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Supporting Information

Synthesis and Self-sensitized Photo-oxidation of 2-Fulleropyrrolines by Palladium(II)-catalyzed Heteroannulation of [60]Fullerene with Benzoyl Hydrazone Esters

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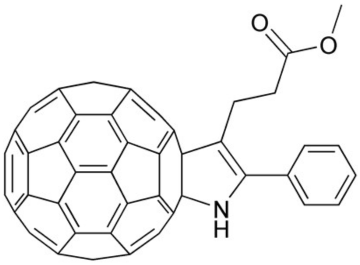
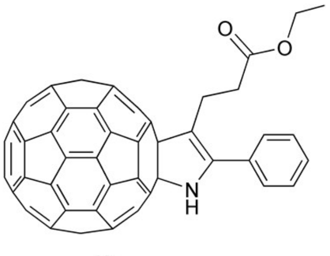
General Procedure for the Synthesis of [60]fullereropyrroline 2a-l.

To a pressure-affordable thick-wall glass tube containing C_{60} (36.0 mg, 0.05 mmol), benzoyl hydrazone esters **1** (0.15 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), and $Cu(OAc)_2$ (27 mg, 0.15 mmol) were added 10 to mL of chlorobenzene, 1 mL of TFA, and a stir bar. The tube was sealed with an O-ring and Teflon cap. After the tube was stirred at 120 °C without loss of TFA (bp 72.4 C) for 12 h. After the reaction was completed, the reaction solution was evaporated under vacuum, and the residue was chromatographed on a silica gel column eluting with CS_2. The first purple band was unreacted C_{60}, and the second brown band was eluted with toluene/hexane (5:2 v/v) to afford the desired product **2**.



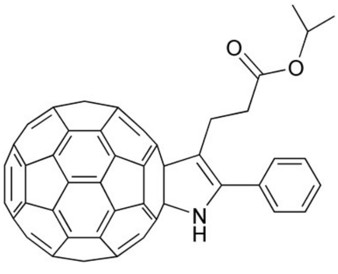
2a

Synthesis of **2a**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1a** (56.1 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2a** (12.8 mg, 28%) as a brown amorphous solid and unreacted C_{60} (18.2 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 7.96 (d, J = 7.1 Hz, 2H), 7.56–7.52 (m, 2H), 7.49–7.45 (m, 1H), 3.61 (s, 3H), 3.33–3.27 (m, 2H), 2.89–2.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 171.82, 150.74, 149.02, 148.17, 147.45, 146.37, 146.25, 146.09, 146.04, 145.96, 145.73, 145.56, 145.48, 145.26, 145.22, 145.16, 144.49, 144.47, 143.00, 142.80, 142.77, 142.41, 142.37, 142.22, 141.97, 141.77, 140.55, 139.94, 137.27, 136.27, 130.37, 130.28, 129.65, 128.88, 128.01, 109.63, 99.71 , 77.51, 68.15, 34.87, 21.96; FT-IR (KBr) ν/cm^{-1}: 3433, 2973, 2920, 1728, 1630, 1447, 1371, 1272, 1182, 1106, 1012, 765, 526; UV-vis ($CHCl_3$) λ/nm (log ε) 254 (5.00), 313 (4.50), 428 (3.44); HRMS (MALDI-TOF) m/z calcd for $C_{72}H_{14}NO_2$ $[M+H]^+$ 924.1020, found 924.1016.



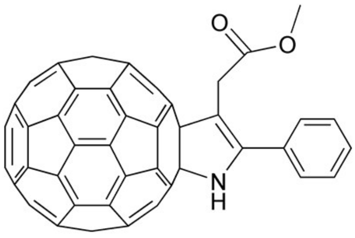
2b

Synthesis of **2b**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1b** (58.2 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2b** (14.2 mg, 30%) as a brown amorphous solid and unreacted C_{60} (19.9 mg, 55%). ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 7.97 (d, J = 8.1 Hz, 2H), 7.58–7.52 (m 2H), 7.48–7.45 (m, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.34–3.26 (m, 2H), 2.87–2.78 (m, 2H), 1.22 (d, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 171.75, 150.90, 149.03, 148.17, 147.46, 146.38, 146.26, 146.10, 146.05, 146.00, 145.73, 145.54, 145.50, 145.27, 145.23, 145.17, 144.52, 144.48, 143.02, 142.82, 142.79, 142.44, 142.39, 142.24, 142.01, 141.79, 140.58, 139.97, 137.24, 136.29, 130.37, 129.63, 129.07, 128.87, 128.31, 128.04, 99.72, 77.55, 60.63, 34.52, 30.29, 22.44, 14.48; FT-IR (KBr) *ν*/cm^{-1}: 3432, 2972, 2921, 1722, 1635, 1385, 1344, 1254, 1190, 1063, 526; UV-vis ($CHCl_3$) λ/nm (log ε) 253 (4.99), 314 (4.51), 429 (3.40); HRMS (MALDI-TOF) *m/z* calcd for $C_{73}H_{16}NO_2$ $[M+H]^+$ 938.1176, found 938.1161.



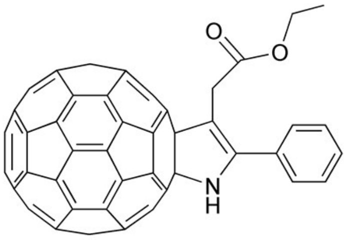
2c

Synthesis of **2c**. By following the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1c** (60.3 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2c** (16.4 mg, 34%) as a brown amorphous solid and unreacted C_{60} (19.2 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.07 (d, J = 7.0 Hz, 2H), 7.65–7.62 (m, 2H), 7.58–7.55(m, 1H), 5.07–5.00 (m, 1H), 3.42–3.33 (m, 2H), 2.95–2.87 (m, 2H), 1.28 (d, J = 6.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 171.63, 150.57, 148.86, 148.00, 147.29, 146.20, 146.08, 145.92, 145.87, 145.79, 145.56, 145.39, 145.30, 145.09, 145.05, 144.99, 144.32, 144.30, 142.83, 142.63, 142.60, 142.24, 142.20, 142.05, 141.80, 141.59, 140.37, 139.77, 130.20, 130.10, 129.49, 128.76, 128.71, 127.85, 109.47, 77.20, 67.98, 38.51, 34.71, 29.08, 22.25, 21.69; FT-IR (KBr) *ν*/cm^{-1}: 3433, 2974, 2920, 1716, 1647, 1450, 1333, 1241, 1111, 1074, 1023, 526; UV-vis ($CHCl_3$) *λ*/nm (log ε) 253 (4.99), 315 (4.50), 427 (3.39); HRMS (MALDI-TOF) *m/z* calcd for $C_{74}H_{18}NO_2$ $[M+H]^+$ 952.1332, found 952.1384.



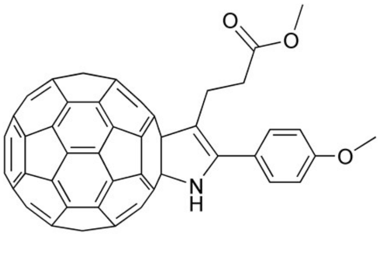
2d

Synthesis of **2d**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1d** (54.0 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2d** (11.1 mg, 24%) as a brown amorphous solid and unreacted C_{60} (16.4 mg, 45%). ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.13 (d, J = 8.1 Hz, 2H), 7.65–7.62 (m, 2H), 7.60–7.58 (m, 1H), 3.98 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 171.58, 153.24, 148.44, 146.29, 146.19, 146.13, 145.98, 145.91, 145.61, 145.39, 145.33, 145.16, 145.12, 145.04, 144.36, 142.87, 142.66, 142.28, 142.23, 141.81, 141.63, 140.23, 139.77, 137.37, 136.06, 134.08, 130.50, 130.40, 129.98, 128.77, 128.69, 128.28, 104.28, 77.19, 52.18, 32.82; UV-vis ($CHCl_3$) λ/nm (log ε) 255 (5.01), 316 (4.48), 427 (3.38); HRMS (MALDI-TOF) *m/z* calcd for $C_{71}H_{12}NO_2$ $[M+H]^+$ 910.0863, found 910.0855.



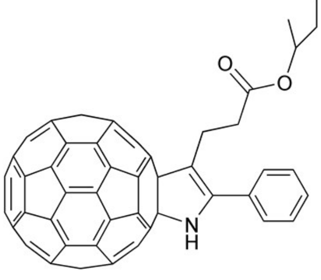
2e

Synthesis of **2e**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1e** (56.1 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2e** (12.3 mg, 27%) as a brown amorphous solid and unreacted C_{60} (19.6 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.11 (d, J = 6.2 Hz, 2H), 7.63–7.53 (m, 3H), 4.18 (q, J = 7.1 Hz, 2H), 3.92 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 170.74, 153.06, 148.36, 147.91, 147.20, 146.12, 146.04, 145.98, 145.82, 145.75, 145.47, 145.45, 145.34, 145.20, 145.01, 144.95, 144.87, 144.21, 142.73, 142.52, 142.49, 142.14, 142.09, 141.96, 141.68, 141.48, 140.09, 139.63, 137.18, 135.96, 129.83, 129.56, 128.85, 128.64, 128.13, 125.16, 104.13, 61.22, 32.96, 29.78, 13.99; FT-IR (KBr) *ν*/cm^{-1}: 3432, 2975, 2926, 1740, 1511, 1430, 1320, 1387, 1260, 1153, 694, 526; UV-vis ($CHCl_3$) λ/nm(log ε) 256 (4.98), 315 (4.52), 428 (3.38); HRMS (MALDI-TOF) *m/z* calcd for $C_{72}H_{14}NO_2$ $[M+H]^+$ 924.1020, found 924.1016.



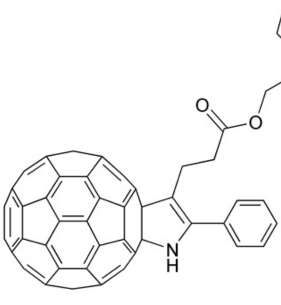
2f

Synthesis of **2f**. By following the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1f** (60.6 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2f** (14.6 mg, 31%) as a brown amorphous solid and unreacted C_{60} (19.0 mg, 53%). ^1H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.33 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 8.9 Hz, 2H), 3.95 (s, 3H), 3.69 (s, 3H), 2.96–2.85 (m, 2H), 2.75–2.70 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 167.29, 150.82, 148.00, 146.79, 146.58, 146.42, 146.36, 146.27, 145.59, 145.48, 145.34, 145.14, 144.81, 144.69, 143.10, 142.81, 142.42, 141.93, 141.44, 141.31, 140.12, 139.50, 139.09, 138.59, 136.47, 132.54, 130.81, 128.86, 121.79, 114.27, 71.69, 55.52. 65.47, 30.01, 19.30; FT-IR (KBr) ν/cm^{-1}: 3433, 2921, 2853, 1718, 1691, 1456, 1411, 1384, 1273, 1032, 525; UV-vis ($CHCl_3$) λ/nm (log ε) 256 (5.00), 316 (4.50), 429 (3.41); HRMS (MALDI-TOF) *m/z* calcd for $C_{73}H_{16}NO_3$ $[M+H]^+$ 954.1125, found 954.1121.



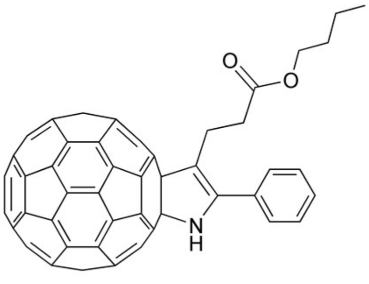
2g

Synthesis of **2g**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1g** (62.4 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2g** (21 mg, 43%) as a brown amorphous solid and unreacted C_{60} (15.4 mg, 43%). ^1H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.08 (d, J = 7.0 Hz, 2H), 7.64–7.62 (m, 2H), 7.58–7.55 (m, 1H), 4.91–4.86 (m, 1H), 3.42–3.37 (m, 2H), 2.96–2.90 (m, 2H), 1.68–1.54 (m, 2H), 1.25 (d, J = 6.3 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 171.86, 150.71, 149.00, 148.17, 147.45, 146.37, 146.25, 146.09, 146.04, 145.95, 145.72, 145.55, 145.48, 145.26, 145.21, 145.16, 144.49, 144.47, 143.14, 143.00, 142.80, 142.77, 142.41, 142.37, 142.22, 141.97, 141.77, 140.56, 139.94, 137.27, 136.27, 130.28, 129.66, 128.89, 128.00, 109.63, 99.70, 77.51, 72.63, 34.91, 29.05, 22.54, 19.57, 9.93; FT-IR (KBr) *v*/cm^{-1}: 3432, 2975, 2926, 1740, 1635, 1511, 1430, 1320, 1213, 1091, 1049, 770, 694, 526. UV-vis ($CHCl_3$) *λ*/nm (log ε) 257 (4.98), 315 (4.48), 427 (3.33); HRMS (MALDI-TOF) *m/z* calcd for $C_{75}H_{20}NO_2$ $[M+H]^+$ 966.1489, found 966.1476.



2h

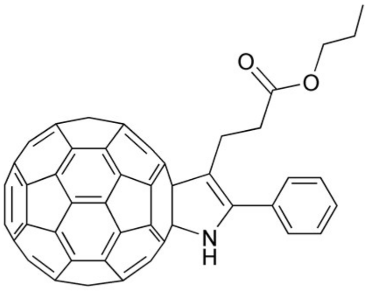
Synthesis of **2h**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1h** (69.6 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2h** (17.8 mg, 37%) as a brown amorphous solid and unreacted C_{60} (18.6 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.05 (d, J = 7.0 Hz, 2H), 7.64-7.61 (m, 2H), 7.58-7.55 (m, 1H), 7.29–7.26 (m, 2H), 7.22 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 6.9 Hz, 2H), 4.31 (t, J = 7.1 Hz, 2H), 3.40–3.33 (m, 2H), 2.95 (t, J = 7.1 Hz, 2H), 2.94–2.91 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 171.96, 150.86, 148.94, 148.17, 147.46, 146.38, 146.26, 146.10, 146.05, 145.92, 145.72, 145.50, 145.25, 145.17, 144.51, 144.47, 143.15, 143.02, 142.82, 142.77, 142.43, 142.38, 142.23, 141.98, 141.78, 140.57, 139.96, 137.60, 137.26, 136.28, 130.27, 129.68, 128.93, 128.91, 128.63, 127.97, 126.72, 109.32, 99.71, 77.48, 65.19, 35.35, 34.50, 22.40; FT-IR (KBr) *v*/cm^{-1}: 3432, 2974, 2926, 1740, 1631, 1461, 1384, 1273, 1050, 590; UV-vis ($CHCl_3$) *λ*/nm (log ε) 255 (4.99), 314 (4.49), 429 (3.45); HRMS (MALDI-TOF) *m/z* calcd for $C_{79}H_{20}NO_2$ $[M+H]^+$ 1014.1489, found 1014.1478.



2i

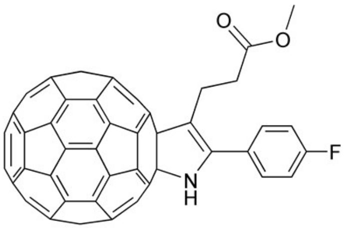
Synthesis of **2i**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1i** (62.4 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2i** (15.1 mg, 31%)

as a brown amorphous solid and unreacted C_{60} (16.1 mg, 45%). ^1H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.07 (d, J = 7.1 Hz, 2H), 7.65–7.62 (m, 2H), 7.58–7.56 (m, 1H), 4.11 (t, J = 6.7 Hz, 2H), 3.43–3.37 (m, 2H), 2.97–2.92 (m, 2H), 1.66–1.61 (m, 2H), 1.42–1.38 (m, 2H), 0.97–0.95 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 192.60, 192.57, 172.35, 150.80, 148.98, 148.17, 147.45, 146.37, 146.25, 146.08, 146.03, 145.92, 145.72, 145.52, 145.47, 145.25, 145.21, 145.16, 144.49, 144.46, 143.13, 142.99, 142.79, 142.76, 142.40, 142.36, 142.21, 141.96, 141.76, 140.55, 139.93, 137.27, 136.26, 130.25, 129.67, 128.90, 127.98, 109.48, 77.49, 64.70, 34.57, 30.83, 22.43, 19.44, 13.95; FT-IR (KBr) *ν*/cm^{-1}: 3433, 2973, 2923, 1731, 1632, 1427, 1272, 1166, 1091, 1050, 881, 767, 526; UV-vis ($CHCl_3$) *λ*/nm (log ε) 256 (4.99), 314 (4.50), 429 (3.42); HRMS (MALDI-TOF) m/z calcd for $C_{75}H_{20}NO_2$ $[M+H]^+$ 966.1489, found 966.1481.



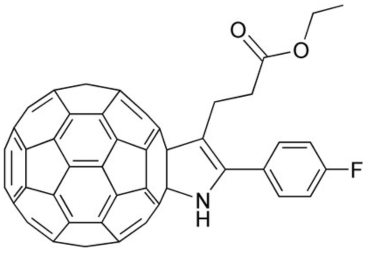
2j

Synthesis of **2j**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1j** (60.3 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2j** (13.1 mg, 28%) as a brown amorphous solid and unreacted C_{60} (15.4 mg, 43%). ^1H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.07 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 4.07 (t, J = 6.7 Hz, 2H), 3.43–3.37 (m, 2H), 2.97–2.91 (m, 2H), 1.71–1.64 (m, 2H), 0.99-0.97 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 172.02, 150.65, 148.81, 148.00, 147.29, 146.21, 146.09, 145.93, 145.88, 145.77, 145.56, 145.36, 145.32, 145.09, 145.05, 145.00, 144.33, 144.30, 142.84, 142.64, 142.61, 142.26, 142.21, 142.06, 141.81, 141.61, 140.40, 139.78, 137.10, 136.11, 130.12, 129.51, 128.75, 127.82, 109.29, 99.54, 77.33, 66.21, 34.37, 22.29, 22.16, 10.53; FT-IR (KBr) *ν*/cm^{-1}: 3434, 2921, 2851, 1730, 1636, 1490, 1423, 1261, 1157, 1015, 803, 525; UV-vis ($CHCl_3$) *λ*/nm (log ε) 255 (5.00), 315 (4.53), 428 (3.36); HRMS (MALDI-TOF) *m/z* calcd for $C_{74}H_{18}NO_2$ $[M+H]^+$ 952.1332, found 952.1312.



2k

Synthesis of **2k**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1k** (58.8 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2k** (9.9 mg, 21%) as a brown amorphous solid and unreacted C_{60} (23.6 mg, 65%) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.03–8.00 (m, 2H), 7.29–7.26 (m, 2H), 3.66 (s, 3H), 3.35–3.30 (m, 2H), 2.91–2.87 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 172.43, 164.18, 162.51, 150.00, 148.80, 148.18, 147.46, 146.38, 146.28, 146.10, 146.05, 145.75, 145.69, 145.50, 145.43, 145.23, 145.17, 144.46, 143.02, 142.82, 142.74, 142.38, 142.22, 141.94, 141.78, 140.59, 139.96, 137.26, 136.26, 130.02, 129.97, 126.42, 116.12, 115.97, 109.20, 99.72, 77.39, 51.79, 34.21, 22.36; FT-IR (KBr) *ν*/cm^{-1}: 3435, 2973, 2925, 1730, 1638, 1440, 1375, 1271, 1181, 1012, 765, 525; UV-vis ($CHCl_3$) *λ*/nm (log ε) 256 (4.99), 314 (4.50), 426 (3.40); HRMS (MALDI-TOF) *m/z* calcd for $C_{72}H_{13}NO_2F$ $[M+H]^+$ 942.0924, found 942.0916.

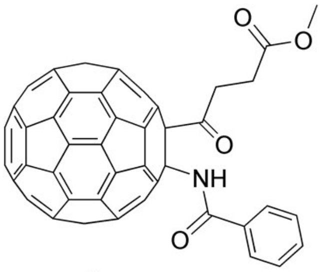


2l

Synthesis of **2l**. According to the general procedure, C_{60} (36.0 mg, 0.05 mmol) with **1l** (60.9 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol), TFA (1 mL) and chlorobenzene (10 mL) were added to a 48 mL pressure-affordable thick-wall glass tube with a magnetic stirring bar. The reaction was stirred at 120 °C for 12 h and purified by column chromatography to afford **2l** (11.5 mg, 24%) as a brown amorphous solid and unreacted C_{60} (20.3 mg, 56%). ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.04–8.01 (m, 2H), 7.29–7.26 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.36–3.30 (m, 2H), 2.90–2.84 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 172.01, 164.17, 162.51, 149.94, 148.85, 148.18, 147.47, 146.39, 146.27, 146.11, 146.06, 145.70, 145.50, 145.47, 145.23, 145.18, 144.49, 143.02, 142.83, 142.80, 142.75, 142.42, 142.38, 142.22, 141.95, 141.78, 140.58, 139.97, 137.25, 136.26, 129.98, 126.45, 116.09, 115.95, 109.34, 99.72, 60.83, 34.44, 22.38, 14.44; FT-IR (KBr) *ν*/cm^{-1}: 3432, 2964, 2918, 1735, 1635, 1450, 1372, 1270, 1175, 1010, 763, 521; UV-vis ($CHCl_3$) *λ*/nm (log ε) 255 (4.98), 317 (4.43), 428 (3.42); HRMS (MALDI-TOF) m/z calcd for $C_{73}H_{15}NO_2F$ $[M+H]^+$ 956.1081, found 956.1076.

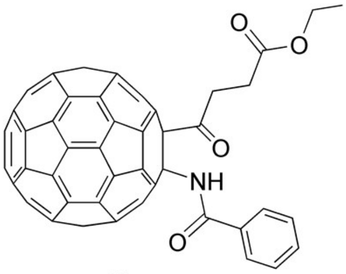
Photo-oxidation of 2a-l.

2-fulleropyrrolines **2** (0.1 mmol) and 25 mL CS_2 was added to a 50-mL round-bottomed flask with a magnetic stirring bar. The reaction was stirred at room temperature for 3-7 day. The reaction was monitored by TLC and stopped at the desired time. After the reaction solution was evaporated under vacuum, and the residue was chromatographed on a silica gel column eluted with toluene/CS_2 (2:5 v/v). The first brown band was unreacted **2**, the second brown band was **3**. Spectral data of compound **3a-j** were as follows.



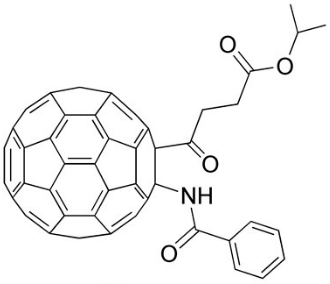
3a

Synthesis of **3a**. According to the general procedure, a solution of **2a** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 3 days at room temperature afforded **3a** (67 mg, 70%) as brown amorphous solid along with unreacted **2a** (18 mg, 18%) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3$/CS_2 (3:1 v/v)) δ 8.32 (d, J = 7.9 Hz, 2H), 7.70–7.67 (m, 1H), 7.59–7.55 (m, 2H), 3.91 (t, J = 6.8 Hz, 2H), 3.60 (s, 3H), 2.66 (t, J = 6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$/CS_2 (3:1 v/v)) δ 200.42, 172.50, 167.48, 150.59, 148.46, 147.65, 147.57, 146.73, 146.51, 146.37, 146.30， , 146.21, 145.56, 145.51, 145.42, 145.38, 145.22, 145.00, 144.72, 144.59, 143.03, 142.76, 142.38, 142.30, 141.85, 141.36, 141.20, 140.08, 139.43, 138.55, 136.35, 134.11, 130.28, 129.48, 128.88, 93.02, 51.82, 38.61, 28.70; FT-IR (KBr) *ν*/cm^{-1}: 3434, 2973, 2917, 1724, 1512, 1432, 1349, 1275, 1101, 526; UV-vis ($CHCl_3$) *λ*/nm (log ε) 255 (5.00), 315 (4.48), 428 (3.45); HRMS (MALDI-TOF) *m/z* calcd for $C_{72}H_{14}NO_4$ $[M+H]^+$ 956.0918, found 956.0921.



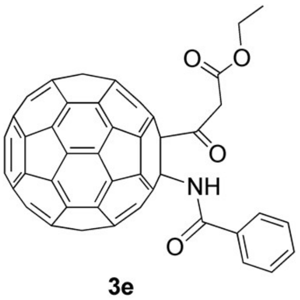
3b

Synthesis of **3b**. According to the general procedure, a solution of **2b** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 4 days at room temperature afforded **3b** (75 mg, 77%) as brown amorphous solid along with unreacted **2b** (14 mg, 14%) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3$/CS_2 (3:1 v/v)) δ 8.39 (d, J = 7.0 Hz, 2H), 7.78–7.74 (t, J = 7.4 Hz, 1H), 7.67–7.63 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$/CS_2 (3:1 v/v)) δ 199.46, 192.58, 171.30, 167.12, 150.93, 148.52, 147.85, 147.70, 146.81, 146.59, 146.47, 146.37, 146.28, 145.69, 145.60, 145.49, 145.45, 145.42, 145.17, 144.84, 144.69, 143.12, 142.85, 142.82, 142.49, 142.45, 142.38, 141.95, 141.47, 141.30, 140.15, 139.50, 138.71, 136.46, 133.98, 130.41, 129.76, 129.11, 128.90, 128.37, 125.49, 92.87, 77.60, 60.68, 38.64, 28.96, 14.58; FT-IR (KBr) *ν*/cm^{-1}: 3434, 2968, 2918, 1733, 1635, 1448, 1349, 1262, 1180, 1094, 1014, 526; UV-vis ($CHCl_3$) λ/nm (log ε) 254 (5.00), 313 (4.47), 427 (3.43); HRMS (MALDI-TOF) *m/z* calcd for $C_{73}H_{16}NO_4$ [M+H]+ 970.1074, found 970.1069.



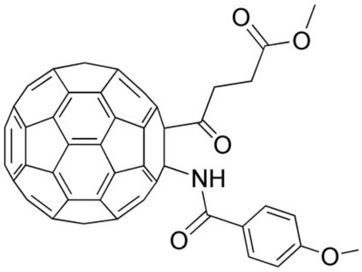
3c

Synthesis of **3c**. According to the general procedure, a solution of **2c** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 4 days at room temperature afforded **3c** (75 mg, 76%) as brown amorphous solid along with unreacted **2c** (16 mg, 16%) after purification by column chromatography; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.39 (d, J = 8.1 Hz, 2H), 7.77–7.72 (m, 1H), 7.65–7.60 (m, 2H), 5.00–4.92 (m, 1H), 3.95 (t, J = 6.6 Hz, 2H), 2.67 (t, J = 6.8 Hz, 2H), 1.22 (d, J = 6.3 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 200.17, 171.34, 167.30, 150.62, 148.37, 147.55, 146.64, 146.43, 146.28, 146.21, 146.12, 145.49, 145.42, 145.33, 145.29, 145.19, 144.93, 144.64, 144.51, 142.94, 142.65, 142.30, 142.26, 142.22, 141.77, 141.28, 141.12, 139.99, 139.33, 138.49, 136.25, 133.95, 77.20, 67.98, 38.51, 29.08, 21.69; FT-IR (KBr) *ν*/cm^{-1}: 3433, 2974, 2920, 1717, 1647, 1450, 1333, 1241, 1111, 1074, 1023, 526; UV-vis ($CHCl_3$) *λ*/nm (log ε) 256 (5.00), 315 (4.53), 427 (3.54); HRMS (MALDI-TOF) *m/z* calcd for $C_{74}H_{18}NO_4$ [M+H]$^+$ 984.1230, found 984.1224.



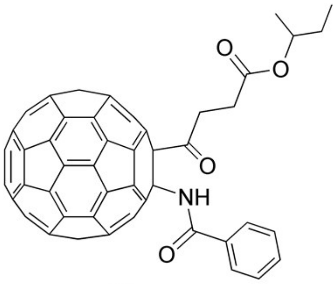
3e

Synthesis of **3e**. According to the general procedure, a solution of **2e** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 7 days at room temperature afforded **3e** (61 mg, 64%) as brown amorphous solid along with unreacted **2e** (10 mg, 10%) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.16 (d, J = 7.3 Hz, 2H), 7.66–7.63 (m, 2H), 7.61–7.58 (m, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.98 (s, 2H), 1.24 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 193.99, 167.09, 165.90, 150.01, 148.51, 147.74, 147.42, 146.82, 146.64, 146.50, 146.40, 146.30, 145.71, 145.62, 145.47, 145.30, 145.13, 144.79, 144.69, 143.17, 142.87, 142.52, 142.46, 142.27, 141.99, 141.51, 141.27, 140.06, 139.49, 138.64, 136.72, 134.07, 130.56, 130.29, 129.66, 129.12, 128.86, 128.36, 95.62, 61.53, 49.51, 31.56; FT-IR (KBr) *v*/cm^{-1}: 3433, 2929, 2891, 1720, 1695, 1528, 1466, 1263, 1032, 724, 526; UV-vis ($CHCl_3$) *λ*/nm (log ε) 255 (4.99), 315(4.48), 428(3.42); HRMS (MALDI-TOF) *m/z* calcd for $C_{72}H_{14}NO_4$ $[M+H]^+$ 956.0918, found 956.0912.



3f

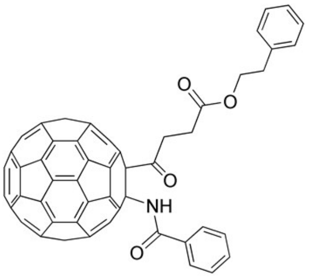
Synthesis of **3f.** According to the general procedure, a solution of **2f** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 3 days at room temperature afforded **3f** (53 mg, 54 %) as brown amorphous solid along with unreacted **2f** (28 mg, 28%) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.32 (d, J = 8.7 Hz, 2H), 7.38–7.32 (m, 2H), 3.98 (s, 3H), 3.89 (s, 3H), 2.74–2.70 (m, 2H), 2.40–2.32 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 198.96, 171.26, 166.19, 163.26, 149.72, 147.40, 146.89, 146.59, 145.68, 145.47, 145.31, 145.24, 145.16, 144.55, 144.47, 144.37, 144.33, 144.24, 144.04, 143.70, 143.57, 141.99, 141.72, 141.69, 141.35, 141.31, 141.26, 140.81, 140.32, 140.20, 139.01, 138.39, 137.97, 137.48, 135.36, 131.44, 131.38, 131.33, 129.70, 129.69, 127.76, 127.75, 91.60, 75.99, 70.58, 64.36, 28.91, 18.21.; FT-IR (KBr) *v*/cm^{-1}: 3429, 2921, 2851, 1710, 1691, 1508, 1476, 1385, 11263, 1032, 724, 526; UV-vis ($CHCl_3$) *λ*/nm (log ε) 255 (5.00), 314 (4.41), 429 (3.36); HRMS (MALDI-TOF) *m/z* calcd for $C_{73}H_{16}NO_5$ $[M+H]^+$ 986.1023, found 986.1015.



3g

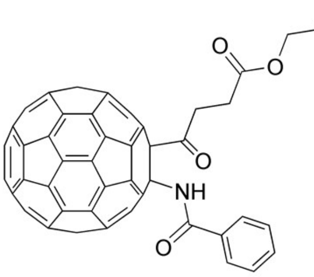
Synthesis of **3g**. According to the general procedure, a solution of **2g** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 5 days at room temperature afforded **3g** (70 mg, 70%) as brown amorphous solid along with unreacted **2g** (16 mg, 16 %) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.33 (d, J = 7.9 Hz, 2H), 7.69–7.67 (m, 1H), 7.58–7.55 (m, 2H), 4.78–4.72 (m, 1H), 3.91 (t, J = 8.3 Hz, 2H), 2.63 (t, J = 8.1 Hz, 2H), 1.54-1.43 (m, 2H), 1.48–1.43 (m, 1H), 1.13 (d, J = 6.3 Hz, 3H), 0.85-0.82 (m, 3H);

^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 199.96, 171.38, 167.31, 150.87, 148.53, 147.79, 147.71, 146.82, 146.60, 146.47, 146.38, 146.29, 145.68, 145.60, 145.50, 145.46, 145.39, 145.13, 144.83, 144.69, 143.17, 143.12, 142.86, 142.83, 142.49, 142.45, 142.39, 141.95, 141.46, 141.30, 140.16, 139.51, 138.70, 136.44, 134.07, 130.41, 129.67, 129.12, 128.93, 128.35, 125.45, 72.58, 38.70, 30.11, 19.57, 10.03; FT-IR (KBr) *ν*/cm^{-1}: 3434, 2931, 2889, 1718, 1685, 1531, 1466, 1260, 1041, 731, 525; UV-vis ($CHCl_3$) *λ*/nm (log ε) 256 (4.98), 315 (4.40), 428 (3.33); HRMS (MALDI-TOF) *m/z* calcd for $C_{75}H_{20}NO_4$ $[M+H]^+$ 998.1386, found 998.1375.



3h

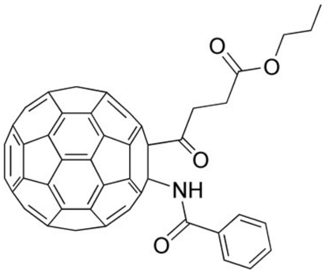
Synthesis of **3h**. According to the general procedure, a solution of **2h** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 4 days at room temperature afforded **3h** (73 mg, 70%) as brown amorphous solid along with unreacted **2h** (16 mg, 16%) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.39 (d, J = 7.0 Hz, 2H), 7.72–7.70 (m, 1H), 7.60–7.58 (m, 2H), 7.25–7.22 (m, 2H), 7.19–7.17 (m, 1H), 7.15 (d, J = 7.0 Hz, 2H), 4.27 (t, J = 7.1 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 2.91 (t, J = 7.1 Hz, 2H), 2.71 (t, J = 6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 195.29, 166.96, 162.63, 146.00, 143.78, 142.98, 142.07, 141.85, 141.72, 141.63, 141.54, 140.91, 140.85, 140.75, 140.71, 140.58, 140.36, 140.07, 139.94, 138.37, 138.11, 138.08, 137.73, 137.69, 137.63, 137.20, 136.71, 136.54, 135.41, 134.77, 133.92, 132.90, 131.70, 125.63, 124.88, 124.35, 124.20, 123.87, 123.58, 121.94, 88.23, 60.52, 33.92, 30.60, 24.24; FT-IR (KBr) *ν*/cm^{-1}: 3437, 2921, 2891, 1721, 1695, 1528, 1469, 1263, 1037, 724, 524; UV-vis ($CHCl_3$) *λ*/nm (log ε) 256 (5.00), 314 (4.45), 429 (3.36); HRMS (MALDI-TOF) *m/z* calcd for $C_{79}H_{20}NO_4$ $[M+H]^+$ 1046.1387, found 1046.1381.



