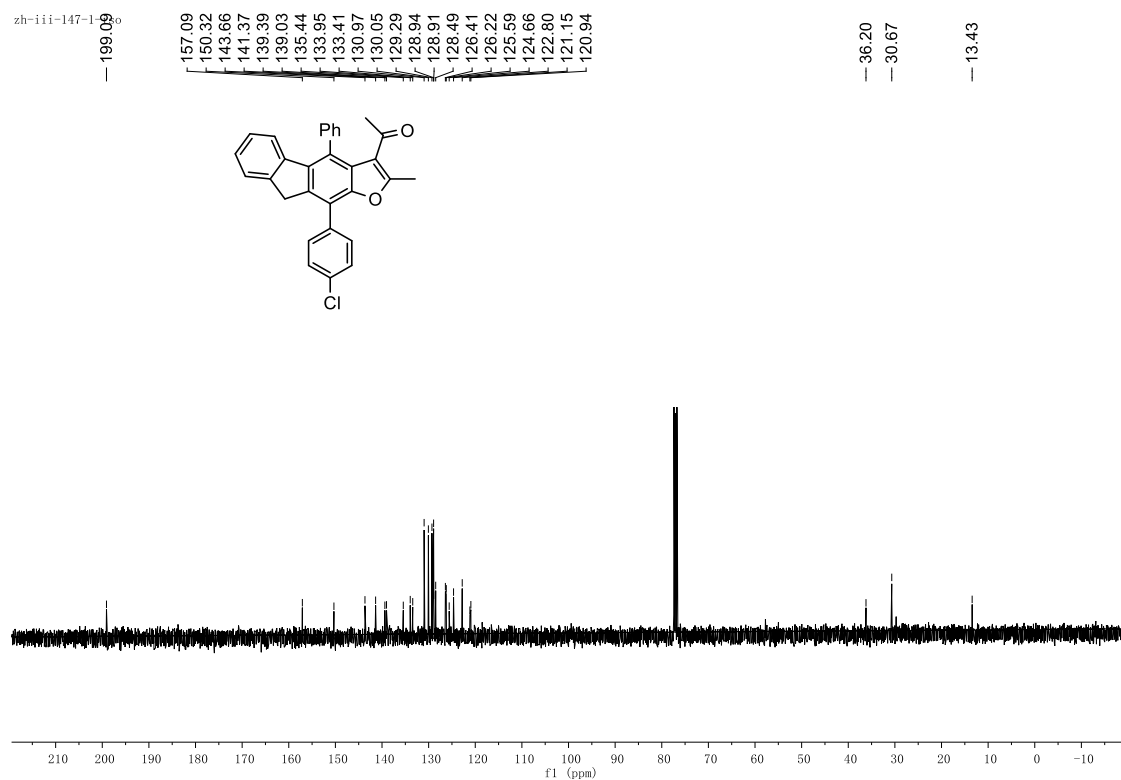
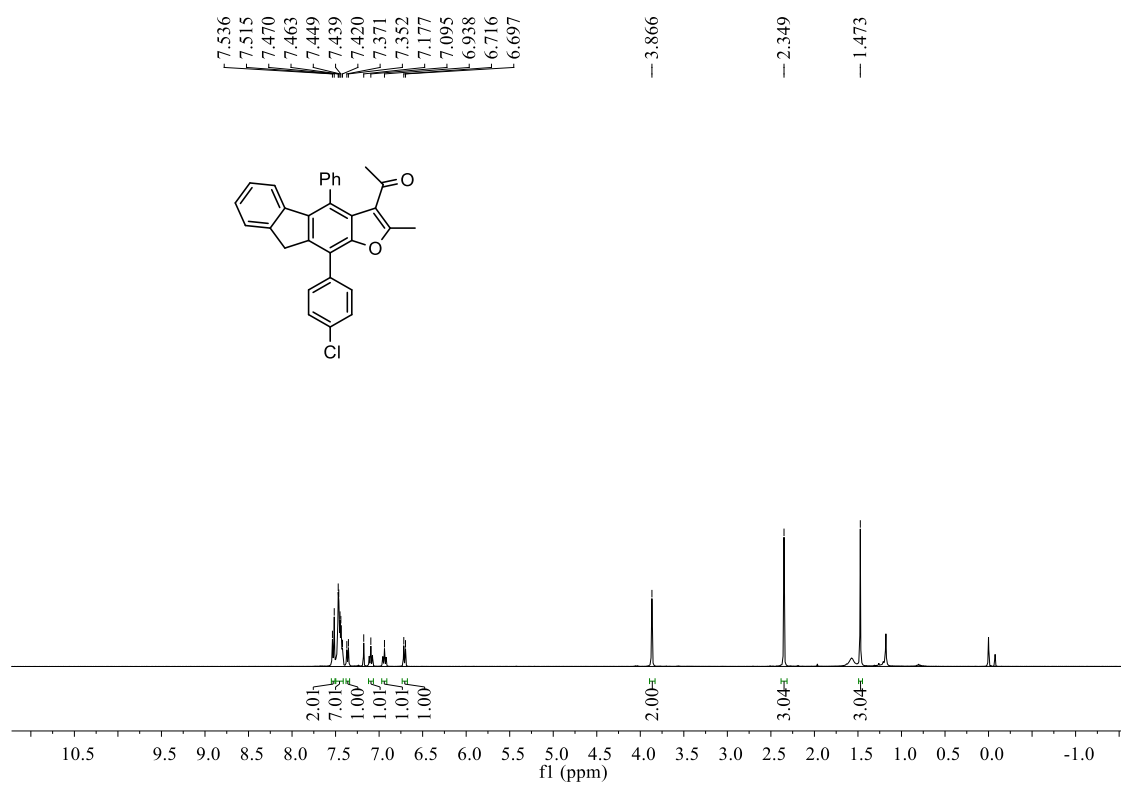


3ad

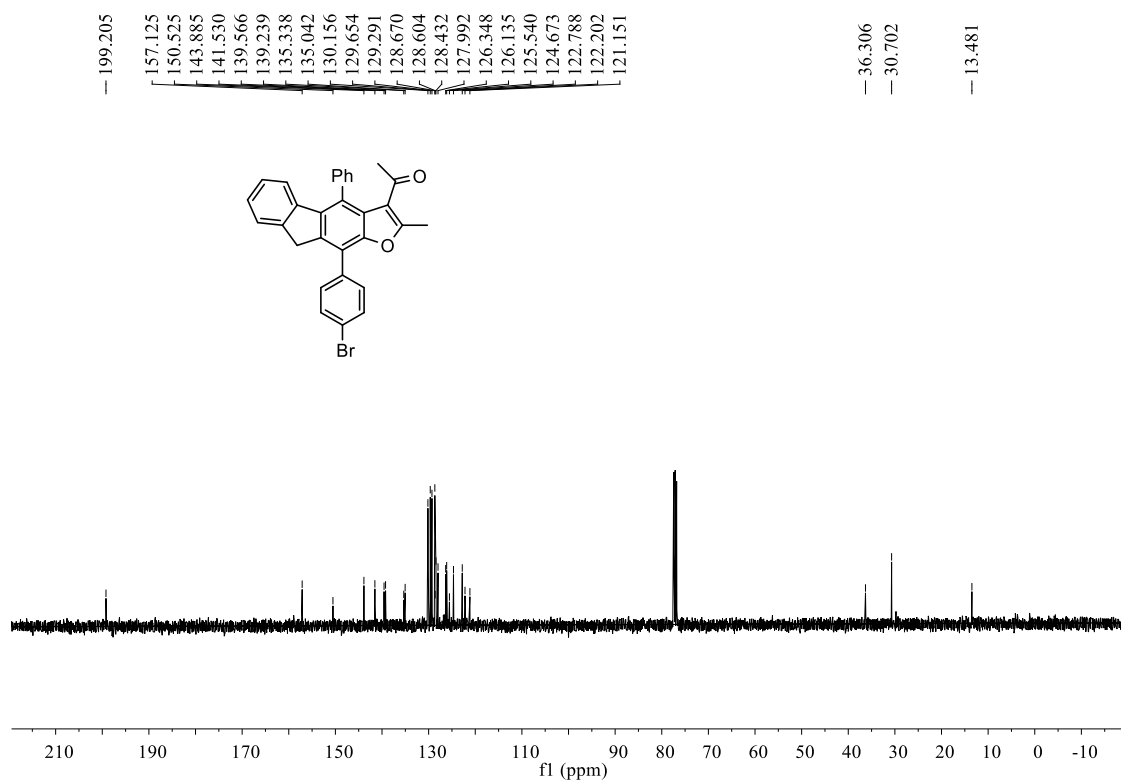
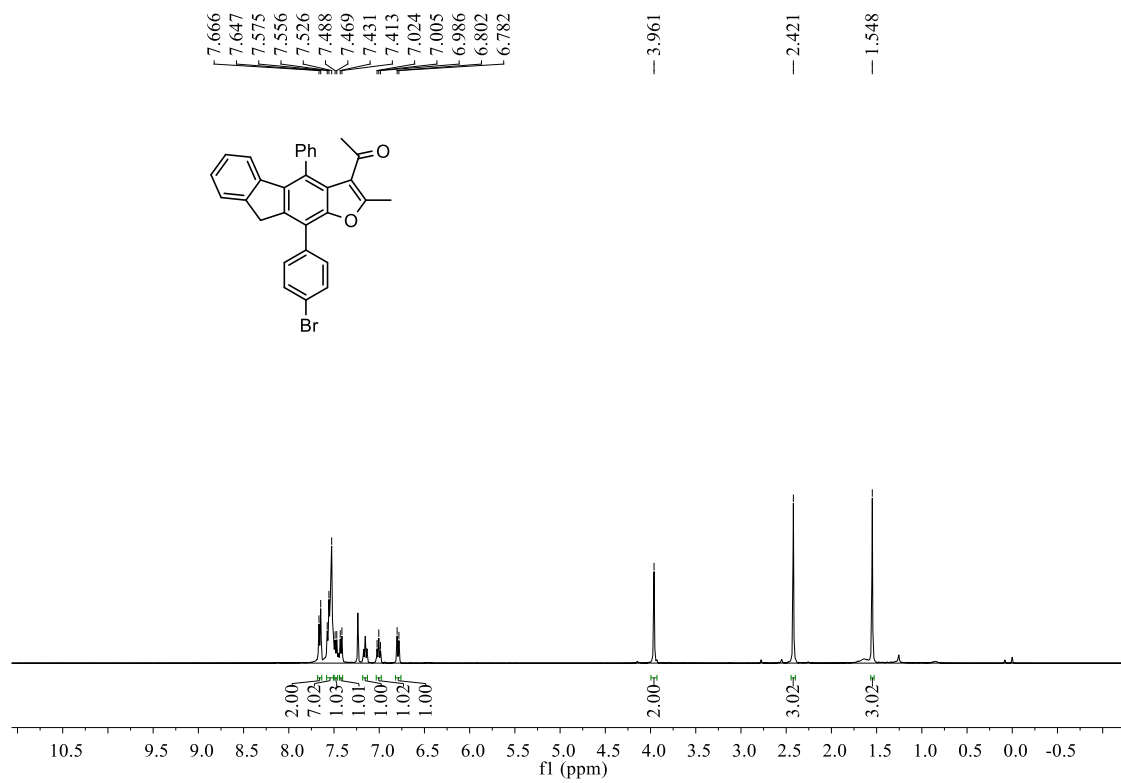




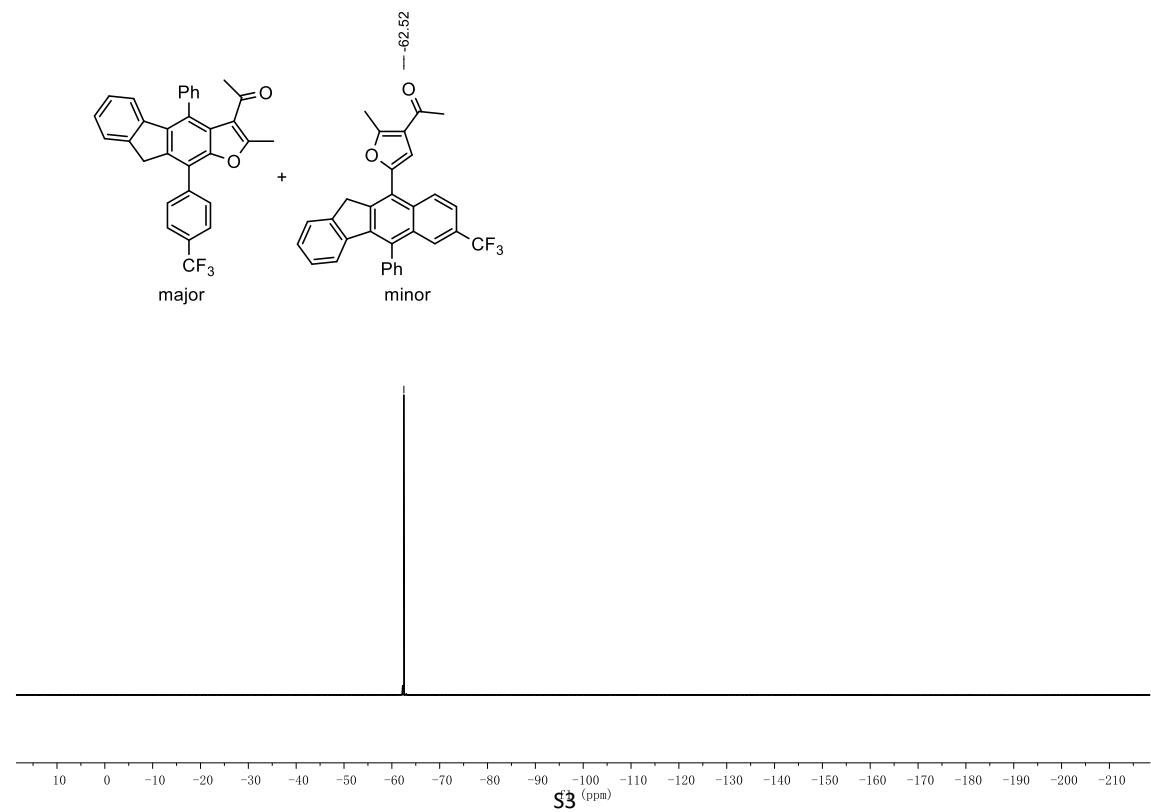
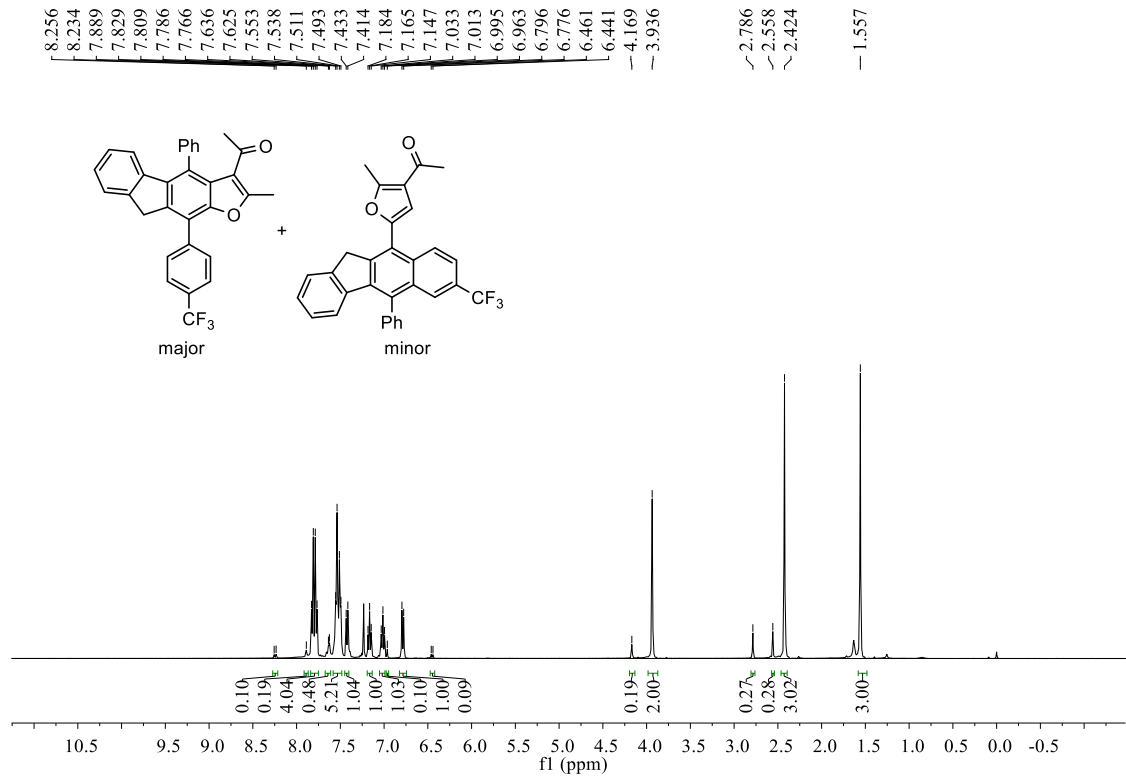
3ae

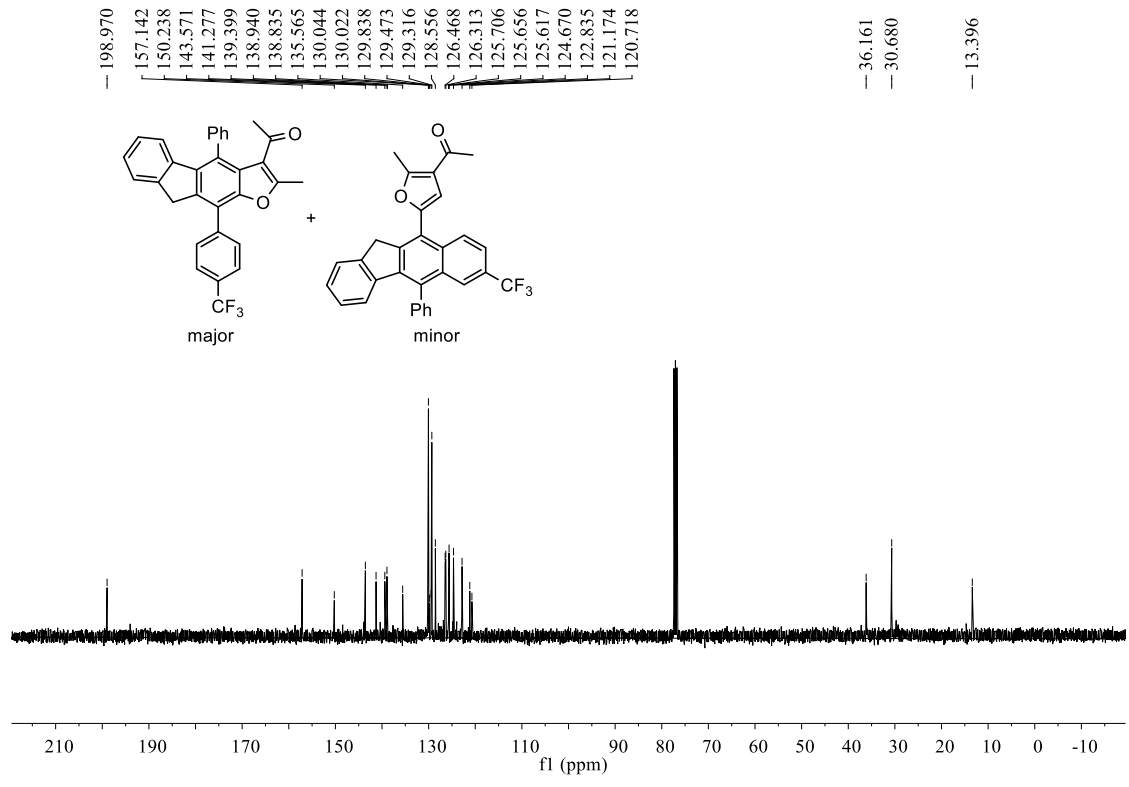


3af

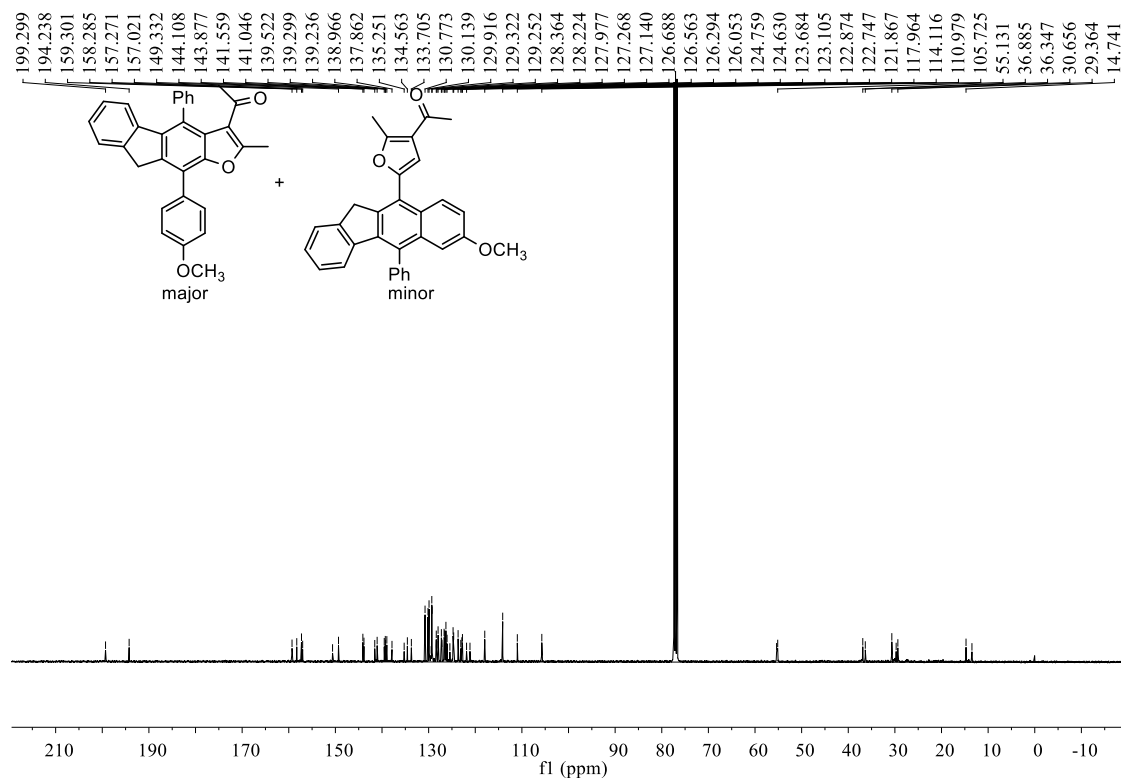
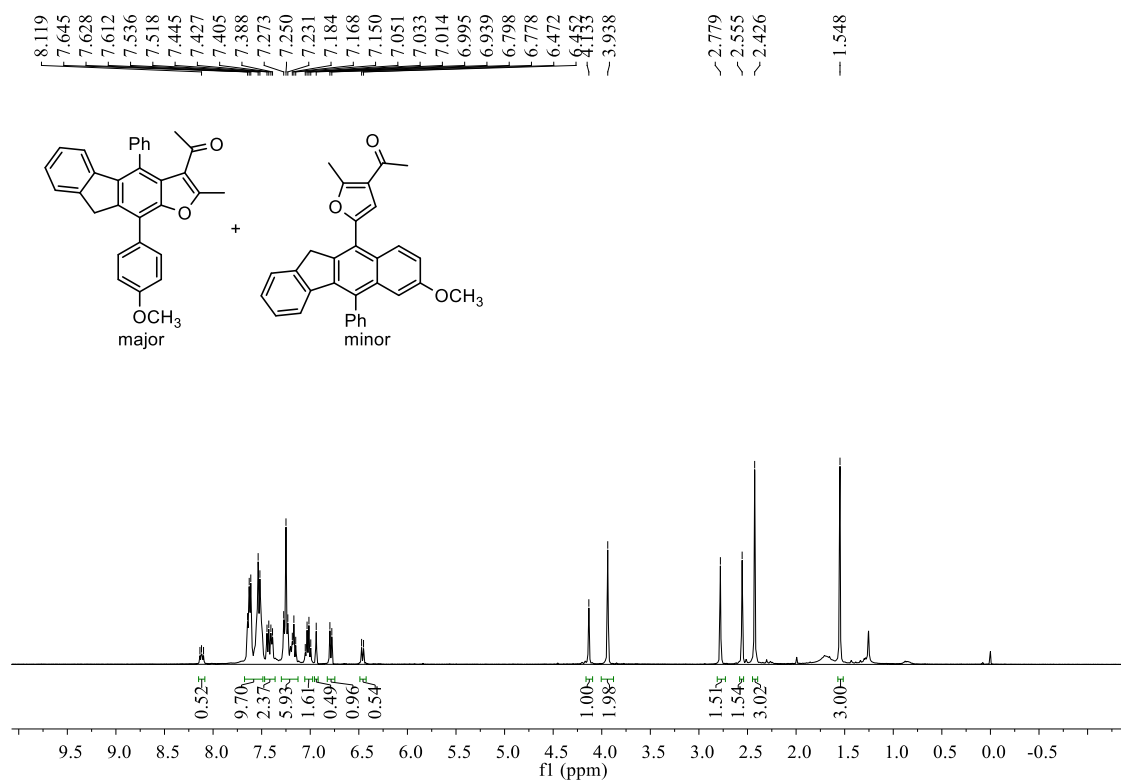


