

Preparation of Dibenzofurtropones *via* Pd-catalyzed cyclization

Yu-Wei Lin and Shiuh-Tzung Liu*

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

Corresponding author. E-mail: stliu@ntu.edu.tw

Supplementary Materials

Contents

Table S1 Physical and Spectral data of **2aa-2ga**

Table S2 Physical and Spectral data of **1aa-1ga**

Figure S1 ^1H NMR spectrum of compound **2aa**

Figure S2 ^1H NMR spectrum of compound **2ab**

Figure S3 ^1H NMR spectrum of compound **2ac**

Figure S4 ^1H NMR spectrum of compound **2ad**

Figure S5 ^1H NMR spectrum of compound **2ae**

Figure S6 ^1H NMR spectrum of compound **2af**

Figure S7 ^1H NMR spectrum of compound **2ag**

Figure S8 ^1H NMR spectrum of compound **2ba**

Figure S9 ^1H NMR spectrum of compound **2ca**

Figure S10 ^1H NMR spectrum of compound **2da**

Figure S11 ^1H NMR spectrum of compound **2ea**

Figure S12 ^1H NMR spectrum of compound **2fa**

Figure S13 ^1H NMR spectrum of compound **2ga**

Figure S14 ^1H NMR spectrum of compound **1aa**

Figure S15 ^1H NMR spectrum of compound **1ab**

Figure S16 ^1H NMR spectrum of compound **1ac**

Figure S17 ^1H NMR spectrum of compound **1ad**

Figure S18 ^1H NMR spectrum of compound **1ae**

Figure S19 ^1H NMR spectrum of compound **1af**

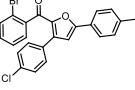
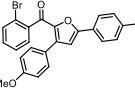
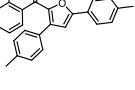
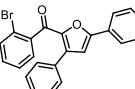
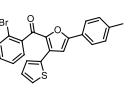
Figure S20 ^1H NMR spectrum of compound **1da**

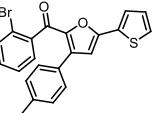
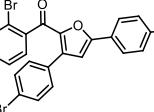
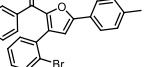
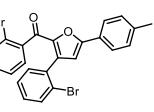
Figure S21 ^1H NMR spectrum of compound **1ea**

Figure S22 ^1H NMR spectrum of compound **1fa**

Figure S23 ^1H NMR spectrum of compound **1ga**

Table S1 Physical and spectral data of **2aa-2ga**

compd	structure	Physical and spectral data
2aa		Pale yellow solid; m.p.: 92-93 °C; Eluent: ethyl acetate : hexane = 3 : 97; (383 mg, 38%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.62 (d, <i>J</i> = 8.2 Hz, 2H), 7.57 (d, <i>J</i> = 8.4 Hz, 3H), 7.48 (dd, <i>J</i> = 7.9, 1.1 Hz 1H), 7.40 (d, <i>J</i> = 7.2 Hz, 1H), 7.33-7.28 (m, 4H), 7.24 (d, <i>J</i> = 8.0Hz, 2H), 6.90 (s, 1H), 2.40 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 183.2, 157.6, 145.1, 140.6, 140.0, 137.8, 134.5, 132.9, 131.2, 130.4, 130.1, 129.6, 129.5, 128.2, 127.0, 126.1, 125.1, 120.2, 109.3, 21.4. IR (KBr) ν _{C=O} 1648 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₇ BrClO ₂ : 451.0095. Found: 451.0090.
2ab		Yellow solid; m.p.: 144-145 °C; Eluent: ethyl acetate : hexane = 3 : 97; (337 mg, 45%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.64 (d, <i>J</i> = 8.2 Hz, 2H), 7.62 (d, <i>J</i> = 8.2 Hz, 2H), 7.58 (dd, <i>J</i> = 7.8, 1.1 Hz, 1H), 7.41 (dd, <i>J</i> = 7.5, 1.9 Hz, 1H), 7.32 (d, <i>J</i> = 7.4, 1.3 Hz, 1H), 7.28 (dd, <i>J</i> = 7.8, 1.9 Hz, 1H), 7.23 (d, <i>J</i> = 8.2 Hz, 2H), 6.92 (s, 1H), 6.89 (d, <i>J</i> = 8.9 Hz, 2H), 3.84 (s, 3H), 2.39 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 183.1, 159.8, 157.4, 144.8, 140.9, 139.7, 138.6, 132.8, 130.9, 130.4, 129.5, 129.5, 126.9, 126.3, 125.1, 123.9, 120.1, 113.5, 109.3, 55.2, 21.4. IR (KBr) ν _{C=O} 1645 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₅ H ₂₀ BrO ₃ : 447.0596. Found: 447.0608.
2ac		Yellow solid; m.p.: 88-89 °C; Eluent: ethyl acetate : hexane = 3 : 97; (349 mg, 53%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.63 (d, <i>J</i> = 8.2 Hz, 2H), 7.54-7.58 (m, 3H), 7.41 (dd, <i>J</i> = 7.4, 1.8Hz, 1H), 7.23-7.32 (m, 4H), 7.18 (d, <i>J</i> = 8.4 Hz, 2H), 6.93 (s, 1H), 2.41 (s, 3H), 2.38 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 183.1, 157.4, 145.0, 140.8, 139.7, 138.8, 138.4, 132.8, 130.9, 129.6, 129.5, 128.9, 128.7, 126.8, 126.3, 125.1, 120.2, 109.5, 21.4, 21.2. IR (KBr) ν _{C=O} 1648 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₅ H ₂₀ BrO ₂ : 431.0647. Found: 431.0641.
2ad		Yellow solid; m.p.: 68-69 °C; Eluent: ethyl acetate : hexane = 3 : 97; (435 mg, 41%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.66 (d, <i>J</i> = 8.2 Hz, 2H), 7.62-7.58 (m, 2H), 7.55 (dd, <i>J</i> = 7.7, 1.1 Hz, 1H), 7.39 (dd, <i>J</i> = 7.4, 1.9 Hz, 1H), 7.34-7.32 (m, 3H), 7.27-7.23 (m, 4H), 6.93 (s, 1H), 2.40 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 183.1, 157.5, 145.1, 140.6, 139.8, 138.8, 132.8, 131.7, 131.1, 129.6, 129.0, 128.4, 128.0, 126.9, 126.2, 125.1, 120.2, 109.6, 21.4. IR (KBr) ν _{C=O} 1648 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₈ BrO ₂ : 417.0490. Found: 417.0485.
2ae		Yellow solid; m.p.: 144-145 °C; Eluent: ethyl acetate : hexane = 3 : 97; (271 mg, 41%). ¹ H NMR (400 MHz, CDCl ₃) δ 8.10 (dd, <i>J</i> = 3.7, 1.1 Hz, 1H), 7.68 (dd, <i>J</i> = 7.9, 1.0 Hz, 1H), 7.56-7.52 (m, 3H), 7.47-7.42 (m, 2H), 7.37 (td, <i>J</i> = 8.0, 1.9 Hz, 1H), 7.22 (d, <i>J</i> = 8.0, 2H), 7.16 (dd, <i>J</i> = 5.1, 3.7 Hz, 1H), 7.09 (s, 1H), 2.39 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 183.1, 157.1, 144.0, 140.9, 139.9, 133.2, 132.9, 131.2,

		131.1, 129.7, 129.5, 129.4, 127.7, 127.6, 127.0, 126.0, 125.0, 120.1, 108.1, 21.4. IR (KBr) $\nu_{C=O}$ 1638 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₂ H ₁₆ BrO ₂ S: 423.0054. Found: 423.0049.
2af		Yellow solid; m.p.: 100-101 °C; Eluent: ethyl acetate : hexane = 3 : 97; (230 mg, 33%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.55 (dd, <i>J</i> = 7.7, 1.0 Hz, 1H), 7.52 (d, <i>J</i> = 8.1 Hz, 2H), 7.44 (d, <i>J</i> = 3.1 Hz, 1H), 7.40-7.37(m, 2H), 7.28 (td, <i>J</i> = 7.3, 1.0 Hz, 1H), 7.24 (td, <i>J</i> = 7.4, 1.8 Hz, 1H), 7.15 (d, <i>J</i> = 8.0 Hz, 2H), 7.09 (dd, <i>J</i> = 4.8, 3.8 Hz, 1H), 6.81 (s, 1H), 2.37 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 182.9, 152.5, 144.7, 140.6, 138.8, 138.5, 132.8, 131.7, 131.0, 129.5, 128.9, 128.7, 128.3, 128.1, 127.2, 126.8, 125.9, 120.2, 109.8, 21.3. IR (KBr) $\nu_{C=O}$ 1644 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₂ H ₁₆ BrO ₂ S: 423.0052. Found: 423.0049.
2ag		Yellow solid; m.p.: 102-103 °C; Eluent: ethyl acetate : hexane = 3 : 97; (363 mg, 52%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.61 (d, <i>J</i> = 7.7 Hz, 2H), 7.56 (d, <i>J</i> = 7.7 Hz, 1H), 7.52 (d, <i>J</i> = 8.3 Hz, 2H), 7.46 (d, <i>J</i> = 8.0 Hz, 2H), 7.40 (d, <i>J</i> = 6.7 Hz, 1H), 7.31-7.20 (m, 4H), 6.89 (s, 1H), 2.38 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 182.8, 157.4, 144.8, 140.3, 139.7, 137.1, 132.7, 131.0, 130.9, 130.5, 130.4, 129.4, 129.3, 126.8, 125.8, 124.9, 122.5, 119.9, 109.0, 21.2. IR (KBr) $\nu_{C=O}$ 1648 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₇ Br ₂ O ₂ : 494.9595. Found: 494.9590.
2ba		Pale yellow solid; m.p.: 86-87 °C; Eluent: ethyl acetate : hexane = 3 : 97; (340 mg, 32%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.98 (dd, <i>J</i> = 8.2, 1.2 Hz, 2H), 7.75 (d, <i>J</i> = 8.2 Hz, 2H), 7.64 (dd, <i>J</i> = 8.0, 1.1 Hz, 1H), 7.51 (tt, <i>J</i> = 5.6, 1.3 Hz, 1H), 7.41 (t, <i>J</i> = 7.7, 2H), 7.33 (dd, <i>J</i> = 7.6, 1.8 Hz, 1H), 7.31-7.29 (m, 1H), 7.29-7.26 (m, 2H), 7.19 (td, <i>J</i> = 7.9, 1.8 Hz, 1H), 6.91 (s, 1H), 2.44 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 182.7, 156.1, 146.7, 139.4, 137.5, 136.0, 134.1, 132.6, 132.0, 131.4, 129.6, 129.5, 129.4, 127.9, 126.9, 126.5, 124.9, 123.0, 109.9, 21.4. IR (KBr) $\nu_{C=O}$ 1727 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₈ BrO ₂ : 417.0490. Found: 417.0485.
2ca		Orange solid; m.p.: 103-104 °C; Eluent: ethyl acetate : hexane = 3 : 97; (112 mg, 41%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.73 (d, <i>J</i> = 8.2 Hz, 2H), 7.51 (dd, <i>J</i> = 7.9, 1.2 Hz, 1H), 7.44 (dd, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.37 (dd, <i>J</i> = 7.6, 2.0 Hz, 1H), 7.30-7.26 (m, 3H), 7.15 (tt, <i>J</i> = 7.4, 1.3 Hz, 2H), 7.12 (dd, <i>J</i> = 7.9, 1.1 Hz, 1H), 7.08 (td, <i>J</i> = 6.1, 1.8 Hz, 1H), 6.85 (s, 1H), 2.42 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 182.4, 157.5, 145.9, 139.9, 139.8, 137.2, 133.3, 1332.6, 132.4, 131.2, 131.0, 129.6, 129.5, 129.1, 126.7, 126.6, 126.2, 125.2, 122.9, 120.1, 110.3, 21.4. IR (KBr) $\nu_{C=O}$ 1708 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₇ Br ₂ O ₂ : 494.9595. Found: 494.9590.

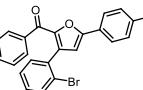
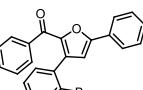
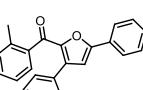
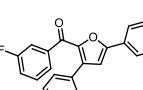
2da		Pale yellow solid; m.p.: 120-121 °C; Eluent: ethyl acetate : hexane = 3 : 97; (131 mg, 42%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.93 (dd, <i>J</i> = 8.5, 1.5 Hz, 2H), 7.77 (d, <i>J</i> = 8.7, 2H), 7.63 (dd, <i>J</i> = 8.0, 1.1 Hz, 1H), 7.50 (tt, <i>J</i> = 7.5, 1.3 Hz, 1H), 7.45 (d, <i>J</i> = 8.7, 2H), 7.39 (t, <i>J</i> = 8.0 Hz, 2H), 7.30 (d, <i>J</i> = 7.5 Hz, 1H), 7.23 (td, <i>J</i> = 7.3, 1.2 Hz, 1H), 7.18 (td, <i>J</i> = 8.0, 2.0 Hz, 1H), 6.94 (s, 1H); ¹³ C NMR (100 MHz, CDCl ₃) δ 182.8, 154.6, 147.1, 137.3, 135.7, 135.1, 133.8, 132.7, 132.2, 131.5, 129.6, 129.4, 129.2, 128.0, 127.7, 127.0, 126.2, 123.0, 110.8. IR (KBr) ν _{C=O} 1730 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₃ H ₁₅ BrClO ₂ : 436.9943. Found: 436.9938.
2ea		Pale yellow solid; m.p.: 126-127 °C; Eluent: ethyl acetate : hexane = 3 : 97; (633 mg, 70%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.96 (d, <i>J</i> = 7.1 Hz, 2H), 7.79 (d, <i>J</i> = 8.8 Hz, 2H), 7.63 (dd, <i>J</i> = 8.0, 1.1Hz, 1H), 7.49 (tt, <i>J</i> = 6.6, 1.3 Hz, 1H), 7.39 (t, <i>J</i> = 7.7 Hz, 2H), 7.32 (dd, <i>J</i> = 7.6, 1.8 Hz, 1H), 7.26 (dd, <i>J</i> = 7.4, 1.3 Hz, 1H), 7.18 (dd, <i>J</i> = 7.4, 1.9 Hz, 1H), 7.01 (d, <i>J</i> = 8.9 Hz, 2H), 6.82 (s, 1H), 3.87 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 182.6, 160.5, 156.1, 146.5, 137.6, 136.2, 134.2, 132.7, 132.0, 131.5, 129.4, 127.9, 126.9, 126.6, 123.1, 122.0, 114.4, 109.2, 55.3. IR (KBr) ν _{C=O} 1644 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₈ BrO ₃ : 433.0442. Found: 433.0434.
2fa		Pale yellow solid; m.p.: 98-99 °C; Eluent: ethyl acetate : hexane = 3 : 97; (116 mg, 50%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.73 (d, <i>J</i> = 8.1 Hz, 1H), 7.54 (dd, <i>J</i> = 7.9, 0.5 Hz, 1H), 7.40 (d, <i>J</i> = 7.6 Hz, 1H), 7.27 (d, <i>J</i> = 8.4 Hz, 1H), 7.23-7.21 (m, 1H), 7.19-7.17 (m, 2H), 7.15-7.10 (m, 2H), 7.02 (t, <i>J</i> = 7.7 Hz, 1H), 6.85 (s, 1H), 2.45 (s, 3H), 2.42 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 185.2, 156.7, 147.0, 139.6, 137.7, 136.9, 136.1, 133.9, 132.5, 131.3, 130.5, 130.2, 129.6, 129.3, 128.6, 126.7, 126.4, 125.1, 124.7, 123.0, 110.0, 21.4, 19.8. IR (KBr) ν _{C=O} 1644 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₅ H ₂₀ BrO ₂ : 431.0620. Found: 431.0641.
2ga		Pale yellow solid; m.p.: 102-103 °C; Eluent: ethyl acetate : hexane = 3 : 97; (284 mg, 58%). ¹ H NMR (400 MHz, CDCl ₃) δ 7.78 (d, <i>J</i> = 8.3 Hz, 1H), 7.75 (d, <i>J</i> = 8.0 Hz, 2H), 7.70 (d, <i>J</i> = 9.5 Hz, 1H), 7.65 (d, <i>J</i> = 8.0 Hz, 1H), 7.41-7.37 (m, 1H), 7.35-7.28 (m, 4H), 7.23-7.18 (m, 2H), 6.90 (s, 1H), 2.43 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 180.9, 162.2 (d, <i>J</i> _{C-F} = 247.0 Hz), 156.5, 146.3, 139.7, 139.4 (d, <i>J</i> _{C-F} = 6.5 Hz), 136.6, 133.9, 132.7, 131.3, 129.6 (d, <i>J</i> _{C-F} = 10.8 Hz), 127.0, 126.2, 125.2, 125.0, 123.0, 118.9 (d, <i>J</i> _{C-F} = 21.4 Hz), 116.2 (d, <i>J</i> _{C-F} = 22.9 Hz), 110.0, 21.4. IR (KBr) ν _{C=O} 1642 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₇ BrFO ₂ : 435.0378. Found: 435.0390.