3i

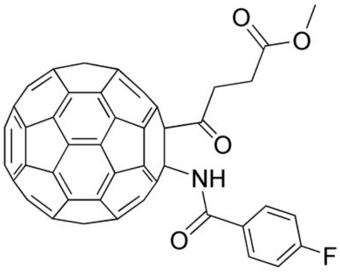
Synthesis of **3i**. According to the general procedure, a solution of **2i** (100 mg, 0.01 mmol) in 25 mL carbon disulfide was photooxygenated for 5 days at room temperature afforded **3i** (75 mg, 75%) as brown amorphous solid along with unreacted **2i** (1.2 mg, 12%) after purification by column chromatography; ^{1}H NMR

(600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.40 (d, J = 8.1 Hz, 2H), 7.75–7.73 (m, 1H), 7.64–7.62 (m, 2H), 4.07 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 2.73 (t, J = 6.8 Hz, 2H), 1.62–1.57 (m, 2H), 1.39–1.33 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 195.47, 167.24, 162.68, 146.01, 143.78, 142.96, 142.06, 141.85, 141.71, 141.62, 141.54, 140.91, 140.84, 140.75, 140.70, 140.59, 140.35, 140.07, 139.93, 138.36, 138.10, 137.72, 137.68, 137.63, 137.19, 136.70, 136.54, 135.40, 134.76, 133.91, 131.68, 129.38, 125.63, 124.86, 124.34, 124.19, 123.56, 120.65, 99.99, 88.27, 72.35, 59.97, 33.97, 26.12, 24.22, 14.71, 9.24; FT-IR (KBr) *v*/cm^{-1}: 3428, 2929, 2898, 1722, 1694, 1532, 1460, 1376, 1260, 1032, 722, 525; UV-vis ($CHCl_3$) *λ*/nm (log ε) 253 (5.01), 315 (4.52), 427 (3.41); HRMS (MALDI-TOF) *m/z* calcd for $C_{75}H_{20}NO_4$ $[M+H]^+$ 998.1386, found 998.1370.



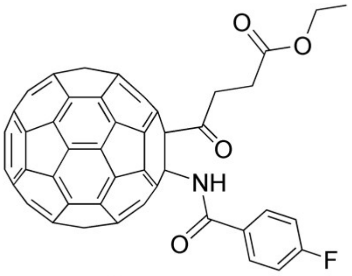
3j

Synthesis of **3j**. According to the general procedure, a solution of **2j** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 4 days at room temperature afforded **3j** (77 mg, 78%) as brown amorphous solid along with unreacted **2j** (12 mg, 12%) after purification by column chromatography; ^1H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.36 (d, J = 8.0 Hz, 2H), 7.78–7.76 (m, 1H), 7.67-7.65 (m, 2H), 3.99 (t, J = 6.7 Hz, 2H), 2.70 (t, J = 6.6 Hz, 2H), 1.69–1.63 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 200.15, 171.91, 167.32, 150.61, 148.40, 147.57, 146.67, 146.45, 146.32, 146.23, 146.15, 145.52, 145.45, 145.36, 145.32, 145.20, 144.96, 144.67, 144.54, 142.97, 142.71, 142.33, 142.29, 142.24, 141.80, 141.31, 141.15, 140.02, 139.37, 138.52, 136.29, 133.99, 130.24, 129.47, 128.95, 128.80, 128.16, 125.25, 92.91, 76.99, 66.27, 38.57, 28.81, 22.10, 10.45; FT-IR (KBr) *v*/cm^{-1}: 3439, 2921, 2895, 1726, 1692, 1534, 1461, 1260, 1029, 723, 525; UV-vis ($CHCl_3$) *λ*/nm (log ε) 255 (4.99), 316 (4.48), 428 (3.34); HRMS (MALDI-TOF) *m/z* calcd for $C_{74}H_{18}NO_4$ $[M+H]^+$ 984.1231, found 984.1221.



3k

Synthesis of **3k**. According to the general procedure, a solution of **2k** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 4 days at room temperature afforded **3k** (69 mg, 71%) as brown amorphous solid along with unreacted **2k** (19 mg, 19 %) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.42–8.40 (m, 2H), 7.28 (t, J = 8.5 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 3.66 (s, 3H), 2.72 (t, J = 6.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 200.38, 172.38, 167.40, 166.57, 165.70, 150.60, 148.55, 147.73, 147.54, 146.82, 146.60, 146.47, 146.38, 146.30, 145.63, 145.60, 145.51, 145.46, 145.28, 144.99, 144.81, 144.66, 143.12, 142.83, 142.36, 141.94, 141.45, 141.25, 140.17, 139.53, 138.65, 136.38, 133.08, 133.02, 129.98, 125.84, 116.27, 116.12, 51.86, 38.63, 28.76; FT-IR (KBr) ν/cm^{-1}: 3442, 2971, 2865, 1743, 1680, 1524, 1466, 1258, 1056, 756, 514; UV-vis ($CHCl_3$) λ/nm (log ε) 256 (5.00), 314 (4.48), 426 (3.48); HRMS (MALDI-TOF) *m/z* calcd for $C_{72}H_{13}NO_4F$ $[M+H]^+$ 974.0823, found 974.0816.



3l

Synthesis of **3l**. According to the general procedure, a solution of **2l** (100 mg, 0.1 mmol) in 25 mL carbon disulfide was photooxygenated for 4 days at room temperature afforded **3l** (66 mg, 67%) as brown amorphous solid along with unreacted **2l** (19 mg, 19 %) after purification by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 8.43–8.41 (m, 2H), 7.29 (t, J = 8.6 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.98 (t, J = 6.8 Hz, 2H), 2.72 (t, J = 6.8 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ (3:1 v/v)) δ 200.45, 171.94, 167.32, 166.51, 165.62, 150.54, 148.46, 147.63, 147.44, 146.73, 146.50, 146.36, 146.29, 146.20, 145.53, 145.50, 145.41, 145.37, 145.20, 144.90, 144.71, 144.56, 143.02, 142.76, 142.36, 142.28, 141.84, 141.34, 141.15, 140.07, 139.43, 138.55, 136.28, 133.00, 132.93, 125.77, 116.18, 116.04, 93.08, 76.93, 60.77, 38.54, 28.86, 14.21;FT-IR (KBr) ν/cm^{-1}: 3424, 2945, 2823, 1730, 1685, 1531, 1432, 1255, 1021, 724, 526; UV-vis ($CHCl_3$) λ/nm (log ε) 254 (4.99), 317 (4.50), 425 (3.46); HRMS (MALDI-TOF) m/z calcd for $C_{73}H_{15}NO_4F$ $[M+H]^+$ 988.0980, found 988.0975.

References:

1. Wang, G.-W.; Li, F.-B. *Org. Biomol. Chem.* **2005,** *3*,794.

^{1}H NMR spectra and ^{13}C NMR spectra of compounds 2a–l.

