

Selective Pd-catalyzed α - and β -Arylations of the Furan Rings of (*ortho*-Bromophenyl)furan-2-yl-methanones: C(CO)–C Bond Cleavage with a Furan Ring as a Leaving Group and Synthesis of Furan-derived Fluorenones

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General Experimental Details.

IR spectra were recorded with FT-IR as a thin film or using KBr pellets and were expressed in cm^{-1} . ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using CDCl_3 as a solvent. Chemical shifts were reported in ppm downfield to tetramethylsilane. Coupling constants were reported and expressed in Hz; splitting patterns were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), dq (double quartet). Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer. Mass spectra were obtained from high resolution ESI mass spectrometer. All reactions were carried out using freshly distilled and dry solvents. Column chromatography was performed over silica gel (100-200 Mesh) using petroleum ether /ethyl acetate as the eluent.

General Procedure for the synthesis of 1a-c, 1j-l, 1r

To a stirred mixture of furans (8.0 mmol) and dry THF (20 mL) was added *n*-BuLi (3.2 mL, 2.5 M, 8.0 mmol) dropwise at $-10\text{ }^\circ\text{C}$. After the stirring of the reaction mixture for 2 h at the same temperature, the aldehyde (4.0 mmol) was added. The reaction was allowed to warm to room temperature over 2.5 h then was quenched with saturated aqueous NH_4Cl (10 mL). The resulting mixture was extracted with EtOAc (3×10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and then concentrated *in vacuo*. The residue was submitted to the next step without further purification.

To the solution of the above-made residue in dry DCM (30 mL) was added MnO_2 (2.61 g, 30 mmol) at room temperature. After 24 h vigorous stirring at the same temperature, the reaction mixture was filtered through a pad of celite and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether = 1:30) to afford the desired product.

General Procedure for the synthesis of 1d-h, 1m-p

2-Phenylfuran or 2-benzylfuran (3.0 mmol) was added to a stirred mixture of ZnO (powder, 243.9 mg, 3.0 mmol) and acid chloride (3.6 mmol) at room temperature. The reaction mixture was kept at this temperature with stirring for a certain period of time as required to complete the reaction (monitored by TLC). The reaction mixture was filtered through a pad of celite and eluted with DCM. The filtrate was washed with saturated NaHCO_3 and dried over Na_2SO_4 . Evaporation

of the solvent furnished the crude product which was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:20) to afford the desired product.

General Procedure for the synthesis of 3

1 (0.5 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol), PCy₃·HBF₄ (14.7 mg, 0.04 mmol), and K₂CO₃ (138.0 mg, 1.0 mmol) were suspended in mesitylene (5 mL) in a Schlenk tube under nitrogen. The reaction mixture was then vigorously stirred at 150 °C for 6 h. After cooling to room temperature, H₂O (10 mL) then was added to the reaction mixture. The resulting mixture was extracted with AcOEt (3 × 10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether = 1/60) to afford **3**.

General Procedure for the synthesis of 4

1 (0.5 mmol), Pd(OAc)₂ (11.2 mg, 0.05 mmol), PPh₃ (26.2 mg, 0.1 mmol), KO^tBu (84.2 mg, 0.75 mmol), KCl (93.2 mg, 1.25 mmol) were suspended in PhMe (5 mL) in a Schlenk tube under nitrogen. The mixture was stirred at 80 °C for 18 h. After cooling to room temperature, the reaction mixture was added H₂O (10 mL). The resulting mixture was extracted with AcOEt (3 × 10 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (ethyl acetate/petroleum ether = 1/50) to obtain **4**.

Procedure for one-pot synthesis of 3e, 3f, 3h and 3s from 1b

1b (100 mg, 0.4 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol), PCy₃·HBF₄ (14.7 mg, 0.04 mmol), K₂CO₃ (138.0 mg, 1.0 mmol) were suspended in mesitylene (3 mL) in a Schlenk tube under nitrogen. The mixture was stirred at 80 °C for 6 hours. After cooling to room temperature, the reaction mixture was added aryl bromide (0.48 mmol) under nitrogen atmosphere. The reaction mixture was stirred for additional 6 hours. After cooling to room temperature, the reaction mixture was added H₂O (10 mL). The resulting mixture was extracted with AcOEt (3 × 10 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (ethyl acetate/petroleum ether = 1:60) to obtain **3n-3p** and **3s**.

Characterization of 1

(2-Bromophenyl)(5-methylfuran-2-yl)methanone (**1a**). Yellow oil (713 mg, 74%); IR (KBr): 2960, 2926, 1656, 1586, 1512, 1436, 1370, 1214, 1024, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 1H), 7.38 (q, $J = 7.2$ Hz, 2H), 7.32 (t, $J = 7.3$ Hz, 1H), 6.86 (d, $J = 2.1$ Hz, 1H), 6.18 (d, $J = 2.1$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.9, 160.0, 150.5, 139.7, 133.4, 131.3, 129.1, 127.0, 124.3, 119.9, 109.6, 14.2; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_9\text{BrNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 286.9678, found 286.9682.

(2-Bromophenyl)(furan-2-yl)methanone (**1b**). Yellow oil (660 mg, 70%); IR (KBr): 3120, 1660, 1587, 1562, 1463, 1430, 1189, 1022, 749 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (s, 1H), 7.66 – 7.60 (m, 1H), 7.44 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 7.07 – 6.98 (m, 1H), 6.59 – 6.53 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.7, 151.8, 148.0, 139.5, 133.4, 131.6, 129.1, 127.1, 121.6, 119.9, 112.6; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_7\text{BrNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 272.9522, found 272.9520.

(2-Bromophenyl)(5-ethylfuran-2-yl)methanone (**1c**). Yellow oil (767 mg, 75%); IR (KBr): 2977, 2929, 1651, 1579, 1507, 1457, 1421, 1314, 1203, 1024, 747 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 1H), 7.43 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 6.88 (d, $J = 3.5$ Hz, 1H), 6.19 (d, $J = 3.5$ Hz, 1H), 2.77 (q, $J = 7.6$ Hz, 2H), 1.30 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.0, 165.4, 150.3, 139.8, 133.3, 131.3, 129.1, 127.0, 124.1, 119.9, 107.9, 21.9, 11.7; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{BrNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 300.9835, found 300.9837.

(5-Benzylfuran-2-yl)(2-bromophenyl)methanone (**1d**). Yellow oil (867 mg, 85%); IR (KBr): 2923, 2862, 1652, 1505, 1465, 1311, 1266, 1024, 743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.8$ Hz, 1H), 7.39 (t, $J = 7.1$ Hz, 2H), 7.36 – 7.30 (m, 3H), 7.27 (d, $J = 7.2$ Hz, 3H), 6.89 (d, $J = 3.3$ Hz, 1H), 6.14 (d, $J = 3.4$ Hz, 1H), 4.07 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.1, 162.3, 150.8, 139.7, 136.2, 133.4, 131.4, 129.2, 129.0, 128.8, 127.1, 127.0, 124.0, 120.0, 109.8, 35.0; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{BrNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 362.9991, found 362.9997.

(2-Bromophenyl)(5-phenylfuran-2-yl)methanone (**1e**). Yellow oil (782 mg, 80%); IR (KBr): 2924, 2846, 1649, 1515, 1471, 1370, 1314, 1267, 1027, 763, 746, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.1$ Hz, 2H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.49 – 7.44 (m, 1H), 7.43 – 7.32 (m, 5H), 7.07 (d, $J = 3.7$ Hz, 1H), 6.80 (d, $J = 3.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.1, 159.5, 150.7, 139.7, 133.4, 131.5, 129.6, 129.3, 129.1, 128.9, 127.1, 125.3, 124.3, 120.0, 107.8; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{11}\text{BrNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 348.9835, found 348.9838.

(2-Bromophenyl)(5-(*p*-tolyl)furan-2-yl)methanone (**1f**). Yellow oil (877 mg, 86%); IR (KBr): 2929, 1648, 1525, 1478, 1369, 1270, 1027, 799, 746 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.21 (s, 1H), 7.05 (d, *J* = 3.1 Hz, 1H), 6.74 (d, *J* = 3.1 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 182.0, 159.9, 150.4, 139.9, 139.8, 133.4, 131.4, 129.6, 129.3, 127.1, 126.4, 125.3, 124.6, 120.1, 107.2, 21.5; HRMS (ESI) *m/z* calcd for C₁₈H₁₃BrNaO₂ [M + Na]⁺ 362.9991, found 362.9995.

(2-Bromophenyl)(5-(*o*-tolyl)furan-2-yl)methanone (**1g**). Yellow oil (765 mg, 75%); IR (KBr): 2931, 1652, 1510, 1463, 1368, 1252, 1029, 762 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 6.7 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 6.4 Hz, 3H), 7.17 (d, *J* = 3.1 Hz, 1H), 6.75 (d, *J* = 3.1 Hz, 1H), 2.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 182.3, 159.4, 150.6, 139.9, 136.0, 133.4, 131.6, 131.5, 129.4, 129.2, 128.5, 128.2, 127.1, 126.3, 123.3, 120.0, 111.1, 21.9; HRMS (ESI) *m/z* calcd for C₁₈H₁₃BrNaO₂ [M + Na]⁺ 362.9991, found 362.9993.

(2-Bromophenyl)(5-(4-fluorophenyl)furan-2-yl)methanone (**1h**). Yellow oil (877 mg, 85%); IR (KBr): 3076, 1646, 1599, 1526, 1475, 1228, 1028, 841, 799, 758 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.72 (m, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.15 – 7.07 (m, 2H), 7.05 (br, 1H), 6.74 (d, *J* = 3.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 182.0, 163.5 (d, *J*_{CF} = 249.3 Hz), 158.5, 150.7, 139.7, 133.4, 131.5, 129.2, 127.3 (d, *J*_{CF} = 8.4 Hz), 127.1, 125.5 (d, *J*_{CF} = 3.3 Hz), 124.3, 120.0, 116.1 (d, *J*_{CF} = 22.0 Hz), 107.5; HRMS (ESI) *m/z* calcd for C₁₇H₁₀BrFNaO₂ [M + Na]⁺ 366.9740, found 366.9741.

Methyl 5-(2-bromobenzoyl)furan-2-carboxylate (**1i**). White solid (505 mg, 82%); mp 72.1 – 72.2 °C; IR (KBr): 2955, 1737, 1666, 1568, 1511, 1433, 1283, 1025, 762 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.34 (m, 3H), 7.25 (d, *J* = 2.3 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 3.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.0, 158.5, 152.9, 147.6, 138.7, 133.6, 132.1, 129.4, 127.3, 120.9, 120.0, 118.7, 52.5; HRMS (ESI) *m/z* calcd for C₁₃H₉BrNaO₄ [M + Na]⁺ 330.9576, found 330.9580.

(2-Bromophenyl)(5-methyl-4-(methylthio)furan-2-yl)methanone (**1j**). Yellow oil (865 mg, 77%); IR (KBr): 2989, 2921, 2834, 1660, 1586, 1510, 1466, 1429, 1351, 1313, 1195, 1048, 747 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.38 – 7.31 (m, 1H),

6.93 (s, 1H), 2.45 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.7, 160.3, 149.7, 139.4, 133.4, 131.5, 129.1, 127.1, 126.4, 119.9, 117.2, 19.0, 12.6; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{BrNaO}_2\text{S} [\text{M} + \text{Na}]^+$ 332.9555, found 332.9563.

Benzofuran-2-yl(2-bromophenyl)methanone (1k). White oil (756 mg, 63%); IR (KBr): 3063, 2928, 1662, 1612, 1588, 1549, 1471, 1432, 1219, 1026, 749 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.65 (s, 1H), 7.62 – 7.56 (m, 1H), 7.52 – 7.34 (m, 4H), 7.33 – 7.27 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.6, 156.4, 151.7, 139.4, 133.5, 131.9, 129.3, 129.0, 127.2, 127.0, 124.2, 123.6, 120.0, 118.0, 112.7; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_9\text{BrNaO}_2 [\text{M} + \text{Na}]^+$ 322.9678, found 322.9684.

(2-Bromo-4-methylphenyl)(5-methylfuran-2-yl)methanone (1l). Yellow oil (792 mg, 76%); IR (KBr): 2925, 2856, 1713, 1649, 1602, 1512, 1447, 1381, 1309, 1211, 1027, 761 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (s, 1H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.16 (d, $J = 7.7$ Hz, 1H), 6.86 (d, $J = 3.5$ Hz, 1H), 6.17 (d, $J = 3.4$ Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.0, 159.7, 150.7, 142.0, 136.8, 133.9, 129.1, 127.7, 124.0, 119.9, 109.4, 21.1, 14.2; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{BrNaO}_2 [\text{M} + \text{Na}]^+$ 300.9835, found 300.9835.

(5-Benzylfuran-2-yl)(2-bromo-4-methylphenyl)methanone (1m). Yellow oil (913 mg, 86%); IR (KBr): 3030, 2921, 1653, 1602, 1507, 1452, 1384, 1310, 1206, 1024, 818, 762, 712 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 7.33 – 7.22 (m, 6H), 7.16 – 7.10 (m, 1H), 6.84 (d, $J = 3.5$ Hz, 1H), 6.07 (d, $J = 3.5$ Hz, 1H), 4.04 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.2, 162.1, 151.0, 142.1, 136.7, 136.3, 133.9, 129.2, 129.0, 128.8, 127.7, 127.0, 123.6, 119.9, 109.7, 35.0, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{BrNaO}_2 [\text{M} + \text{Na}]^+$ 377.0148, found 377.0156.

(2-Bromo-4-methylphenyl)(5-phenylfuran-2-yl)methanone (1n). Yellow oil (816 mg, 80%); IR (KBr): 3061, 2922, 2850, 1649, 1602, 1565, 1516, 1474, 1373, 1269, 1029, 816, 763, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.3$ Hz, 2H), 7.46 (s, 1H), 7.41 – 7.32 (m, 4H), 7.17 (d, $J = 7.7$ Hz, 1H), 7.05 (d, $J = 3.7$ Hz, 1H), 6.78 (d, $J = 3.7$ Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.2, 159.3, 150.9, 142.3, 136.8, 134.0, 129.5, 129.3, 129.2, 128.9, 127.8, 125.3, 124.0, 120.0, 107.7, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{BrNaO}_2 [\text{M} + \text{Na}]^+$ 362.9991, found 362.9996.

(2-Bromo-4-methylphenyl)(5-(o-tolyl)furan-2-yl)methanone (1o). Yellow oil (807 mg, 76%); IR (KBr): 2967, 2924, 2854, 1650, 1612, 1461, 1372, 1315, 1260, 1029, 802, 741 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 6.9$ Hz, 1H), 7.48 (s, 1H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.30 – 7.23

(m, 3H), 7.19 (d, $J = 7.7$ Hz, 1H), 7.13 (d, $J = 2.4$ Hz, 1H), 6.70 (d, $J = 2.4$ Hz, 1H), 2.50 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.4, 159.2, 150.8, 142.2, 136.9, 135.9, 133.9, 131.5, 129.3, 129.3, 128.6, 128.2, 127.8, 126.2, 123.1, 120.0, 111.0, 21.9, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 377.0148, found 377.0153.

(2-Bromo-4-methylphenyl)(5-(4-fluorophenyl)furan-2-yl)methanone (1p). Yellow oil (891 mg, 83%); IR (KBr): 2924, 2864, 1650, 1602, 1525, 1485, 1418, 1372, 1234, 1030, 815, 759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.73 (m, 2H), 7.49 (s, 1H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.20 (d, $J = 7.7$ Hz, 1H), 7.15 – 7.07 (m, 2H), 7.06 (d, $J = 3.6$ Hz, 1H), 6.74 (d, $J = 3.6$ Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.2, 163.4 (d, $J_{\text{CF}} = 249.2$ Hz), 158.3, 150.9, 142.3, 136.7, 134.0, 129.3, 127.8, 127.3 (d, $J_{\text{CF}} = 8.4$ Hz), 125.6 (d, $J_{\text{CF}} = 3.3$ Hz), 124.1, 120.0, 116.1 (d, $J_{\text{CF}} = 22.0$ Hz), 107.4, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{BrFNaO}_2$ $[\text{M} + \text{Na}]^+$ 380.9897, found 380.9901.

(2-Bromo-4-fluorophenyl)(5-ethylfuran-2-yl)methanone (1r). Yellow oil (755 mg, 66%); IR (KBr): 2978, 2939, 1657, 1578, 1463, 1401, 1314, 1259, 1025, 828, 759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.54 (m, 1H), 7.19 – 7.11 (m, 1H), 7.11 – 7.02 (m, 1H), 6.95 (br, 1H), 6.23 (d, $J = 2.6$ Hz, 1H), 2.78 (q, $J = 7.5$ Hz, 2H), 1.30 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.4, 165.8, 161.3 (d, $J_{\text{CF}} = 248.1$ Hz), 149.8, 141.2 (d, $J_{\text{CF}} = 6.4$ Hz), 134.8 (d, $J_{\text{CF}} = 7.7$ Hz), 124.4, 118.6 (d, $J_{\text{CF}} = 22.2$ Hz), 116.4 (d, $J_{\text{CF}} = 24.0$ Hz), 114.2 (d, $J_{\text{CF}} = 3.5$ Hz), 108.2, 21.9, 11.6; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{BrFNaO}_2$ $[\text{M} + \text{Na}]^+$ 318.9740, found 318.9745.

Characterization of 4

(5-Methylfuran-2-yl)(2-(5-methylfuran-2-yl)phenyl)methanone (4a). Yellow oil (36 mg, 55%); IR (KBr): 2923, 2854, 1654, 1592, 1511, 1440, 1367, 1310, 1211, 1023, 759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.9$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 1H), 6.70 (d, $J = 3.0$ Hz, 1H), 6.37 (d, $J = 3.1$ Hz, 1H), 6.05 (d, $J = 3.0$ Hz, 1H), 5.92 (d, $J = 3.0$ Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.9, 158.8, 152.6, 151.5, 150.0, 135.4, 130.1, 129.3, 128.4, 126.6, 126.2, 122.6, 109.7, 109.0, 107.8, 14.1, 13.5; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}_3$ $[\text{M} + \text{H}]^+$ 267.1016, found 267.1014.

Furan-2-yl(2-(furan-2-yl)phenyl)methanone (4b). Yellow oil (32 mg, 54%); IR (KBr): 2926, 2853, 1657, 1598, 1564, 1499, 1462, 1223, 1018, 762 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J =$

7.9 Hz, 1H), 7.57 (s, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.33 (s, 1H), 6.85 (d, $J = 2.9$ Hz, 1H), 6.49 (d, $J = 2.9$ Hz, 1H), 6.43 (d, $J = 1.3$ Hz, 1H), 6.34 (d, $J = 1.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.3, 152.6, 151.8, 147.3, 142.8, 135.8, 130.4, 129.1, 128.4, 127.3, 126.9, 120.3, 112.2, 111.6, 108.6; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 261.0522, found 261.0523.

(5-Ethylfuran-2-yl)(2-(5-ethylfuran-2-yl)phenyl)methanone (4c). Yellow oil (44 mg, 60%); IR (KBr): 2975, 2937, 1653, 1594, 1512, 1462, 1377, 1311, 1208, 1022, 760 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 7.9$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 6.71 (br, 1H), 6.41 (br, 1H), 6.05 (br, 1H), 5.93 (br, 1H), 2.70 (q, $J = 7.6$ Hz, 2H), 2.54 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H), 1.10 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.0, 164.1, 158.2, 151.3, 150.1, 135.5, 130.0, 129.3, 128.4, 126.6, 126.1, 122.3, 109.1, 107.4, 106.2, 21.7, 21.3, 12.0, 11.7; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{19}\text{O}_3$ $[\text{M} + \text{H}]^+$ 295.1329, found 295.1327.

(5-Benzylfuran-2-yl)(2-(5-benzylfuran-2-yl)phenyl)methanone (4d). Yellow oli (53 mg, 51%); IR (KBr): 2924, 2853, 1649, 1596, 1503, 1454, 1386, 1271, 1024, 761, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.9$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.33 – 7.23 (m, 6H), 7.20 (d, $J = 7.5$ Hz, 3H), 7.12 (d, $J = 7.3$ Hz, 2H), 6.69 (d, $J = 3.0$ Hz, 1H), 6.39 (d, $J = 3.1$ Hz, 1H), 5.96 (d, $J = 3.3$ Hz, 1H), 5.91 (d, $J = 3.0$ Hz, 1H), 3.97 (s, 2H), 3.80 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.0, 161.0, 155.1, 151.8, 150.7, 137.8, 136.5, 135.6, 130.1, 129.2, 128.9, 128.7, 128.7, 128.5, 128.4, 126.9, 126.8, 126.4, 126.4, 122.1, 109.5, 109.3, 108.4, 34.9, 34.5; HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{22}\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 441.1461, found 441.1459.

(5-Phenylfuran-2-yl)(2-(5-phenylfuran-2-yl)phenyl)methanone (4e). Yellow oil (43 mg, 44%); IR (KBr): 2924, 2853, 1652, 1599, 1567, 1516, 1473, 1450, 1369, 1269, 1027, 761, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.9$ Hz, 1H), 7.71 (d, $J = 7.5$ Hz, 2H), 7.59 – 7.47 (m, 4H), 7.43 – 7.31 (m, 4H), 7.24 (t, $J = 7.5$ Hz, 2H), 7.15 (t, $J = 7.3$ Hz, 1H), 6.94 (d, $J = 2.8$ Hz, 1H), 6.66 (d, $J = 2.8$ Hz, 1H), 6.63 (d, $J = 3.5$ Hz, 1H), 6.57 (d, $J = 3.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.9, 158.6, 154.3, 151.7, 151.3, 135.8, 130.3, 129.3, 129.2, 128.9, 128.8, 128.6, 128.5, 127.4, 127.2, 126.3, 125.2, 123.7, 122.8, 110.5, 107.5, 107.0; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 413.1148, found 413.1149.

(5-(p-Tolyl)furan-2-yl)(2-(5-(p-tolyl)furan-2-yl)phenyl)methanone (4f). Yellow oil (47 mg, 45%); IR (KBr): 2924, 2853, 1650, 1601, 1510, 1468, 1367, 1253, 1032, 799, 761 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.9$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 2H), 7.57 – 7.49 (m, 2H), 7.43 – 7.35 (m, 3H), 7.19 (d, $J = 7.7$ Hz, 2H), 7.07 (d, $J = 7.7$ Hz, 2H), 6.94 (br, 1H), 6.64 (d, $J = 2.4$ Hz, 1H), 6.59 (d, $J = 3.4$ Hz, 1H), 6.52 (d, $J = 3.1$ Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.9, 159.0, 154.5, 151.5, 150.9, 139.5, 137.3, 135.8, 130.2, 129.5, 129.3, 129.0, 128.5, 127.6, 127.0, 126.6, 126.3, 125.2, 123.7, 12,3.0, 110.5, 106.9, 106.3, 21.4, 21.2; HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{22}\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 441.1461, found 441.1465.

(5-(o-Tolyl)furan-2-yl)(2-(5-(o-tolyl)furan-2-yl)phenyl)methanone (4g). Yellow oil (49 mg, 47%); IR (KBr): 2957, 2926, 2857, 1658, 1599, 1566, 1510, 1478, 1310, 1252, 1032, 762 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.9$ Hz, 1H), 7.64 (d, $J = 7.5$ Hz, 1H), 7.58 – 7.48 (m, 3H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 7.1$ Hz, 3H), 7.13 (d, $J = 3.5$ Hz, 3H), 7.02 (br, 1H), 6.66 (br, 1H), 6.56 (d, $J = 2.2$ Hz, 1H), 6.50 (s, 1H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.0, 158.6, 153.8, 151.5, 150.9, 136.0, 135.8, 134.3, 131.3, 131.1, 130.3, 129.6, 129.1, 128.9, 128.7, 128.4, 128.2, 127.5, 127.2, 126.8, 126.6, 126.1, 126.0, 122.1, 110.8, 110.5, 21.9, 21.7; HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{22}\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 441.1461, found 441.1467.

(5-(4-Fluorophenyl)furan-2-yl)(2-(5-(4-fluorophenyl)furan-2-yl)phenyl)methanone (4h). Yellow oil (60 mg, 56%); IR (KBr): 2925, 2854, 1650, 1600, 1485, 1416, 1234, 1028, 839, 761 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.9$ Hz, 1H), 7.72 – 7.63 (m, 2H), 7.54 (dd, $J = 15.4, 7.6$ Hz, 2H), 7.49 – 7.43 (m, 2H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.07 (t, $J = 8.2$ Hz, 2H), 6.98 – 6.87 (m, 3H), 6.65 (d, $J = 3.1$ Hz, 1H), 6.58 (d, $J = 3.2$ Hz, 1H), 6.51 (d, $J = 3.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.9, 163.3 (d, $J_{\text{CF}} = 248.9$ Hz), 162.2 (d, $J_{\text{CF}} = 246.1$ Hz), 157.6, 153.4, 151.7, 151.4, 135.7, 130.3, 128.8, 128.5, 127.4, 127.1 (d, $J_{\text{CF}} = 8.3$ Hz), 126.6 (d, $J_{\text{CF}} = 3.3$ Hz), 126.3, 125.54 (d, $J_{\text{CF}} = 3.3$ Hz), 125.4 (d, $J_{\text{CF}} = 8.0$ Hz), 122.7, 116.0 (d, $J_{\text{CF}} = 22.0$ Hz), 115.6 (d, $J_{\text{CF}} = 21.8$ Hz), 110.4, 107.1, 106.7; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{16}\text{F}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 449.0960, found 449.0962.

(4-Methyl-2-(5-methylfuran-2-yl)phenyl)(5-methylfuran-2-yl)methanone (4i). Yellow oil (28 mg, 40%); IR (KBr): 2922, 2853, 1651, 1607, 1513, 1447, 1366, 1309, 1210, 1024, 817, 792, 768 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (s, 1H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 6.69 (d, $J = 3.2$ Hz, 1H), 6.35 (d, $J = 3.1$ Hz, 1H), 6.03 (d, $J = 2.7$ Hz, 1H), 5.91 (d, $J = 2.7$ Hz,

1H), 2.43 (s, 3H), 2.35 (s, 3H), 2.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 158.5, 152.4, 151.7, 150.2, 140.3, 132.9, 129.3, 128.6, 127.4, 126.8, 122.2, 109.6, 108.9, 107.7, 21.4, 14.1, 13.5; HRMS (ESI) m/z calcd for C₁₈H₁₆NaO₃ [M + Na]⁺ 303.0992, found 303.0996.

(5-Benzylfuran-2-yl)(2-(5-benzylfuran-2-yl)-4-methylphenyl)methanone (4m). Yellow oil (59 mg, 55%); IR (KBr): 2923, 2855, 1652, 1605, 1541, 1509, 1453, 1425, 1383, 1307, 1205, 1023, 816, 792, 769, 708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 1H), 7.35 – 7.27 (m, 4H), 7.24 – 7.18 (m, 5H), 7.13 (d, *J* = 6.7 Hz, 3H), 6.69 (d, *J* = 3.4 Hz, 1H), 6.38 (d, *J* = 3.3 Hz, 1H), 5.95 (d, *J* = 3.5 Hz, 1H), 5.90 (d, *J* = 3.3 Hz, 1H), 3.97 (s, 2H), 3.81 (s, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.1, 160.8, 155.0, 151.9, 150.9, 140.3, 137.8, 136.5, 133.1, 129.3, 128.9, 128.7, 128.7, 128.6, 128.4, 127.7, 127.0, 126.9, 126.4, 121.8, 109.4, 109.2, 108.3, 34.8, 34.4, 21.4; HRMS (ESI) m/z calcd for C₃₀H₂₄NaO₃ [M + Na]⁺ 455.1618, found 455.1622.

(4-Methyl-2-(5-phenylfuran-2-yl)phenyl)(5-phenylfuran-2-yl)methanone (4n). Yellow oil (53 mg, 53%); IR (KBr): 2926, 2852, 1654, 1600, 1515, 1471, 1371, 1311, 1267, 1070, 815, 761, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 1.5 Hz, 1H), 7.70 (s, 1H), 7.60 (s, 1H), 7.53 (t, *J* = 1.6 Hz, 1H), 7.50 (d, *J* = 2.9 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.27 (m, 4H), 7.26 – 7.12 (m, 3H), 6.95 (d, *J* = 3.6 Hz, 1H), 6.64 (t, *J* = 3.3 Hz, 2H), 6.57 (d, *J* = 3.5 Hz, 1H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.1, 158.4, 154.1, 151.9, 151.6, 140.5, 133.3, 130.3, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.1, 127.4, 126.9, 125.1, 123.7, 122.4, 110.4, 107.4, 107.0, 21.5; HRMS (ESI) m/z calcd for C₂₈H₂₀NaO₃ [M + Na]⁺ 427.1305, found 427.1310.

(4-Methyl-2-(5-(o-tolyl)furan-2-yl)phenyl)(5-(o-tolyl)furan-2-yl)methanone (4o). Yellow oil (53 mg, 49%); IR (KBr): 2924, 2853, 1649, 1510, 1462, 1374, 1308, 1256, 1030, 815, 760 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.62 (m, 1H), 7.61 (s, 1H), 7.57 – 7.54 (m, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.18 (m, 4H), 7.17 – 7.11 (m, 3H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.65 (d, *J* = 3.5 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 6.50 (d, *J* = 3.5 Hz, 1H), 2.48 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.1, 158.3, 153.7, 151.7, 151.2, 140.5, 135.8, 134.3, 133.4, 131.3, 131.0, 129.7, 129.0, 128.8, 128.7, 128.1, 128.1, 127.4, 127.2, 126.8, 126.1, 126.0, 121.8, 110.8, 110.7, 110.3, 22.0, 21.7, 21.5; HRMS (ESI) m/z calcd for C₃₀H₂₄NaO₃ [M + Na]⁺ 455.1618, found 455.1621.

(5-(4-Fluorophenyl)furan-2-yl)(2-(5-(4-fluorophenyl)furan-2-yl)-4-methylphenyl)methanone (4p). Yellow oil (62 mg, 57%); IR (KBr): 2923, 2852, 1649, 1604, 1529, 1477, 1232, 1026, 836, 810,

766 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.71 – 7.63 (m, 2H), 7.57 (s, 1H), 7.49 – 7.41 (m, 3H), 7.22 (d, $J = 7.8$ Hz, 1H), 7.07 (t, $J = 8.6$ Hz, 2H), 6.98 – 6.90 (m, 3H), 6.62 (d, $J = 3.5$ Hz, 1H), 6.56 (d, $J = 3.7$ Hz, 1H), 6.50 (d, $J = 3.5$ Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.0, 163.2 (d, $J_{CF} = 248.7$ Hz), 162.1 (d, $J_{CF} = 245.8$ Hz), 157.4, 153.3, 151.9, 151.6, 140.6, 133.2, 128.9, 128.8, 128.2, 127.0, 127.0 (d, $J_{CF} = 8.3$ Hz), 126.7 (d, $J_{CF} = 3.2$ Hz), 125.6 (d, $J_{CF} = 3.3$ Hz), 125.4 (d, $J_{CF} = 8.0$ Hz), 122.3, 116.0 (d, $J_{CF} = 22.0$ Hz), 115.6 (d, $J_{CF} = 21.8$ Hz), 110.3, 107.1, 106.6, 21.5; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{18}\text{F}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 463.1116, found 463.1117.

Characterization of 3

*2-Methyl-8H-indeno[2,1-*b*]furan-8-one (3a)*. Yellow solid (83 mg, 90%); mp 65.8 – 66.1 $^\circ\text{C}$; IR (KBr): 2922, 2854, 1708, 1609, 1562, 1506, 1414, 1311, 1272, 1025, 759 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 7.1$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 7.1$ Hz, 1H), 6.16 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.5, 164.5, 152.4, 148.9, 136.1, 135.5, 133.0, 128.5, 123.6, 119.8, 103.8, 14.6; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_8\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ 207.0417, found 207.0418.

*8H-indeno[2,1-*b*]furan-8-one (3b)*. Yellow solid (73 mg, 86%); mp 86.3 – 86.7 $^\circ\text{C}$; IR (KBr): 2923, 2851, 1705, 1611, 1452, 1415, 1273, 1033, 750 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (br, 1H), 7.37 (d, $J = 7.1$ Hz, 1H), 7.28 (t, $J = 5.8$ Hz, 1H), 7.14 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 7.1$ Hz, 1H), 6.54 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.4, 154.2, 152.6, 147.0, 135.9, 135.3, 133.5, 128.6, 124.0, 120.1, 106.9; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_6\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ 193.0260, found 193.0258.

*2-Ethyl-8H-indeno[2,1-*b*]furan-8-one (3c)*. Yellow solid (91 mg, 92%); mp 79.5 – 79.8 $^\circ\text{C}$; IR (KBr): 2975, 2915, 1695, 1608, 1503, 1453, 1423, 1378, 1328, 1145, 1106, 763 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 7.1$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 7.1$ Hz, 1H), 6.18 (s, 1H), 2.72 (q, $J = 7.6$ Hz, 2H), 1.29 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.7, 170.0, 152.3, 148.7, 136.1, 135.6, 133.0, 128.5, 123.6, 119.7, 102.3, 22.4, 11.7; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{O}_2$ $[\text{M} + \text{H}]^+$ 199.0754, found 199.0756.

2-Benzyl-8H-indeno[2,1-b]furan-8-one (3d). Yellow solid (124 mg, 95%); mp 70.5 – 70.9 °C; IR (KBr): 3029, 2922, 1708, 1610, 1498, 1453, 1419, 1386, 1272, 1021, 762, 717 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.27 (m, 6H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.17 (s, 1H), 4.03 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 177.8, 166.8, 152.8, 148.5, 136.0, 135.9, 135.4, 133.1, 128.8, 128.9, 128.6, 127.2, 123.7, 119.8, 104.1, 35.5; HRMS (ESI) *m/z* calcd for C₁₈H₁₂NaO₂ [M + Na]⁺ 283.0730, found 283.0730.

2-Phenyl-8H-indeno[2,1-b]furan-8-one (3e). Yellow solid (93 mg, 76%); mp 118.5 – 119.0 °C; IR (KBr): 3063, 2929, 2848, 1700, 1611, 1466, 1417, 1311, 1235, 1021, 757, 713 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.32 (m, 4H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.75 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 177.8, 164.3, 152.8, 148.8, 136.3, 135.1, 133.2, 129.7, 129.3, 129.0, 128.8, 125.0, 123.7, 120.1, 101.6; HRMS (ESI) *m/z* calcd for C₁₇H₁₀NaO₂ [M + Na]⁺ 269.0573, found 269.0575.

2-(p-Tolyl)-8H-indeno[2,1-b]furan-8-one (3f). Yellow solid (95 mg, 73%); mp 136.7 – 137.2 °C; IR (KBr): 2918, 2851, 1703, 1611, 1467, 1415, 1372, 1146, 1020, 809, 755 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 1H), 7.22 (t, *J* = 8.1 Hz, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.1 Hz, 1H), 6.69 (s, 1H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 164.7, 152.5, 149.0, 140.1, 136.5, 135.1, 133.1, 129.7, 128.8, 126.6, 125.0, 123.6, 120.0, 101.0, 21.5; HRMS (ESI) *m/z* calcd for C₁₈H₁₂NaO₂ [M + Na]⁺ 283.0730, found 283.0733.

2-(o-Tolyl)-8H-indeno[2,1-b]furan-8-one (3g). Yellow solid (91 mg, 70%); mp 116.7 – 117.2 °C; IR (KBr): 3052, 1703, 1610, 1481, 1374, 1274, 1020, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.1 Hz, 1H), 6.68 (s, 1H), 2.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 164.4, 152.6, 148.6, 136.3, 135.9, 135.3, 133.2, 131.6, 129.5, 128.8, 128.7, 128.0, 126.3, 123.8, 120.0, 105.1, 22.0; HRMS (ESI) *m/z* calcd for C₁₈H₁₂NaO₂ [M + Na]⁺ 283.0730, found 283.0729.

2-(4-Fluorophenyl)-8H-indeno[2,1-b]furan-8-one (3h). Yellow solid (106 mg, 80%); mp 159.2 – 159.8 °C; IR (KBr): 2922, 2853, 1714, 1605, 1516, 1469, 1422, 1225, 1022, 811, 753 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.63 (m, 2H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 17.7, 8.4 Hz, 3H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.65 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 177.7, 163.4 (d, *J*_{CF} = 249.6 Hz), 163.2, 152.7, 148.8, 136.2, 134.9, 133.2, 128.8, 126.9

(d, J_{CF} = 8.4 Hz), 125.63 (d, J_{CF} = 3.3 Hz), 123.7, 120.1, 116.2 (d, J_{CF} = 22.1 Hz), 101.3; HRMS (ESI) m/z calcd for $C_{17}H_9FNaO_2$ [M + Na]⁺ 287.0479, found 287.0474.

Methyl 8-oxo-8H-indeno[2,1-b]furan-2-carboxylate (3i). Yellow solid (82 mg, 72%); mp 172.8 – 172.9 °C; IR (KBr): 3009, 1711, 1613, 1451, 1387, 1256, 1119, 752 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 7.2 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.11 (d, J = 7.2 Hz, 1H), 3.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.8, 158.6, 156.0, 152.2, 145.6, 135.1, 134.7, 134.3, 129.2, 124.5, 120.7, 112.4, 52.6; HRMS (ESI) m/z calcd for $C_{13}H_9O_4$ [M + H]⁺ 229.0495, found 229.0493.

2-Methyl-3-(methylthio)-8H-indeno[2,1-b]furan-8-one (3j). Yellow solid (101 mg, 88%); mp 117.3 – 117.8 °C; IR (KBr): 2923, 2854, 1706, 1610, 1505, 1474, 1417, 1141, 1022, 762 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, J = 7.1 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.10 (d, J = 6.9 Hz, 1H), 7.06 – 6.99 (m, 1H), 2.35 (s, 3H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.2, 166.5, 151.5, 149.8, 135.6, 135.0, 133.2, 128.7, 123.8, 120.0, 112.4, 19.4, 12.9; HRMS (ESI) m/z calcd for $C_{13}H_{10}NaO_2S$ [M + Na]⁺ 253.0294, found 253.0296.