Table S2. Physical and spectral data of tropones **1aa-1ga**

compd	structure	Physical and spectral data
1aa		Pale yellow solid; m.p.: 194-195 °C; Eluent: ethyl acetate : hexane = 5 : 95; (65.9 mg, 89%). ¹ H NMR (400 MHz, CDCl ₃): δ 8.42 (dd, <i>J</i> = 7.7, 1.7 Hz, 1H), 7.93 (d, <i>J</i> = 8.0 Hz, 1H), 7.90 (s, 1H), 7.81 (t, <i>J</i> = 8.1 Hz, 3H), 7.72 (td, <i>J</i> = 7.3, 1.1 Hz, 1H), 7.66 (t, <i>J</i> = 7.0 Hz, 1H), 7.53 (dd, <i>J</i> = 8.5, 1.8 Hz, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 7.20 (s, 1H), 2.41(s,3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 178.6, 158.1, 149.3, 139.9, 138.4, 138.0, 136.1, 133.9, 132.0, 131.8, 131.6, 131.4, 129.6, 129.5, 129.2, 128.8, 128.6, 126.8, 126.1, 125.3, 104.0, 21.4. IR (KBr) ν _{C=O} 1628 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₆ ClO ₂ : 371.0833. Found: 371.0823.
1ab		Pale yellow solid; m.p.: 170-171 °C; Eluent: ethyl acetate : hexane = 5 : 95; (60.2 mg, 83%). ¹ H NMR (400 MHz, CDCl ₃): δ 8.43 (d, <i>J</i> = 7.5 Hz, 1H), 7.91 (d, <i>J</i> = 6.5 Hz, 1H), 7.74 (m, 3H), 7.66 (t, <i>J</i> = 7.1 Hz, 1H), 7.61 (t, <i>J</i> = 7.4 Hz, 1H), 7.33 (s, 1H), 7.22 (d, <i>J</i> = 7.4 Hz, 2H), 7.12 (d, <i>J</i> = 3.5 Hz, 1H), 7.05 (s, 1H), 3.87 (s, 3H), 2.38 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 178.5, 158.9, 157.7, 148.5, 139.5, 138.1, 137.9, 137.1, 132.9, 131.4, 131.3, 129.4, 129.3, 129.3, 128.2, 126.2, 125.2, 121.4, 117.0, 114.7, 104.0, 55.3, 21.3. IR (KBr) ν _{C=O} 1610 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₅ H ₁₉ O ₃ : 367.1329. Found: 367.1322.
1ac		Pale yellow solid; m.p.: 178-179 °C; Eluent: ethyl acetate : hexane = 5 : 95; (58.3 mg, 83%). ¹ H NMR (400 MHz, CDCl ₃): δ 8.43 (dd, <i>J</i> = 7.9, 1.6 Hz, 1H), 7.97 (d, <i>J</i> = 8.0 Hz, 1H), 7.78 (d, <i>J</i> = 8.0 Hz, 1H), 7.72 (s, 1H), 7.69 (td, <i>J</i> = 7.6, 1.8 Hz, 1H), 7.62 (td, <i>J</i> = 7.2, 1.2 Hz, 1H), 7.38 (d, <i>J</i> = 8.0 Hz, 1H), 7.27 (d, <i>J</i> = 8.0 Hz, 1H), 7.23 (s, 1H), 2.50 (s, 3H), 2.41 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 178.9, 157.8, 149.1, 139.7, 138.3, 138.1, 137.5, 136.3, 132.9, 132.8, 131.5, 131.3, 129.5, 129.3, 128.1, 127.7, 126.3, 125.6, 125.3, 104.1, 21.4. IR (KBr) ν _{C=O} 1624 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₅ H ₁₉ O ₂ : 351.1380. Found: 351.1375.
1ad		Pale yellow solid; m.p.: 119-120 °C; Eluent: ethyl acetate : hexane = 5 : 95; (57.1 mg, 85%). ¹ H NMR (400 MHz, CDCl ₃): δ 8.41 (dd, <i>J</i> = 7.8, 1.5 Hz, 1H), 7.97 (d, <i>J</i> = 7.9, 1.1 Hz, 1H), 7.92 (t, <i>J</i> = 9.4, 1.6 Hz, 2H), 7.81 (d, <i>J</i> = 8.1 Hz, 2H), 7.68 (td, <i>J</i> = 7.2, 1.6 Hz, 1H), 7.62 (td, <i>J</i> = 7.9, 1.6 Hz, 1H), 7.57 (td, <i>J</i> = 7.4, 1.5 Hz, 1H), 7.52 (td, <i>J</i> = 7.9, 1.8 Hz, 1H), 7.27 (s, 1H), 7.26 (s, 1H), 7.25 (s, 1H), 2.40 (s, 3H); ¹³ C NMR (100 MHz, CDCl ₃) δ 179.0, 157.9, 149.4, 139.7, 138.3, 137.4, 136.4, 132.7, 132.3, 131.6, 131.4, 129.5, 129.3, 128.5, 128.2, 127.7, 126.2, 125.3, 104.1, 21.4. IR (KBr) ν _{C=O} 1627 cm ⁻¹ . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for C ₂₄ H ₁₇ O ₂ : 337.1223. Found: 337.1230.
1ae		Pale yellow solid; m.p.: 161-162 °C; Eluent: ethyl acetate : hexane = 5 : 95; (50.1 mg, 73%). ¹ H NMR (400 MHz, CDCl ₃): δ 8.88 (dd, <i>J</i> = 8.1, 1.1Hz, 1H), 8.25 (d, <i>J</i> = 8.1 Hz, 1H), 7.87 (m, 3H), 7.75 (t, <i>J</i> = 7.5 Hz, 1H), 7.65 (t, <i>J</i> = 8.0 Hz, 1H), 7.52

		(d, $J = 5.4$ Hz, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.09 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.4, 159.2, 147.8, 140.2, 137.7, 135.5, 132.7, 132.0, 131.6, 131.5, 129.6, 129.4, 129.3, 128.6, 128.1, 125.9, 125.6, 125.2, 103.8, 21.6. IR (KBr) $\nu_{\text{C=O}}$ 1609 cm^{-1} . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for $\text{C}_{22}\text{H}_{15}\text{O}_2\text{S}$: 343.0787. Found: 343.0788.
1af		Pale yellow solid; m.p.: 75-76 °C; Eluent: ethyl acetate : hexane = 5 : 95; (53.8 mg, 79%). ^1H NMR (400 MHz, CDCl_3): δ 8.41 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.99 (dd, $J = 8.0, 0.9$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.72 (s, 1H), 7.69 (td, $J = 7.2, 1.6$ Hz, 1H), 7.62 (m, 2H), 7.41 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.38 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.13 (t, $J = 3.7$ Hz, 1H), 7.12 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.7, 153.0, 138.3, 137.4, 136.4, 132.8, 131.7, 131.5, 131.3, 129.5, 129.3, 128.1, 128.0, 127.7, 127.1, 126.1, 125.3, 104.6, 21.4. IR (KBr) $\nu_{\text{C=O}}$ 1622 cm^{-1} . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for $\text{C}_{22}\text{H}_{15}\text{O}_2\text{S}$: 343.0787. Found: 343.0790.
1da		Pale yellow solid; m.p.: 200-201 °C; Eluent: ethyl acetate : hexane = 5 : 95; (53.1 mg, 74%). ^1H NMR (400 MHz, CDCl_3): δ 8.42 (dd, $J = 7.9, 1.6$ Hz, 1H), 8.00 (d, $J = 8.0, 1$ H), 7.97 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.94 (tt, $J = 7.7, 1.7$ Hz, 1H), 7.88 (d, $J = 8.7$ Hz, 2H), 7.73 (td, $J = 7.3, 1.7$ Hz, 1H), 7.66 (d, $J = 7.8, 1.2$ Hz, 1H), 7.56-7.62 (m, 2H), 7.47 (d, $J = 8.7$ Hz, 2H), 7.34 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 179.1, 156.3, 149.7, 138.2, 137.4, 136.4, 135.4, 132.4, 131.6, 131.5, 129.2, 129.1, 128.5, 128.3, 128.2, 127.8, 127.6, 127.4, 126.5, 125.3, 105.1. IR (KBr) $\nu_{\text{C=O}}$ 1628 cm^{-1} . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for $\text{C}_{23}\text{H}_{14}\text{ClO}_2$: 357.0677. Found: 357.0679.
1ea		Pale yellow solid; m.p.: 122-123 °C; Eluent: ethyl acetate : hexane = 5 : 95; (63.4 mg, 90%). ^1H NMR (400 MHz, CDCl_3): δ 8.43 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.96 (dd, $J = 7.9, 0.6$ Hz, 1H), 7.91 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.89-7.84 (m, 3H), 7.68 (td, $J = 7.2, 1.7$ Hz, 1H), 7.62 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.55 (dd, $J = 7.4, 1.5$ Hz, 1H), 7.51 (dd, $J = 7.4, 1.5$ Hz, 1H), 7.17 (s, 1H), 6.97 (d, $J = 8.9$ Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.7, 160.7, 157.8, 149.2, 138.2, 137.4, 136.4, 132.9, 132.3, 131.5, 131.3, 129.2, 128.4, 128.1, 127.7, 126.9, 121.7, 114.3, 103.3, 55.3. IR (KBr) $\nu_{\text{C=O}}$ 1625 cm^{-1} . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for $\text{C}_{24}\text{H}_{17}\text{O}_3$: 353.1172. Found: 353.1165.
1fa		Pale yellow solid; m.p.: 158-159 °C; Eluent: ethyl acetate : hexane = 5 : 95; (59.0 mg, 84%). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.9$ Hz, 1H), 7.80-7.75 (m, 3H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.55-7.51 (m, 1H), 7.49-7.43 (m, 3H), 7.27 (d, $J = 7.9$ Hz, 2H), 7.15 (s, 1H), 2.77 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.7, 155.9, 150.0, 138.2, 137.3, 137.0, 136.0, 131.4, 130.5, 129.3, 128.8, 128.4, 127.2, 126.5, 125.8, 125.5, 124.0, 102.2, 21.5, 20.3. IR (KBr) $\nu_{\text{C=O}}$ 1645 cm^{-1} . HRMS (ESI-TOF) m/z [M+H] ⁺ Calcd. for $\text{C}_{25}\text{H}_{19}\text{O}_2$: 351.1380. Found: 351.1378.

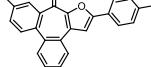
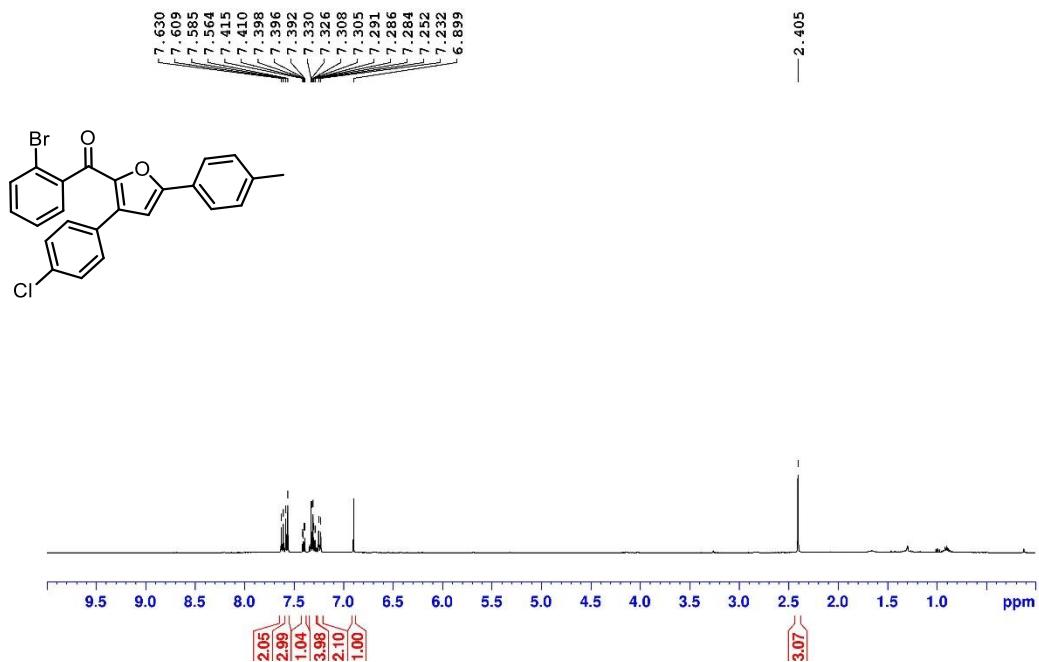
1ga	 <p>Pale yellow solid; m.p.: 148 -149 °C; Eluent: ethyl acetate : hexane = 5 : 95; (24.1 mg, 35%). ^1H NMR (400 MHz, (CDCl_3)) δ 8.13 (d, J = 7.9 Hz, 1H), 7.96 (t, J = 8.0 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.61-7.54 (m, 2H), 7.50-7.43 (m, 2H), 7.29 (d, J = 7.4 Hz, 2H), 7.25 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, (CDCl_3)) δ 178.2, 160.4 (d, $J_{\text{C}-\text{F}}$ = 250.1 Hz), 158.1, 149.3, 141.4, 139.8, 134.0, 133.9 (d, $J_{\text{C}-\text{F}}$ = 11.6 Hz), 129.5, 129.2, 129.1, 128.9, 128.6, 127.8, 126.8, 126.1, 125.8 (d, $J_{\text{C}-\text{F}}$ = 10.5 Hz), 125.2, 124.8, 119.5 (d, $J_{\text{C}-\text{F}}$ = 26.1 Hz), 104.1, 21.3. IR (KBr) $\nu_{\text{C=O}}$ 1636 cm^{-1}. HRMS (ESI-TOF) m/z [M+H]$^+$ Calcd. for $\text{C}_{24}\text{H}_{16}\text{FO}_2$: 355.1129. Found: 355.1123.</p>
------------	--

Figure S1 ^1H NMR spectrum of compound **2aa** (400 MHz, CDCl_3)



¹³C NMR spectrum of compound **2aa** (100 MHz, CDCl₃)