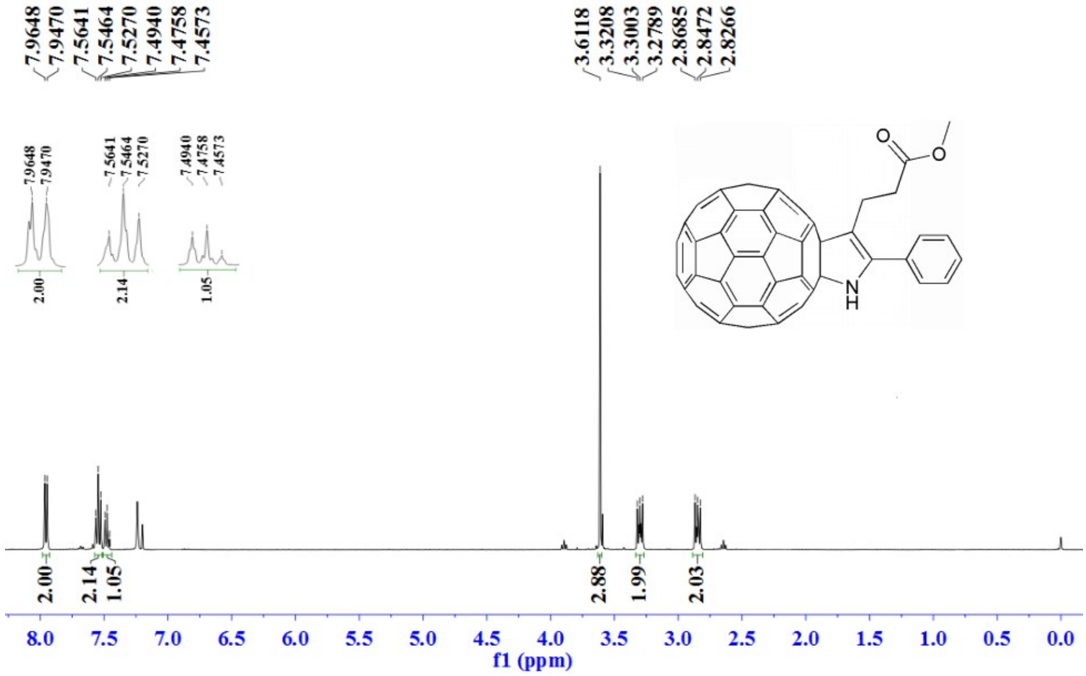


Figure S1. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2a

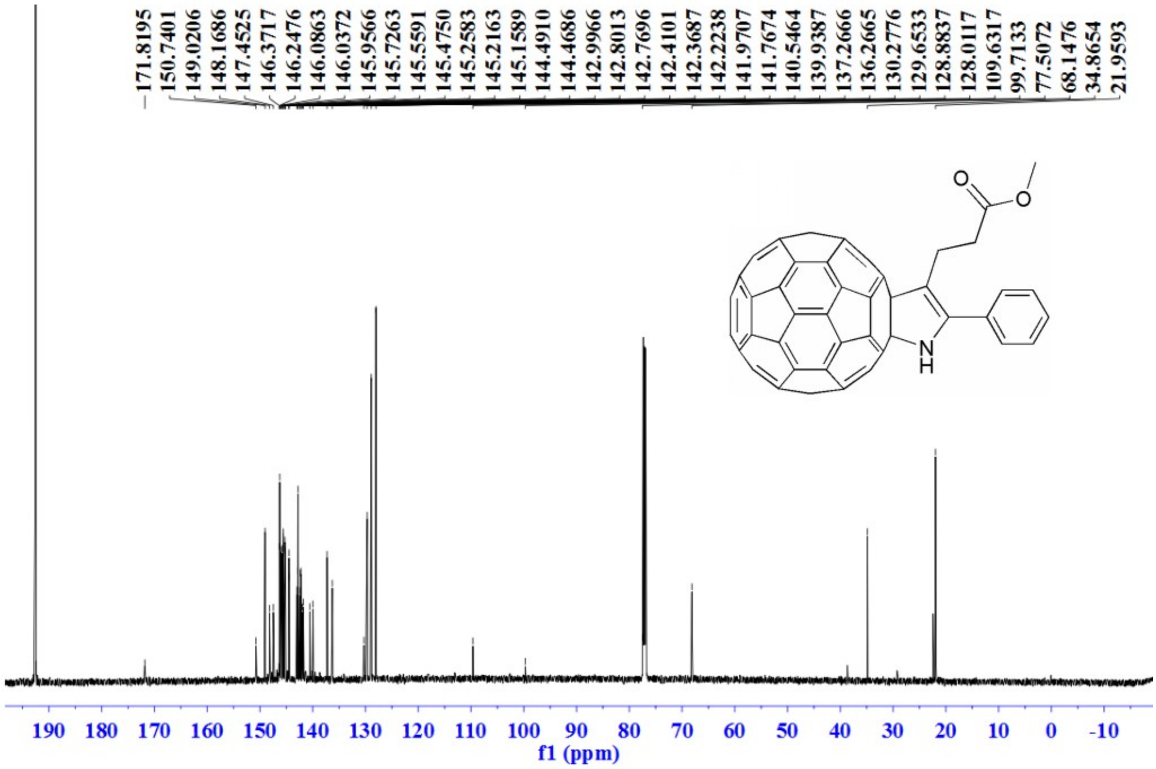


Figure S2. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2a

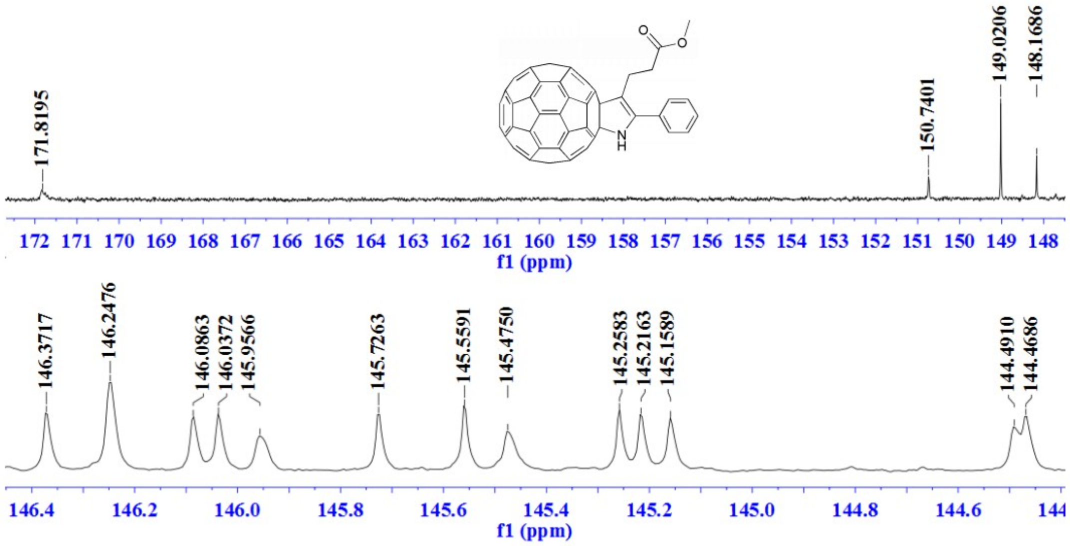


Figure S2-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2a

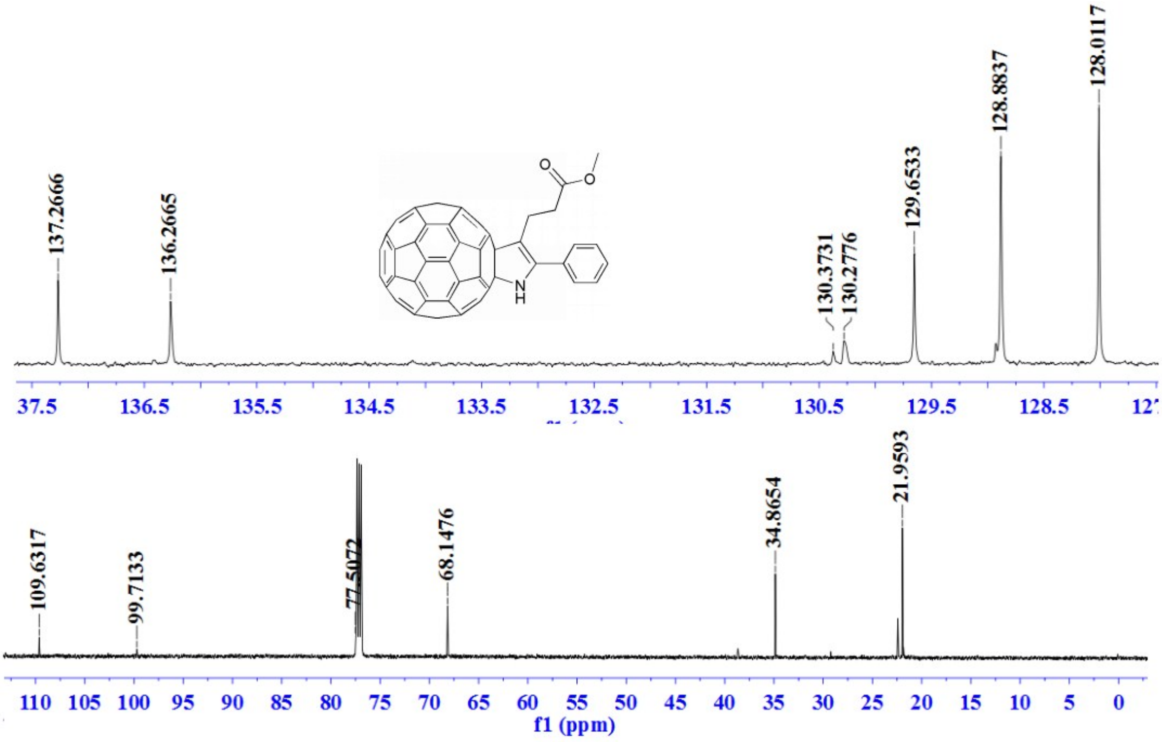


Figure S2-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2a

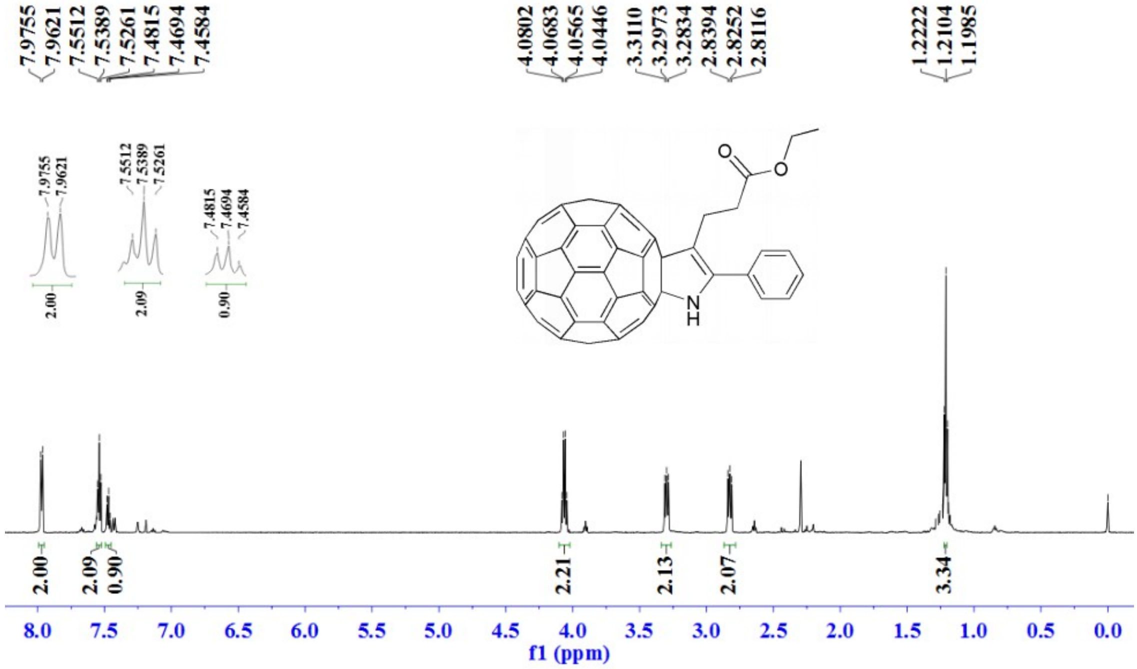


Figure S3. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) of compound 2b

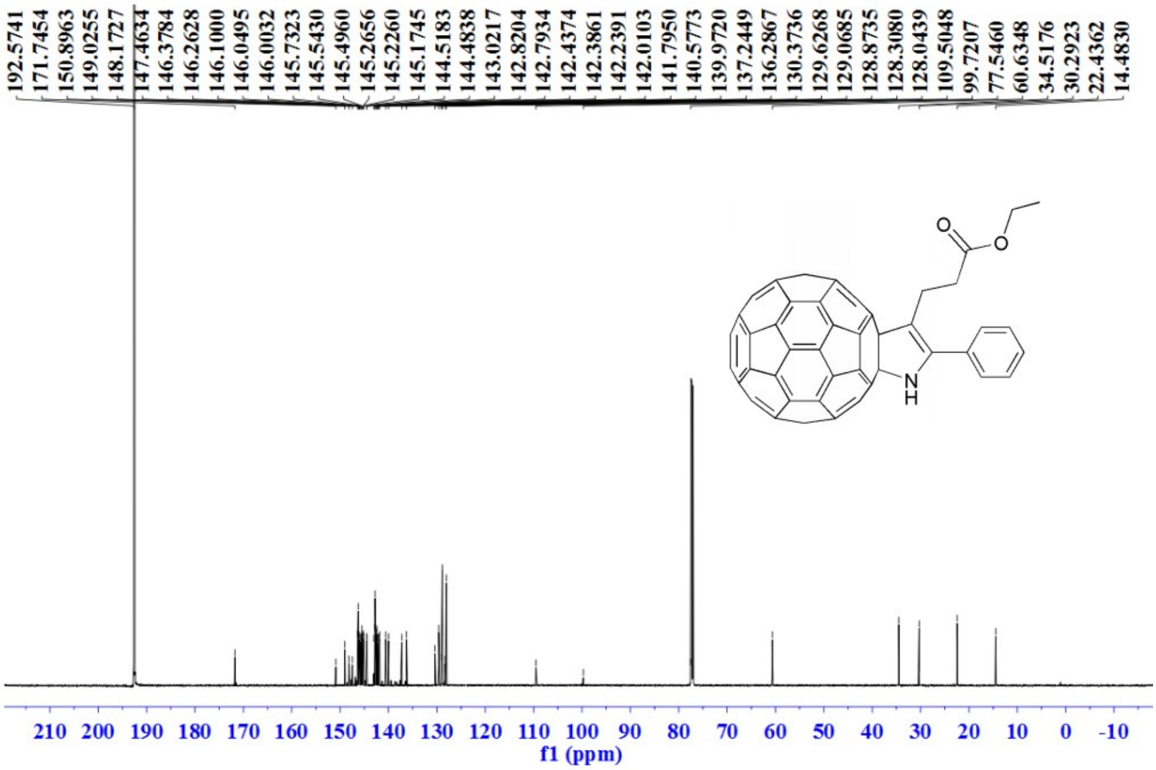


Figure S4. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$) of compound 2b

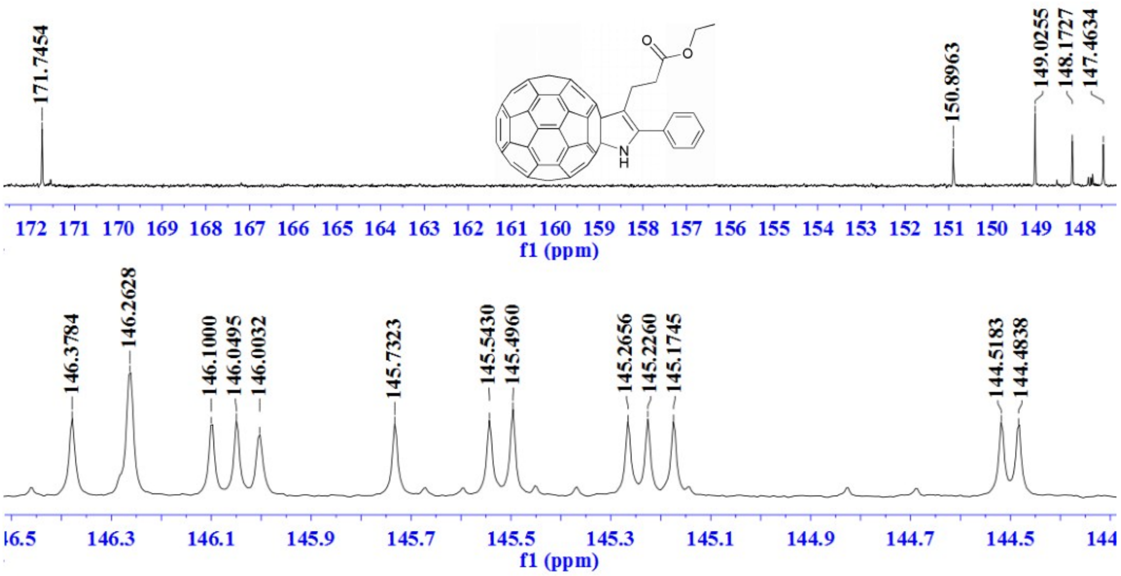


Figure S4-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2b

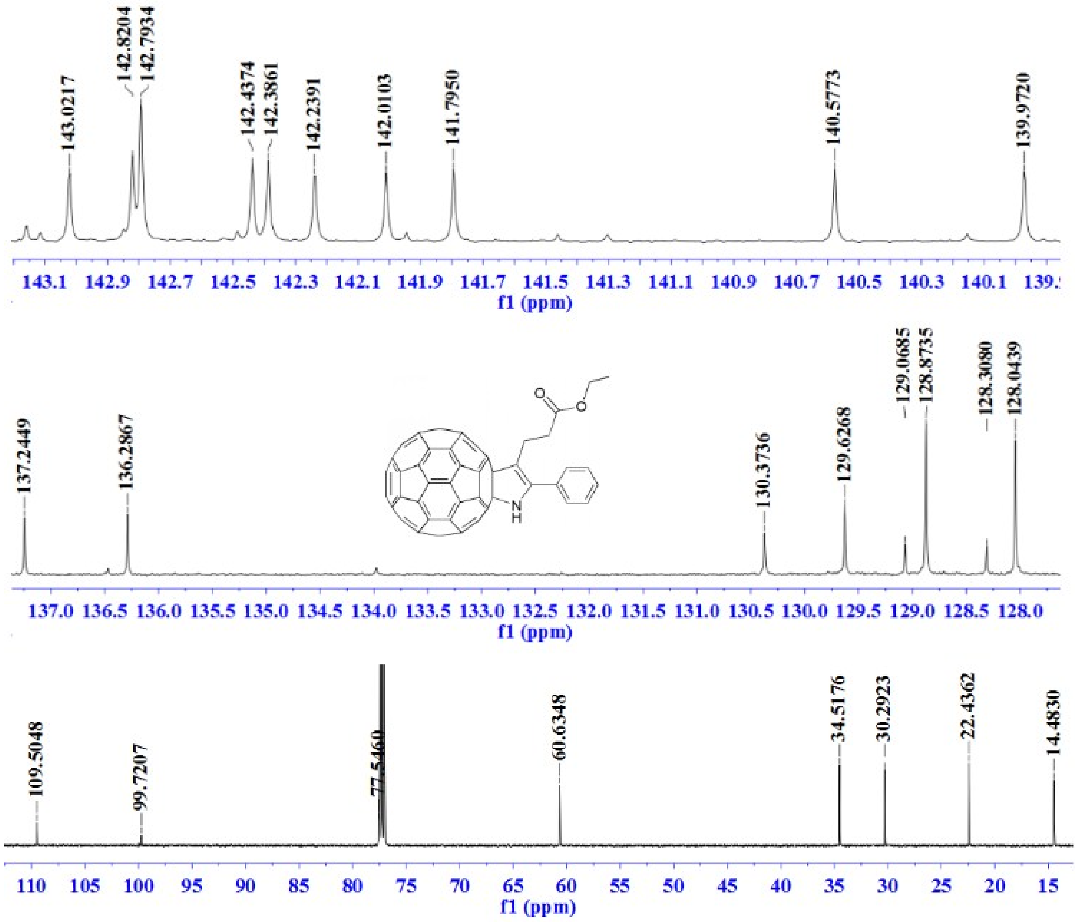


Figure S4-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2b

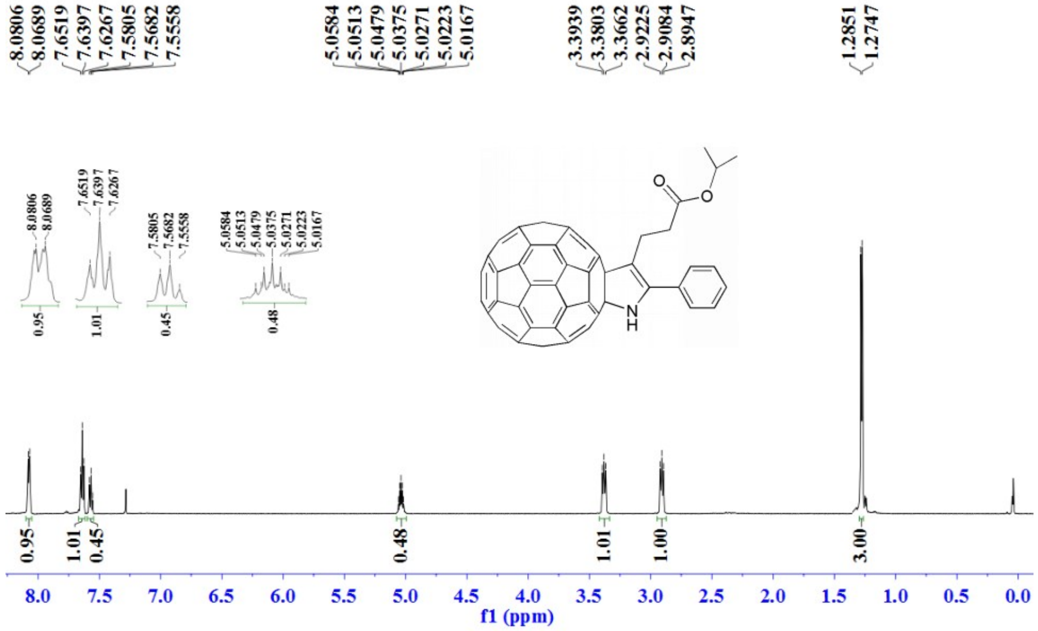


Figure S5. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) of compound 2c

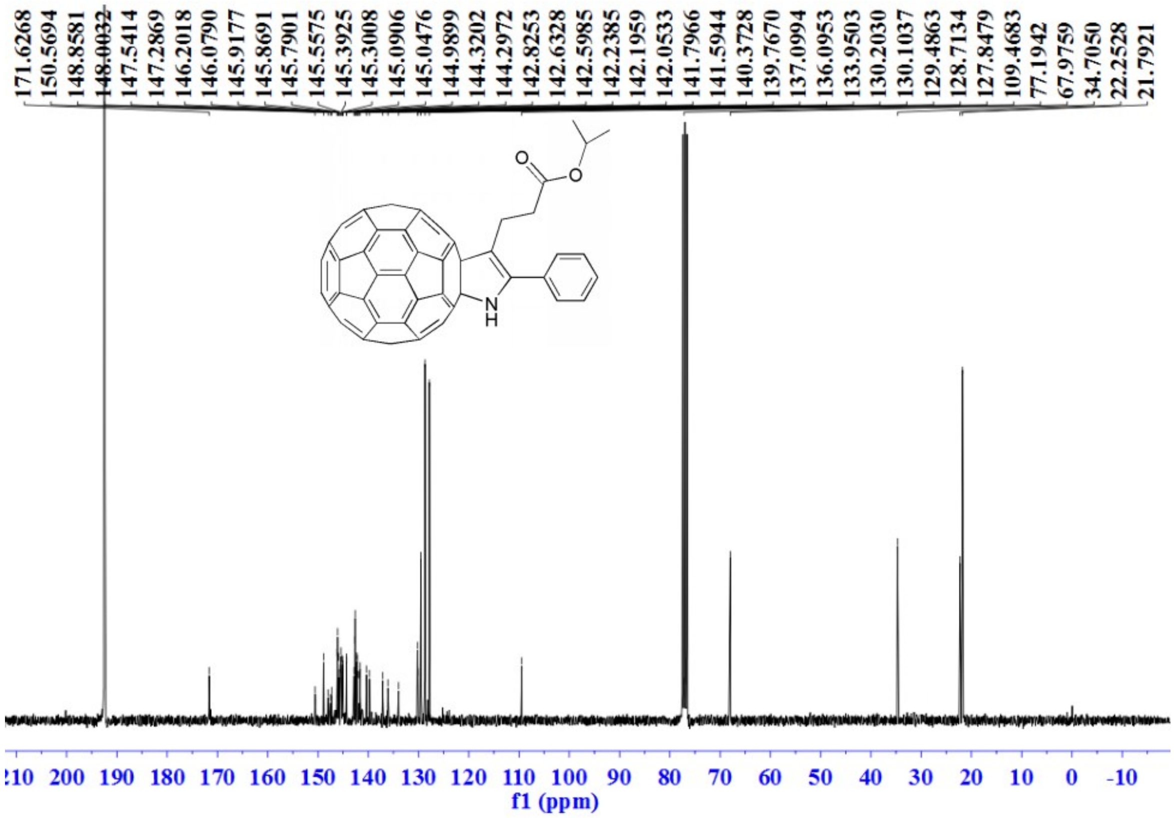


Figure S6. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$) of compound 2c

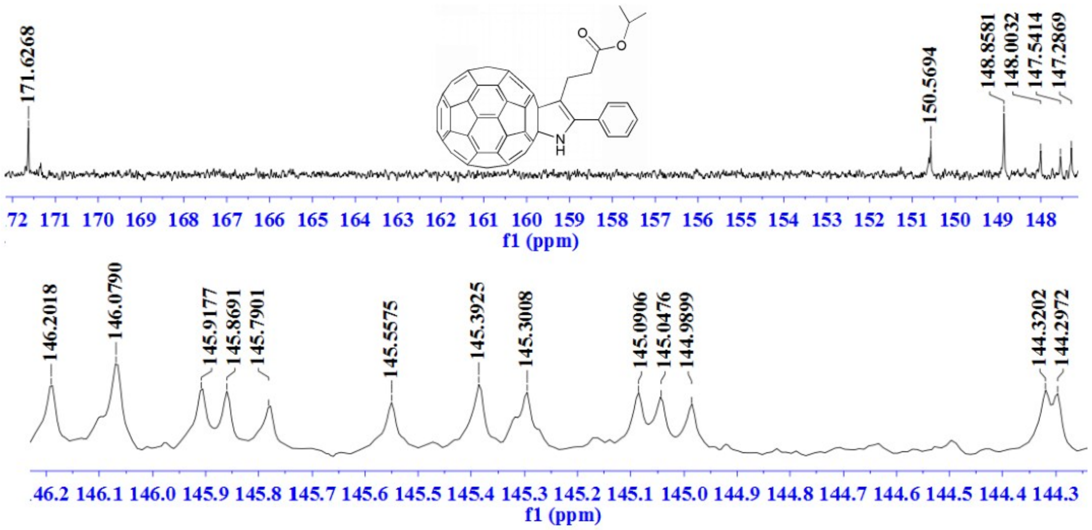


Figure S6-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2c

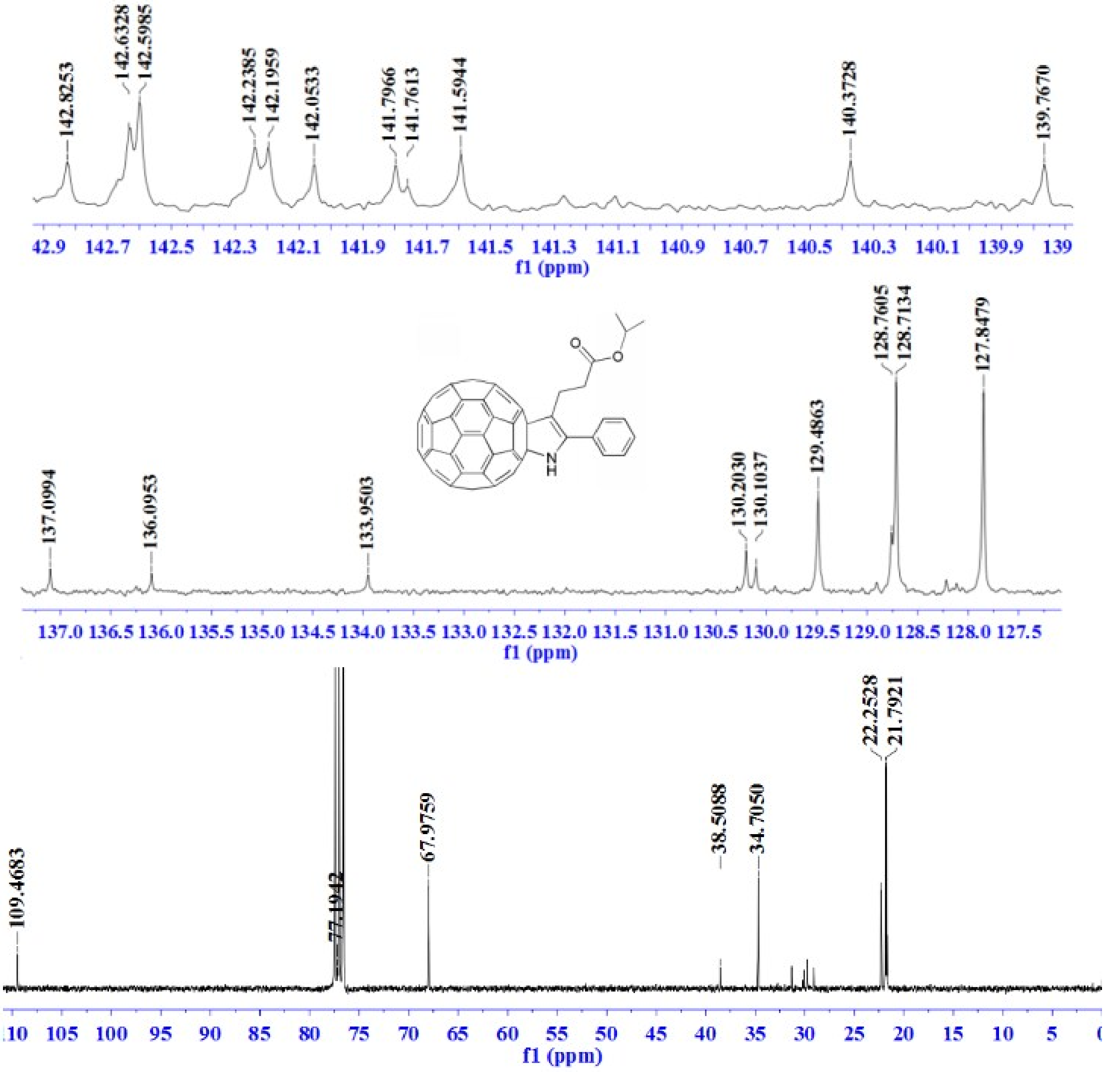


Figure S6-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2c

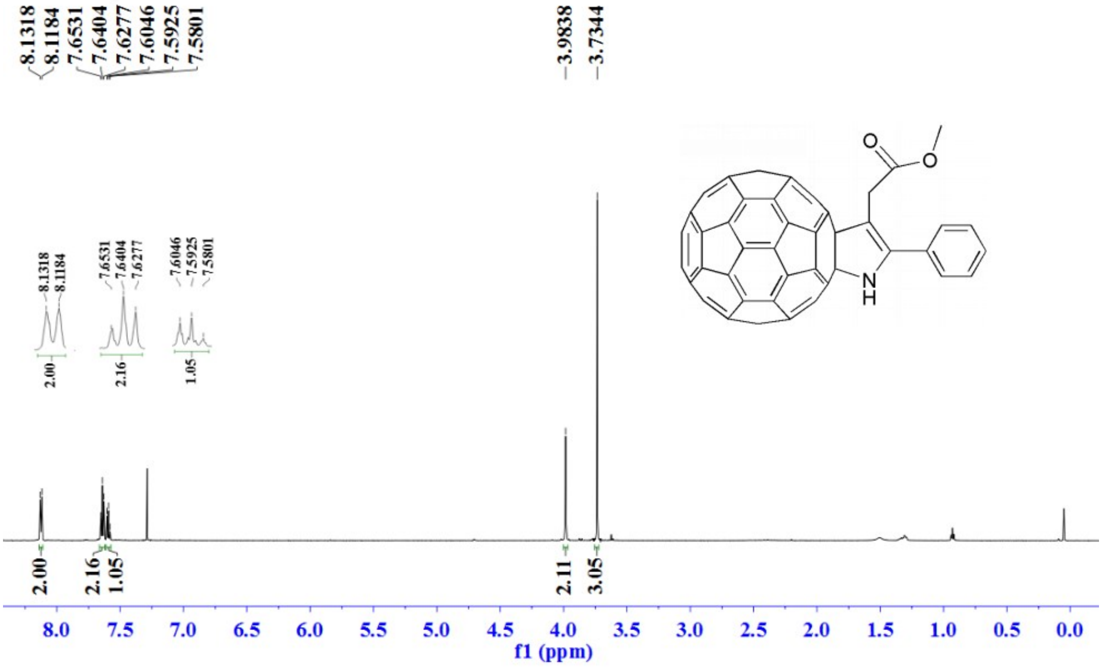


Figure S7. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) of compound 2d

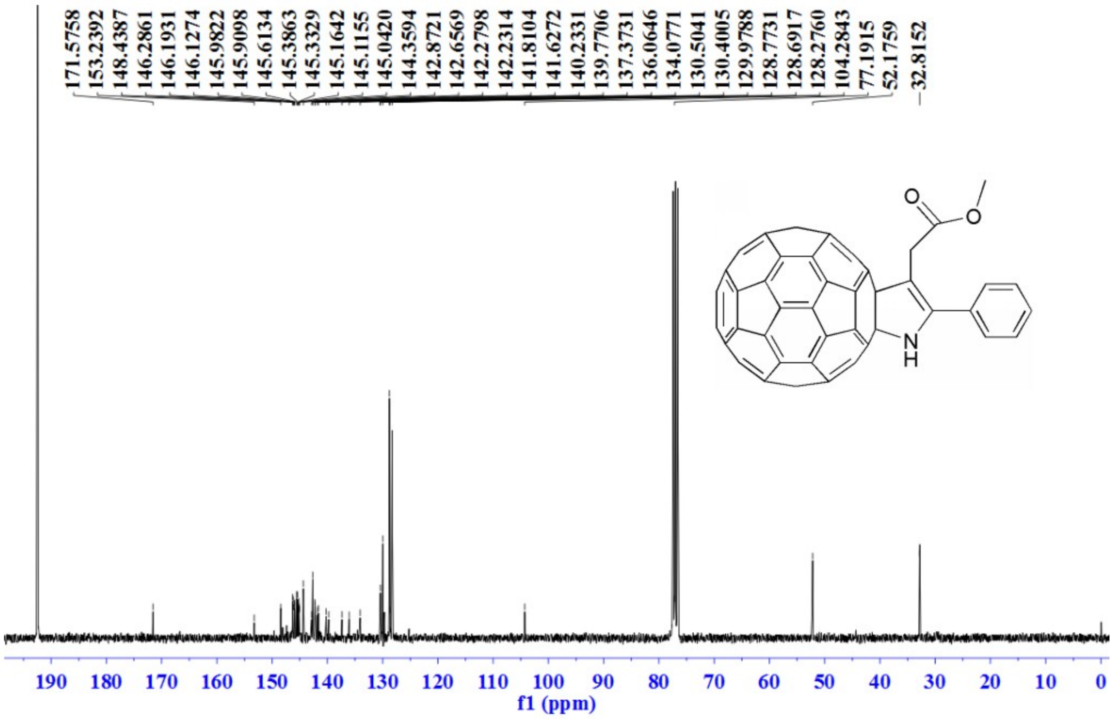


Figure S8. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$) of compound 2d

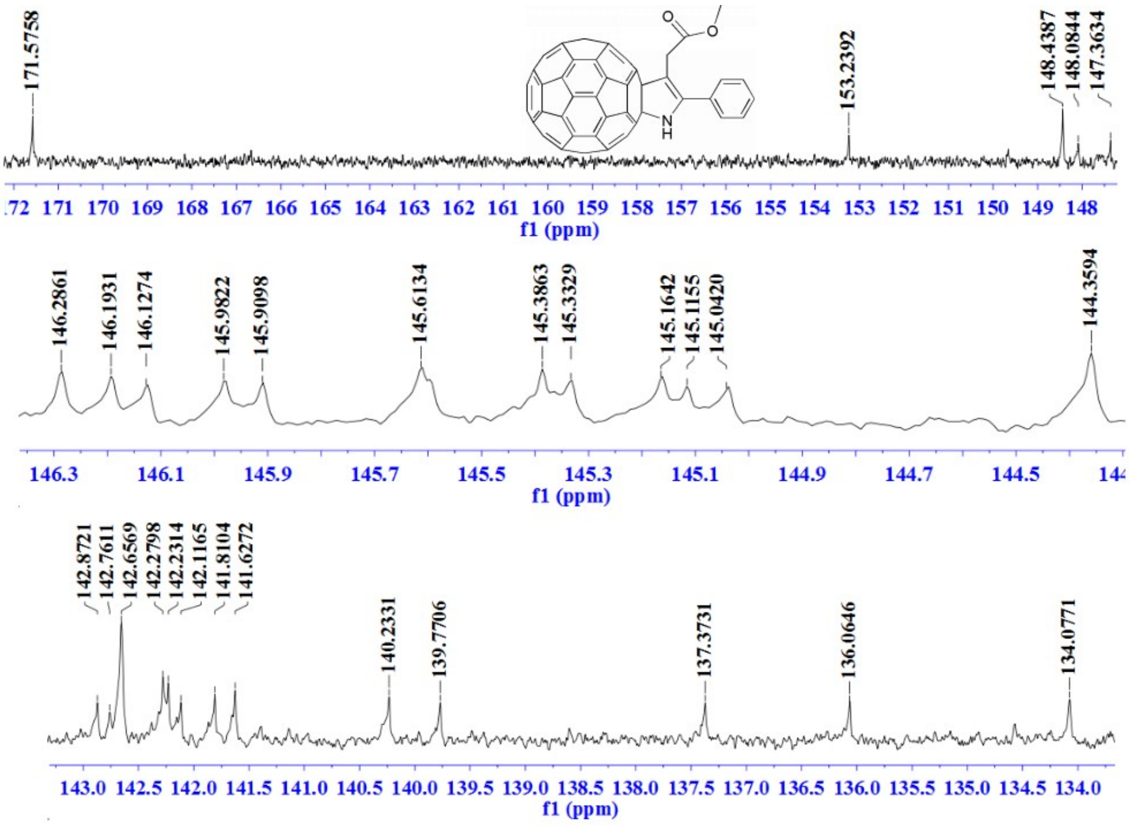


Figure S8-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2d

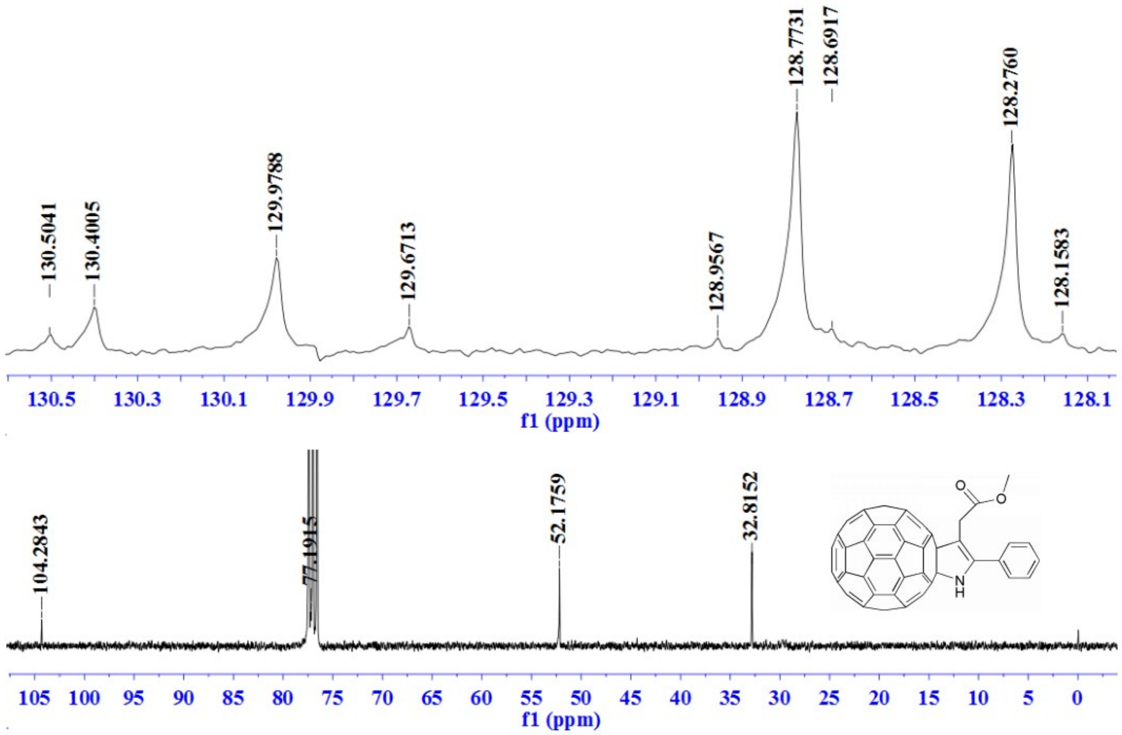


Figure S8-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2d