6H-indeno[2,1-b]benzofuran-6-one (3k). Yellow solid (99 mg, 90%); mp 107.8 – 108.2 °C; IR (KBr): 2923, 2852, 1715, 1610, 1547, 1493, 1450, 1400, 1260, 1020, 745 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.42 – 7.28 (m, 3H), 7.19 (d, J = 7.1 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 180.6, 161.6, 154.7, 141.3, 136.0, 134.9, 133.8, 128.7, 128.6, 124.8, 124.1, 122.0, 122.0, 120.2, 113.8; HRMS (ESI) m/z calcd for $C_{15}H_8NaO_2$ [M + Na]⁺ 243.0417, found 243.0415.

2,5-Dimethyl-8H-indeno[2,1-b]furan-8-one (3l). Yellow solid (92 mg, 93%); mp 100.5 – 100.9 °C; IR (KBr): 2953, 2921, 1716, 1697, 1613, 1561, 1507, 1477, 1401, 1271, 1021, 832, 798, 766 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, J = 7.3 Hz, 1H), 6.86 (d, J = 7.3 Hz, 1H), 6.77 (s, 1H), 6.13 (s, 1H), 2.37 (s, 3H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.7, 164.1, 152.7, 148.3, 143.8, 135.8, 133.5, 128.1, 123.7, 121.3, 103.6, 21.9, 14.6; HRMS (ESI) m/z calcd for $C_{13}H_{10}NaO_2$ [M + Na]⁺ 221.0573, found 221.0574.

2-Benzyl-5-methyl-8H-indeno[2,1-b]furan-8-one (3m). Yellow solid (126 mg, 92%); mp 107.9 – 108.3 °C; IR (KBr): 2923, 2856, 1699, 1617, 1563, 1498, 1446, 1409, 1367, 1244, 1017, 770, 730, 701 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 2H), 7.28 – 7.24 (m, 3H), 7.19 (d, J = 7.3 Hz, 1H), 6.85 (d, J = 7.3 Hz, 1H), 6.73 (s, 1H), 6.10 (s, 1H), 3.99 (s, 2H), 2.26 (s, 3H); ¹³C NMR

(100 MHz, CDCl₃) δ 178.0, 166.4, 153.2, 147.9, 144.0, 136.1, 135.7, 133.3, 128.9, 128.8, 128.2, 127.1, 123.8, 121.4, 104.0, 35.5, 22.0; HRMS (ESI) m/z calcd for C₁₉H₁₄NaO₂ [M + Na]⁺ 297.0886, found 297.0892.

5-Methyl-2-phenyl-8H-indeno[2,1-b]furan-8-one (3n). Yellow solid (117 mg, 90%); mp 122.9 – 123.2 °C; IR (KBr): 2920, 2856, 1698, 1614, 1443, 1407, 1368, 1213, 1119, 752, 712 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.68 (m, 2H), 7.46 – 7.34 (m, 3H), 7.23 (d, J = 7.3 Hz, 1H), 6.90 (d, J = 7.4 Hz, 1H), 6.85 (s, 1H), 6.71 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 178.0, 163.9, 153.2, 148.3, 144.1, 135.3, 133.7, 129.5, 129.4, 129.0, 128.5, 124.9, 123.8, 121.6, 101.5, 22.0; HRMS (ESI) m/z calcd for C₁₈H₁₃O₂ [M + H]⁺ 261.0910, found 261.0908.

5-Methyl-2-(o-tolyl)-8H-indeno[2,1-b]furan-8-one (3o). Yellow solid (111 mg, 81%); mp 140.4 – 140.5 °C; IR (KBr): 2921, 2851, 1691, 1618, 1461, 1270, 1019, 848, 816, 755, 714 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.69 (m, 1H), 7.31 – 7.25 (m, 4H), 6.96 – 6.88 (m, 2H), 6.65 (s, 1H), 2.56 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.2, 164.1, 153.1, 148.0, 144.1, 135.8, 135.6, 133.8, 131.6, 129.4, 128.9, 128.4, 128.0, 126.3, 123.9, 121.6, 105.0, 22.0; HRMS (ESI) m/z calcd for C₁₉H₁₄NaO₂ [M + Na]⁺ 297.0886, found 297.0878.

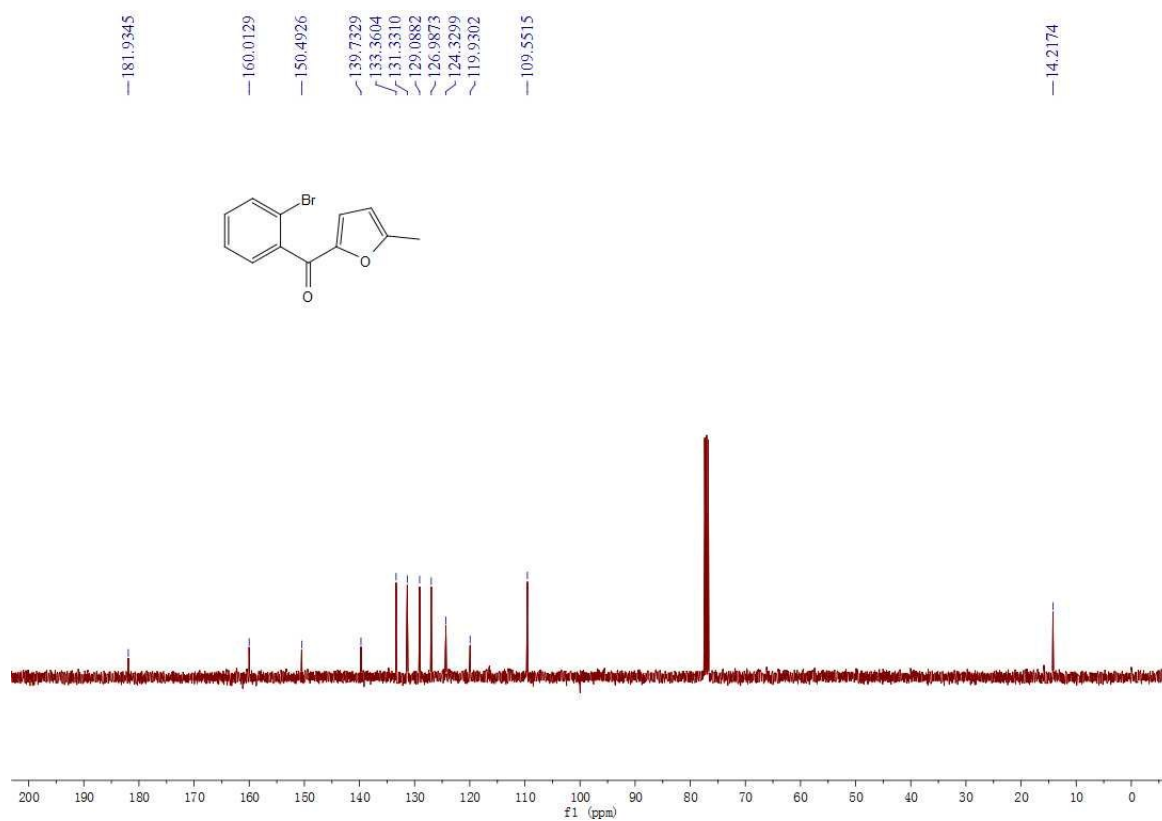
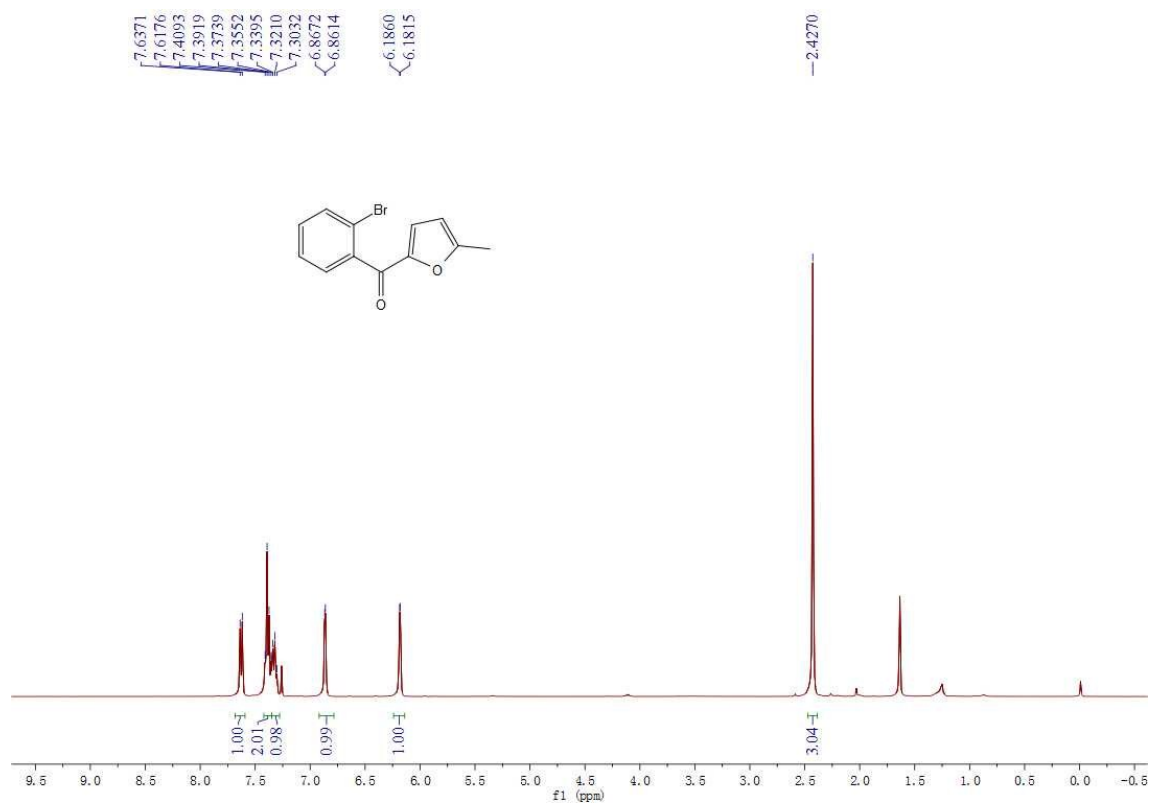
2-(4-Fluorophenyl)-5-methyl-8H-indeno[2,1-b]furan-8-one (3p). Yellow solid (124 mg, 89%); mp 155.6 – 155.9 °C; IR (KBr): 2922, 2850, 1693, 1615, 1469, 1421, 1231, 1013, 828, 761 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.69 (m, 2H), 7.25 (d, J = 7.4 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.92 (d, J = 7.4 Hz, 1H), 6.87 (s, 1H), 6.68 (s, 1H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 163.4 (d, J_{CF} = 249.4 Hz), 163.0, 153.2, 148.3, 144.2, 135.2, 133.7, 128.6, 126.9 (d, J_{CF} = 8.4 Hz), 125.8 (d, J_{CF} = 3.3 Hz), 123.9, 121.6, 116.2 (d, J_{CF} = 22.1 Hz), 101.2, 22.0; HRMS (ESI) m/z calcd for C₁₈H₁₂FO₂ [M + H]⁺ 279.0816, found 279.0824.

2-Ethyl-5-fluoro-8H-indeno[2,1-b]furan-8-one (3r). Yellow solid (91 mg, 84%); mp 59.3 – 59.5 °C; IR (KBr): 2921, 2851, 1708, 1659, 1633, 1451, 1415, 1380, 1198, 1111, 769 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.08 – 7.01 (m, 1H), 6.93 – 6.81 (m, 2H), 6.17 (s, 1H), 2.72 (q, J = 7.5 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.6, 170.7, 163.2 (d, J_{CF} = 247.8 Hz), 152.0, 148.8, 138.7 (d, J_{CF} = 6.7 Hz), 131.1 (d, J_{CF} = 3.9 Hz), 120.7 (d, J_{CF} = 7.5 Hz), 117.6 (d, J_{CF} = 22.5 Hz), 112.9 (d, J_{CF} = 25.2 Hz), 102.4, 22.4, 11.6; HRMS (ESI) m/z calcd for C₁₃H₉FNaO₂ [M + Na]⁺ 239.0479, found 239.0482.

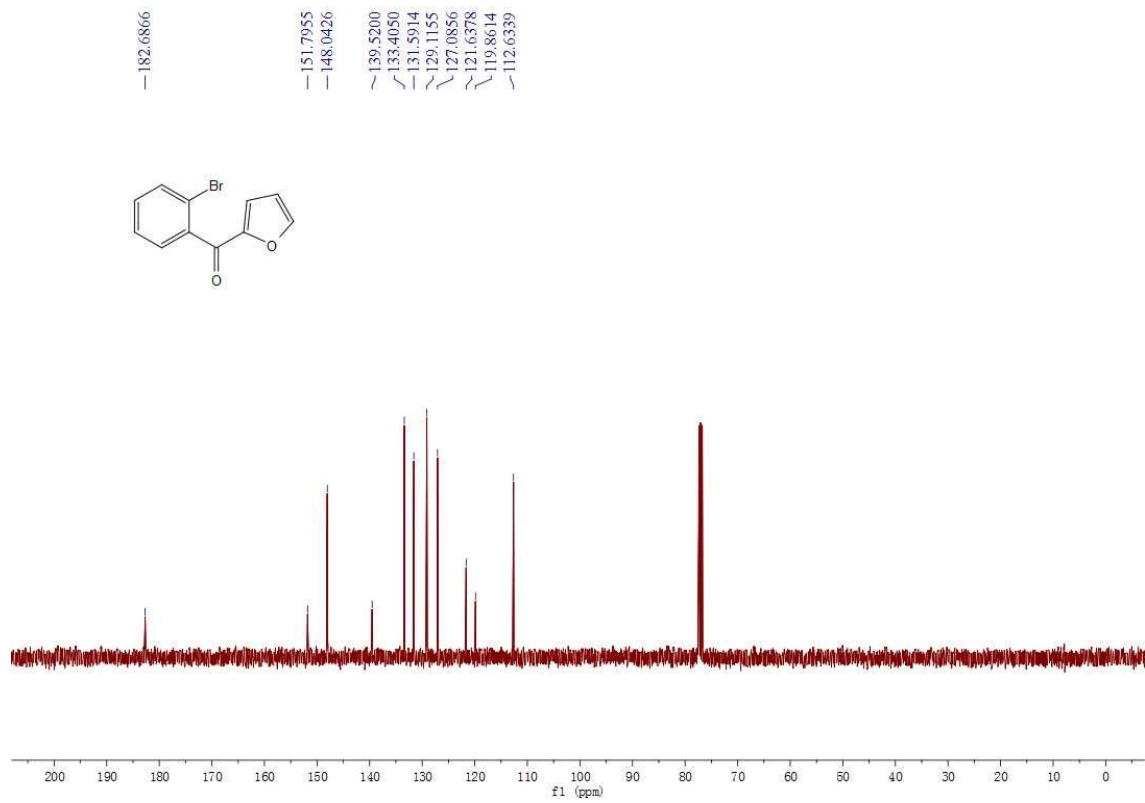
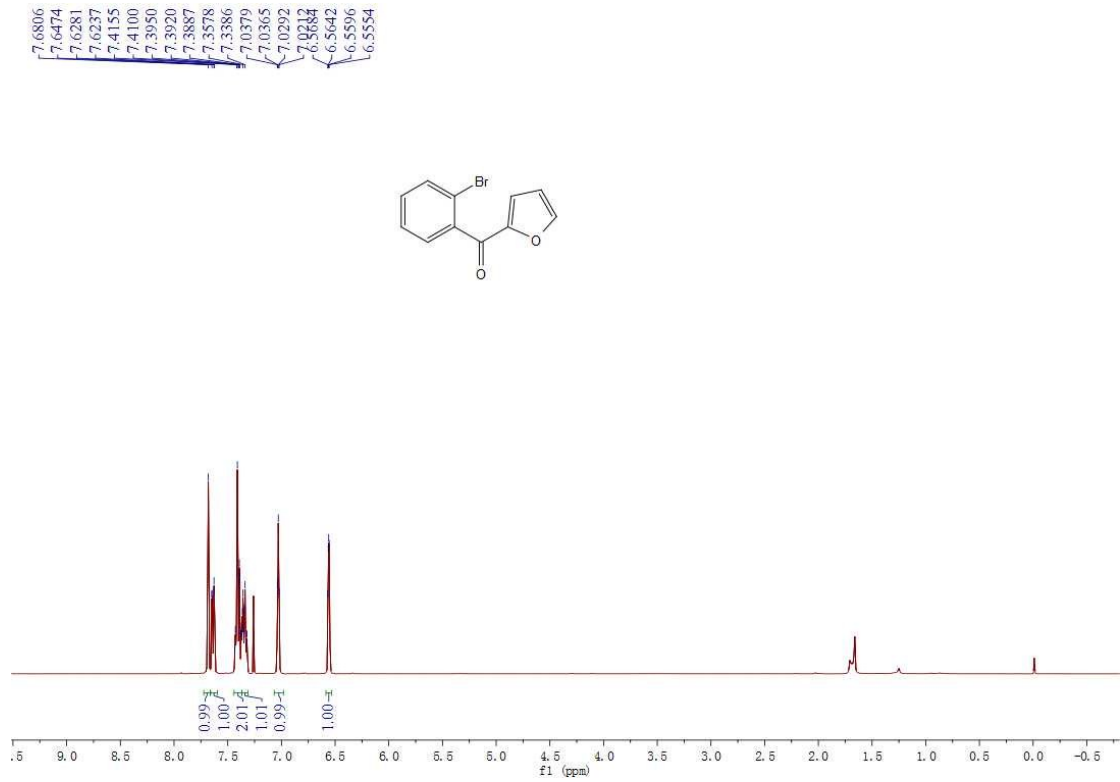
2-(4-methoxyphenyl)-8H-indeno[2,1-b]furan-8-one(3s). Yellow solid (76 mg, 72%); mp 144.4 – 144.5 °C; IR (KBr): 3110, 2923, 2854, 1691, 1603, 1515, 1461, 1423, 1250, 816, 746; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.65 (s, 1H), 3.85 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.44, 164.70, 160.91, 152.15, 149.35, 136.62, 135.09, 133.01, 128.79, 126.71, 123.58, 122.13, 119.97, 114.51, 100.25, 55.43; HRMS (ESI) *m/z* calcd for C₁₈H₁₃O₃[M-H]⁻ 277.0853, found 277.0859.

NMR Spectra for All Compounds

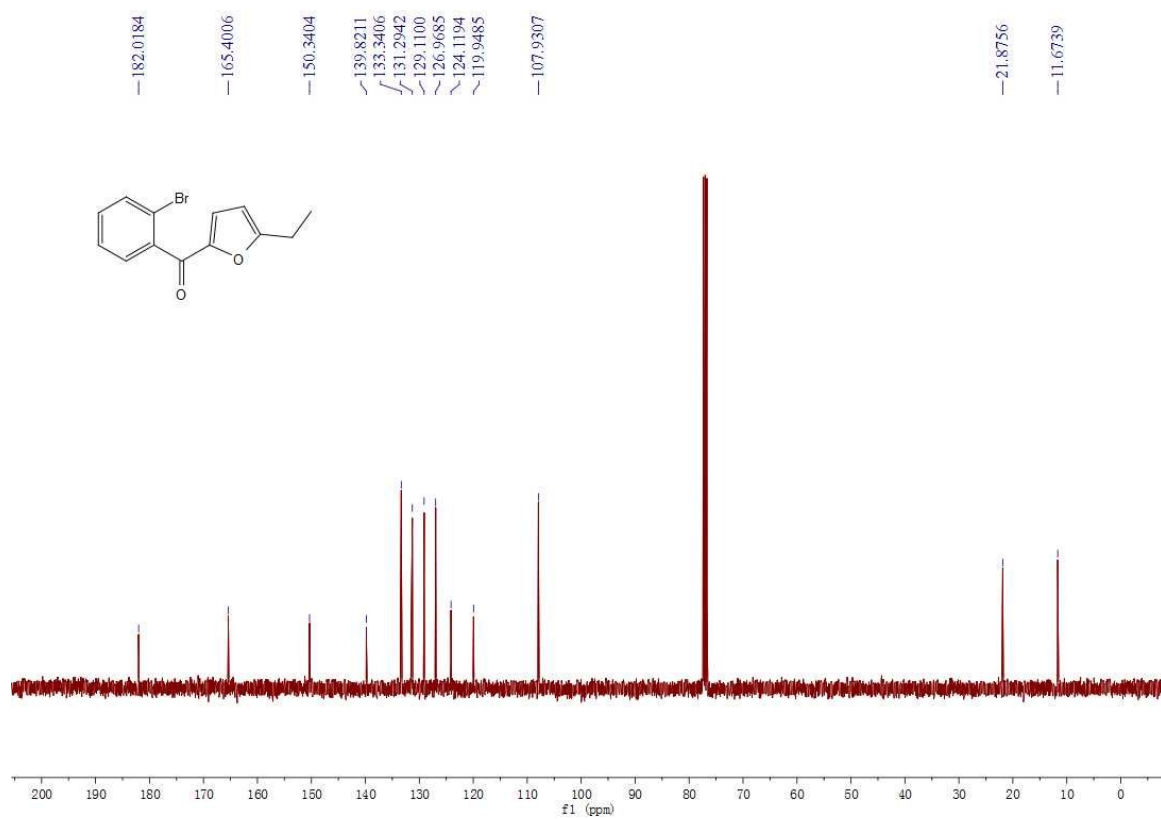
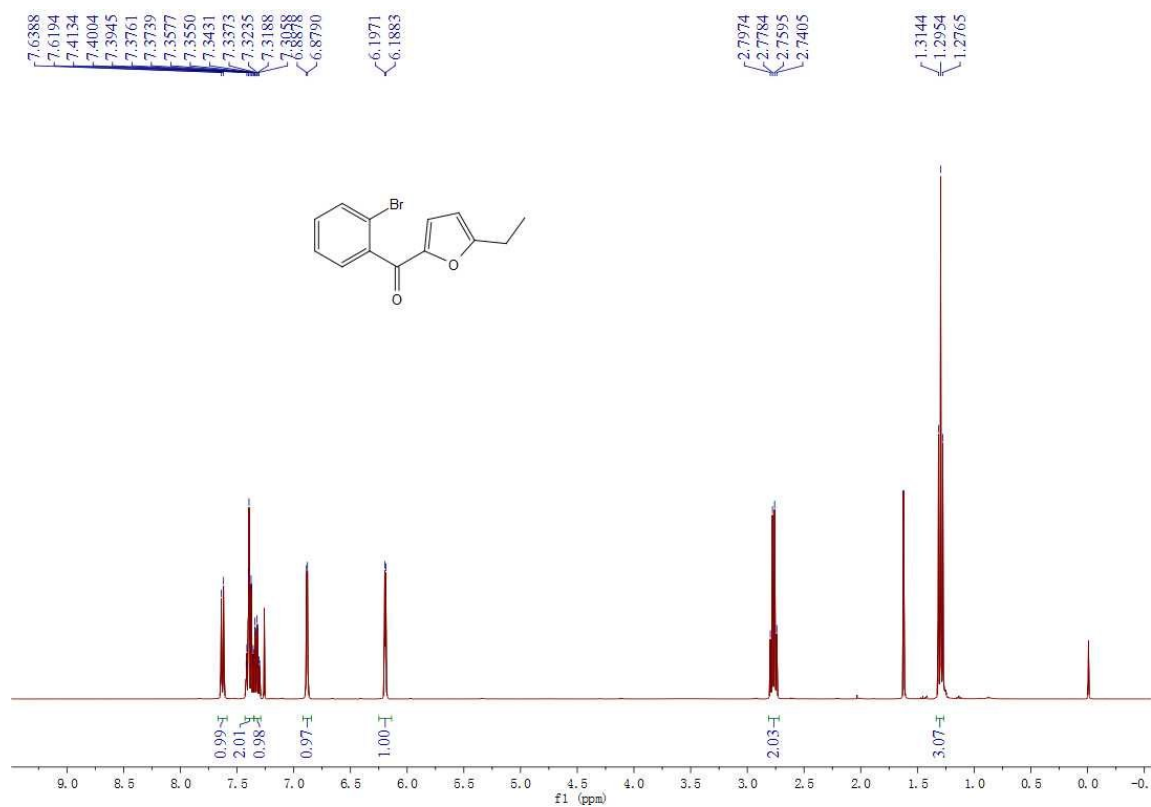
^1H NMR and ^{13}C NMR of 1a



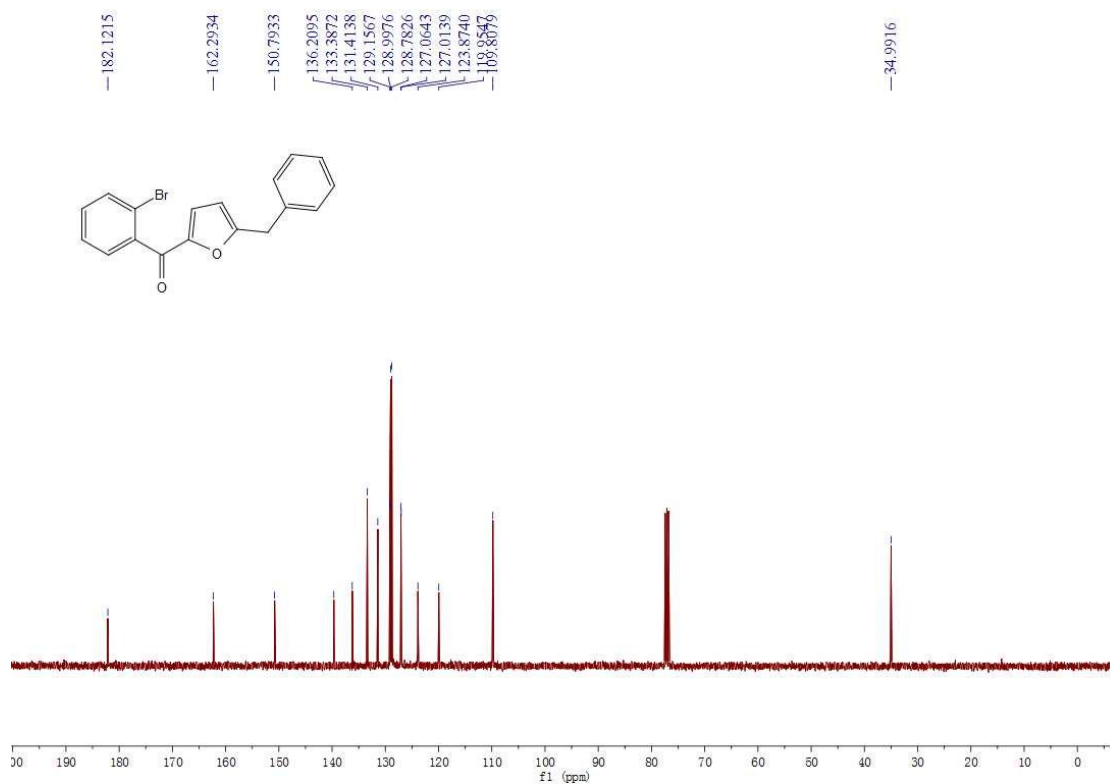
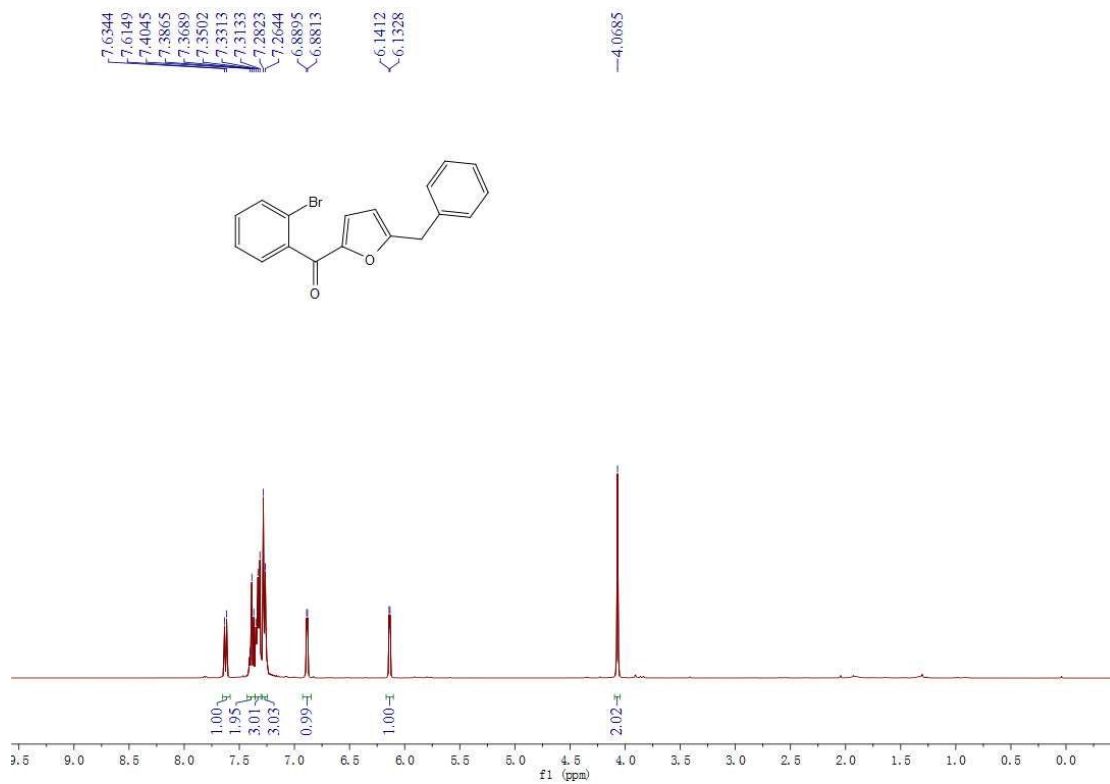
¹H NMR and ¹³C NMR of 1b