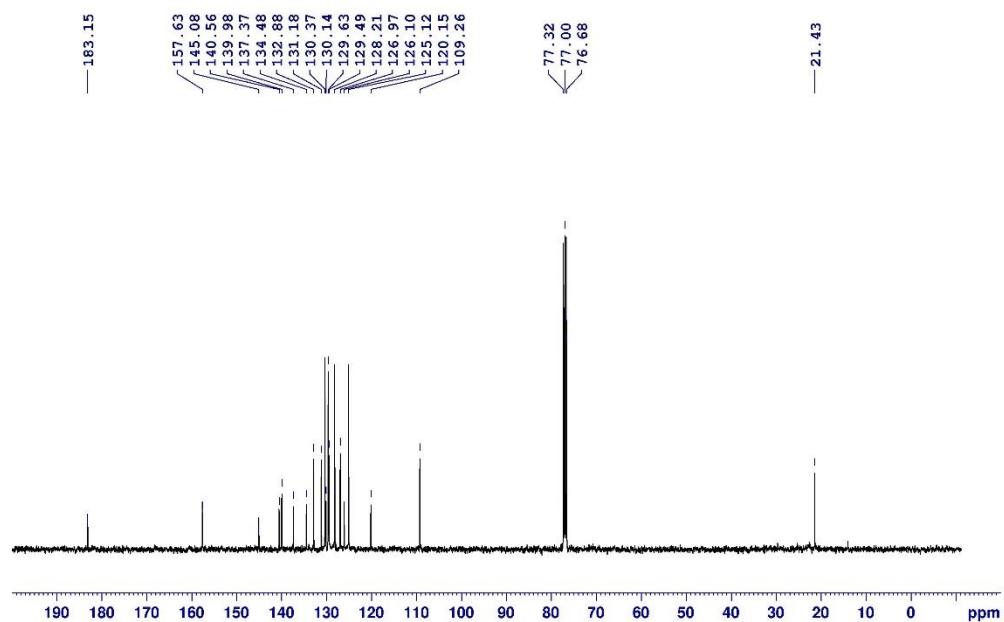
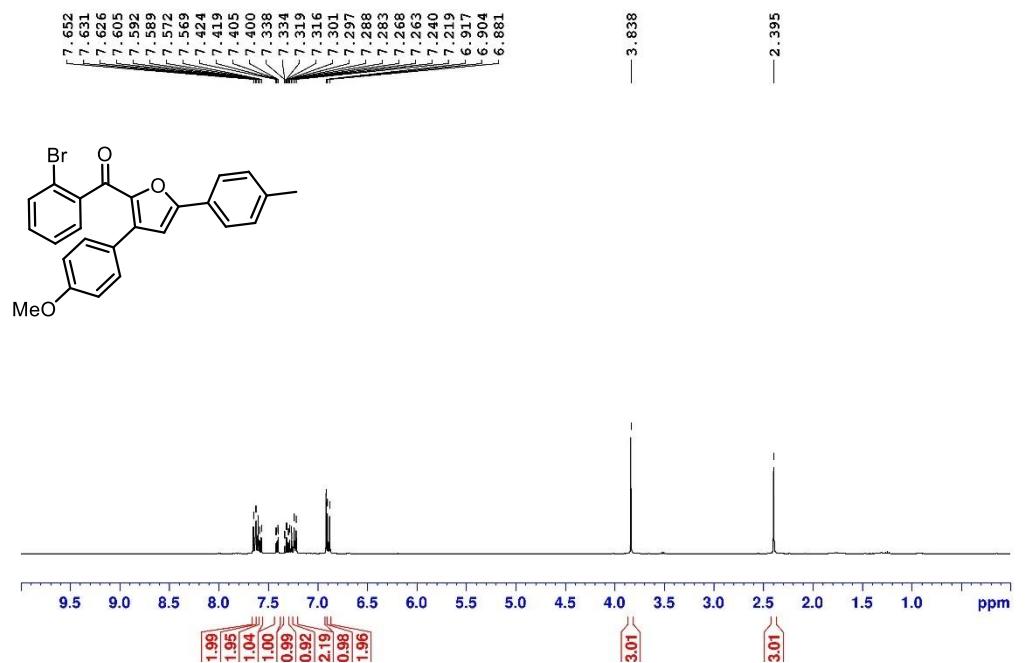


Figure S2 ^1H NMR spectrum of compound **2ab** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2ab** (100 MHz, CDCl_3)

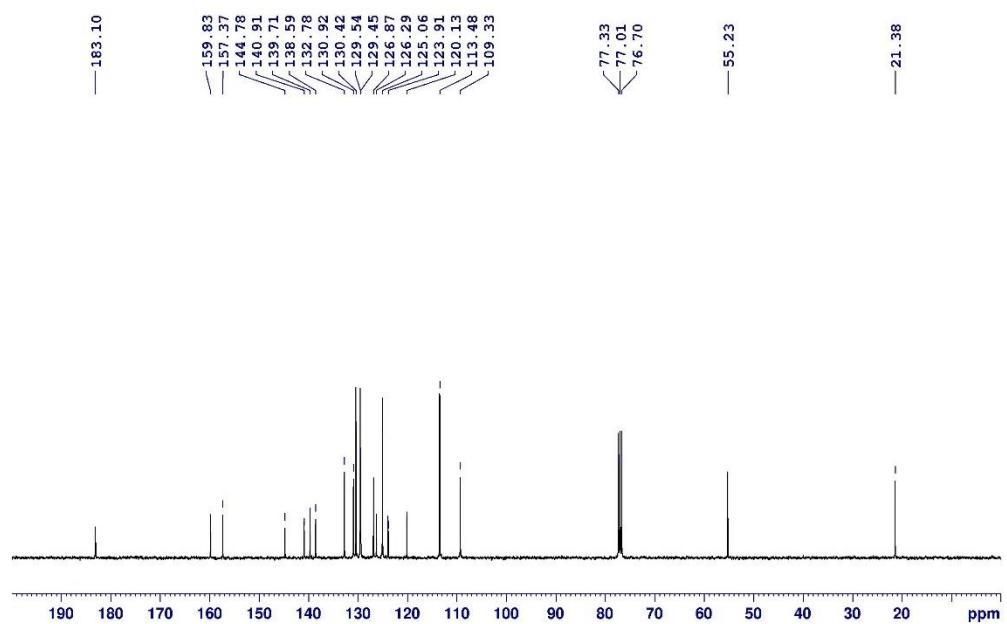
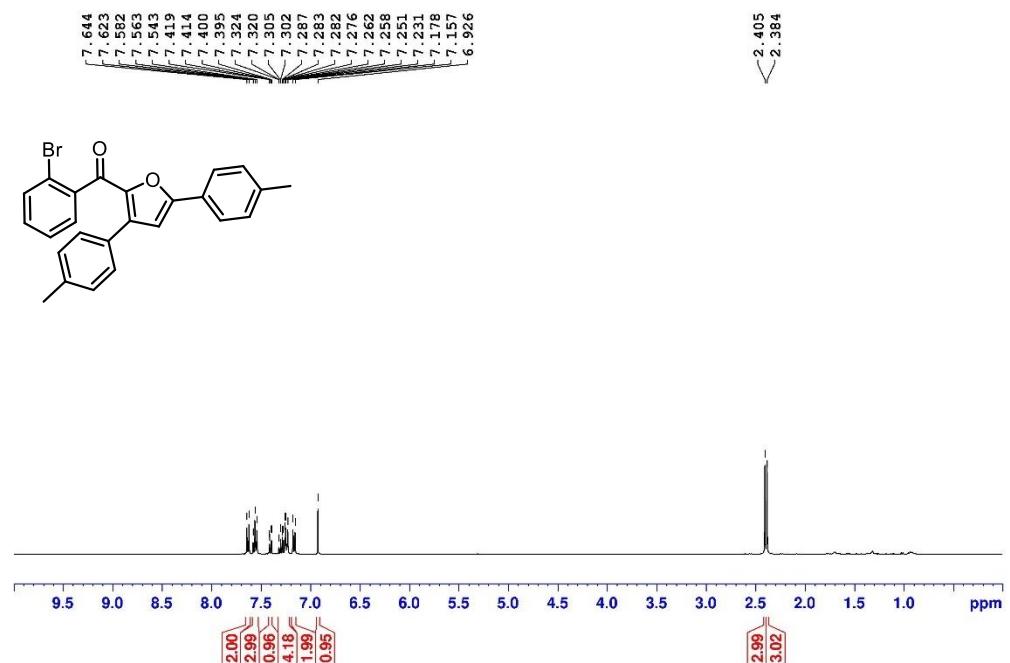


Figure S3 ^1H NMR spectrum of compound **2ac** (400 MHz, CDCl_3)



¹³C NMR spectrum of compound **2ac** (100 MHz, CDCl₃)

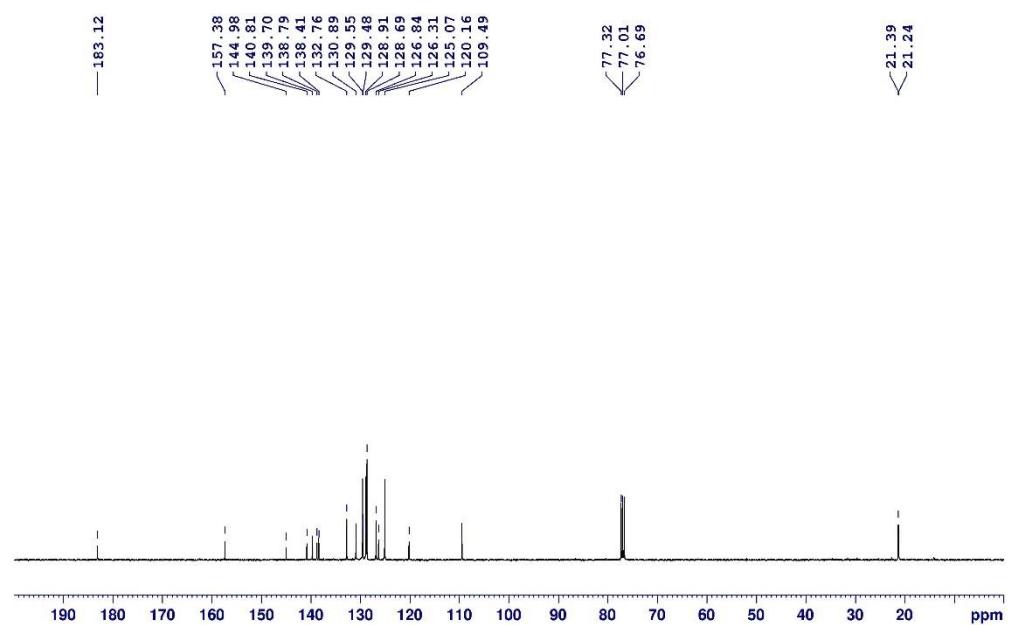
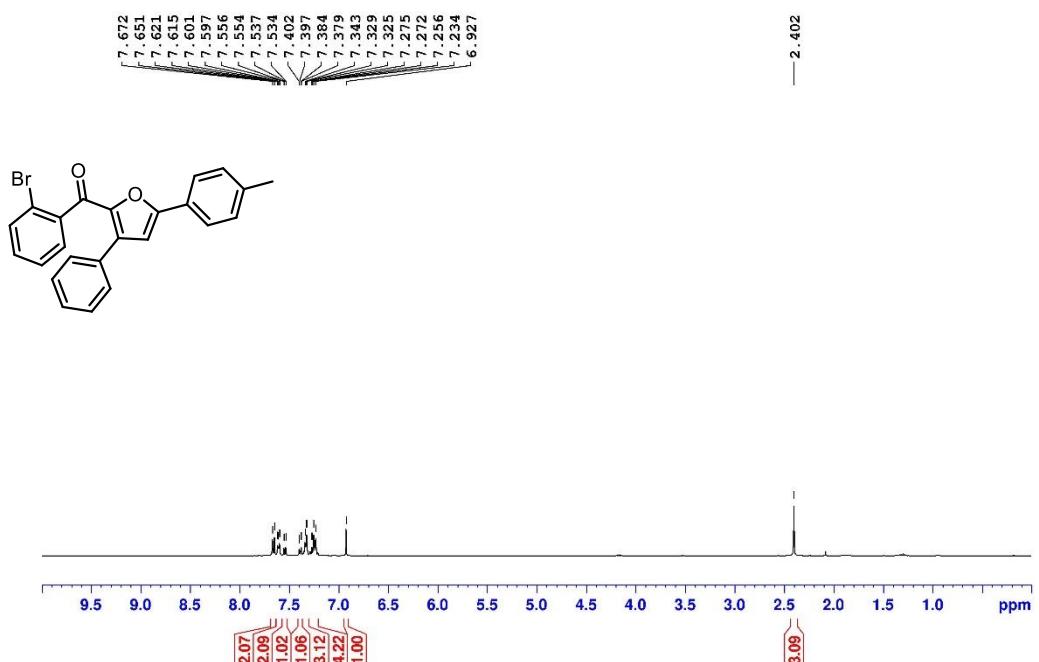


Figure S4 ^1H NMR spectrum of compound **2ad** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2ad** (100 MHz, CDCl_3)

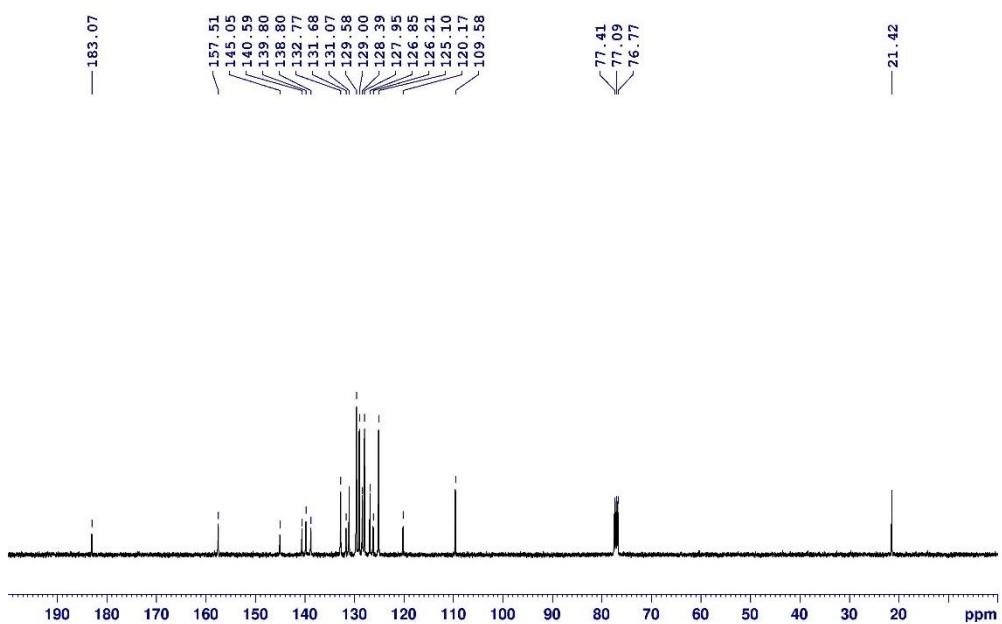
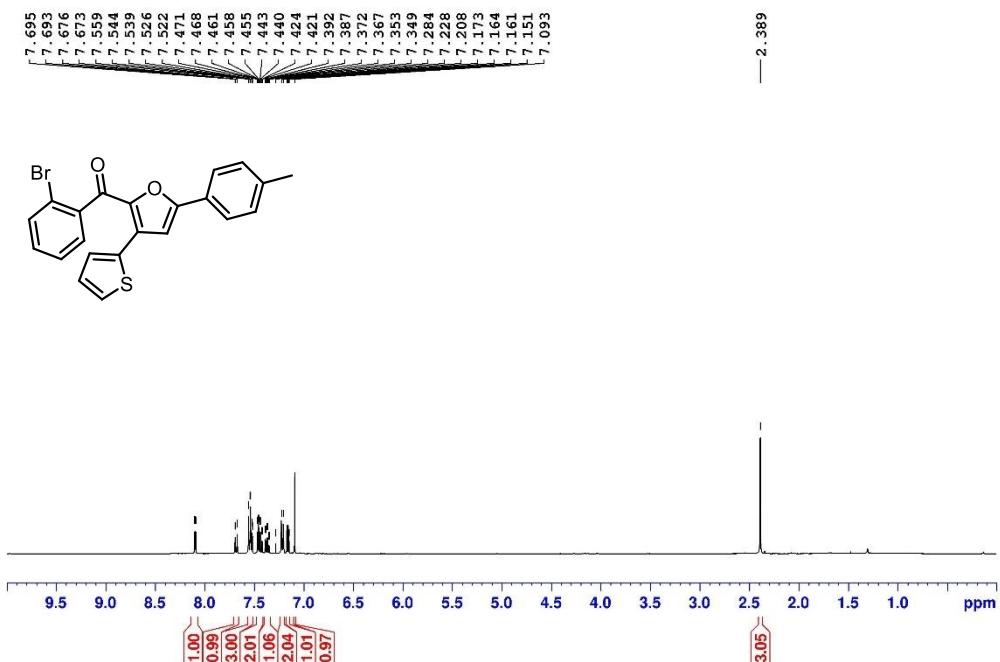