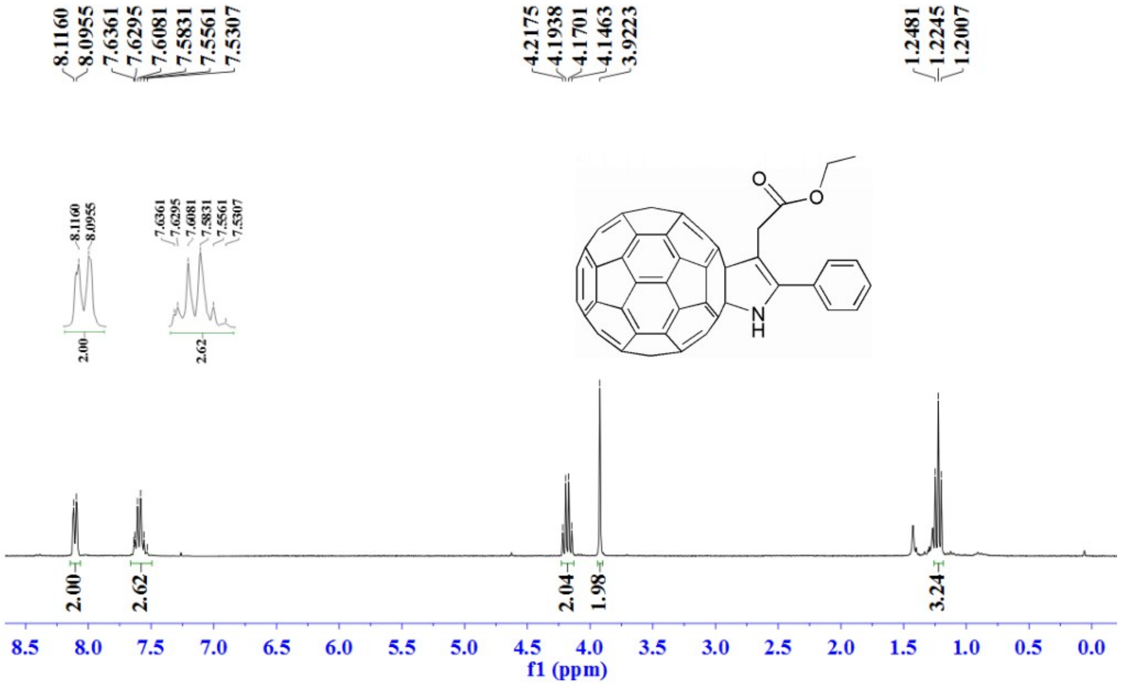


Figure S9. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2e

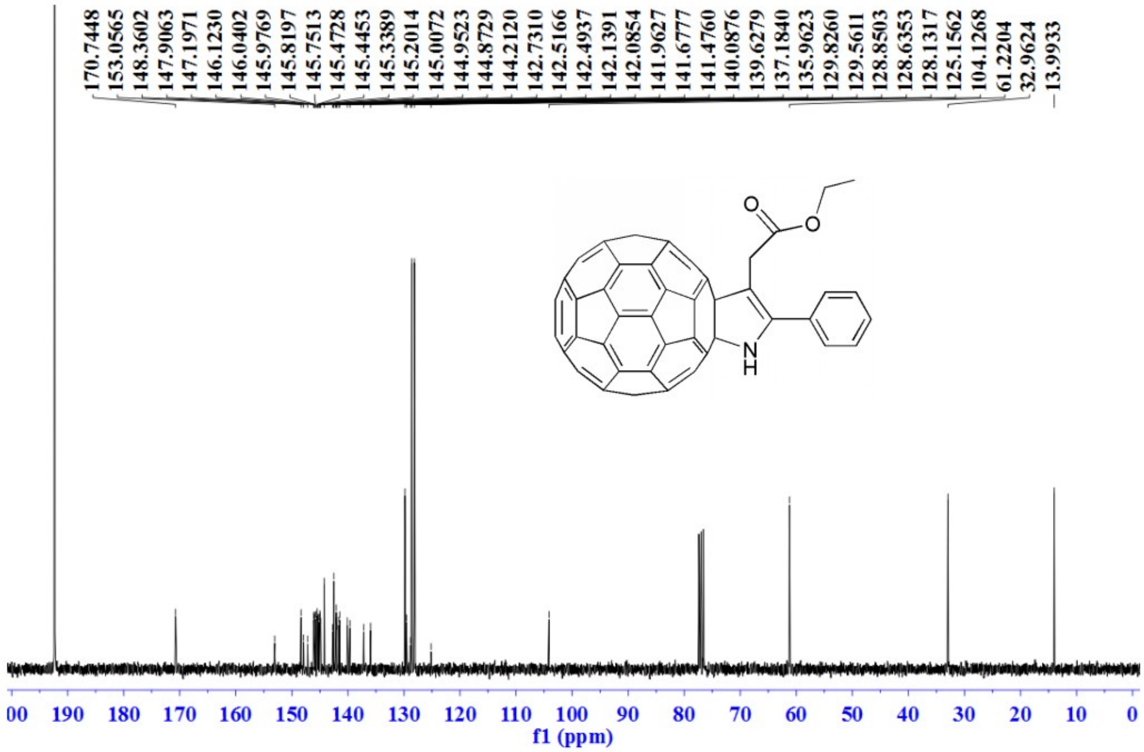


Figure S10. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2e

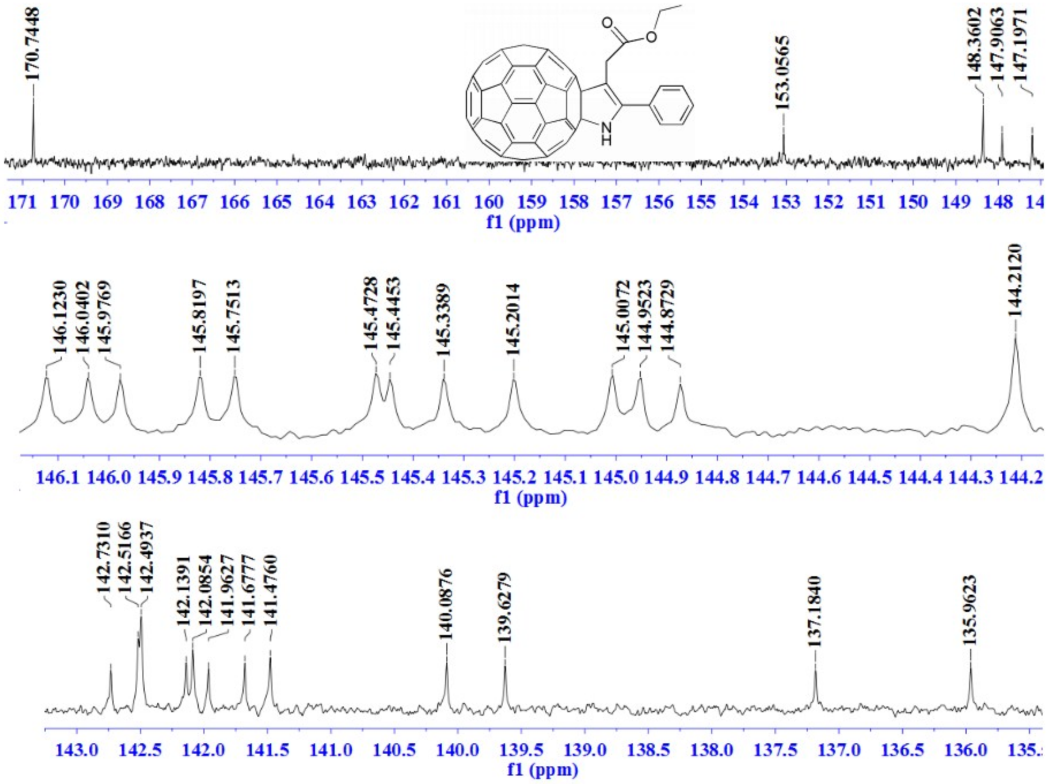


Figure S10-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2e

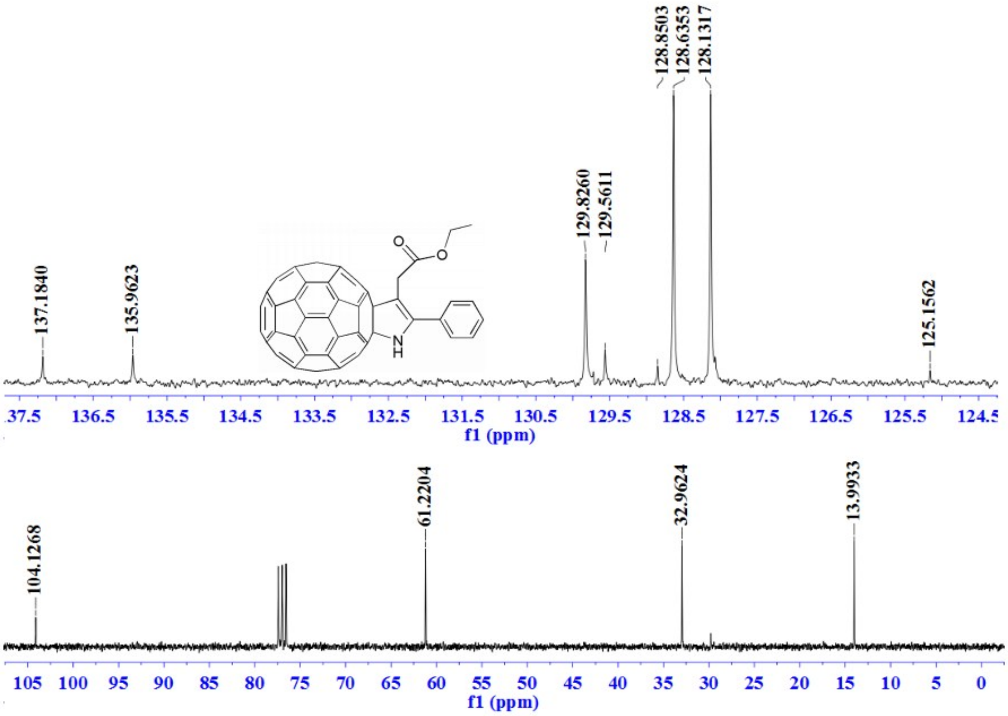


Figure S10-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2e

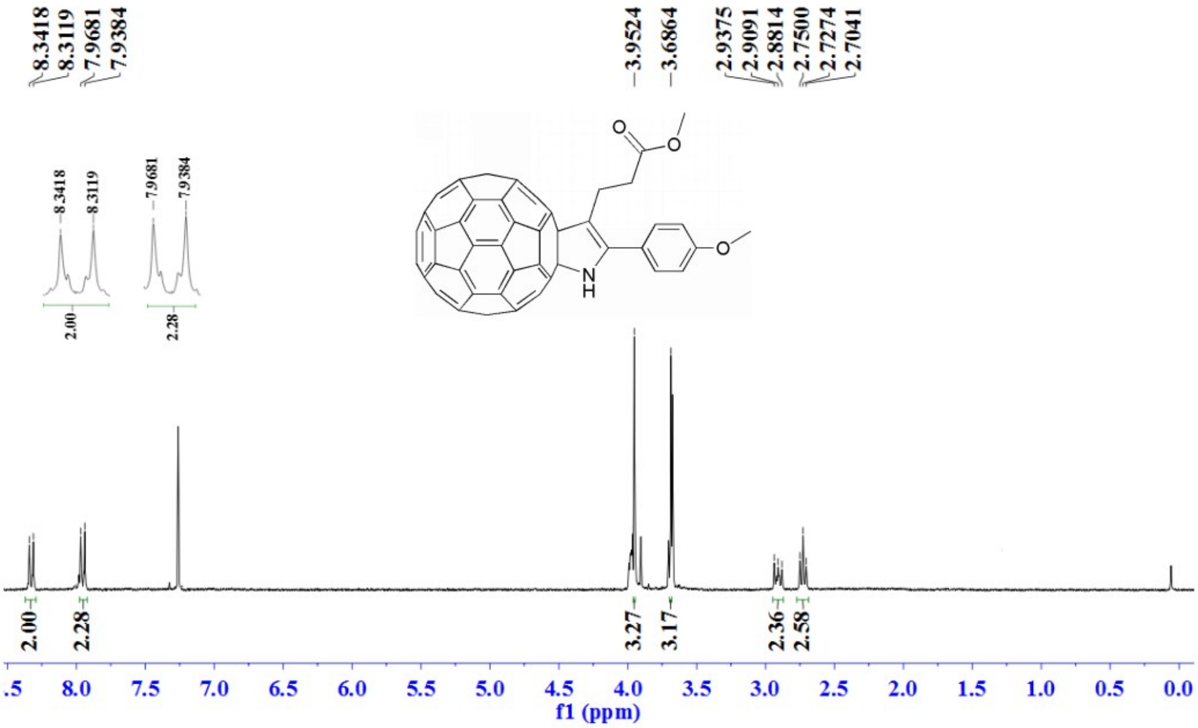


Figure S11. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2f

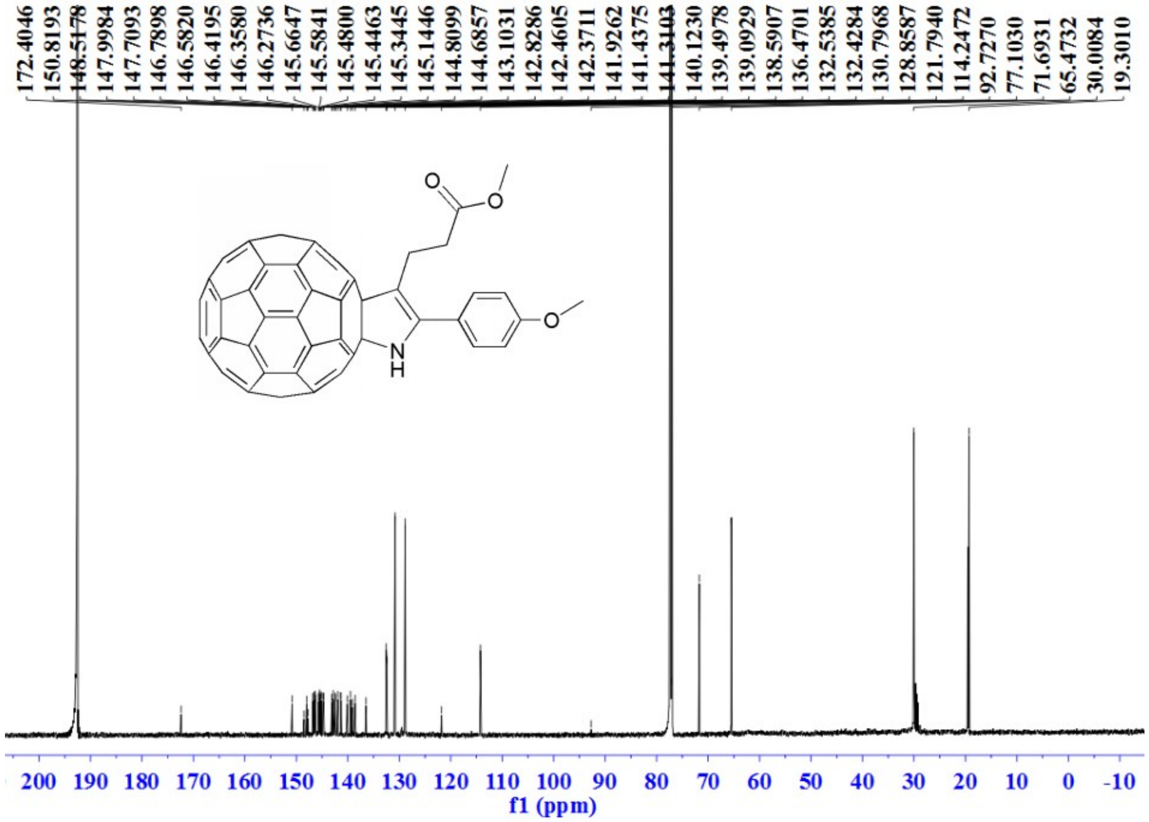


Figure S12. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2f

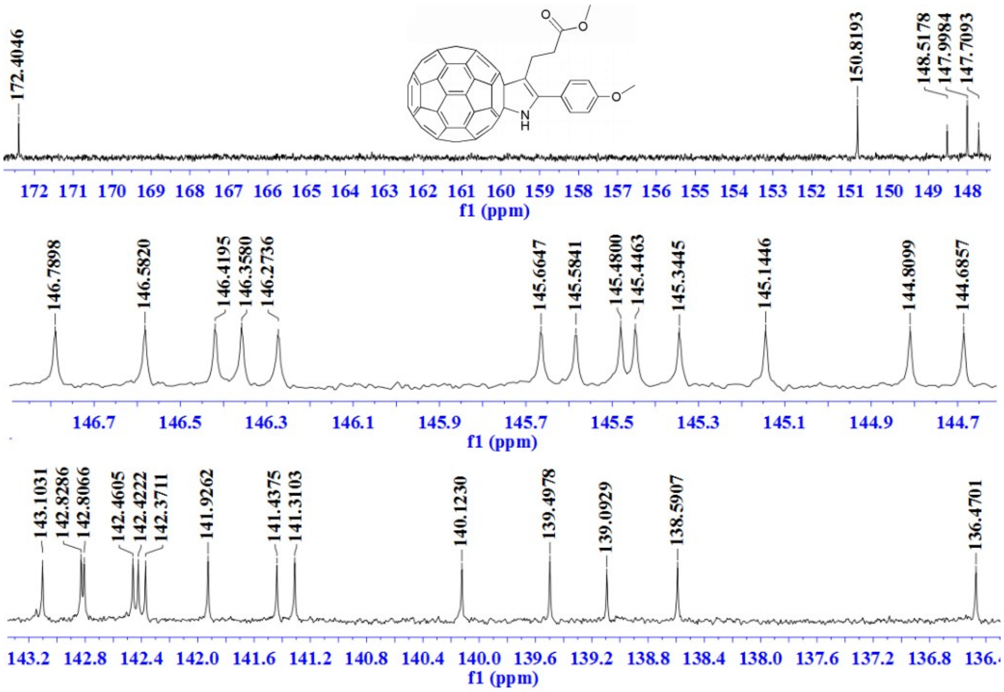


Figure S12-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2f

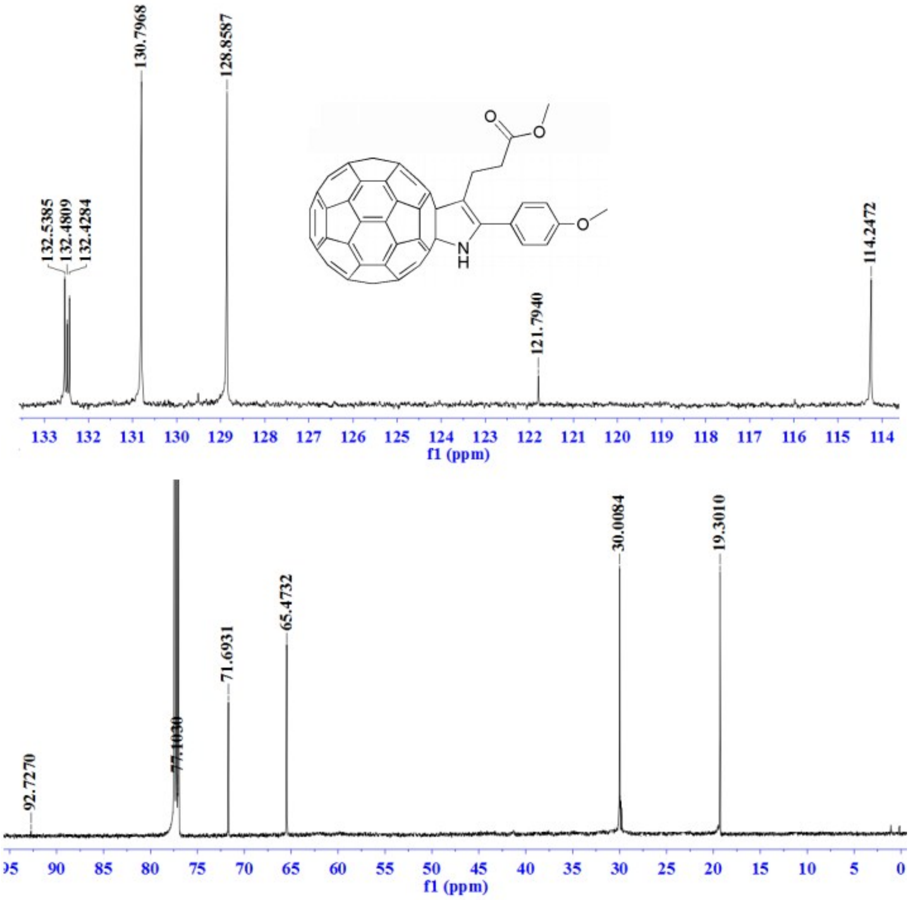


Figure S12-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2f

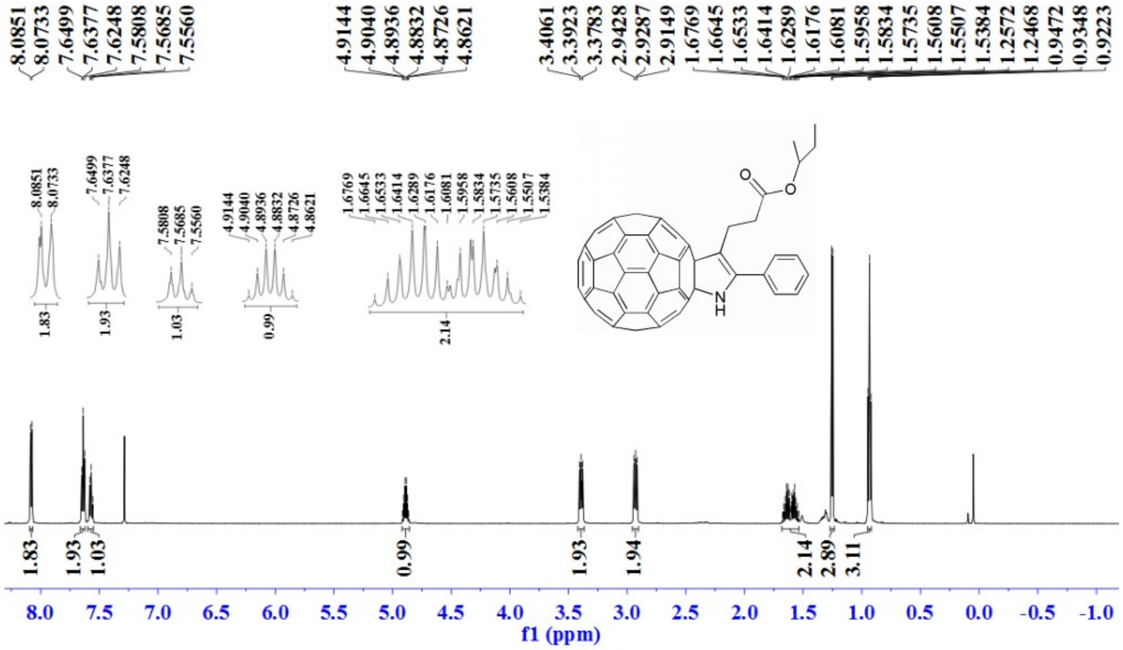


Figure S13. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2g

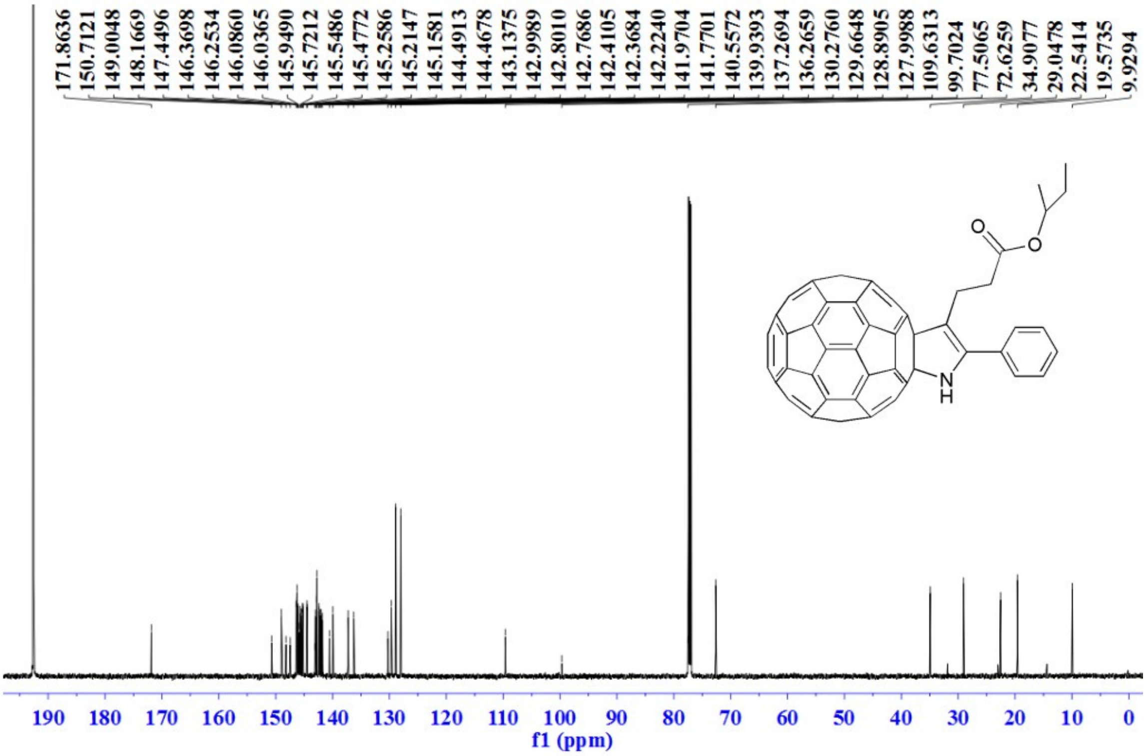


Figure S14. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2g

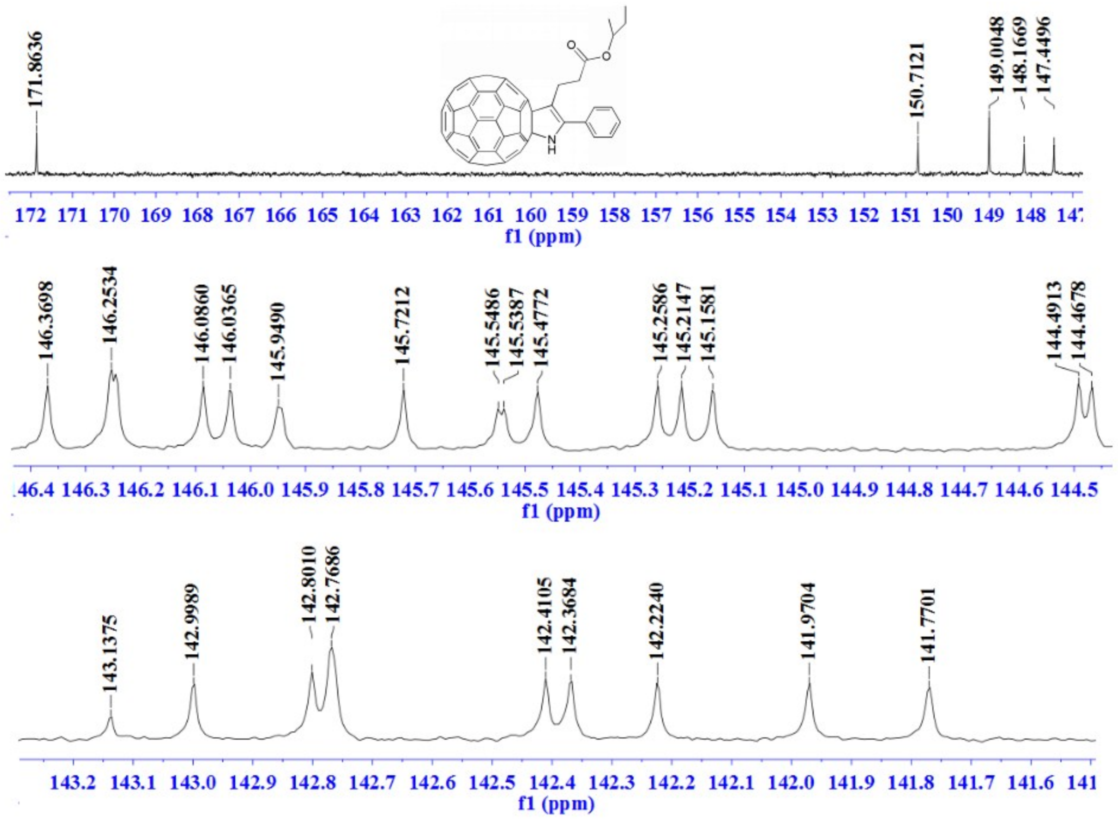


Figure S14-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2g

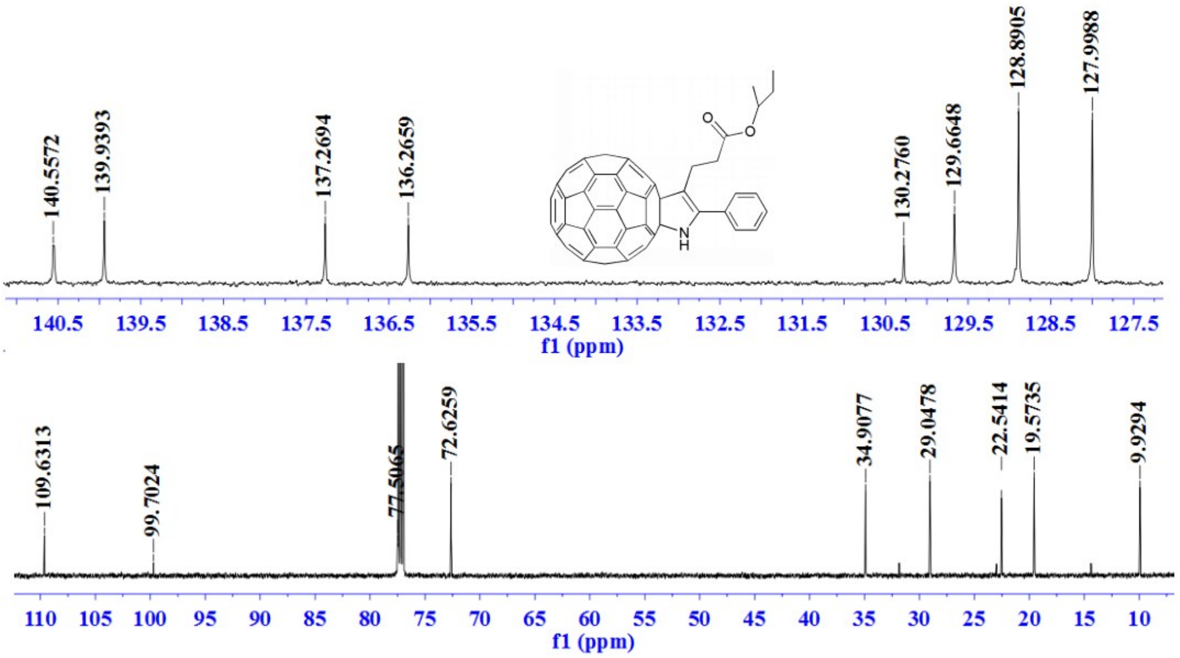


Figure S14-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2g

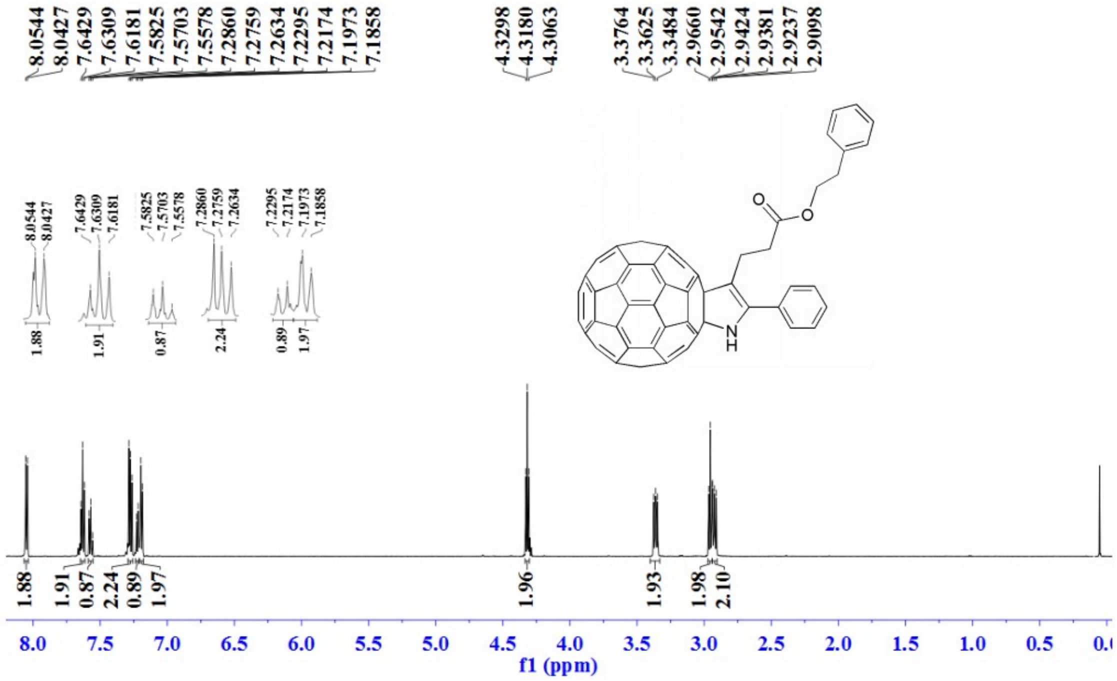


Figure S15. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2h

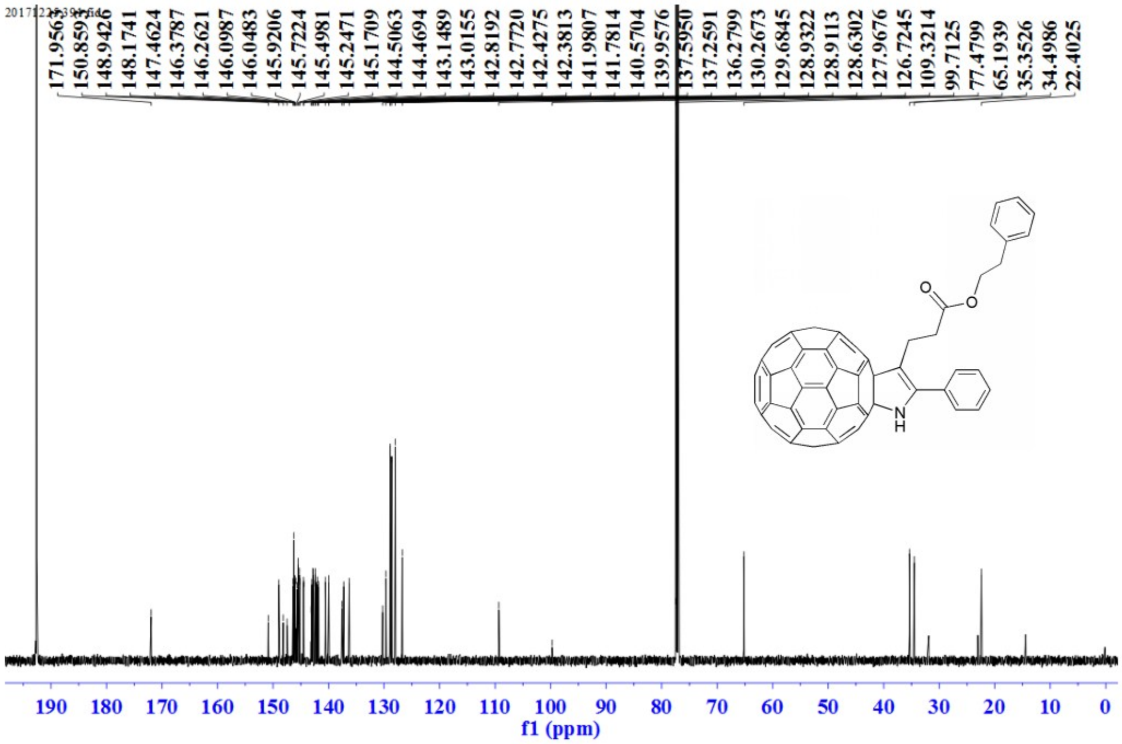


Figure S16. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2h

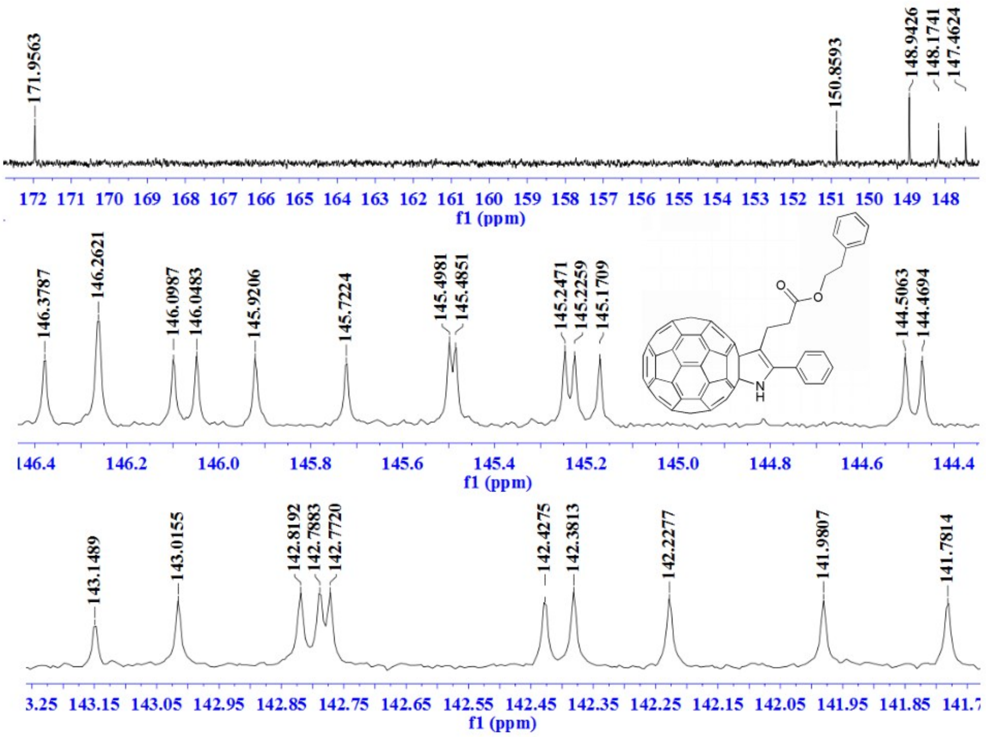


Figure S16-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2h

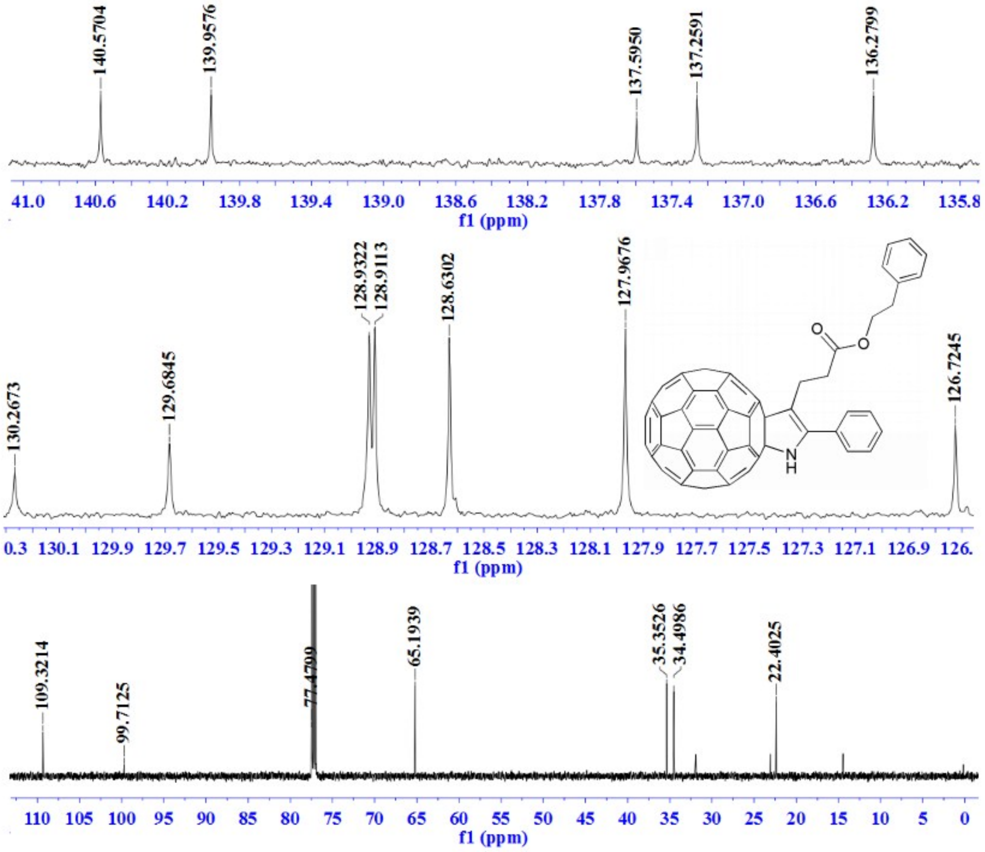


Figure S16-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2h

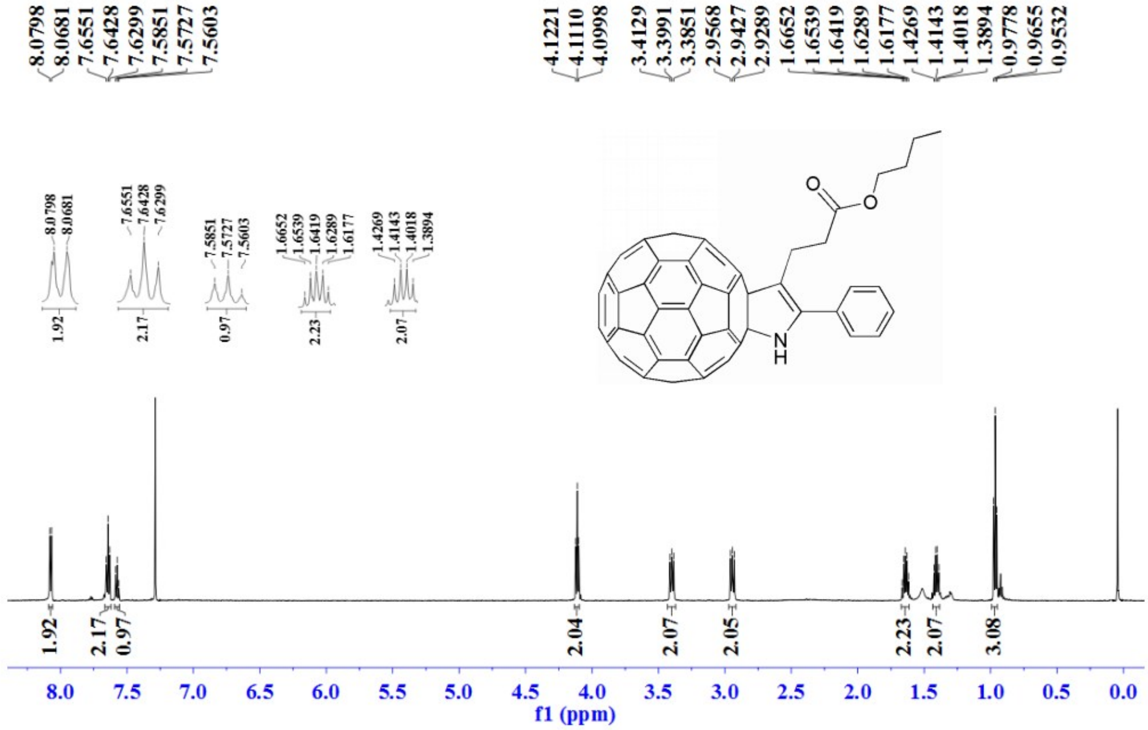