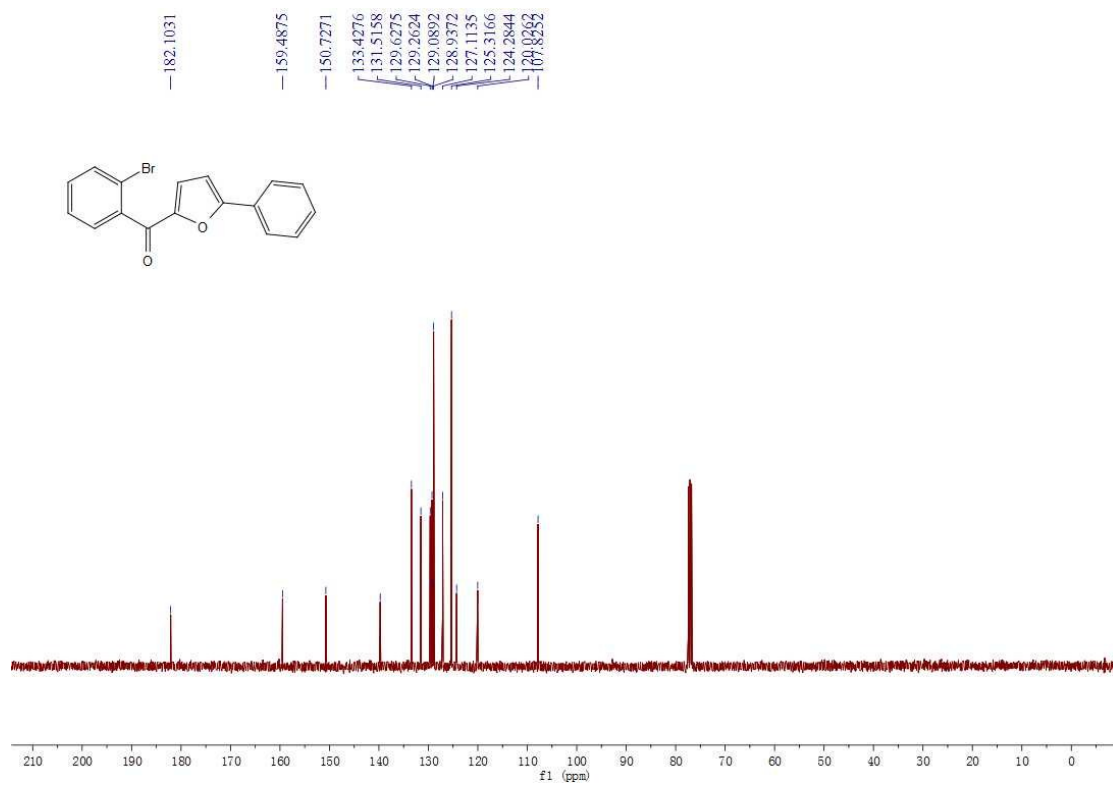
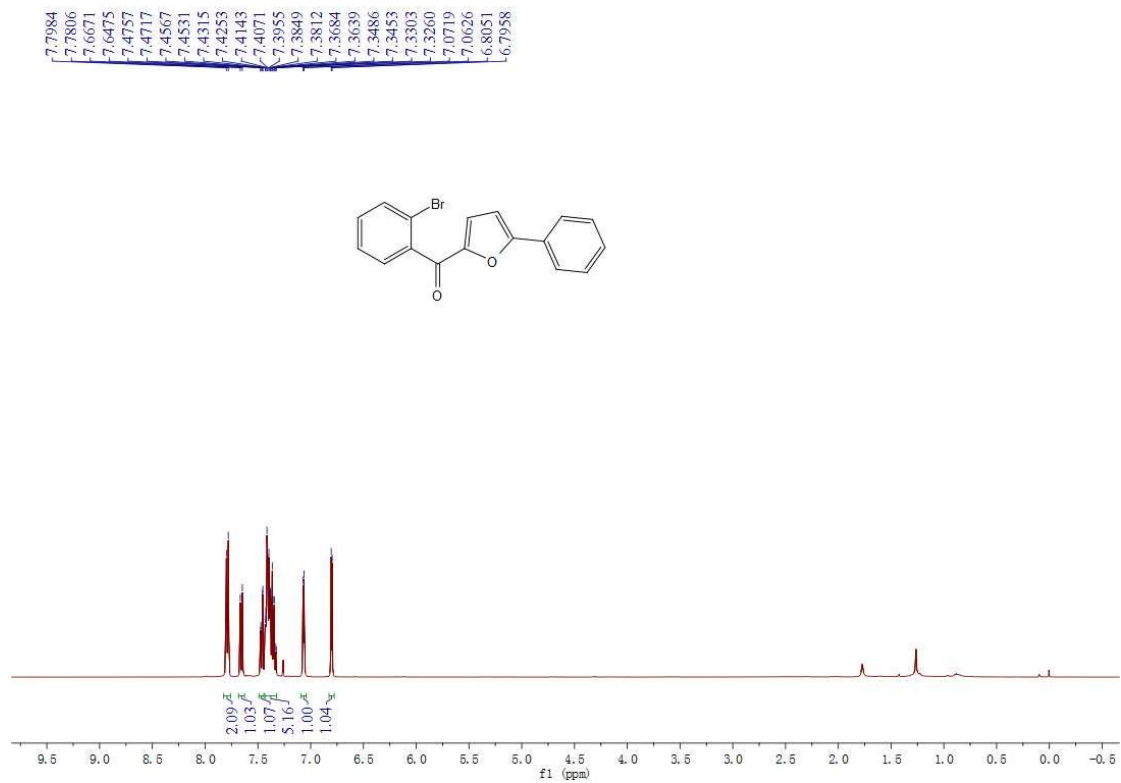
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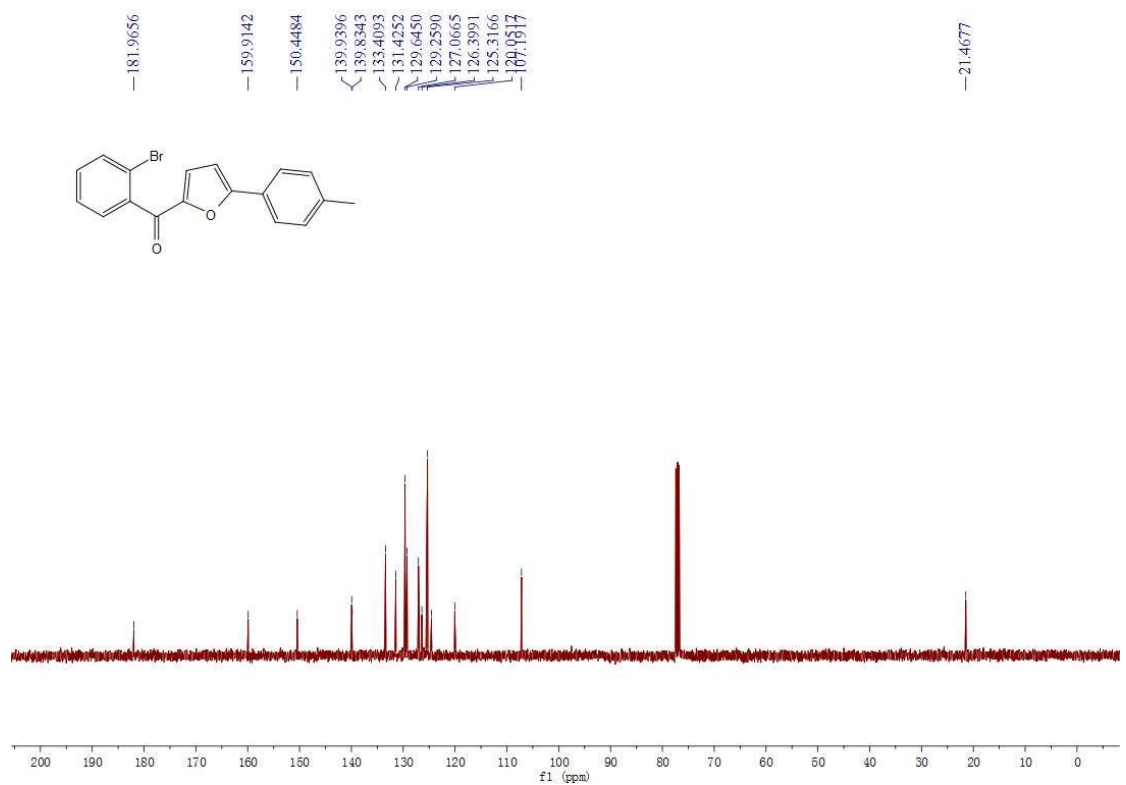
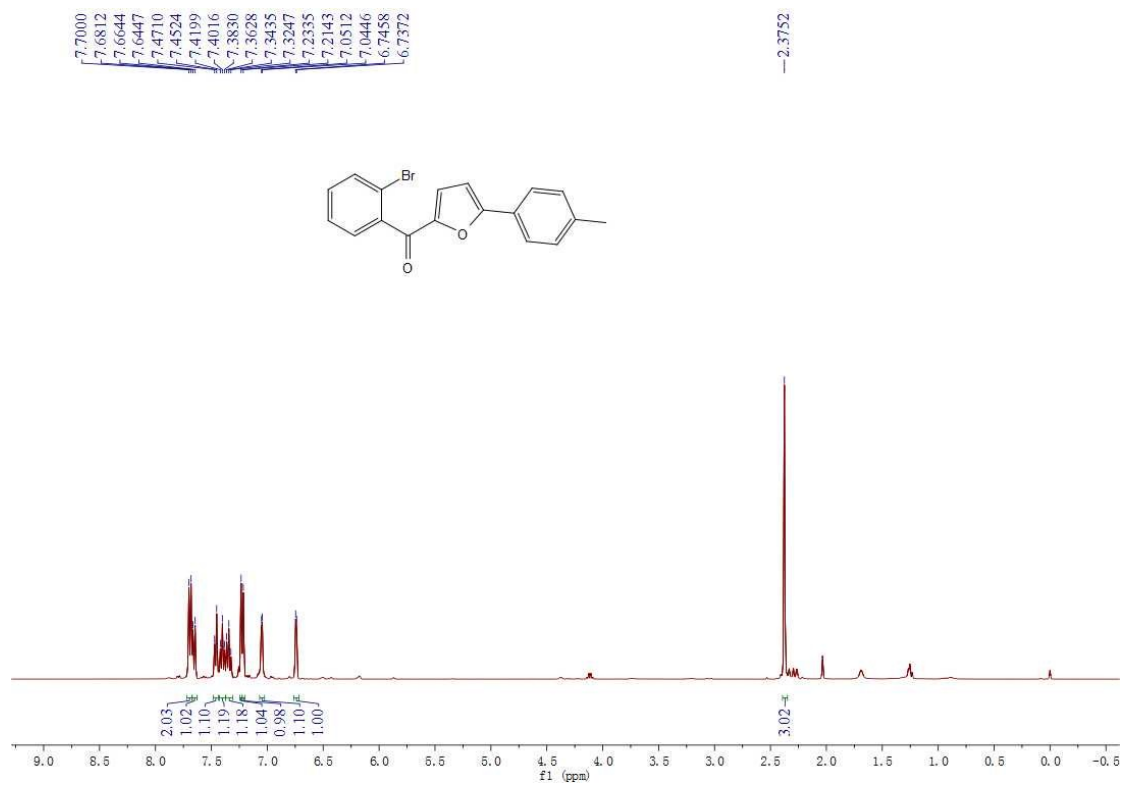
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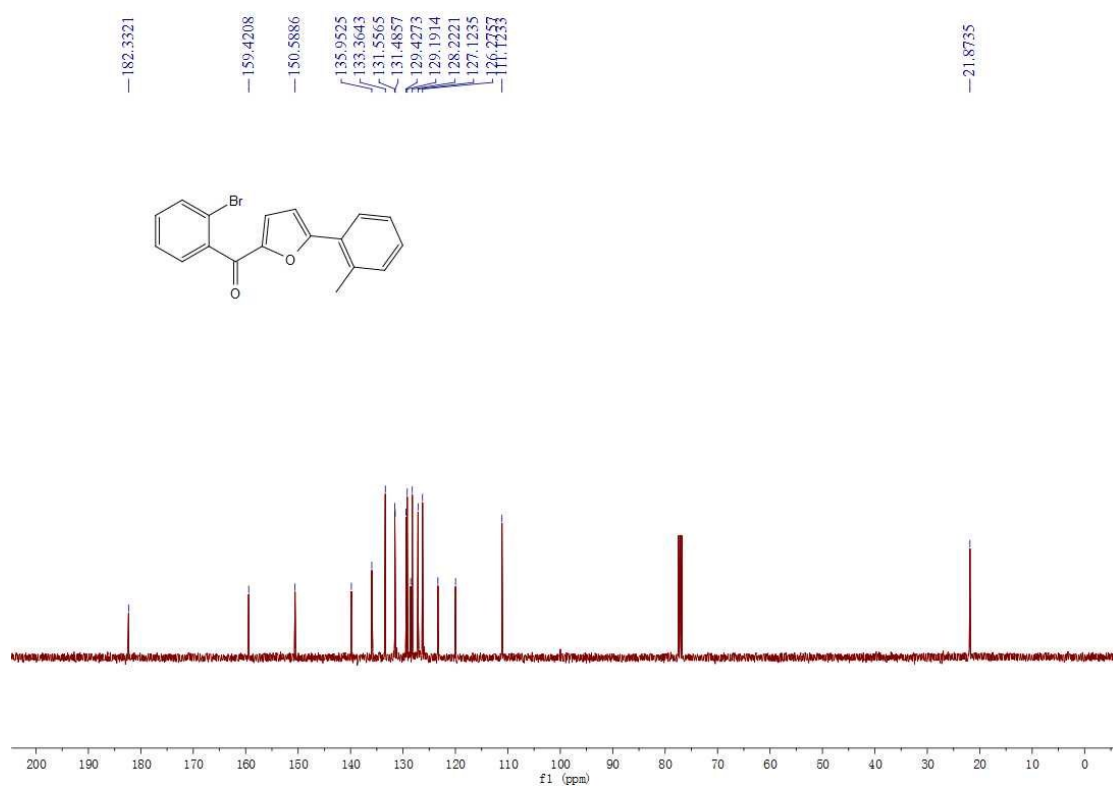
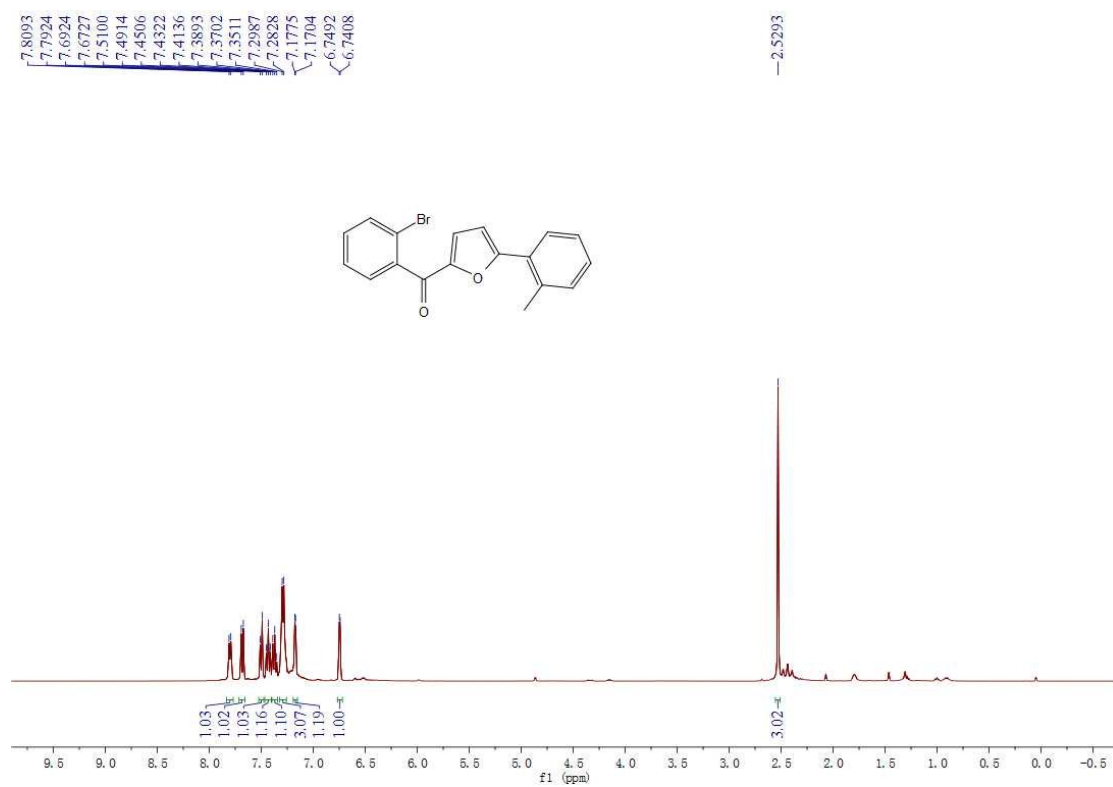
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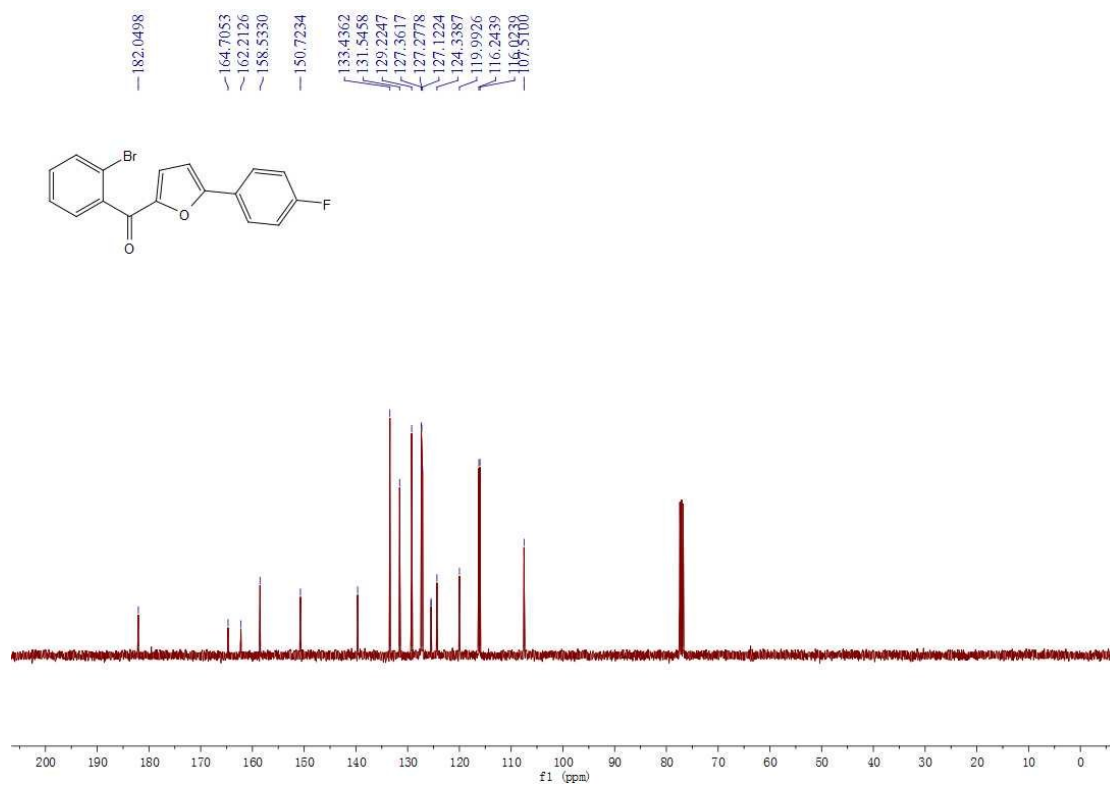
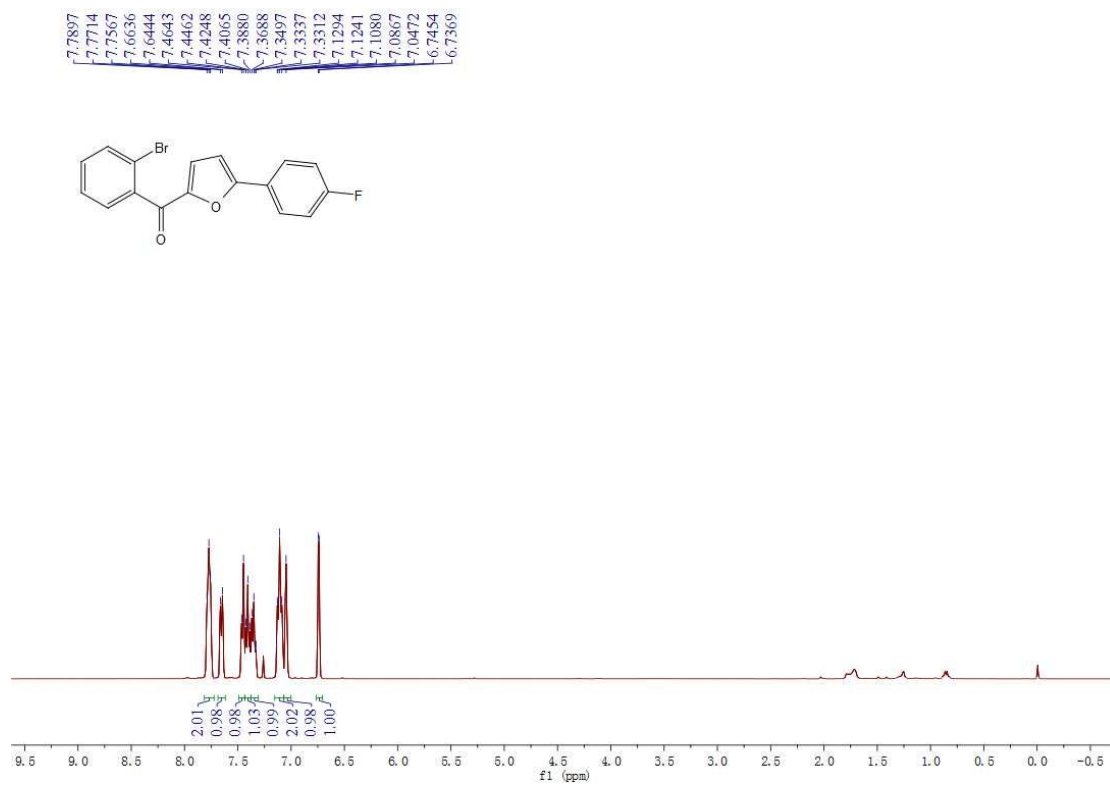
^1H NMR and ^{13}C NMR of 1f



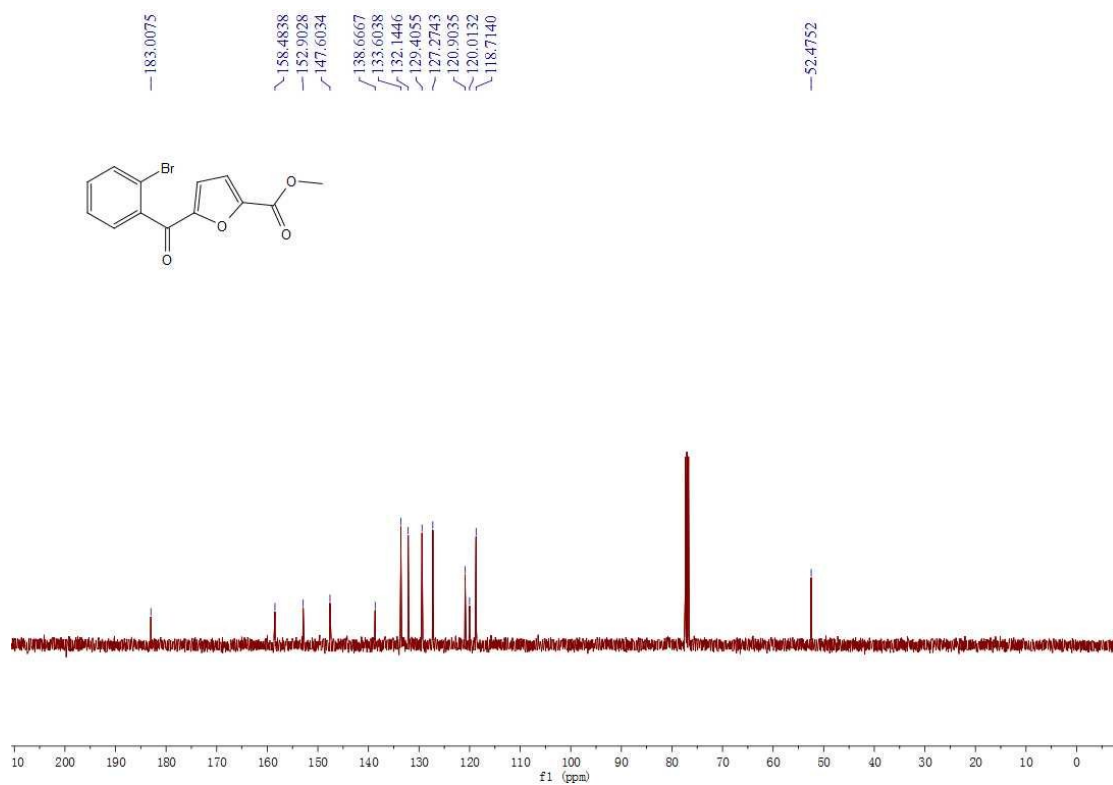
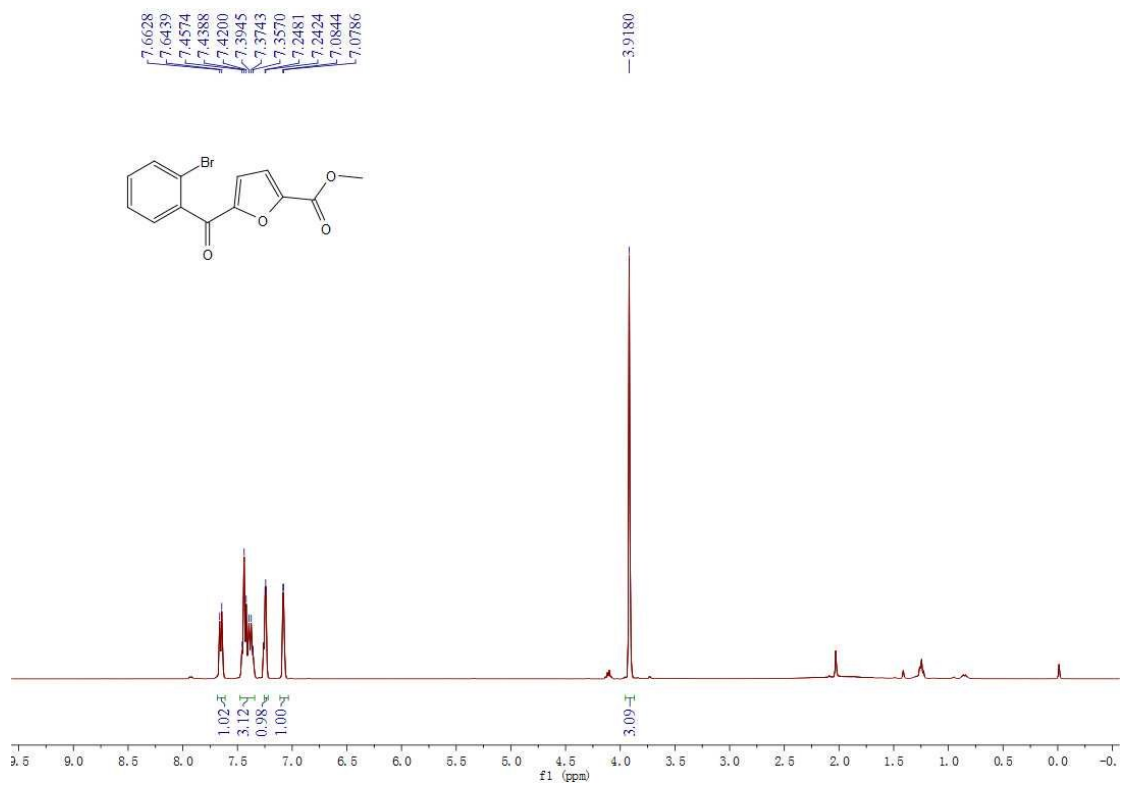
^1H NMR and ^{13}C NMR of 1g



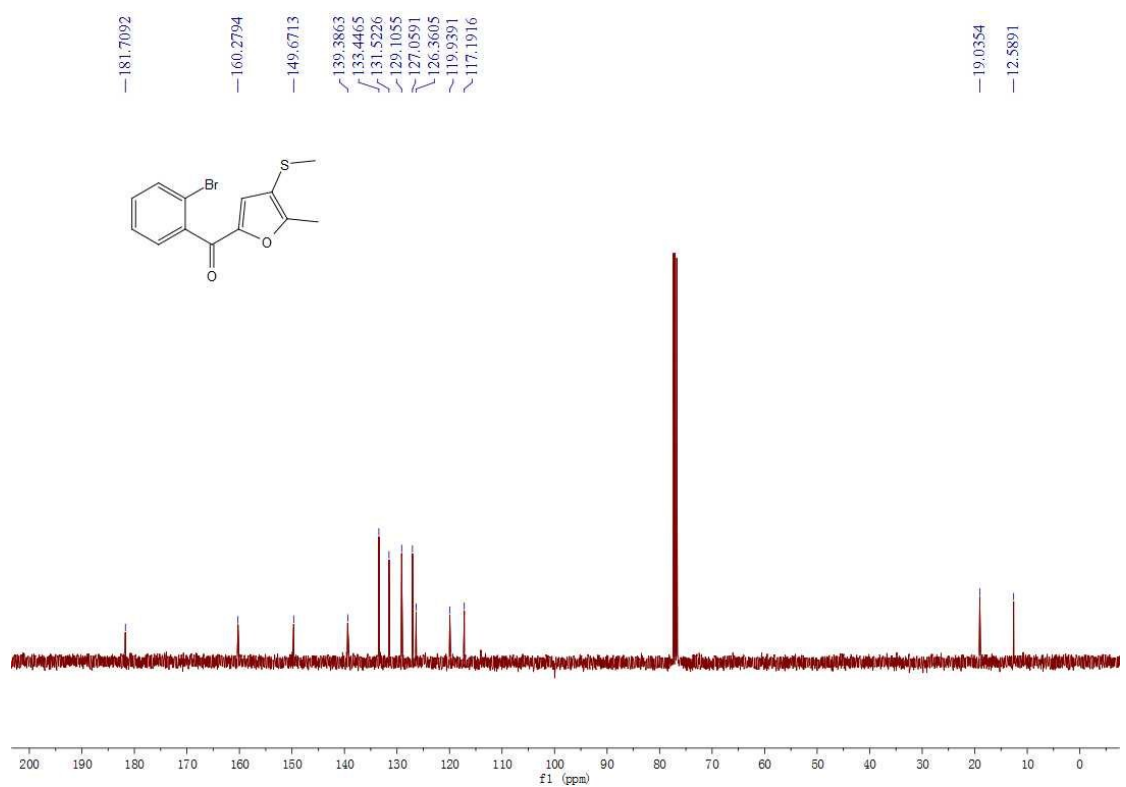
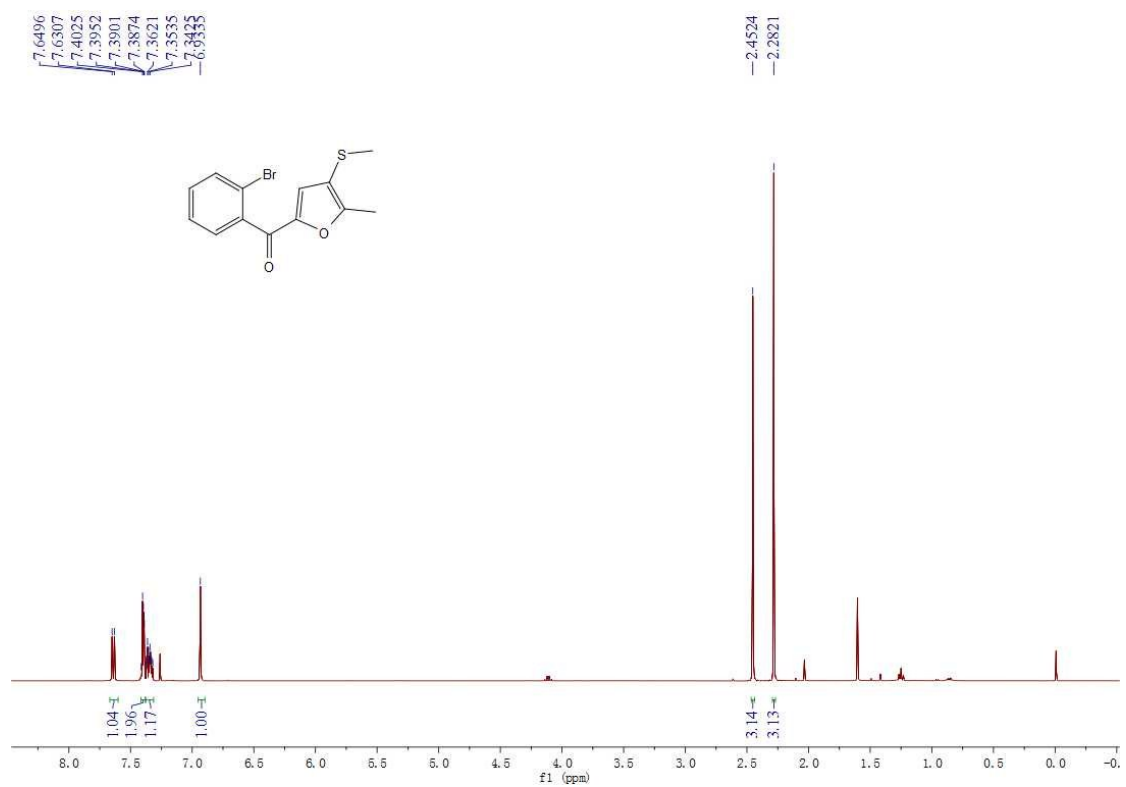
¹H NMR and ¹³C NMR of 1h



^1H NMR and ^{13}C NMR of 1i

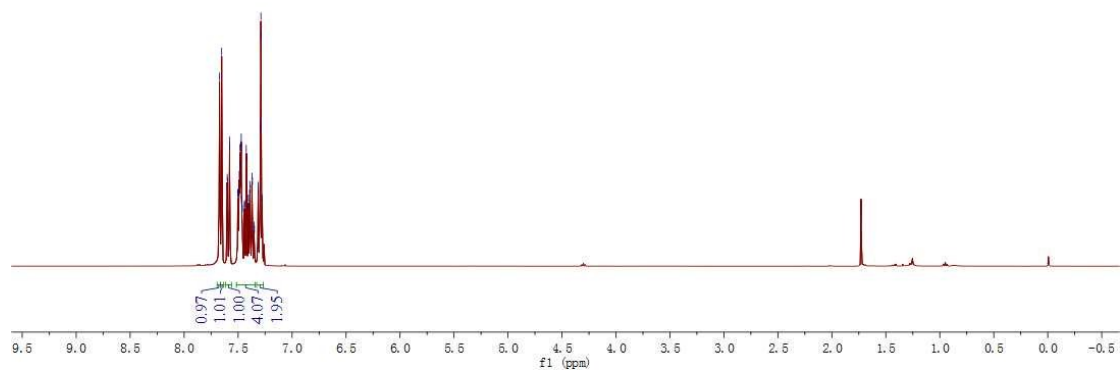


^1H NMR and ^{13}C NMR of 1j

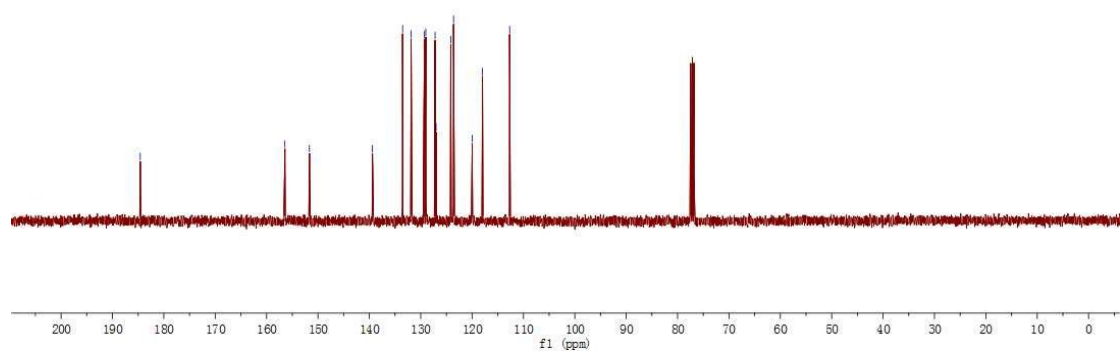
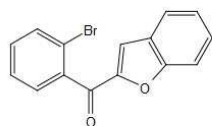


¹H NMR and ¹³C NMR of 1k

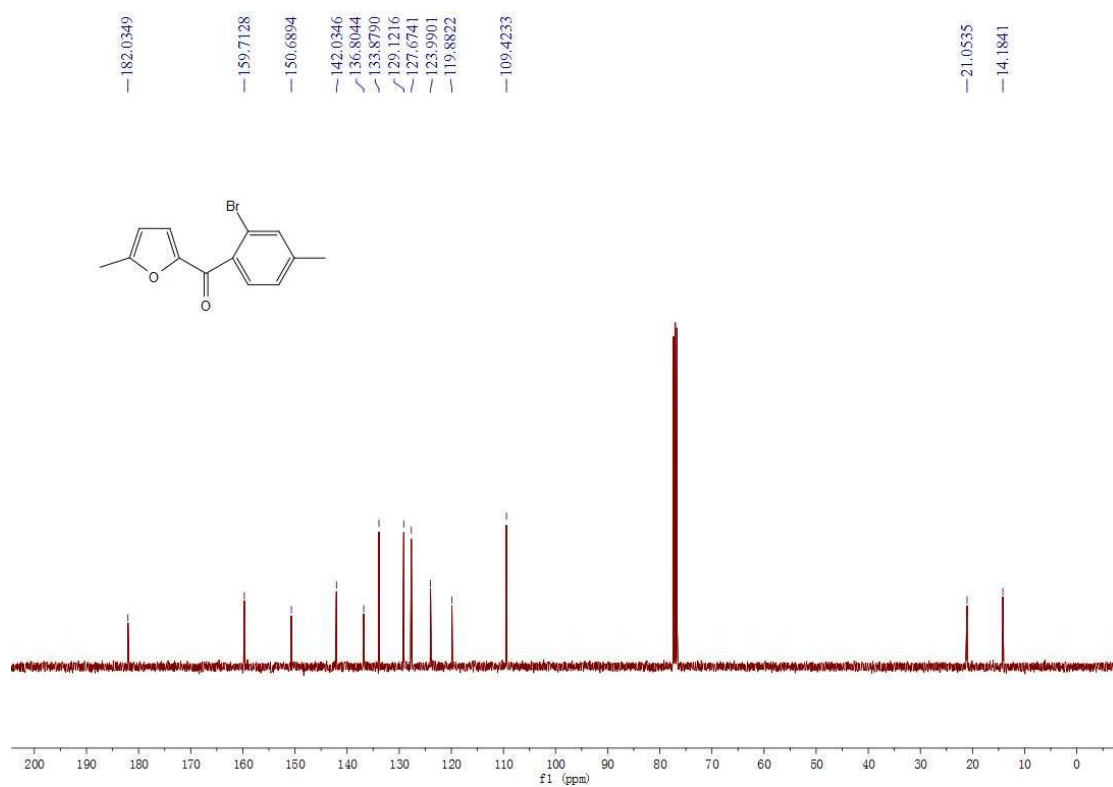
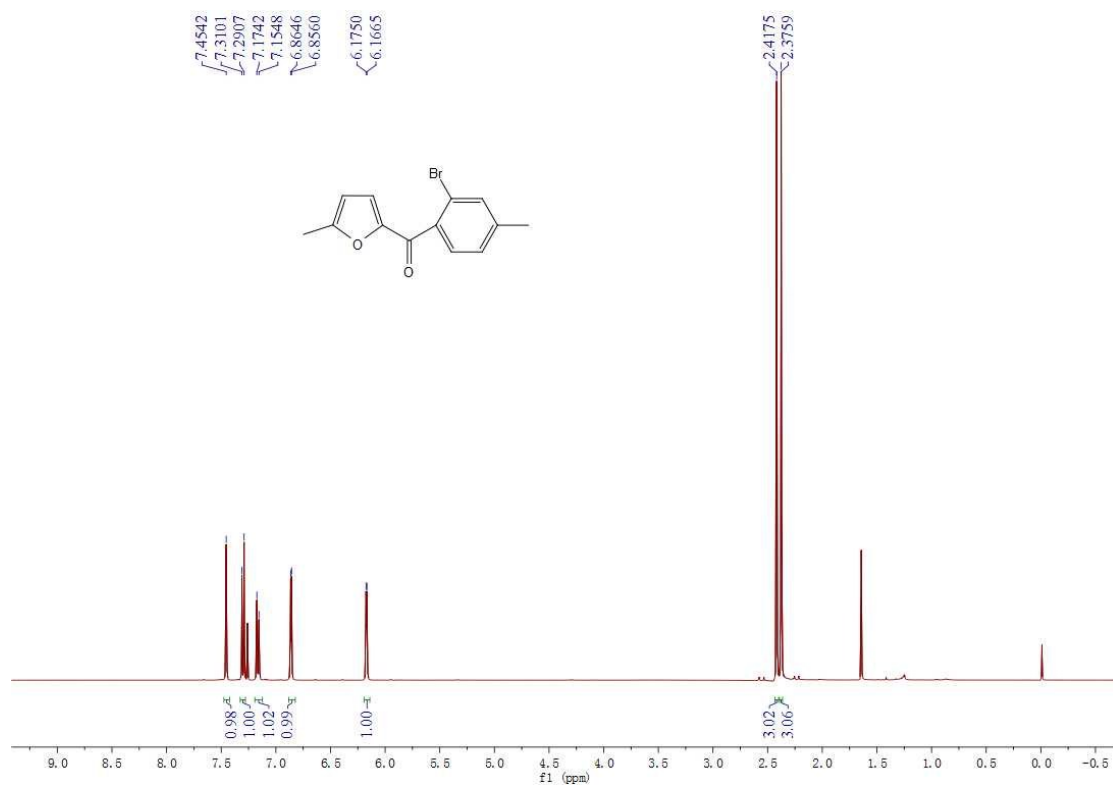
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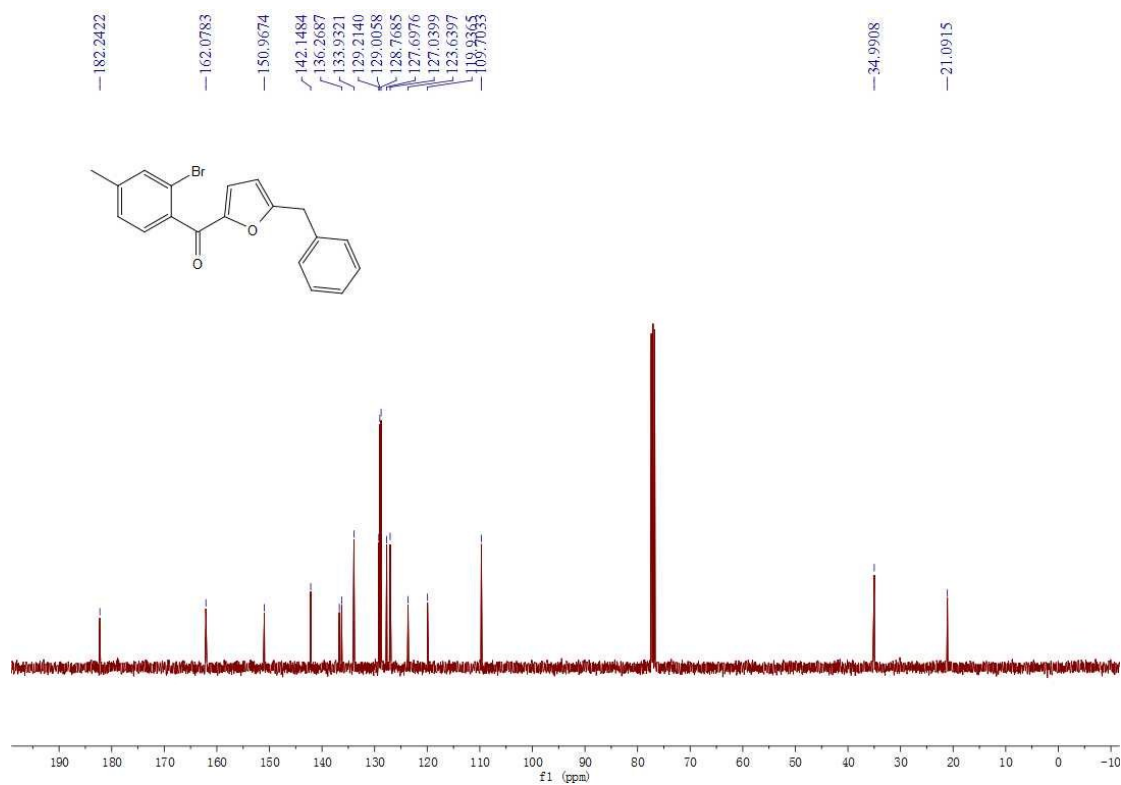
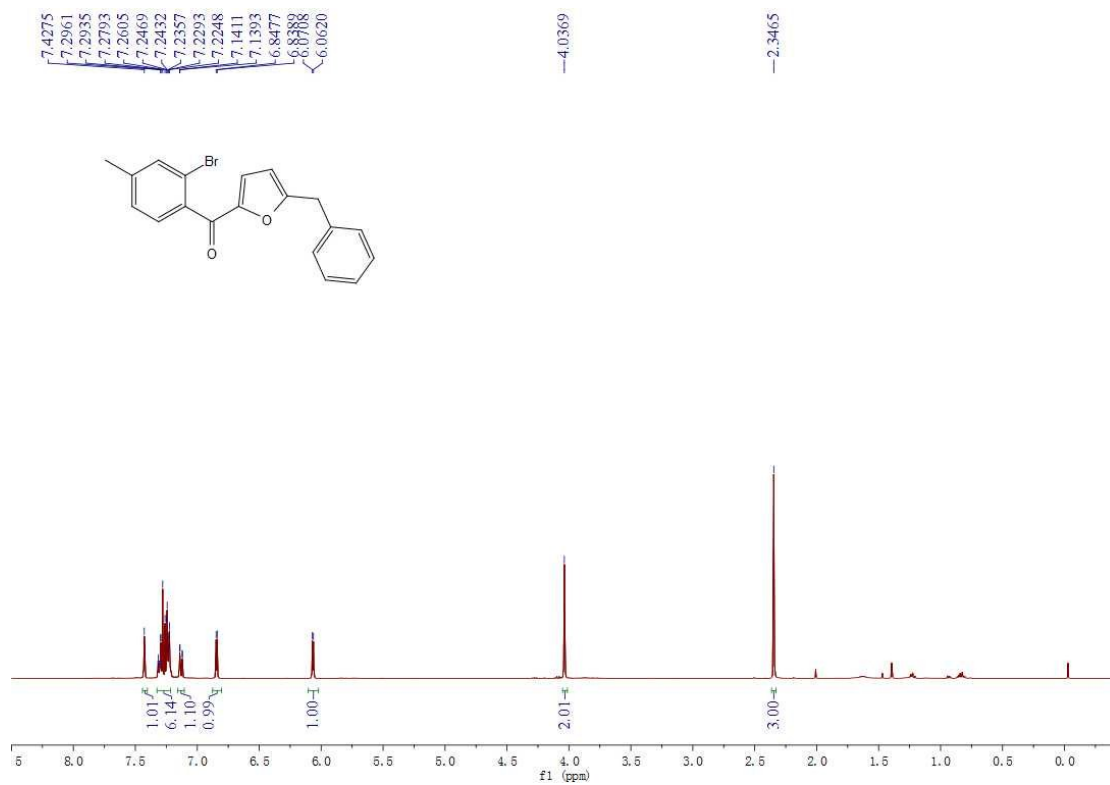
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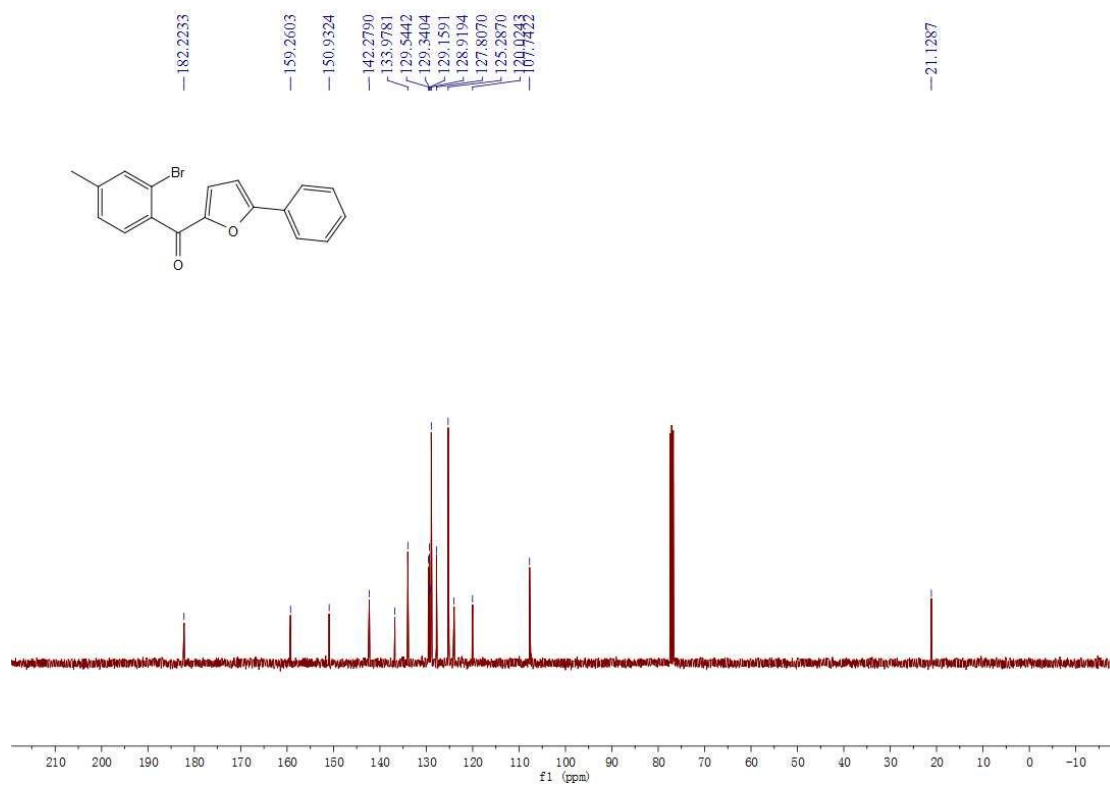
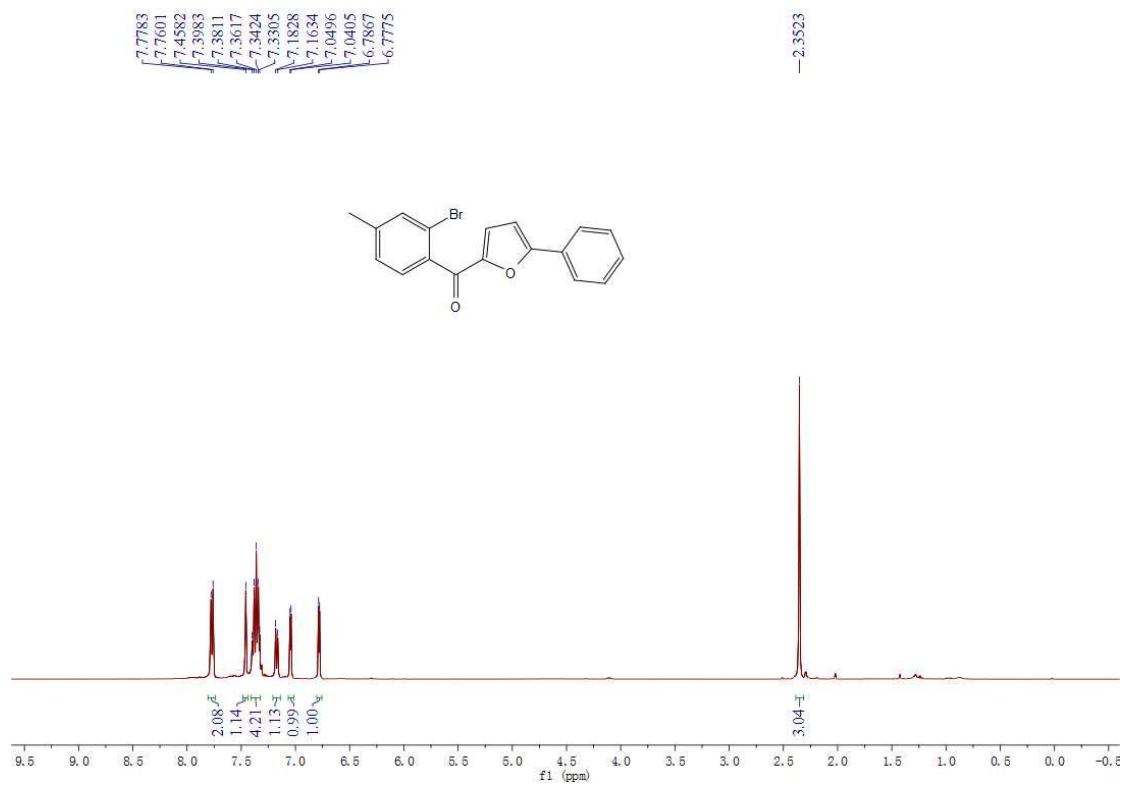
^1H NMR and ^{13}C NMR of 11