3ag

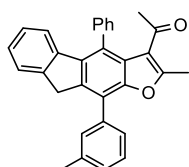
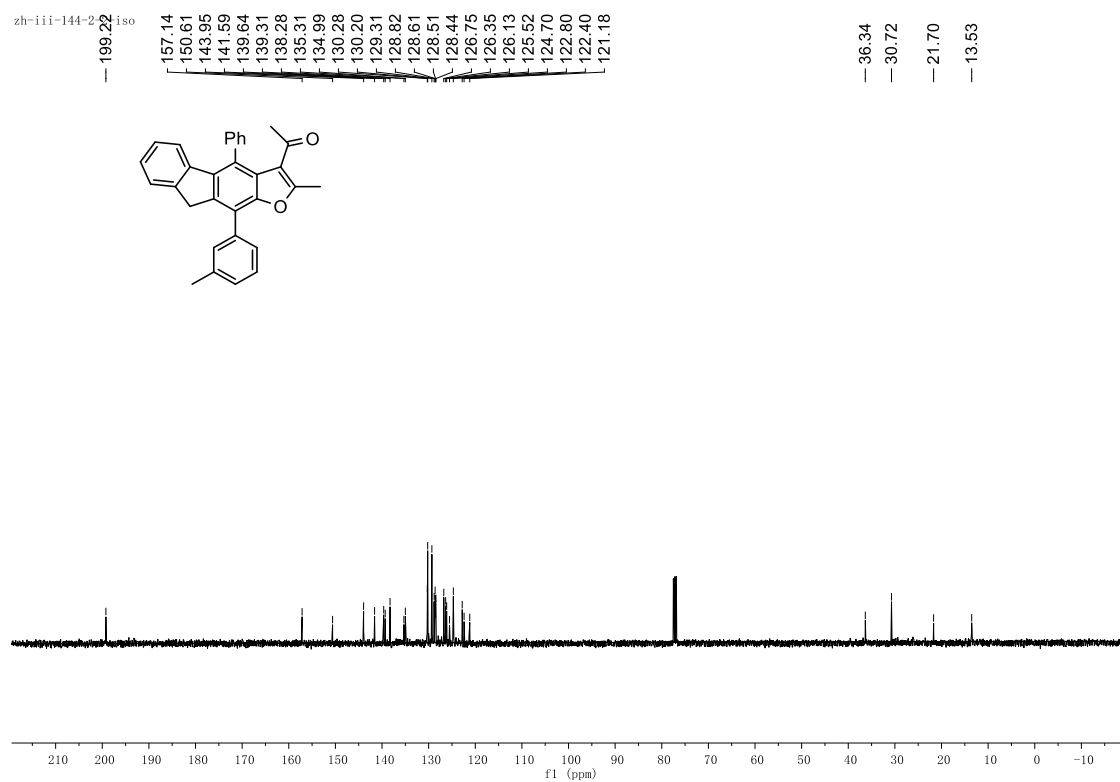
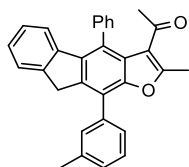
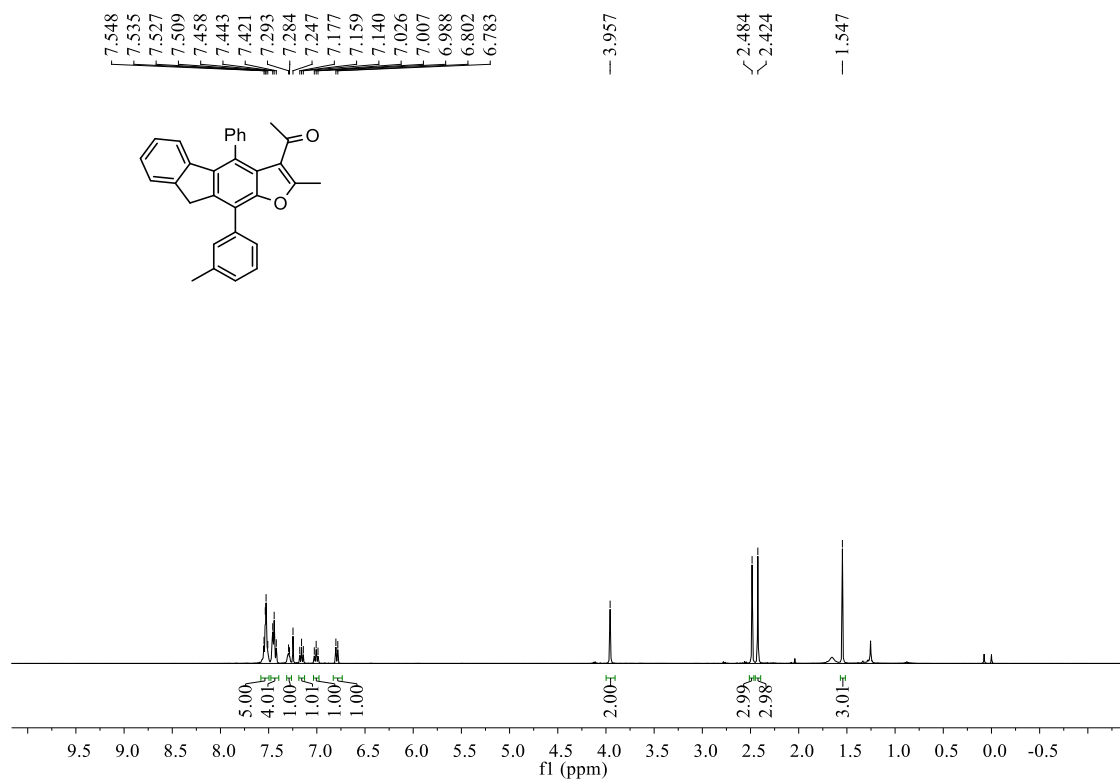




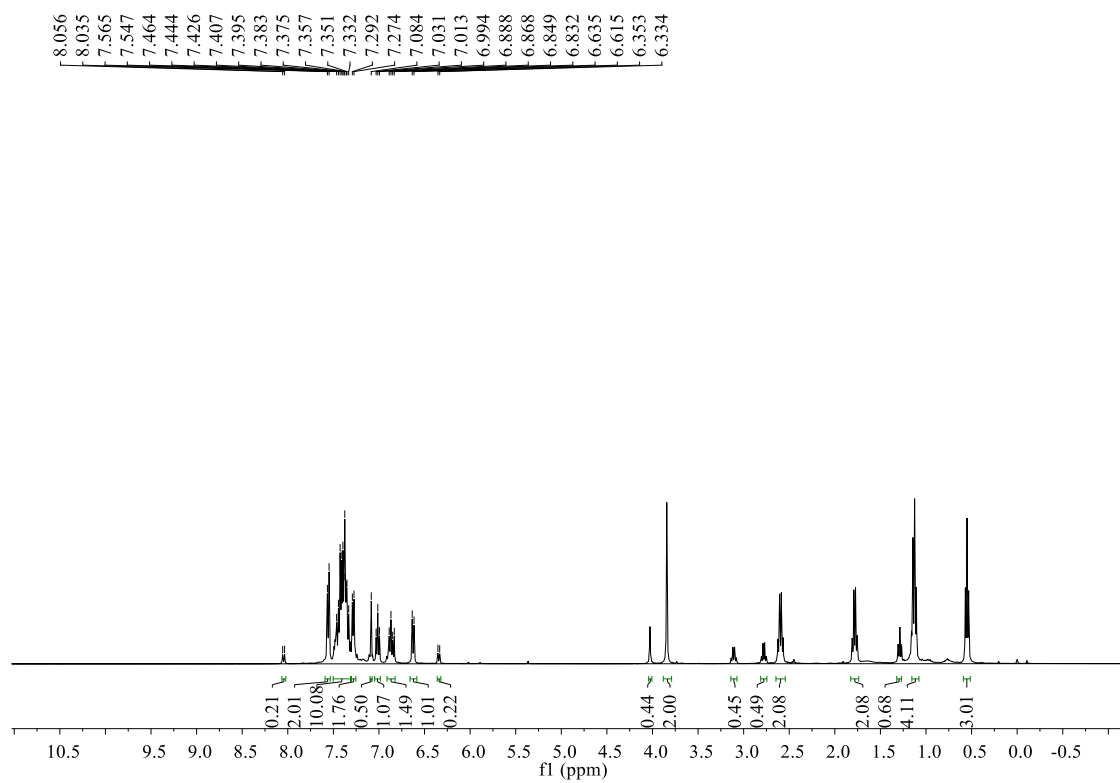
3ah

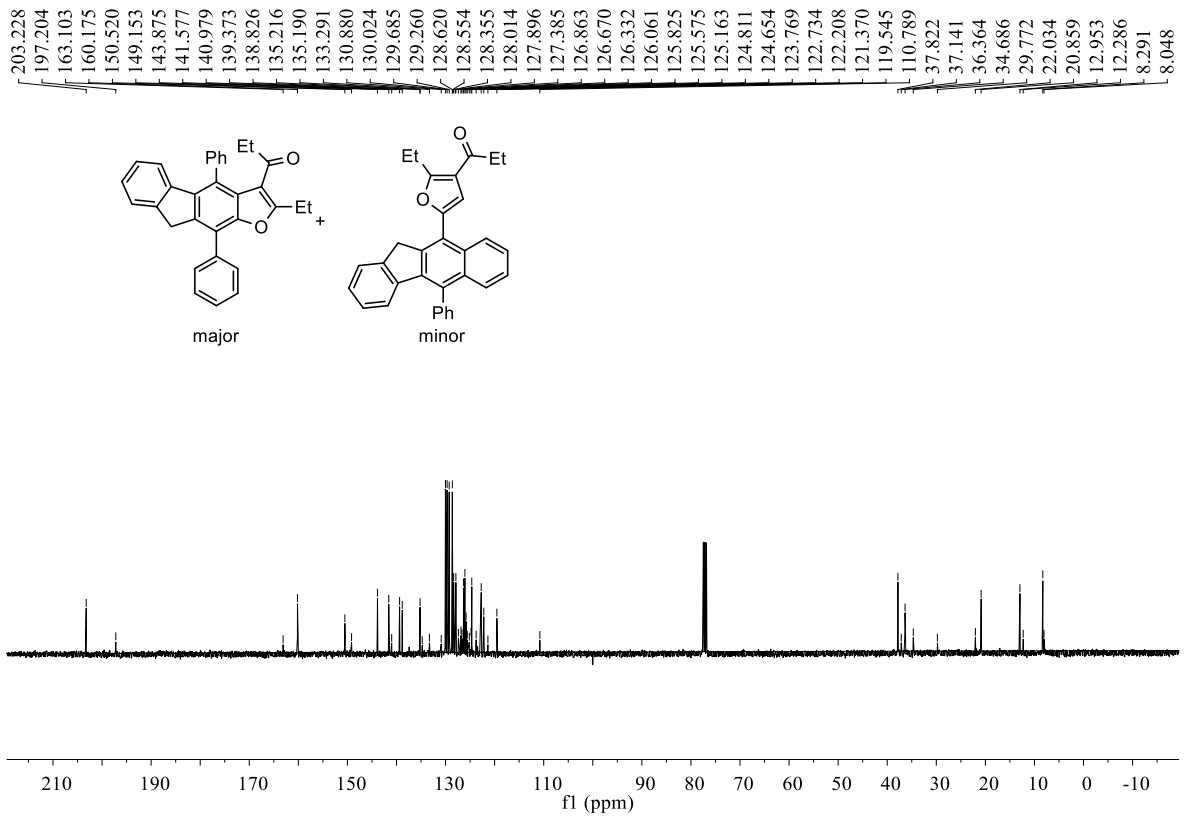


3ai

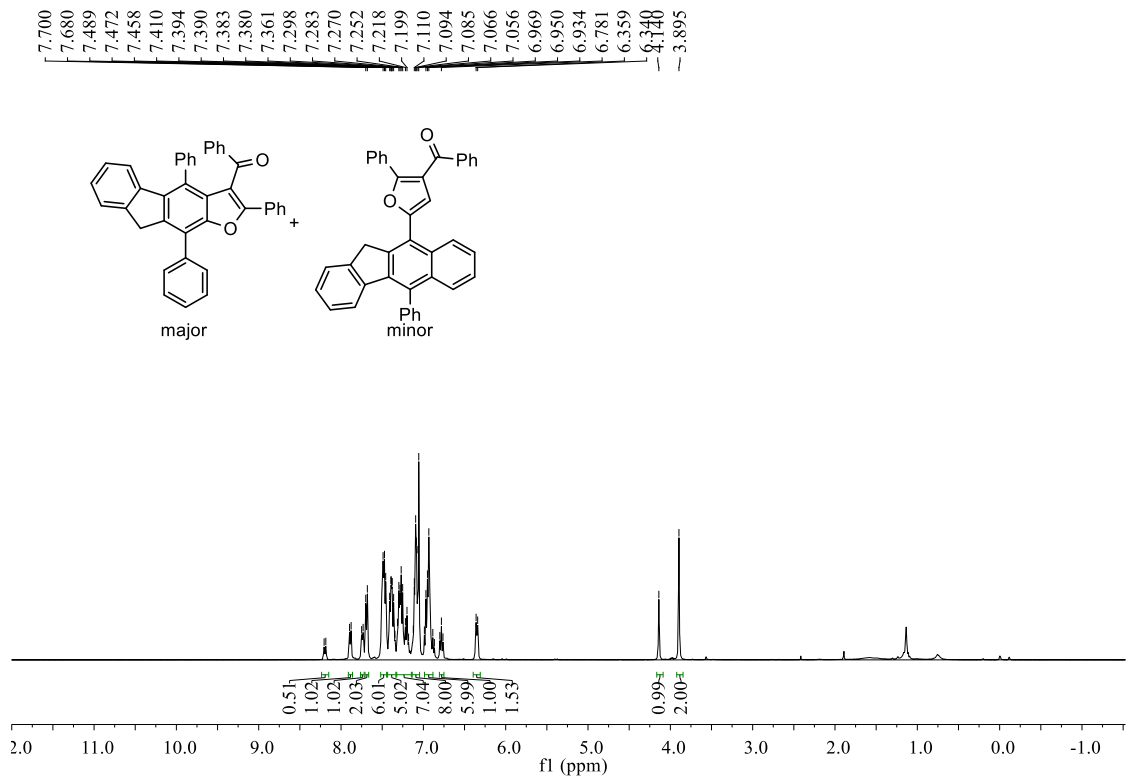


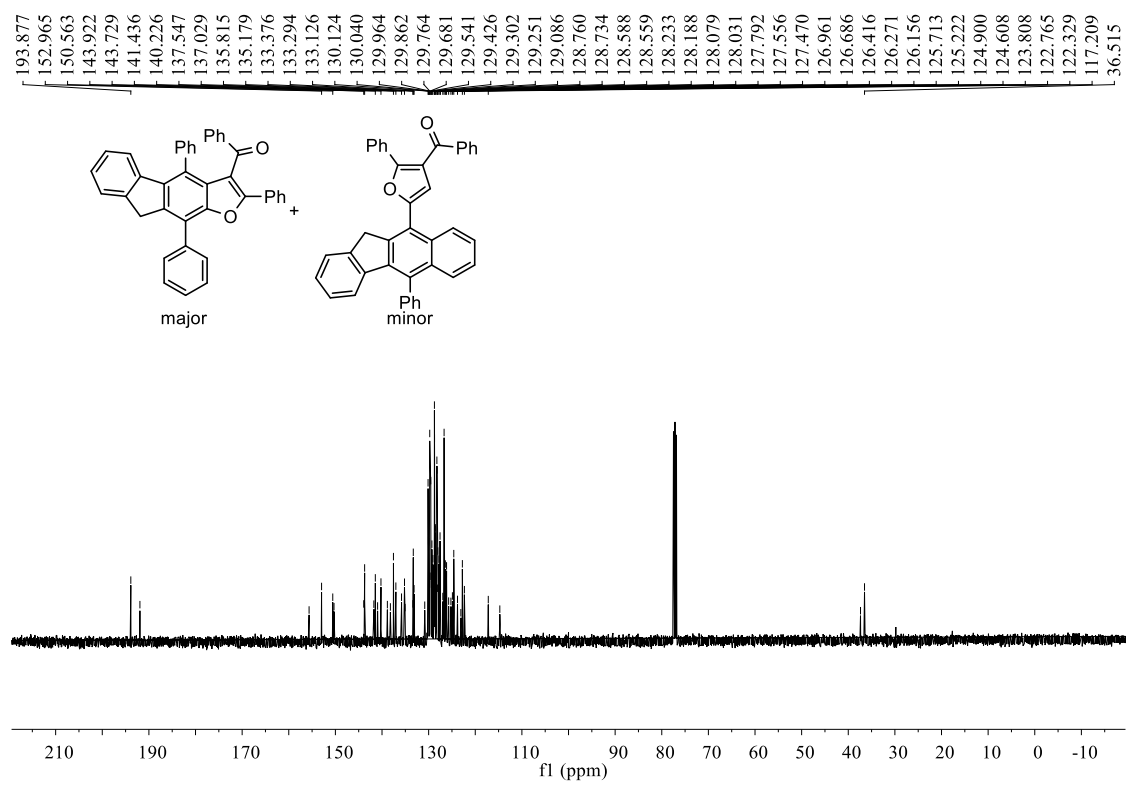
3aj



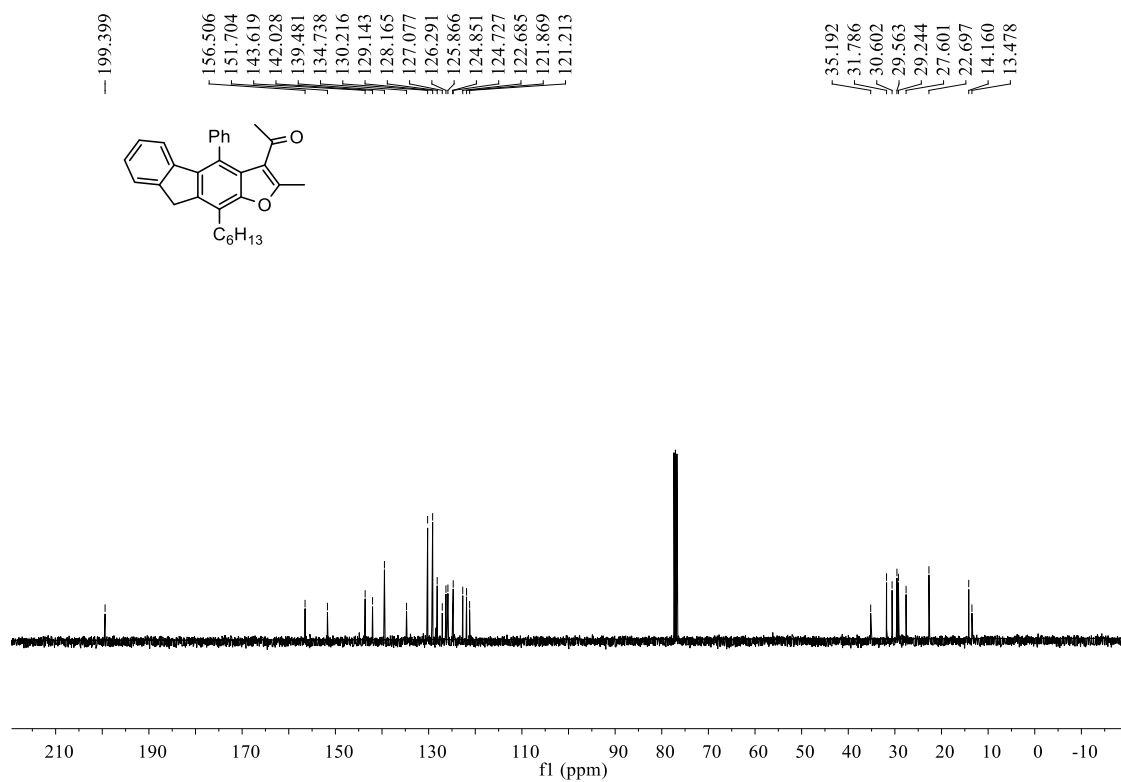
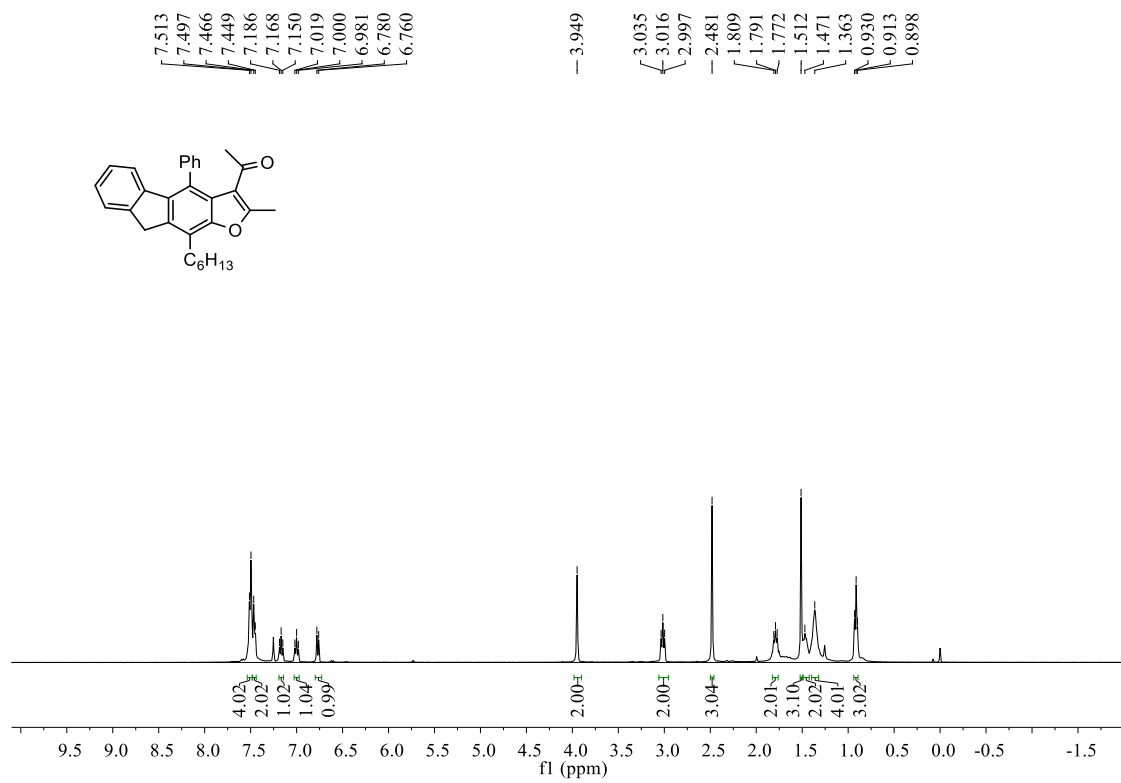