Figure S17. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2i

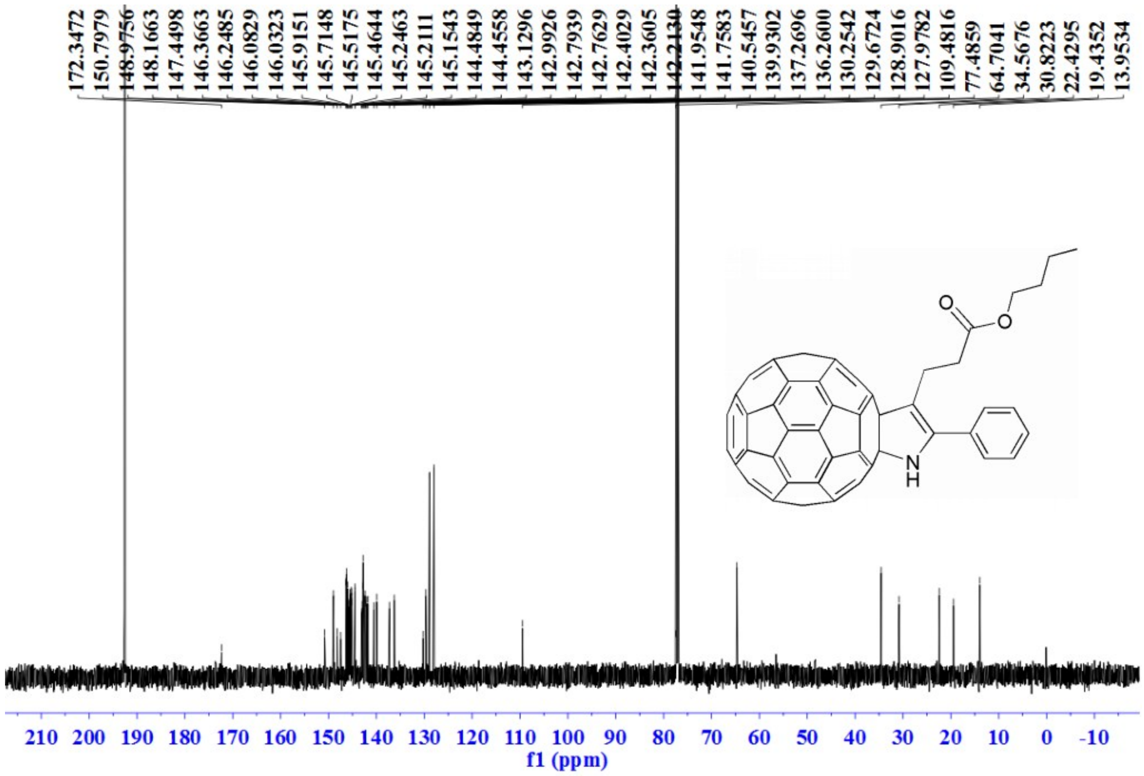


Figure S18. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2i

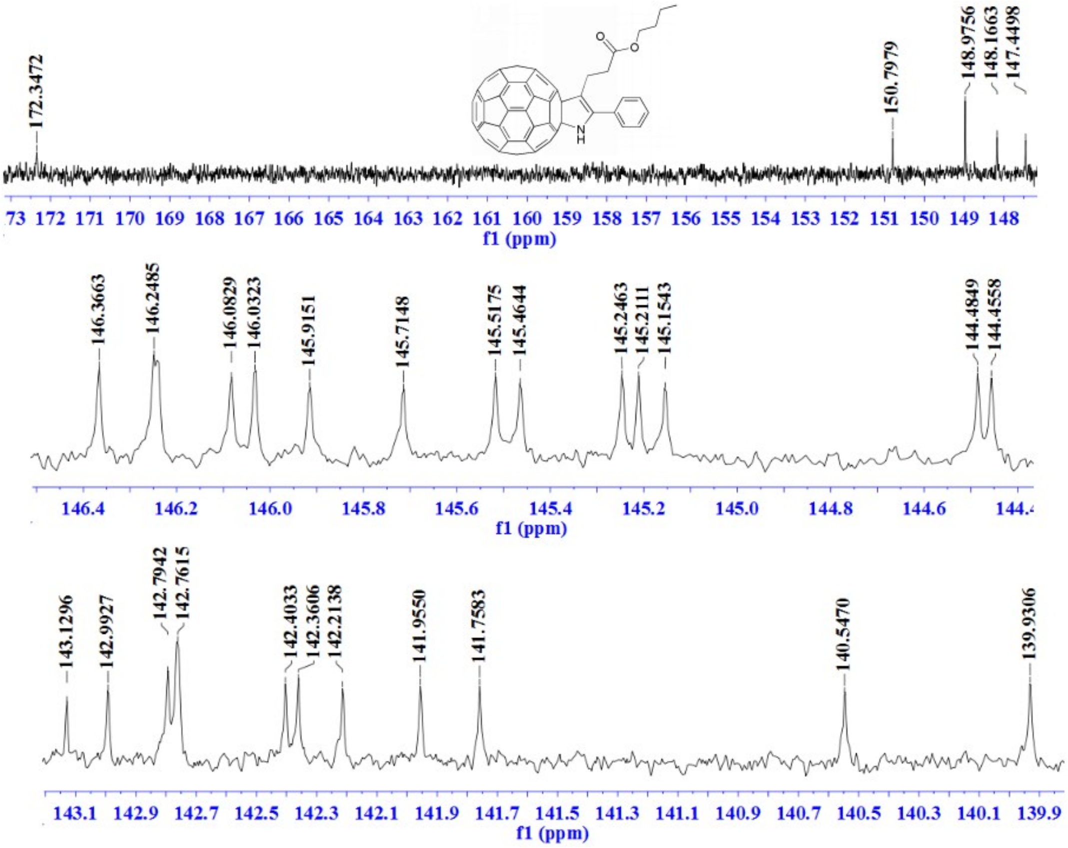


Figure S18-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2i

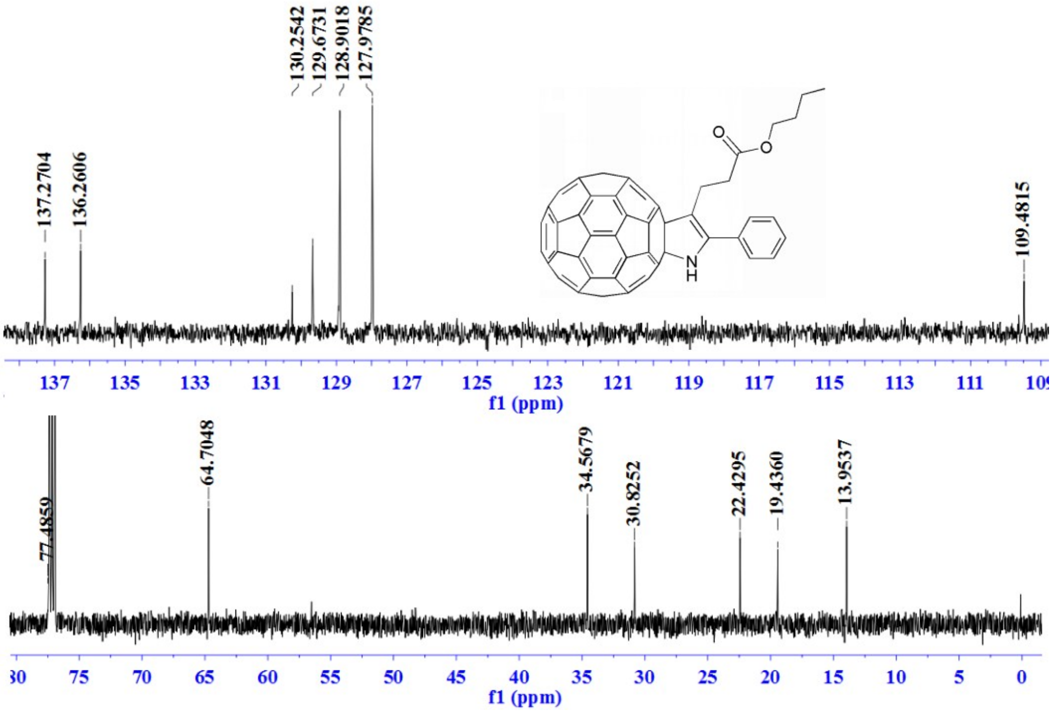


Figure S18-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2i

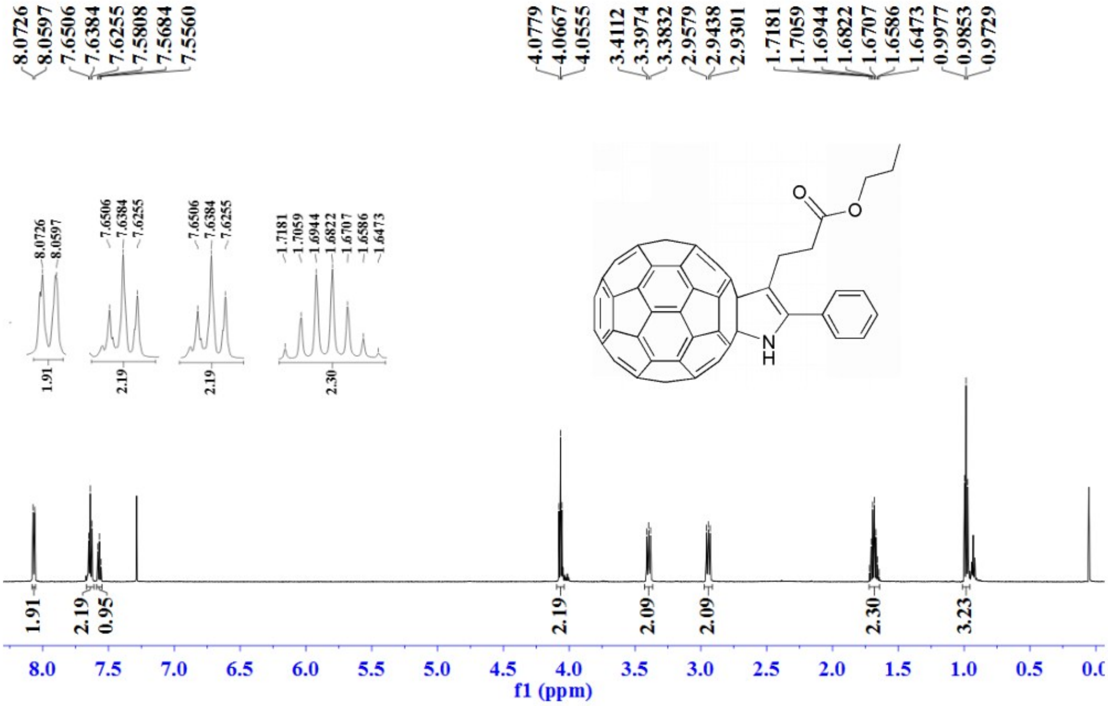


Figure S19. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2j

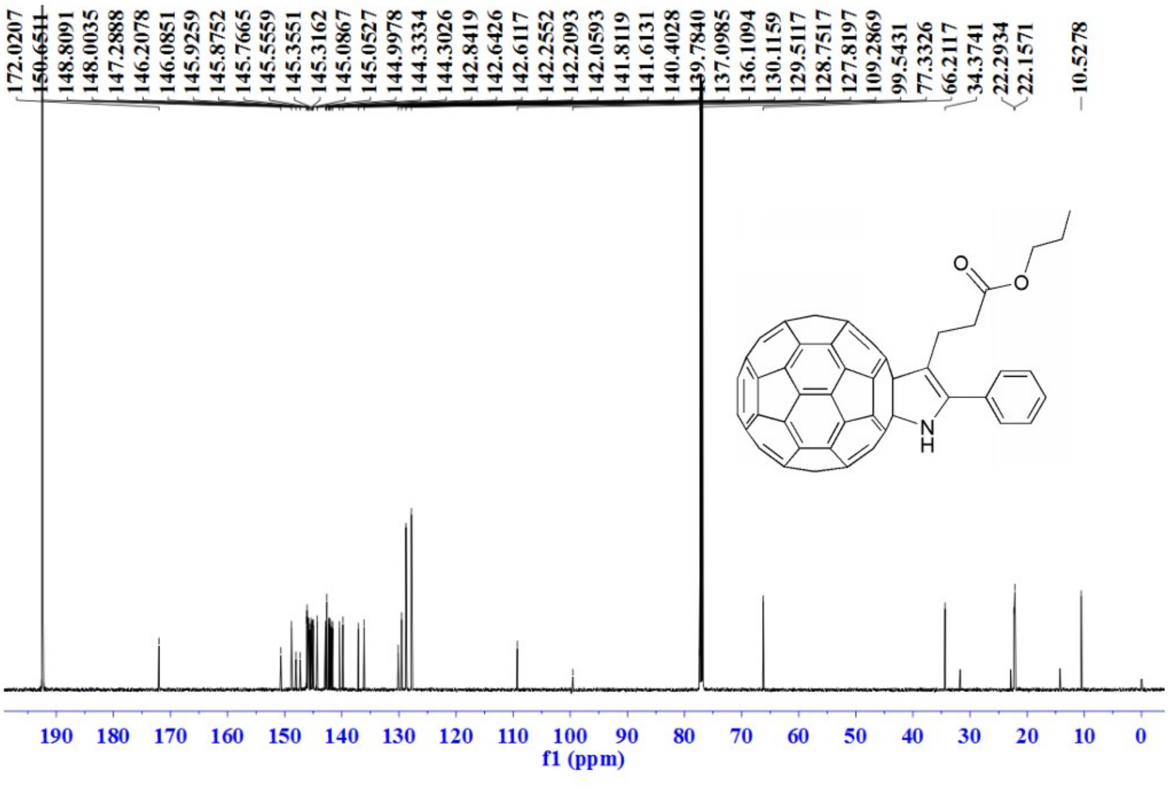


Figure S20. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2j

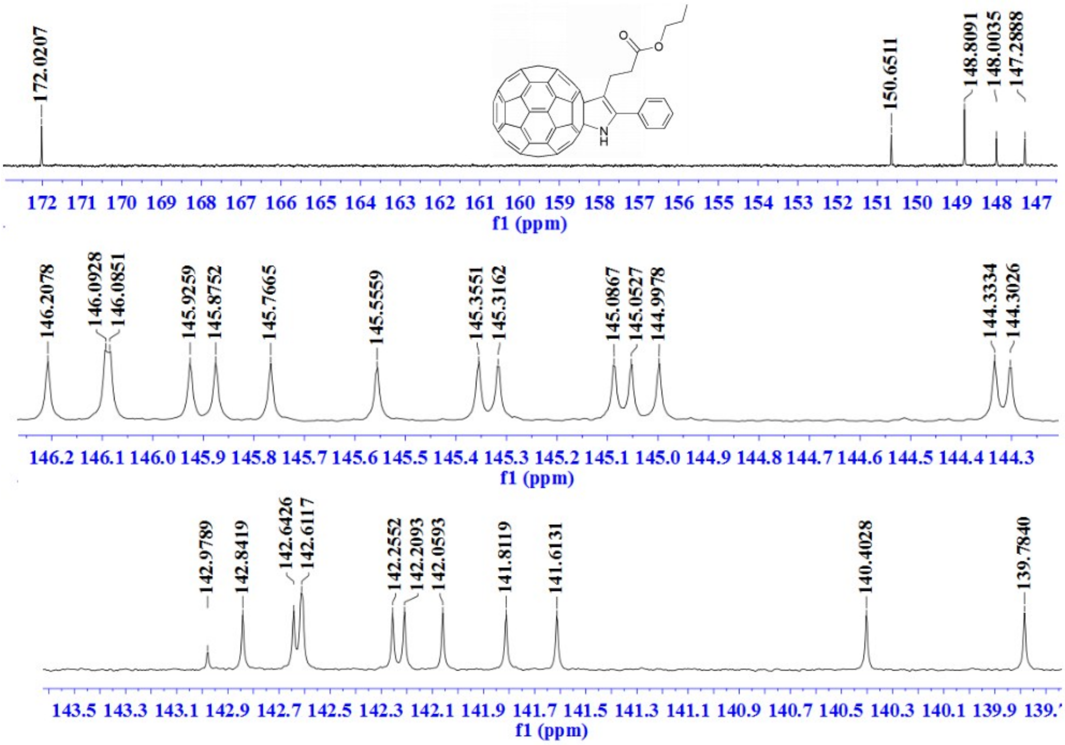


Figure S20-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2j

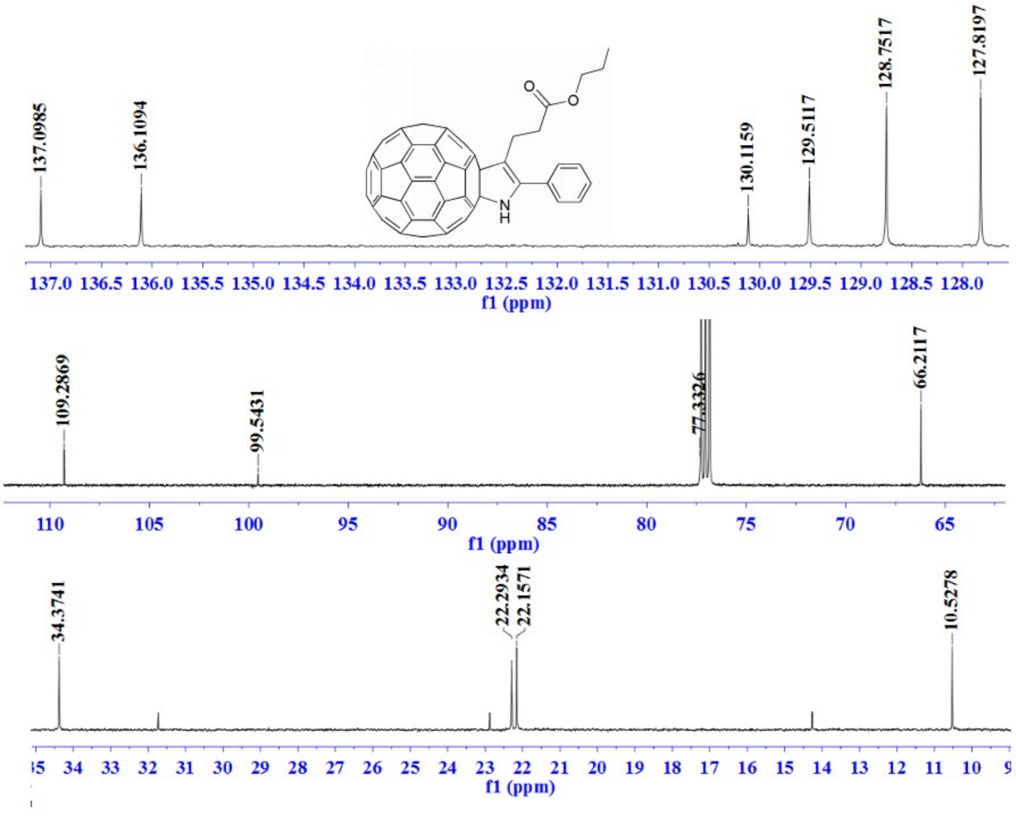


Figure S20-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2j

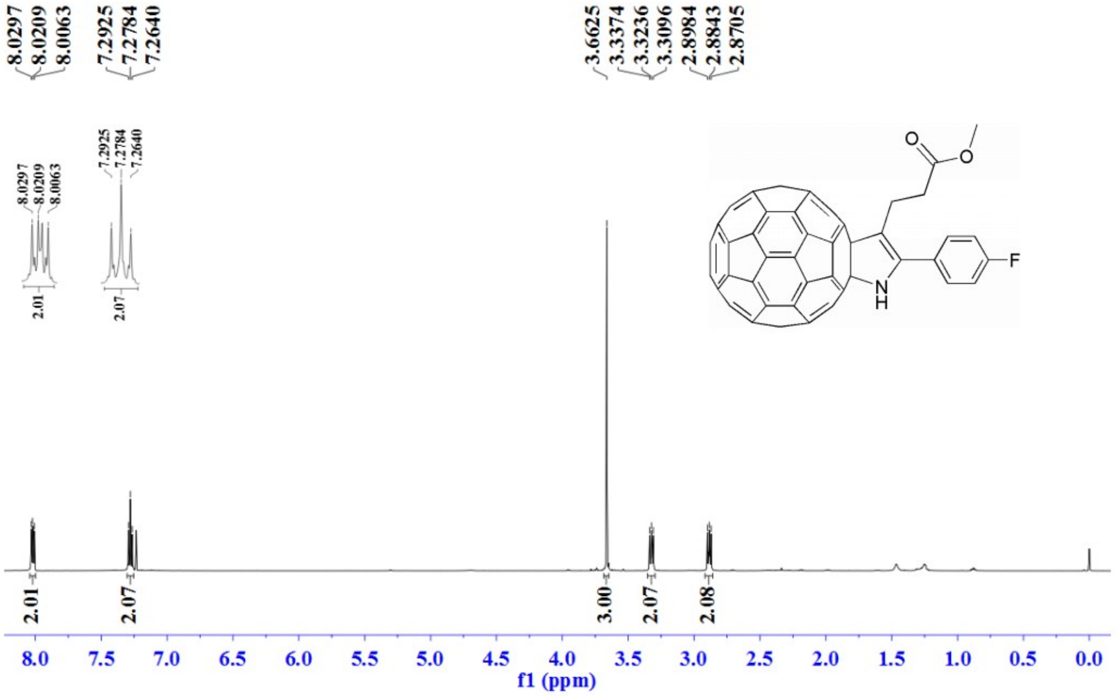


Figure S21. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) of compound 2k

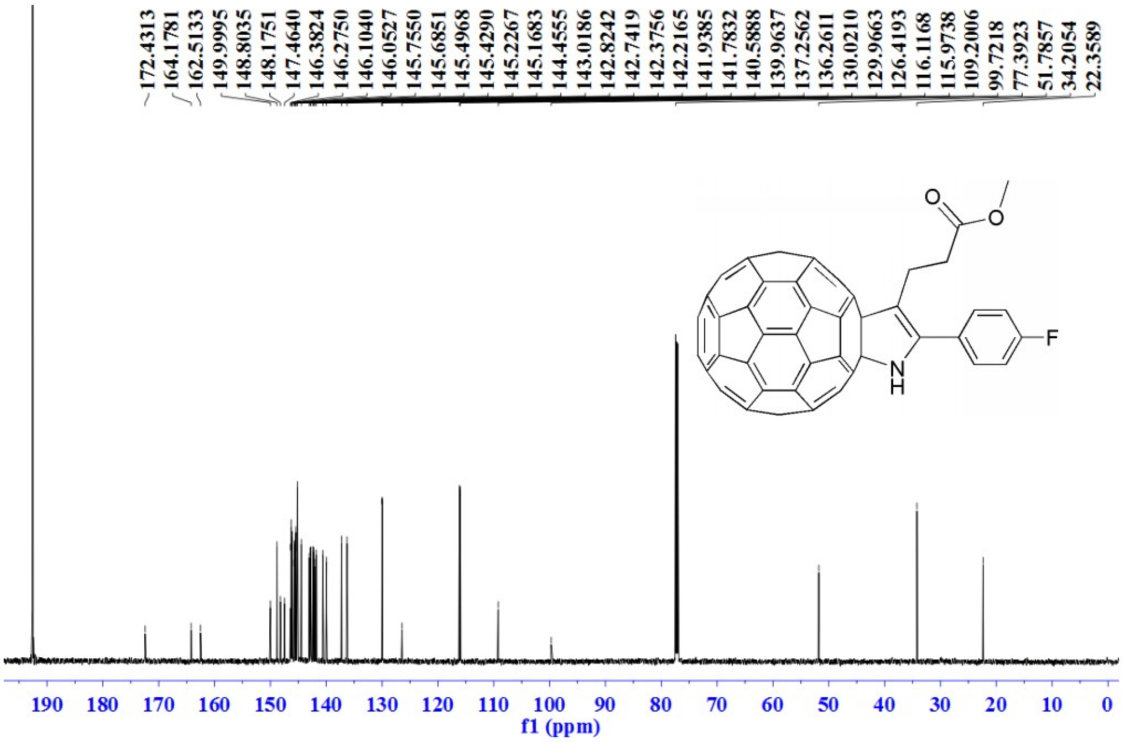


Figure S22. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$) of compound 2k

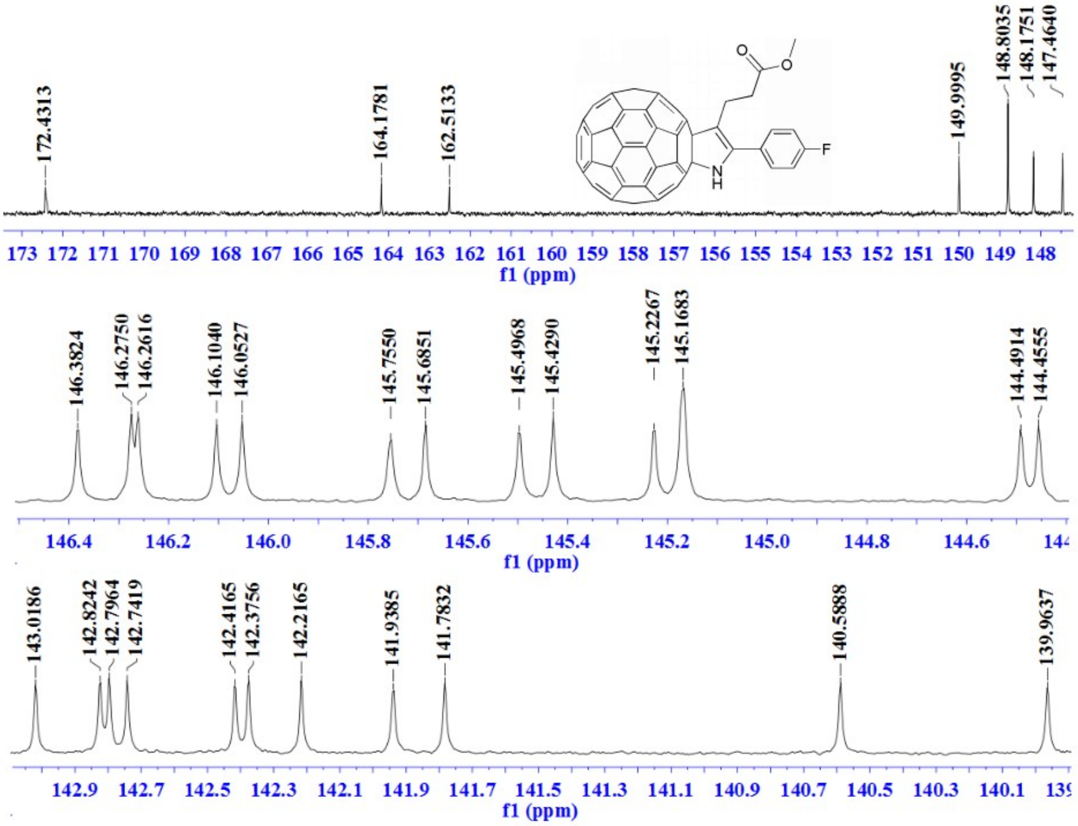


Figure S22-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2k

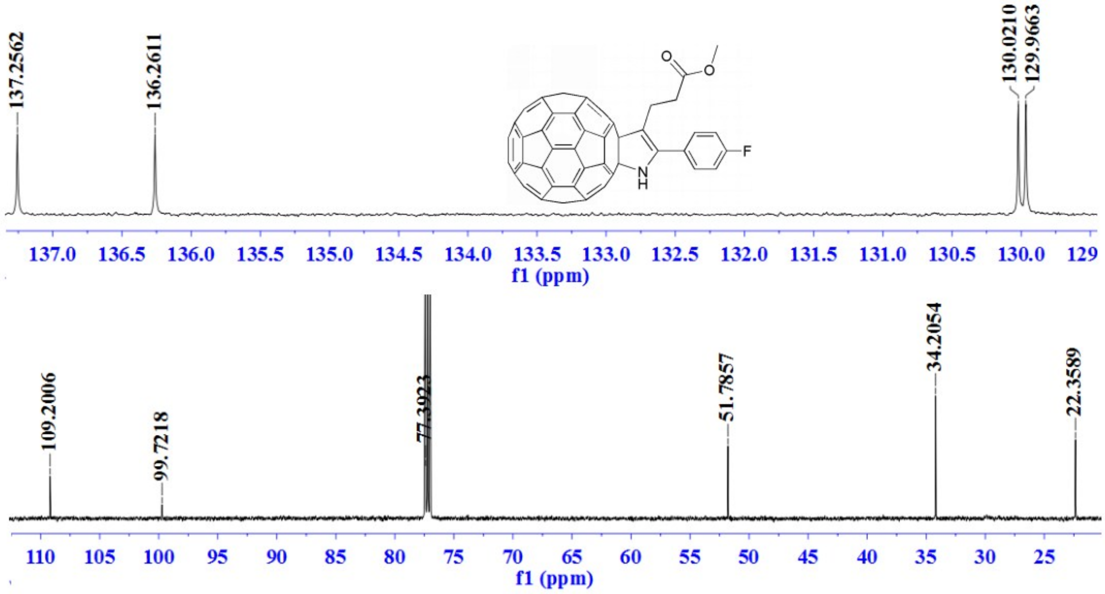


Figure S22-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2k

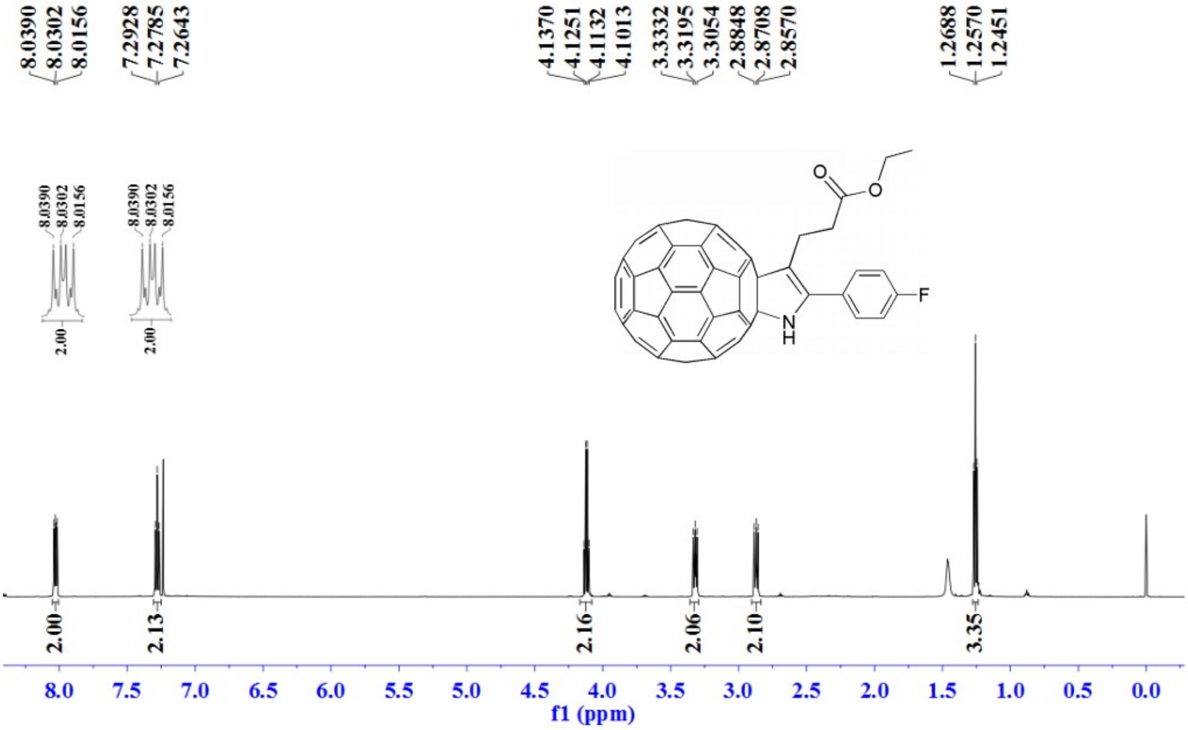


Figure S23. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2l

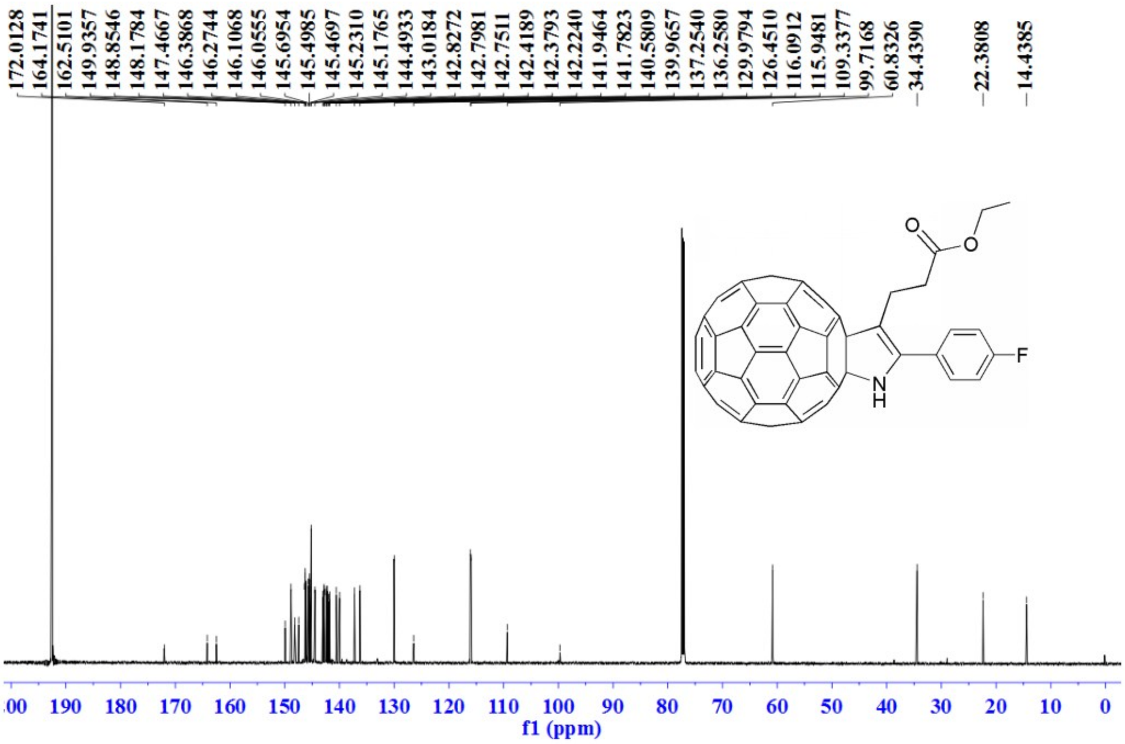


Figure S24. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2l

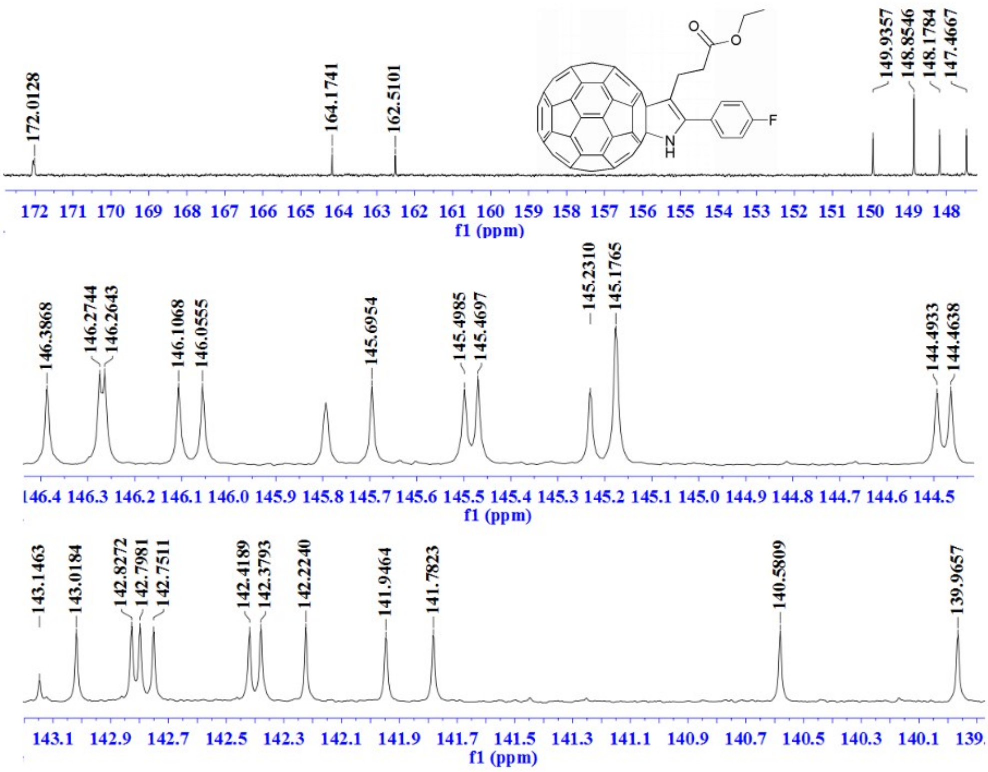


Figure S24-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2l

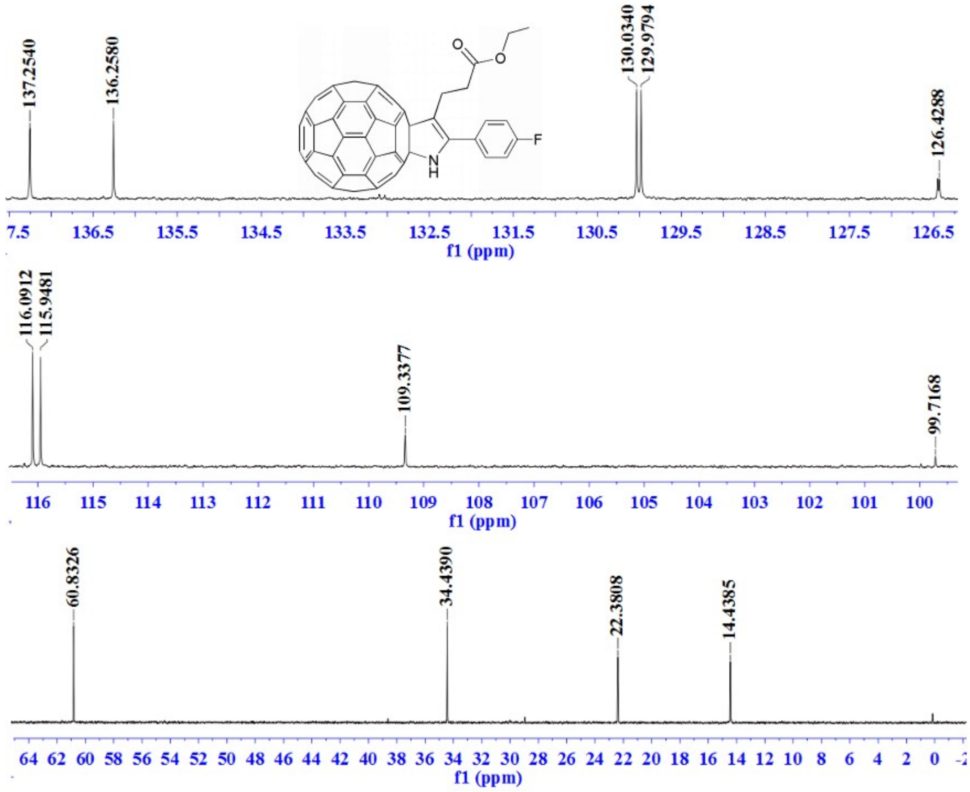


Figure S24-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 2l

^{1}H NMR spectra and ^{13}C NMR spectra of compounds 3a–l.