Figure S5 ^1H NMR spectrum of compound **2ae** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2ae** (100 MHz, CDCl_3)

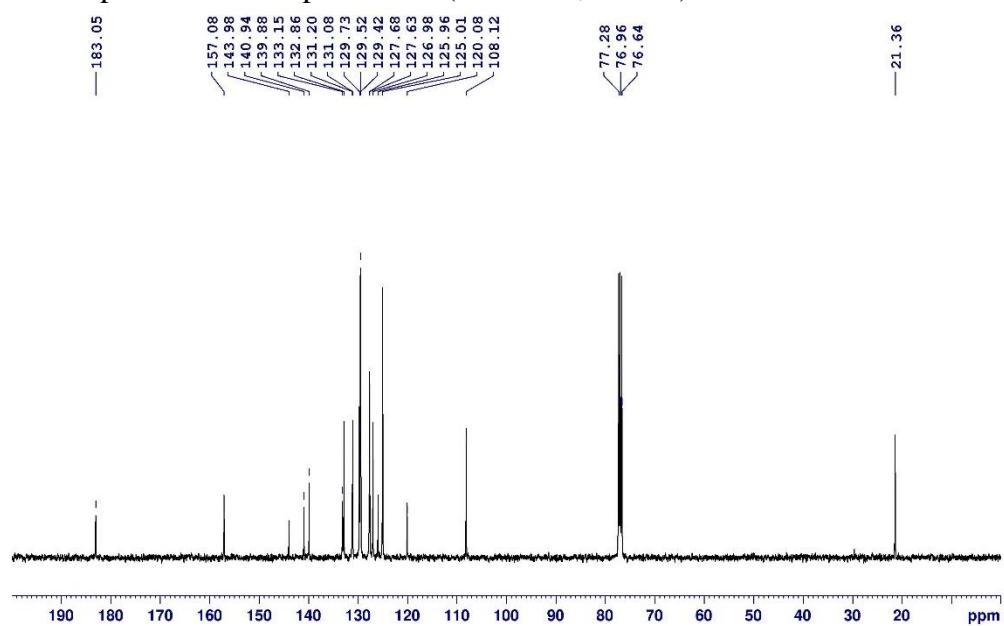
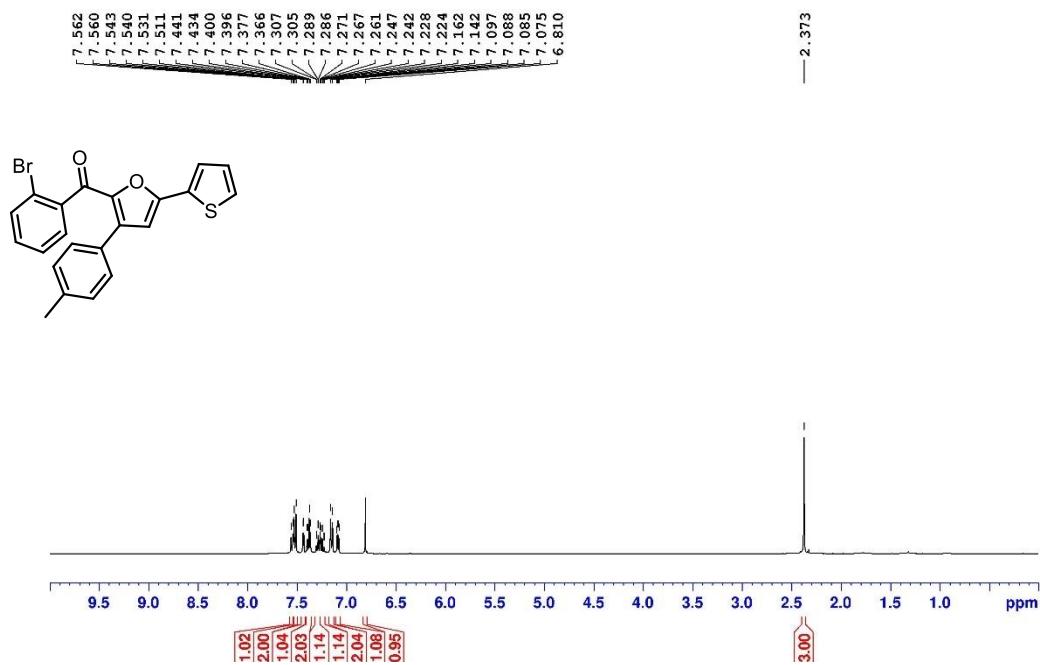


Figure S6 ^1H NMR spectrum of compound **2af** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2af** (100 MHz, CDCl_3)

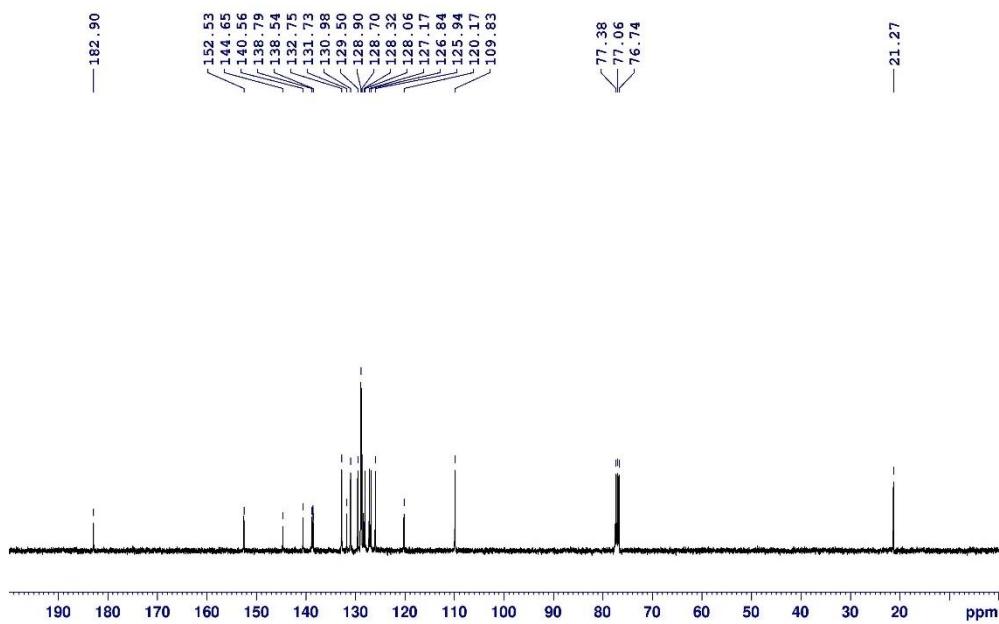
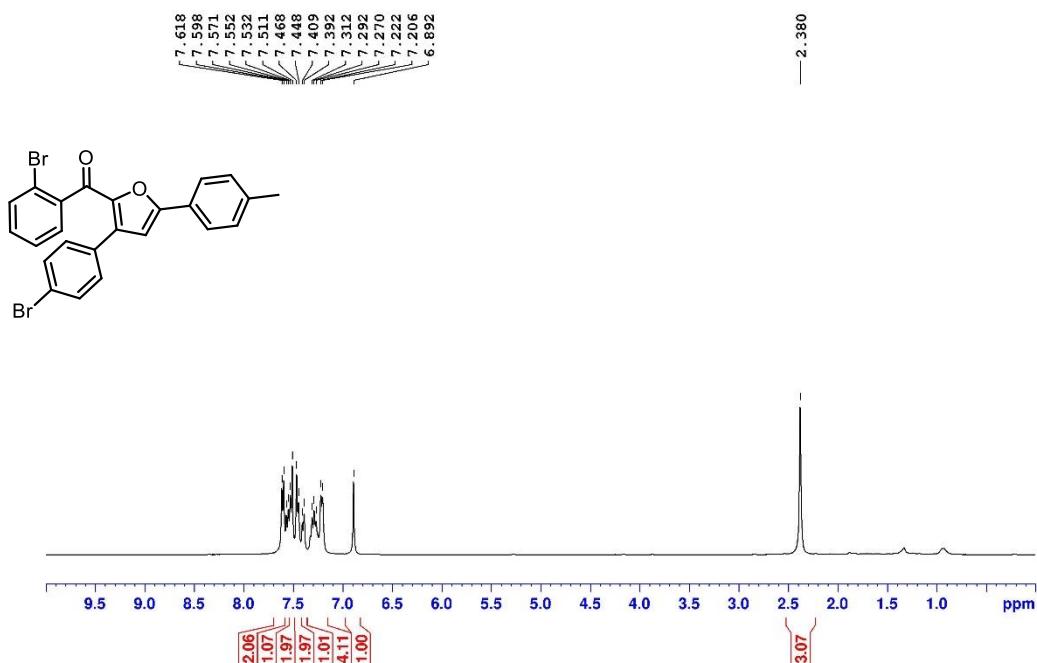


Figure S7 ^1H NMR spectrum of compound **2ag** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2ag** (100 MHz, CDCl_3)

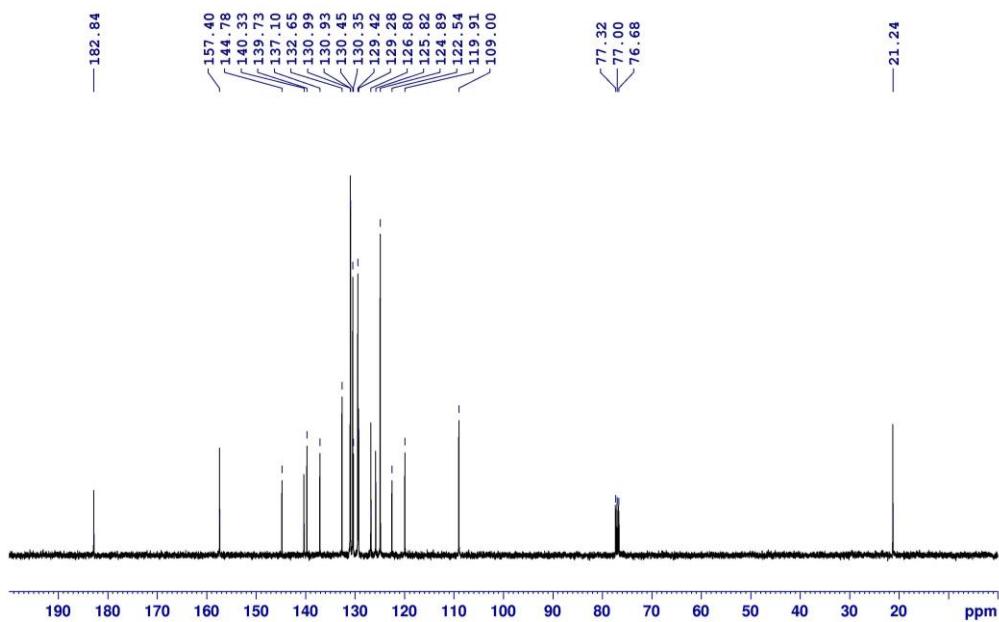
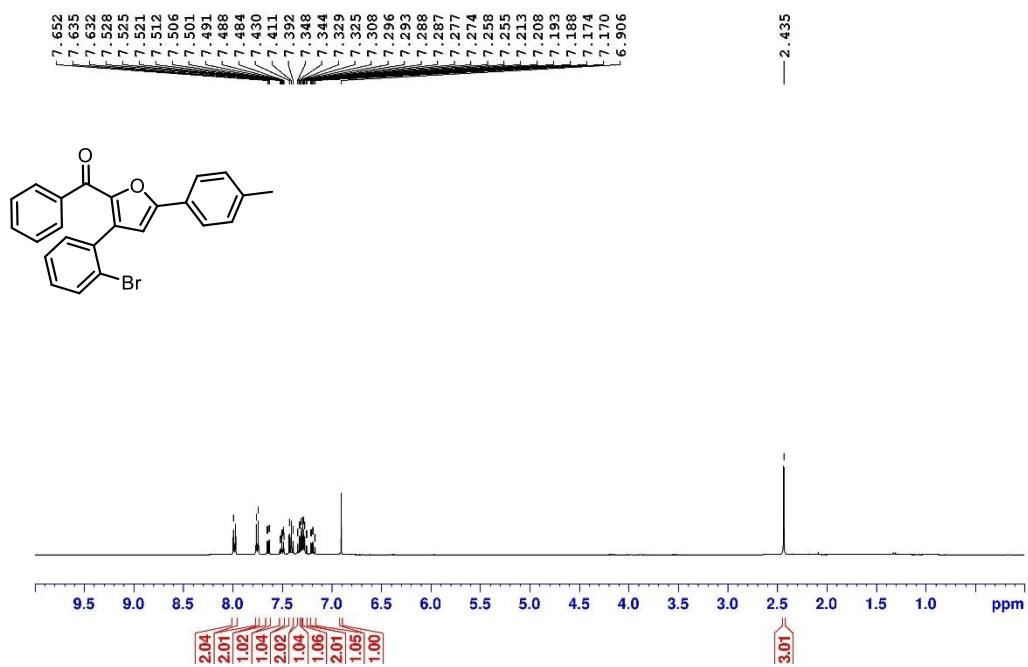


Figure S8 ^1H NMR spectrum of compound **2ba** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2ba** (100 MHz, CDCl_3)