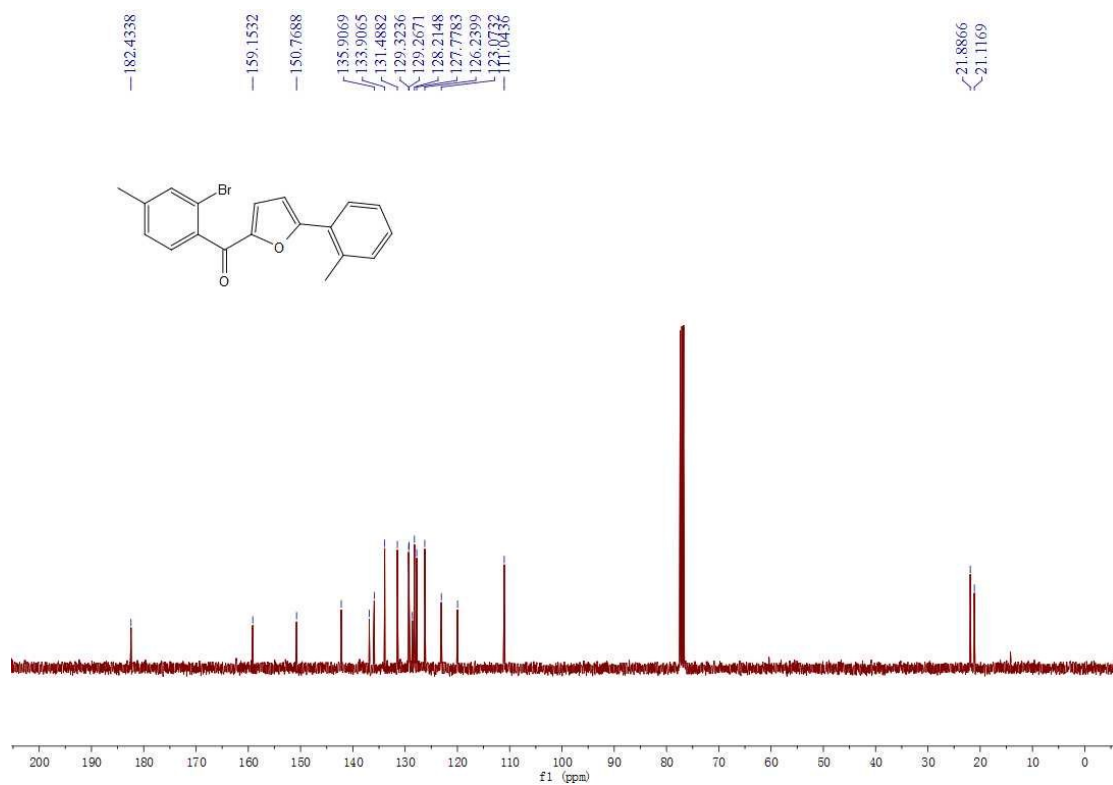
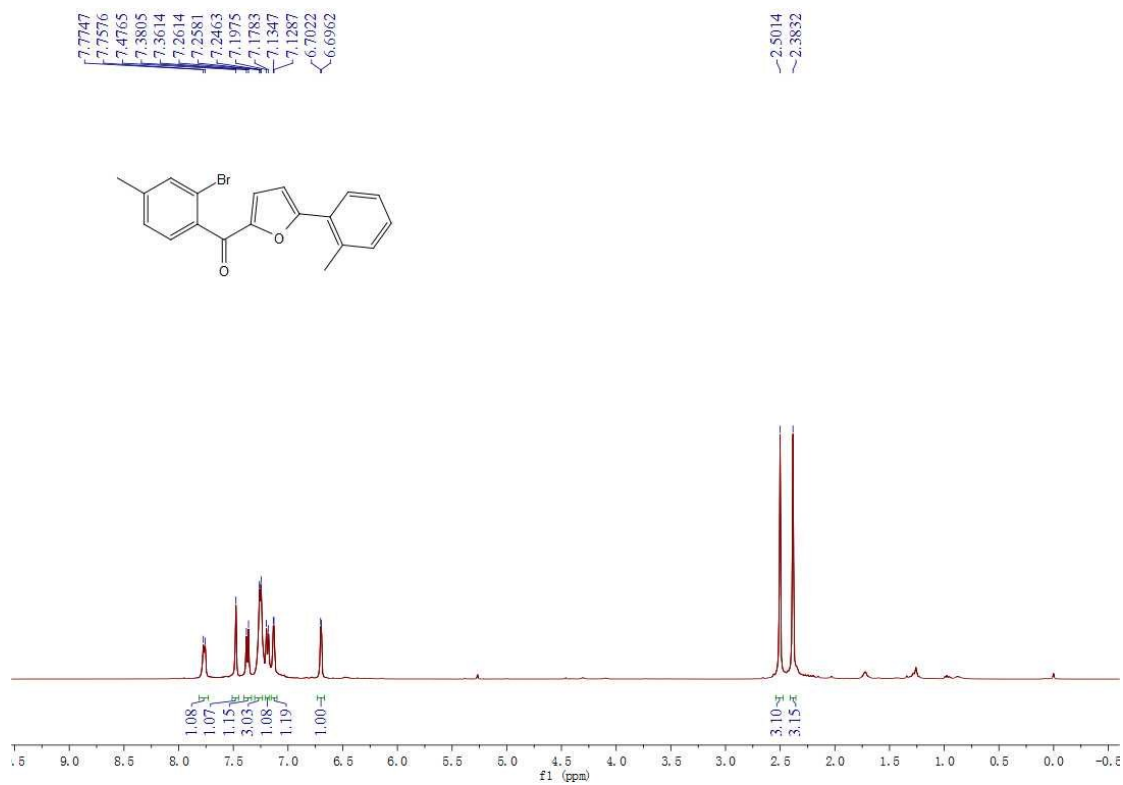
¹H NMR and ¹³C NMR of 1m



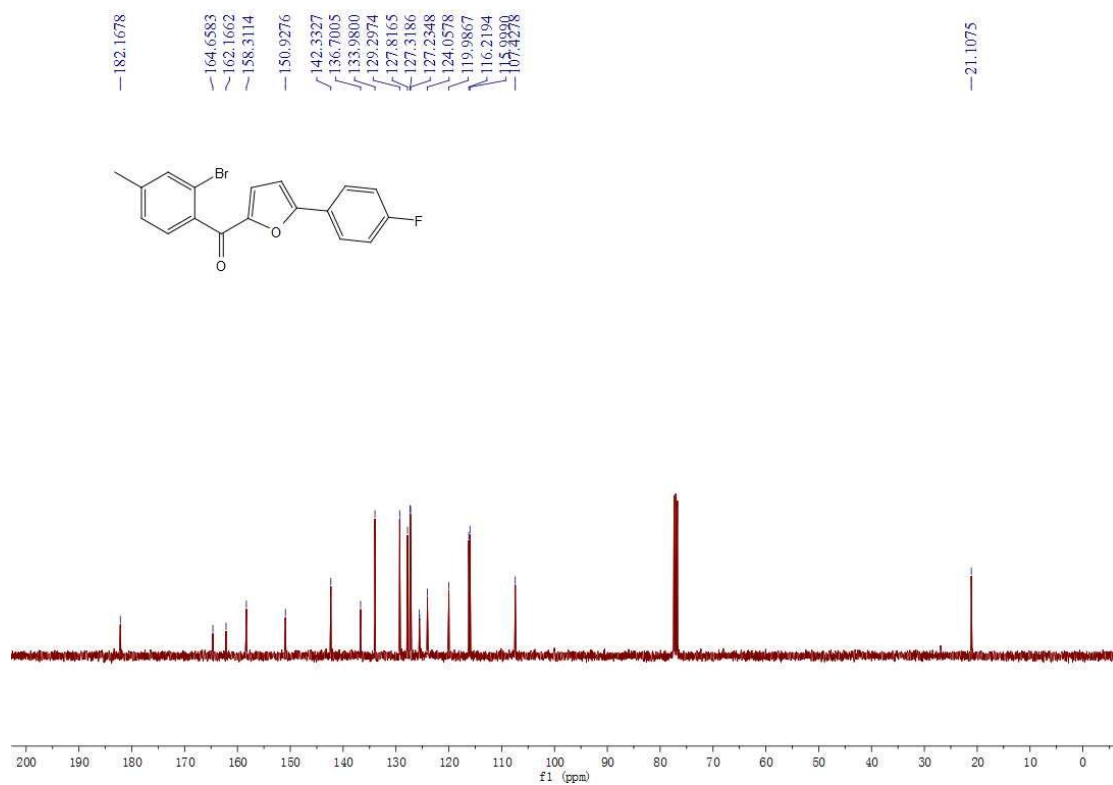
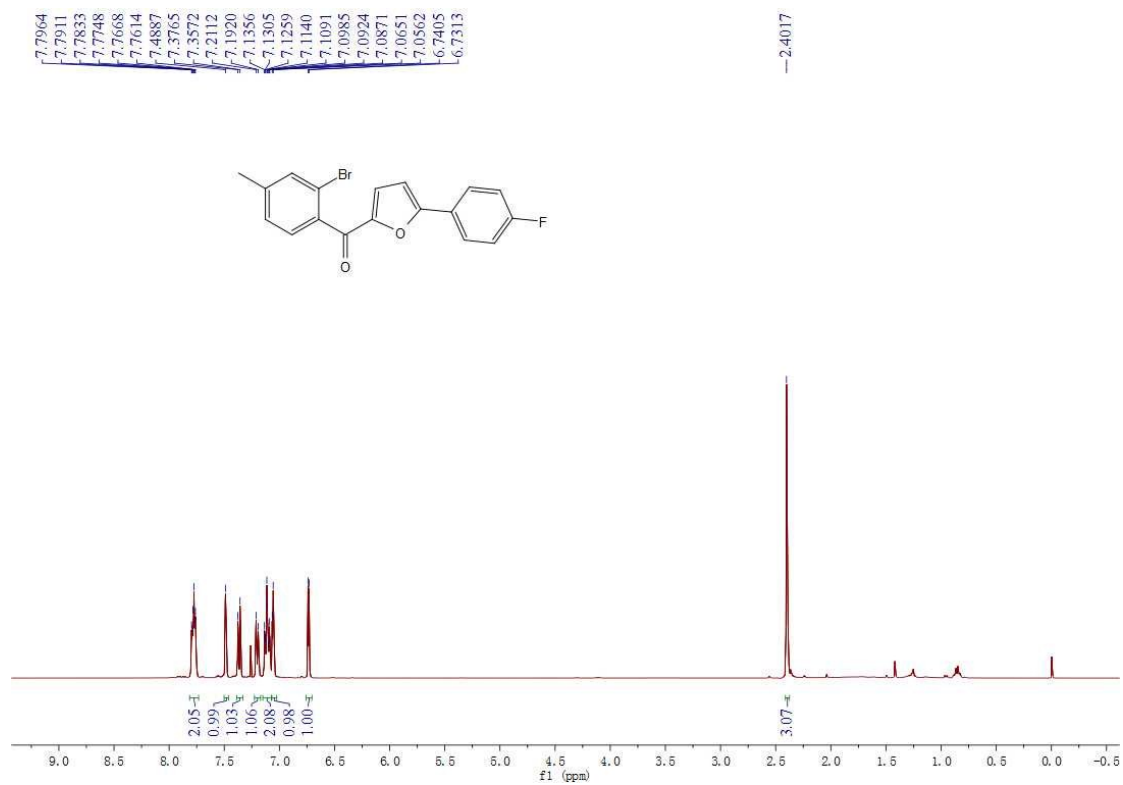
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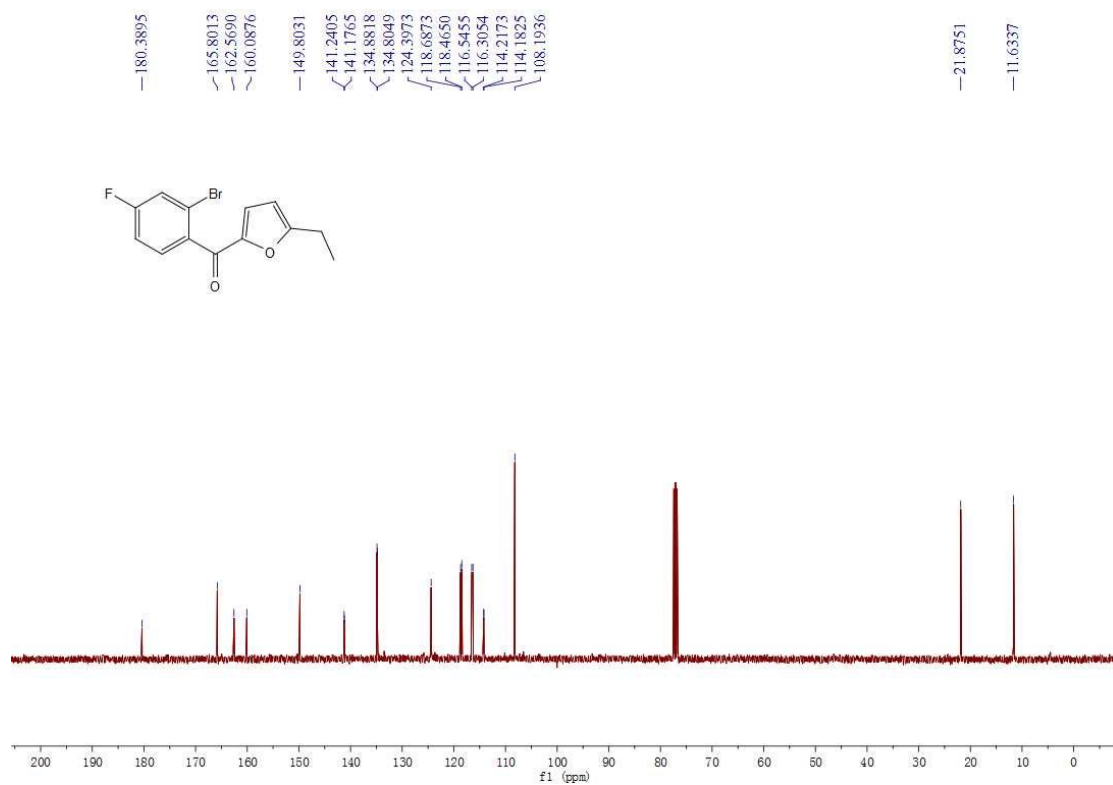
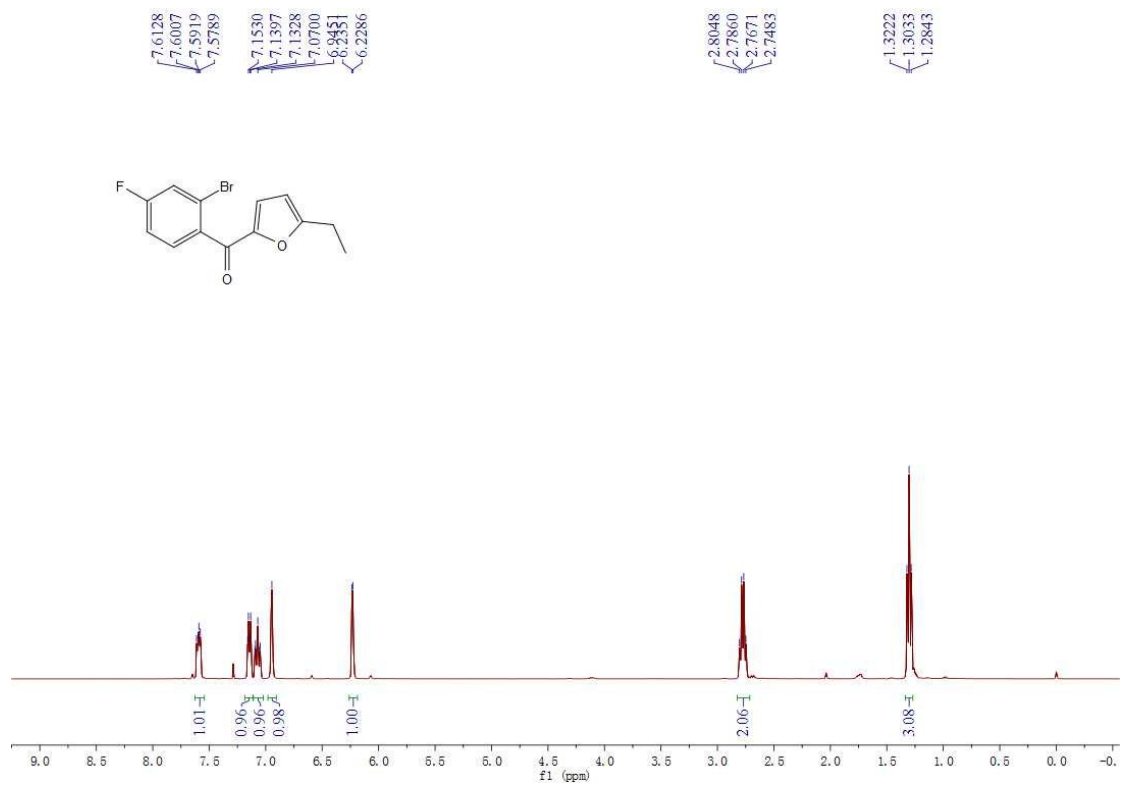
¹H NMR and ¹³C NMR of 1o



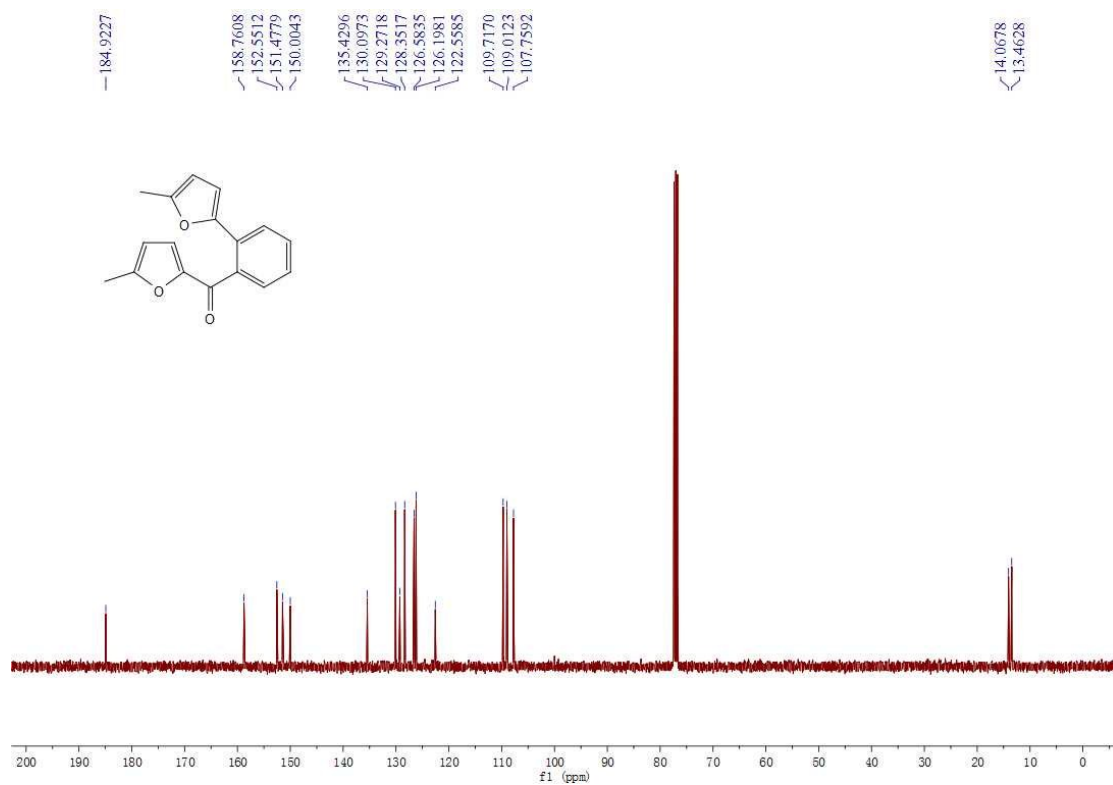
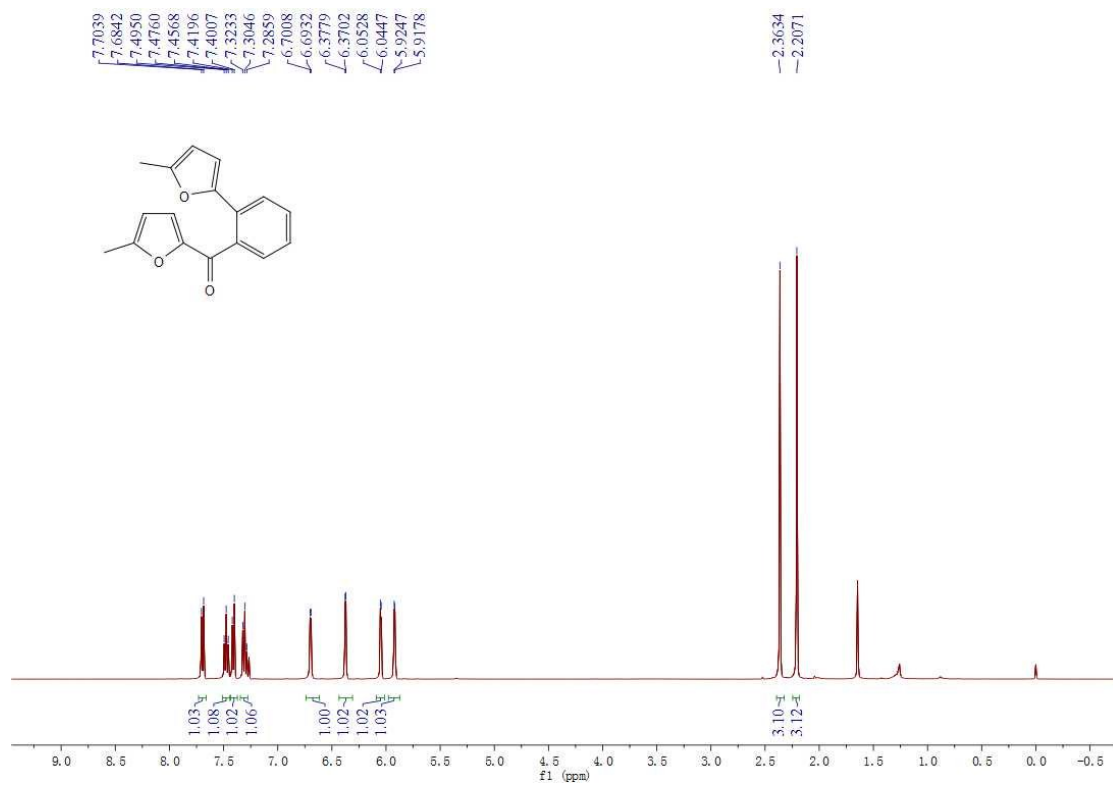
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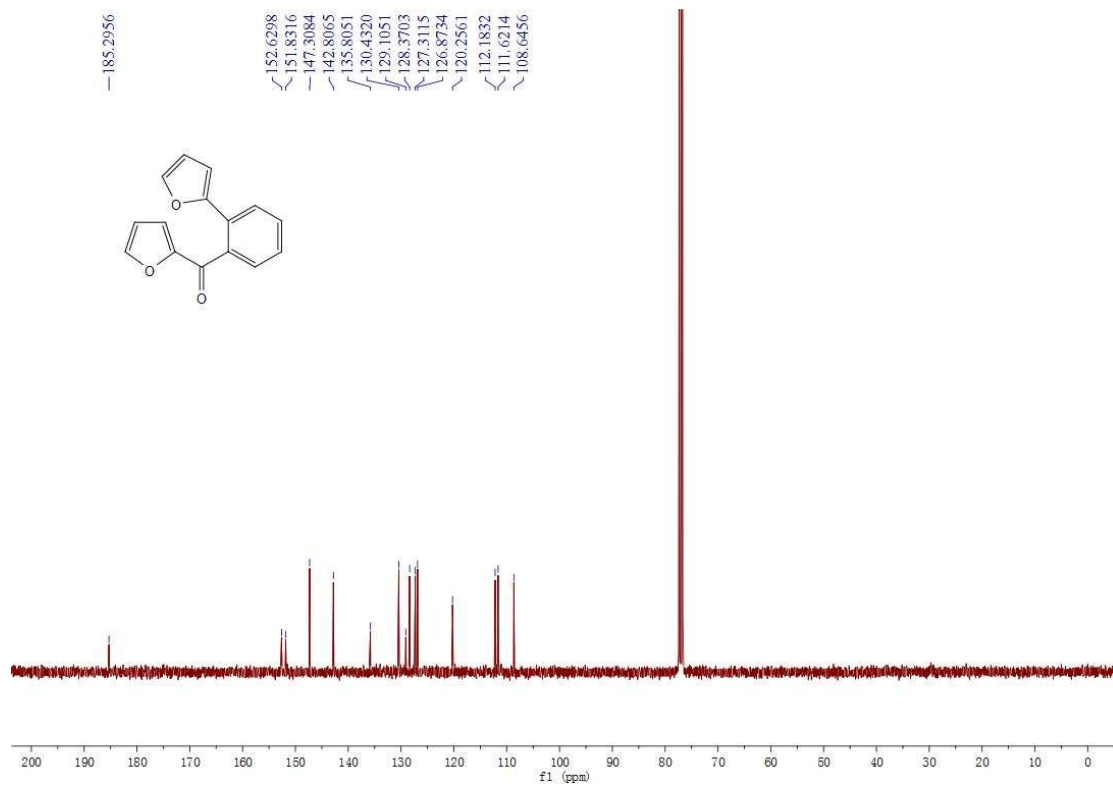
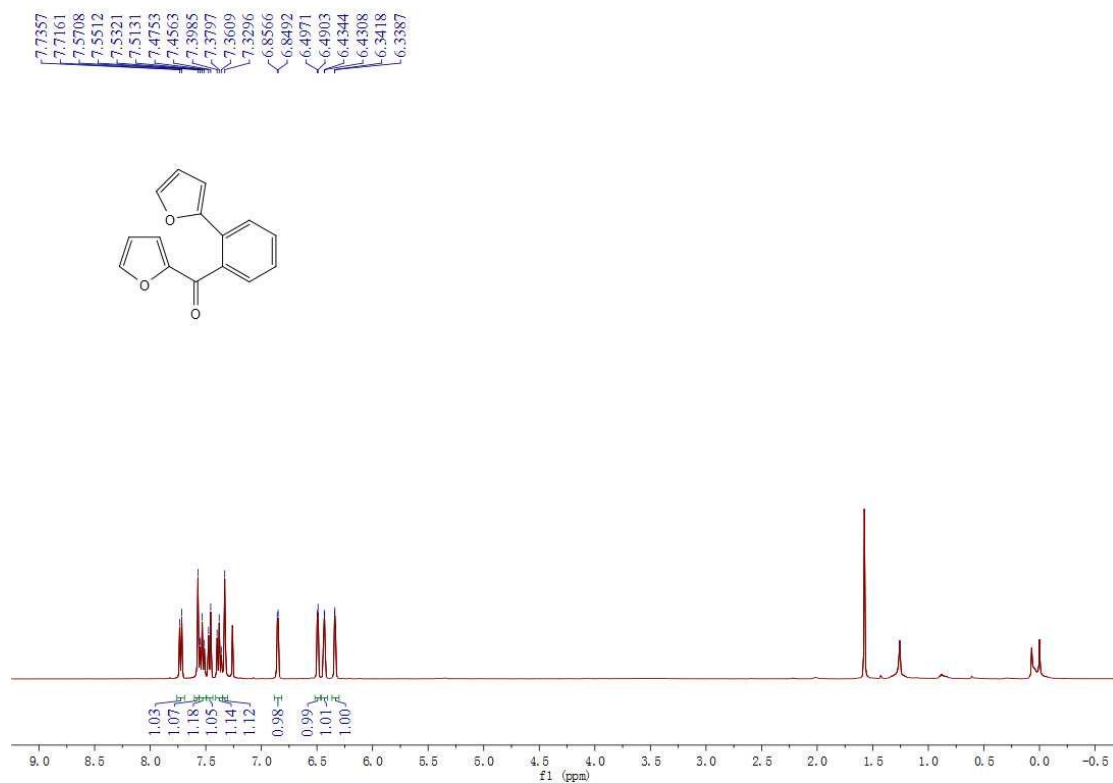
¹H NMR and ¹³C NMR of 1r