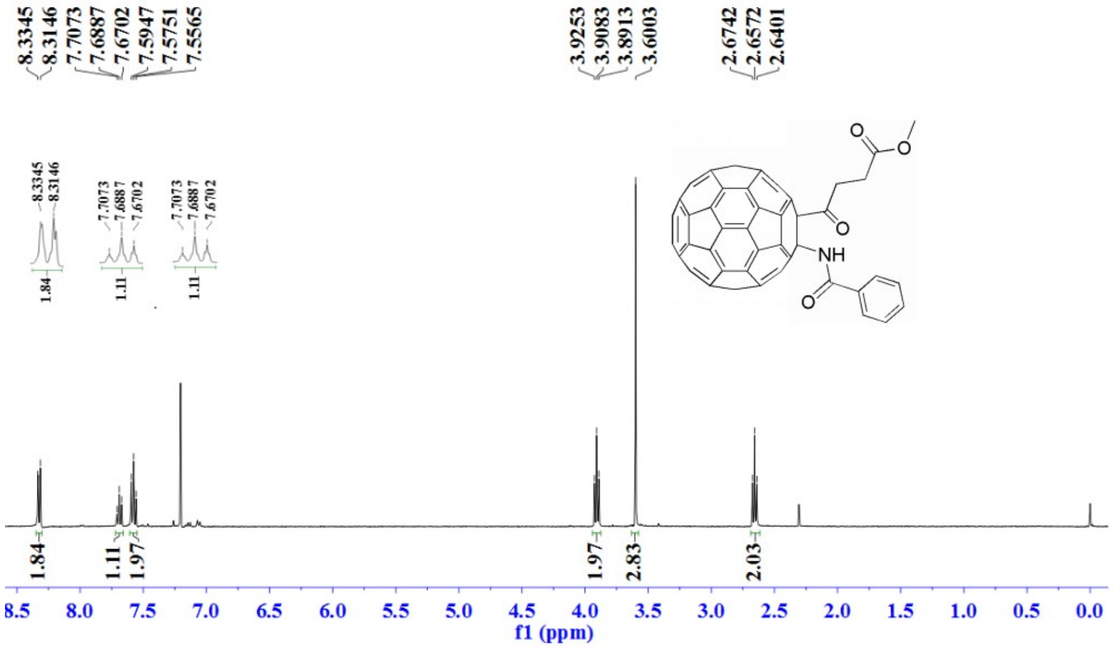


Figure S25. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3a

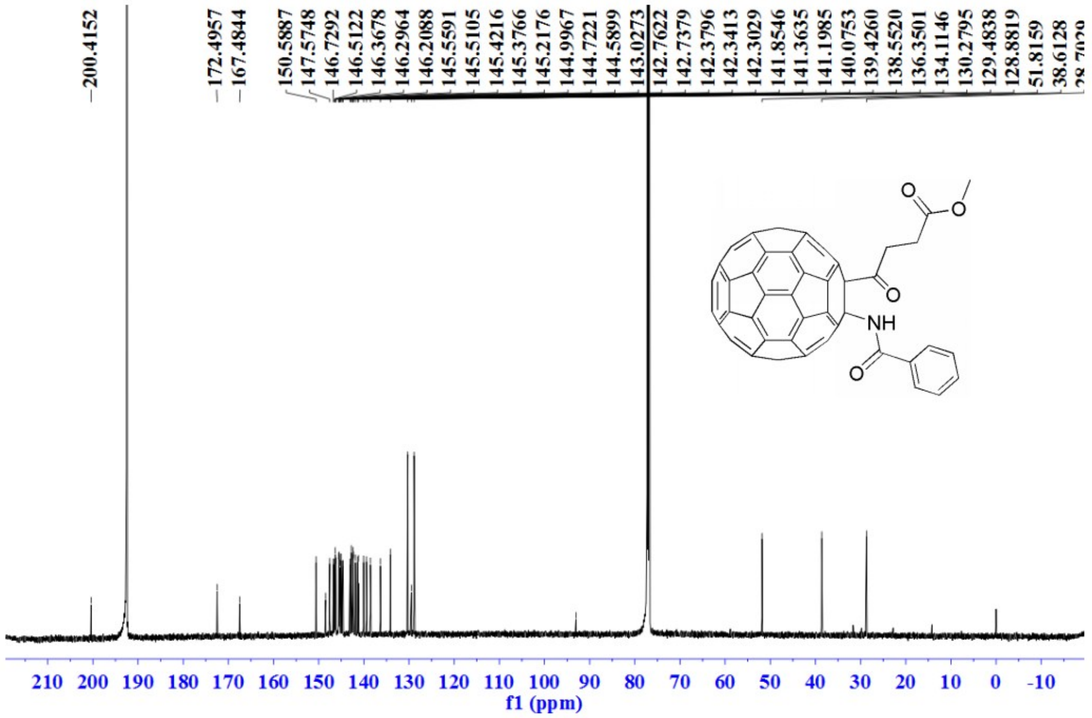


Figure S26. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3a

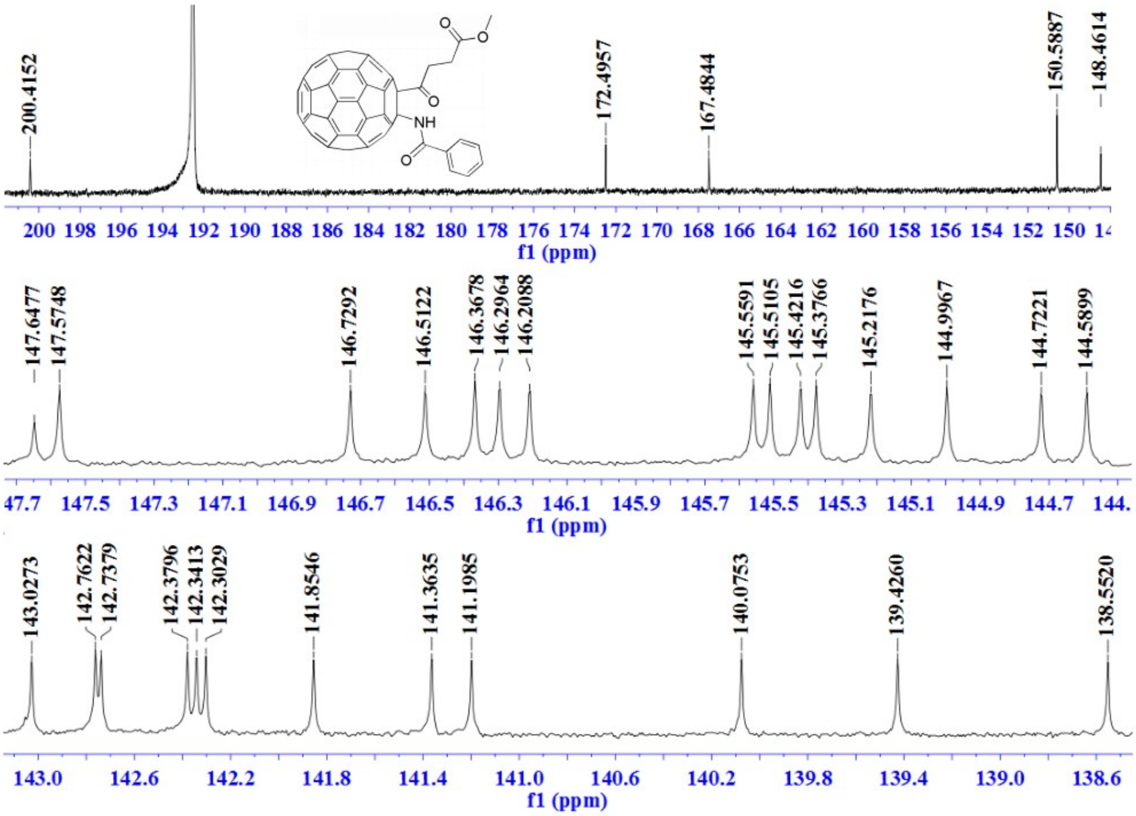


Figure S26-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3a

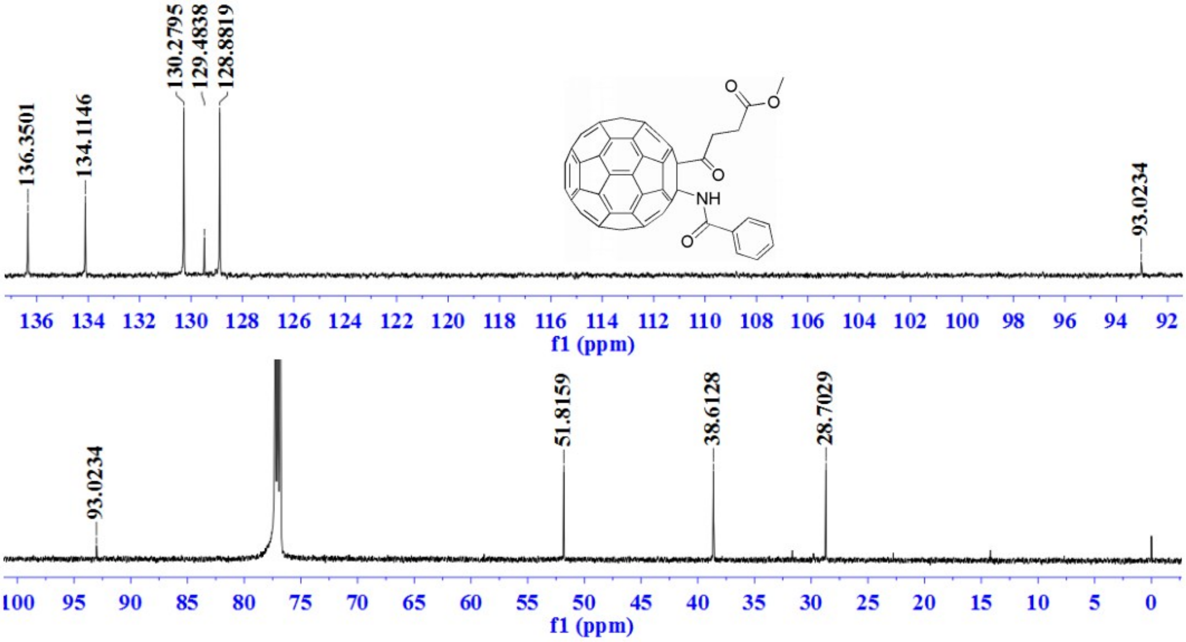


Figure S26-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3a

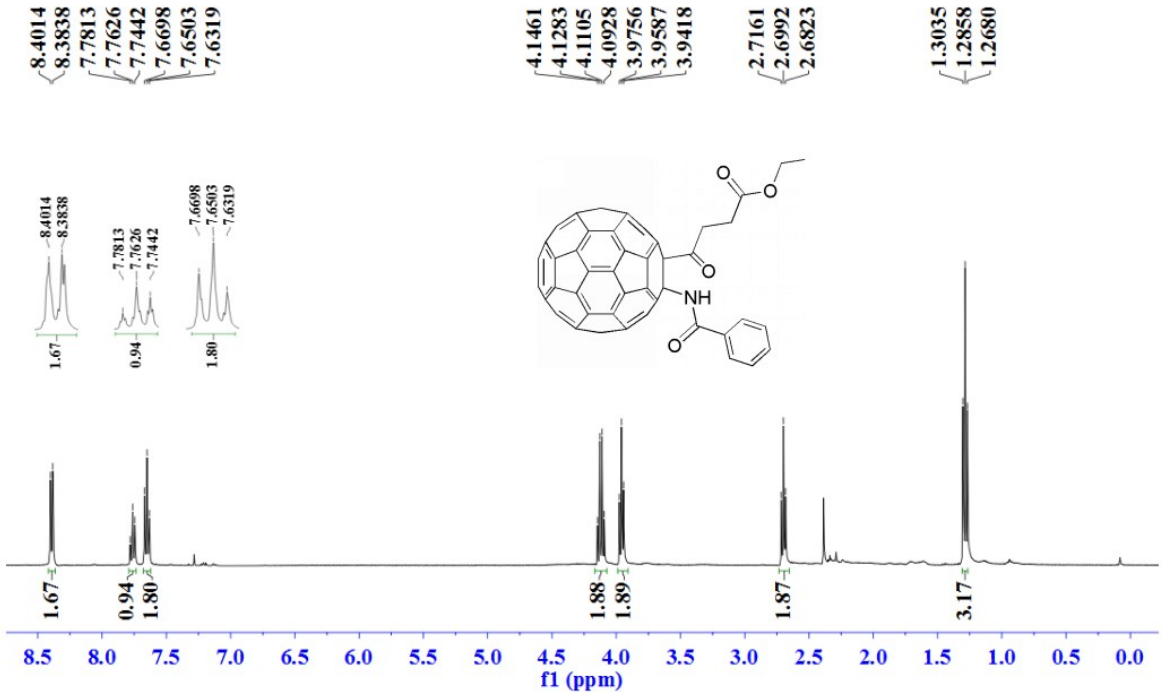


Figure S27. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3b

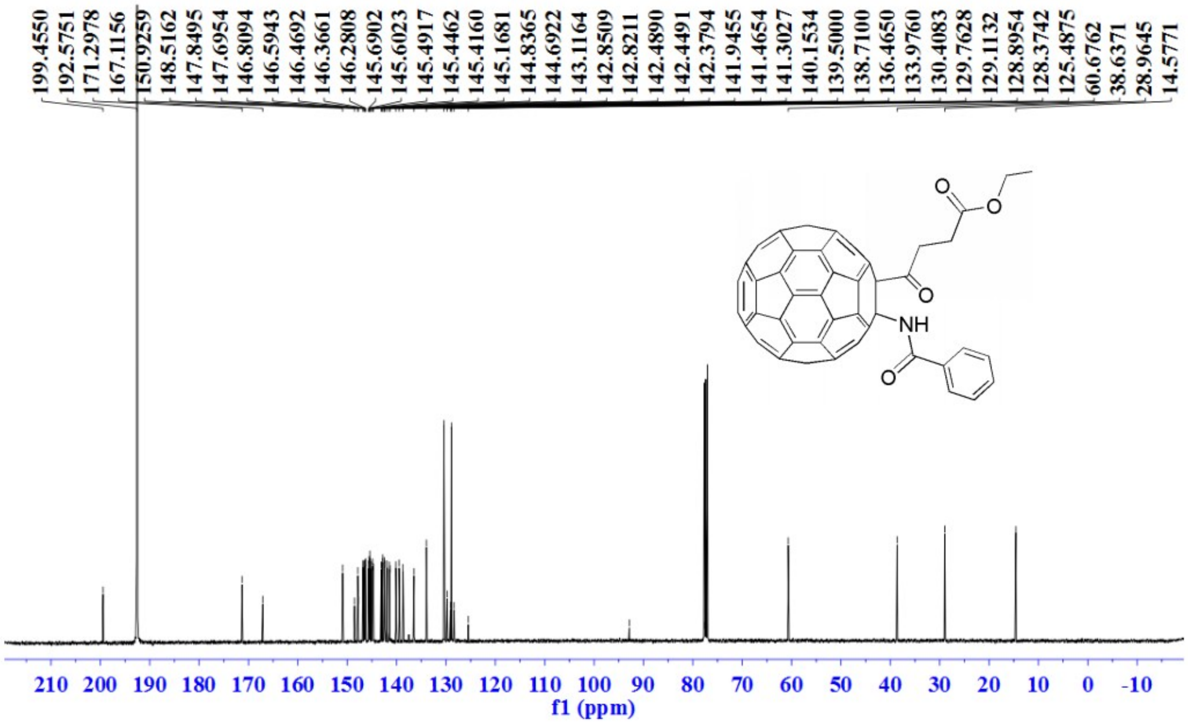


Figure S27. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3b

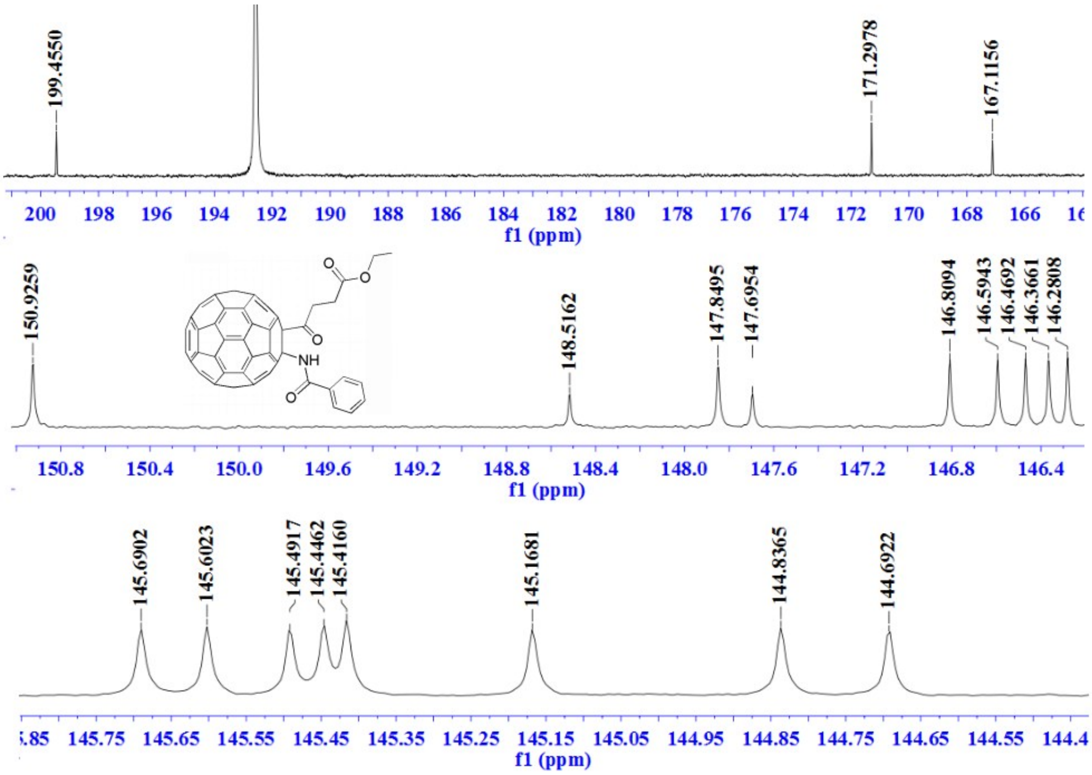


Figure S28-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3b

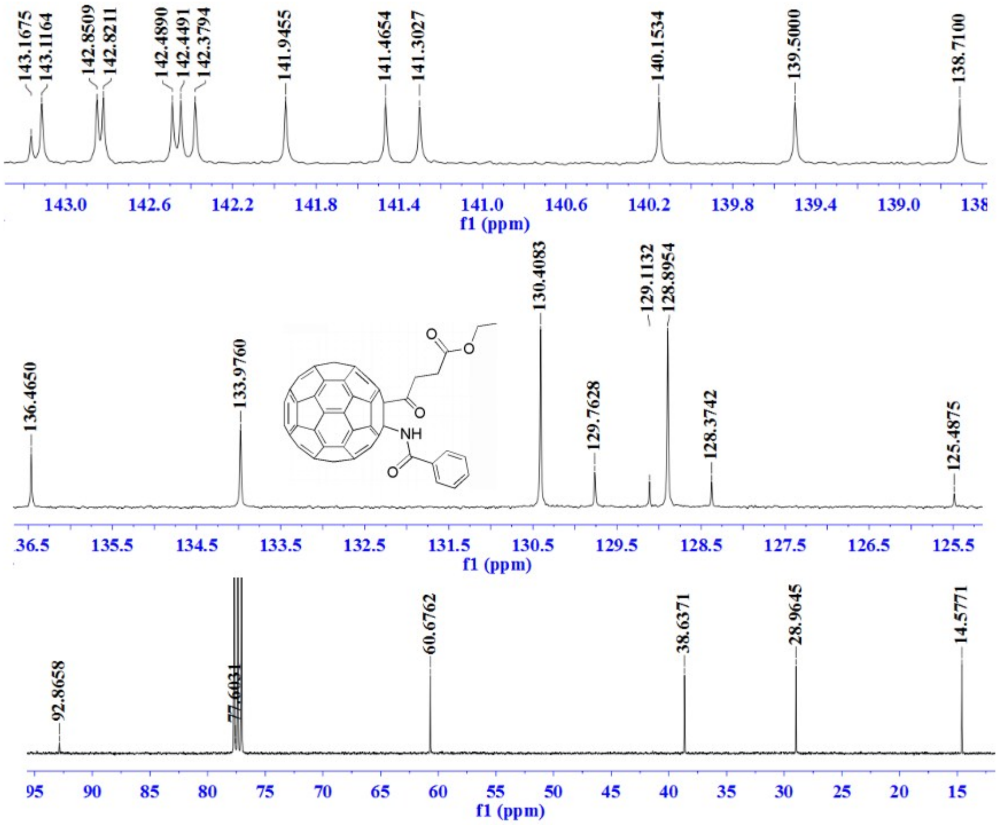


Figure S28-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3b

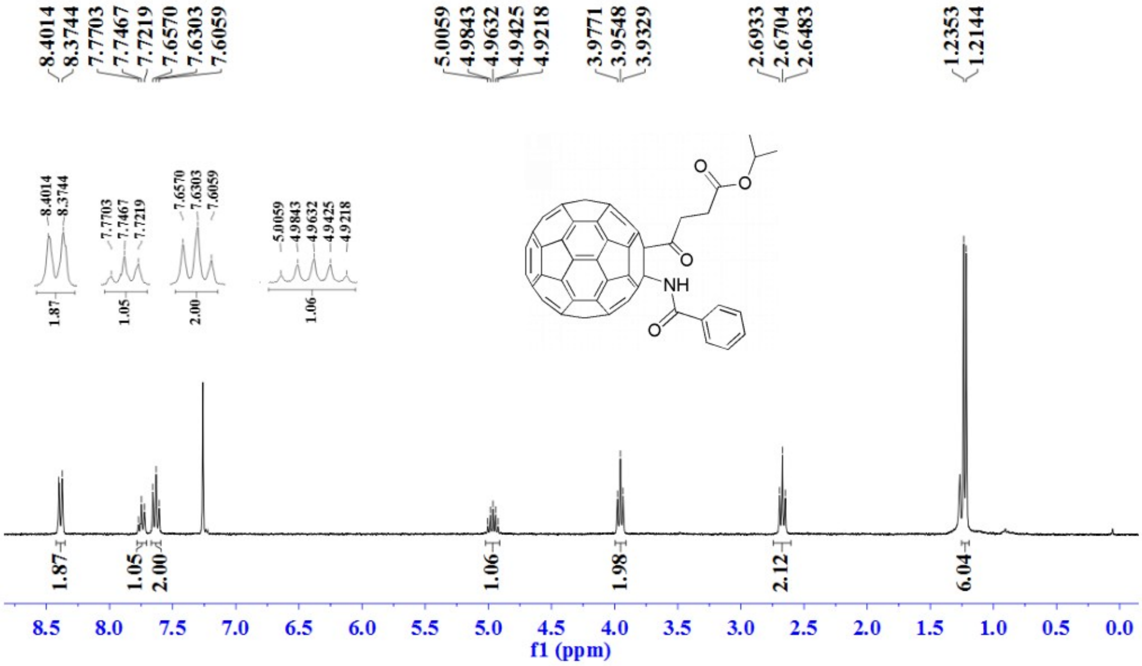


Figure S29. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) of compound 3c

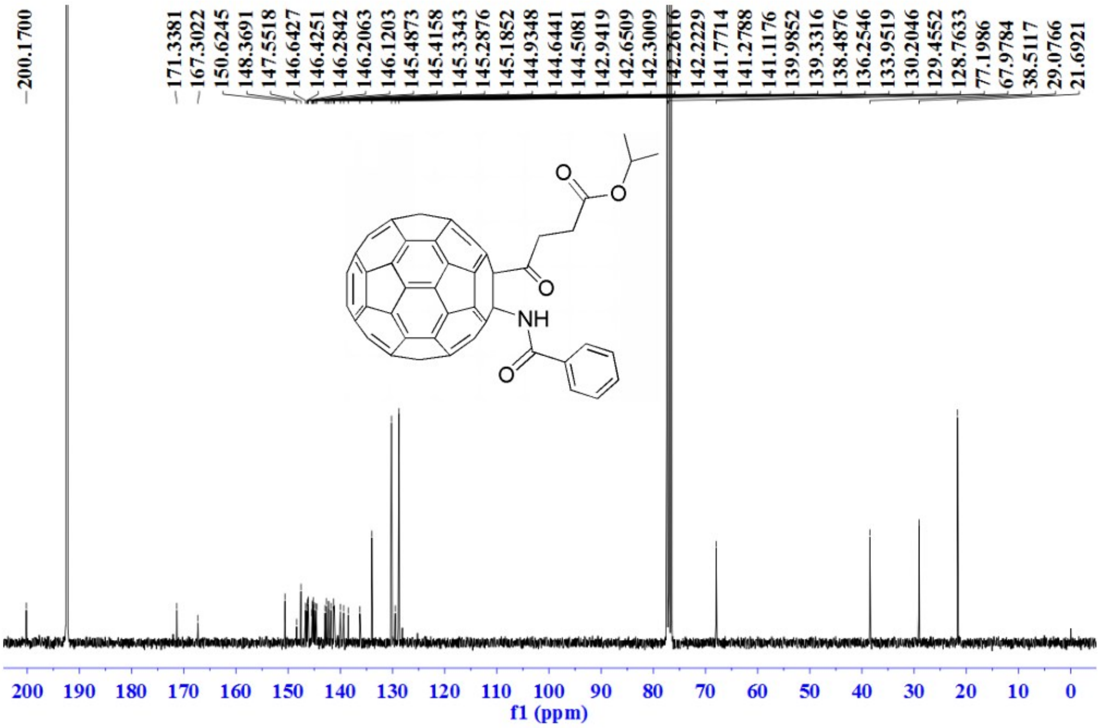


Figure S30. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$) of compound 3c