3ak

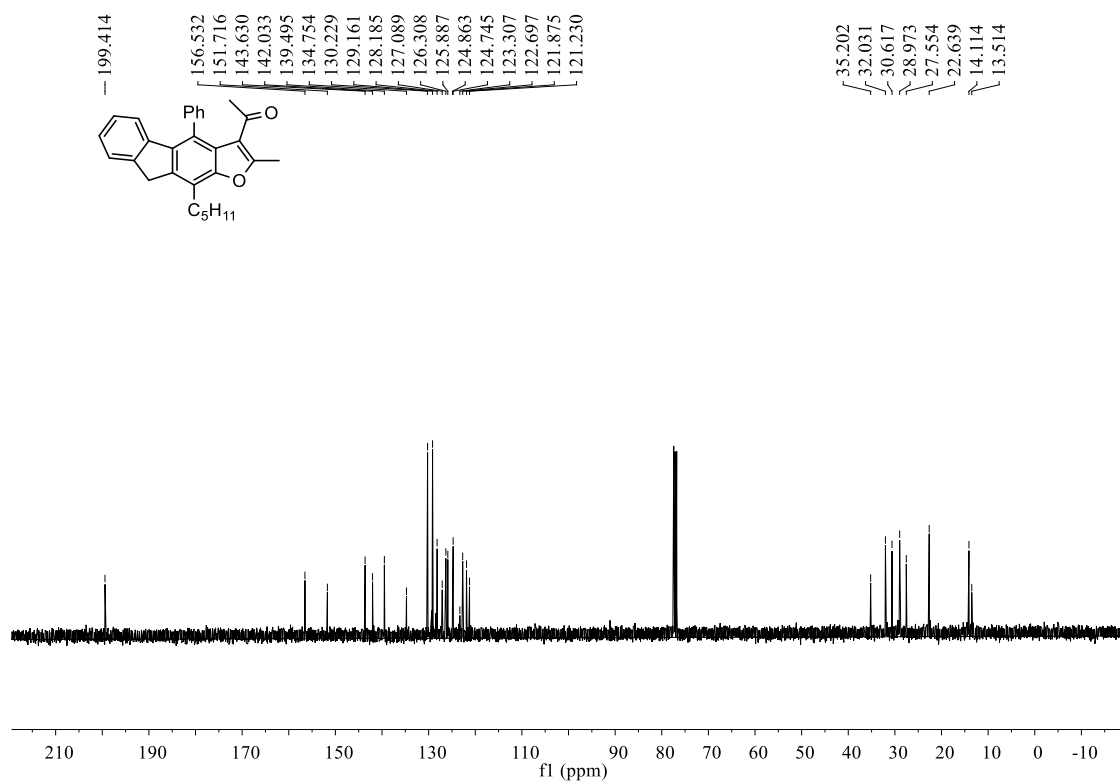
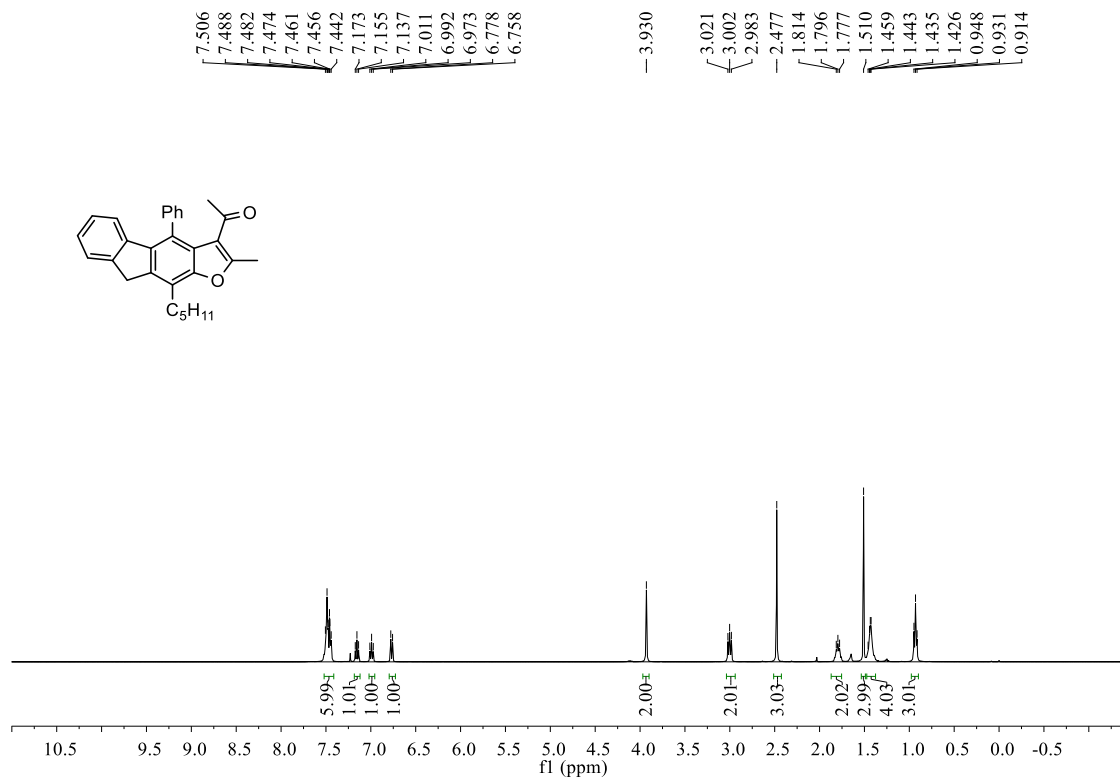




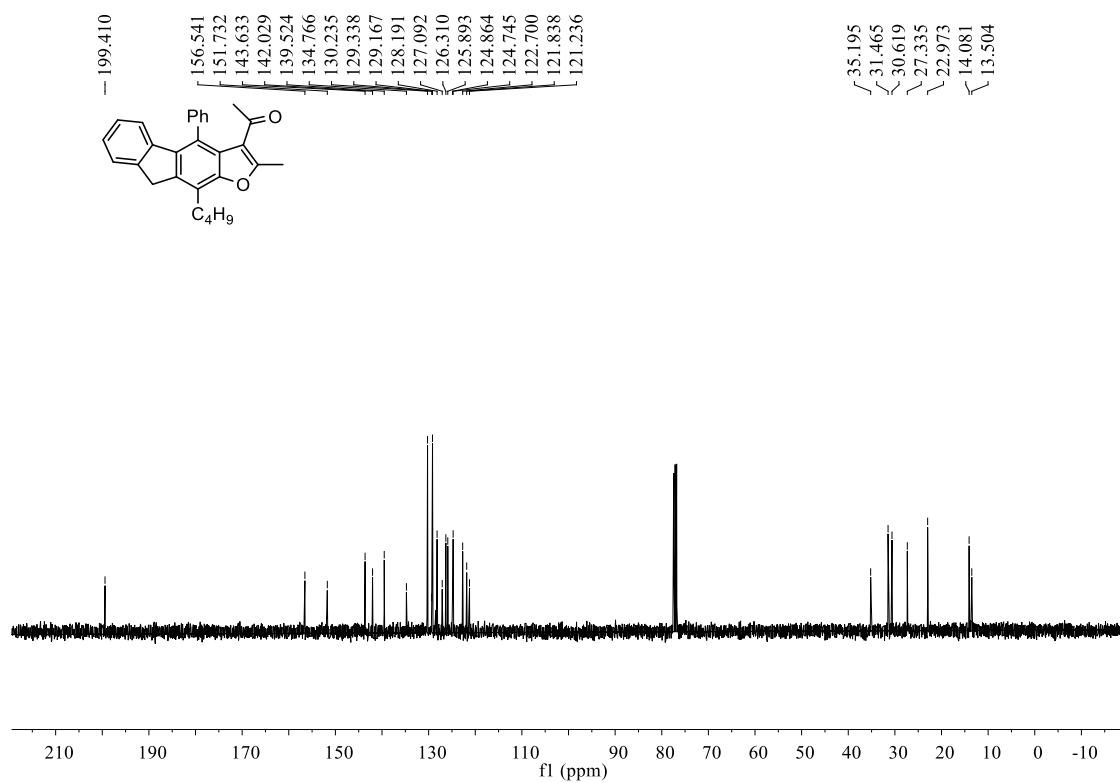
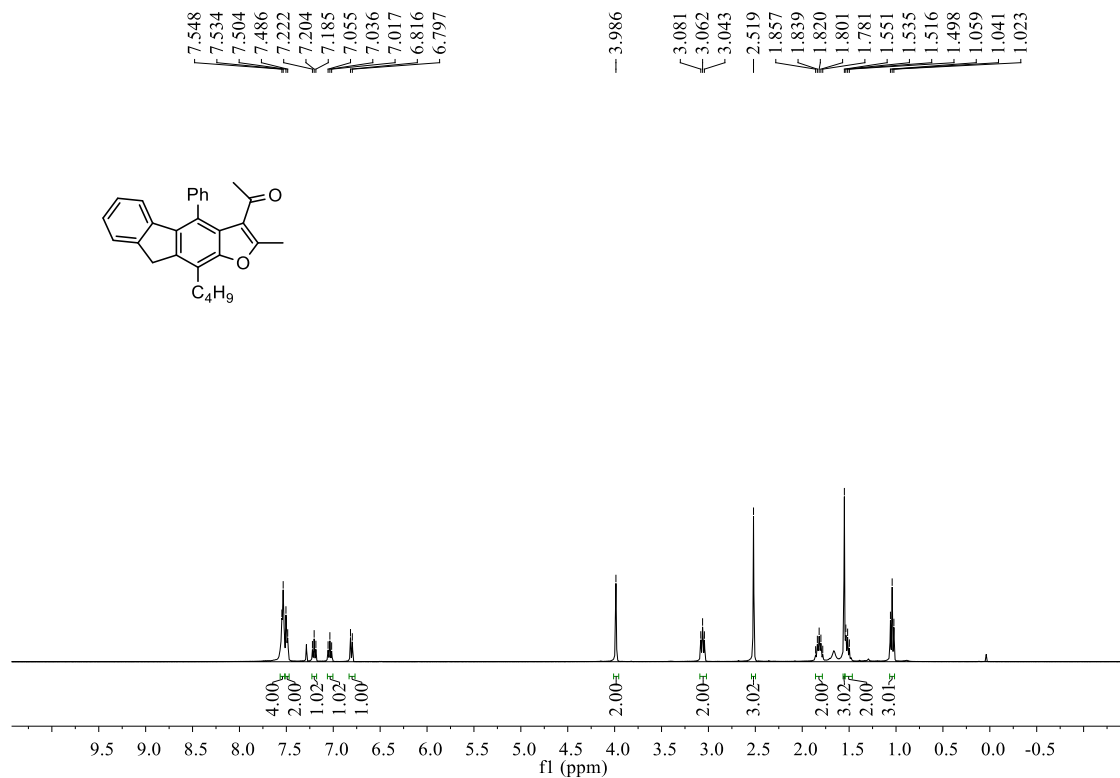
3a



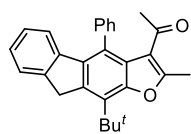
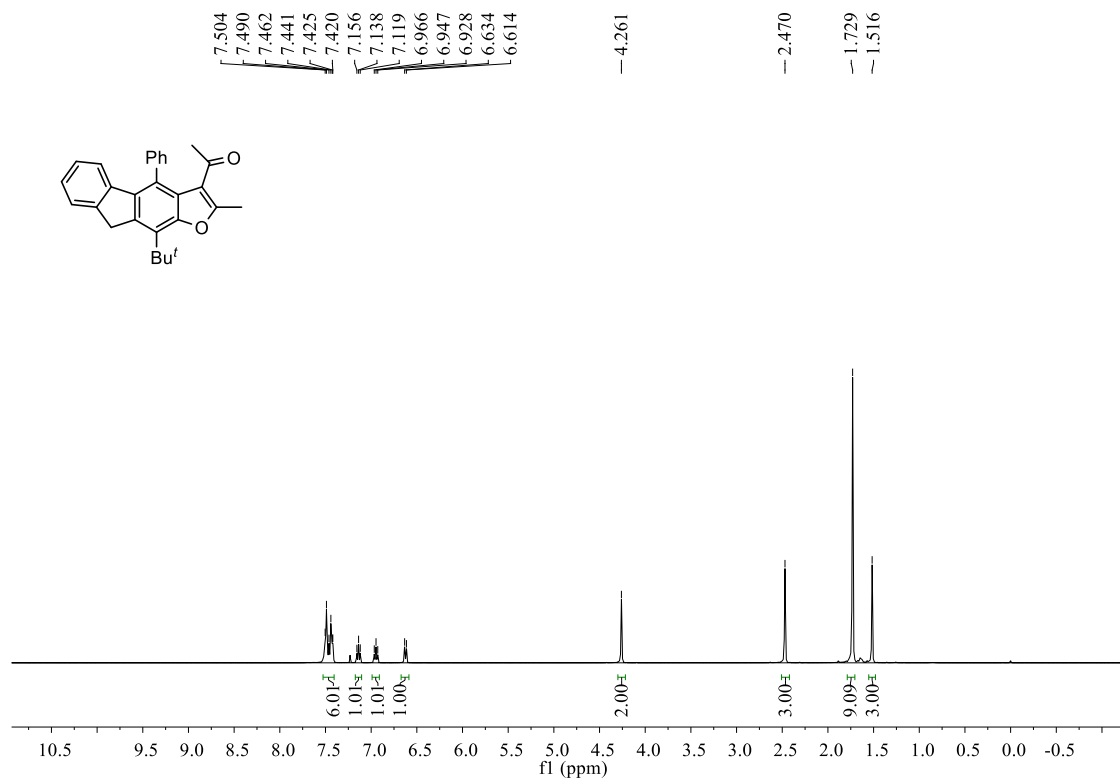
3am

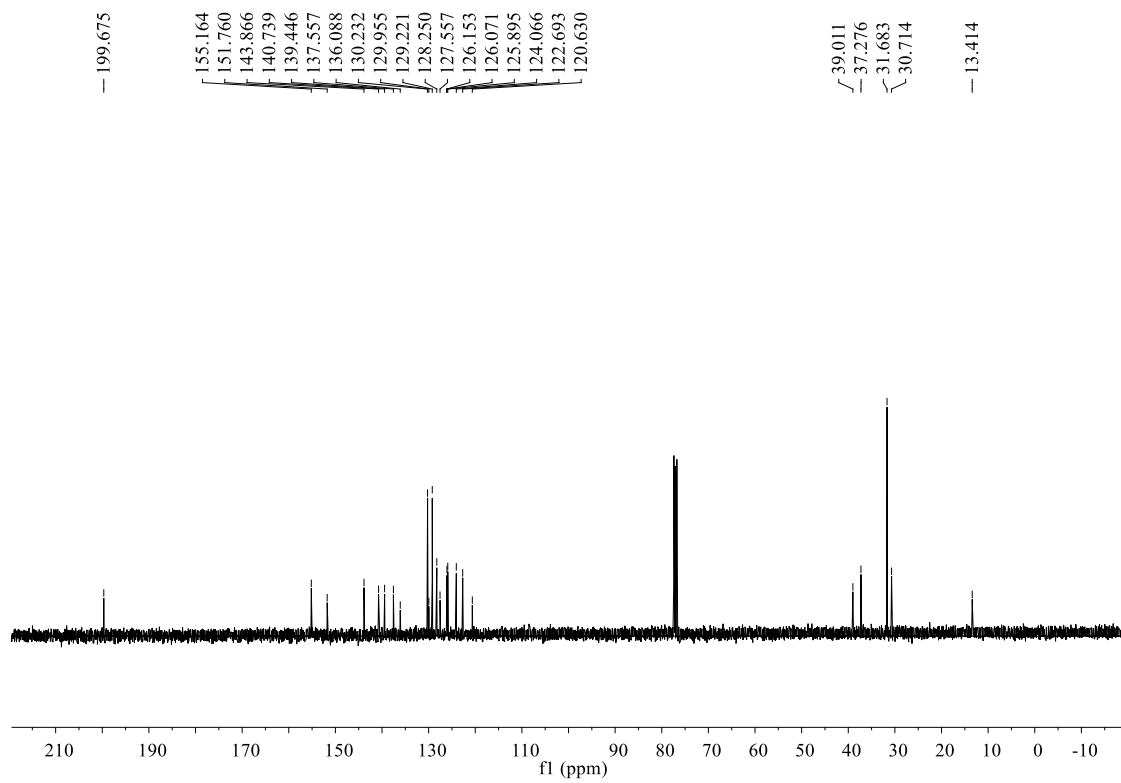


3an

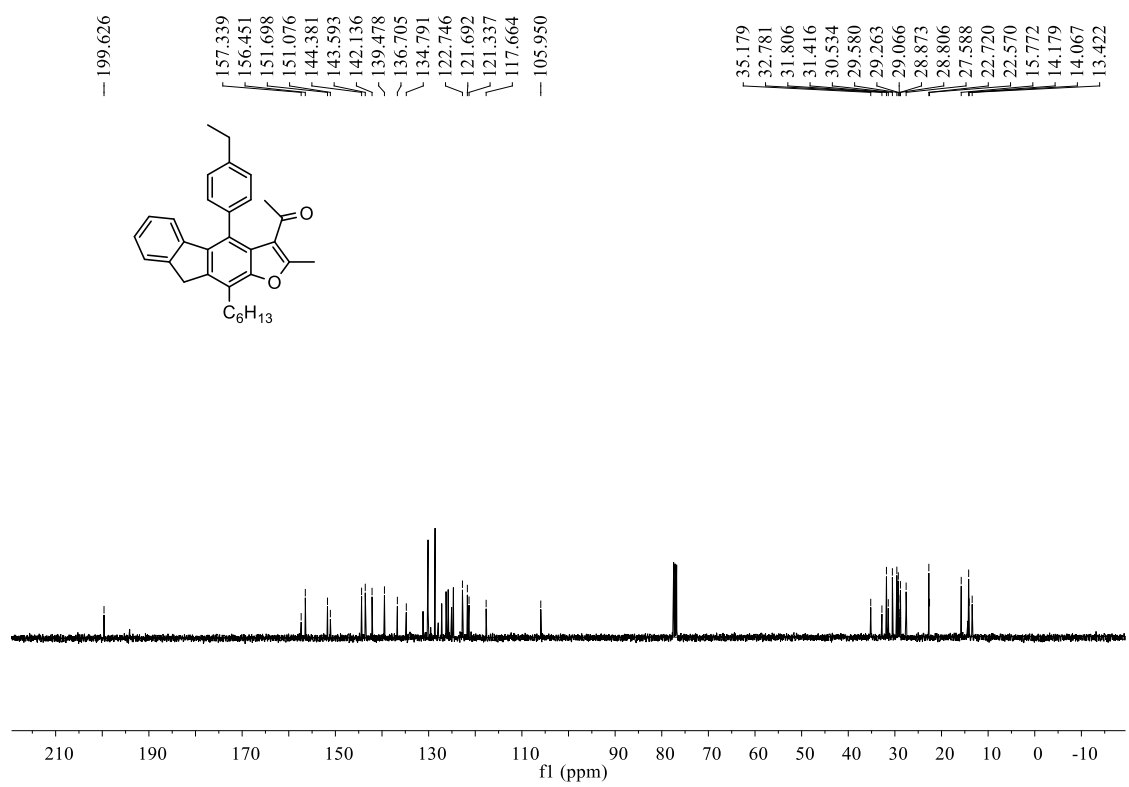
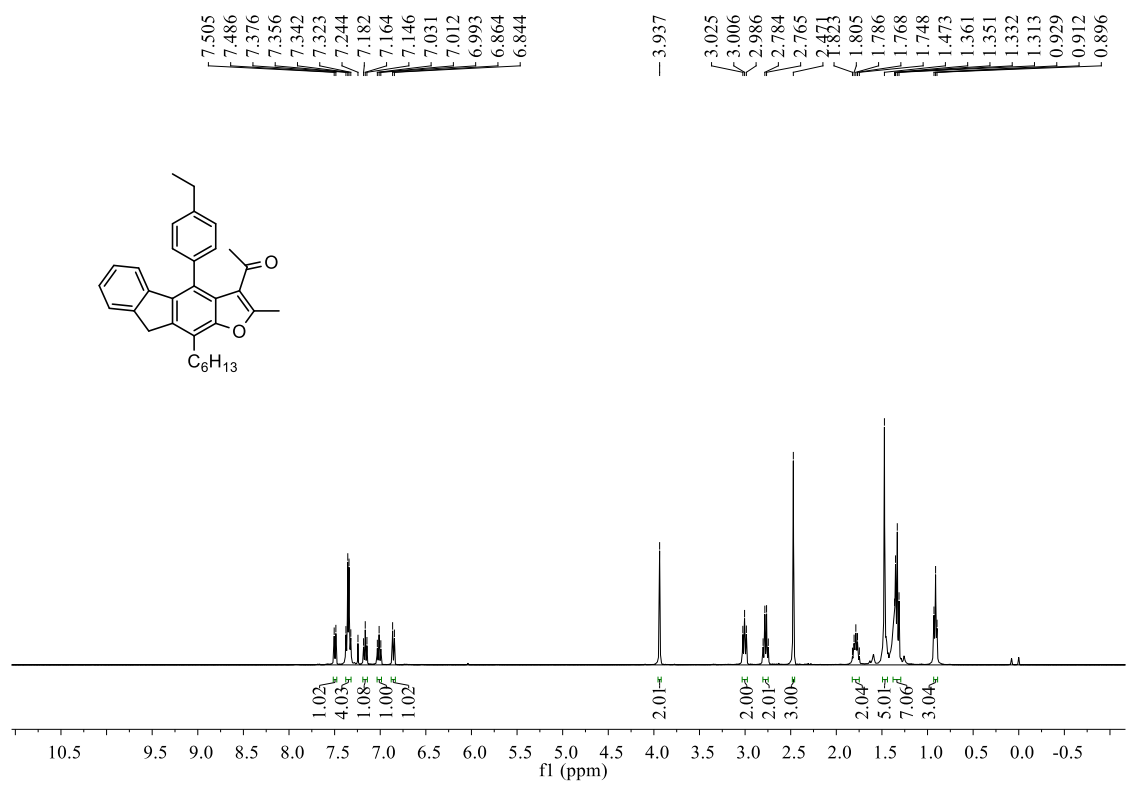