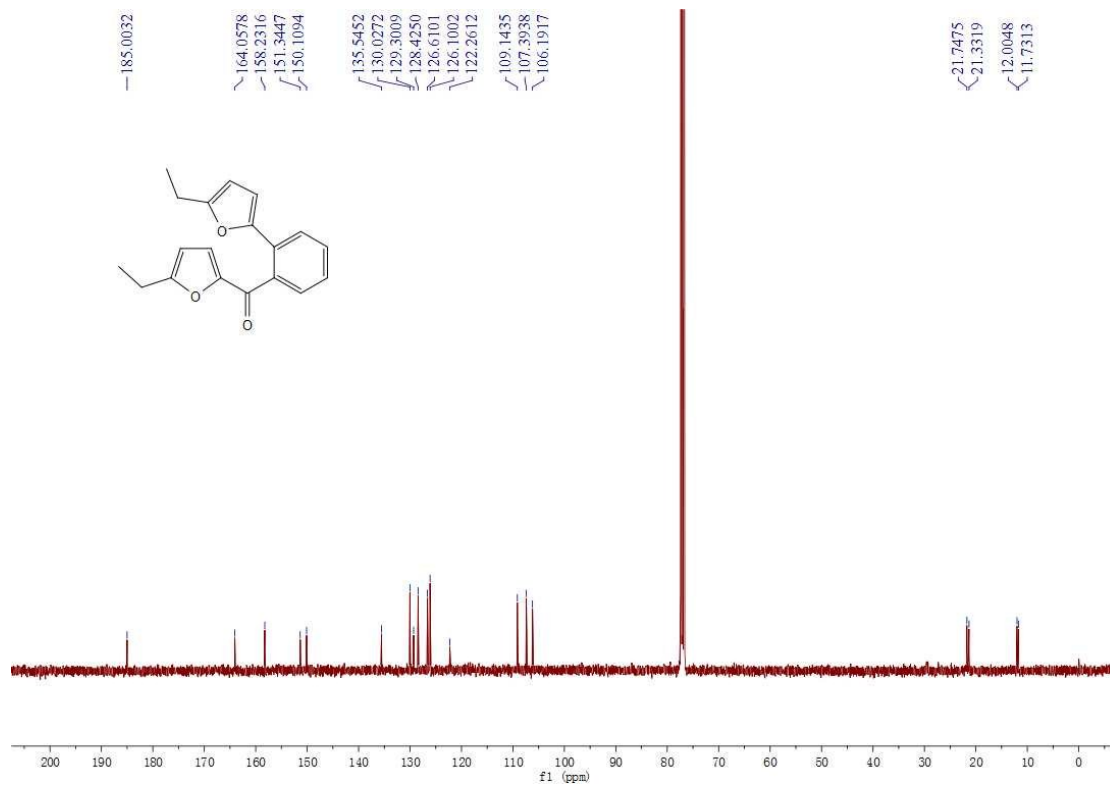
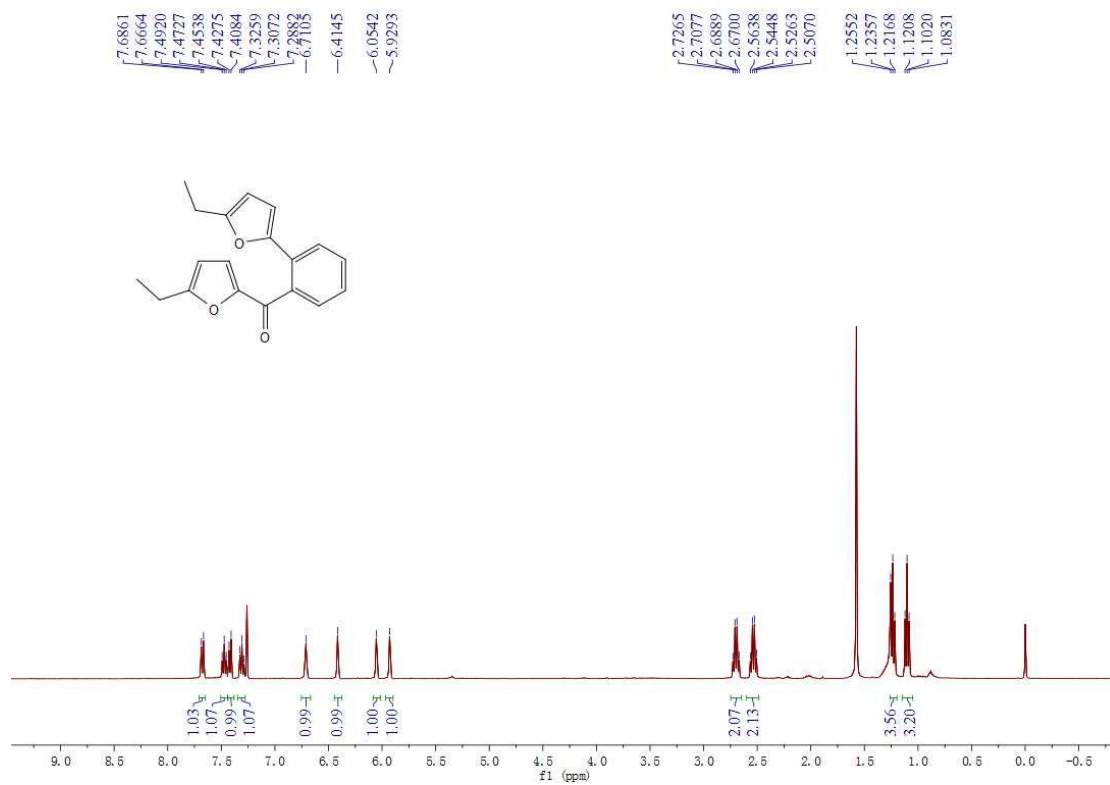
¹H NMR and ¹³C NMR of 4a



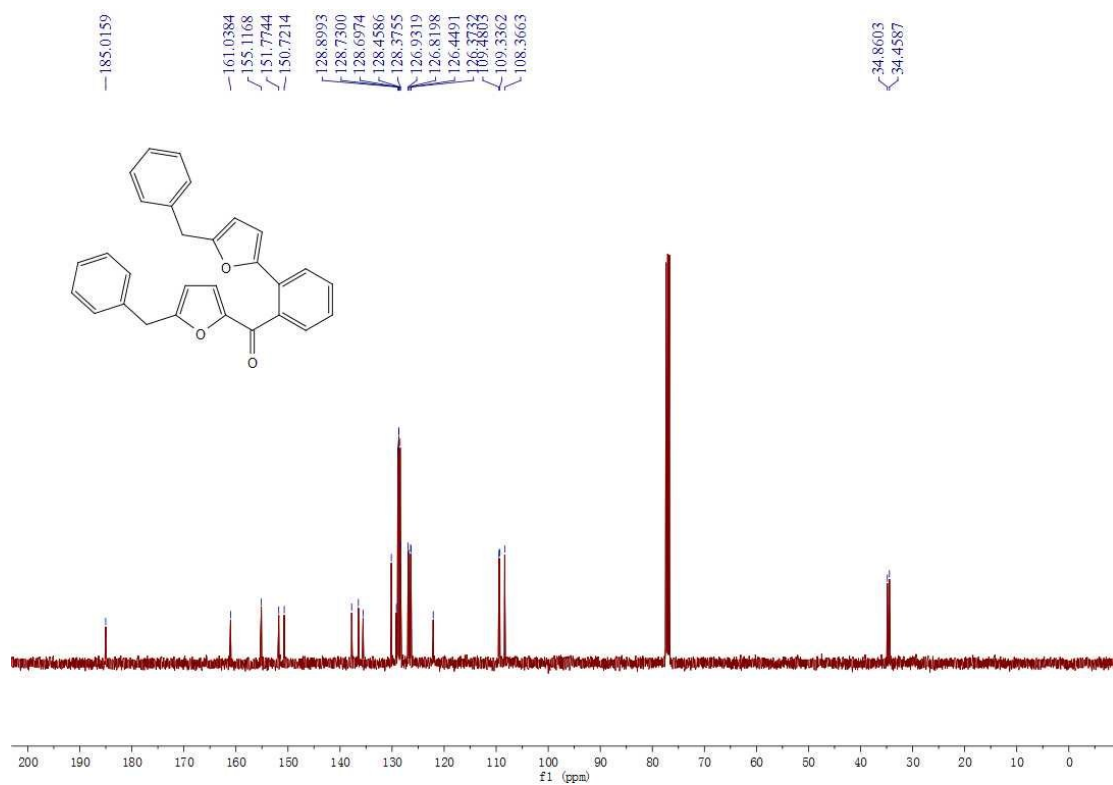
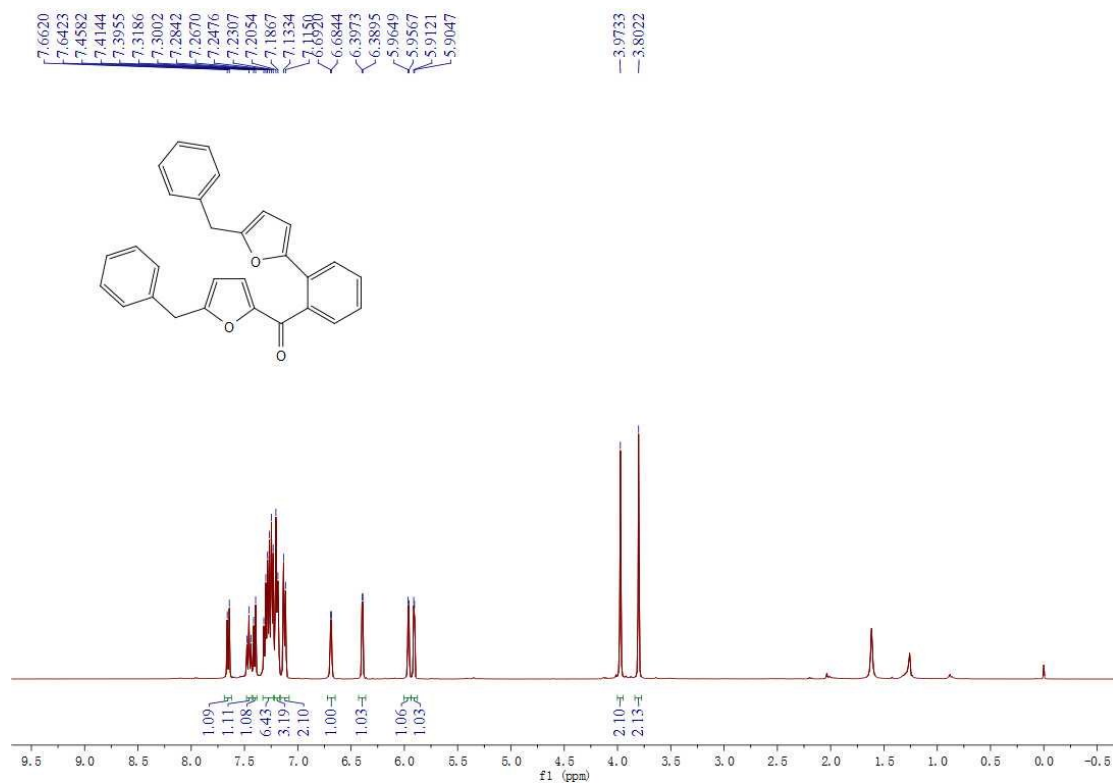
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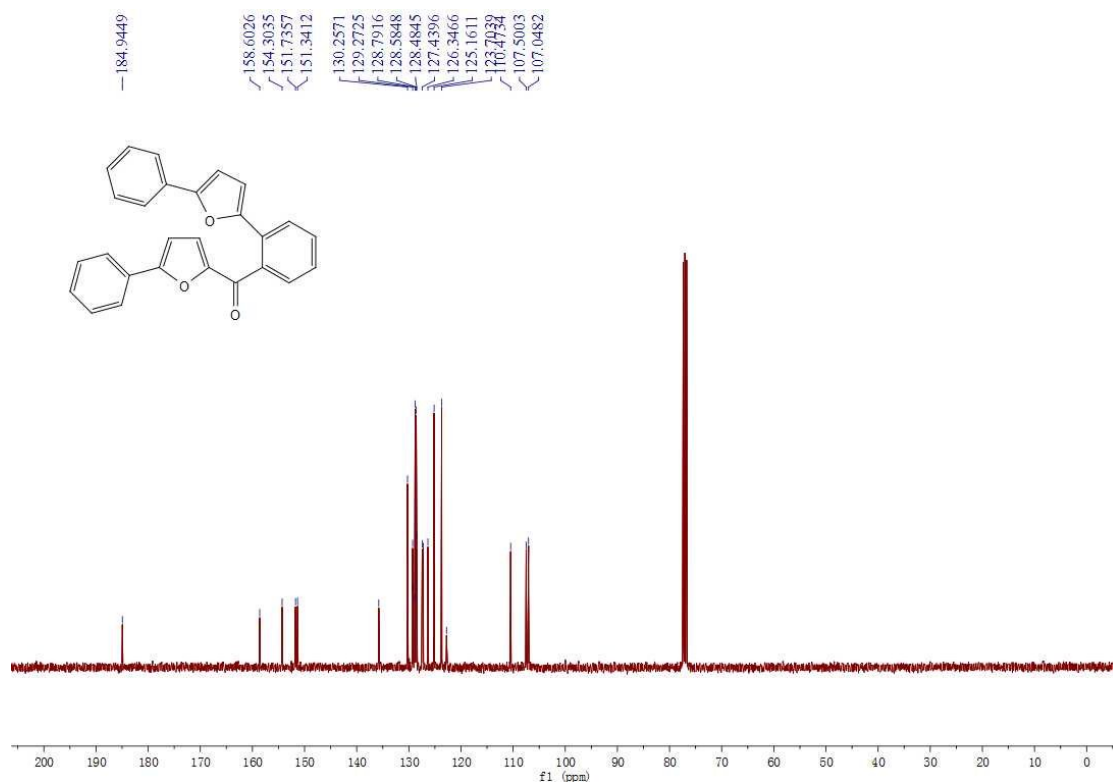
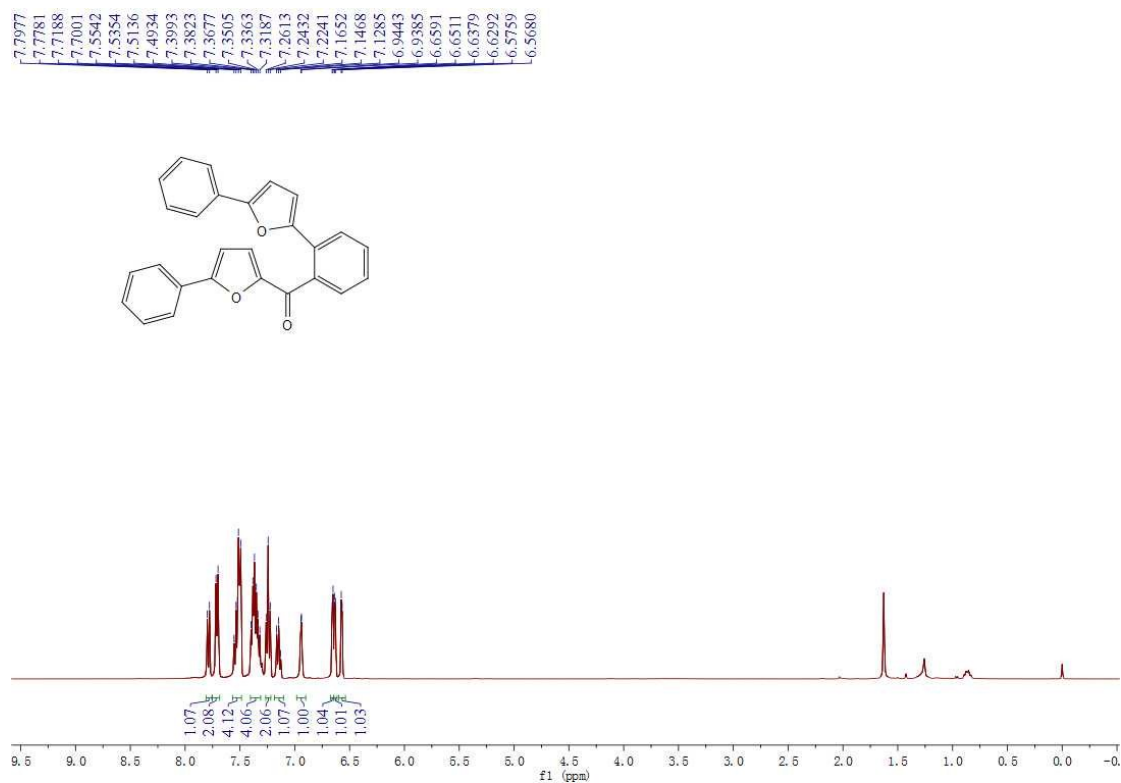
^1H NMR and ^{13}C NMR of 4c



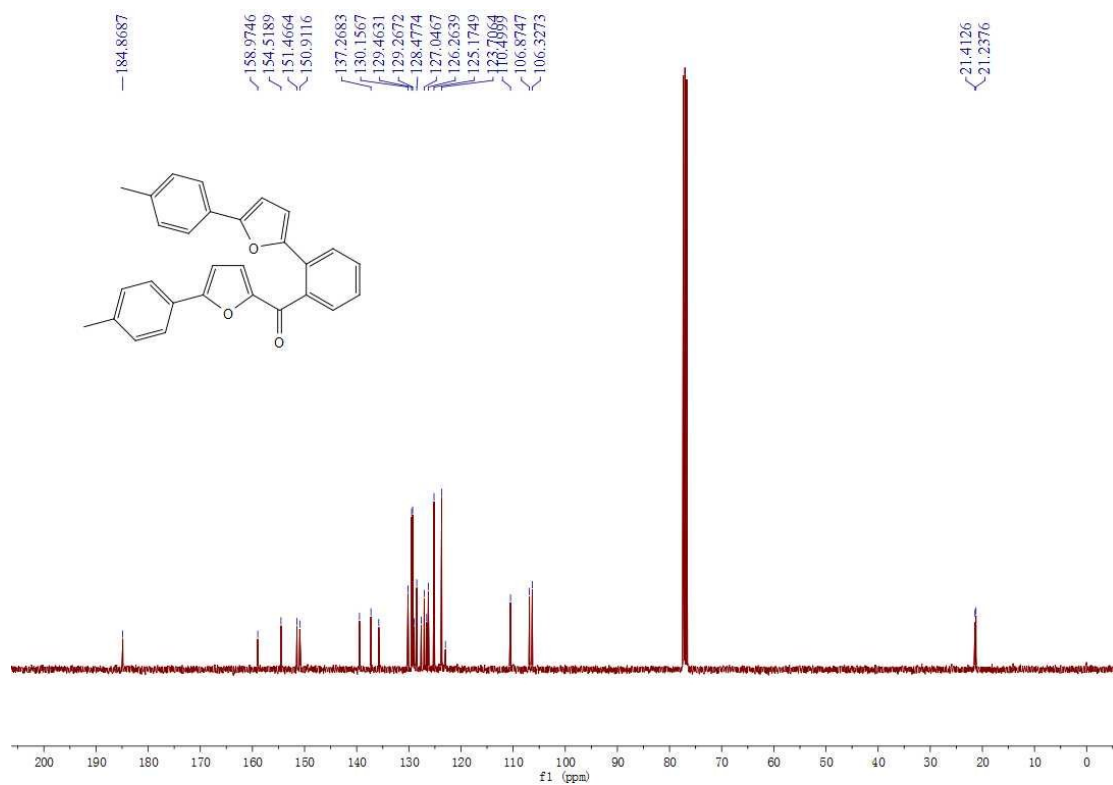
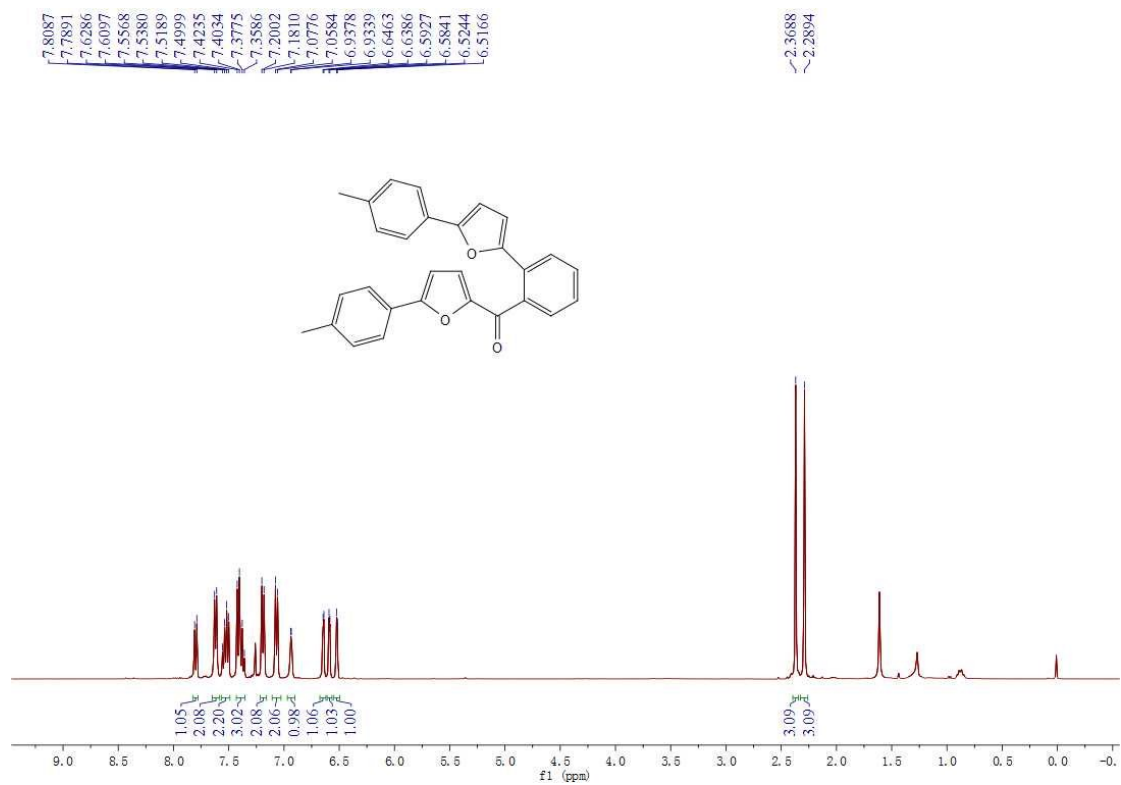
¹H NMR and ¹³C NMR of 4d



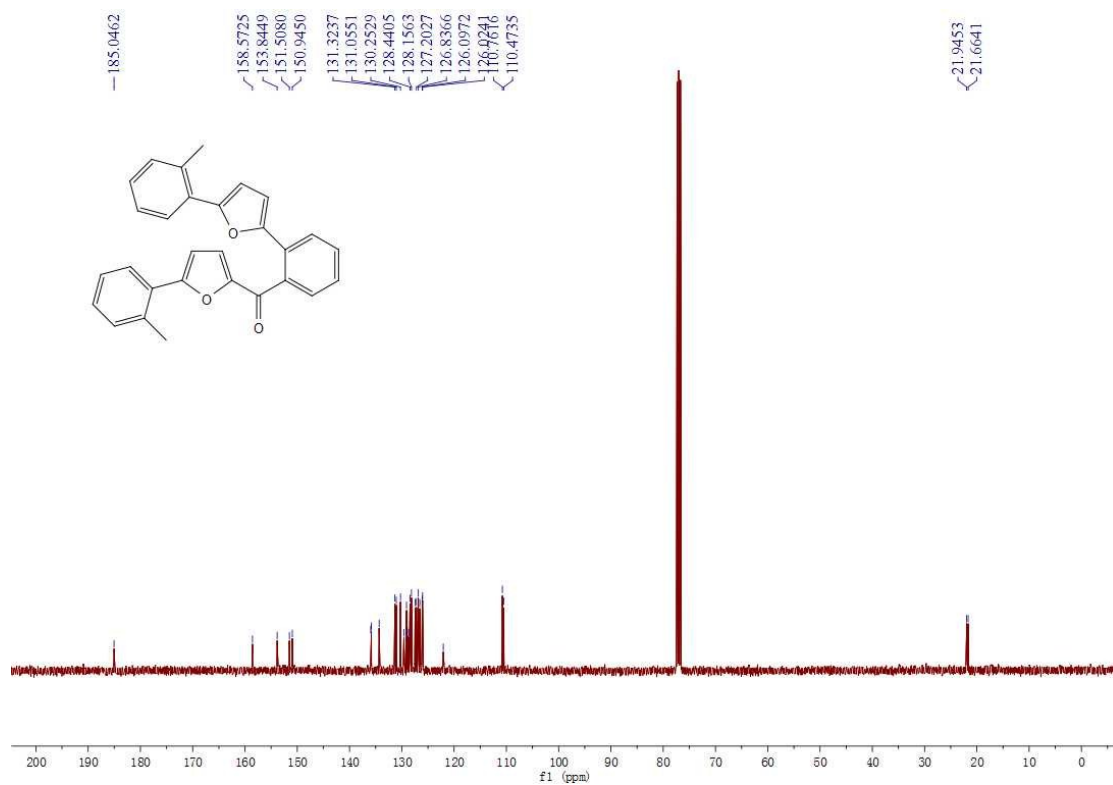
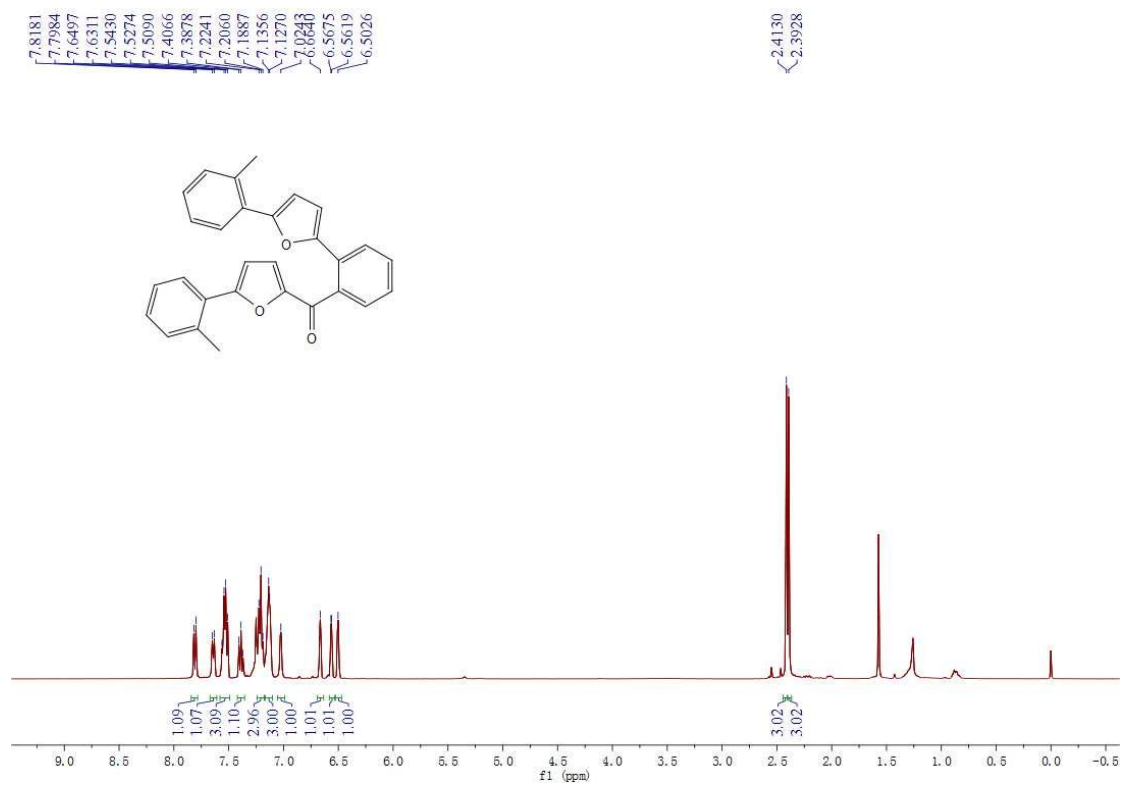
¹H NMR and ¹³C NMR of 4e



^1H NMR and ^{13}C NMR of 4f

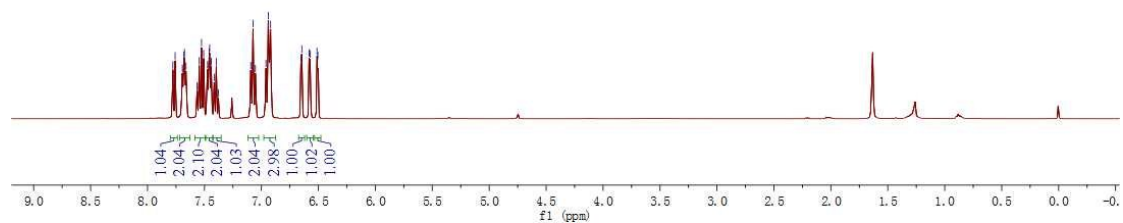
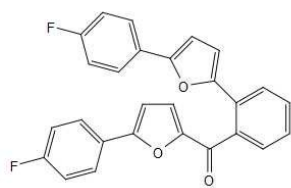


¹H NMR and ¹³C NMR of 4g

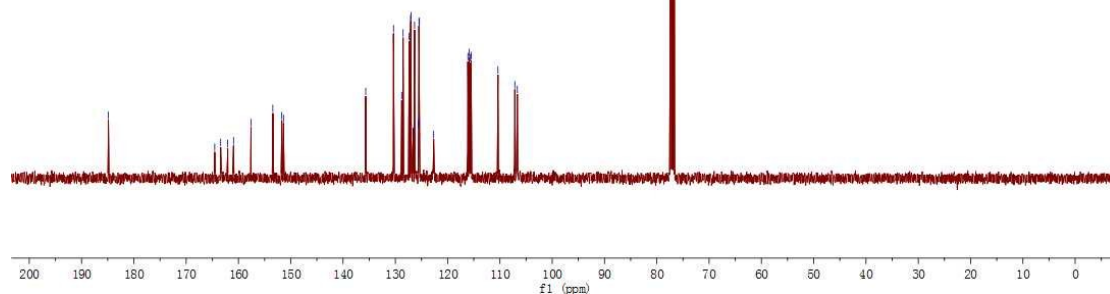
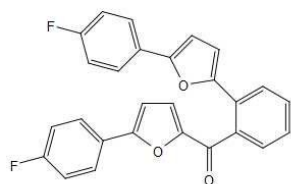


¹H NMR and ¹³C NMR of 4h

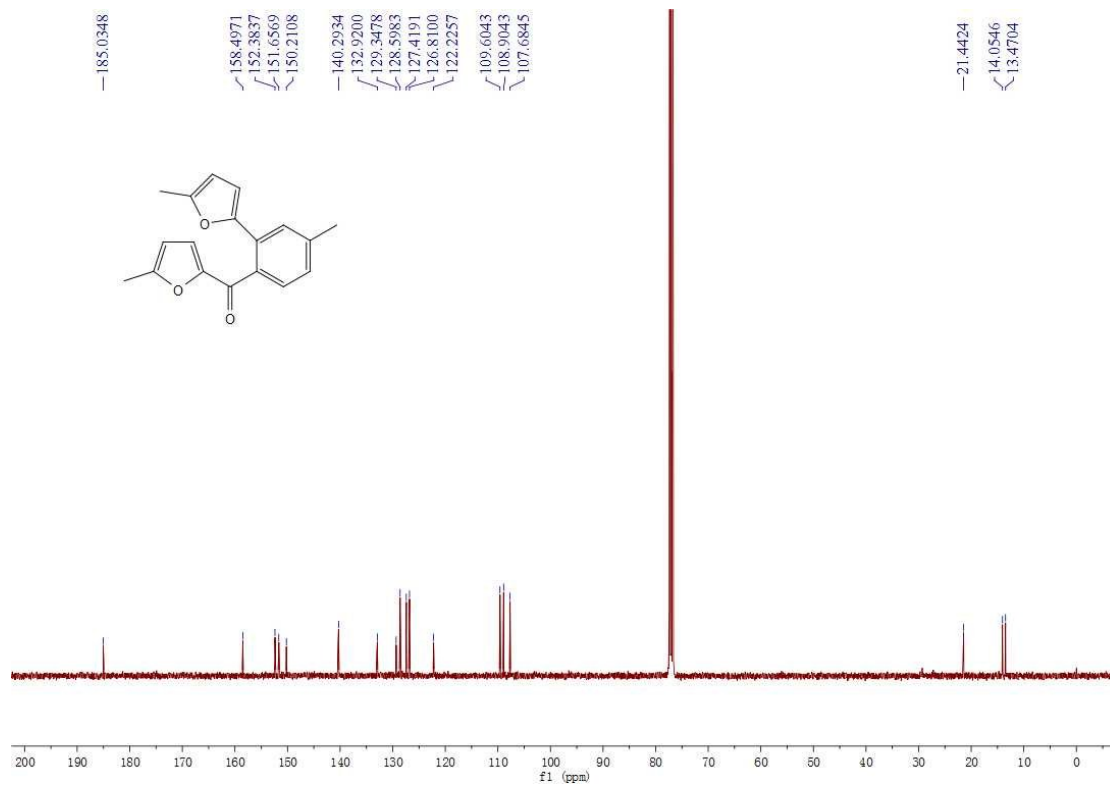
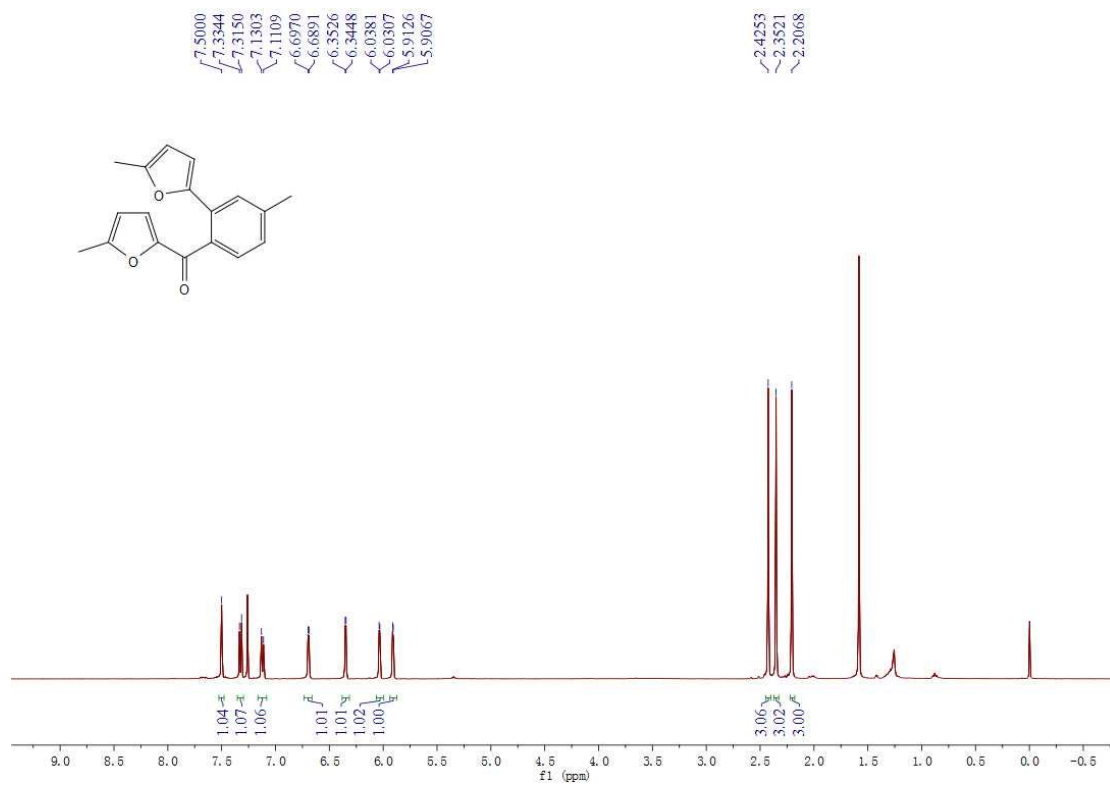
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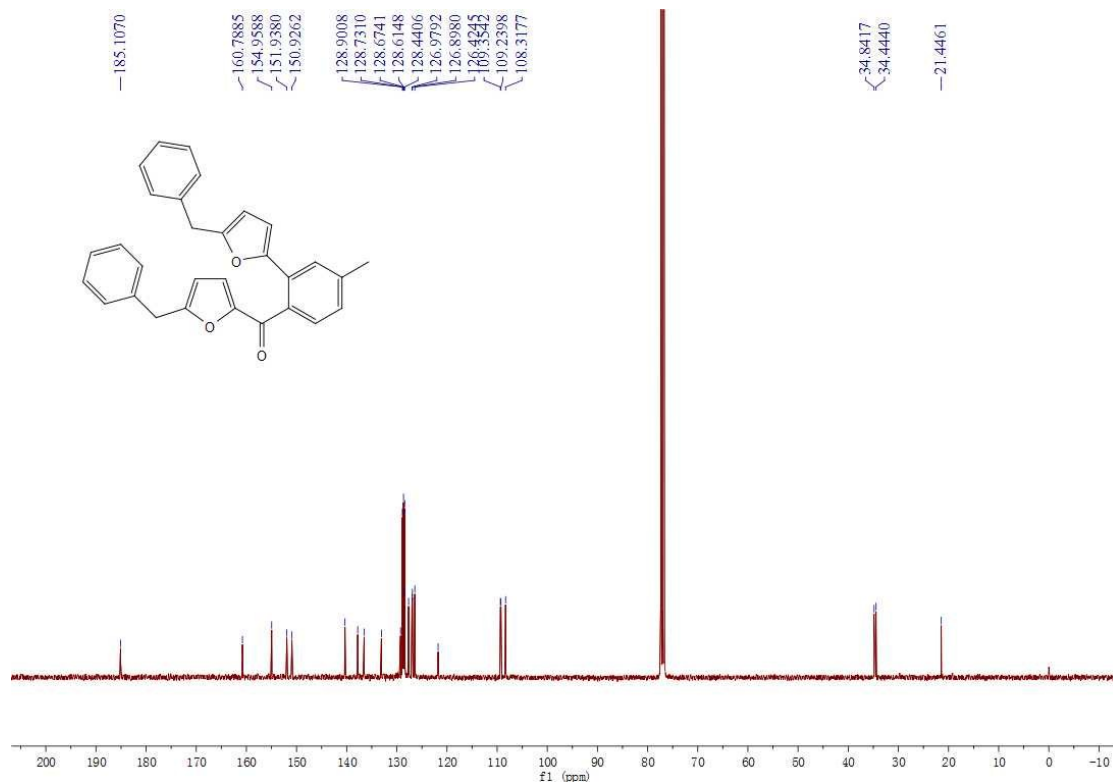
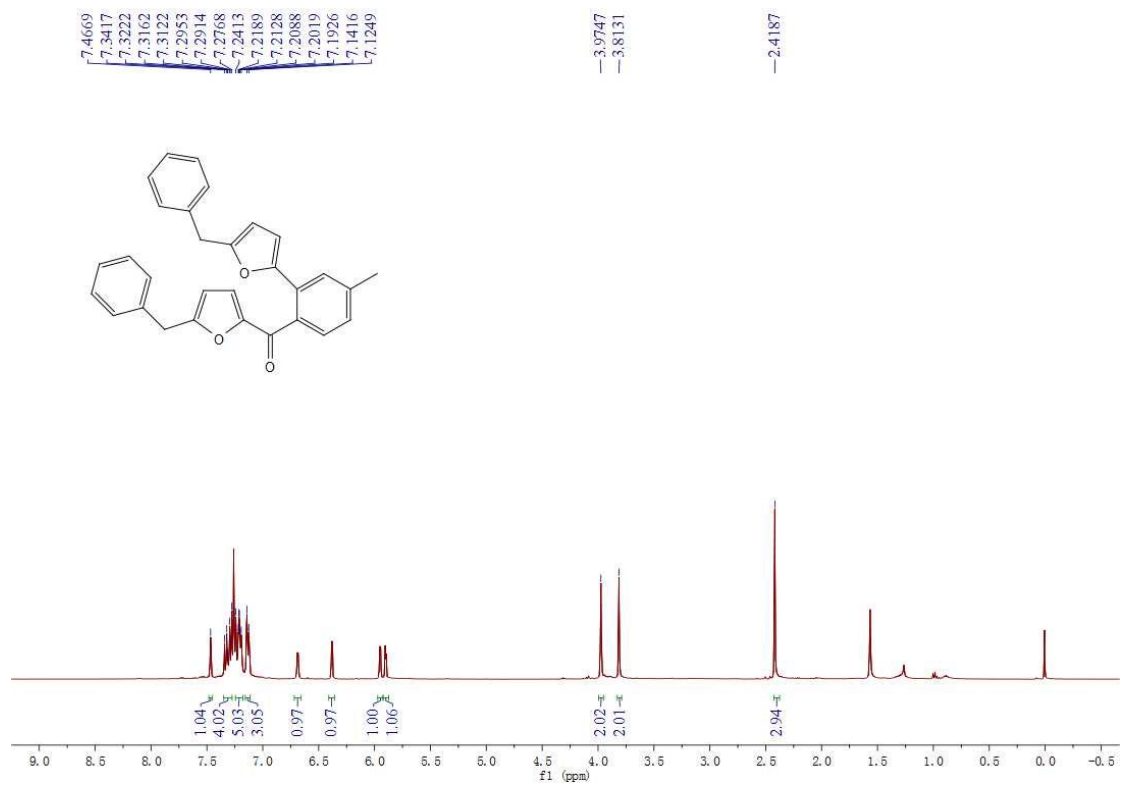
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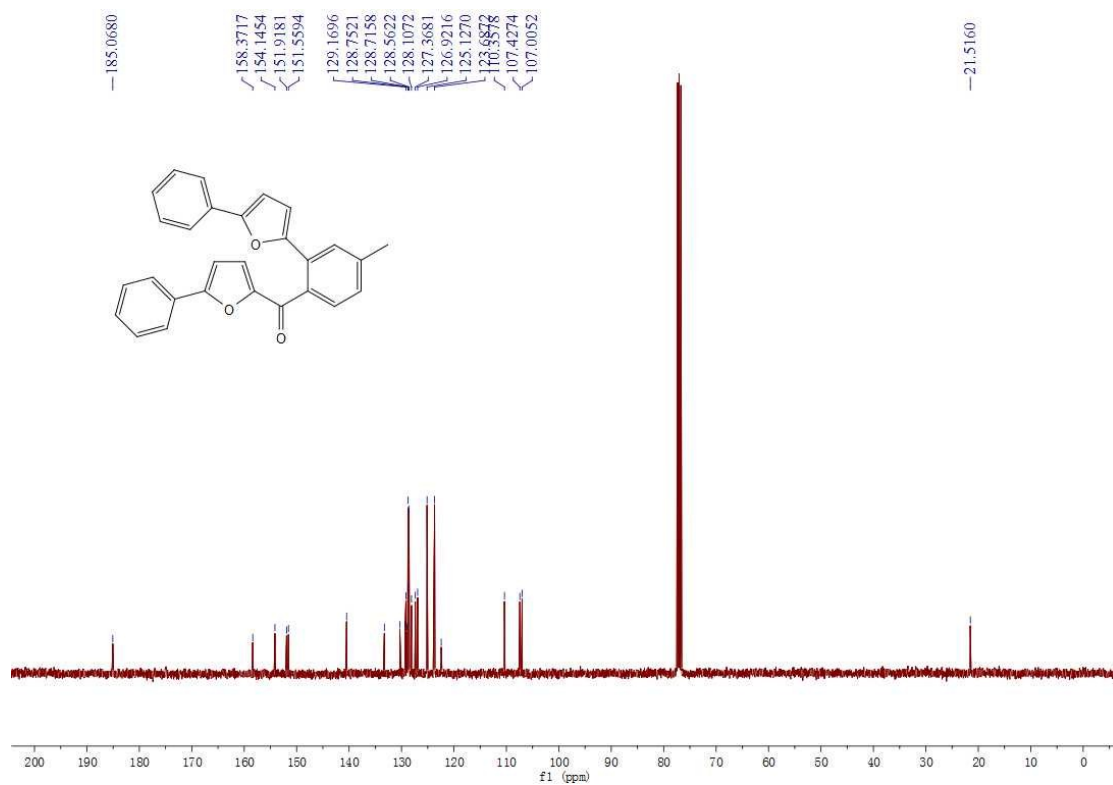
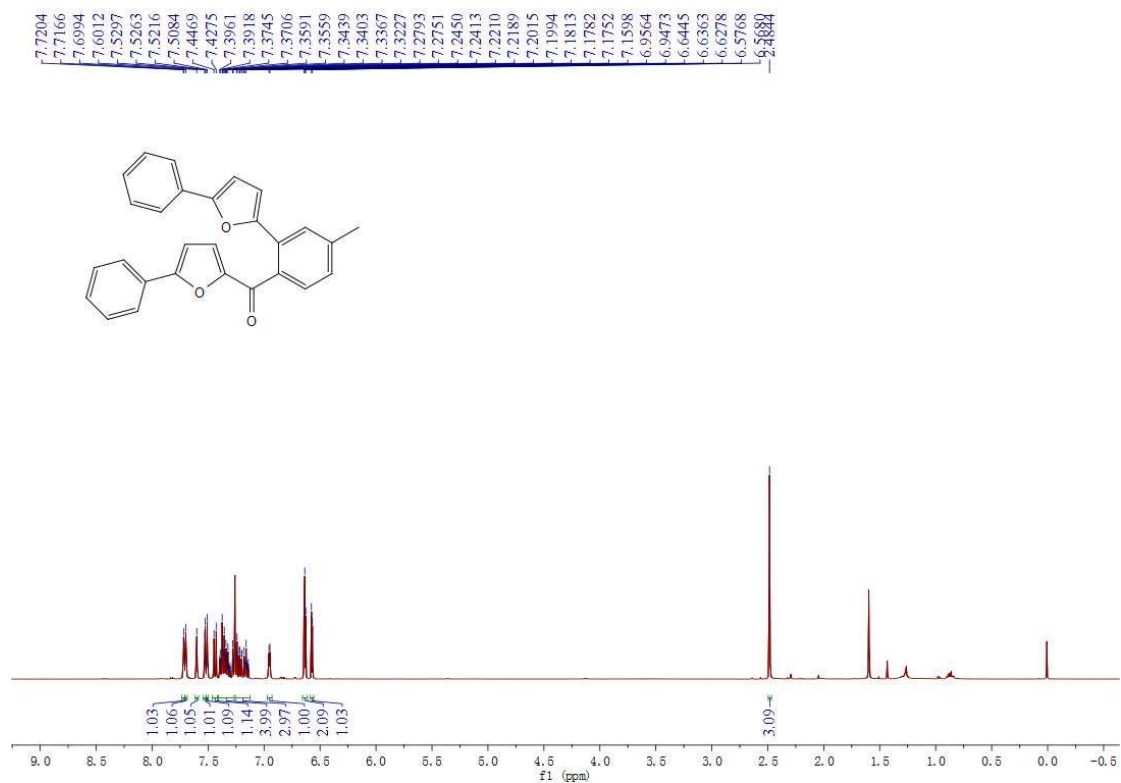
^1H NMR and ^{13}C NMR of 4l