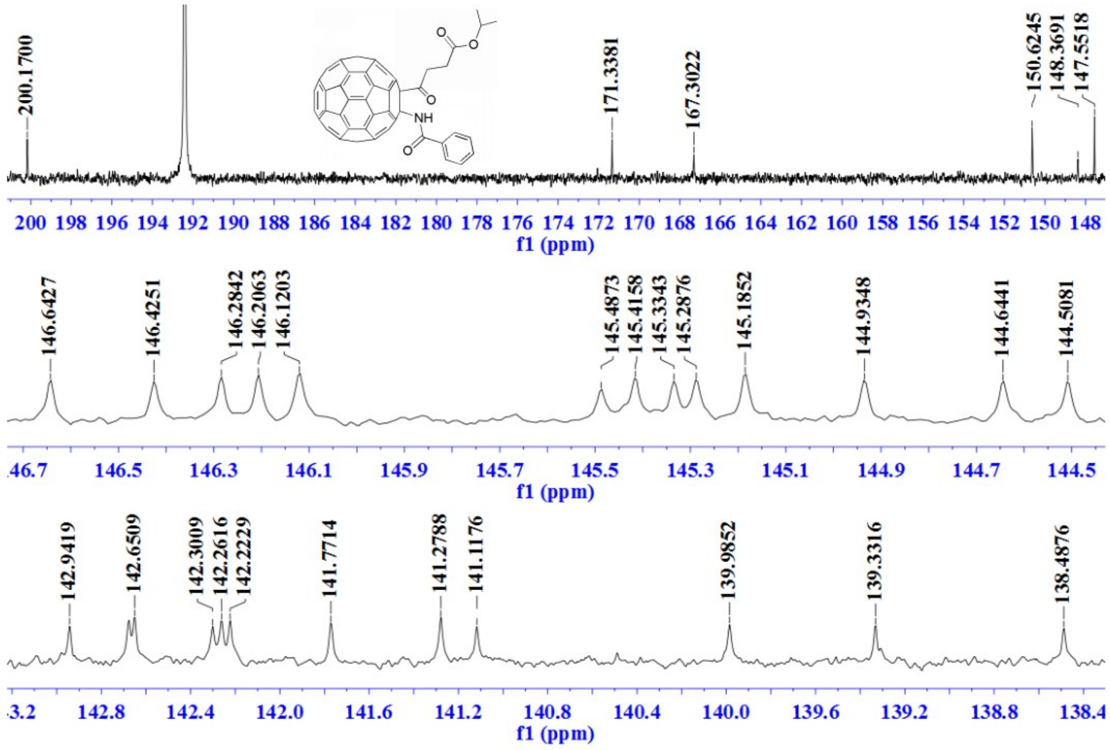


Figure S30-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3c

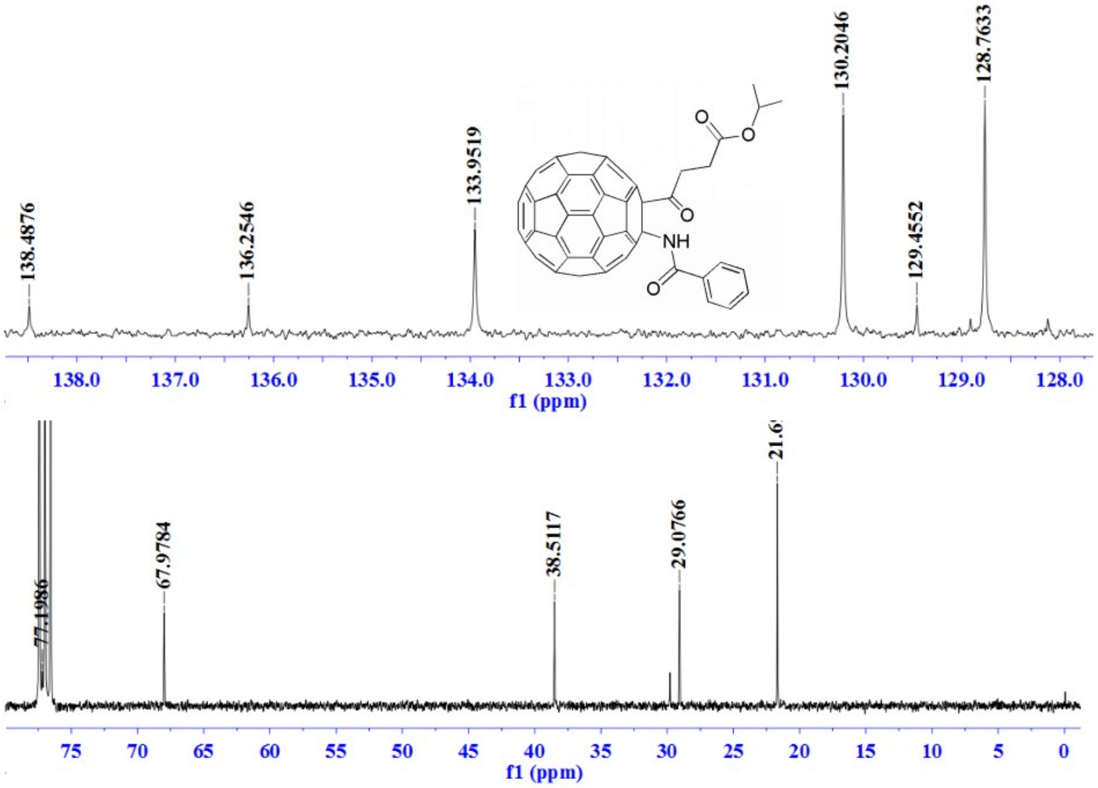


Figure S30-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3c

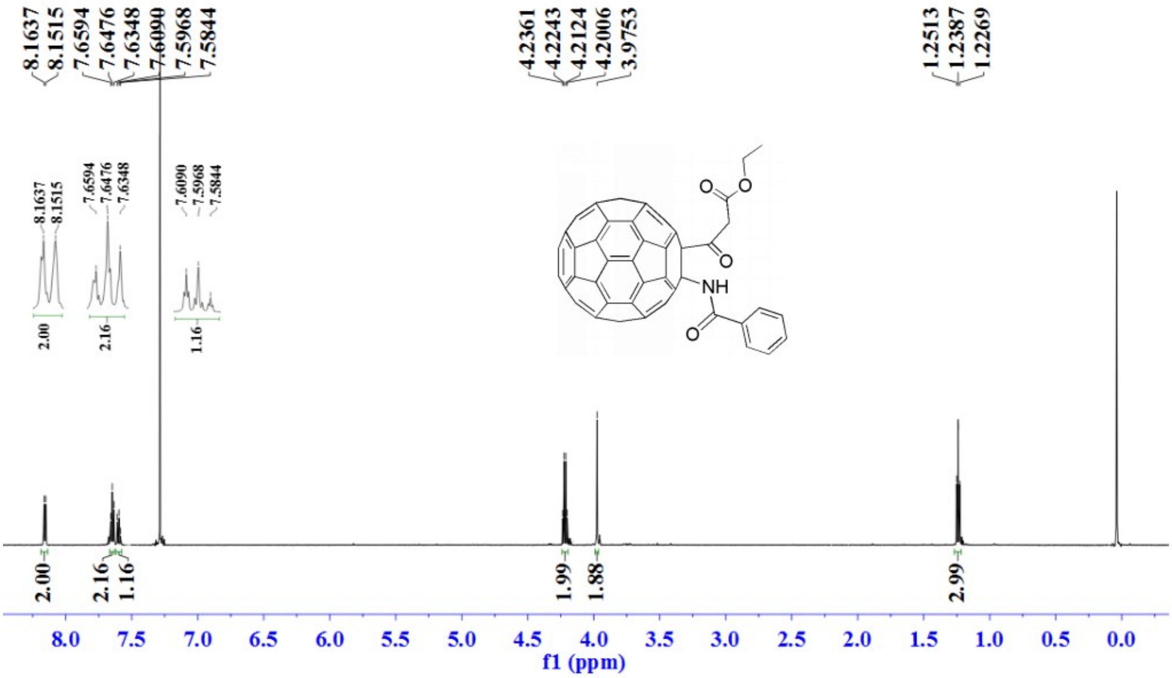


Figure S31. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3e

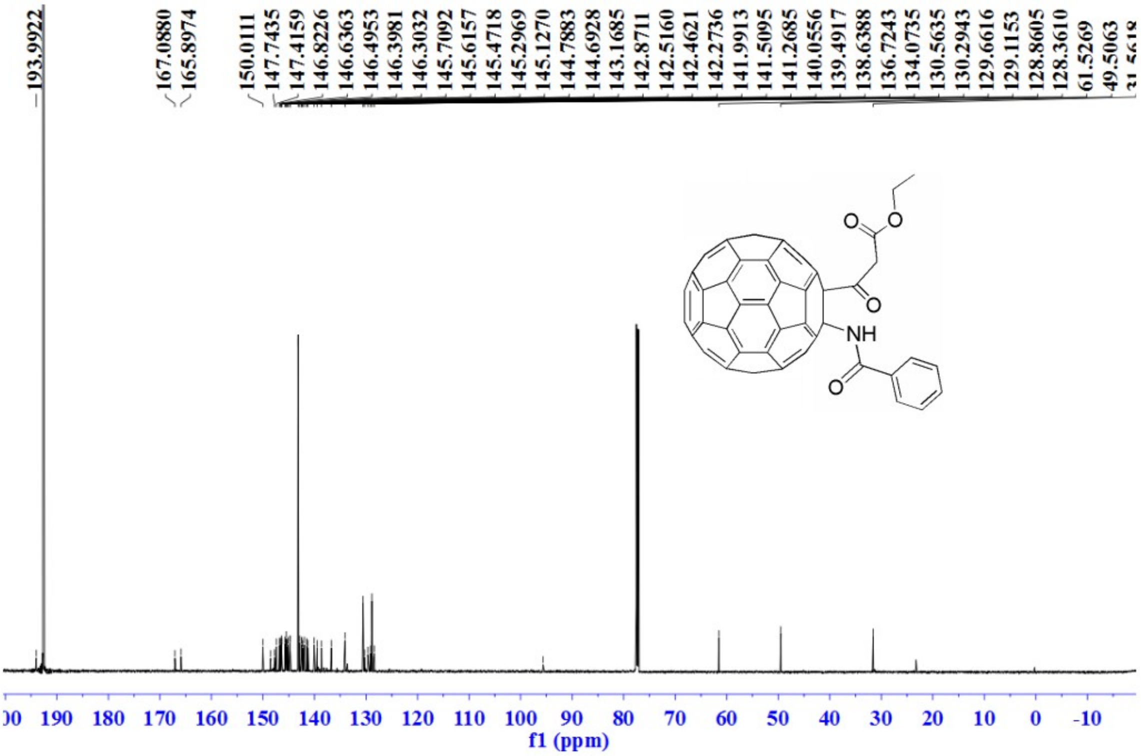


Figure S32. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3e

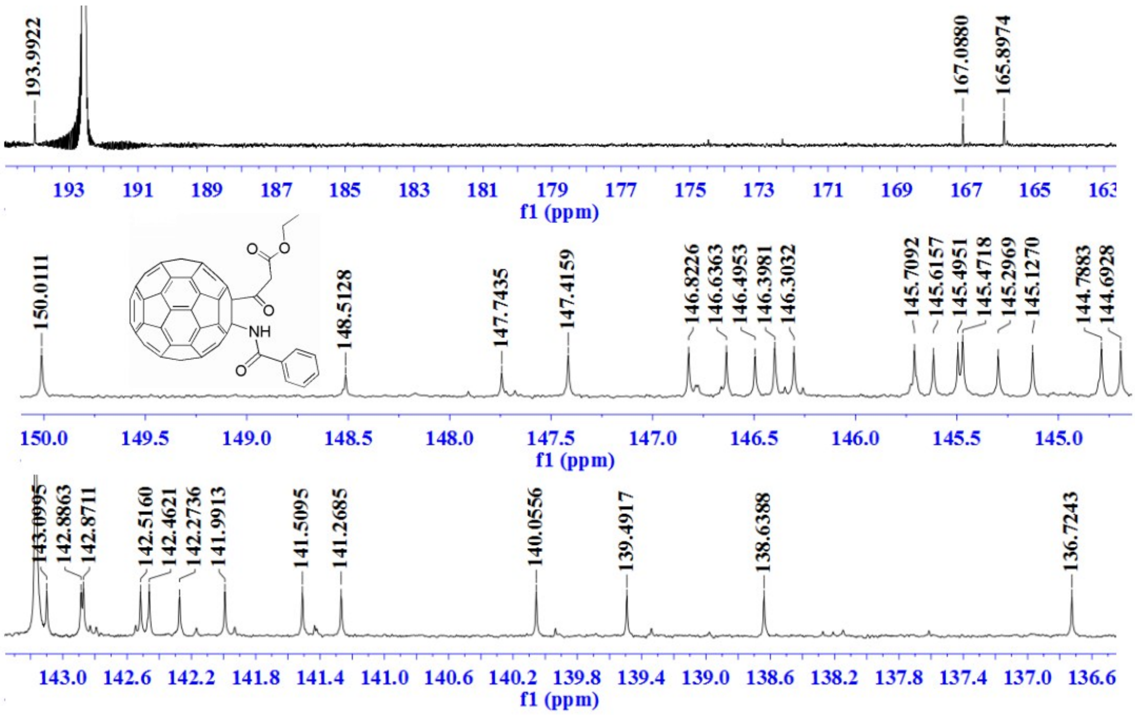


Figure S32-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3e

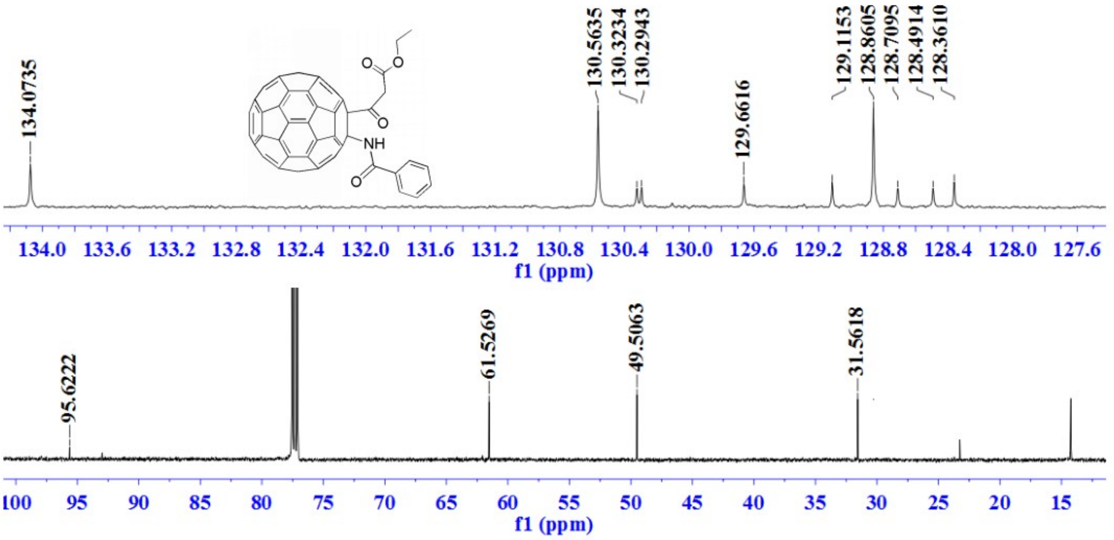


Figure S32-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3e

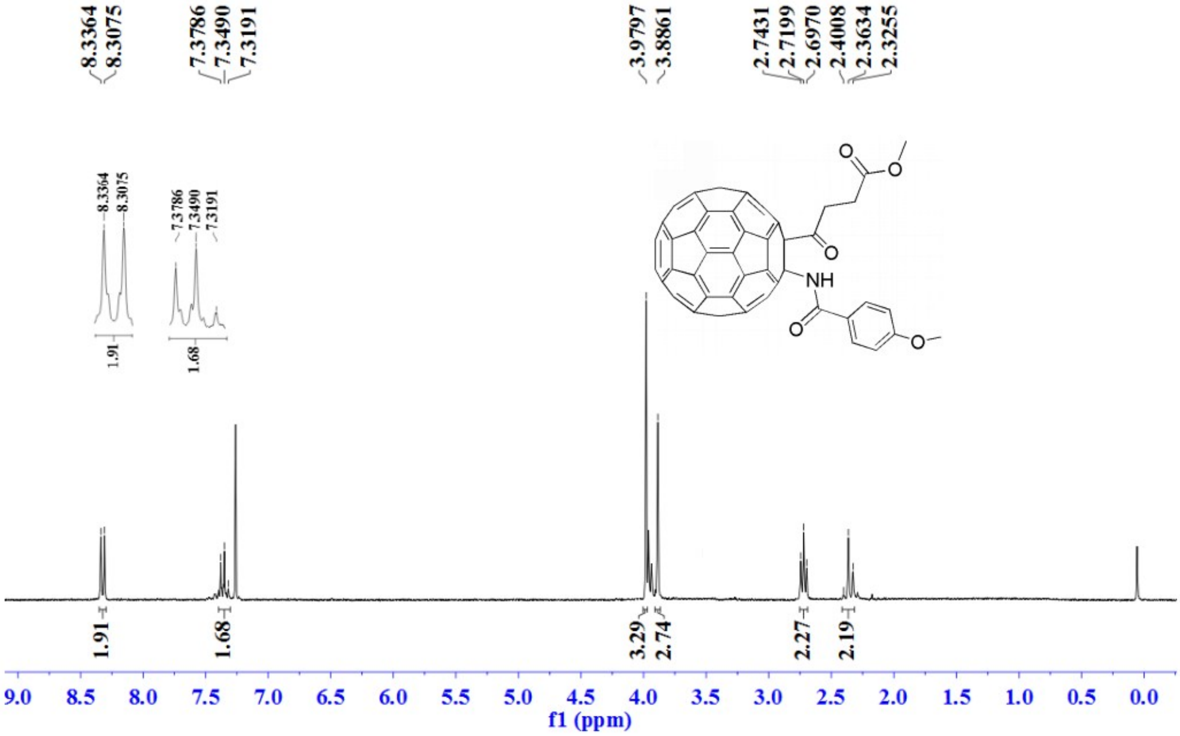


Figure S33. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3f

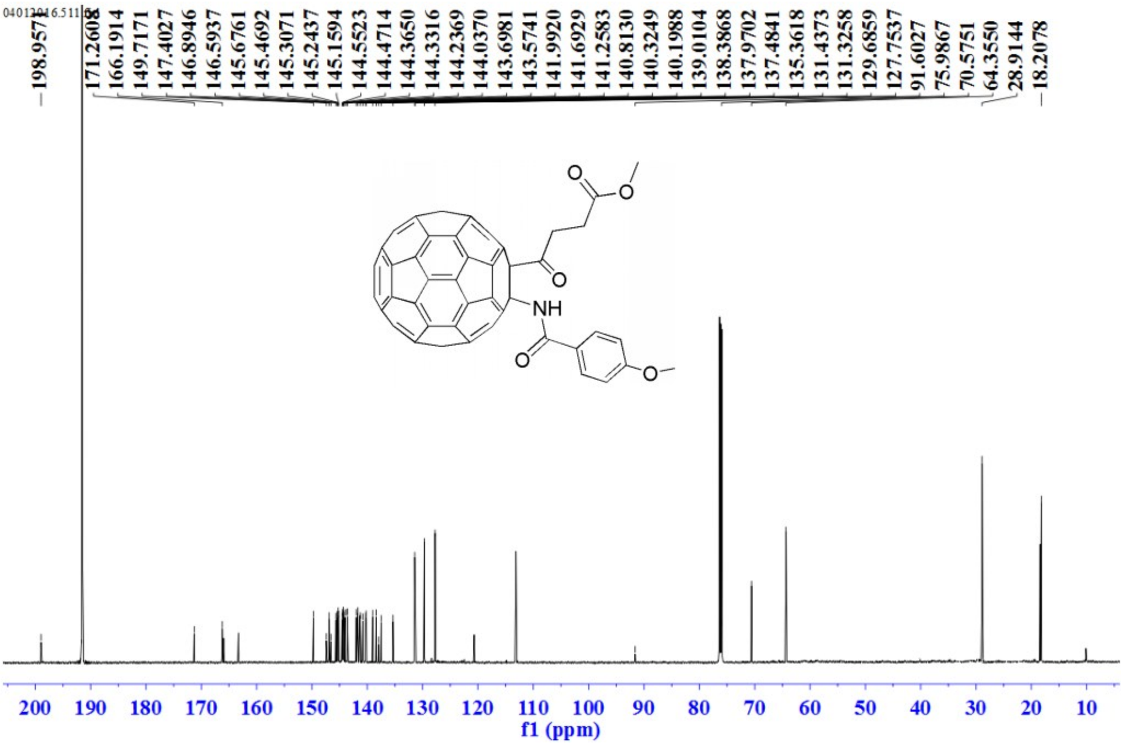


Figure S34. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3f

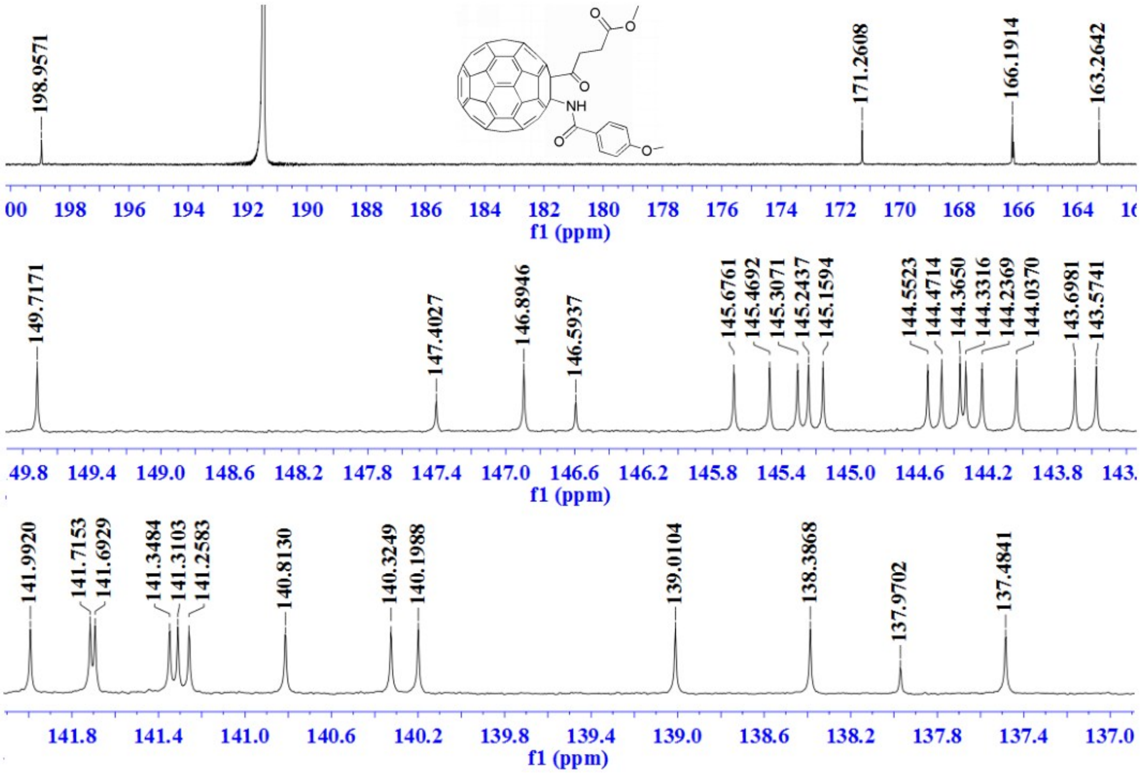


Figure S34-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3f

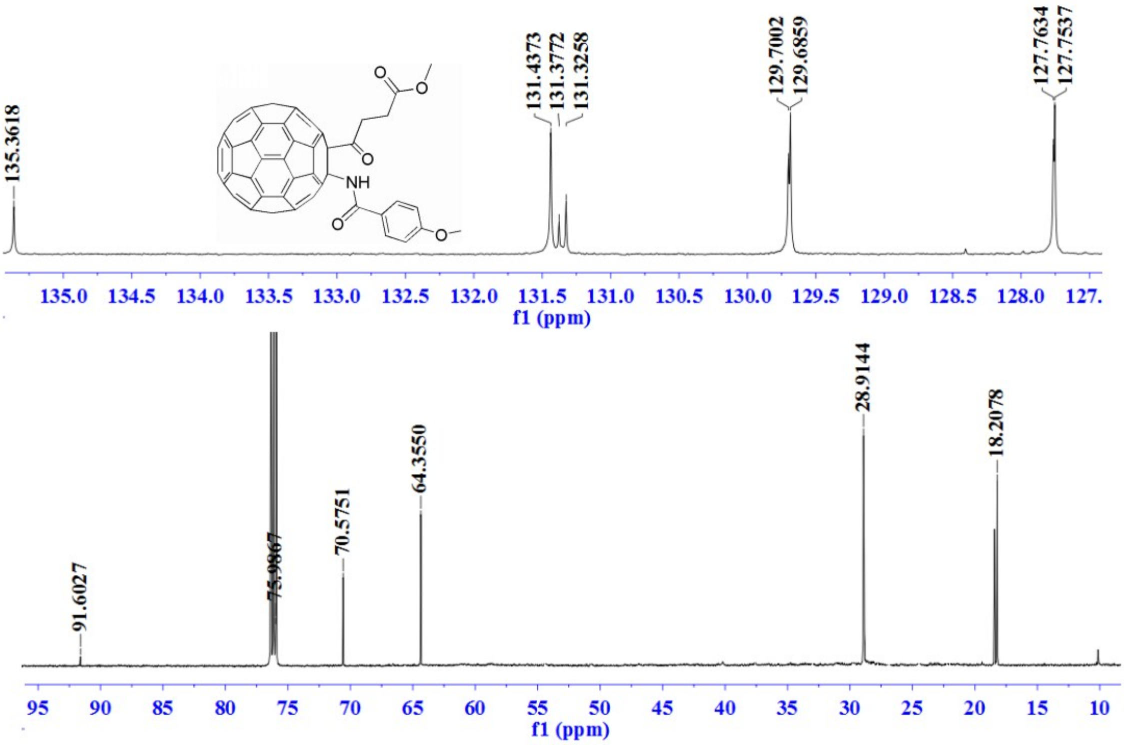


Figure S34-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3f

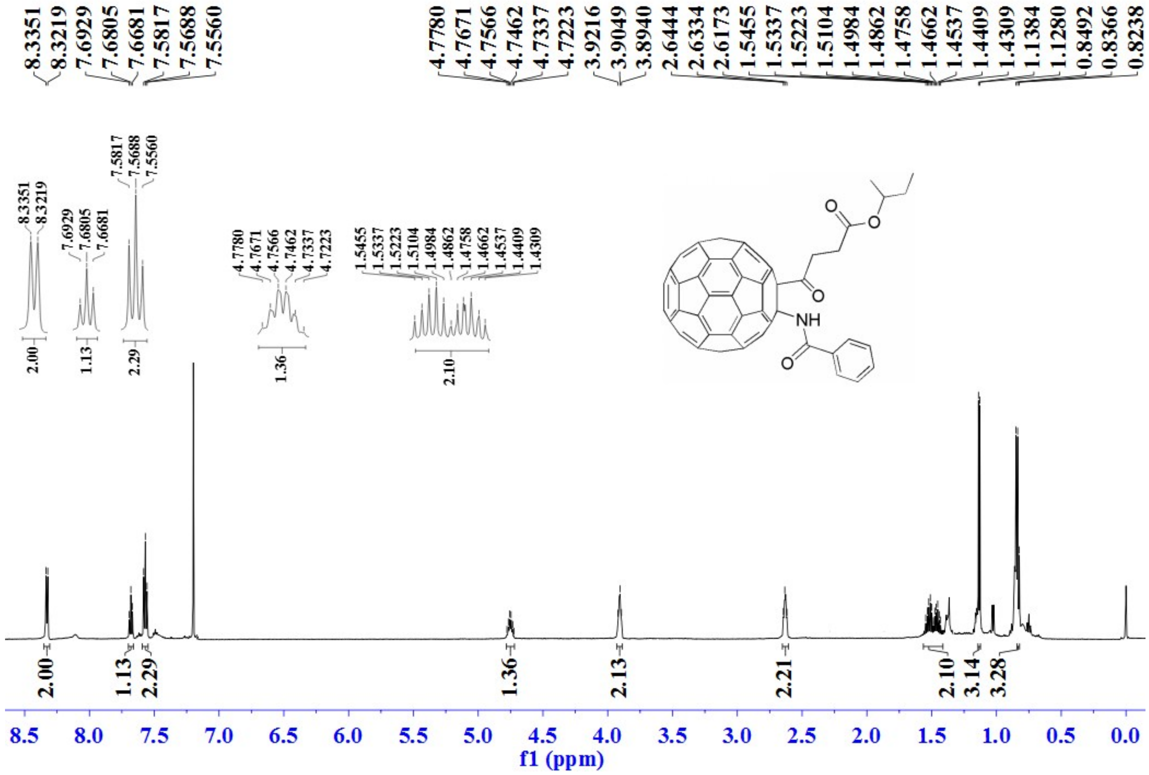


Figure S37. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3g

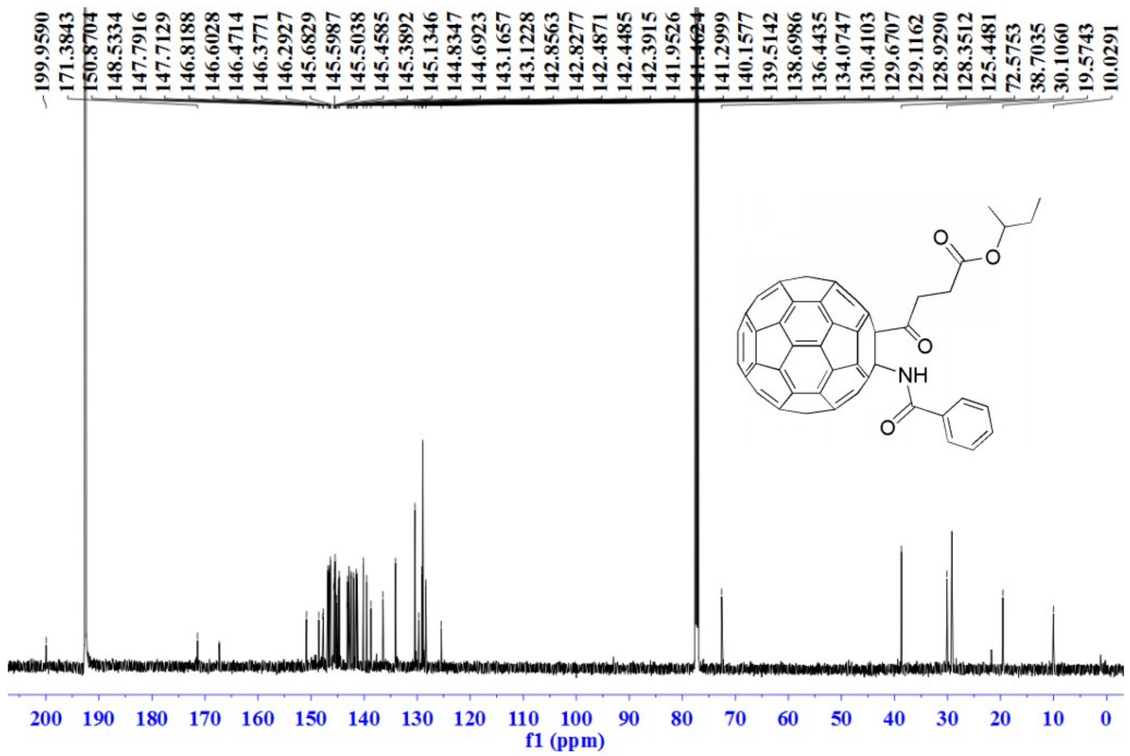


Figure S38. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3g

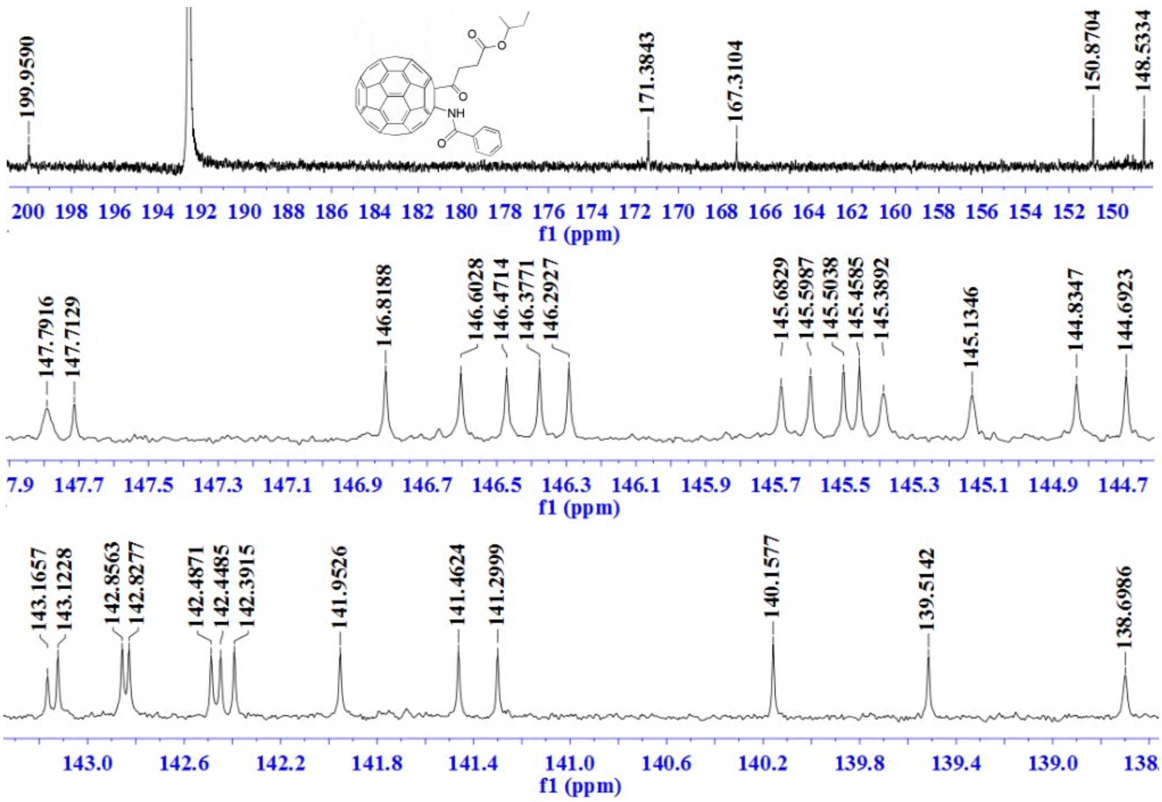


Figure S38-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3g

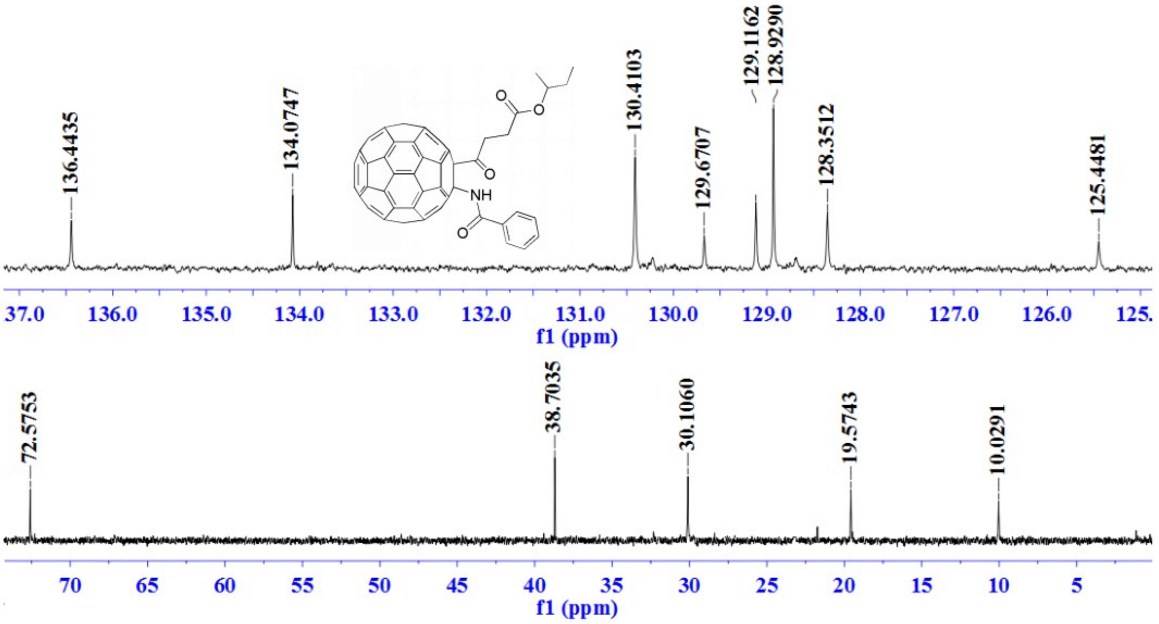


Figure S38-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3g

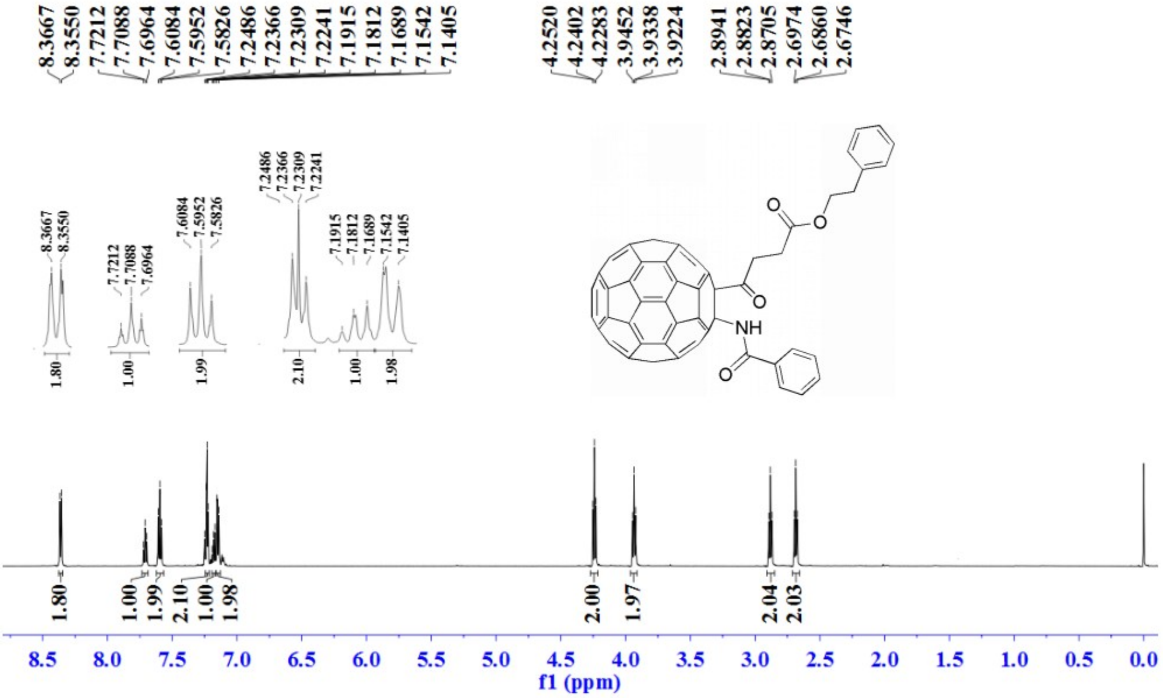


Figure S39. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3h

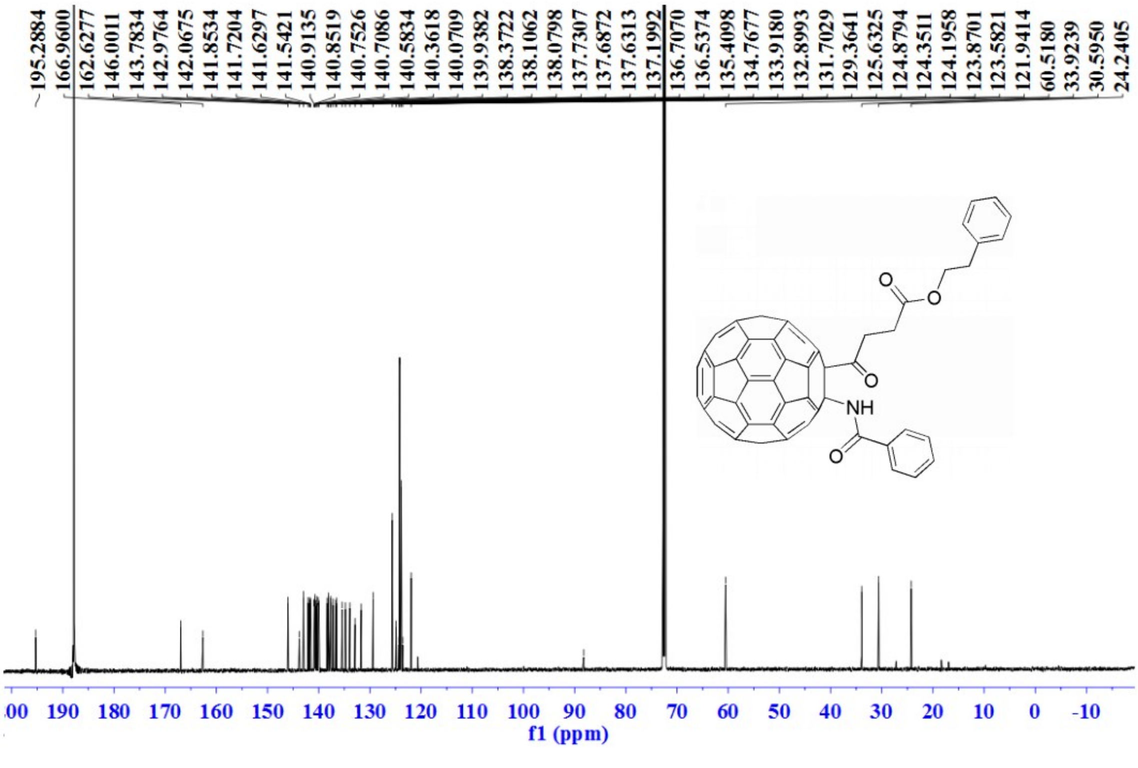


Figure S40. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3h