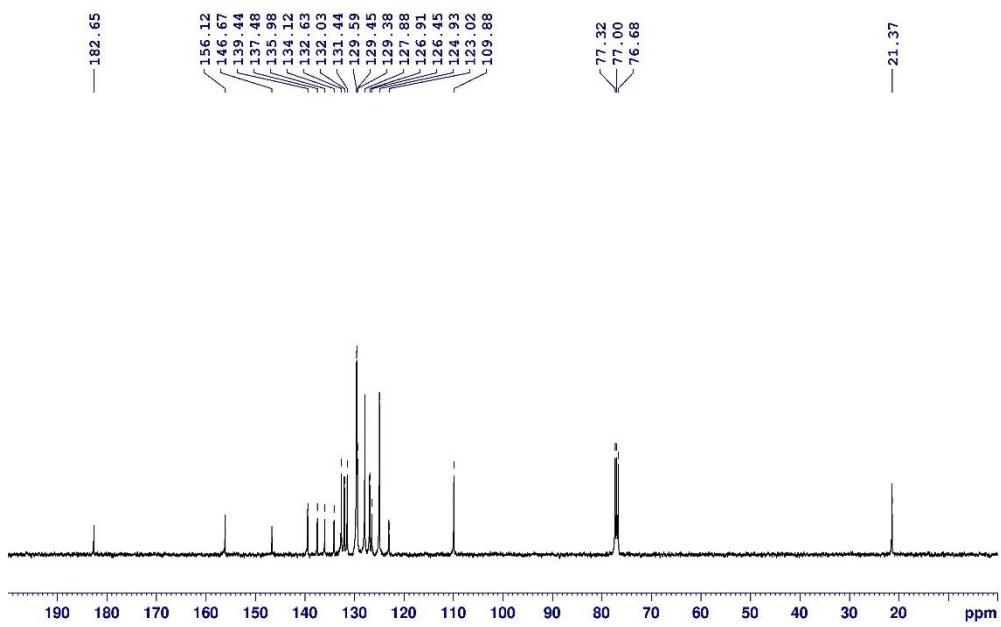
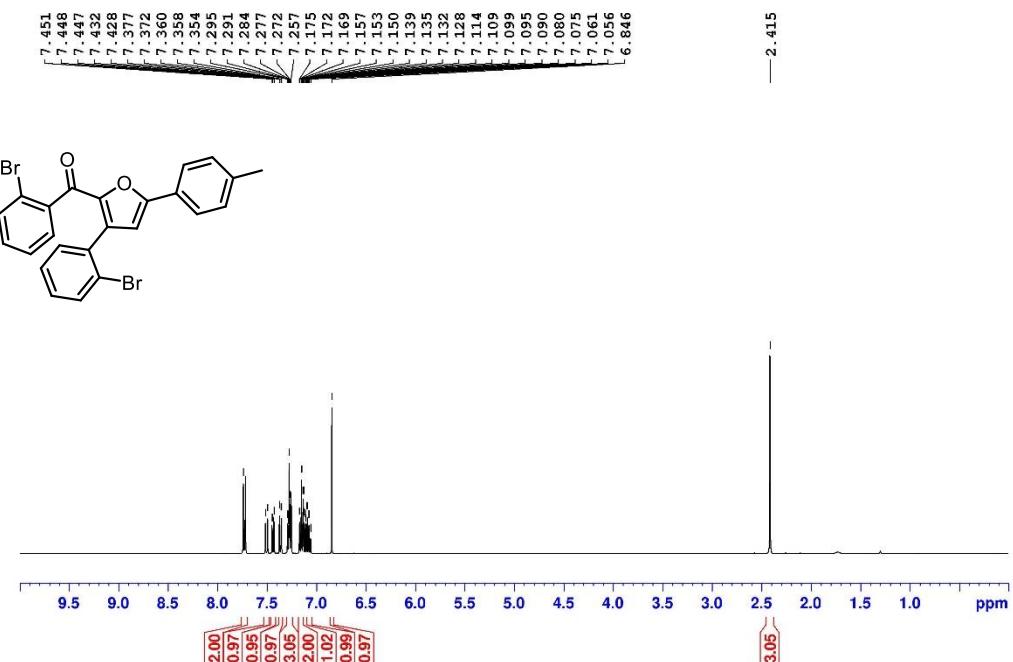


Figure S9 ^1H NMR spectrum of compound **2ca** (400 MHz, CDCl_3)



¹³C NMR spectrum of compound **2ca** (100 MHz, CDCl₃)

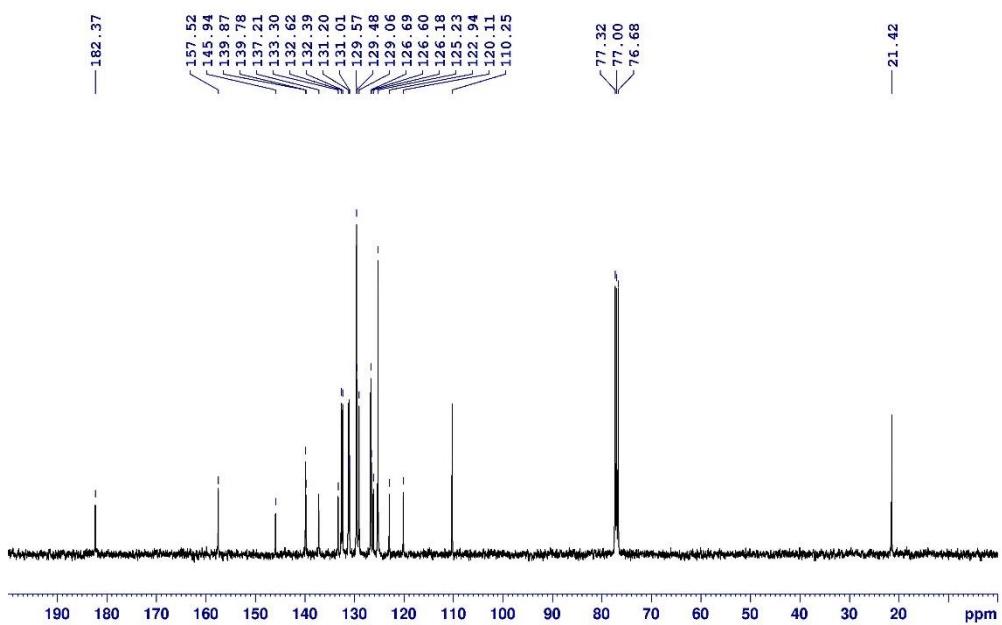
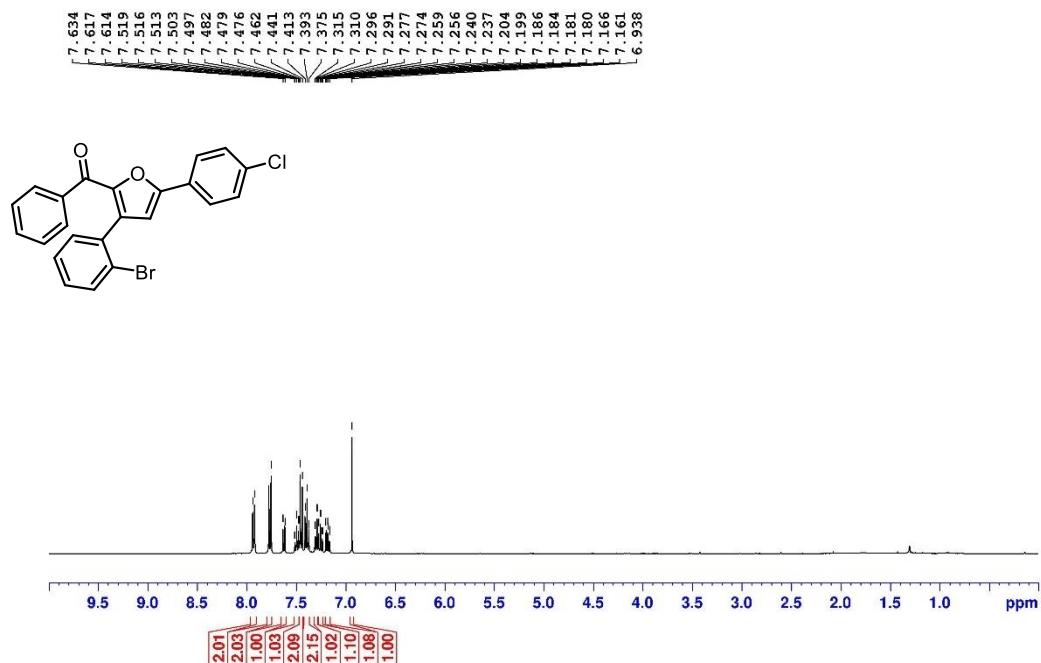


Figure S10 ^1H NMR spectrum of compound **2da** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2da** (100 MHz, CDCl_3)

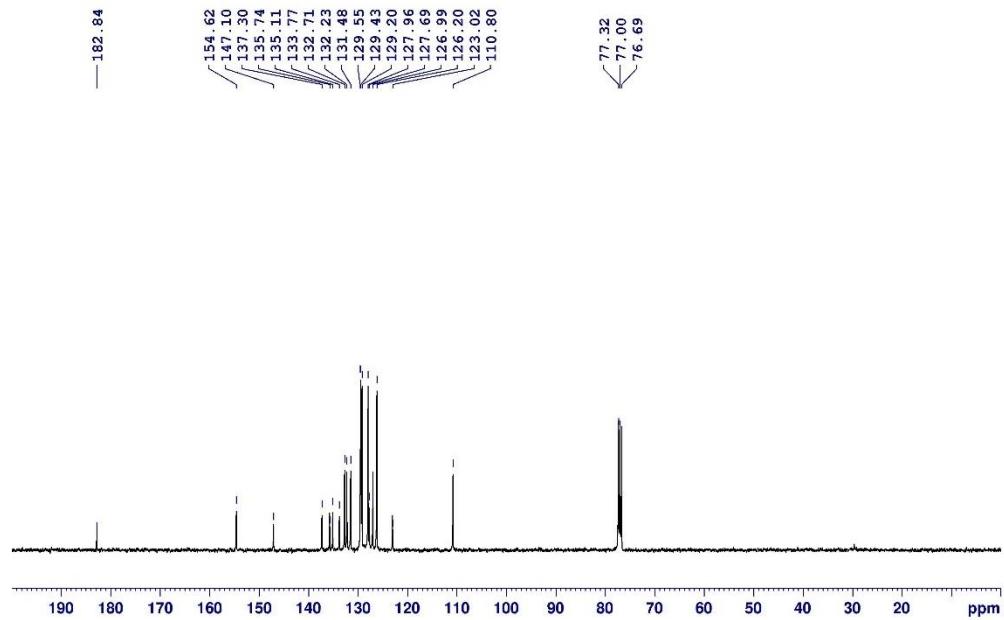
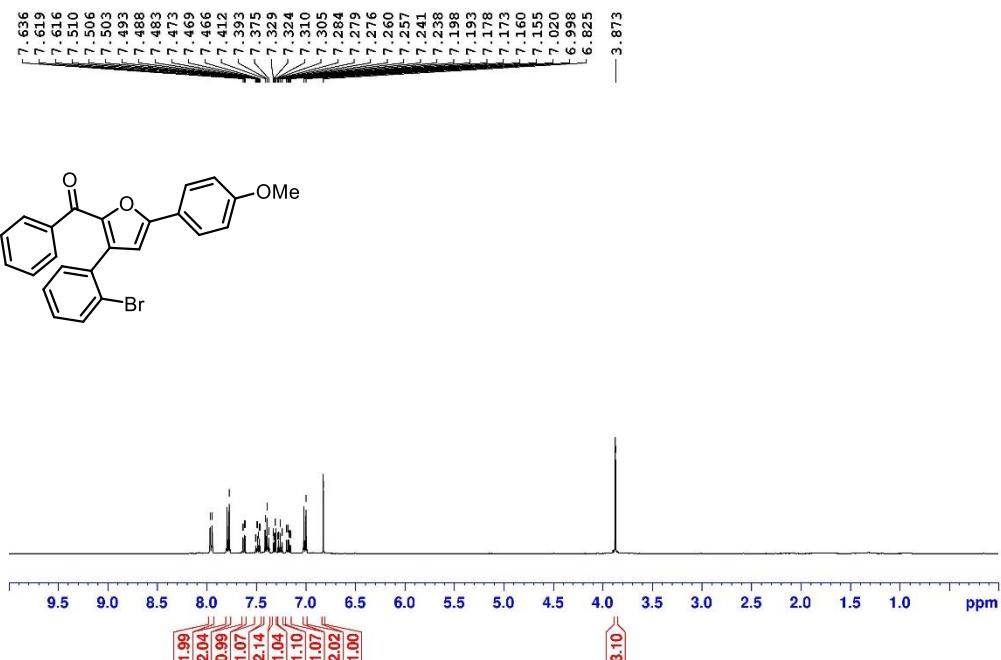


Figure S11 ^1H NMR spectrum of compound **2ea** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2ea** (100 MHz, CDCl_3)

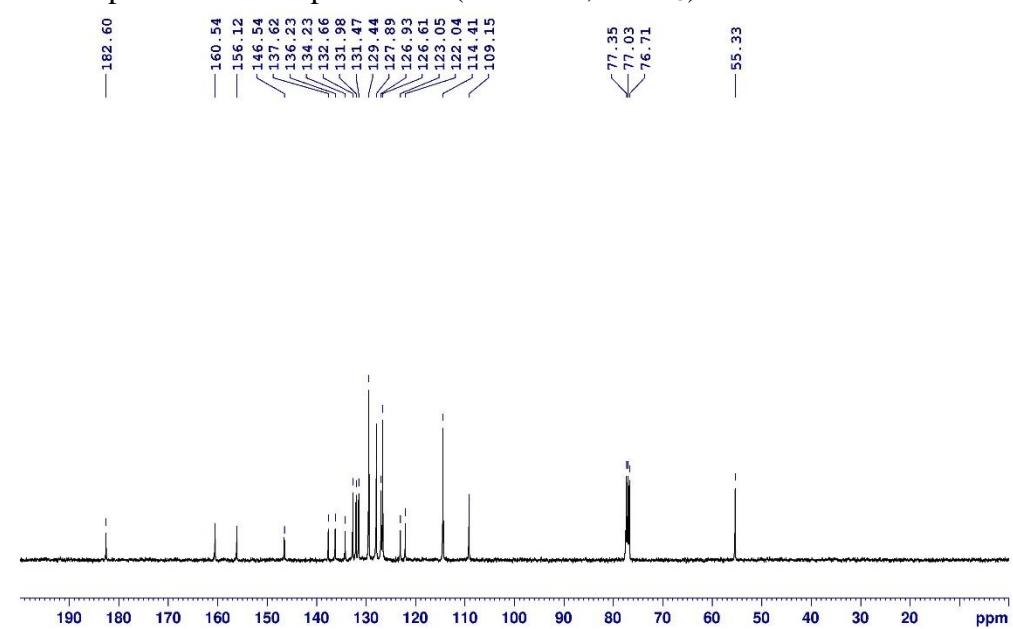
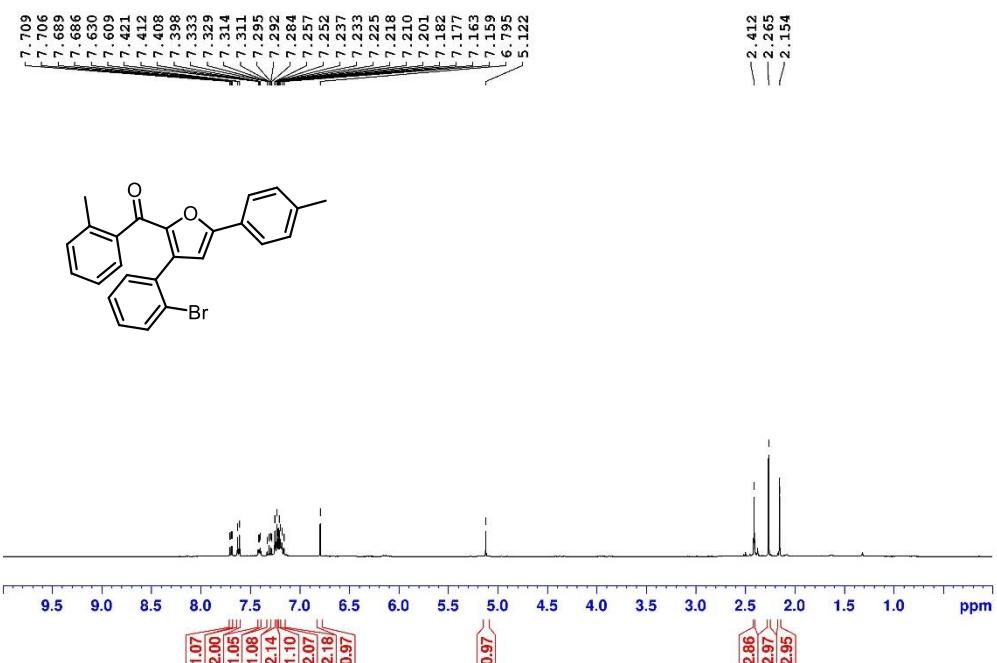