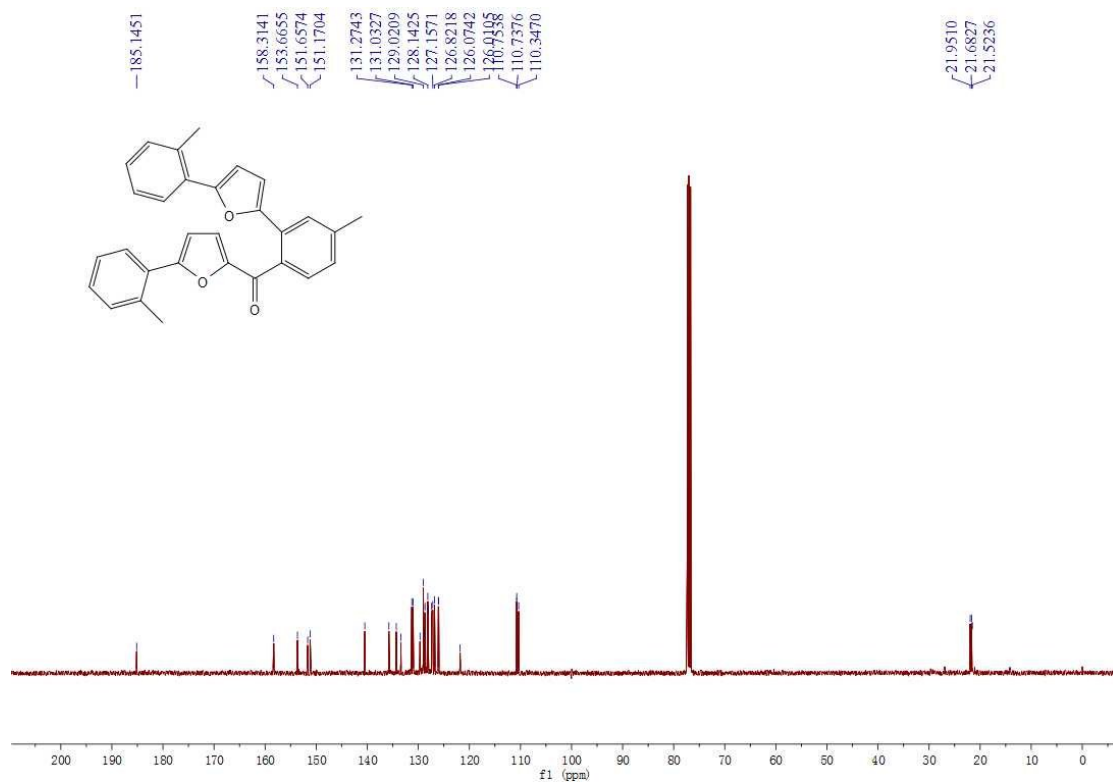
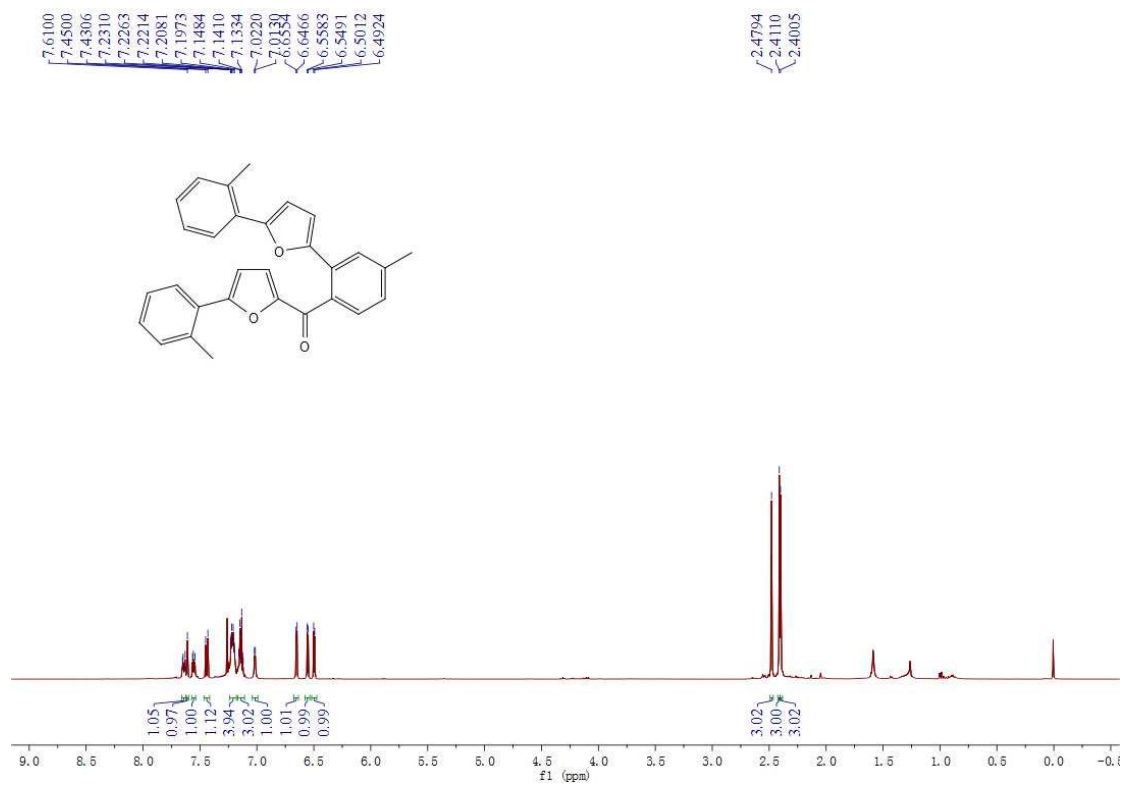
¹H NMR and ¹³C NMR of 4m



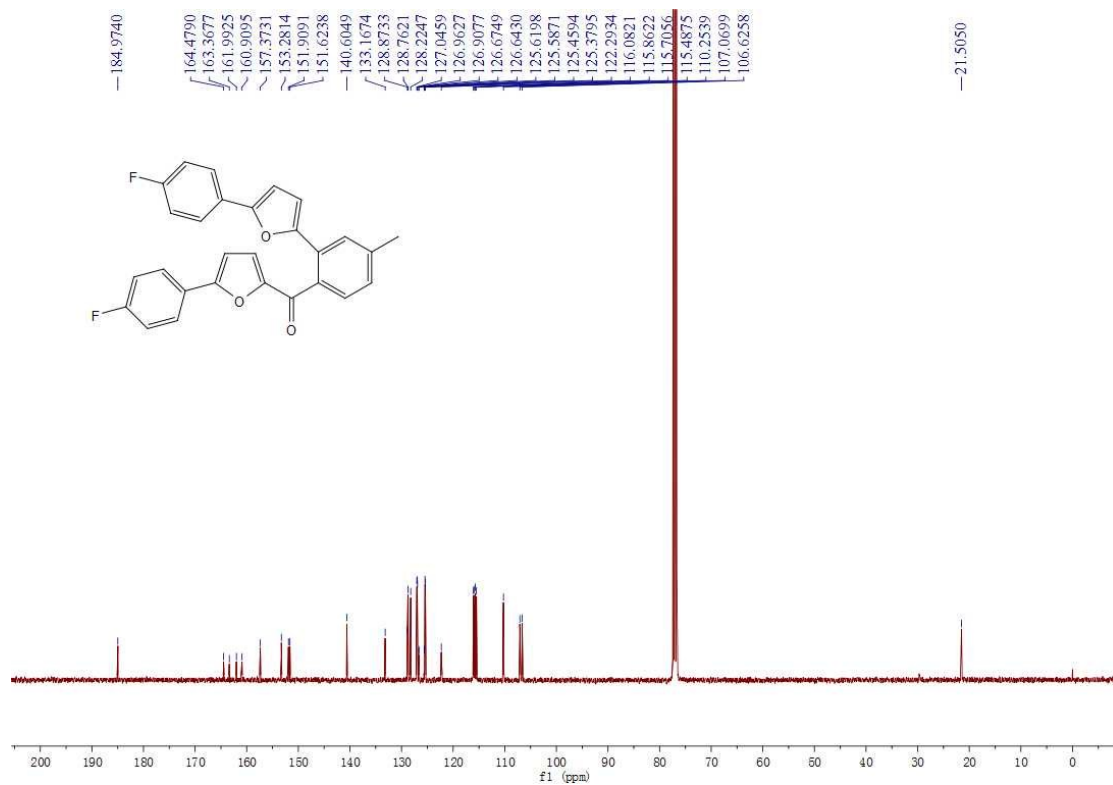
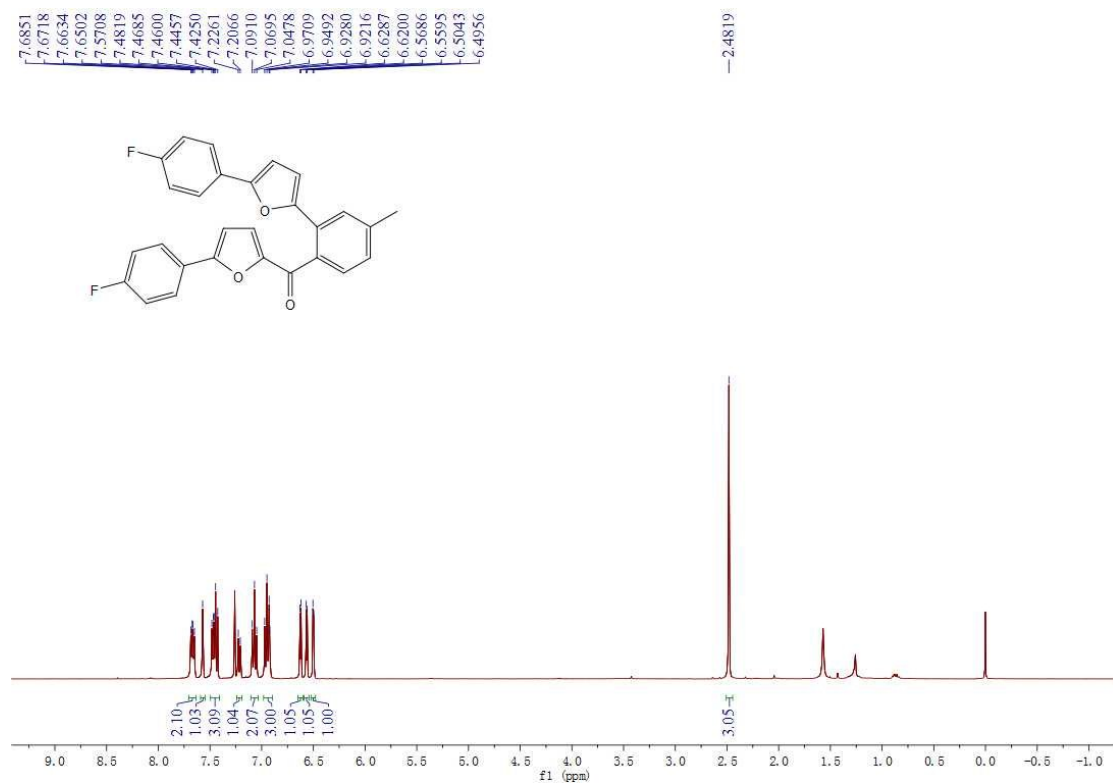
¹H NMR and ¹³C NMR of 4n



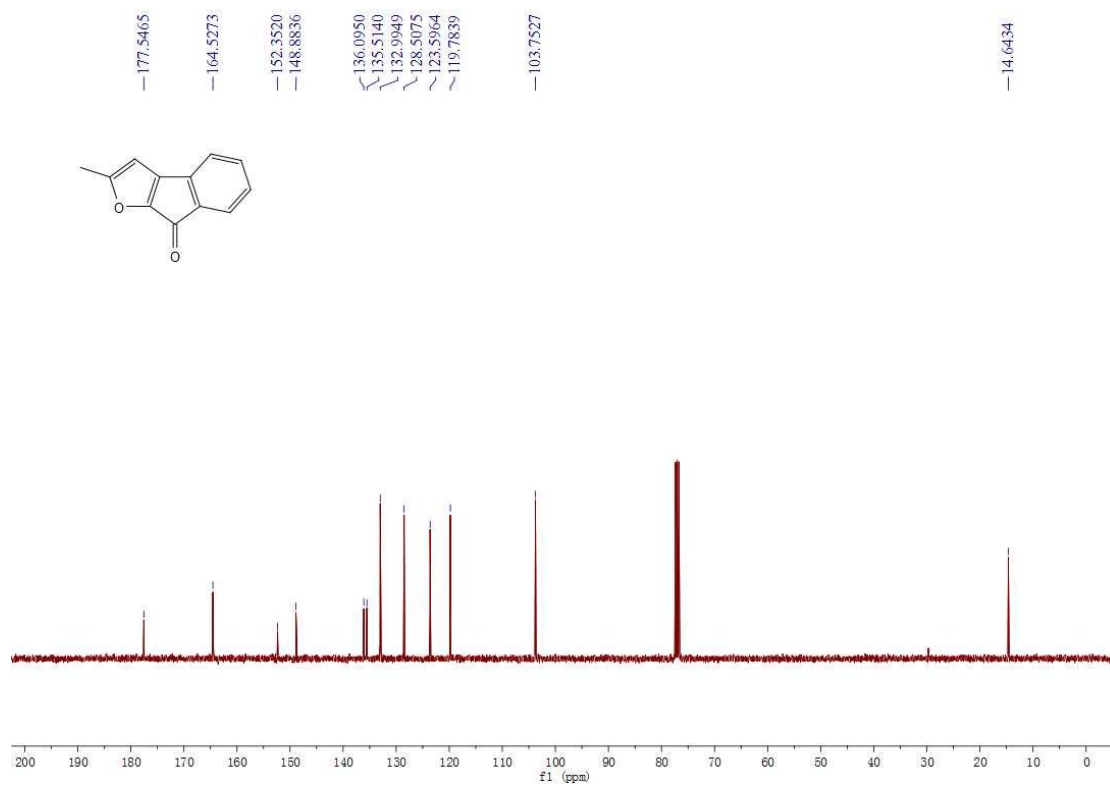
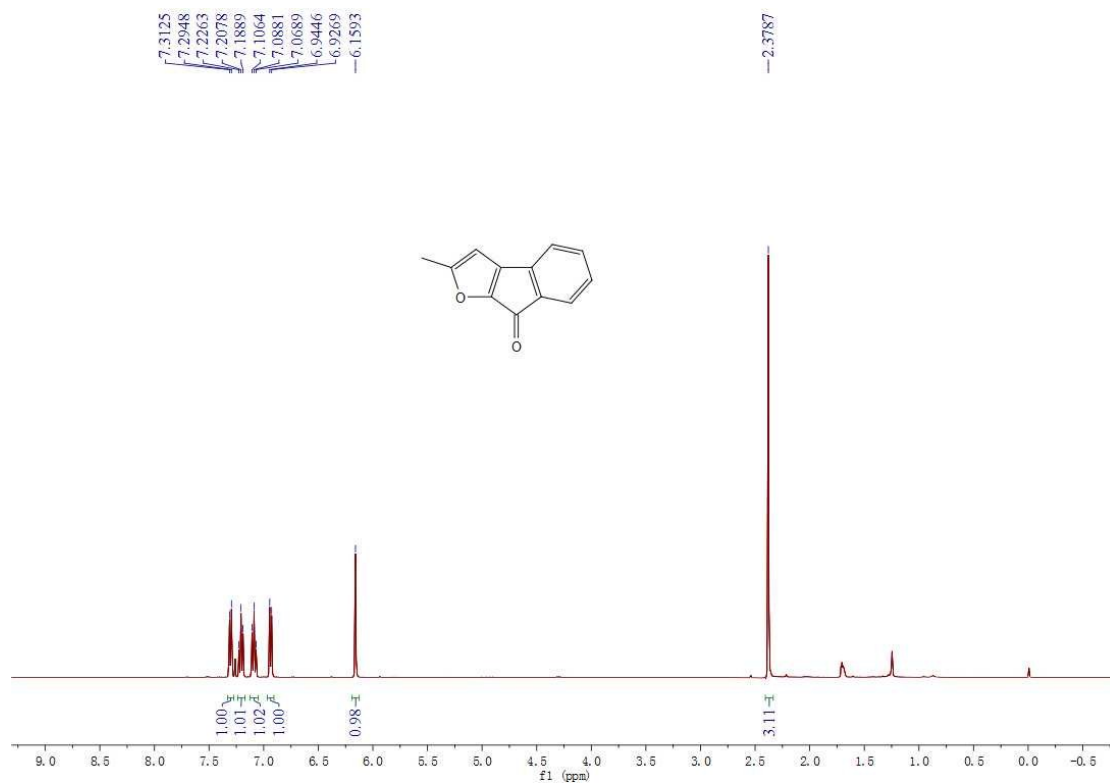
¹H NMR and ¹³C NMR of 4o



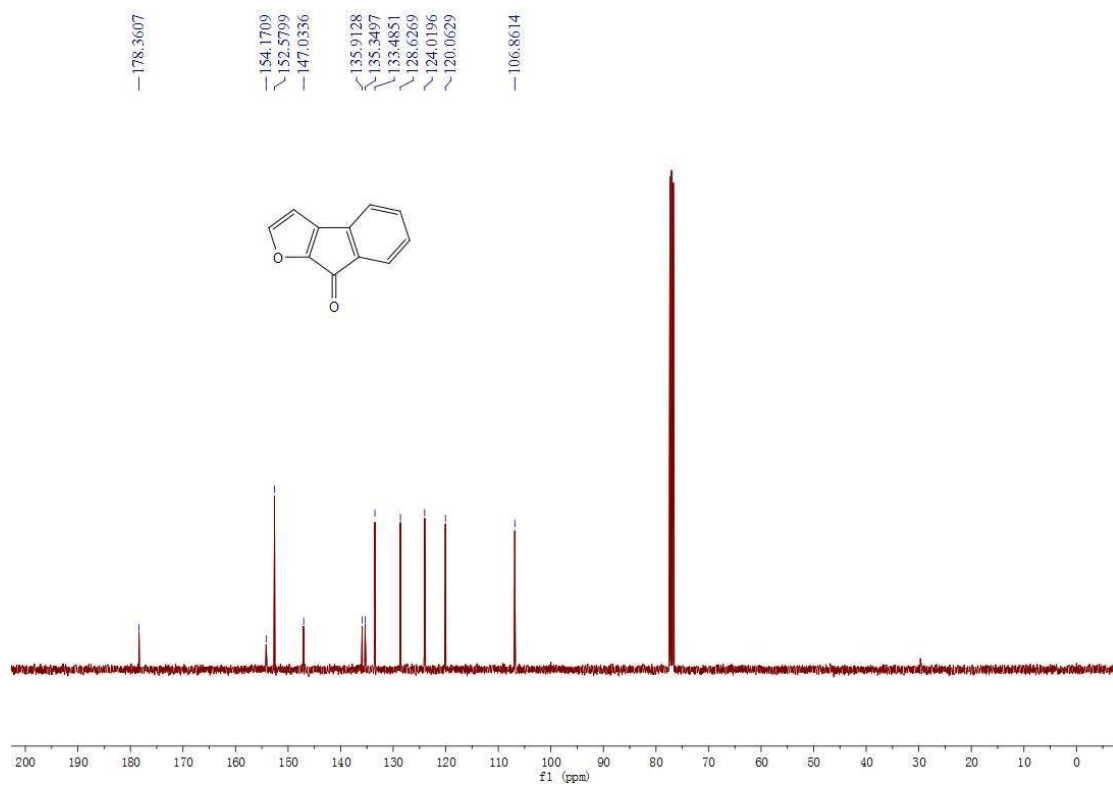
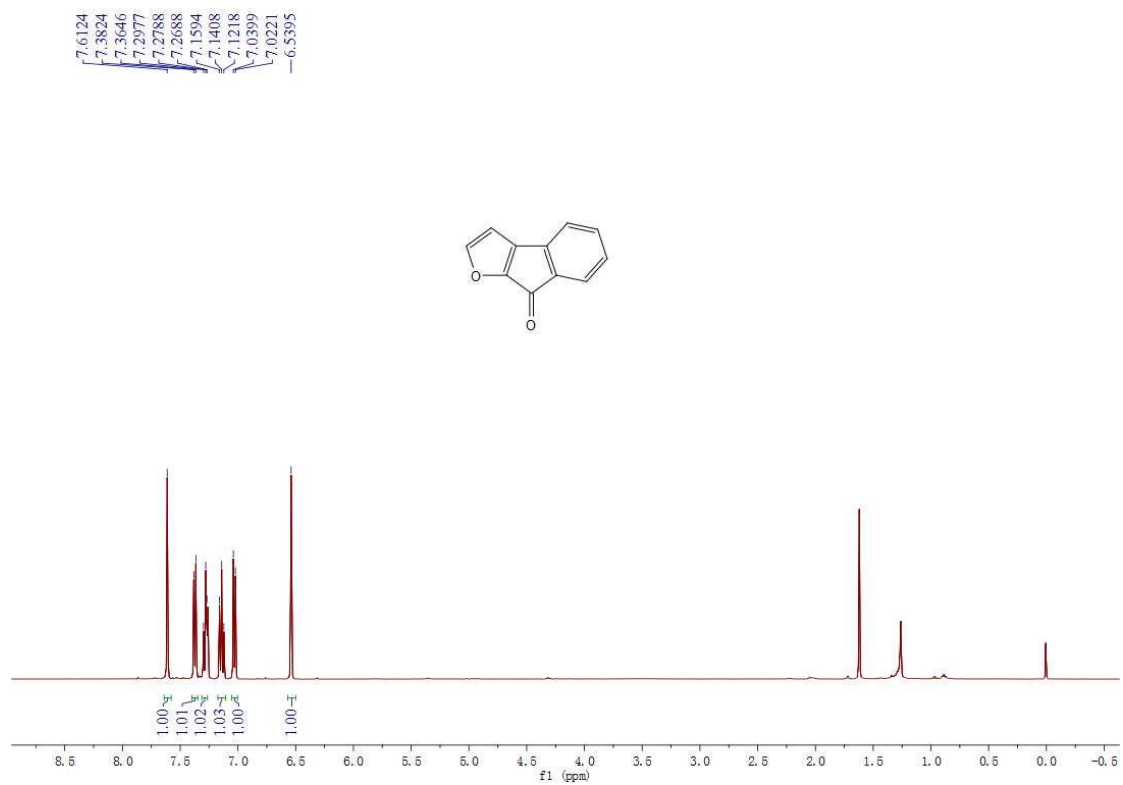
¹H NMR and ¹³C NMR of 4p



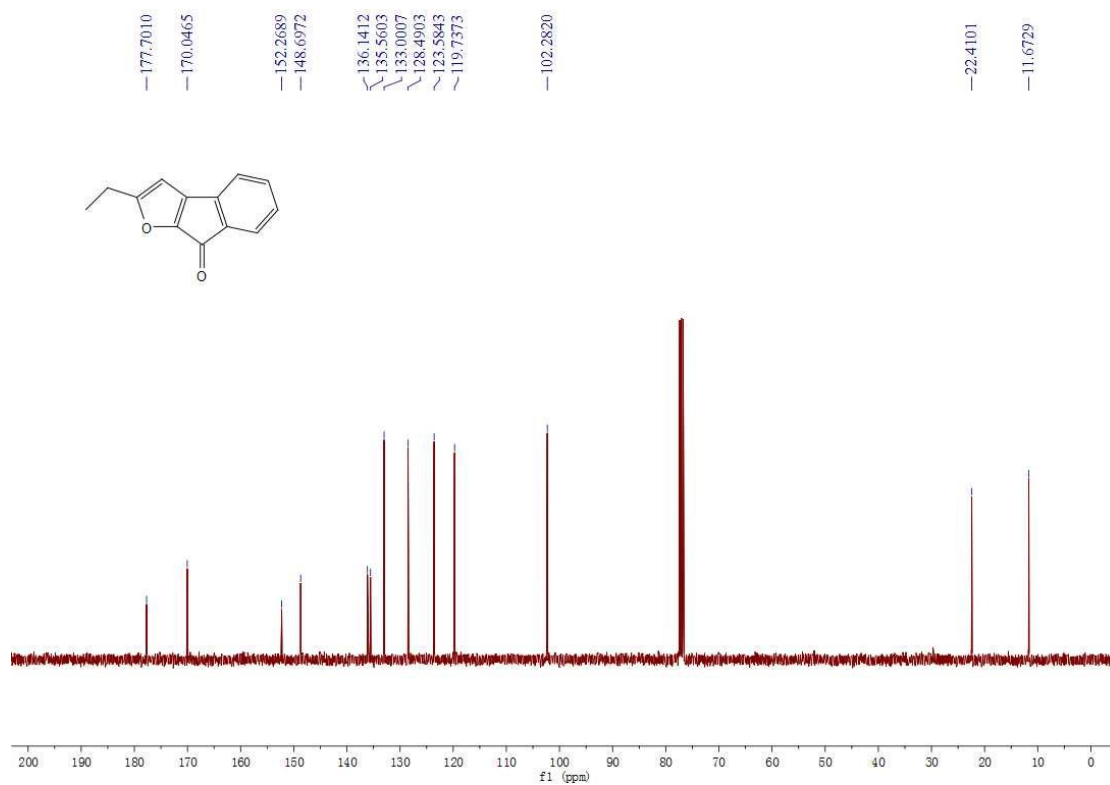
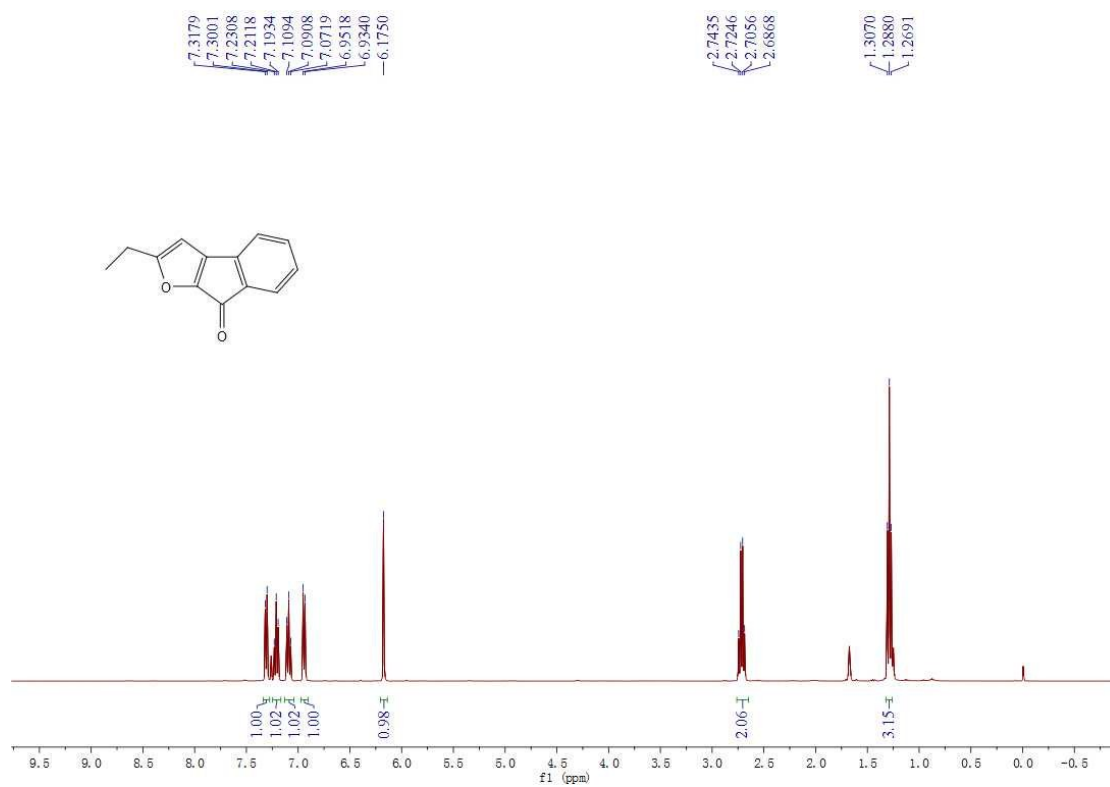
¹H NMR and ¹³C NMR of 3a



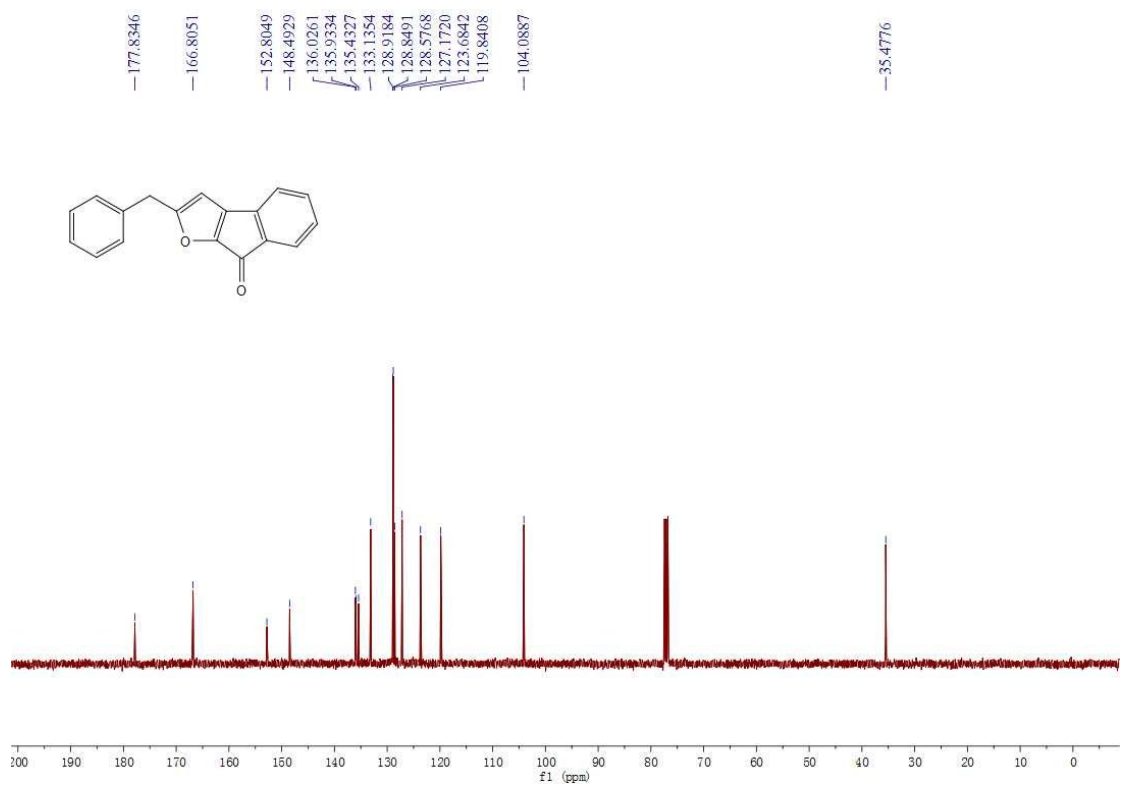
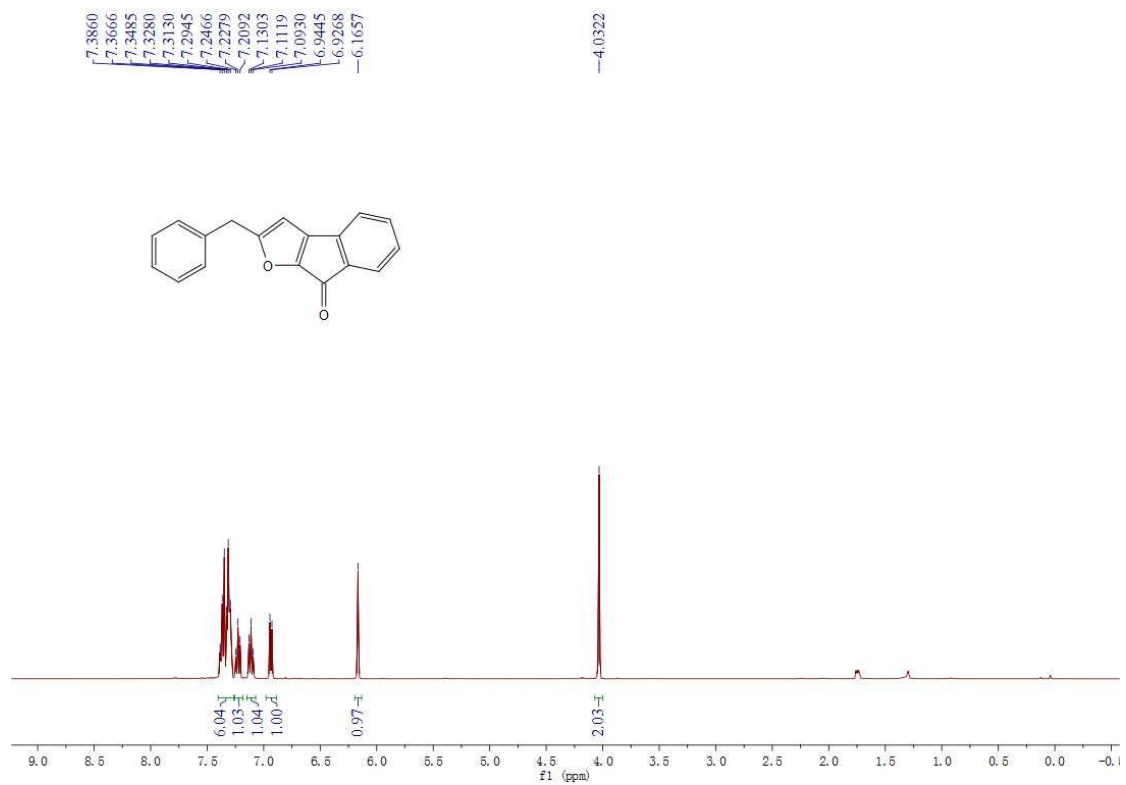
¹H NMR and ¹³C NMR of 3b