3ao

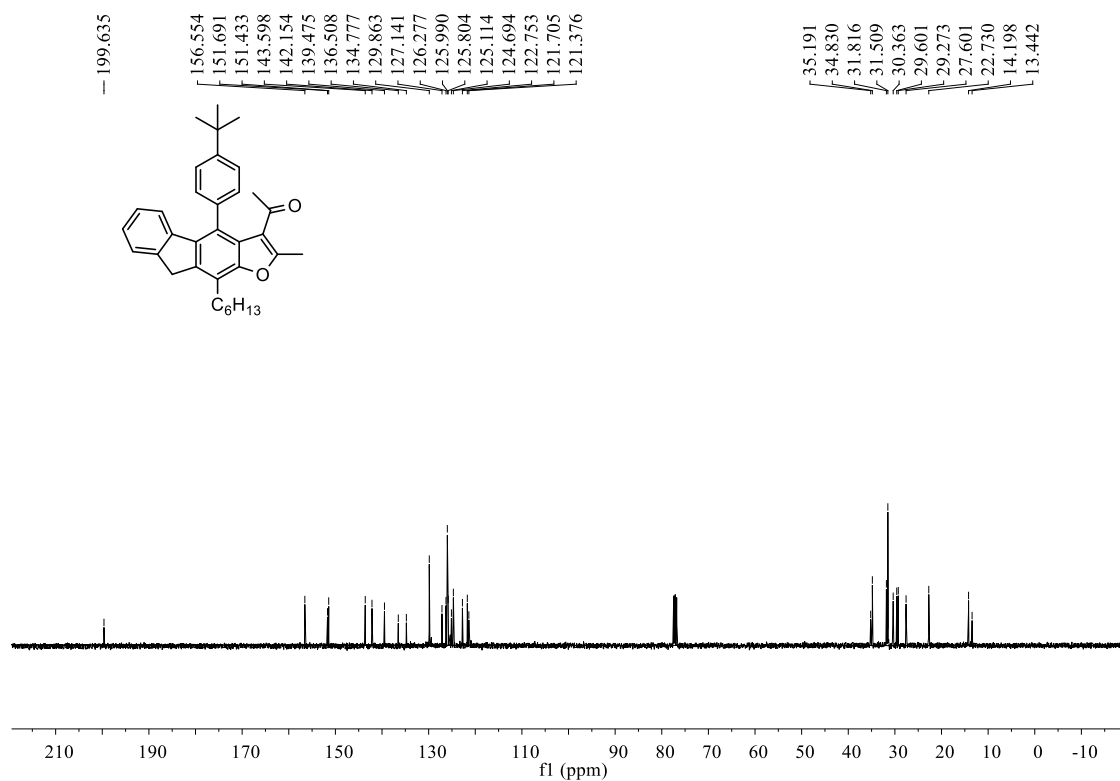
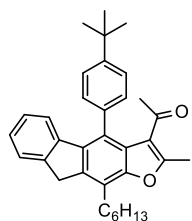
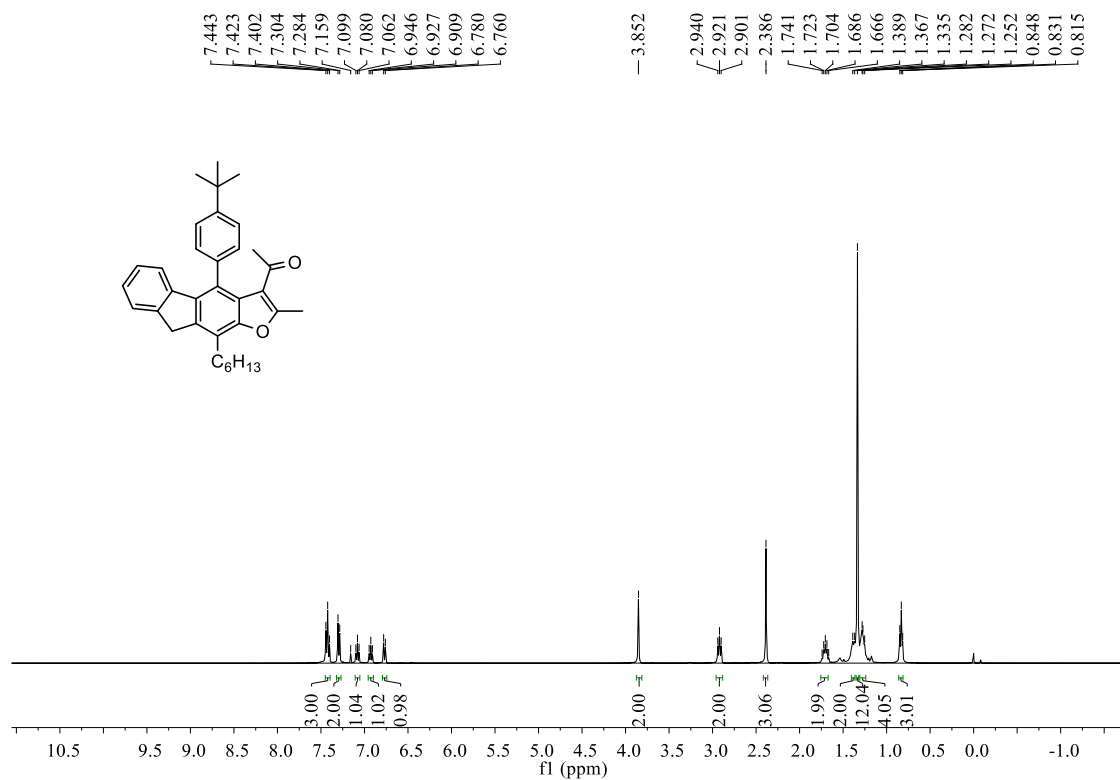




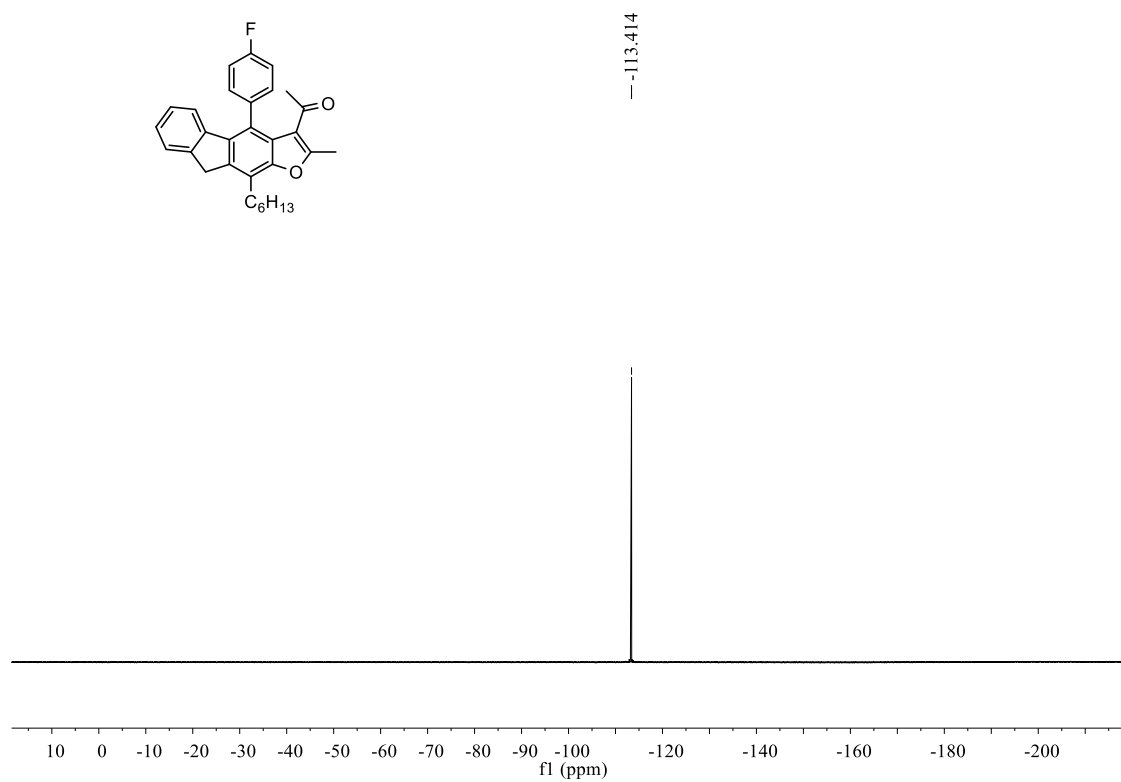
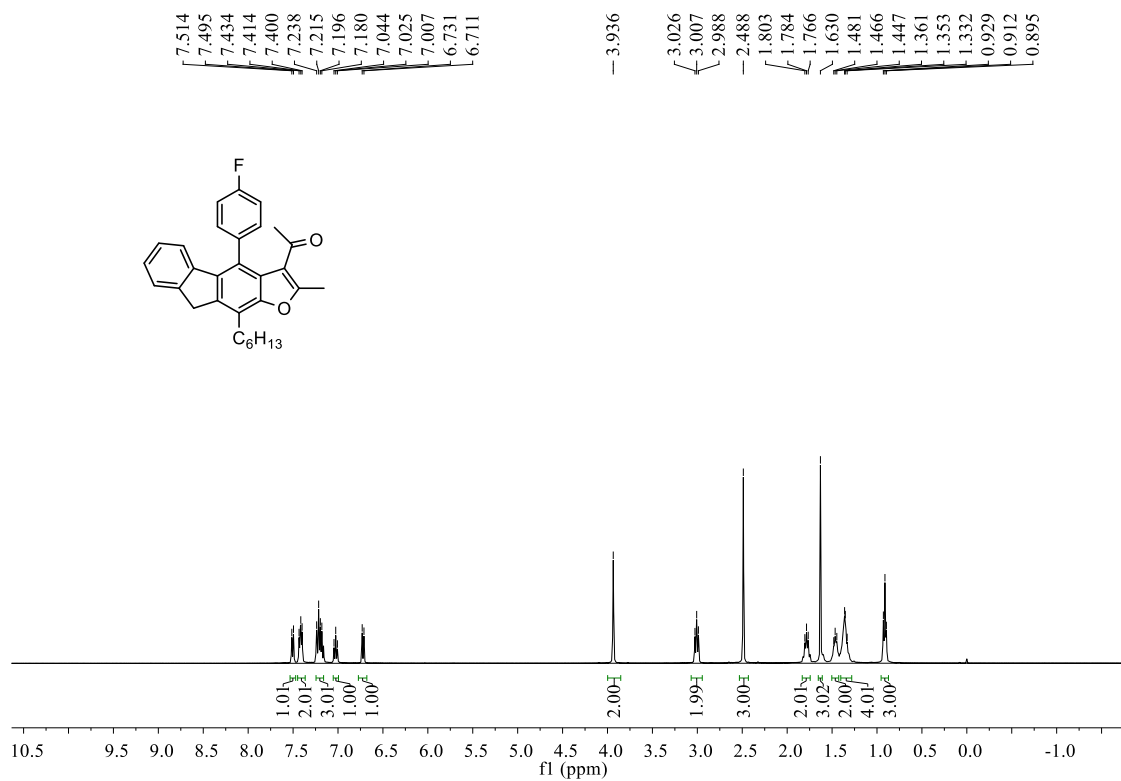
3ba

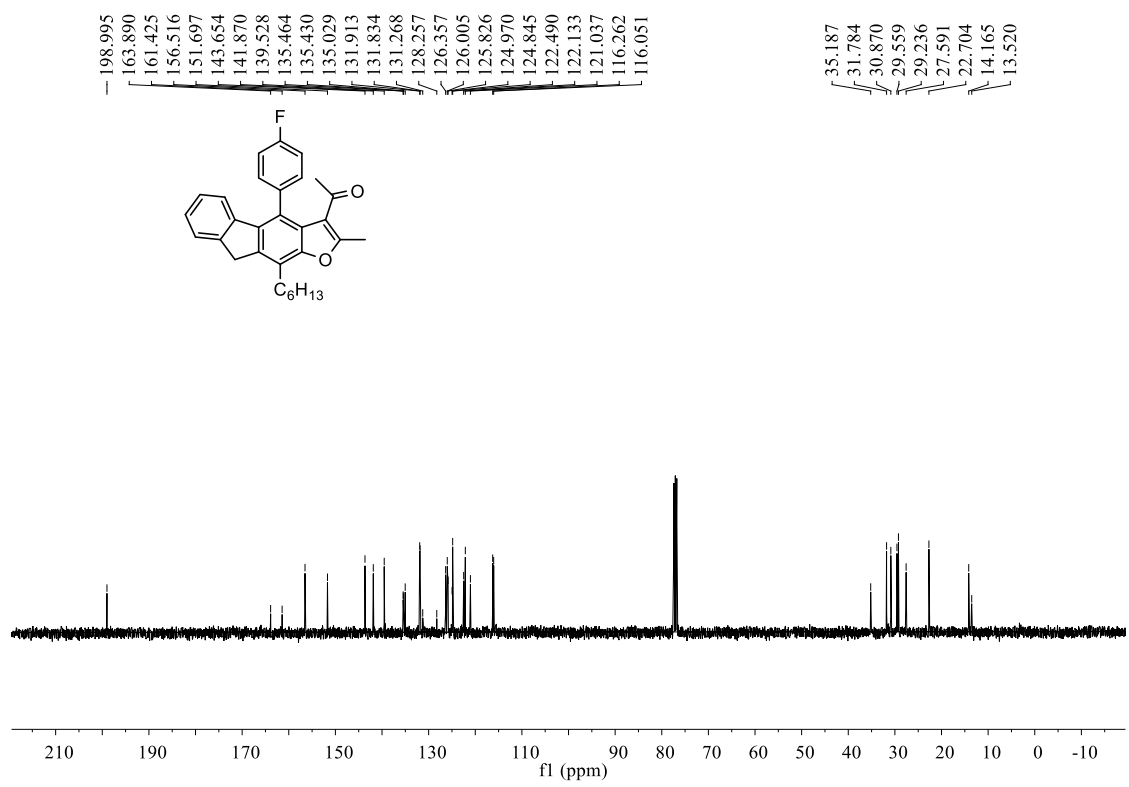


3bb

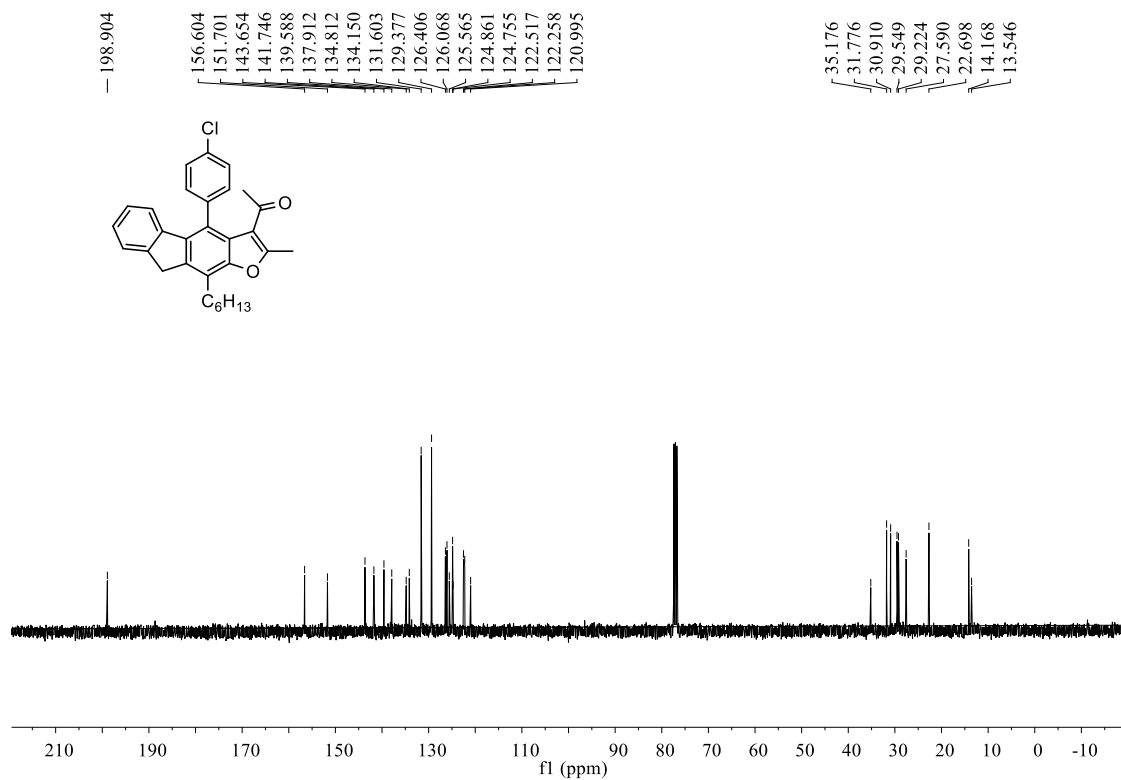
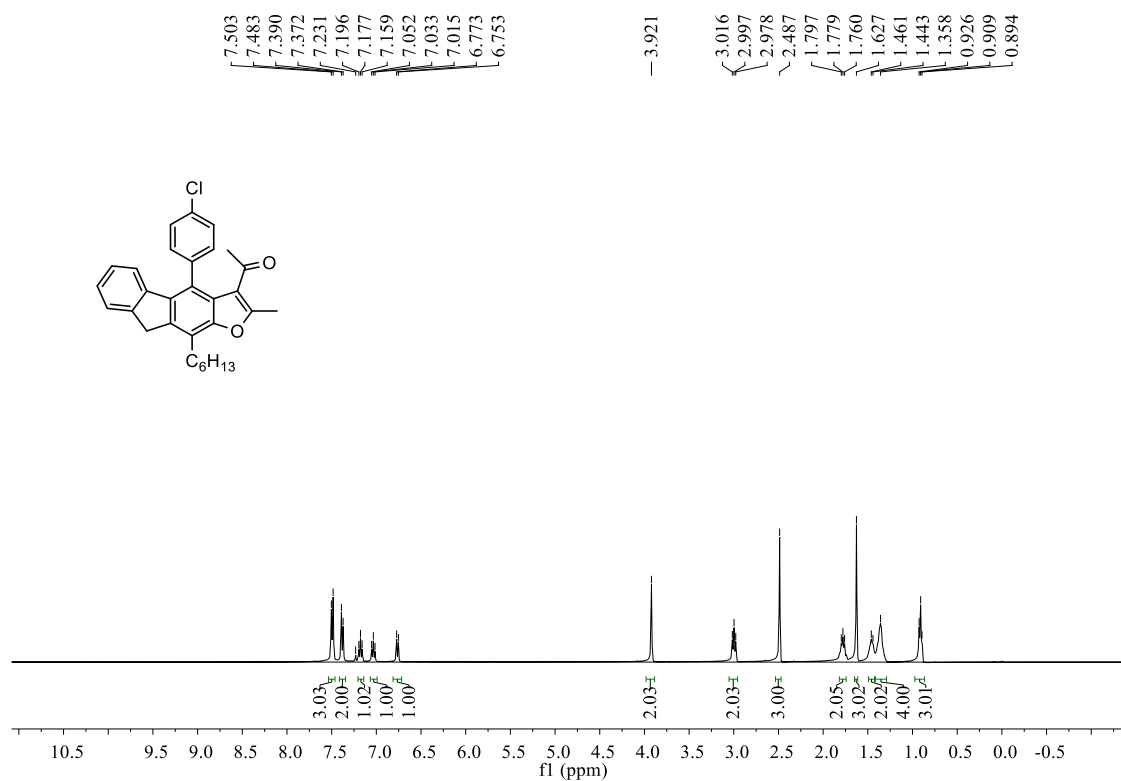


3bc

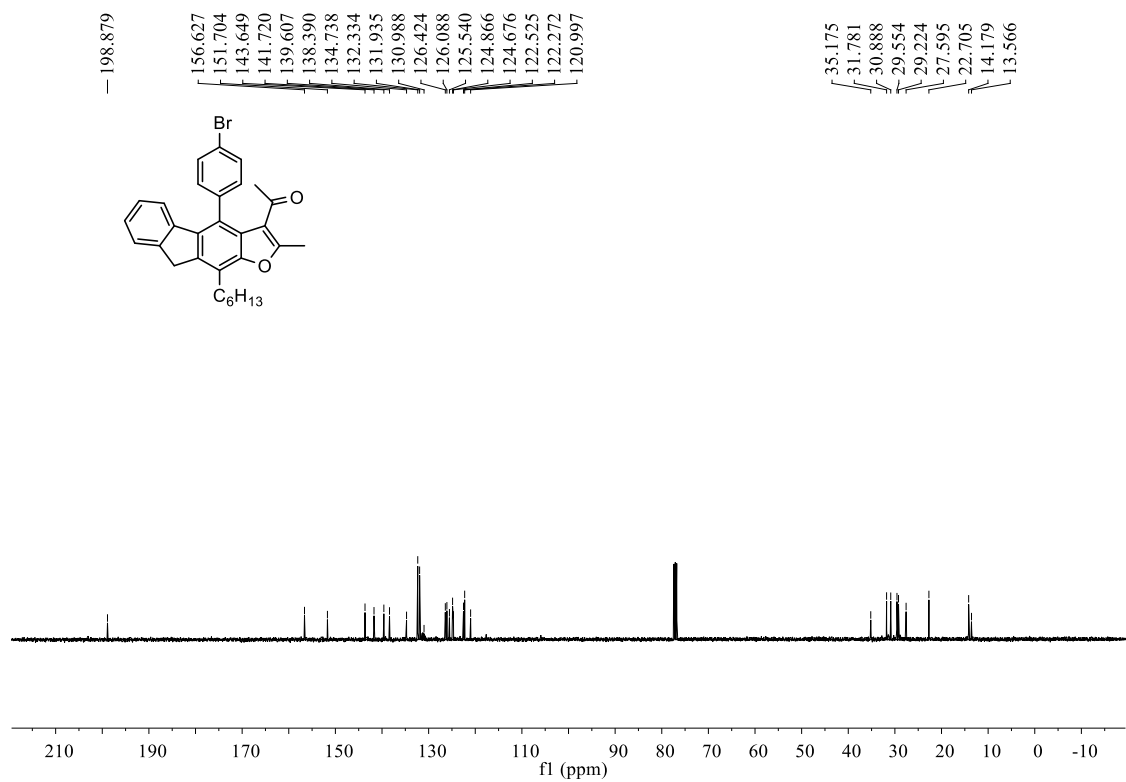
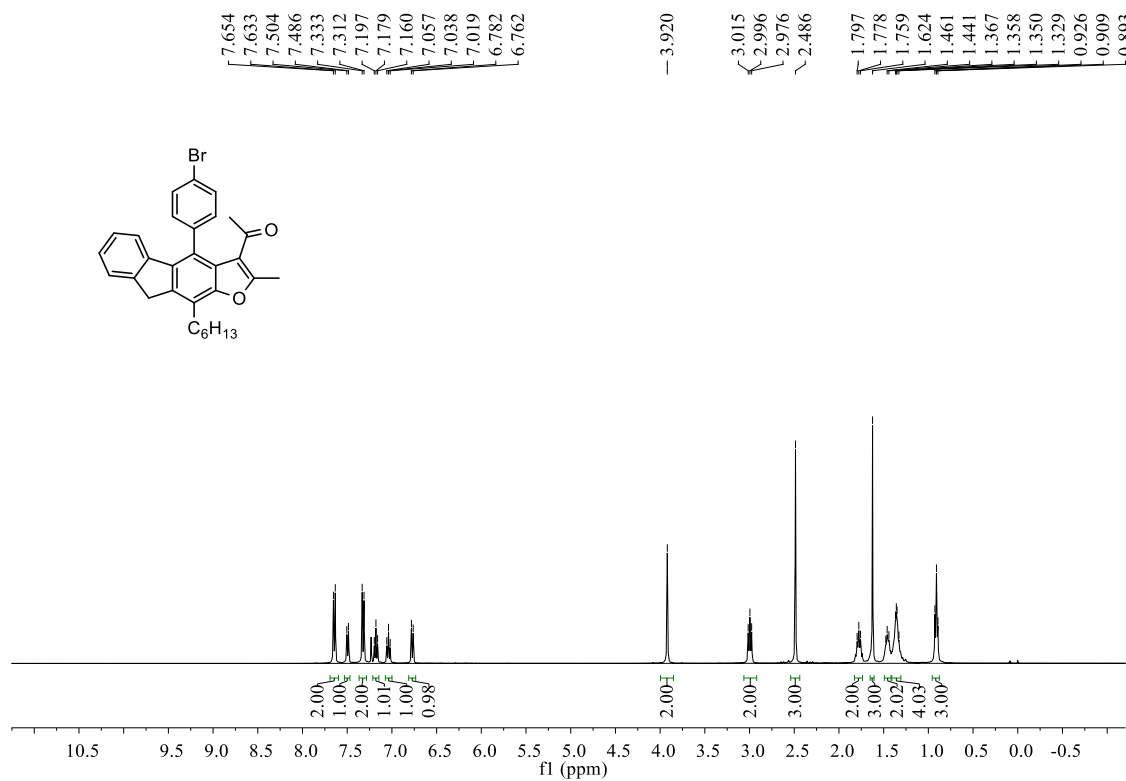




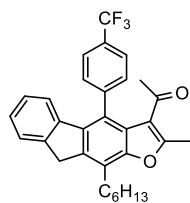
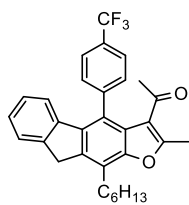
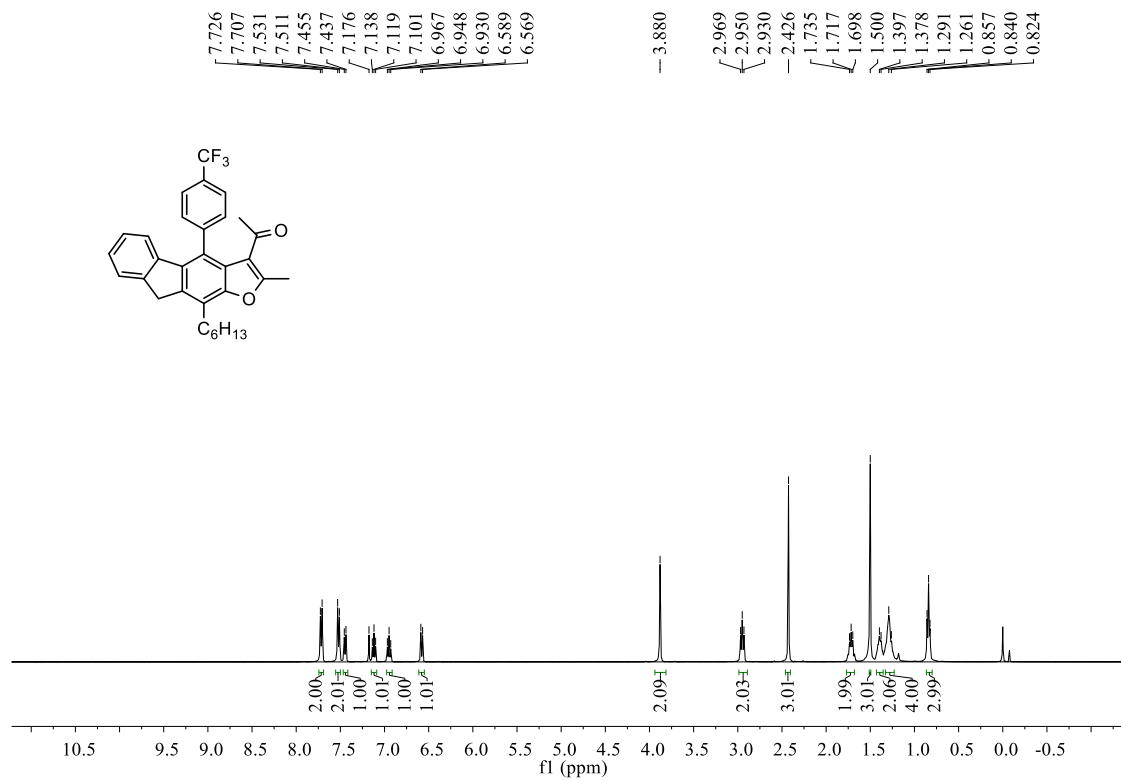
3bd