Figure S12 ^1H NMR spectrum of compound **2fa** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2fa** (100 MHz, CDCl_3)

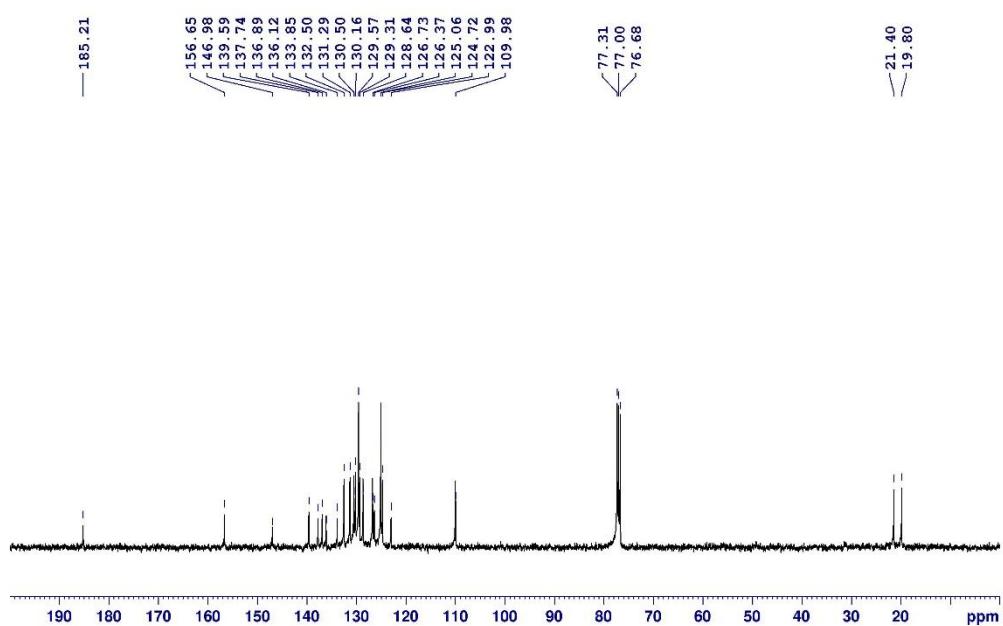
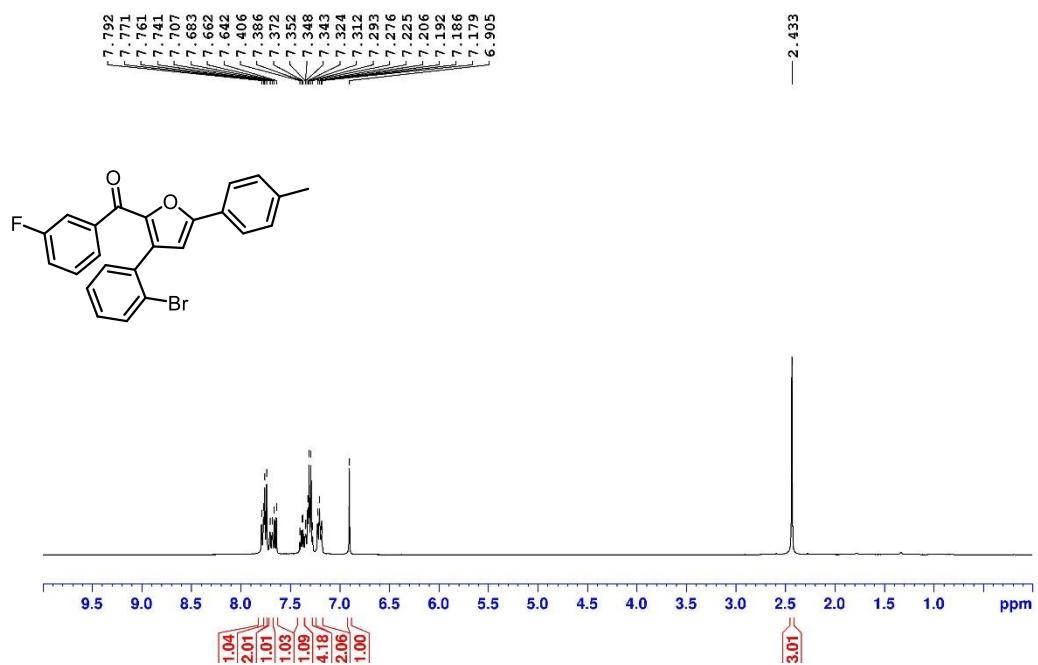


Figure S13 ^1H NMR spectrum of compound **2ga** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **2ga** (100 MHz, CDCl_3)

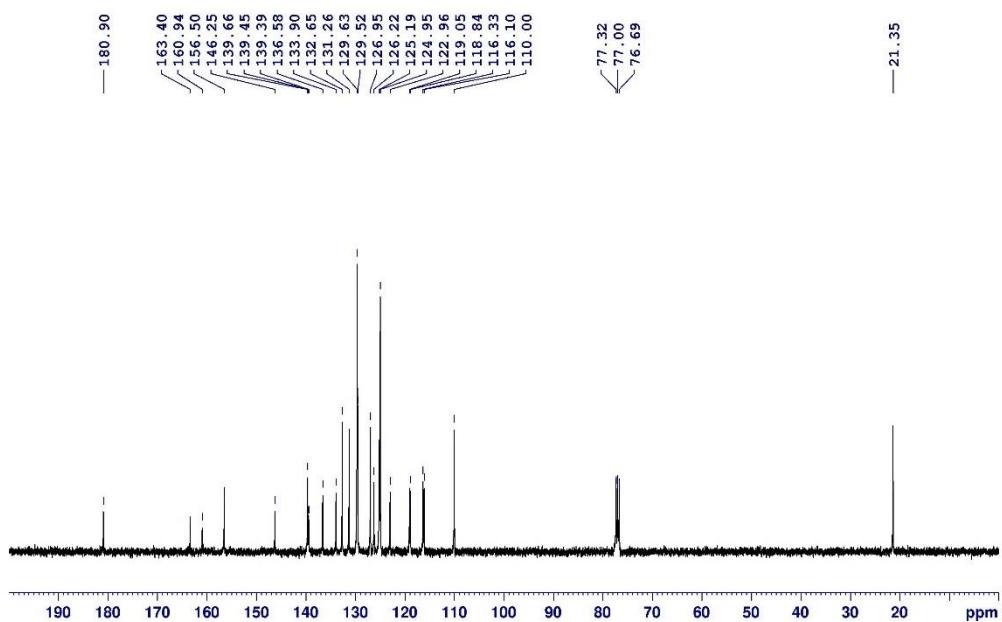
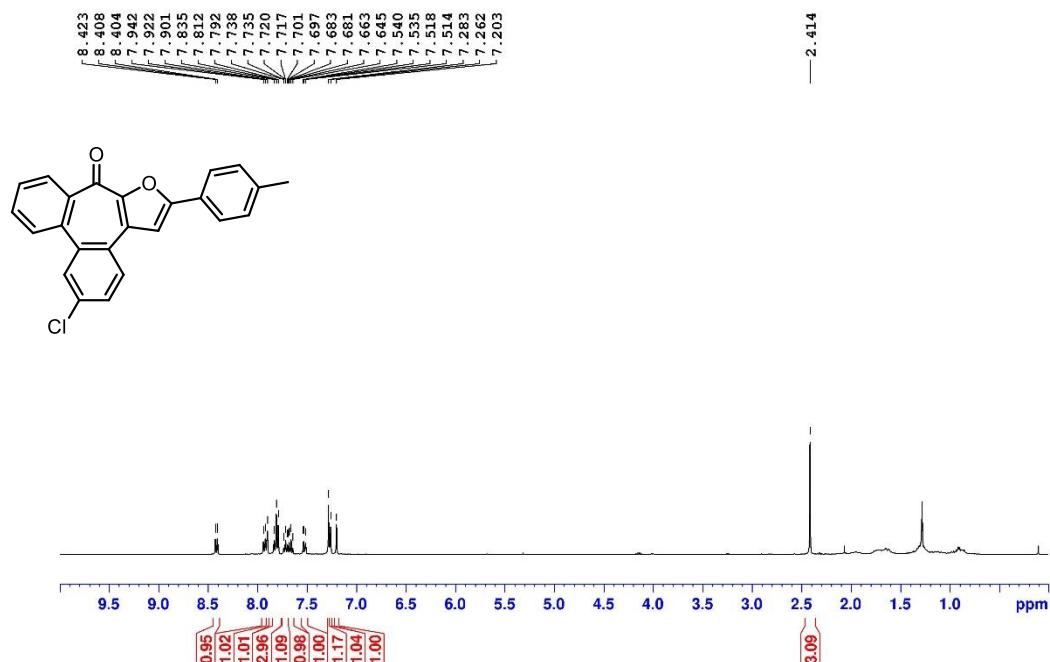


Figure S14 ^1H NMR spectrum of compound **1aa** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1aa** (100 MHz, CDCl_3)

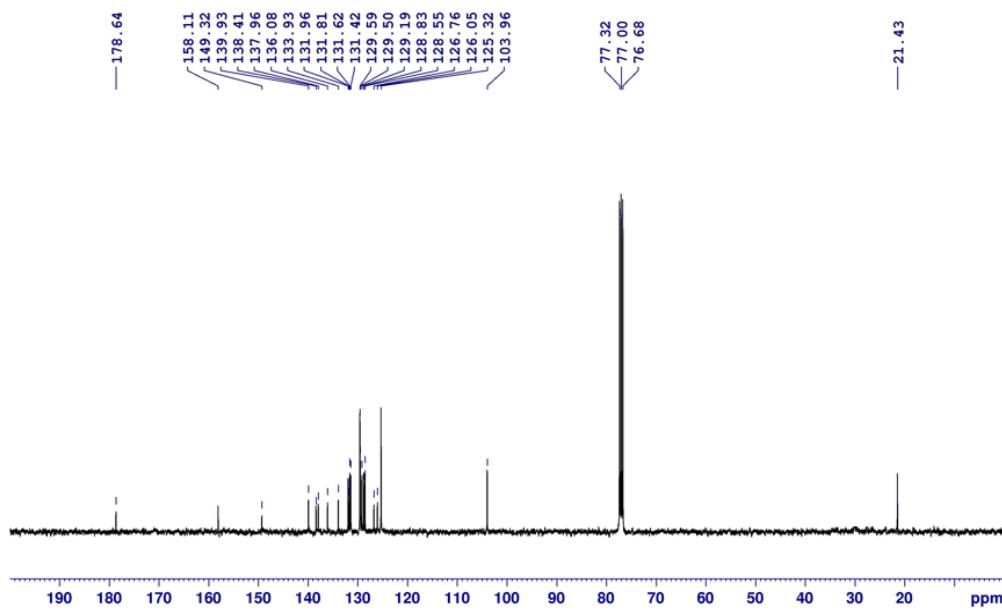
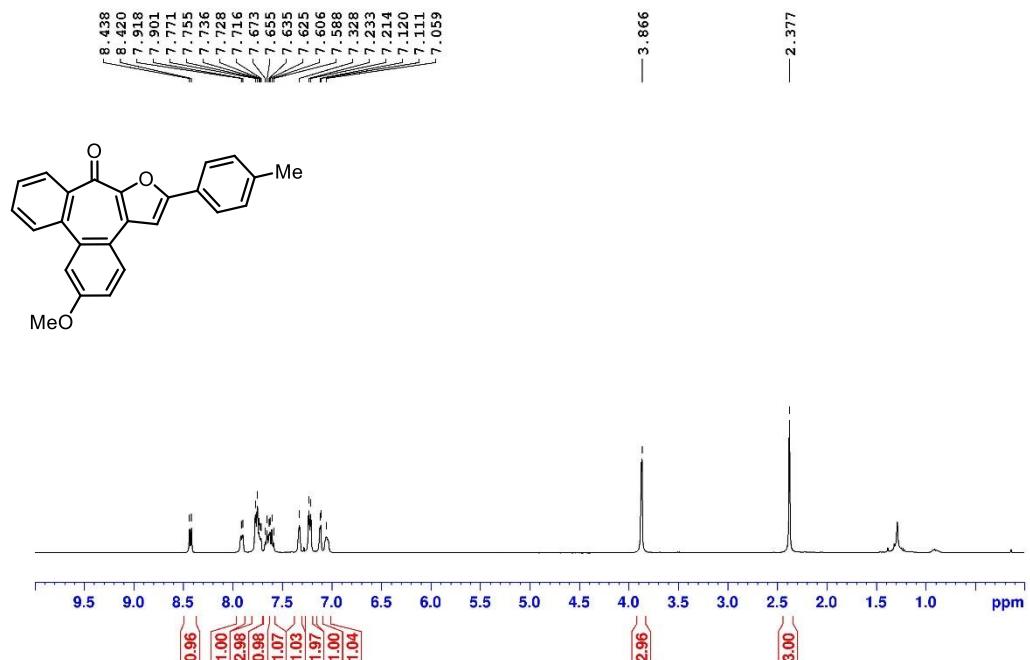


Figure S15 ^1H NMR spectrum of compound **1ab** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1ab** (100 MHz, CDCl_3)

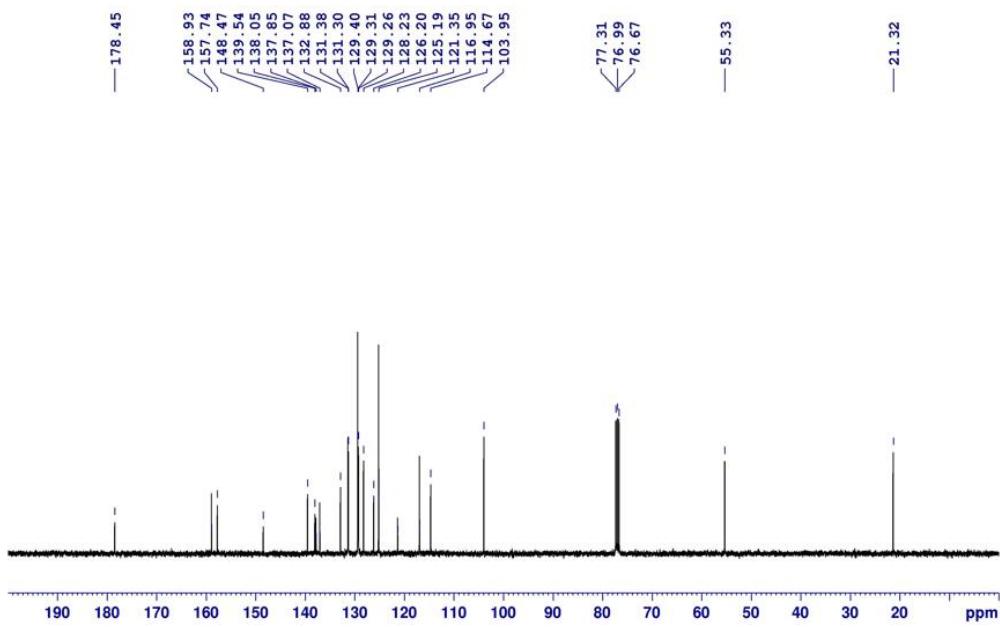
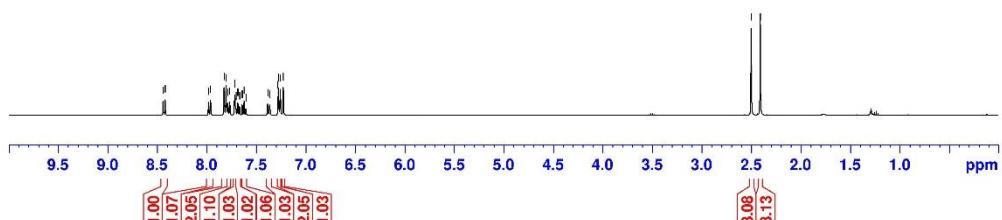
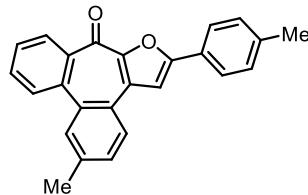
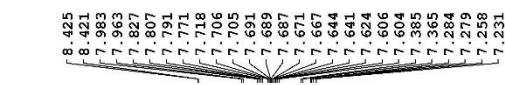