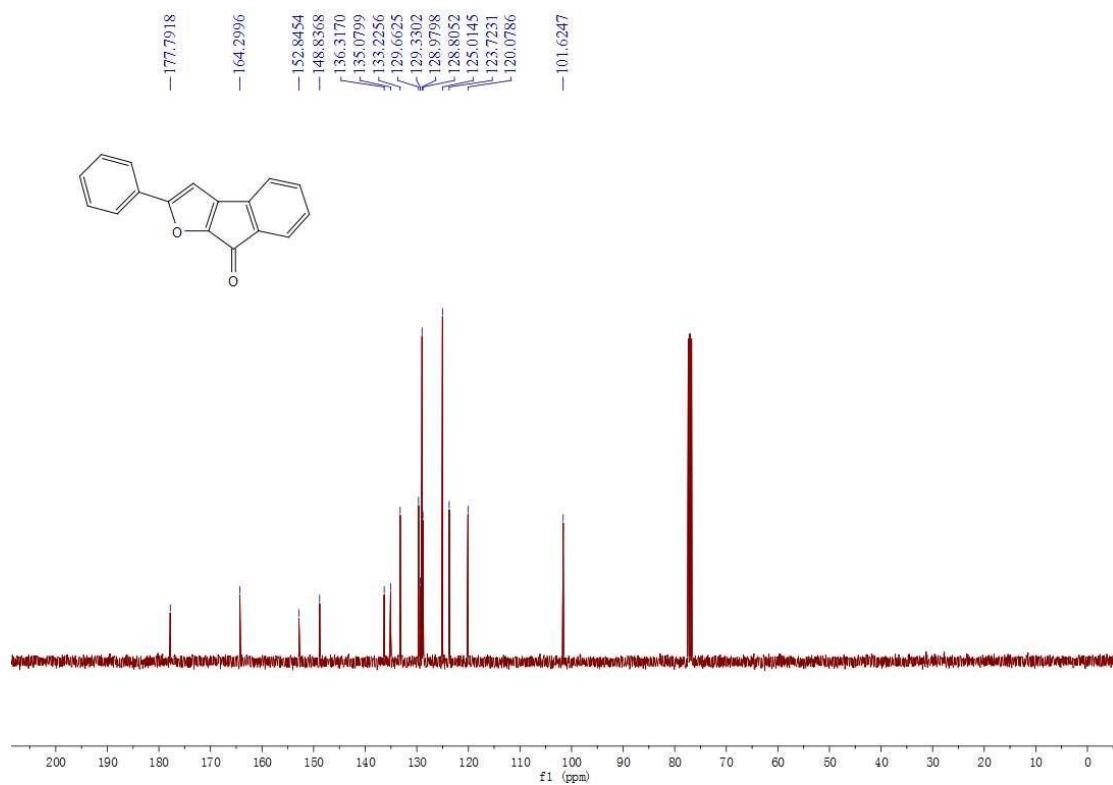
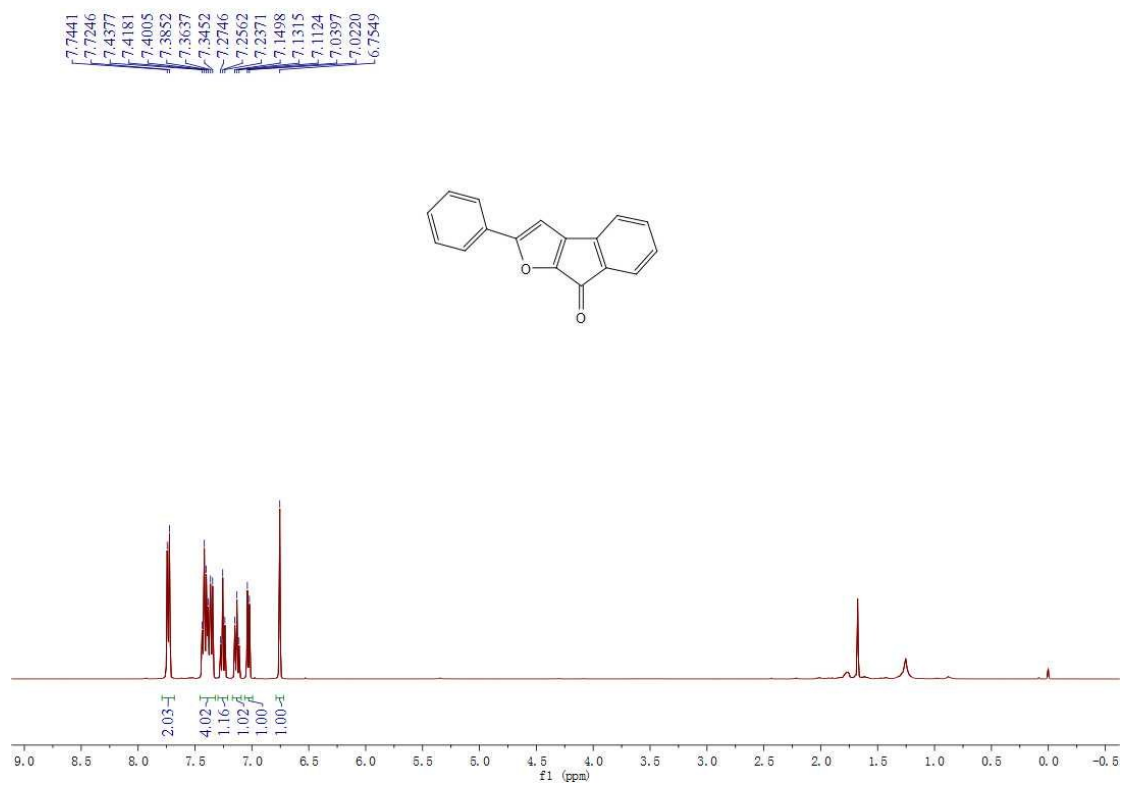
¹H NMR and ¹³C NMR of 3c



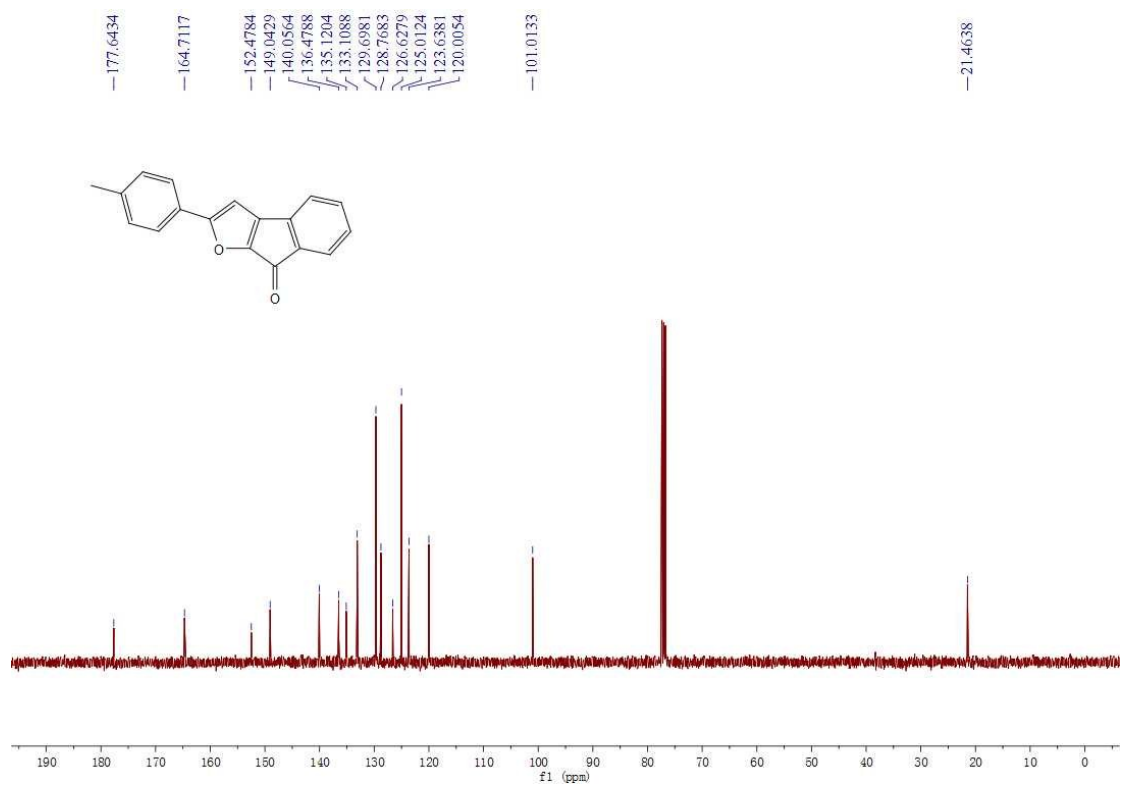
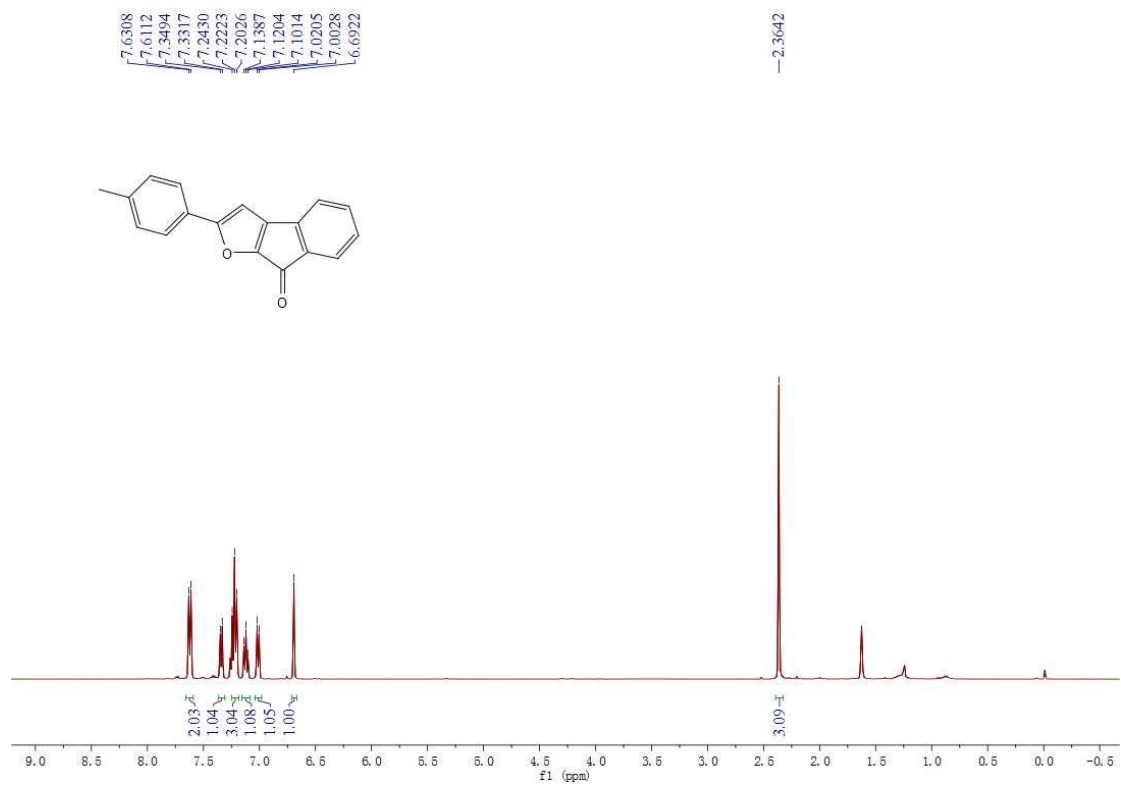
¹H NMR and ¹³C NMR of 3d



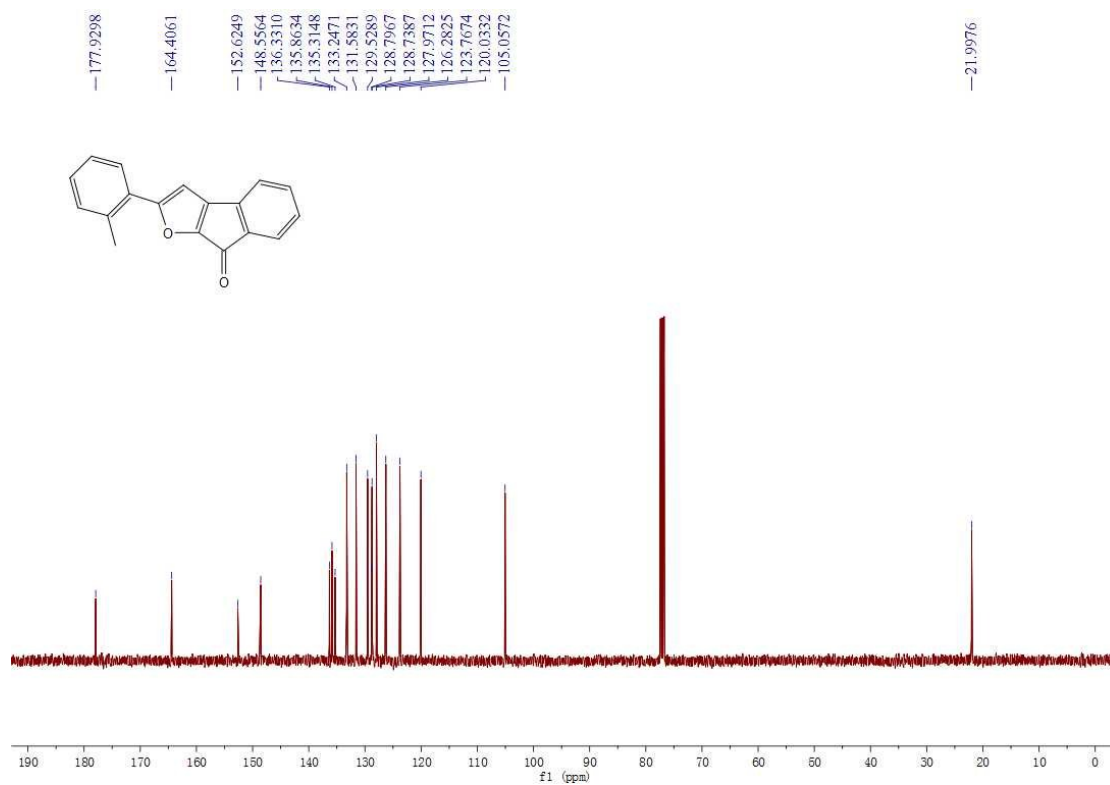
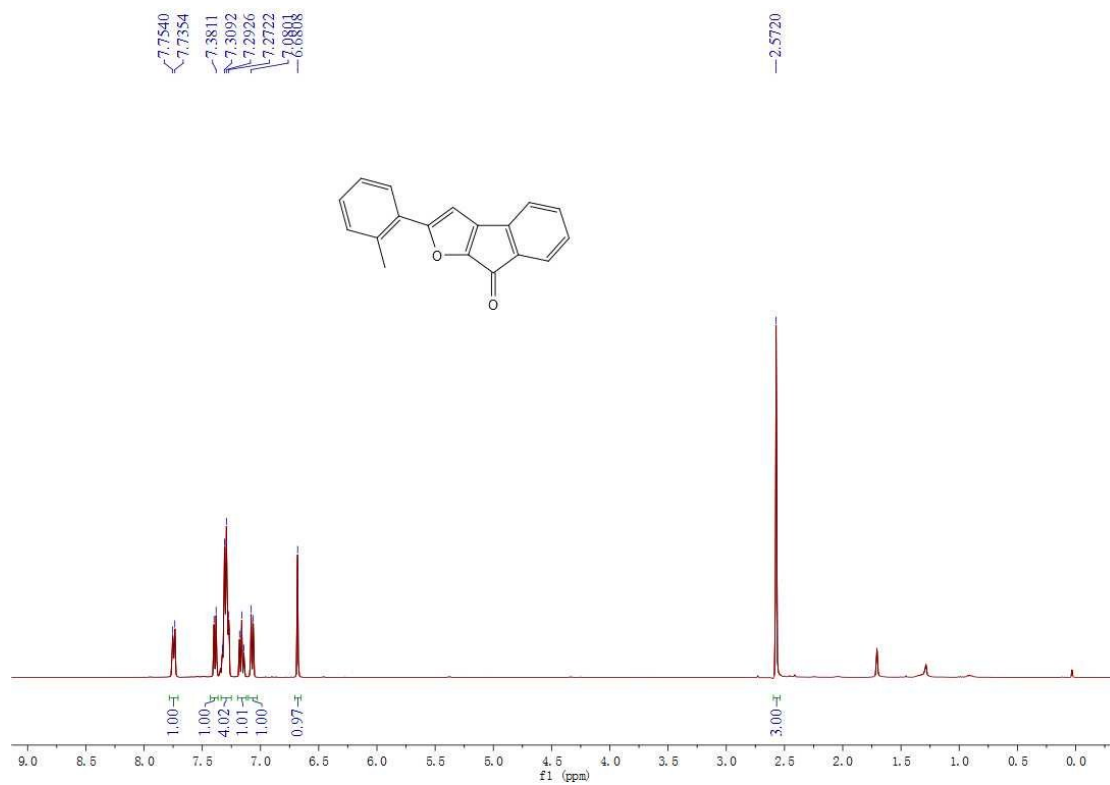
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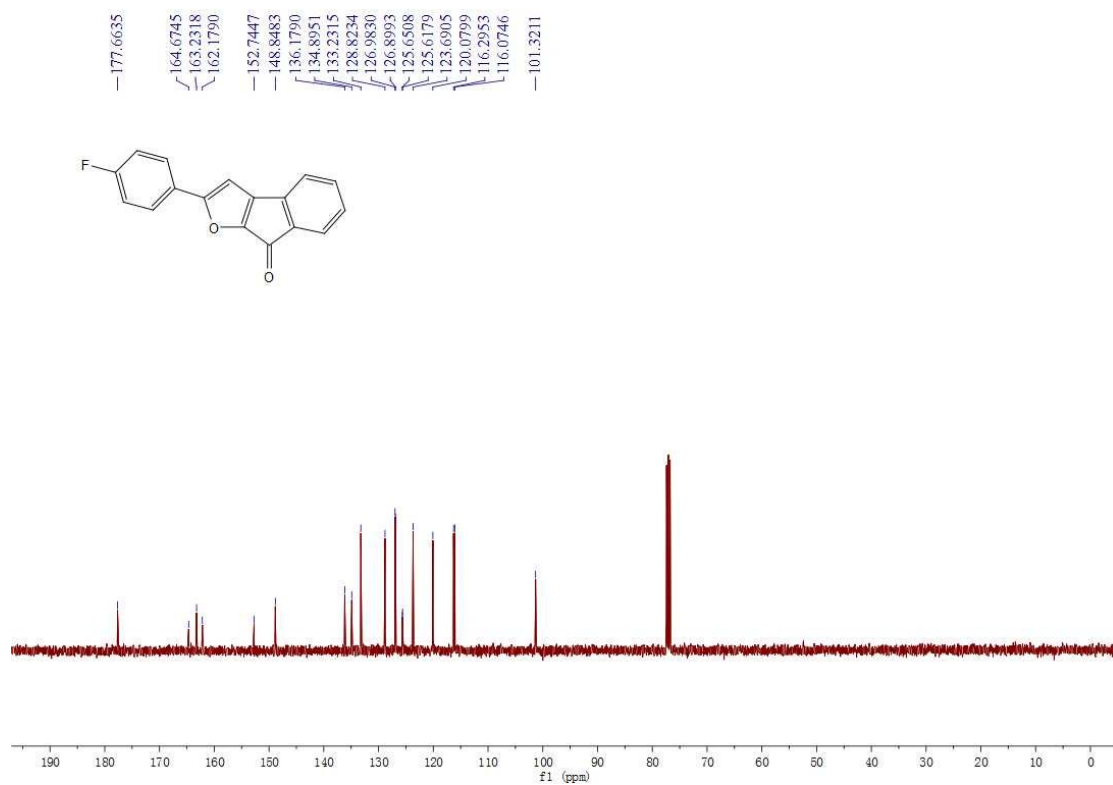
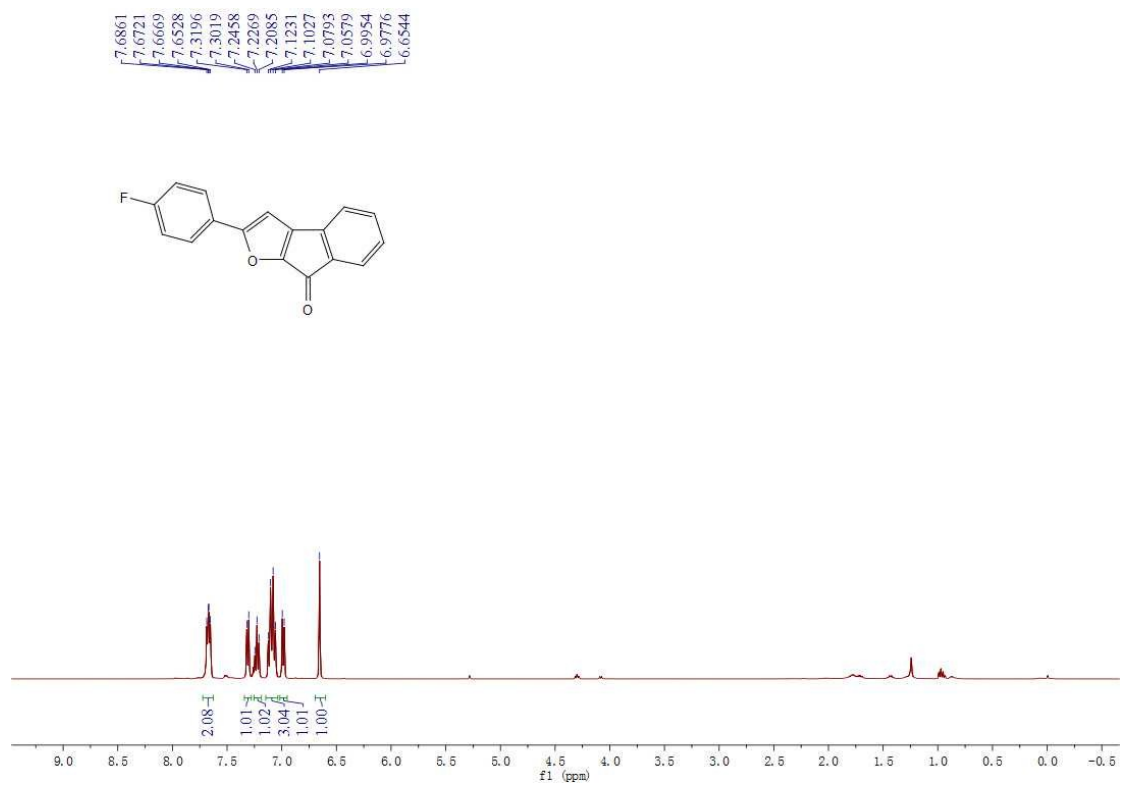
¹H NMR and ¹³C NMR of 3f



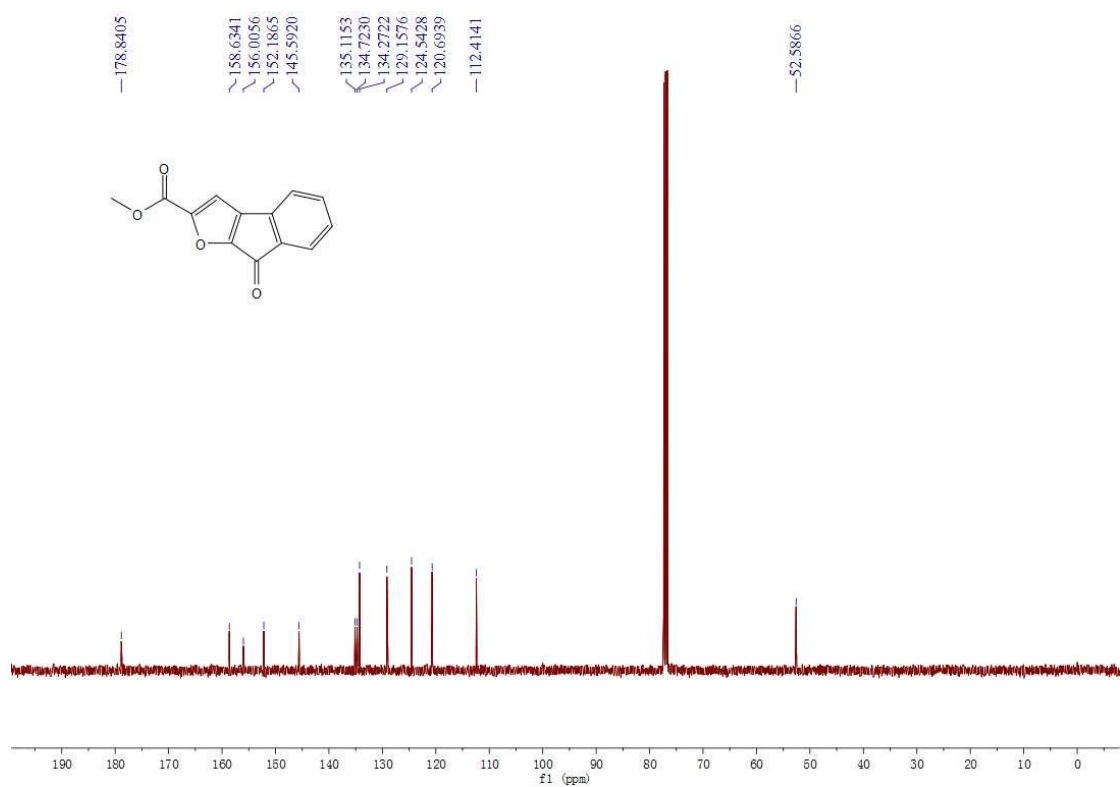
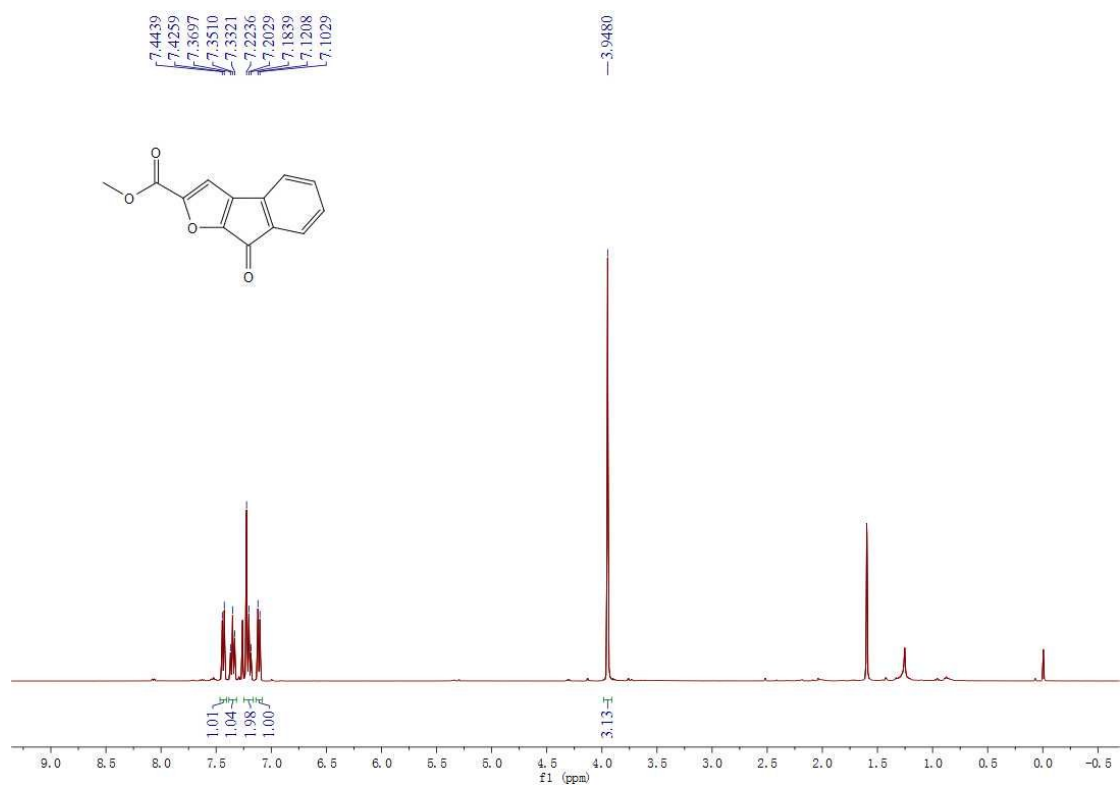
¹H NMR and ¹³C NMR of 3g



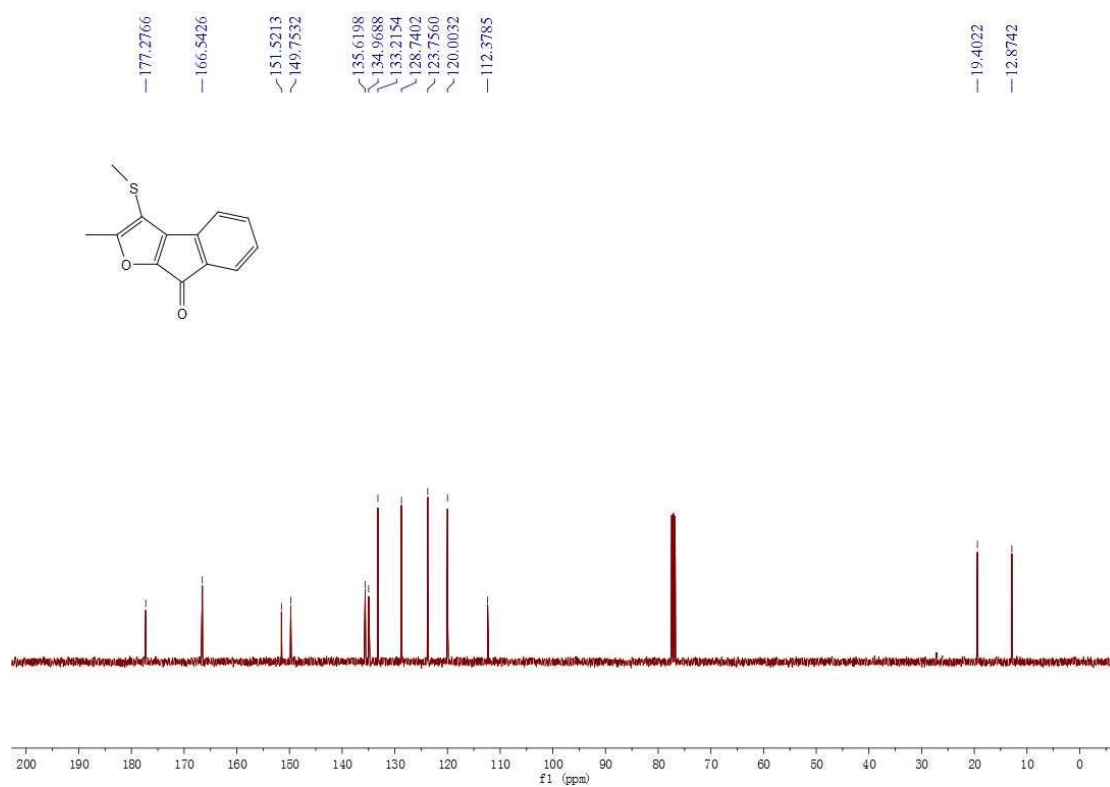
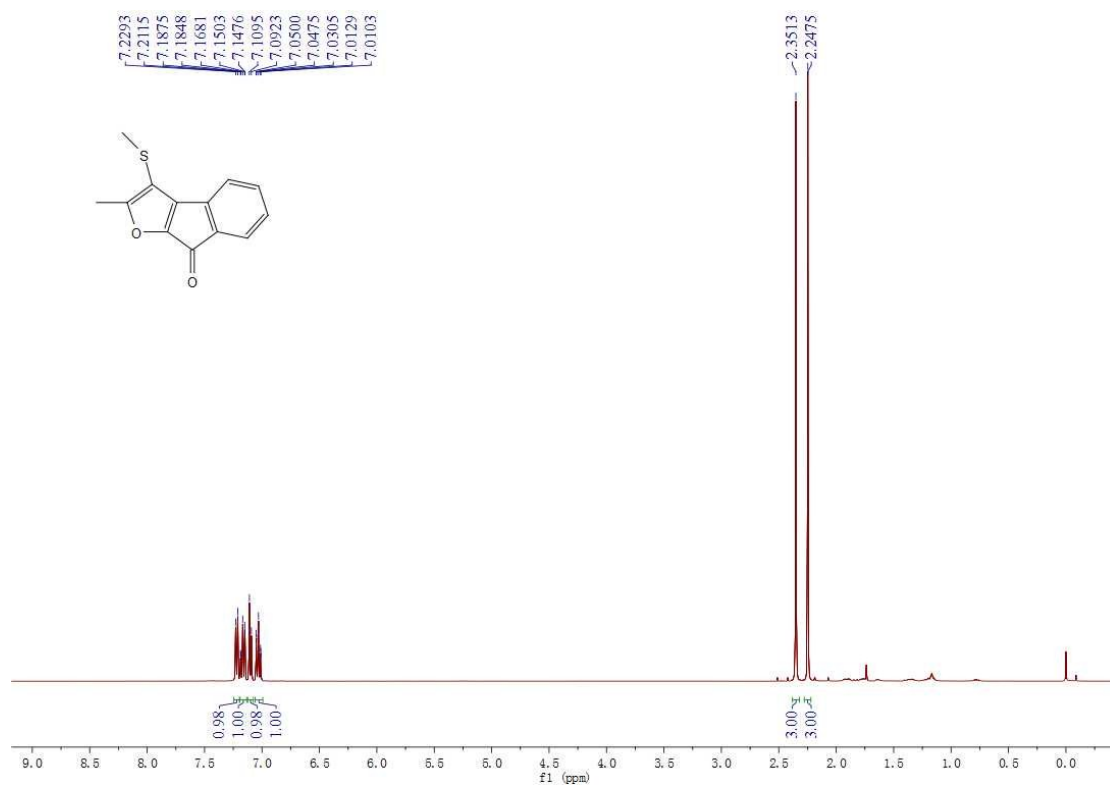
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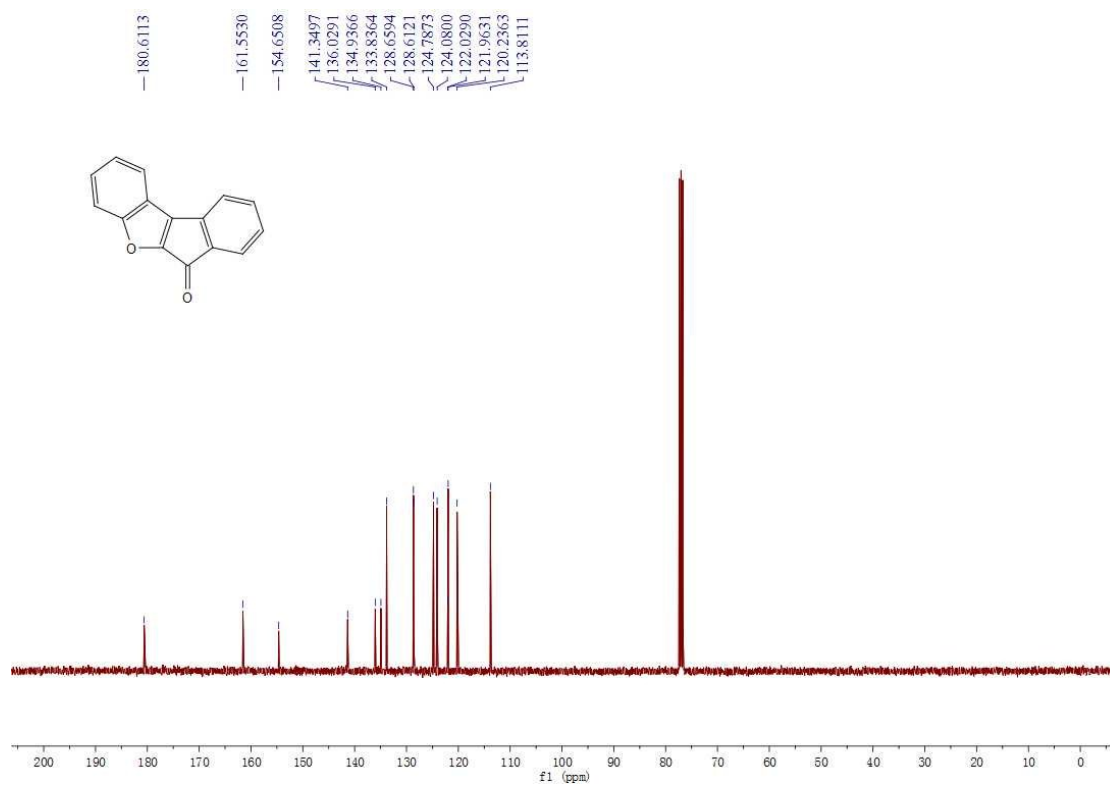
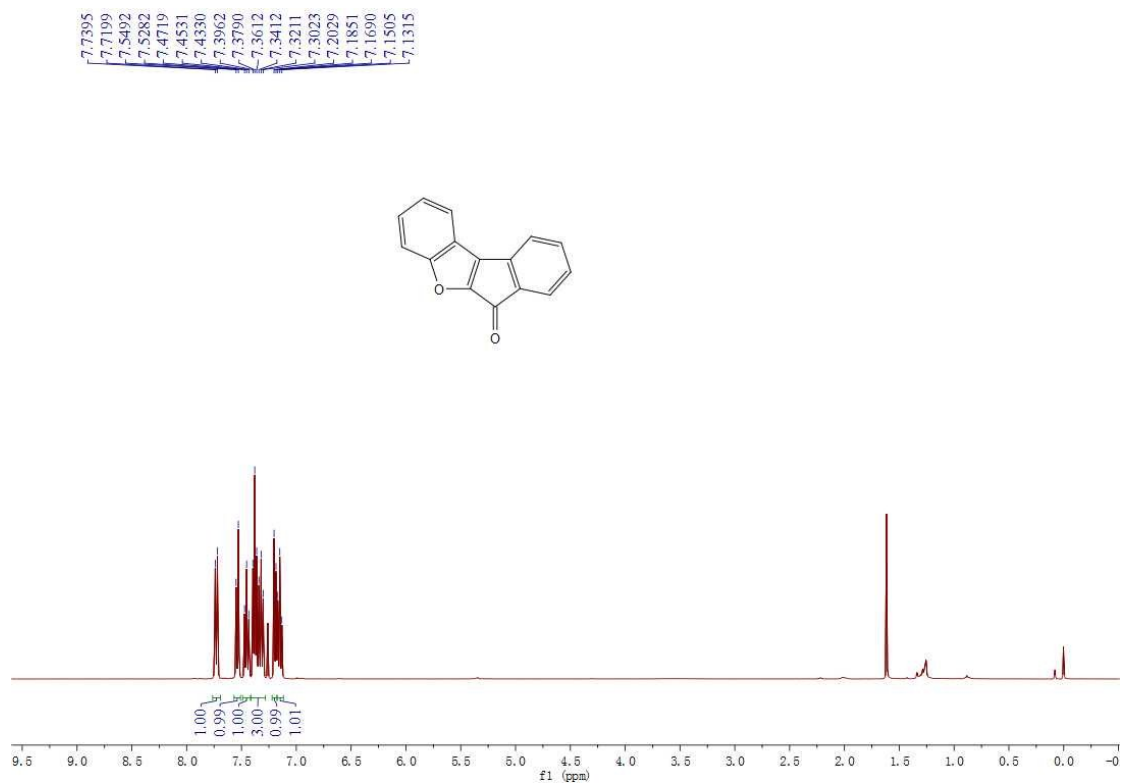
¹H NMR and ¹³C NMR of 3i