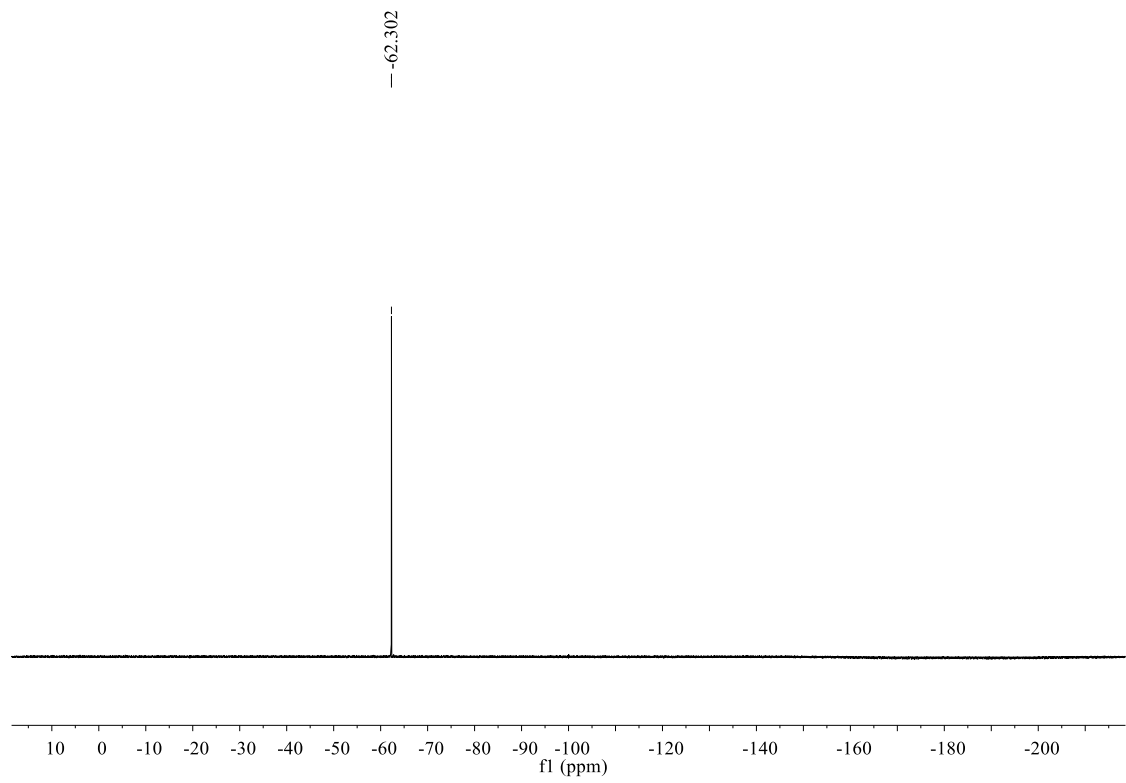


3be



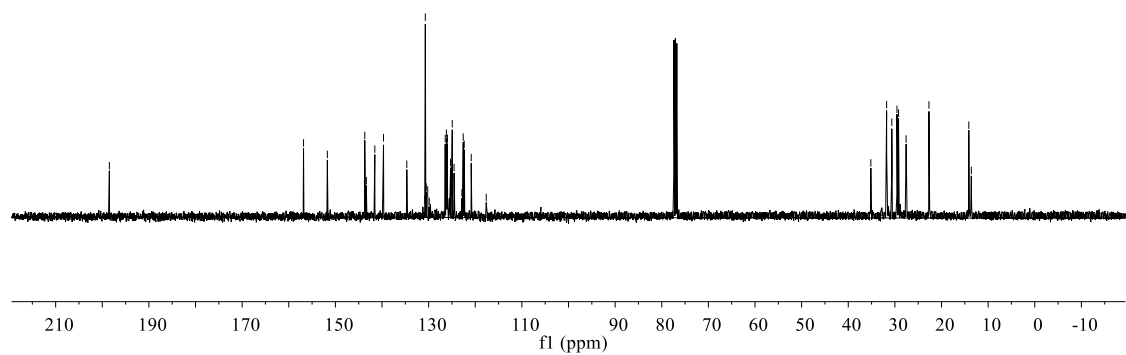
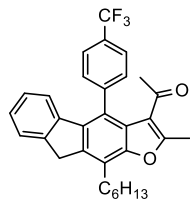
3bf



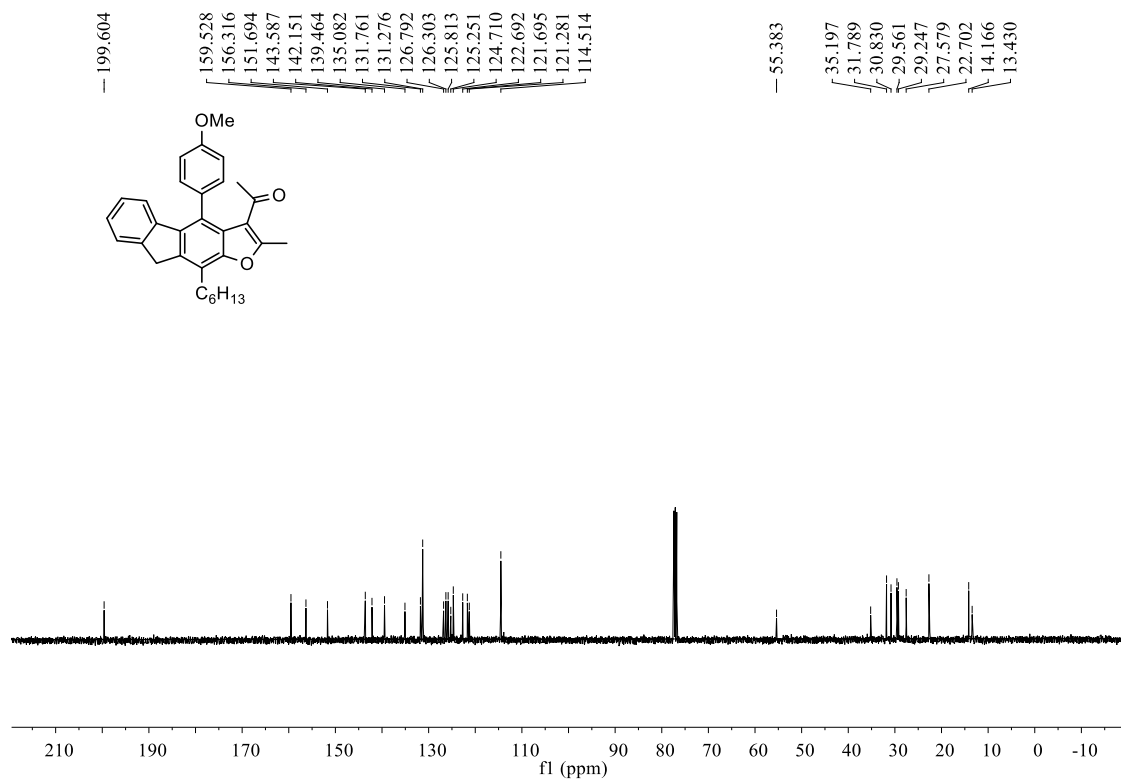
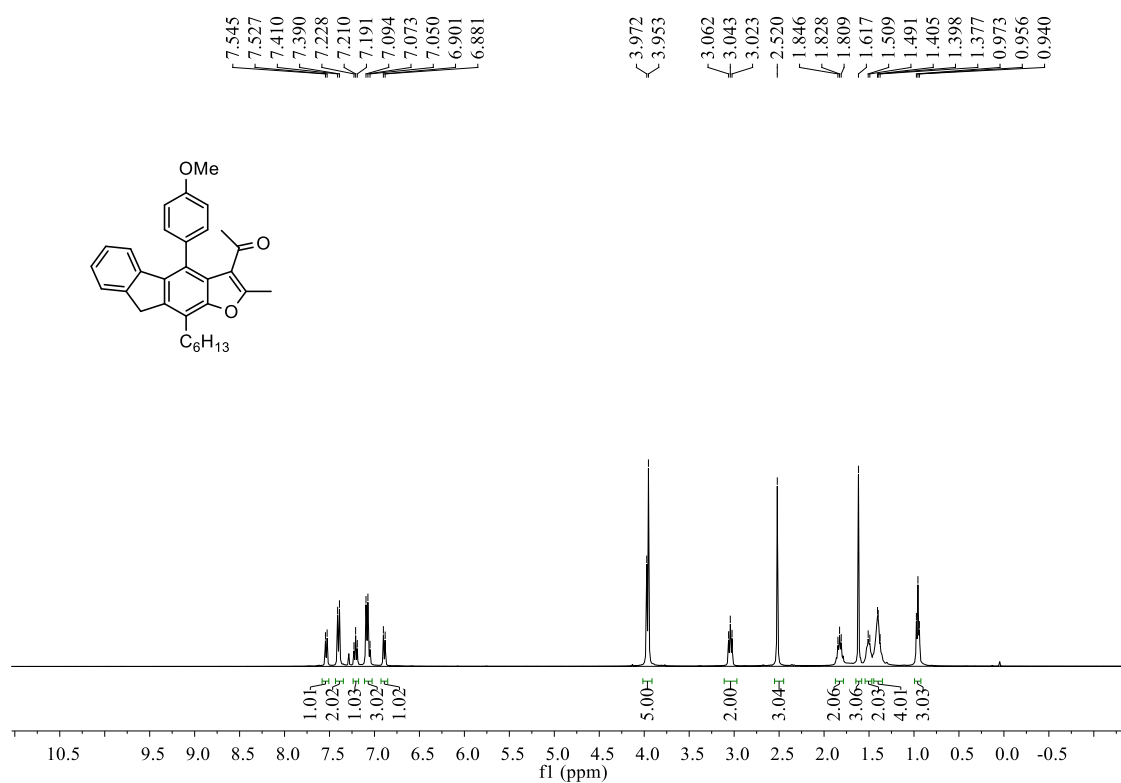


198.474
156.834
151.728
143.703
143.365
141.544
139.680
134.685
130.842
130.715
130.517
130.193
129.870
126.447
126.188
126.062
126.027
125.990
125.953
125.301
124.934
124.547
122.866
122.584
122.373
120.866
117.652

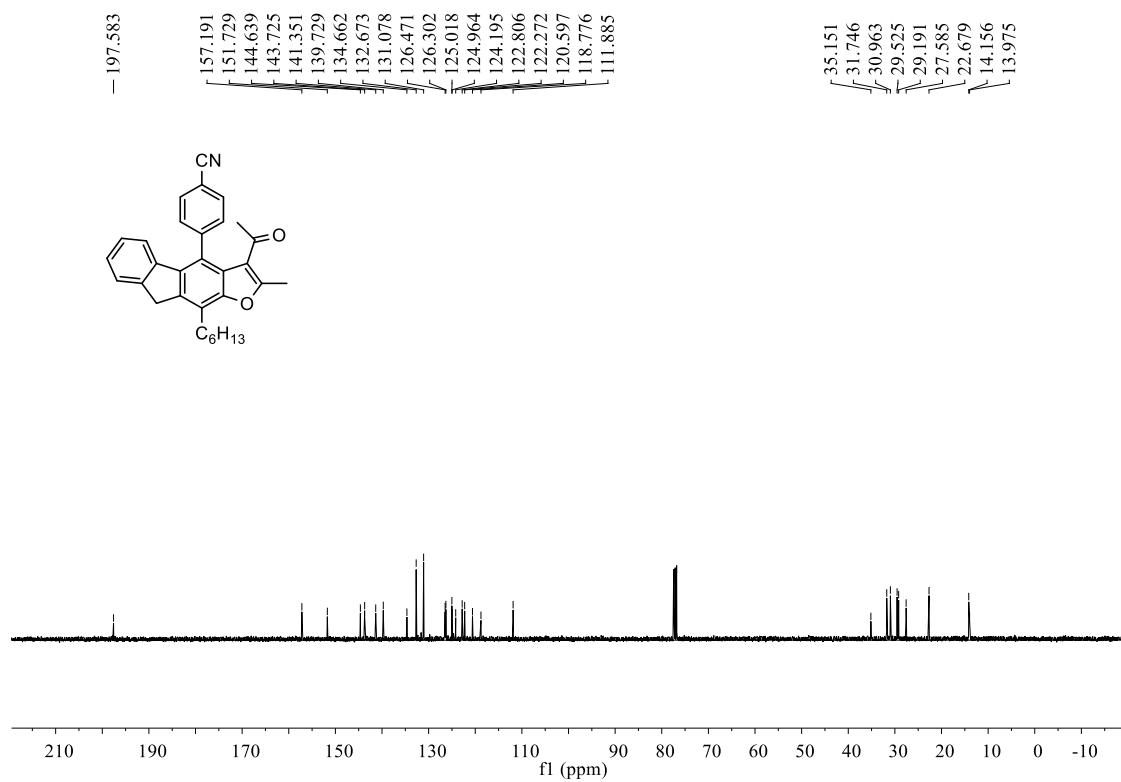
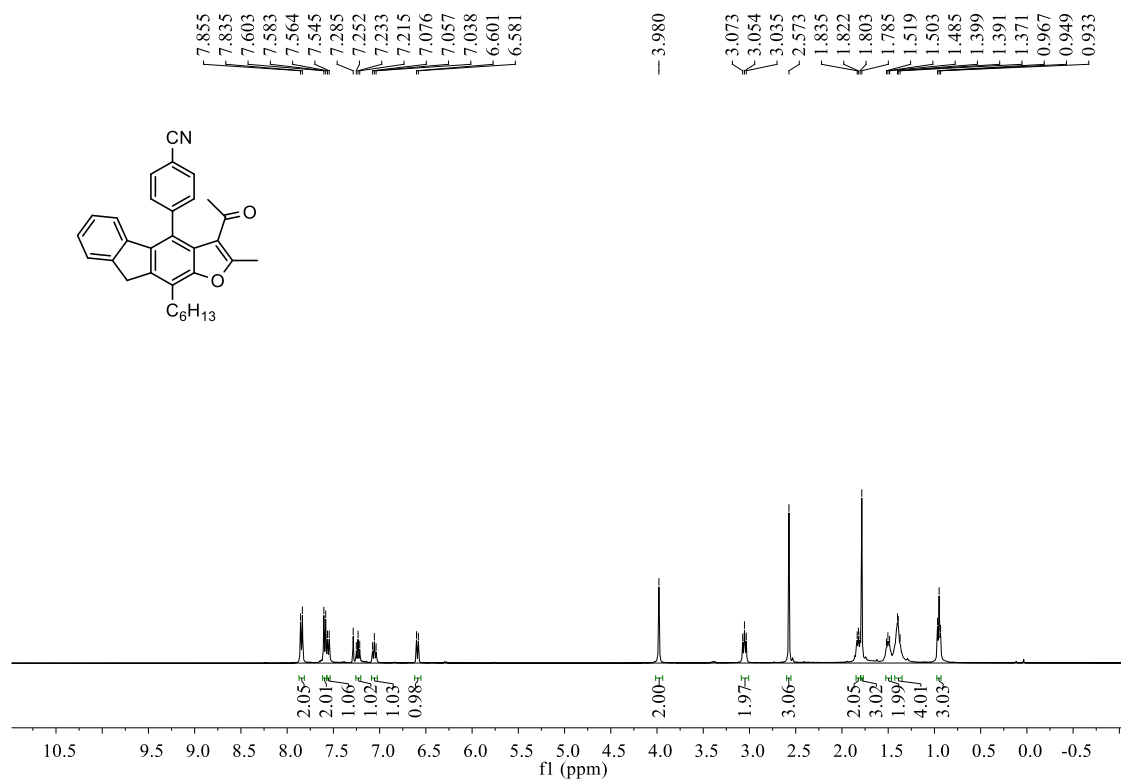
35.159
31.772
30.660
29.554
29.218
27.594
22.696
14.144
13.610



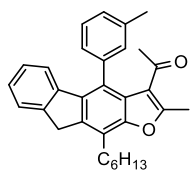
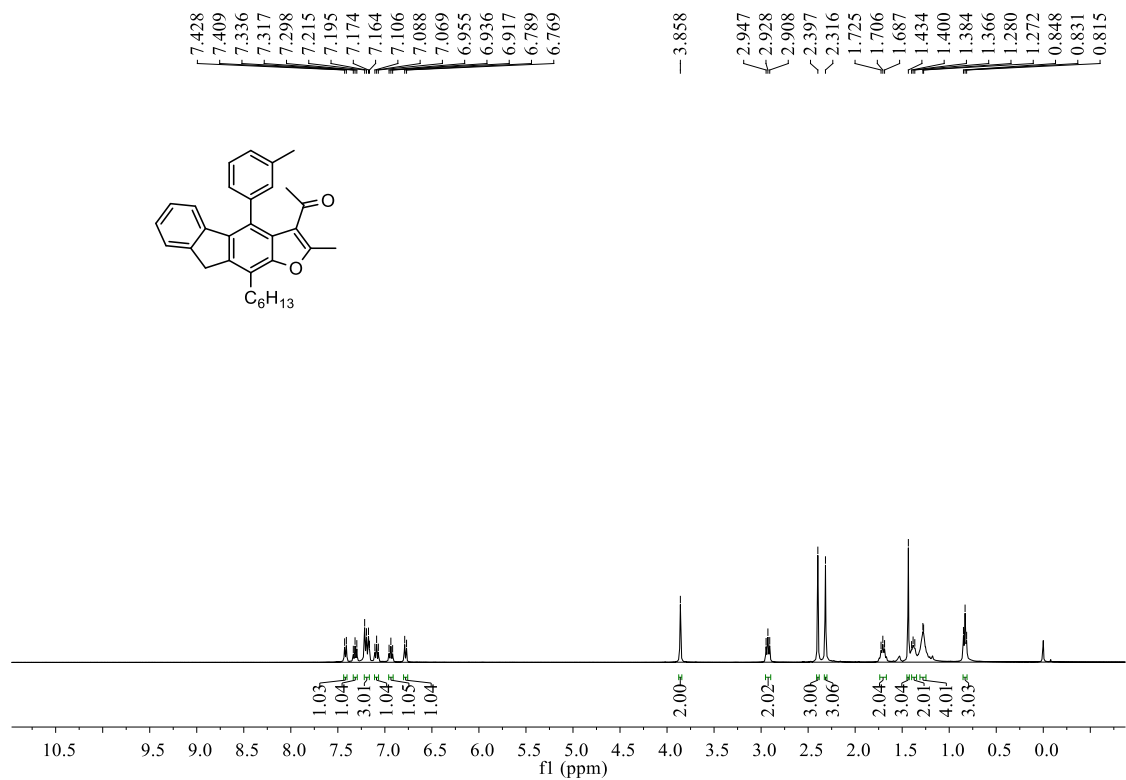
3bg

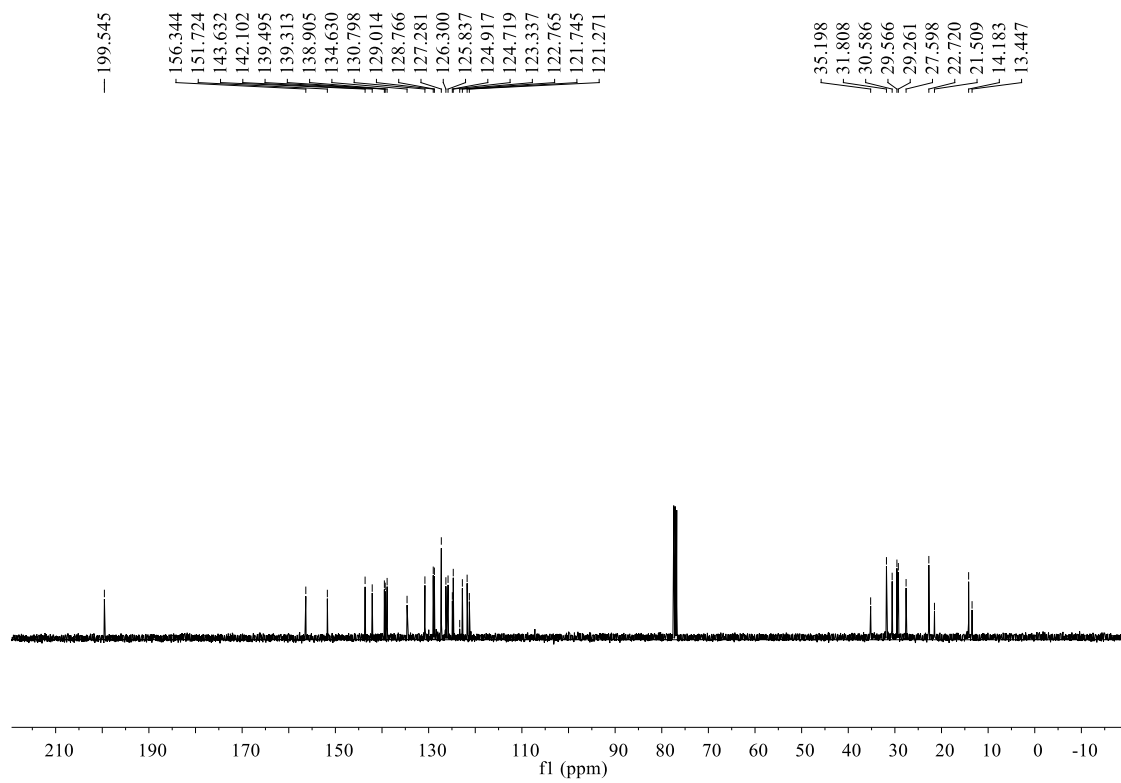


3bh

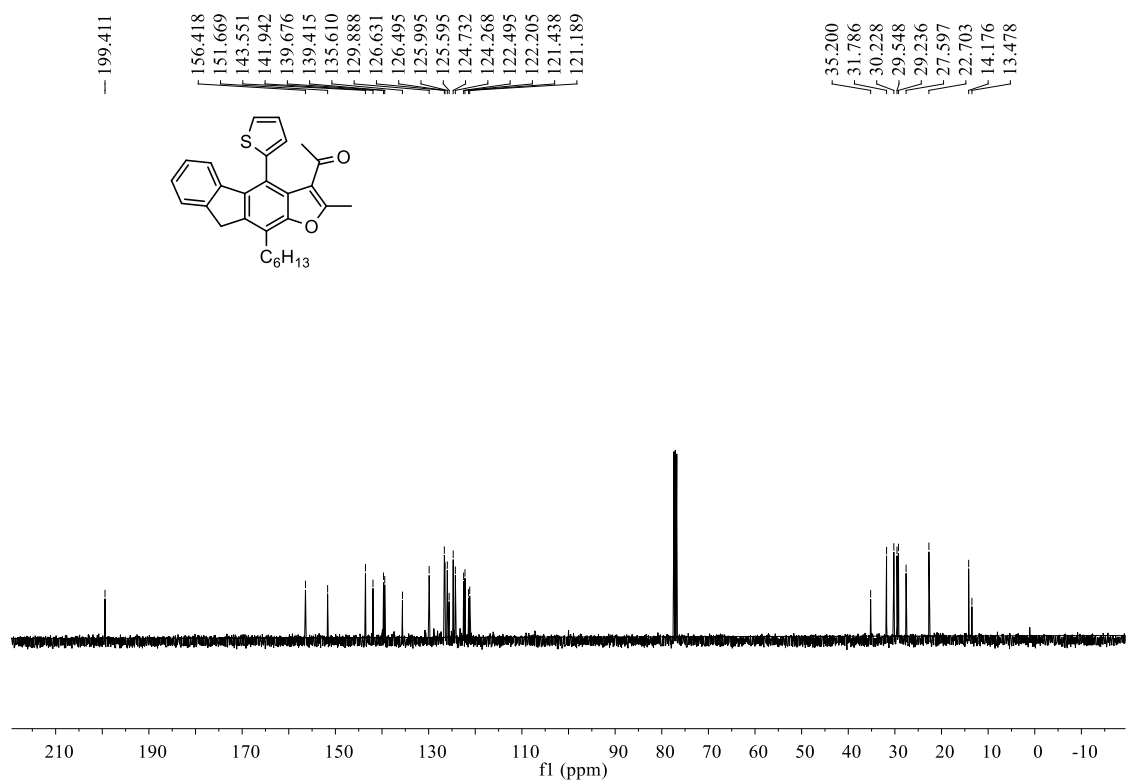
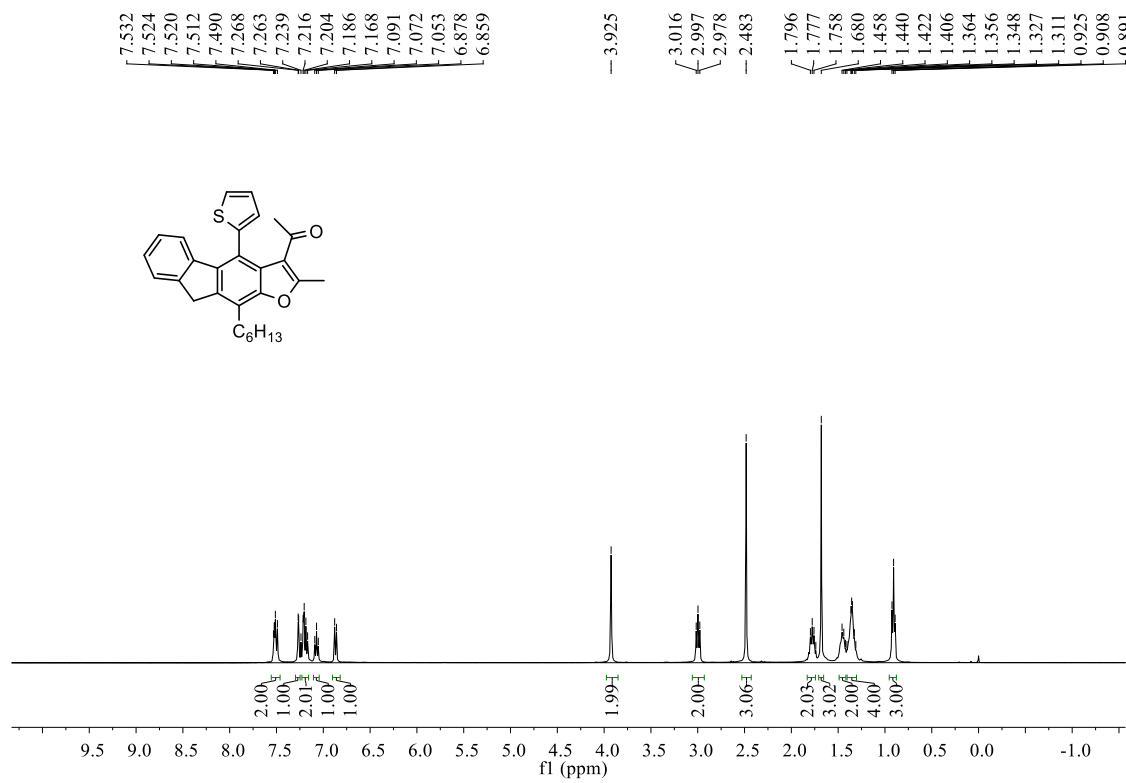