Figure S16 ^1H NMR spectrum of compound **1ac** (400 MHz, CDCl_3)



¹³C NMR spectrum of compound **1ac** (100 MHz, CDCl₃)

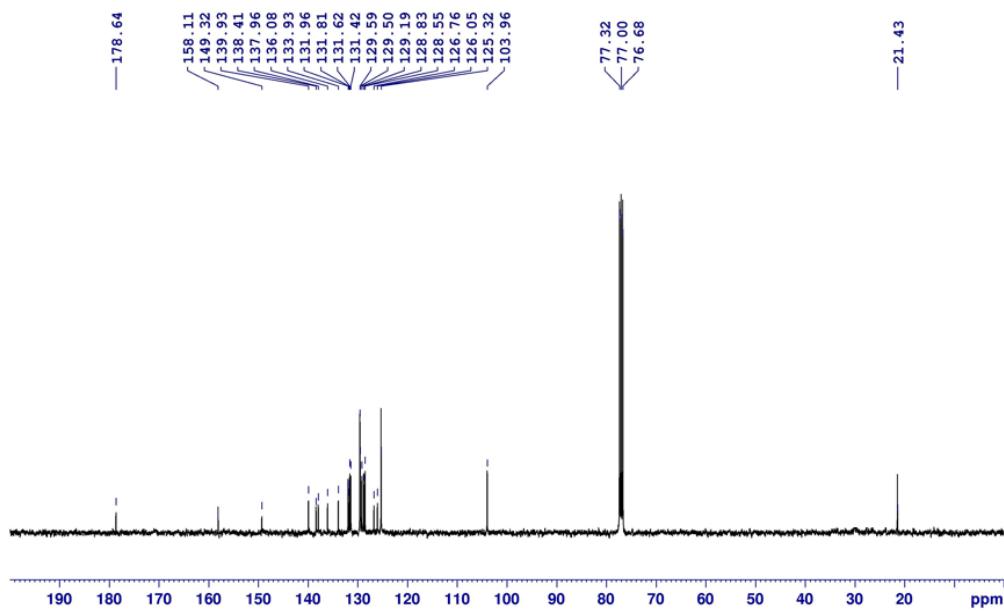
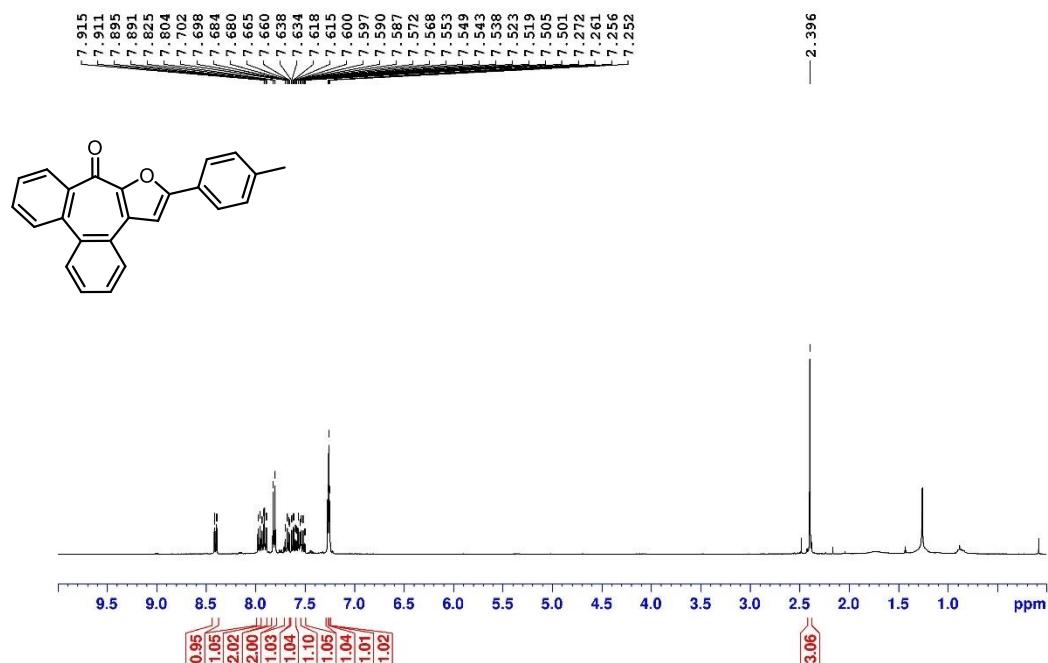


Figure S17 ^1H NMR spectrum of compound **1ad** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1ad** (100 MHz, CDCl_3)

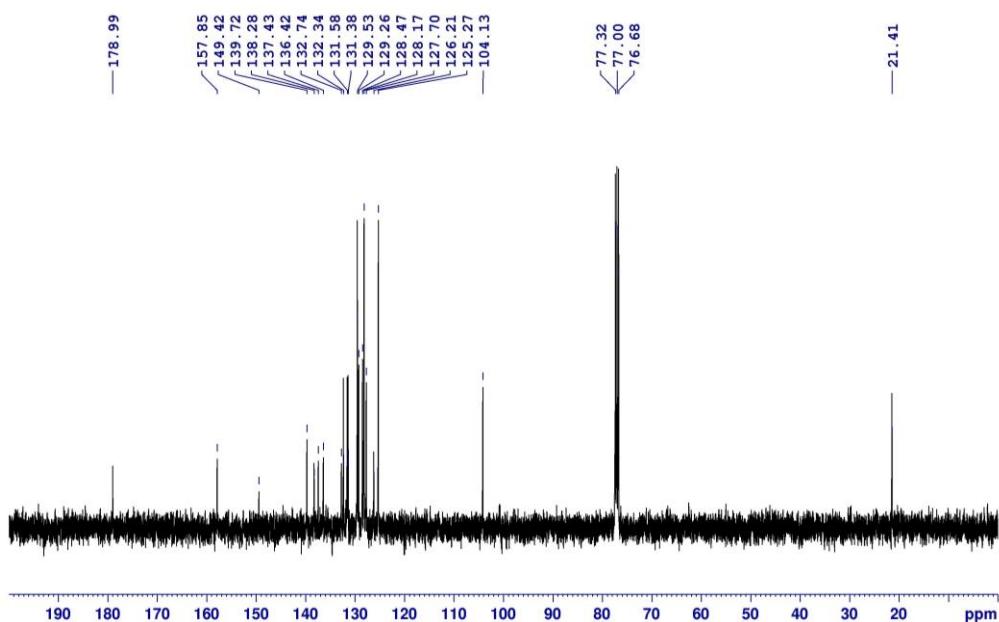
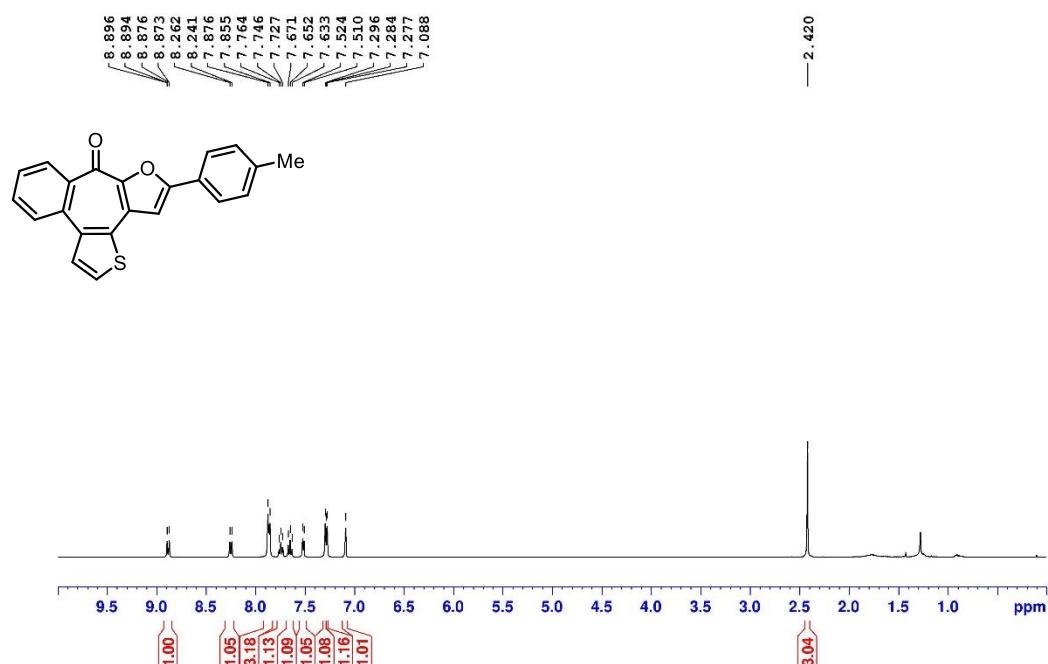


Figure S18 ^1H NMR spectrum of compound **1ae** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1ae** (100 MHz, CDCl_3)

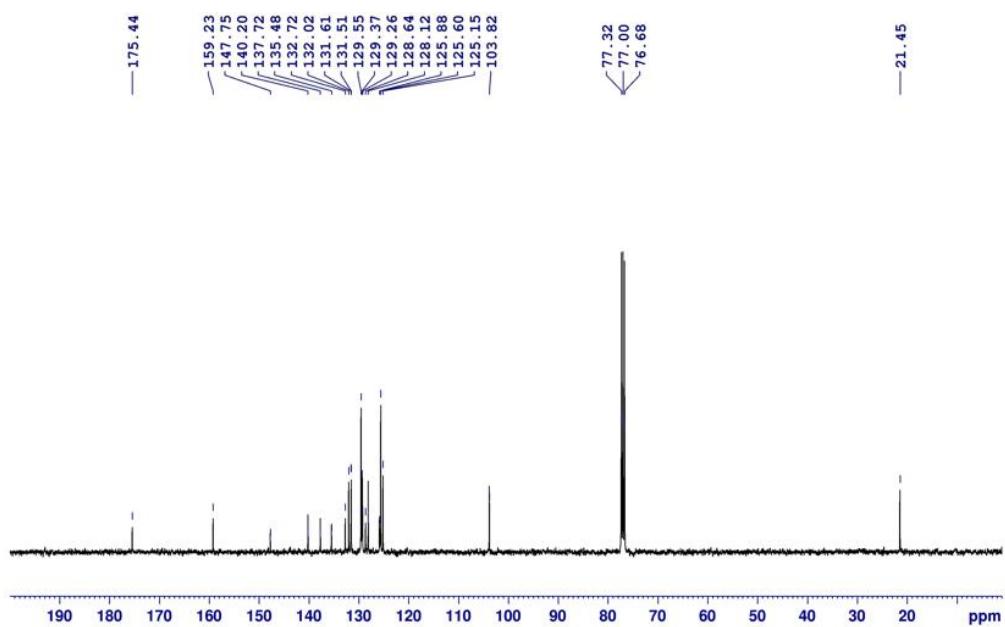
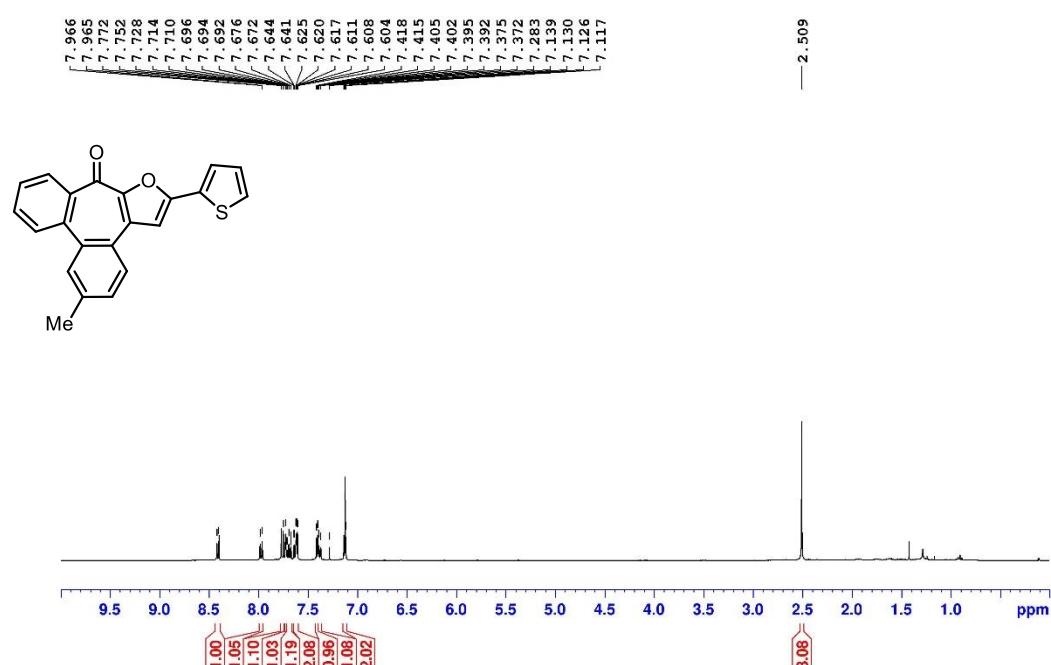


Figure S19 ^1H NMR spectrum of compound **1af** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1af** (100 MHz, CDCl_3)