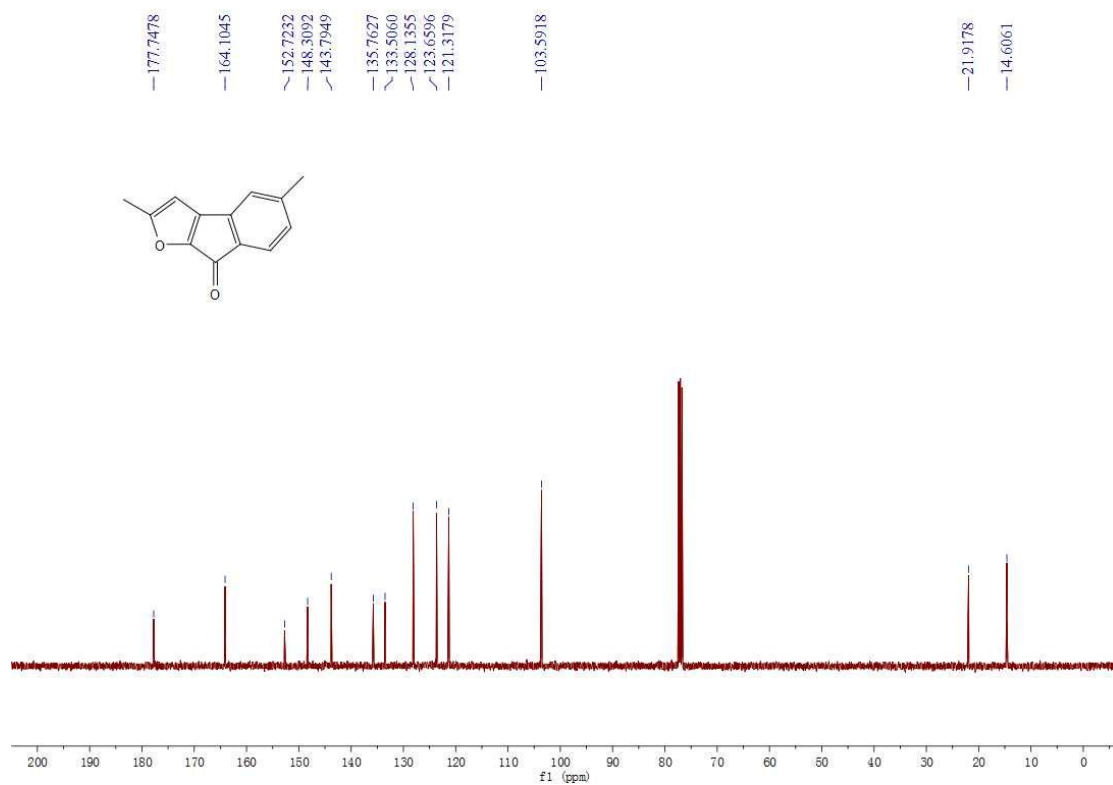
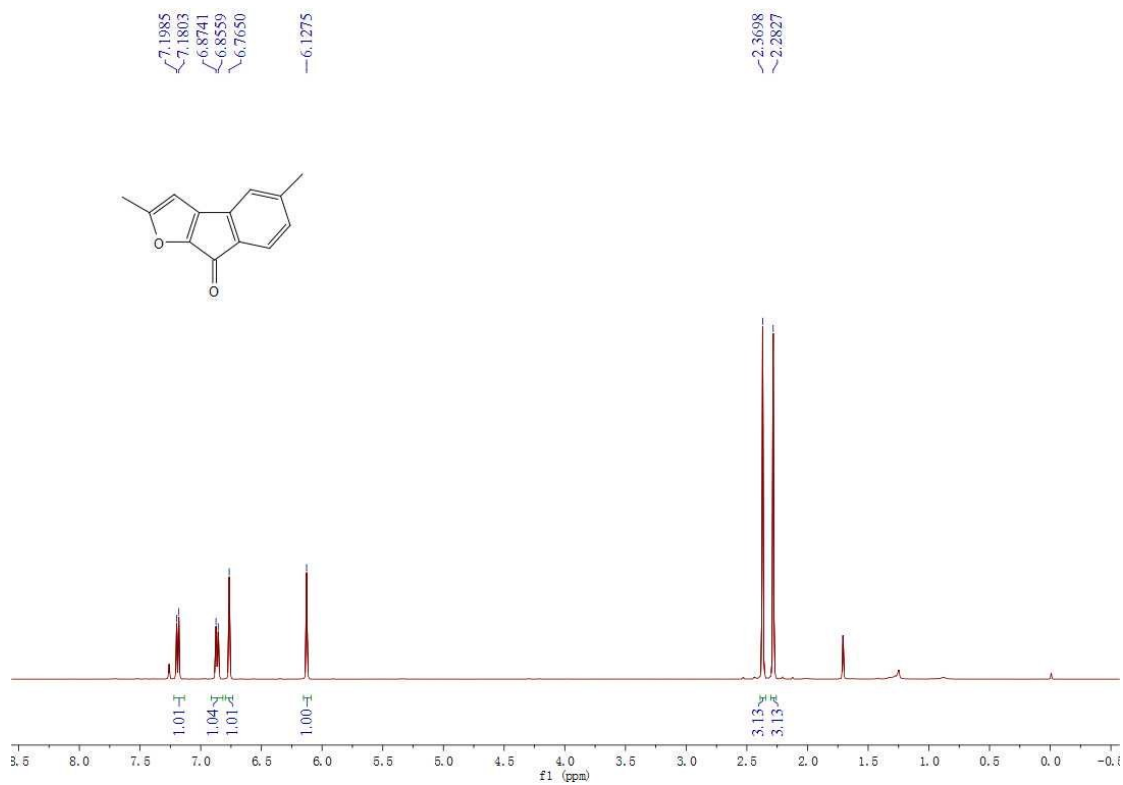
^1H NMR and ^{13}C NMR of 3j



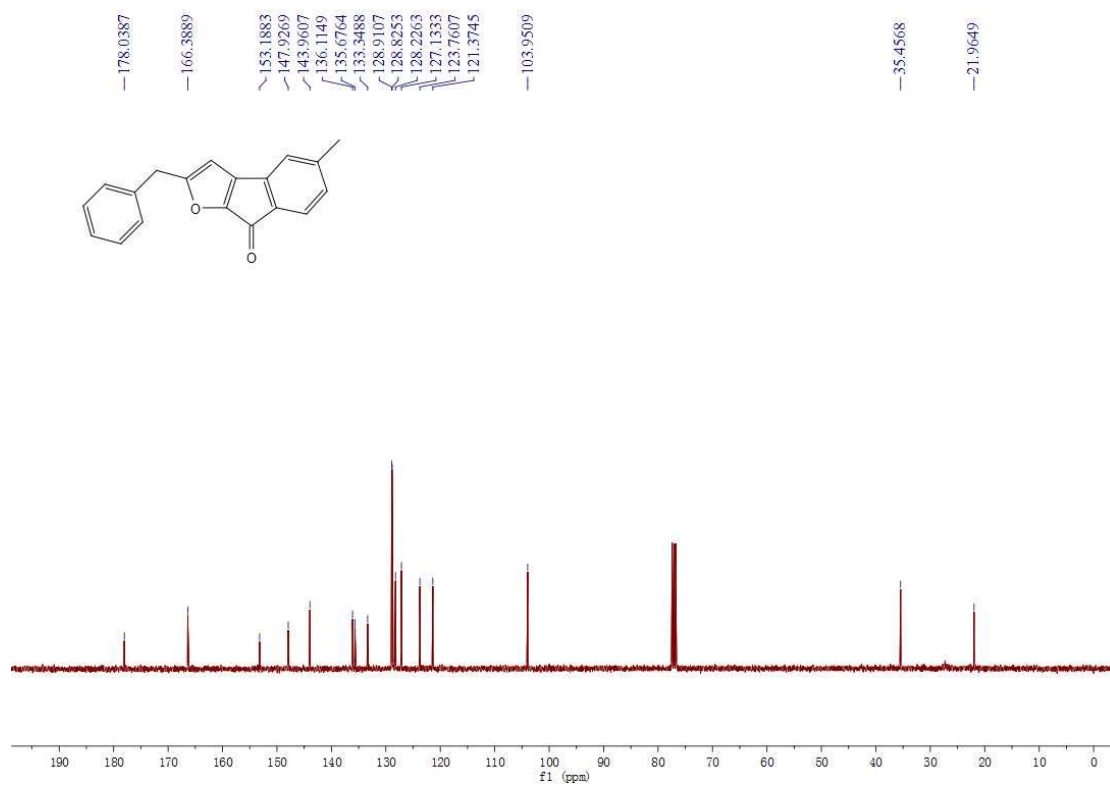
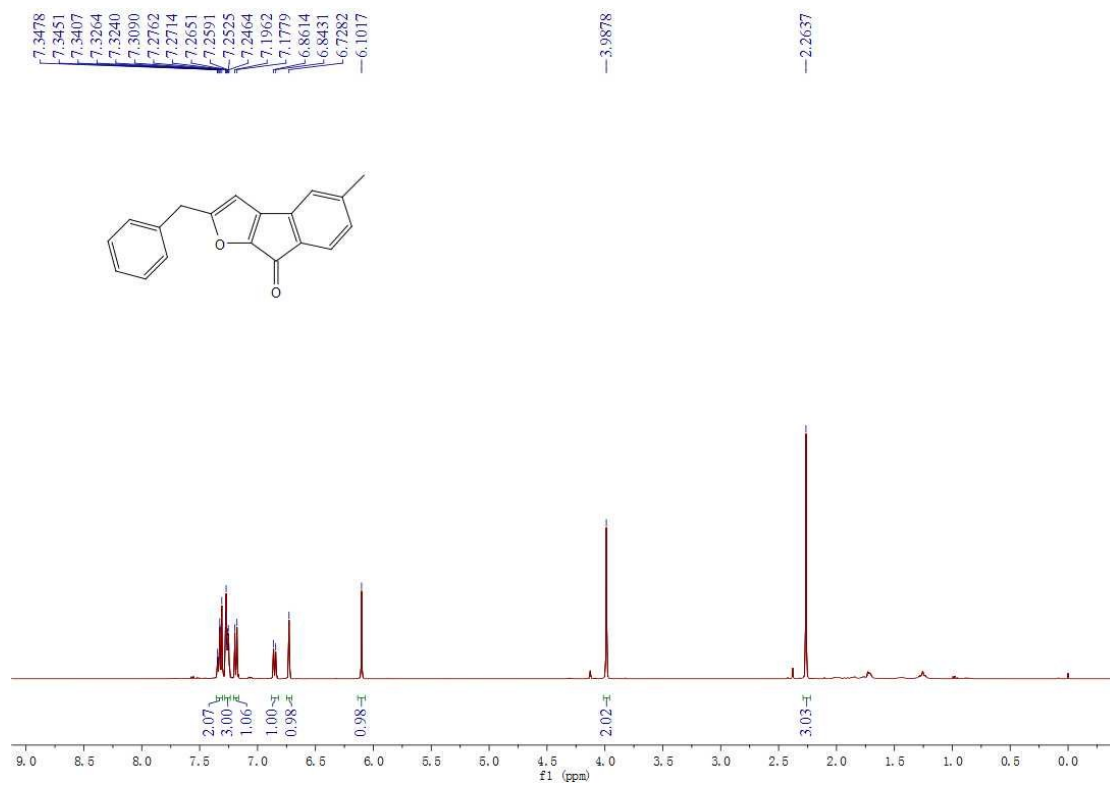
¹H NMR and ¹³C NMR of 3k



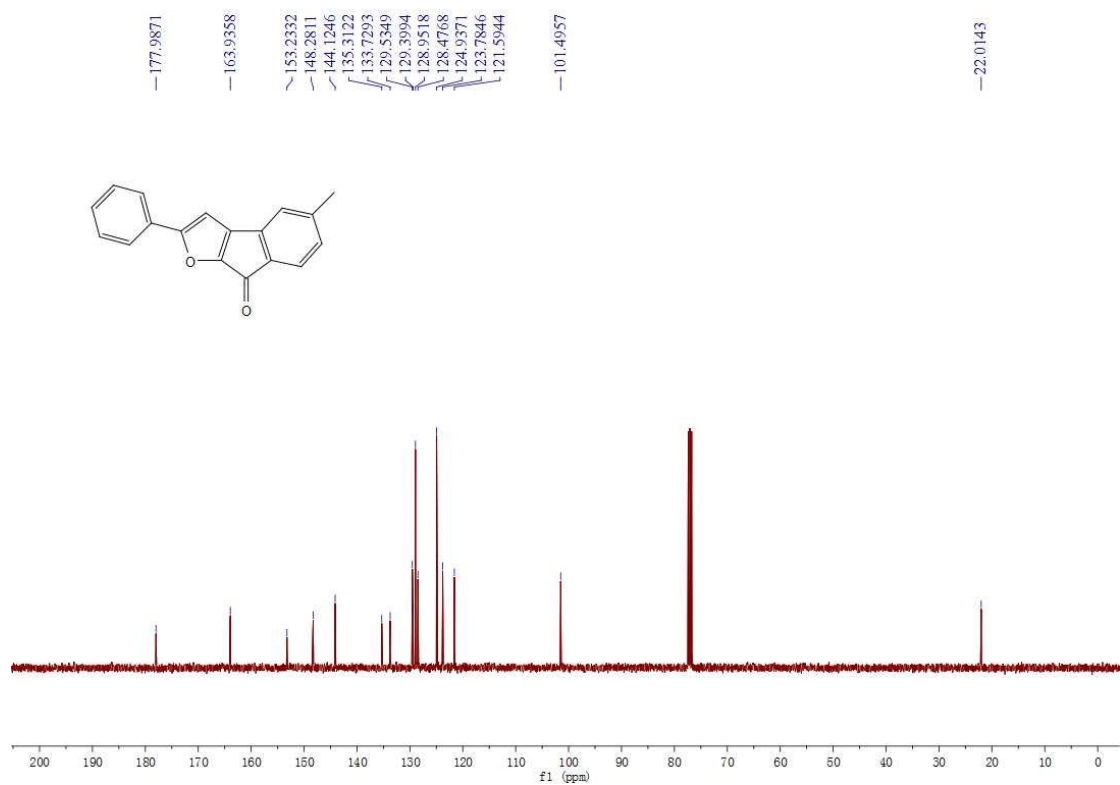
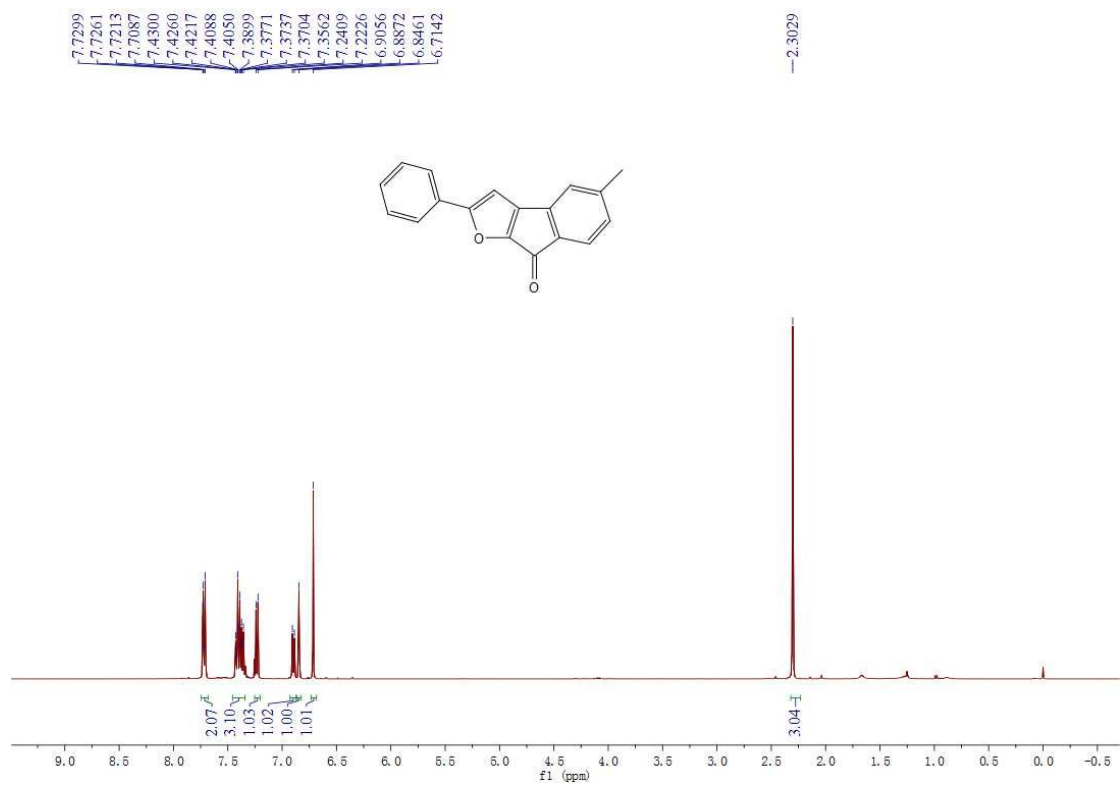
¹H NMR and ¹³C NMR of 31



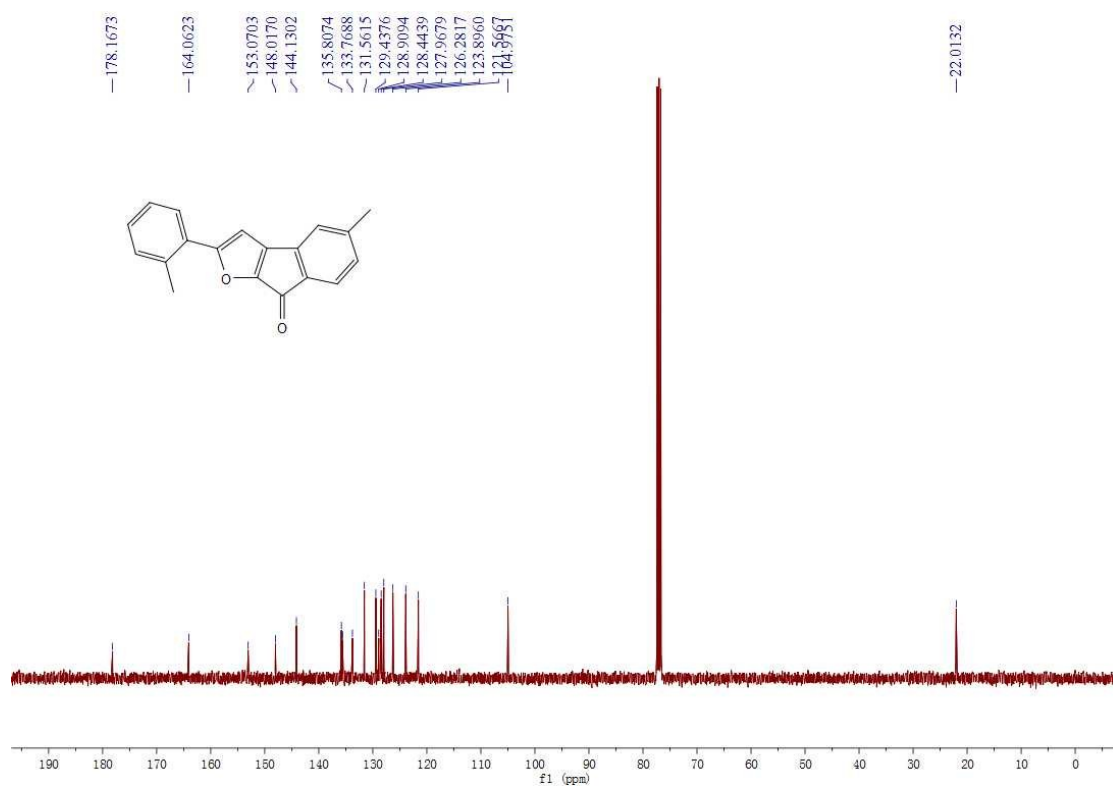
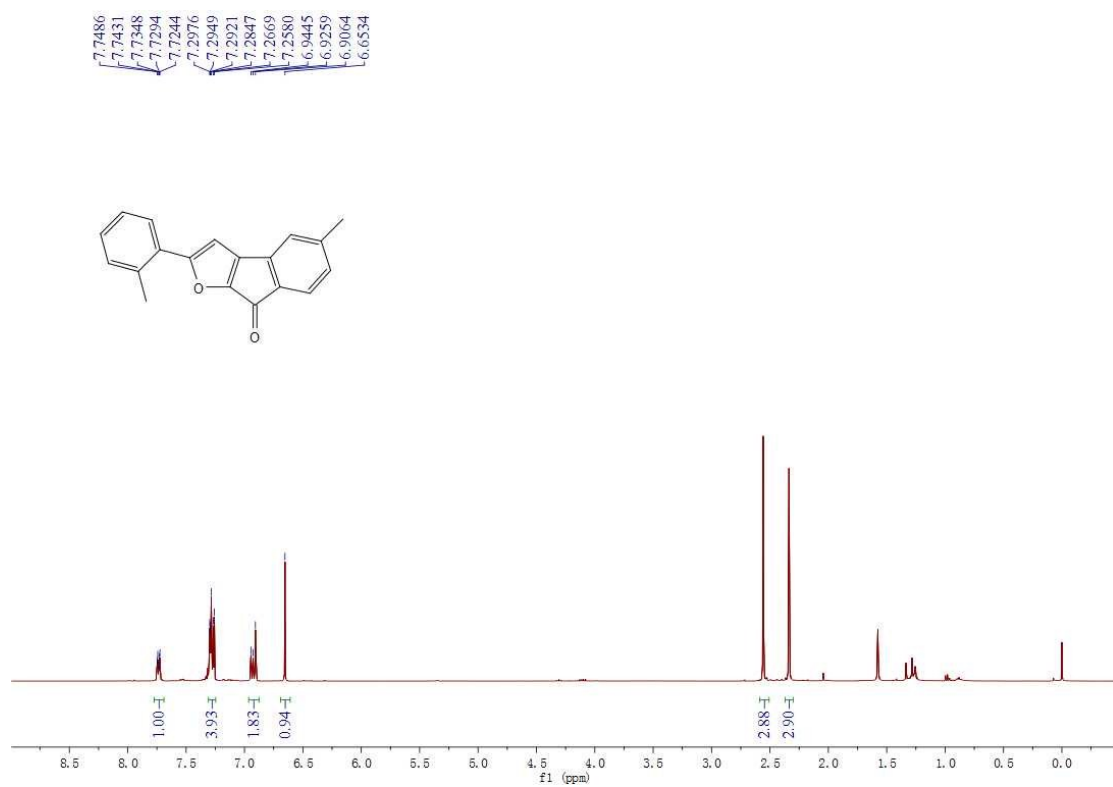
^1H NMR and ^{13}C NMR of 3m



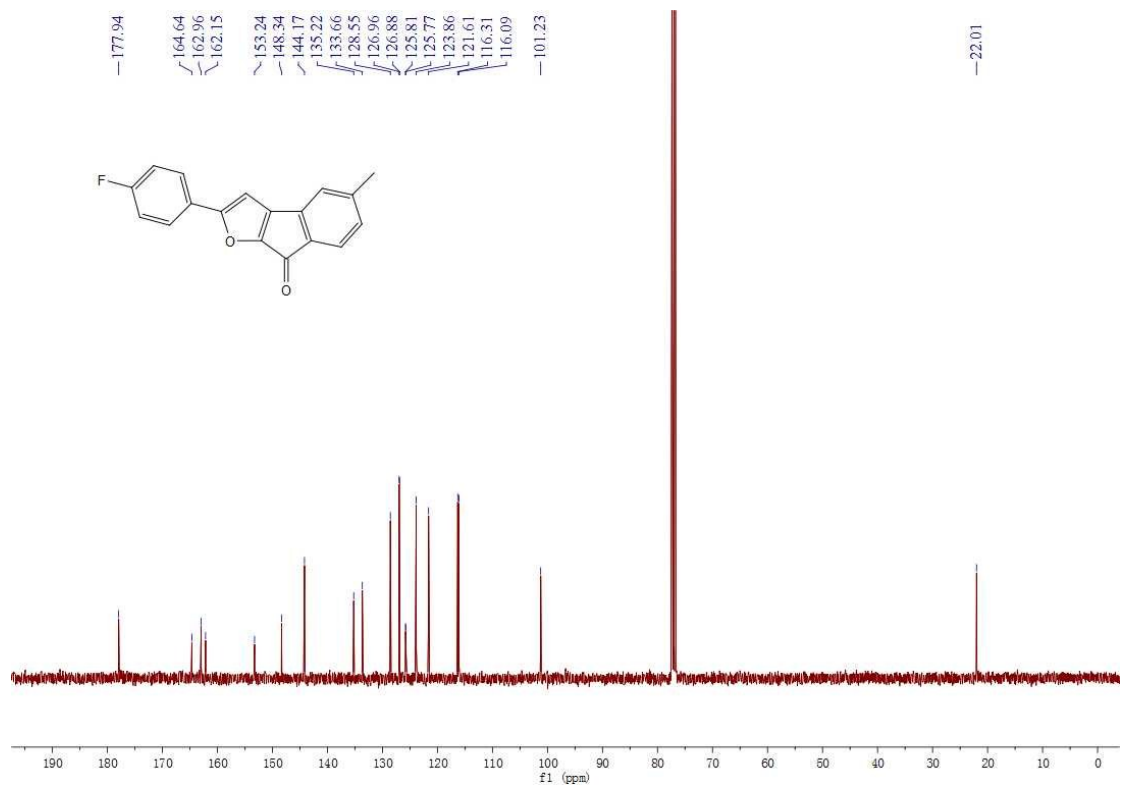
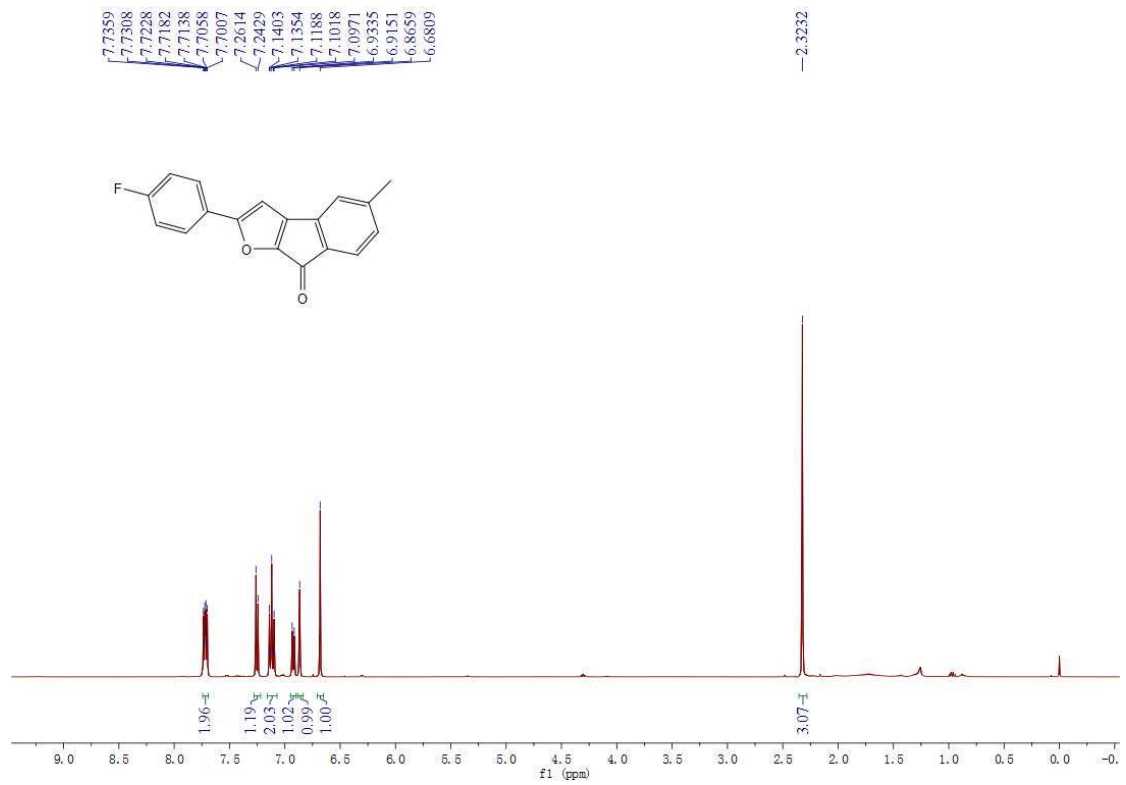
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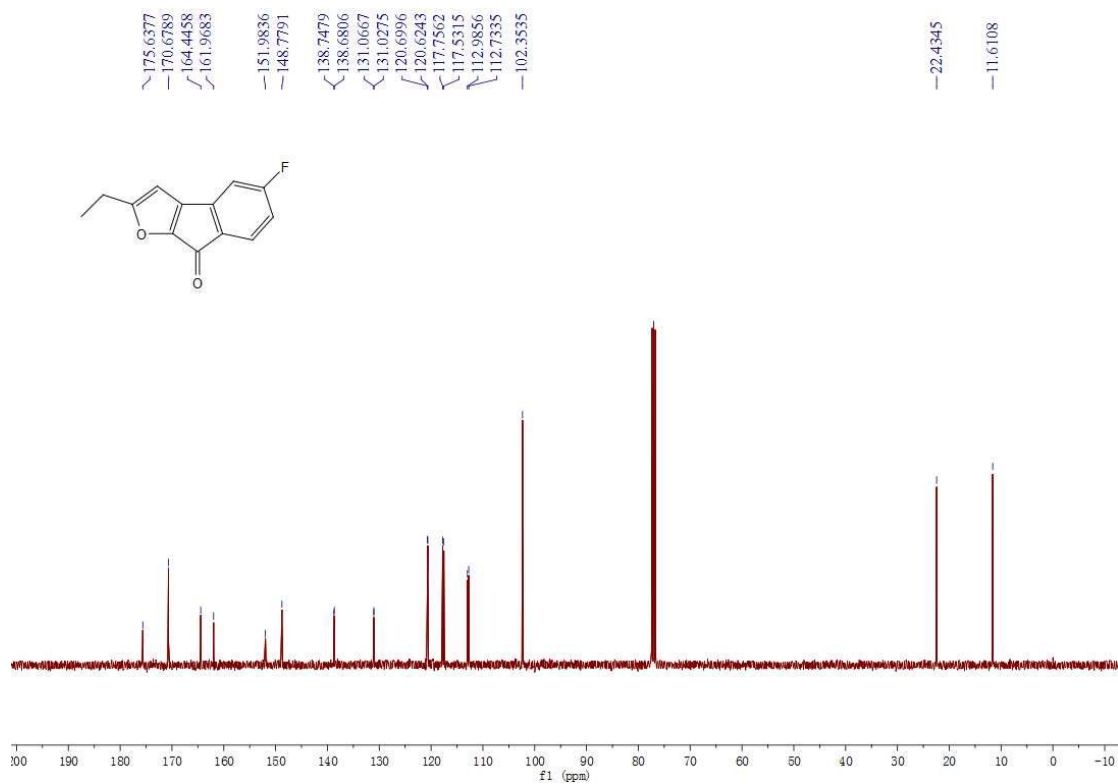
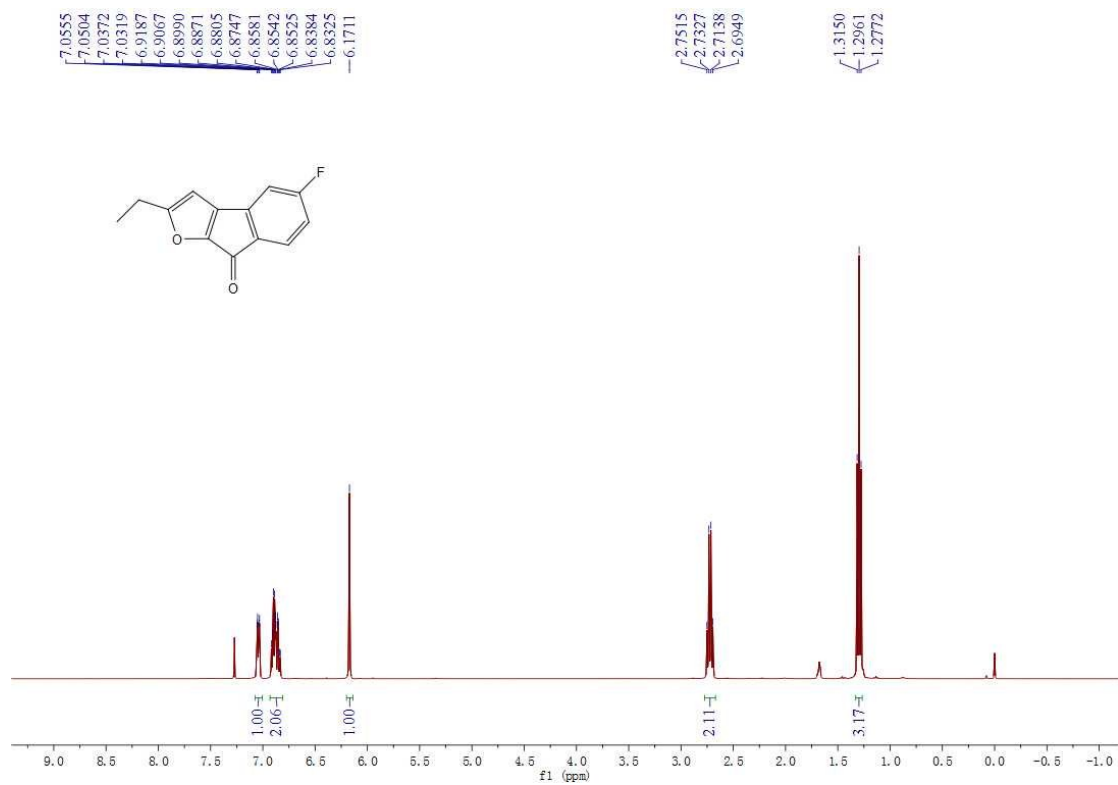
¹H NMR and ¹³C NMR of 3o



¹H NMR and ¹³C NMR of 3p



¹H NMR and ¹³C NMR of 3r



¹H NMR and ¹³C NMR of 3s