3bi

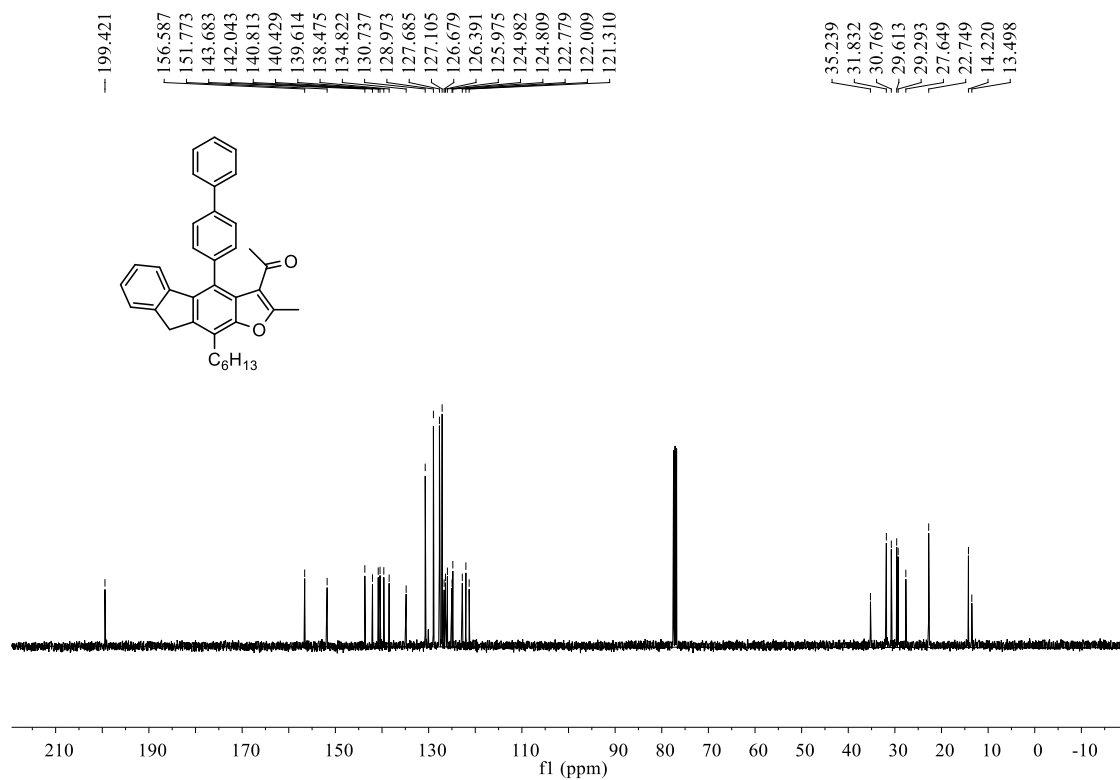
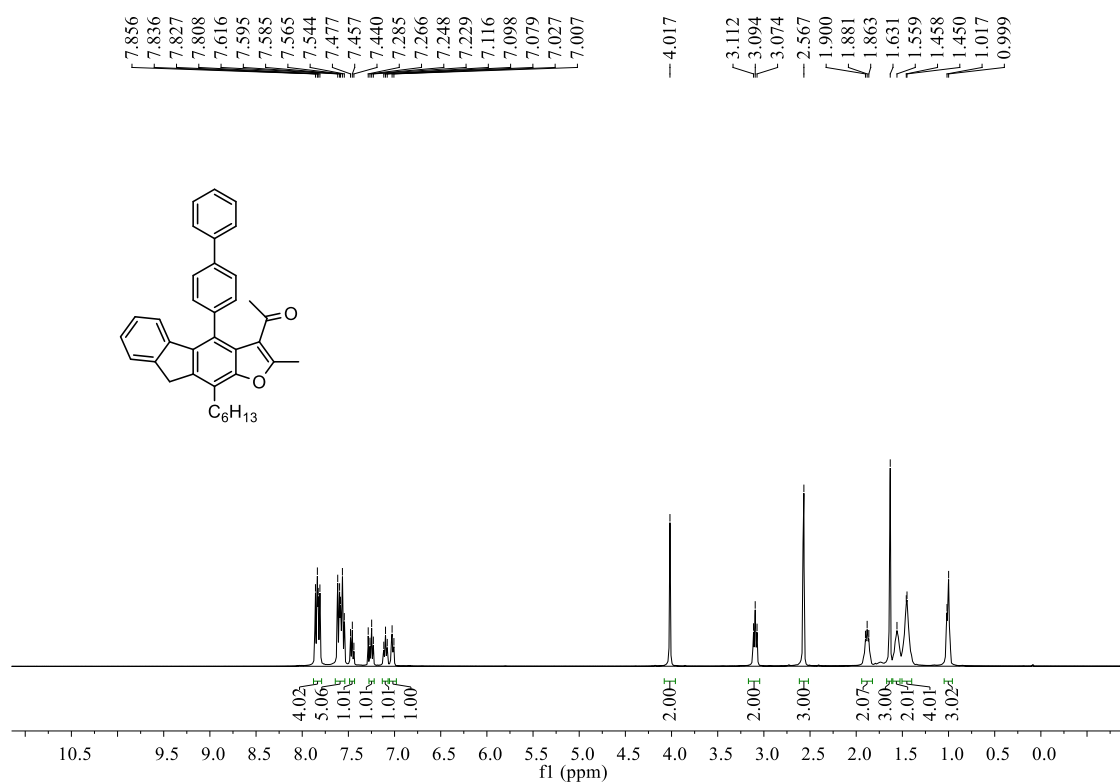




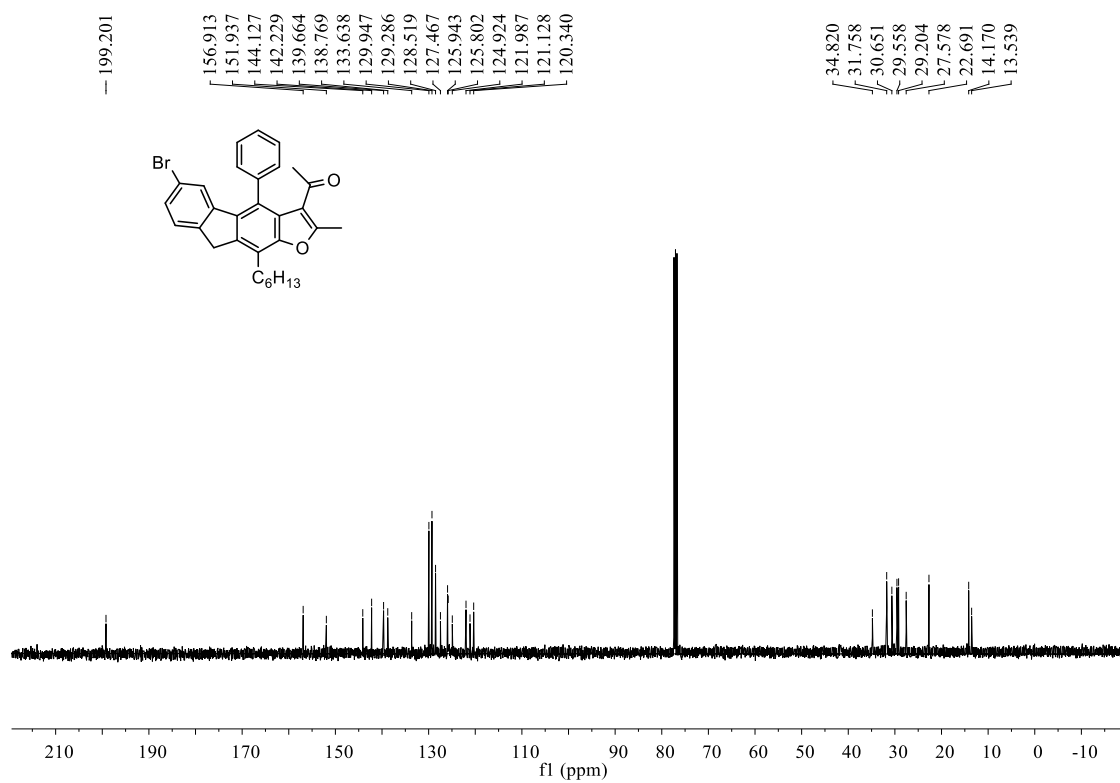
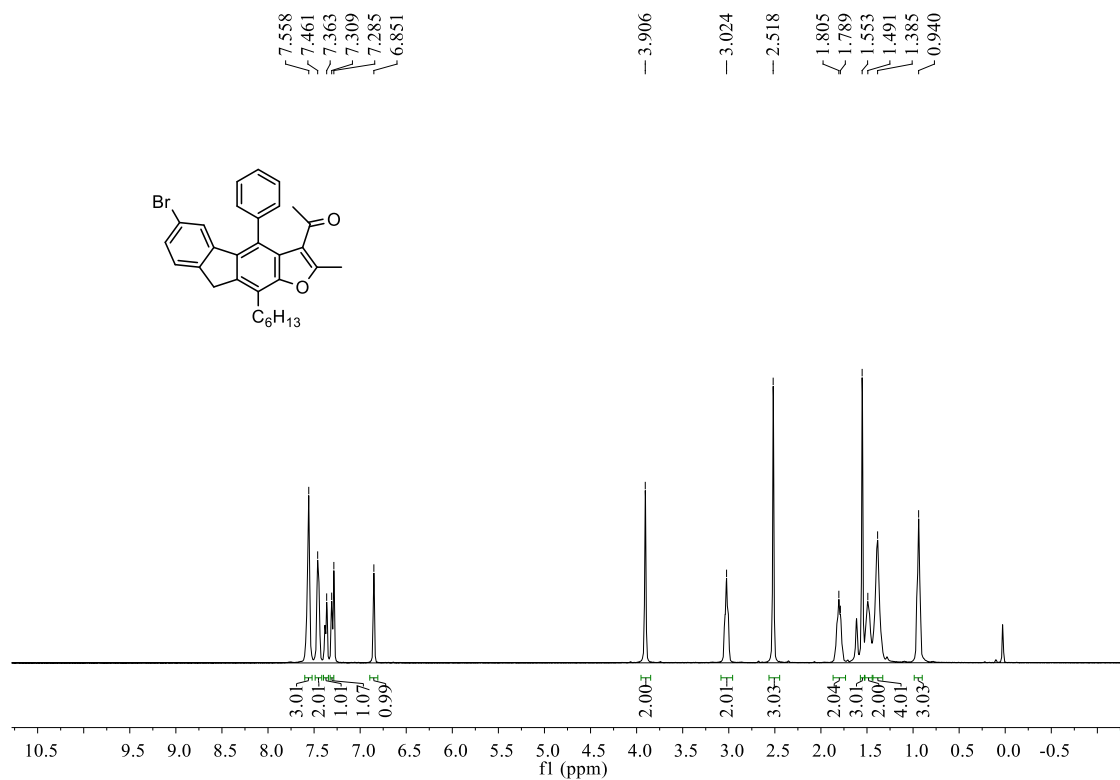
3bj



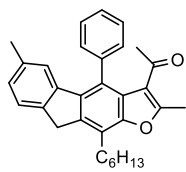
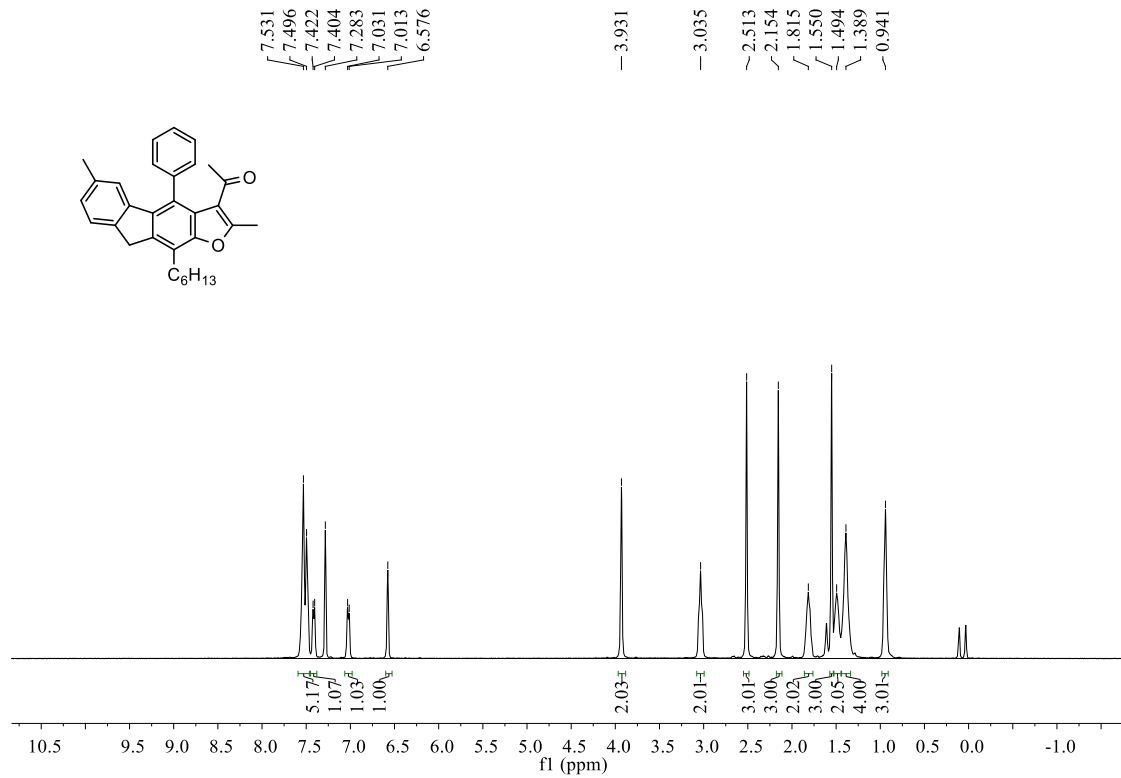
3bk

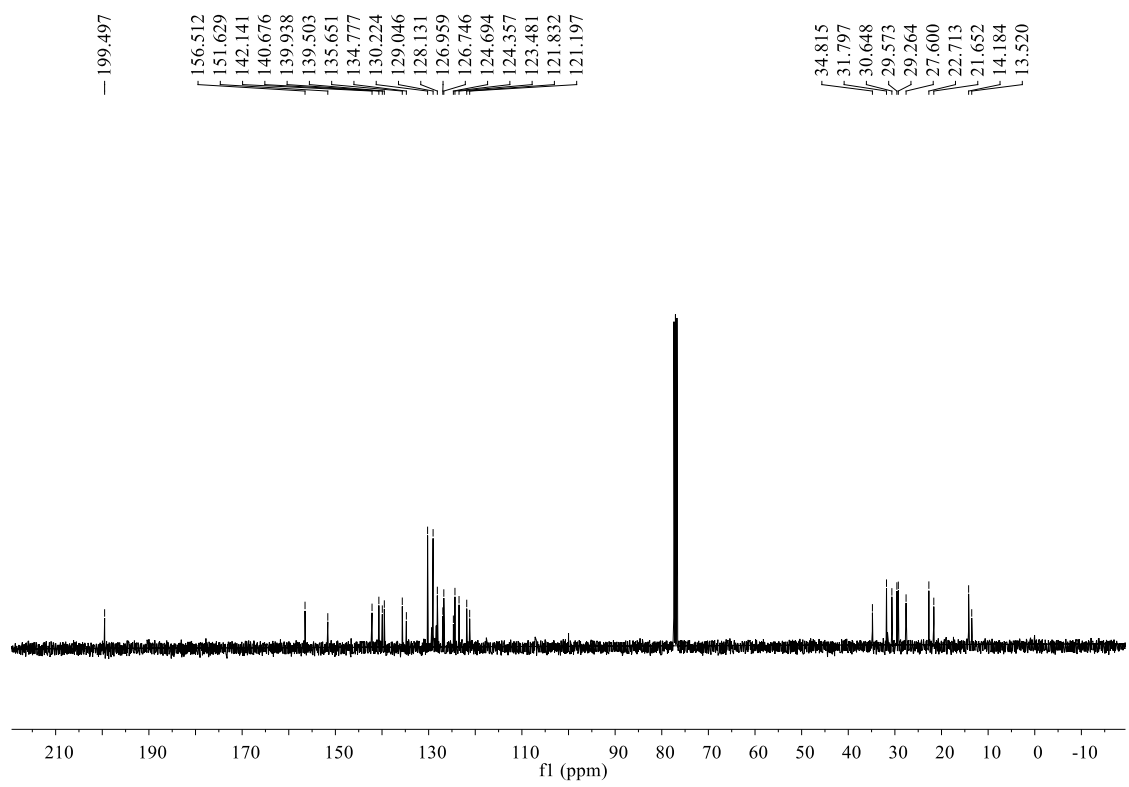


3bl

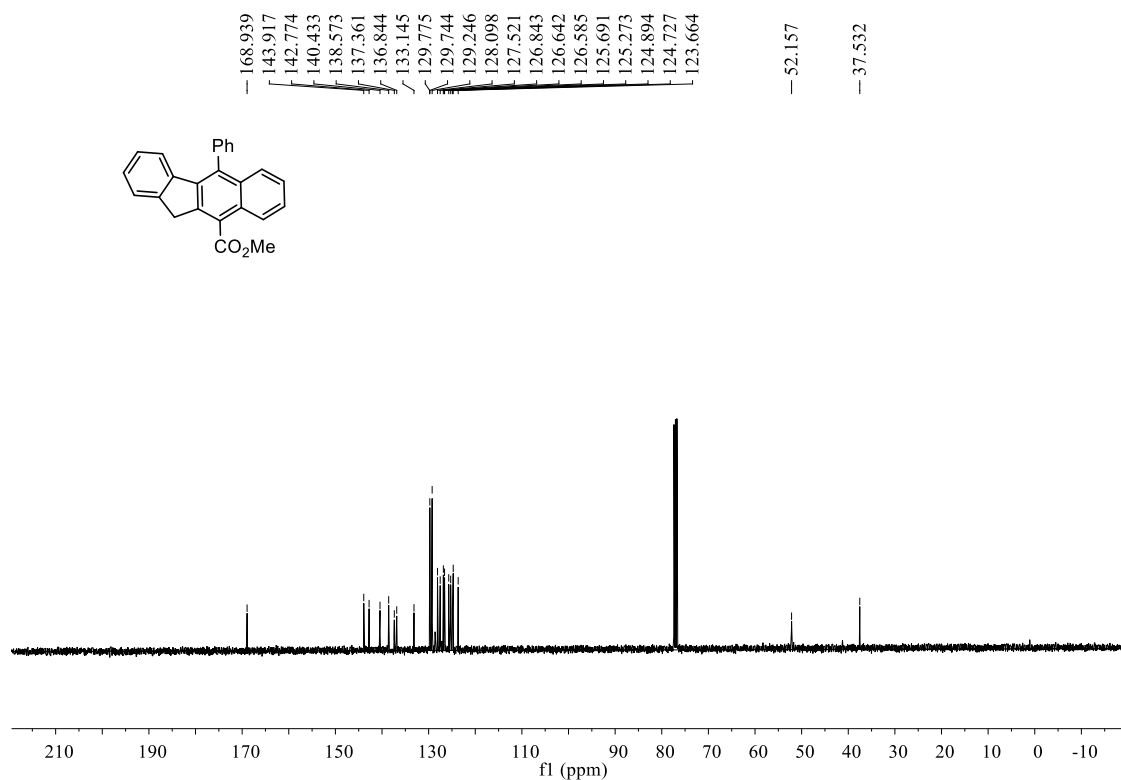
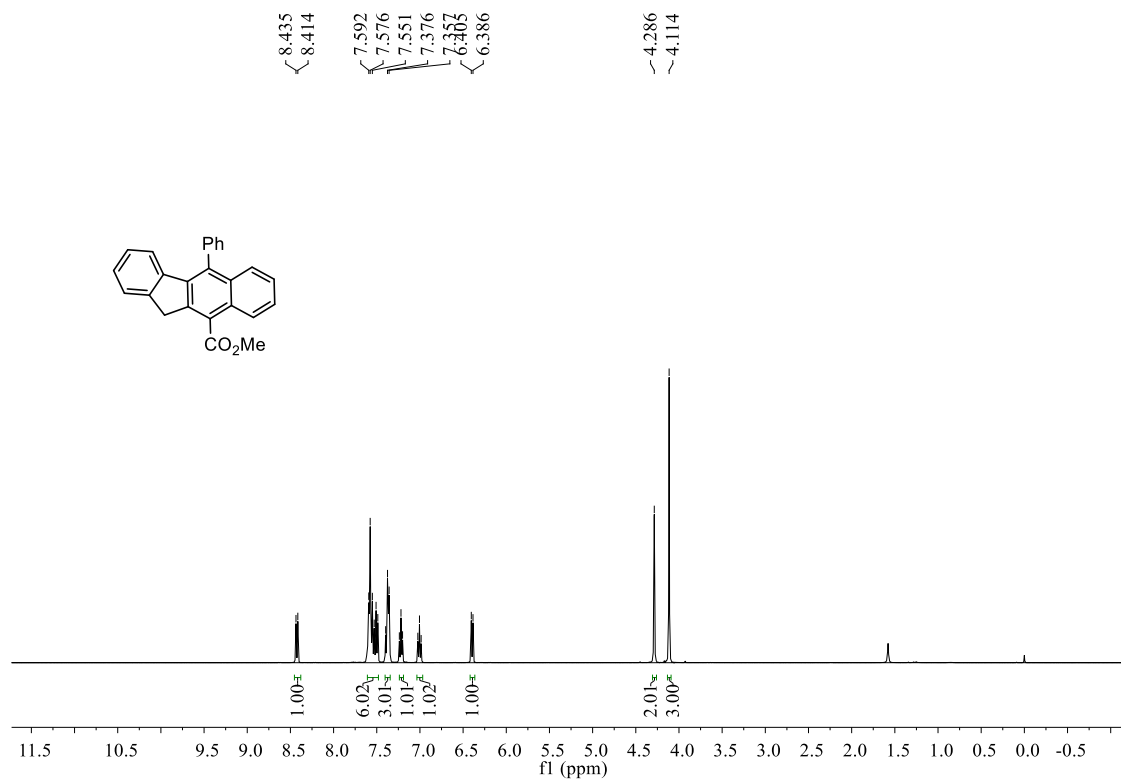