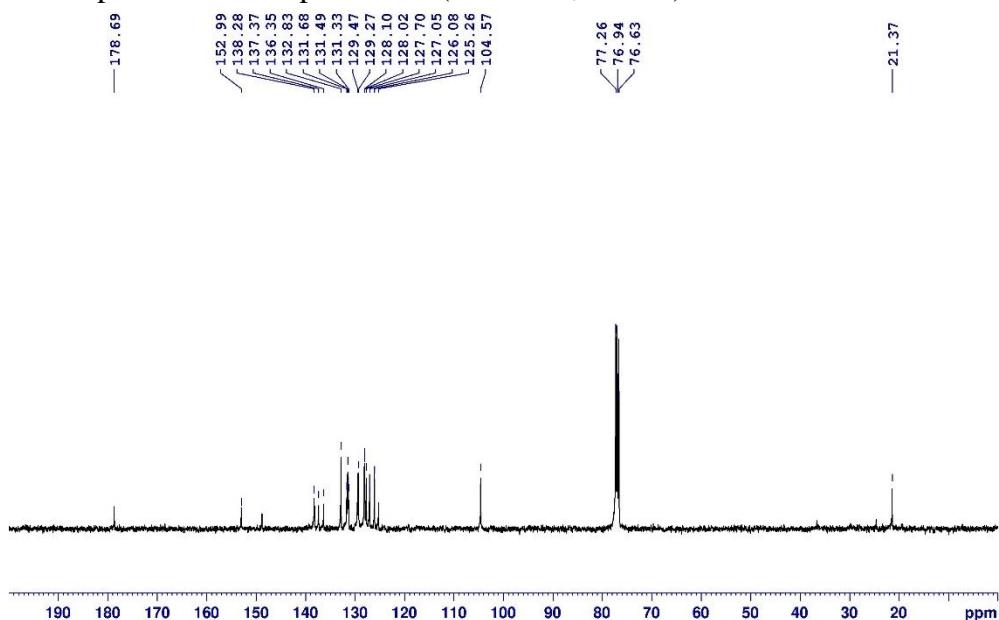
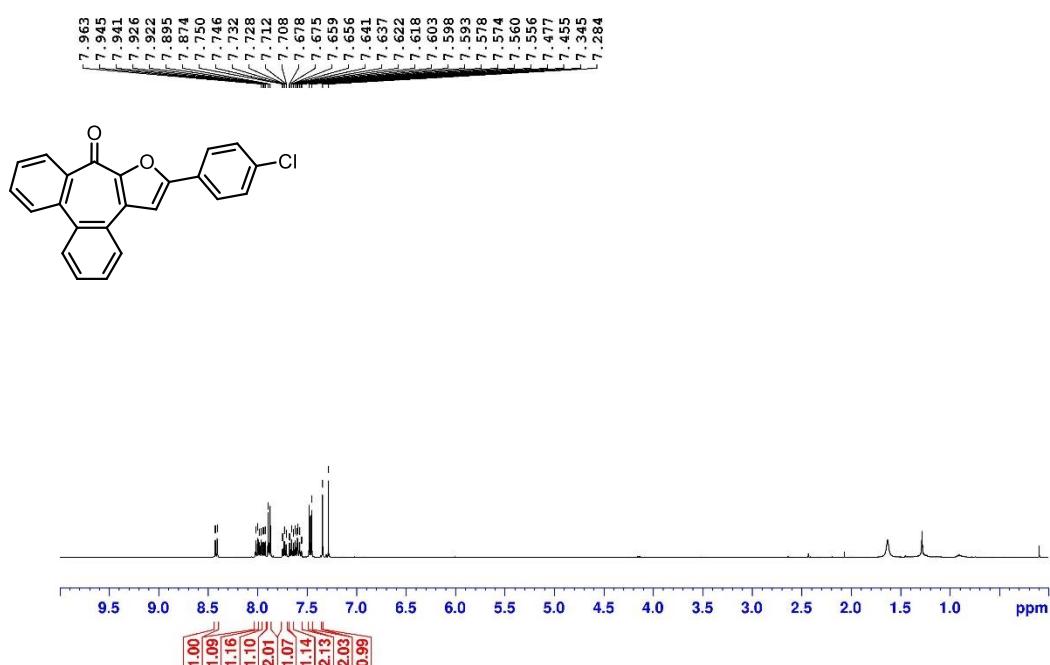


Figure S20 ^1H NMR spectrum of compound **1da** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1da** (100 MHz, CDCl_3)

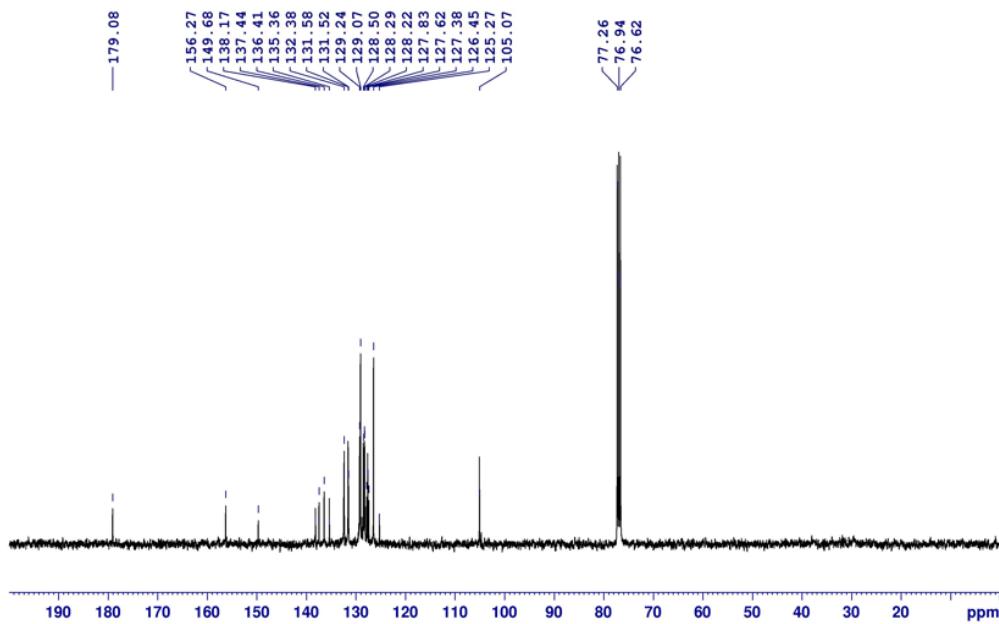
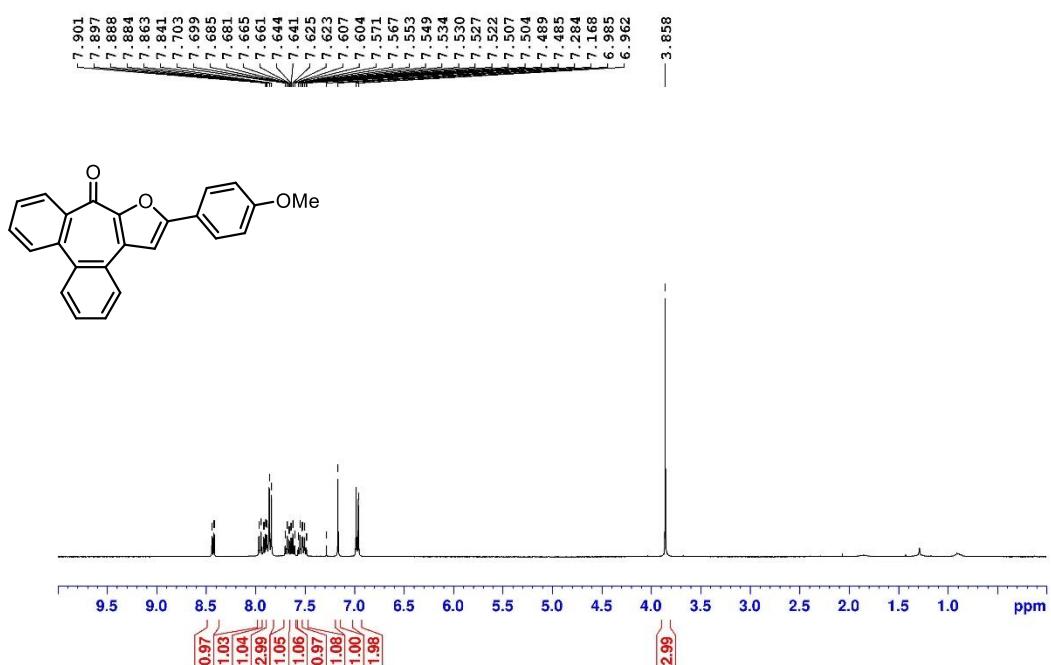


Figure S21 ^1H NMR spectrum of compound **1ea** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1ea** (100 MHz, CDCl_3)

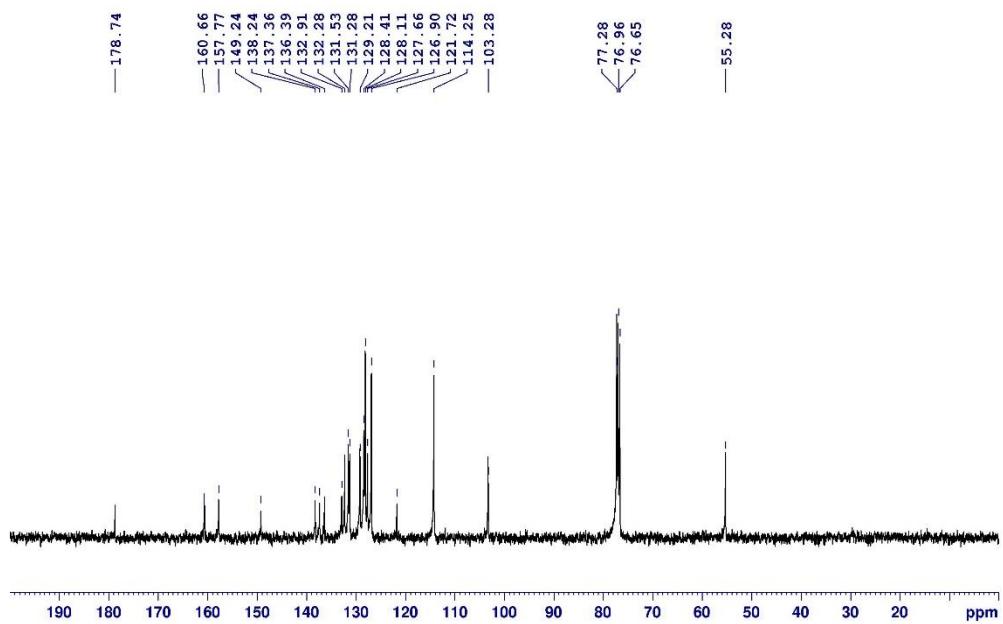
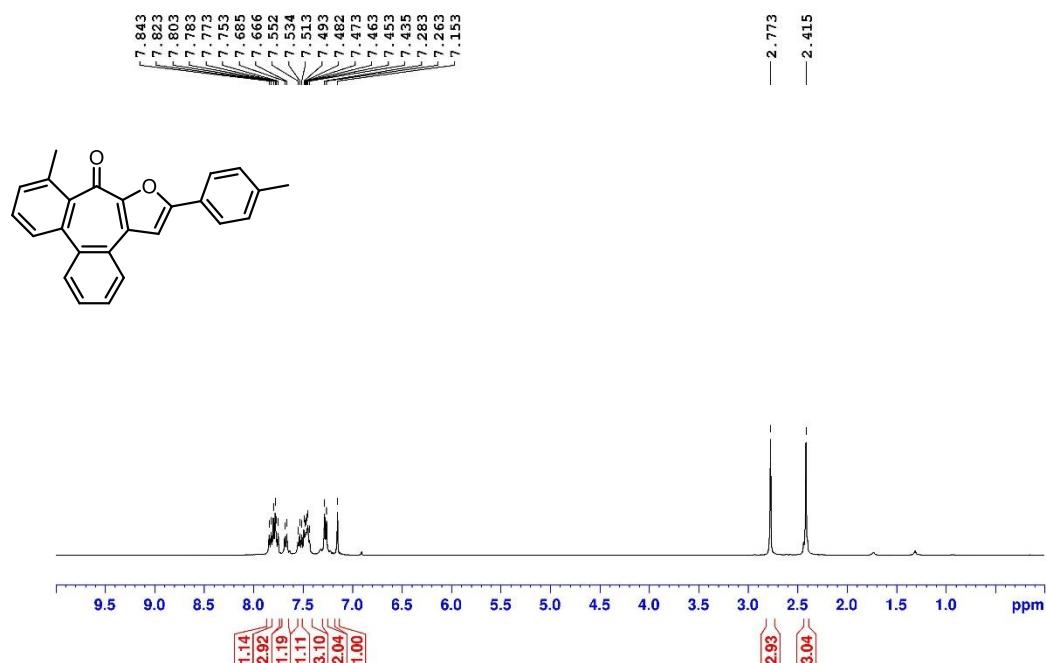


Figure S22 ^1H NMR spectrum of compound **1fa** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1fa** (100 MHz, CDCl_3)

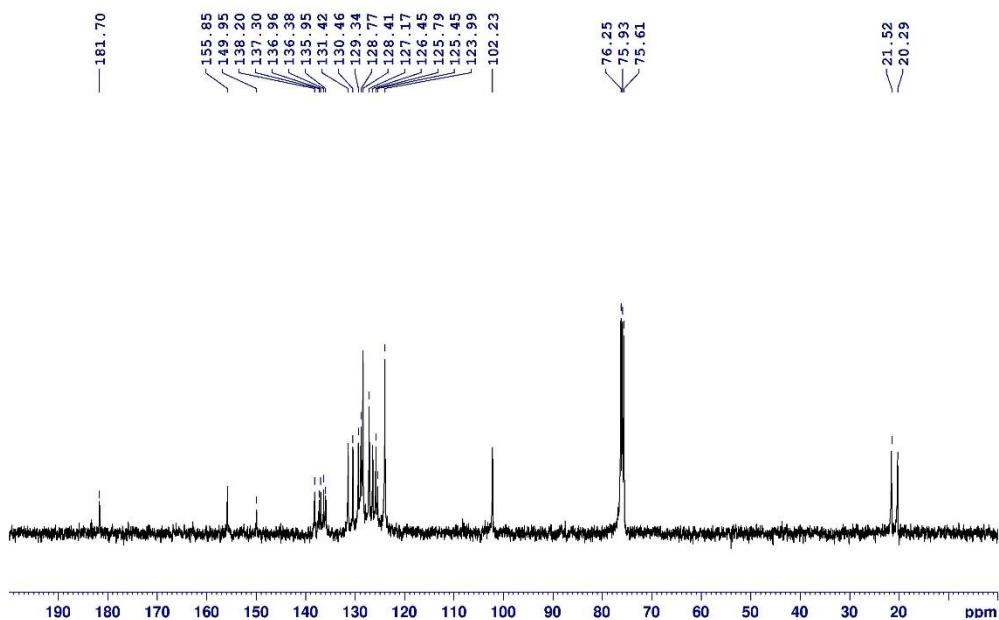
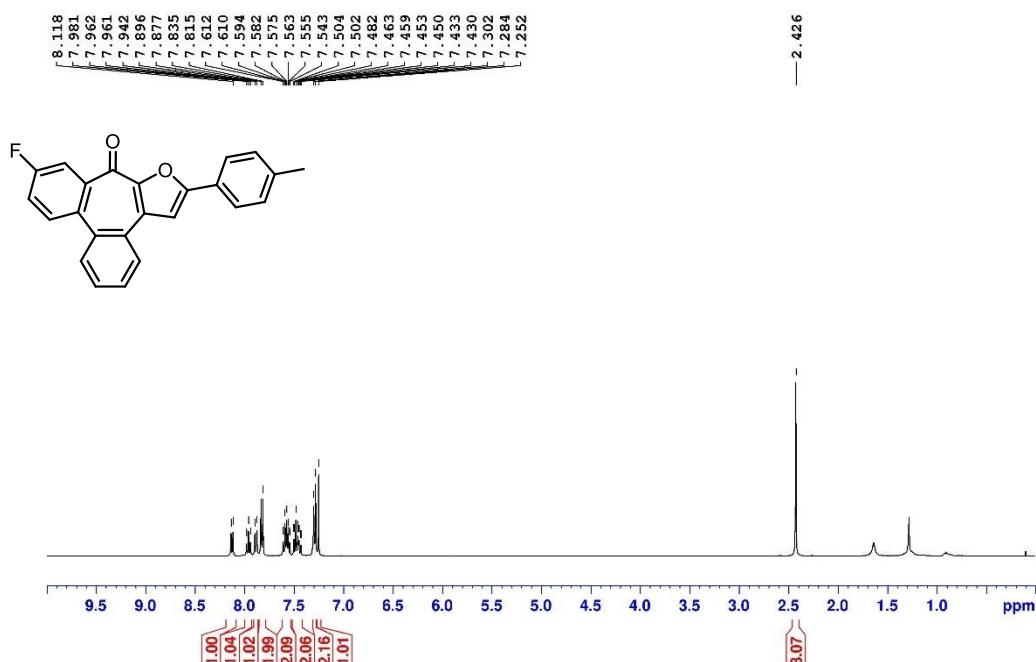


Figure S23 ^1H NMR spectrum of compound **1ga** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **1ga** (100 MHz, CDCl_3)