3bm

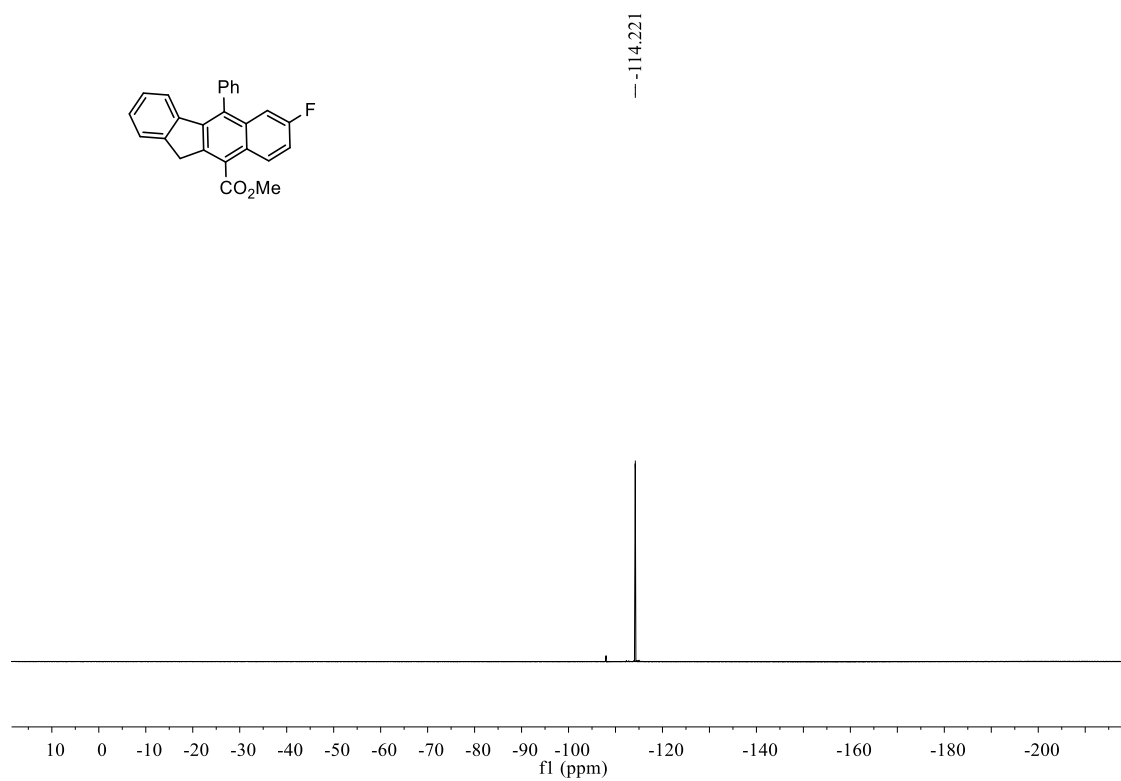
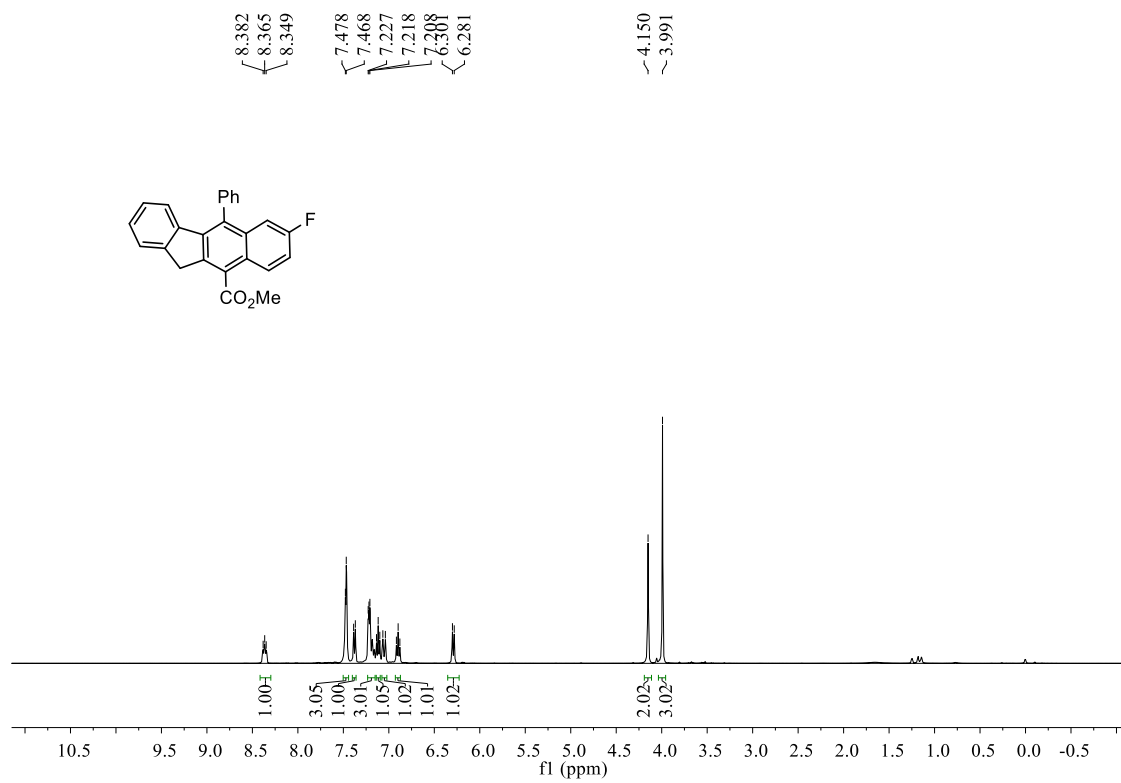


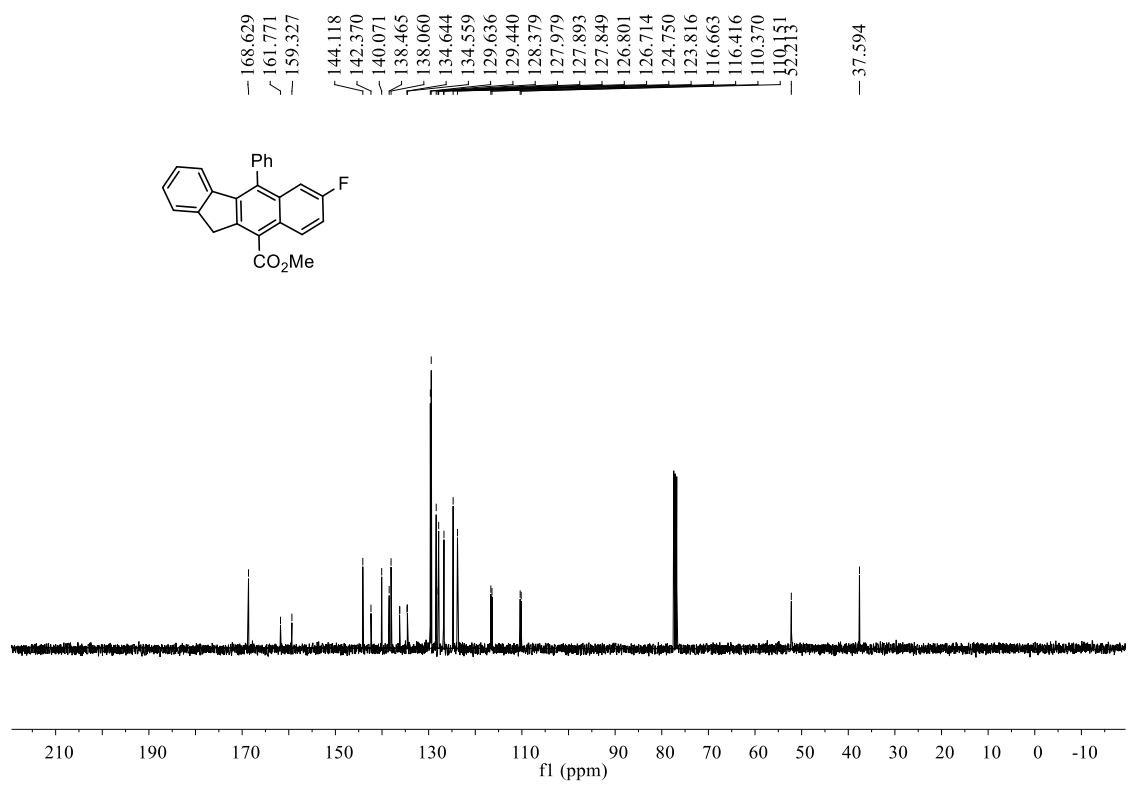


6a

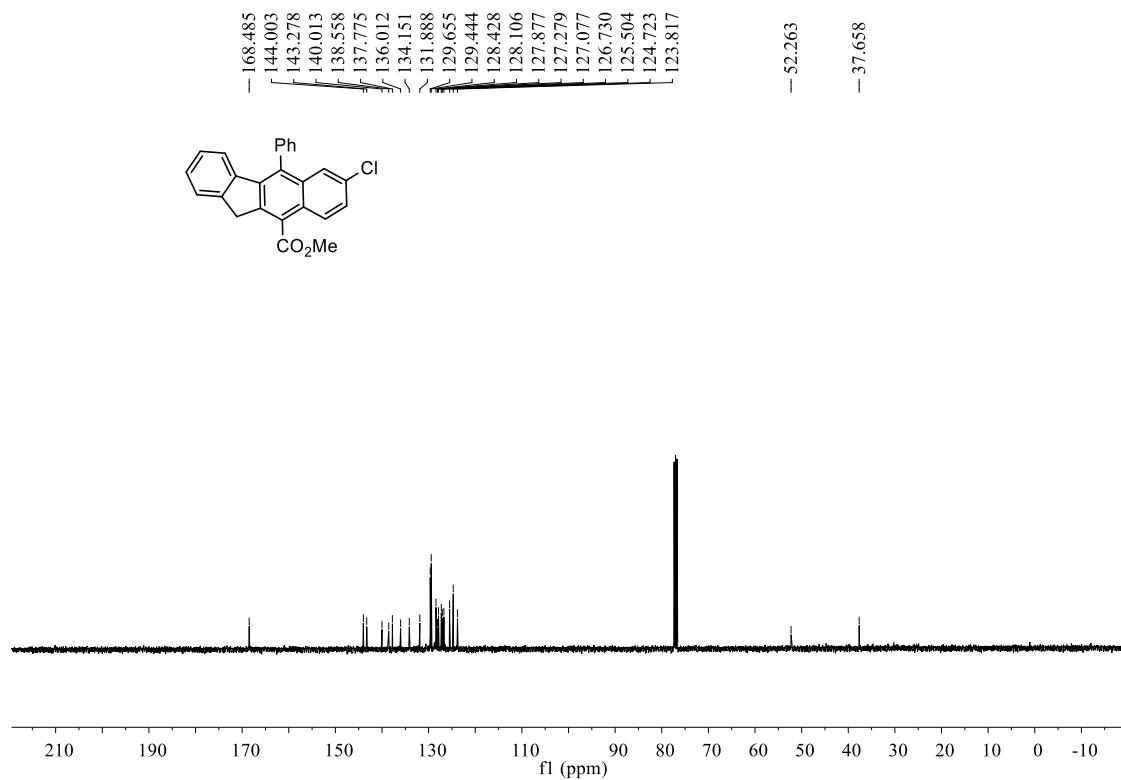
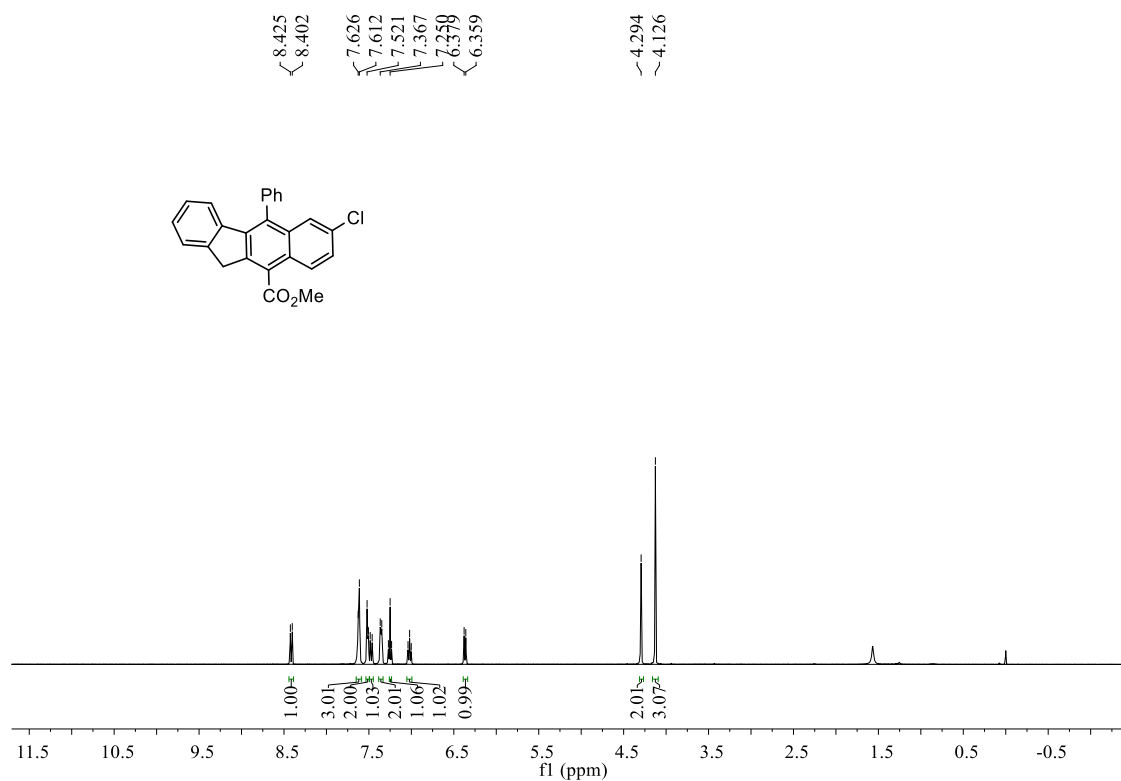


6b

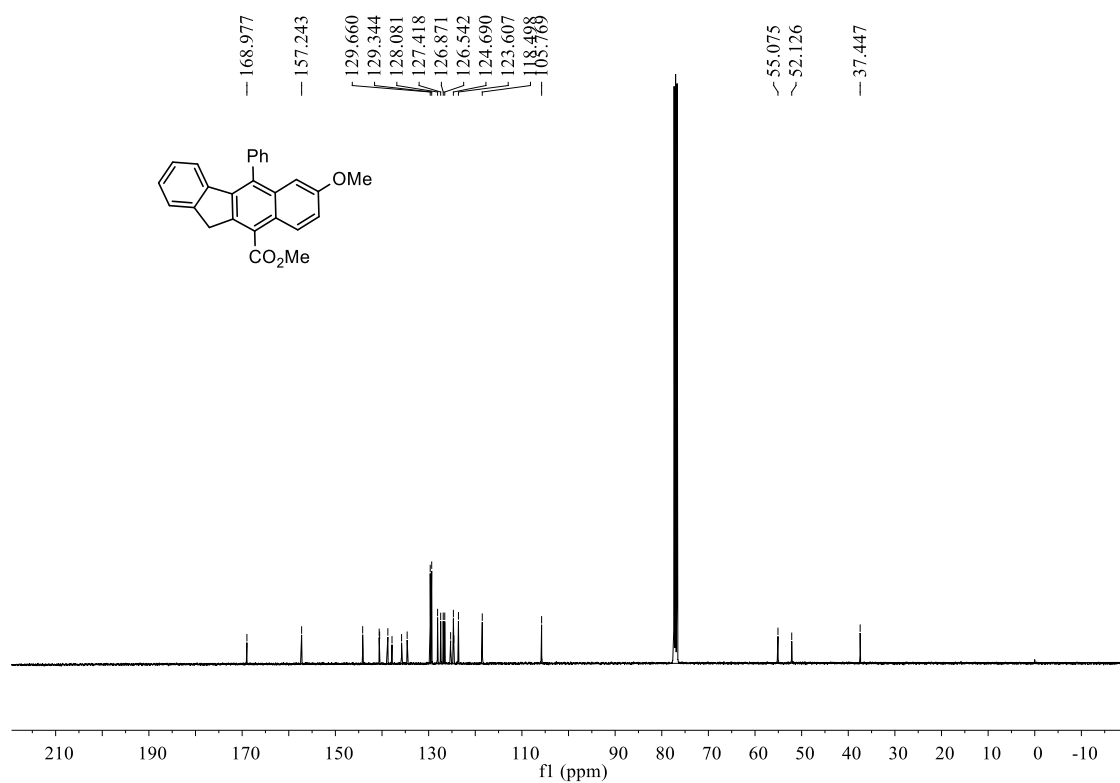
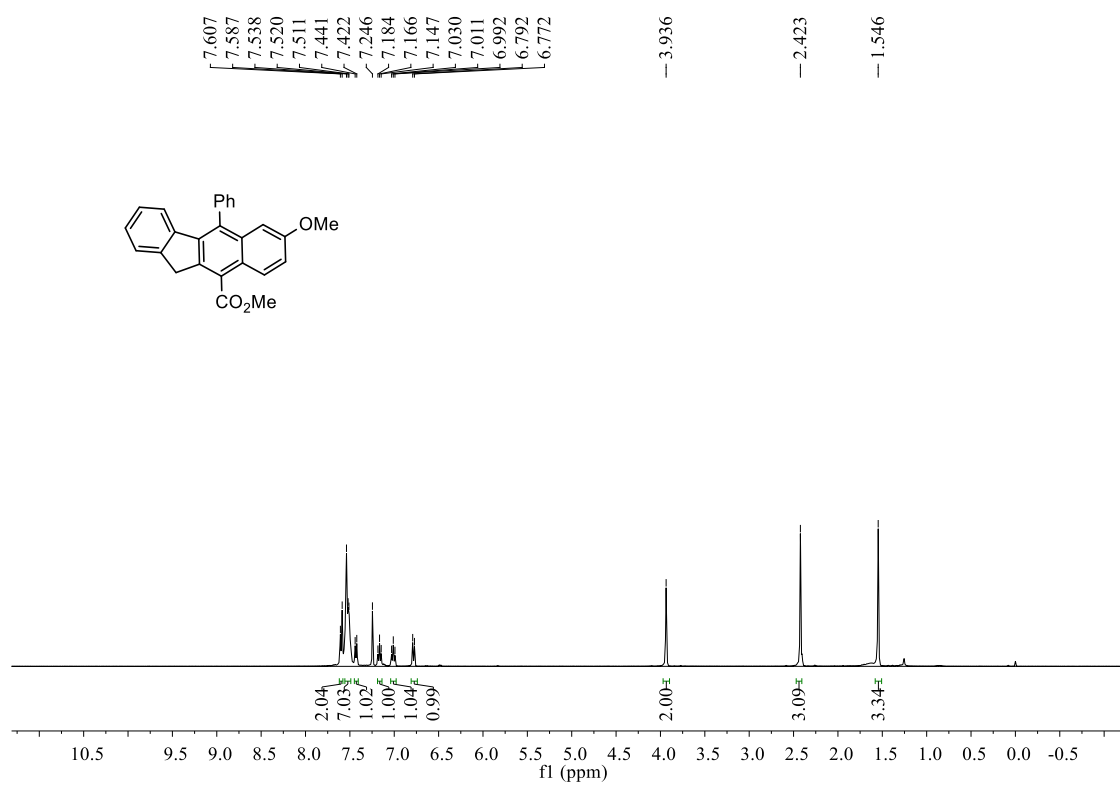




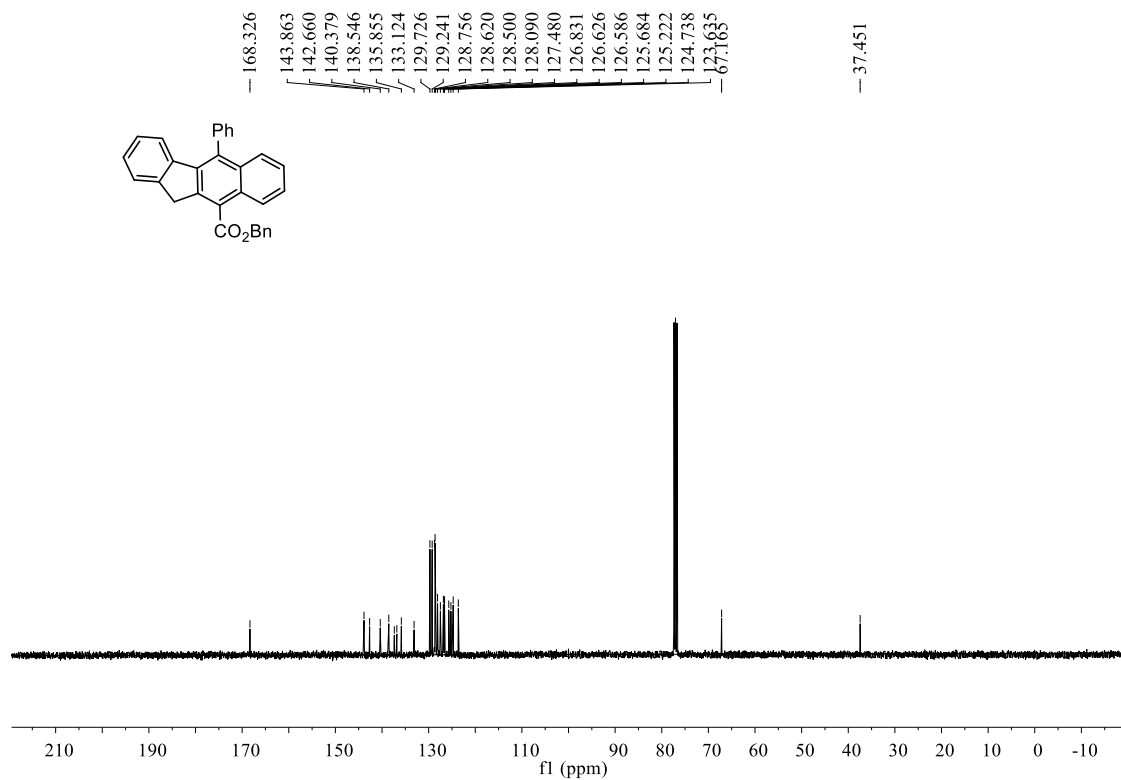
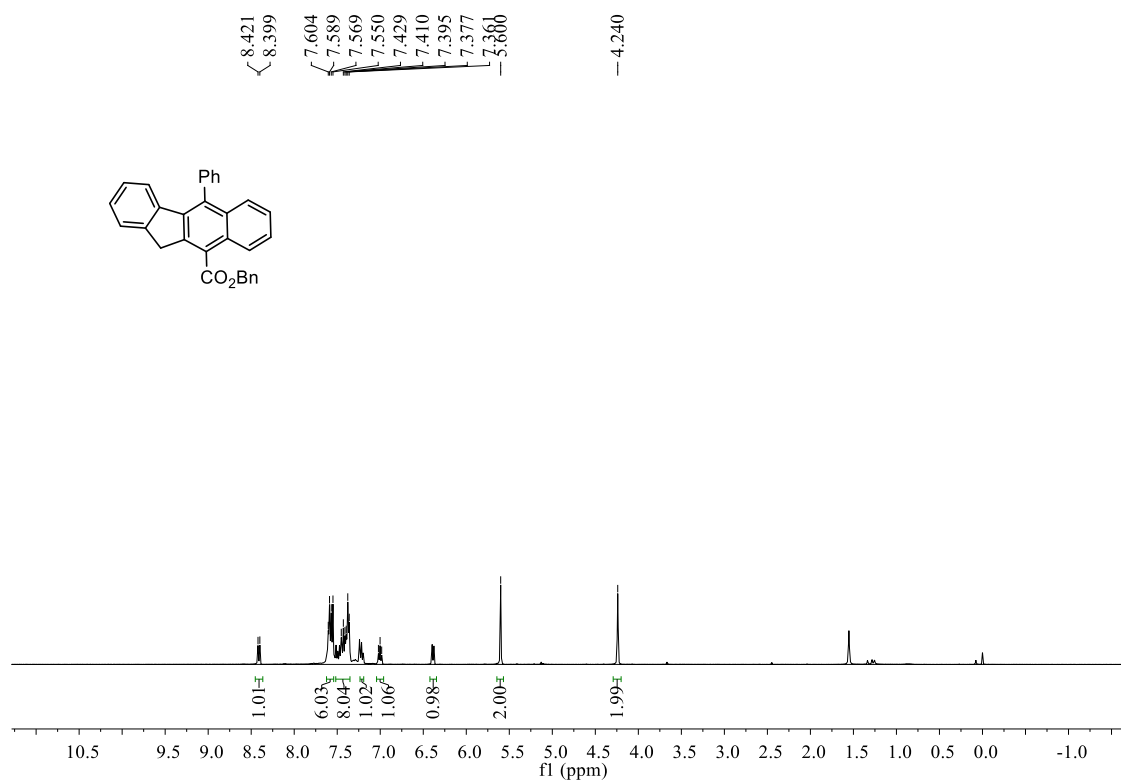
6c



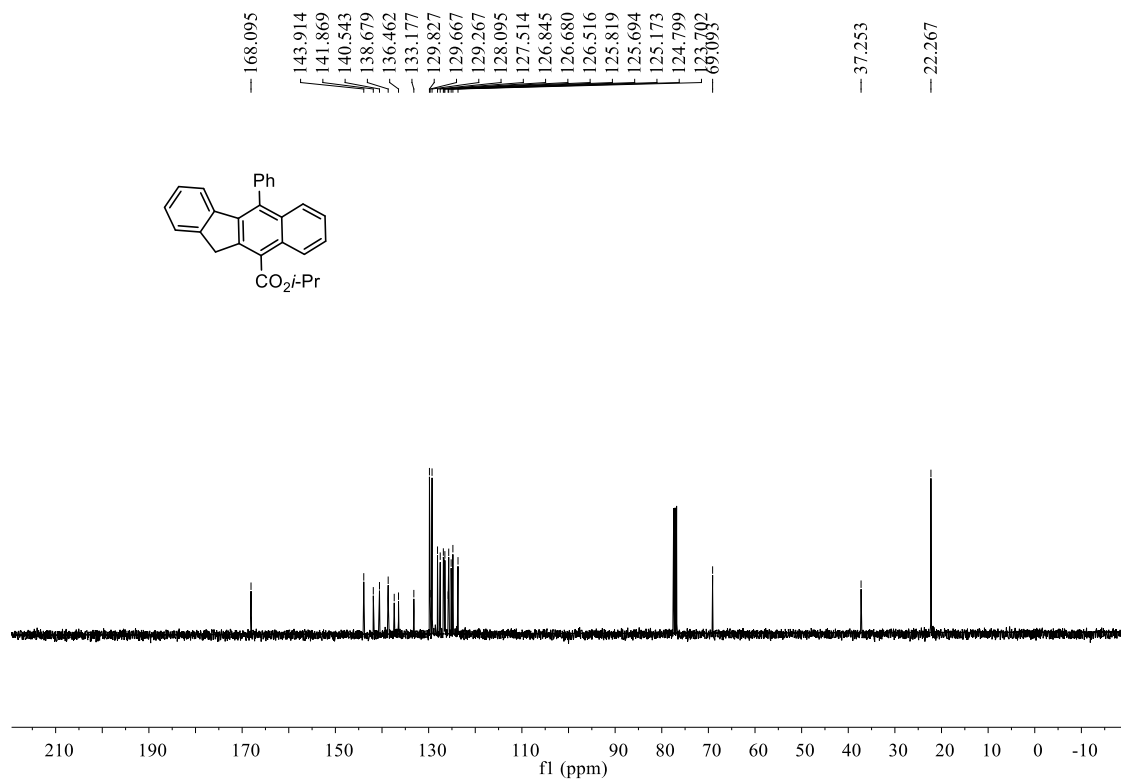
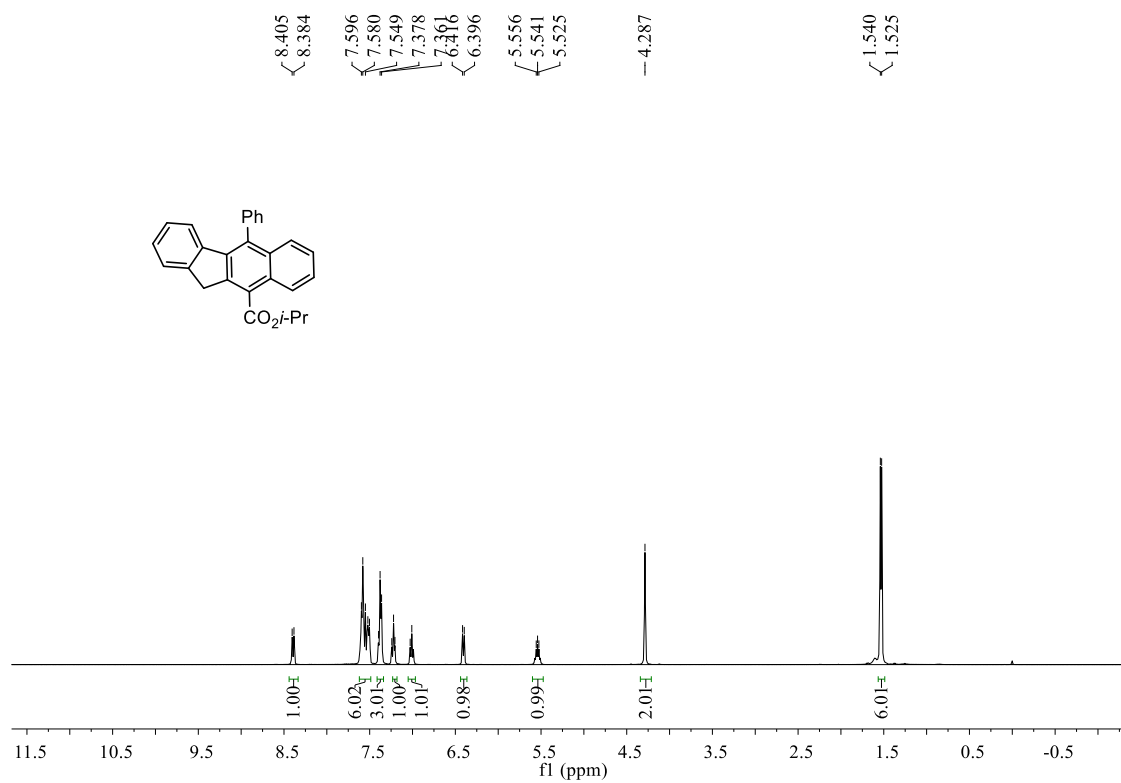
6d



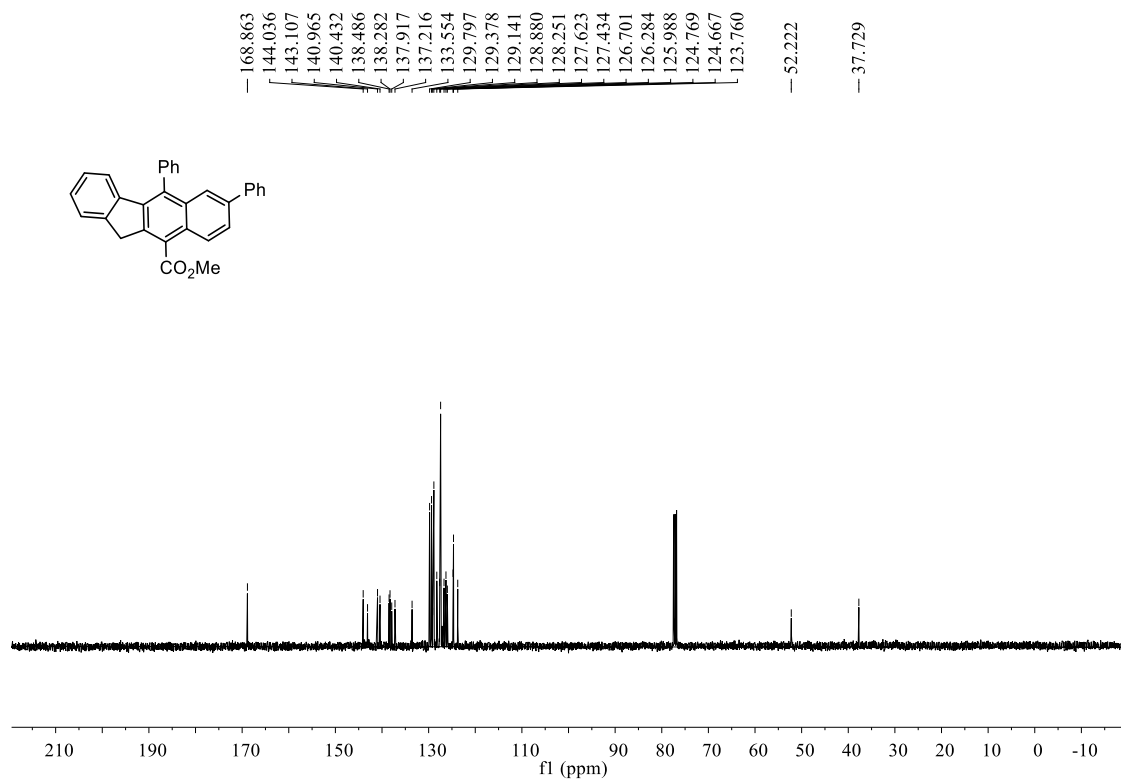
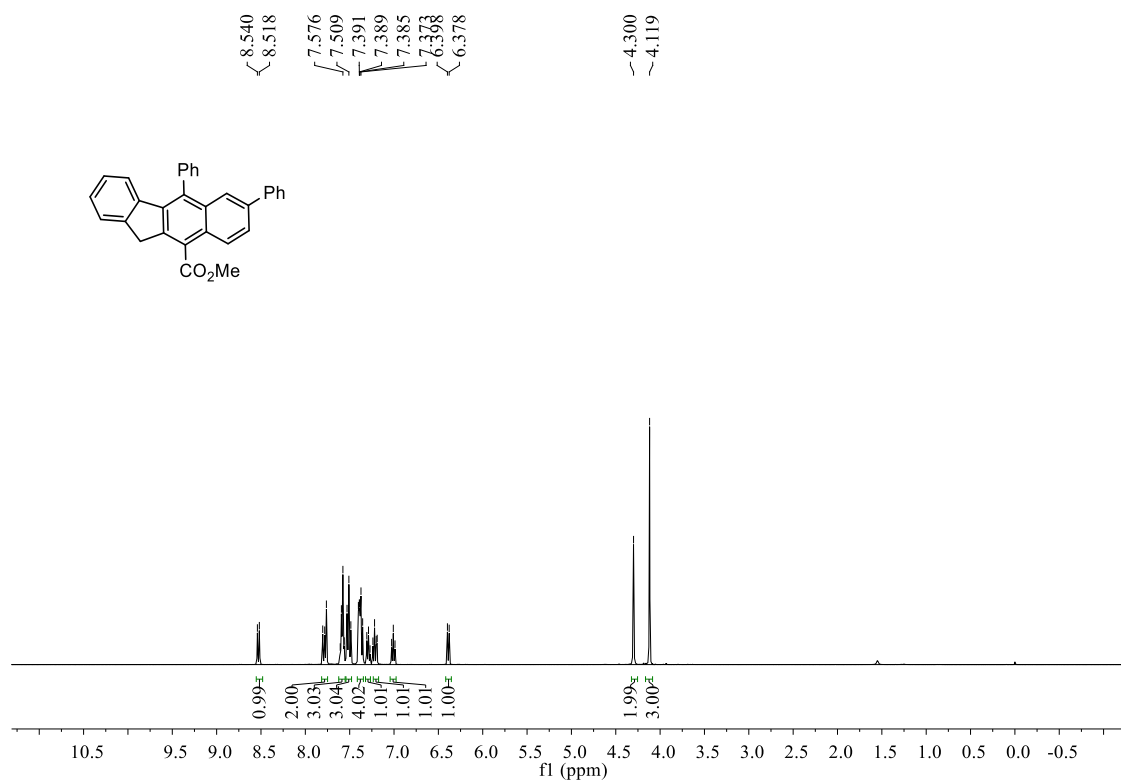
6e



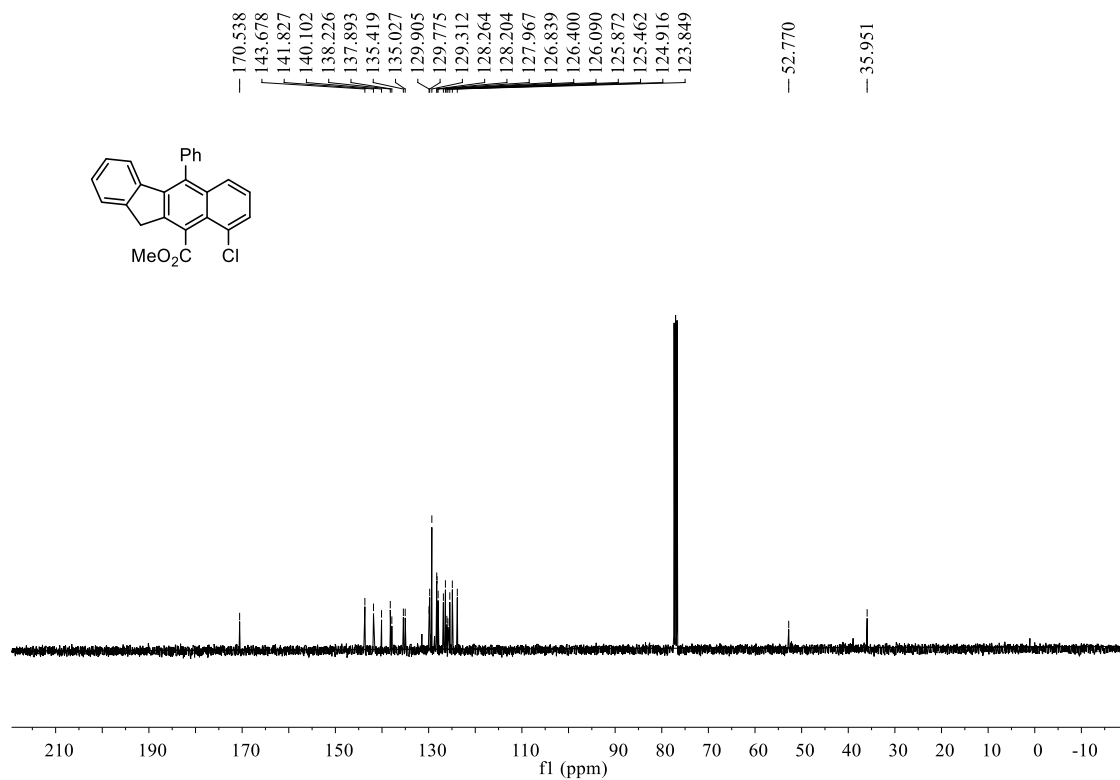
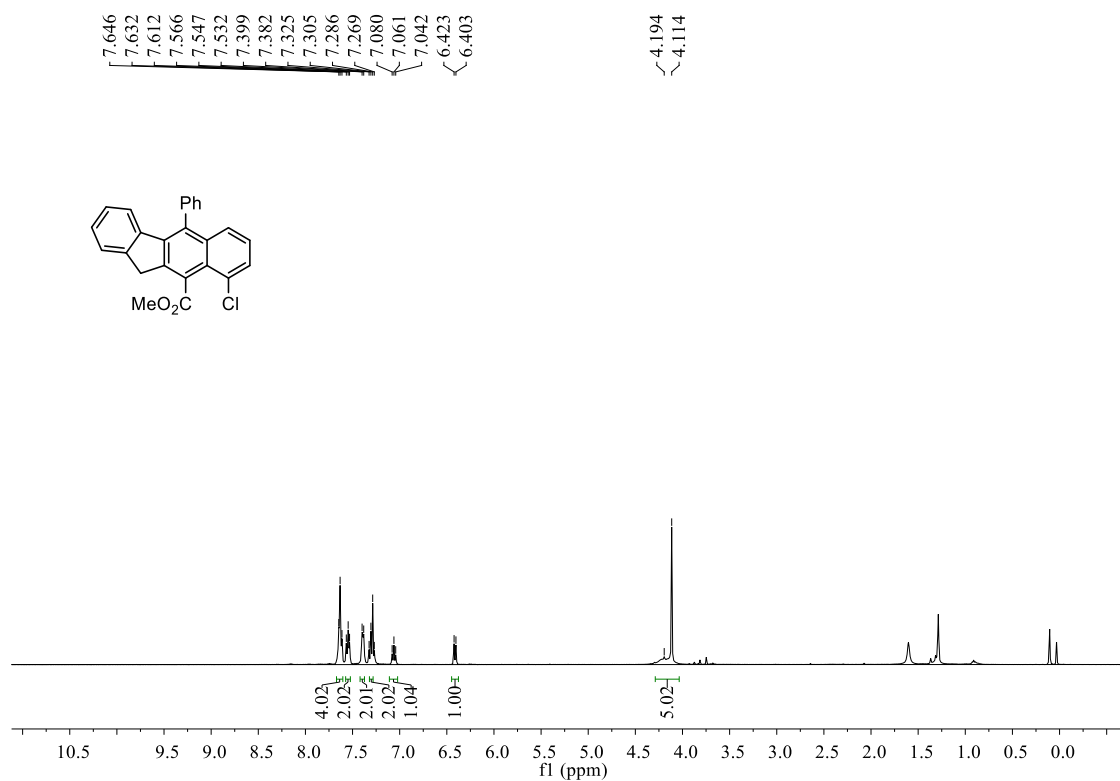
6f



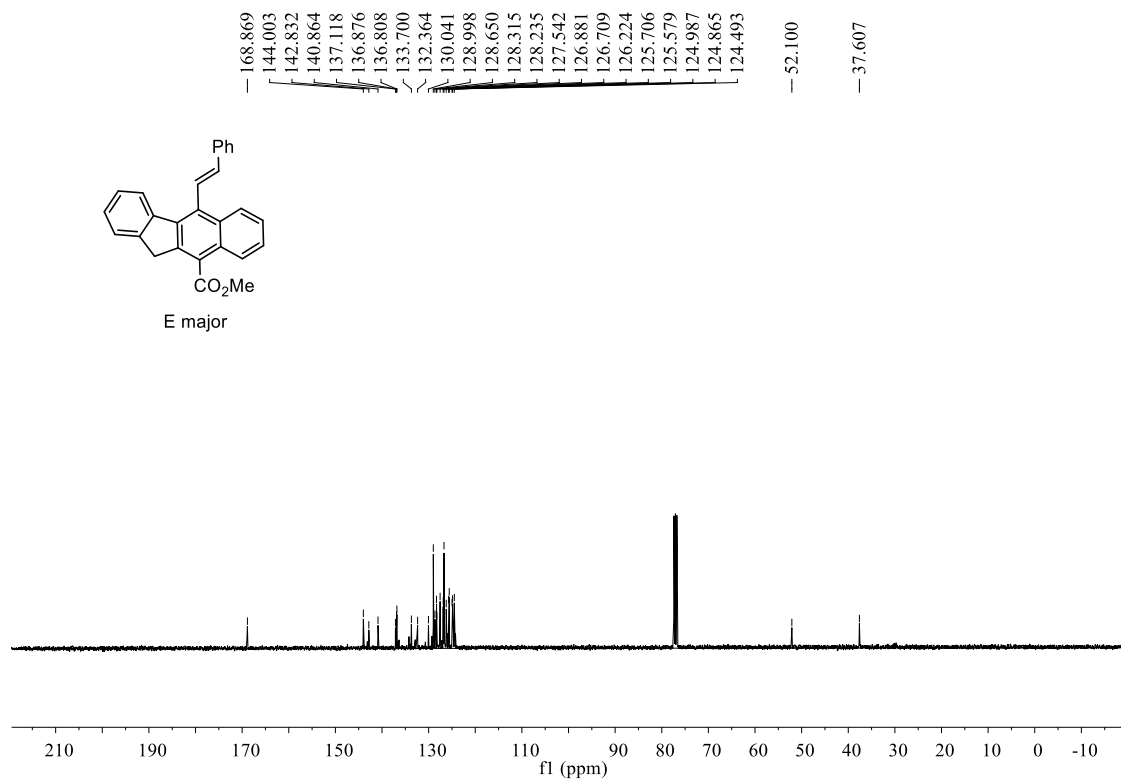
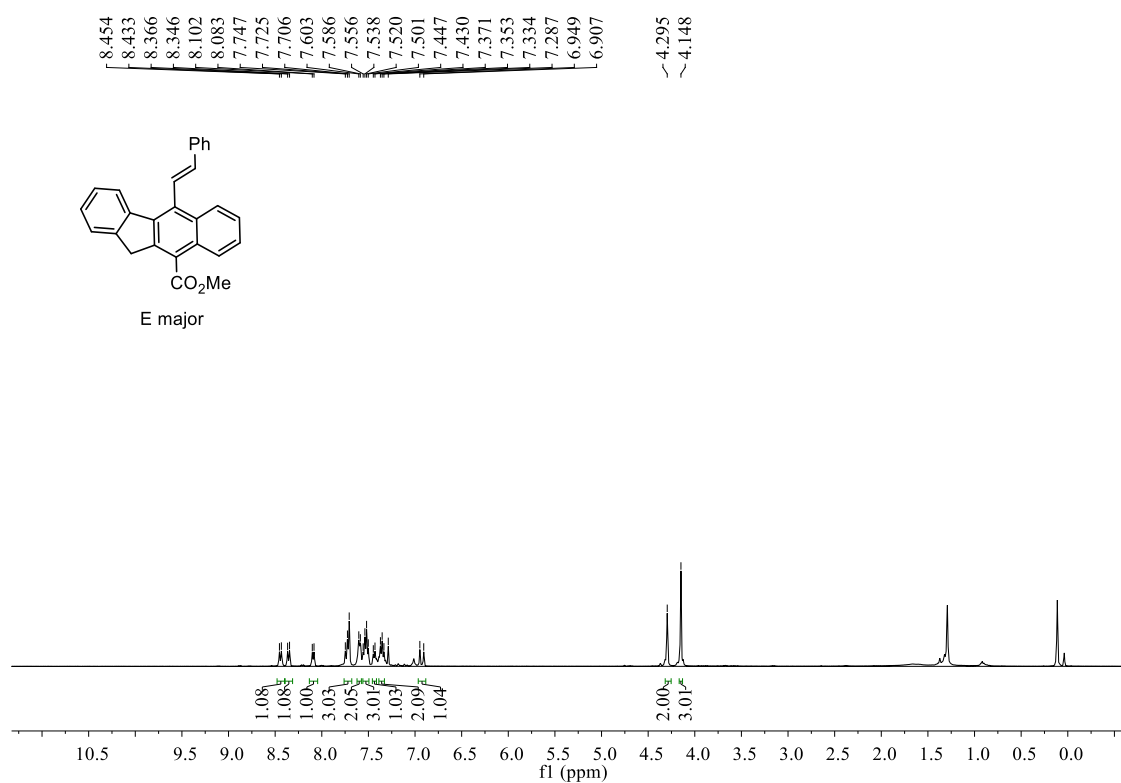
6g



6h



6i (*E* major)



6j