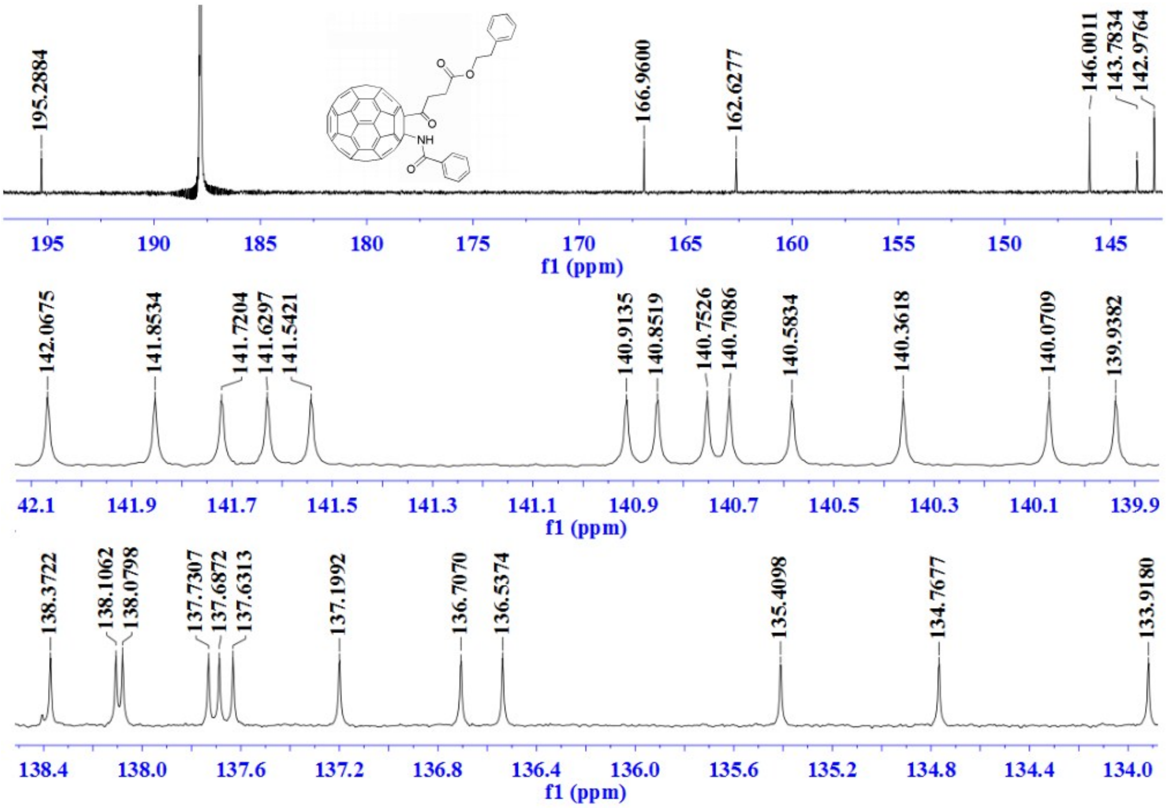


Figure S40-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3h

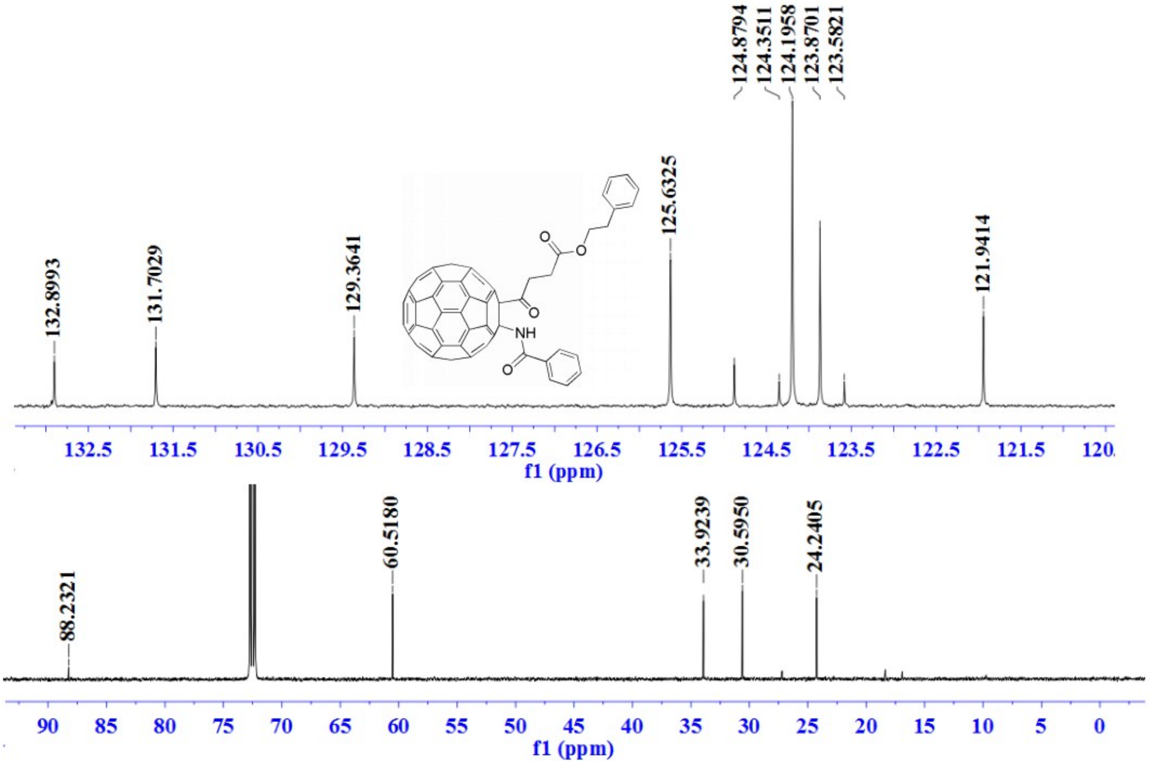


Figure S40-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3h

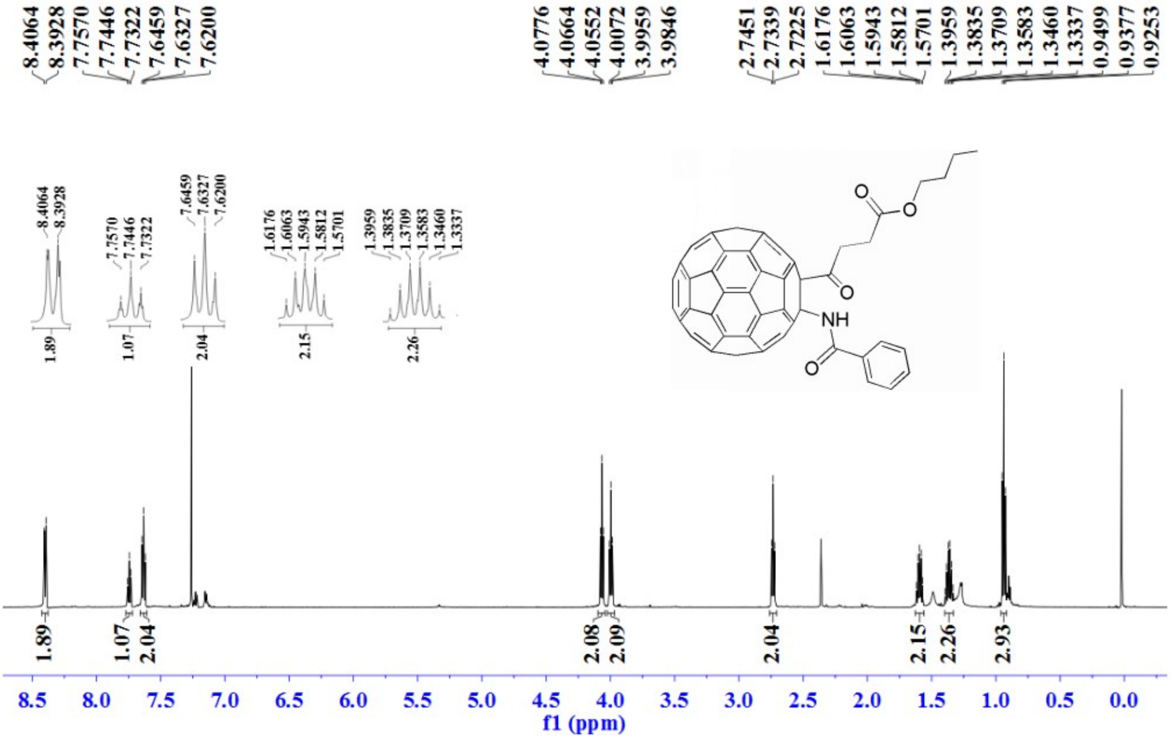


Figure S41. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3i

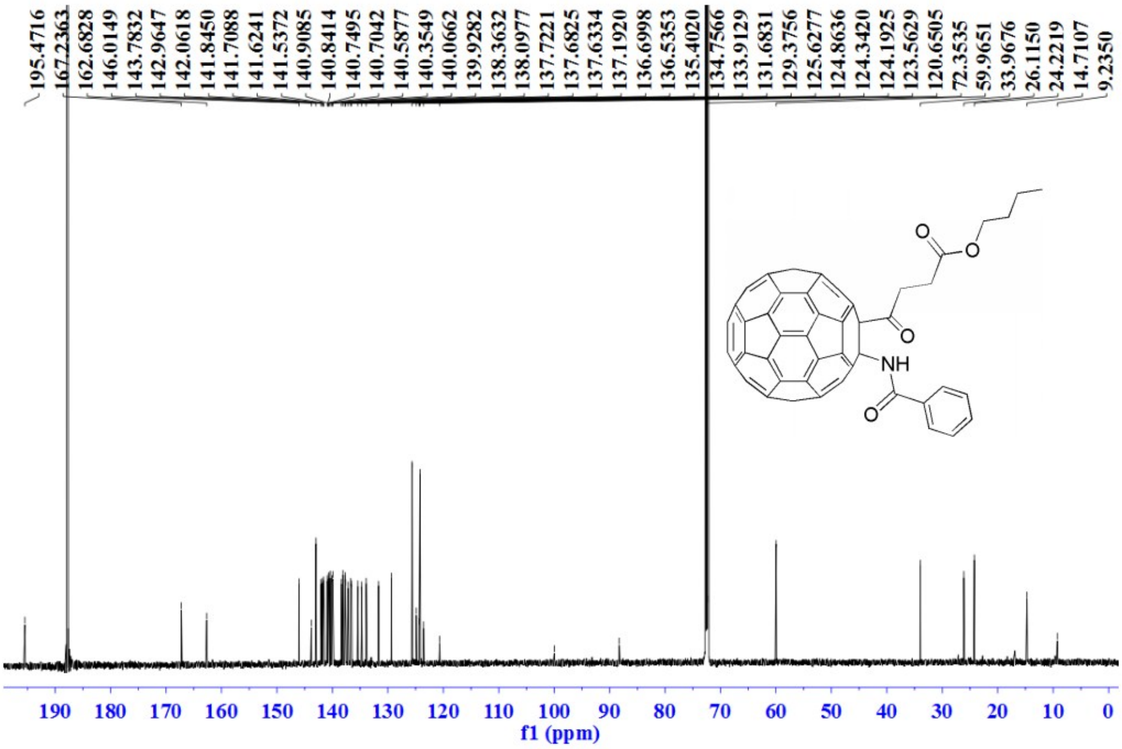


Figure S42. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3i

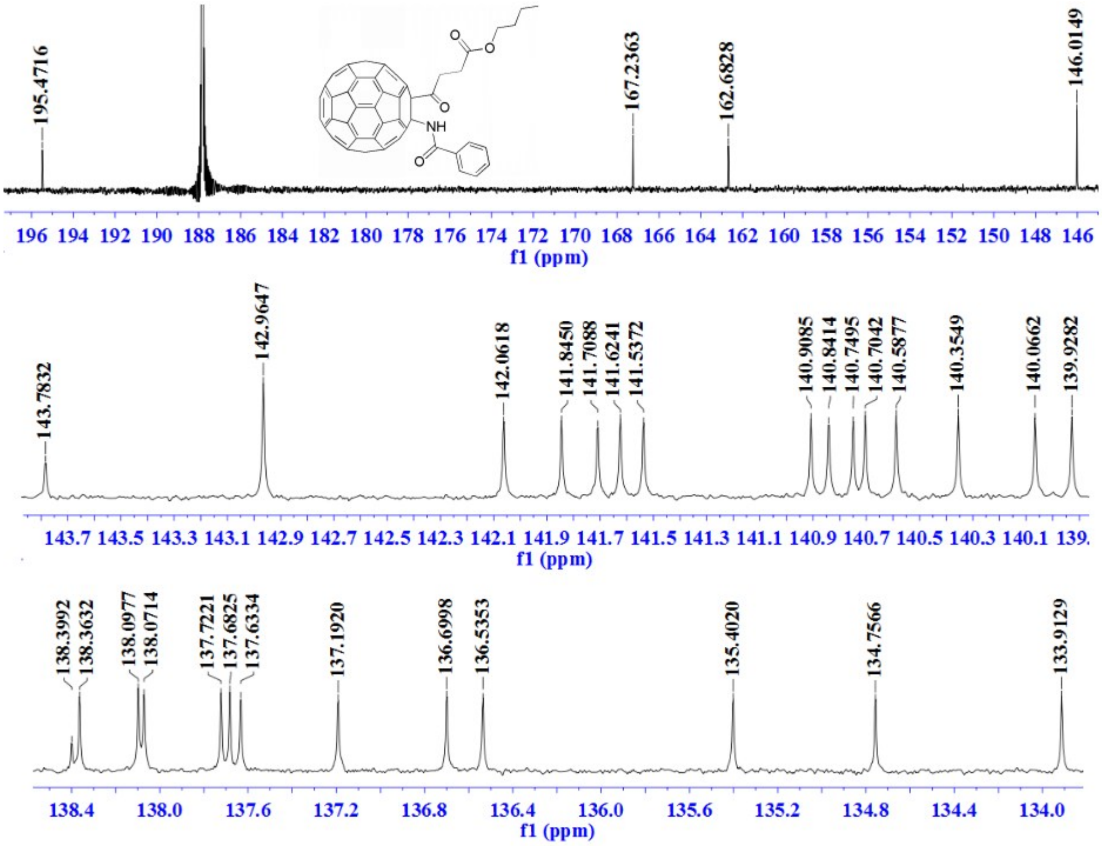


Figure S42-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3i

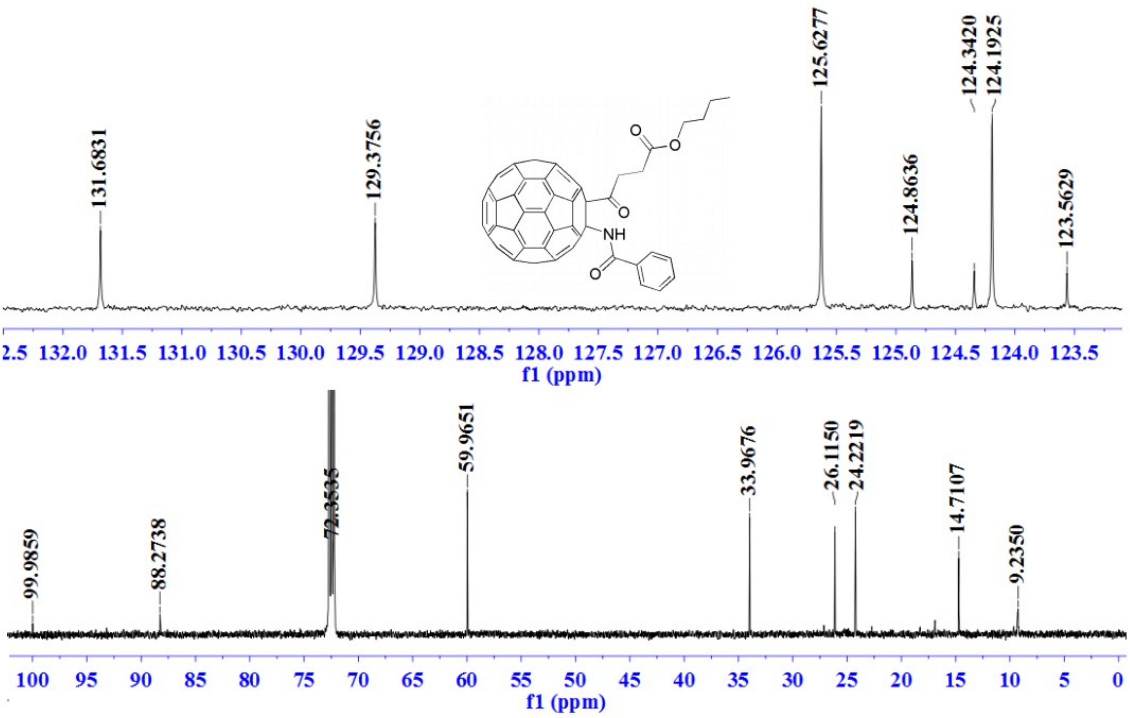


Figure S42-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3i

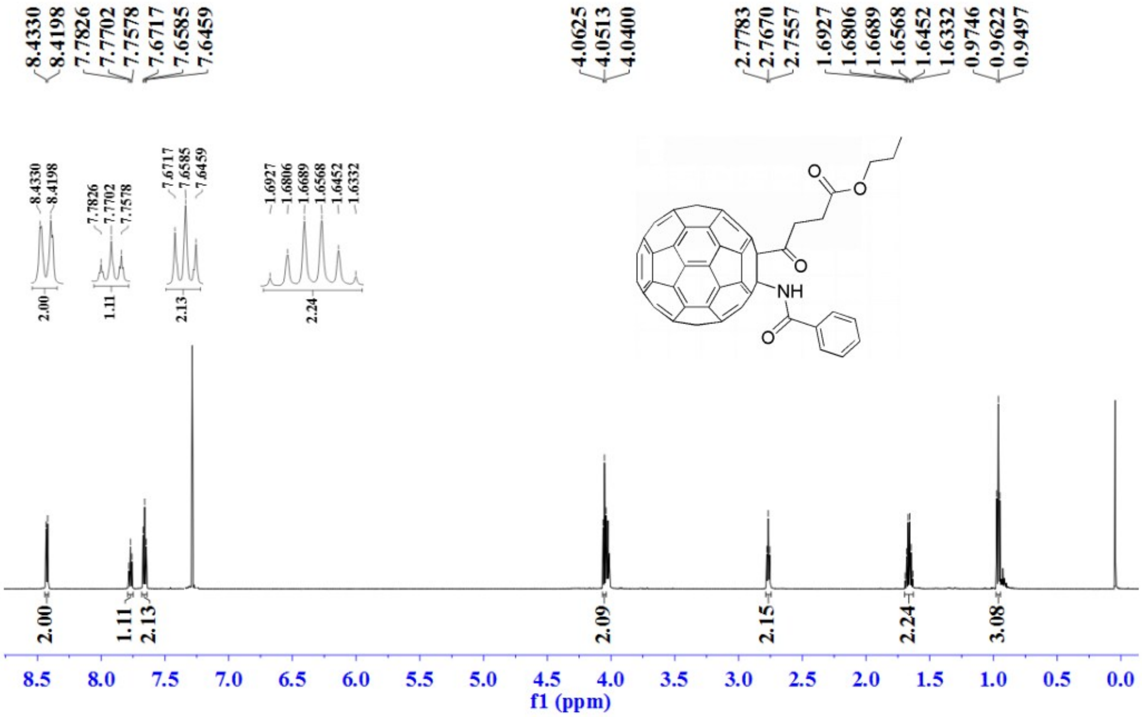


Figure S43. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3j

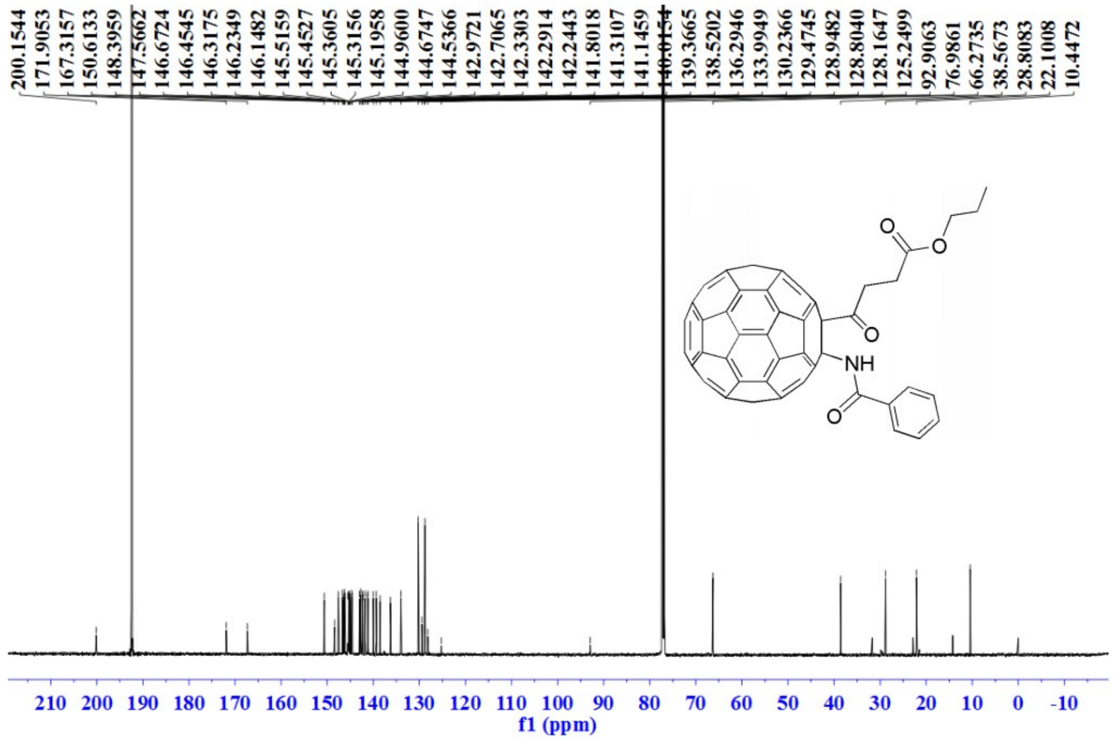


Figure S44. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3j

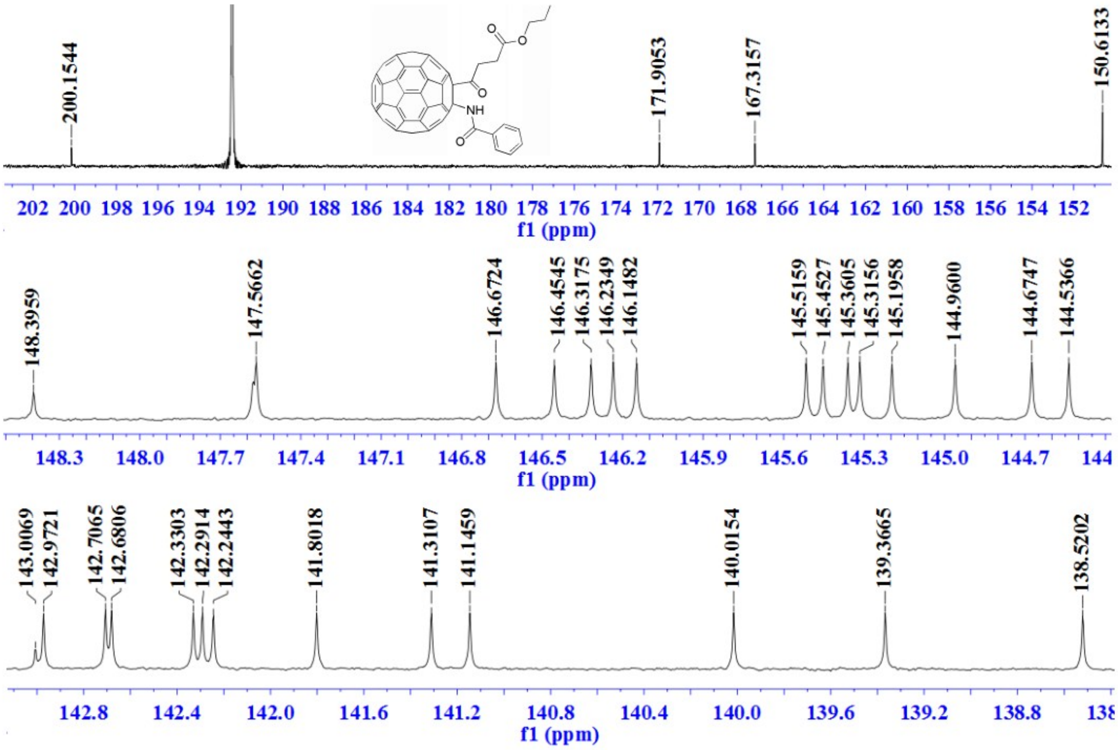


Figure S44-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3j

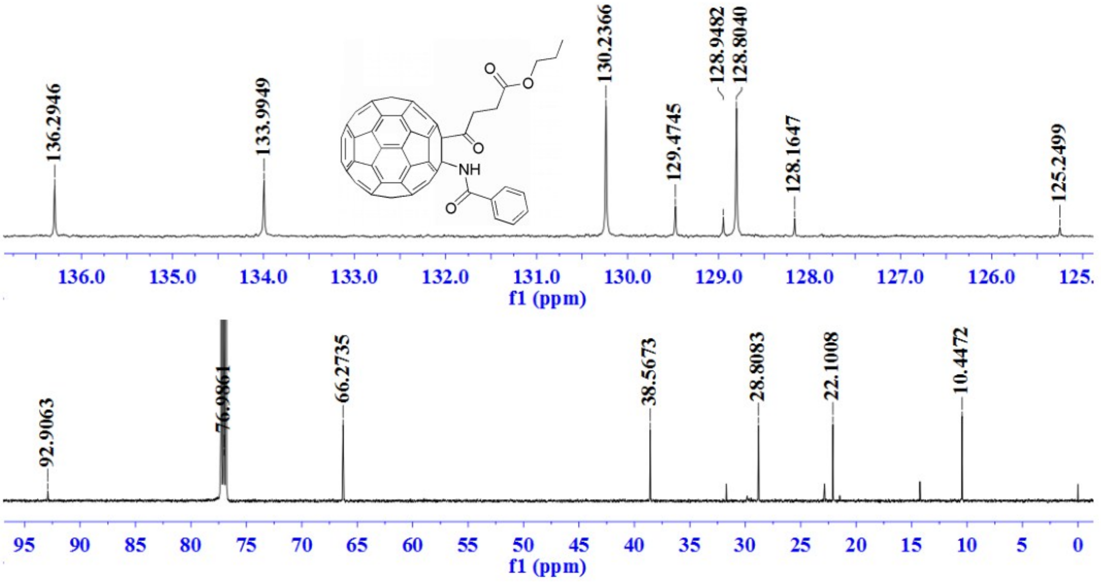


Figure S44-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3j

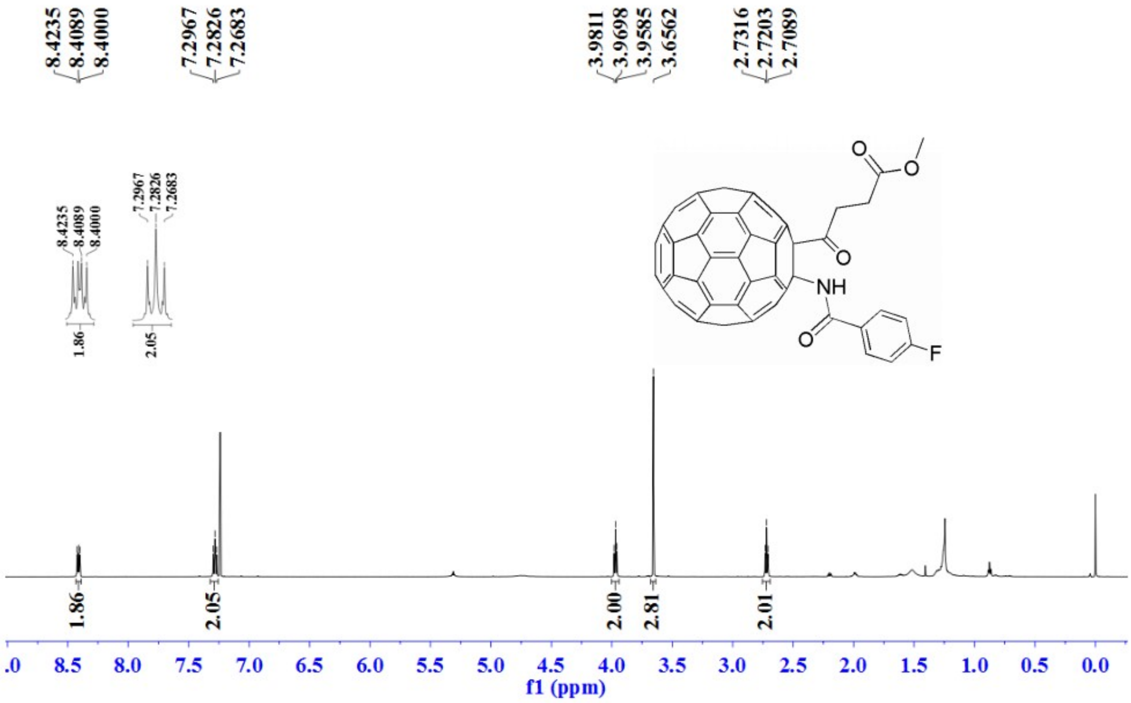


Figure S45. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3k

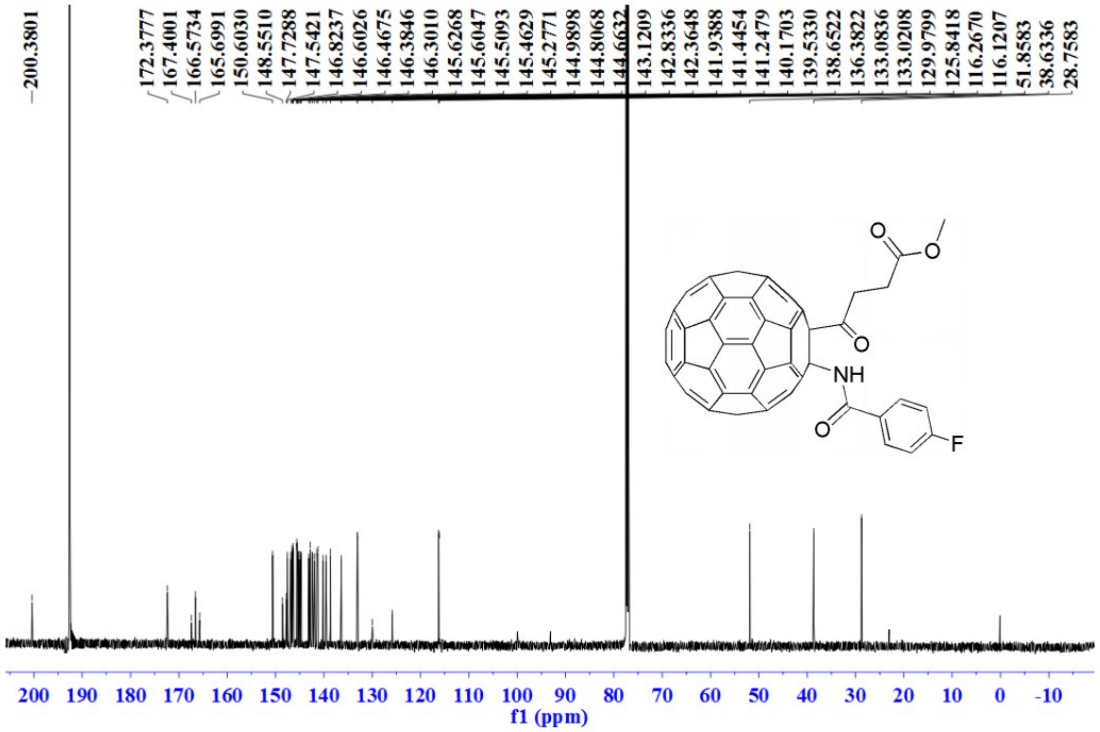


Figure S46. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3k

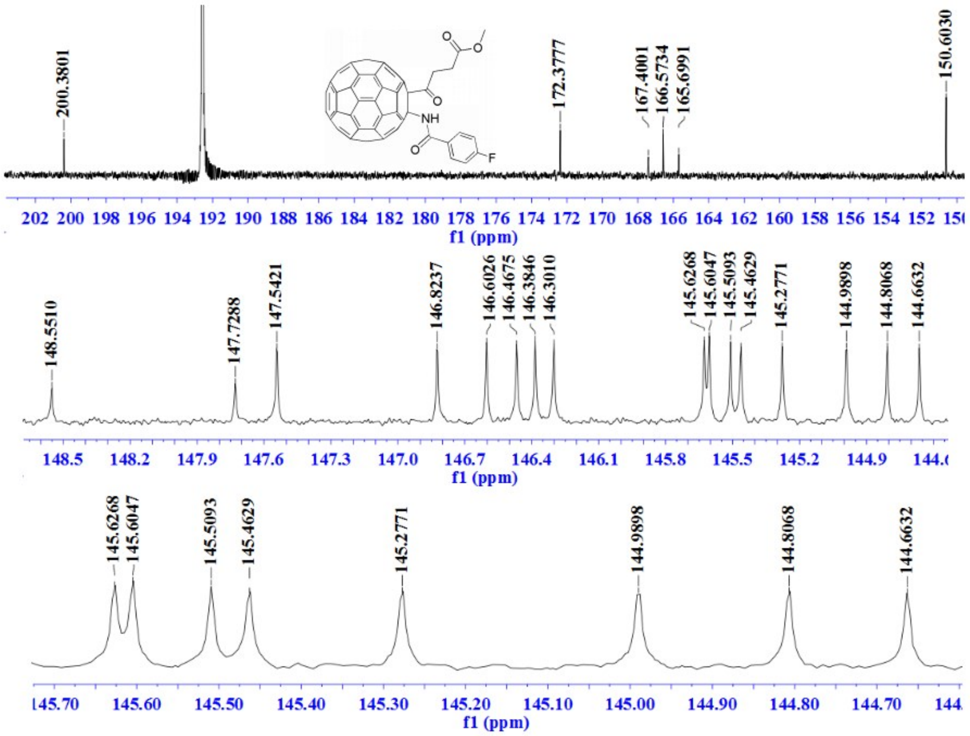


Figure S46-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3k

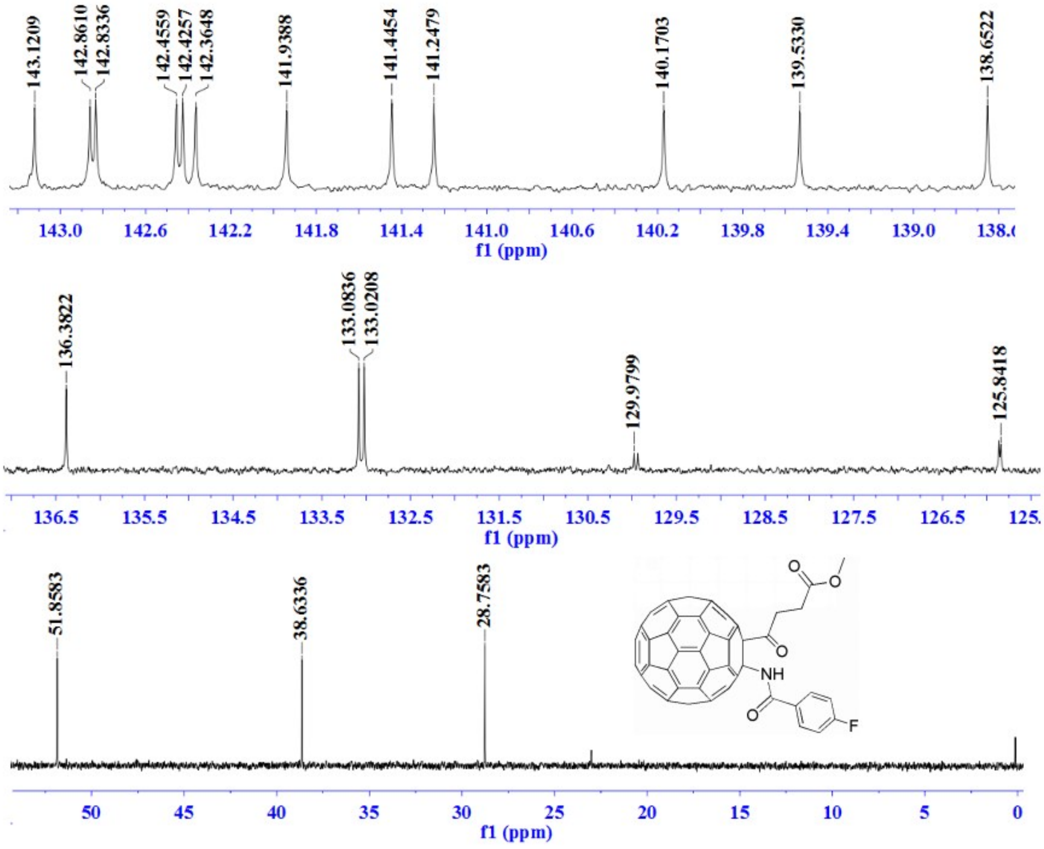


Figure S46-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3k

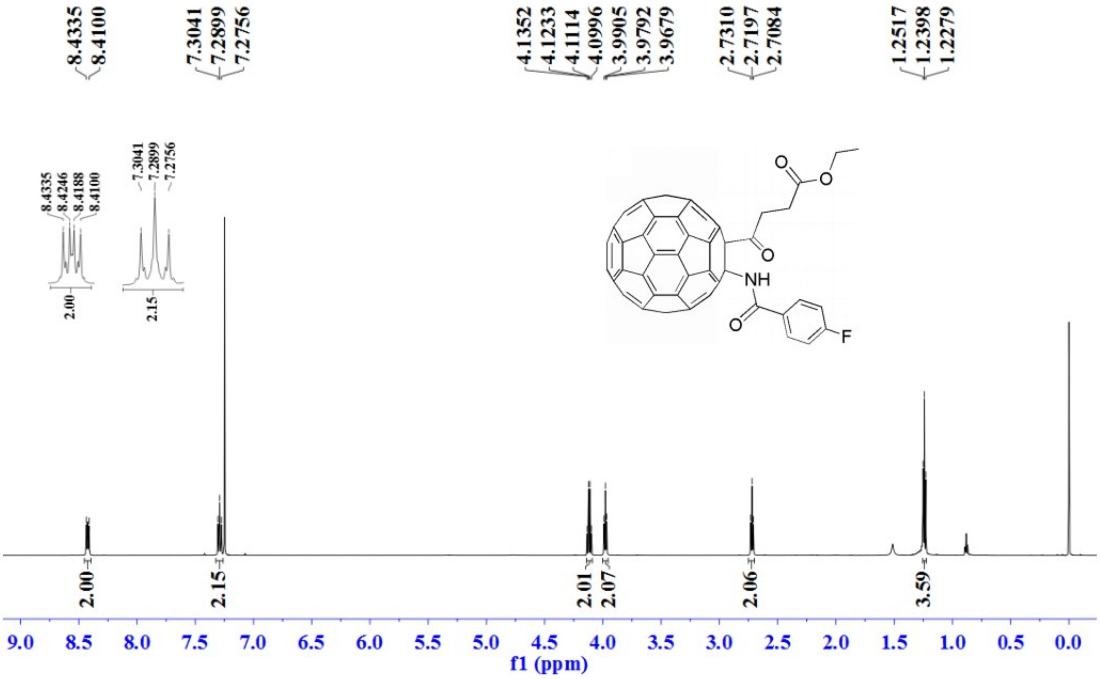


Figure S47. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 3l

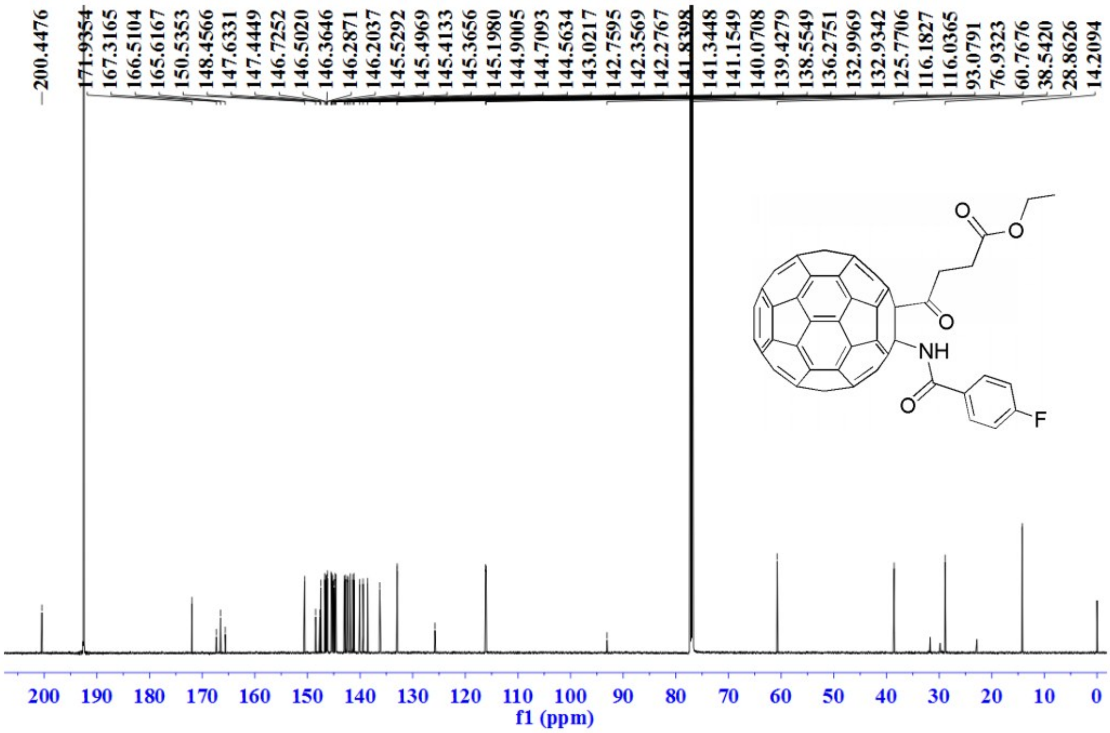


Figure S48. ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3l

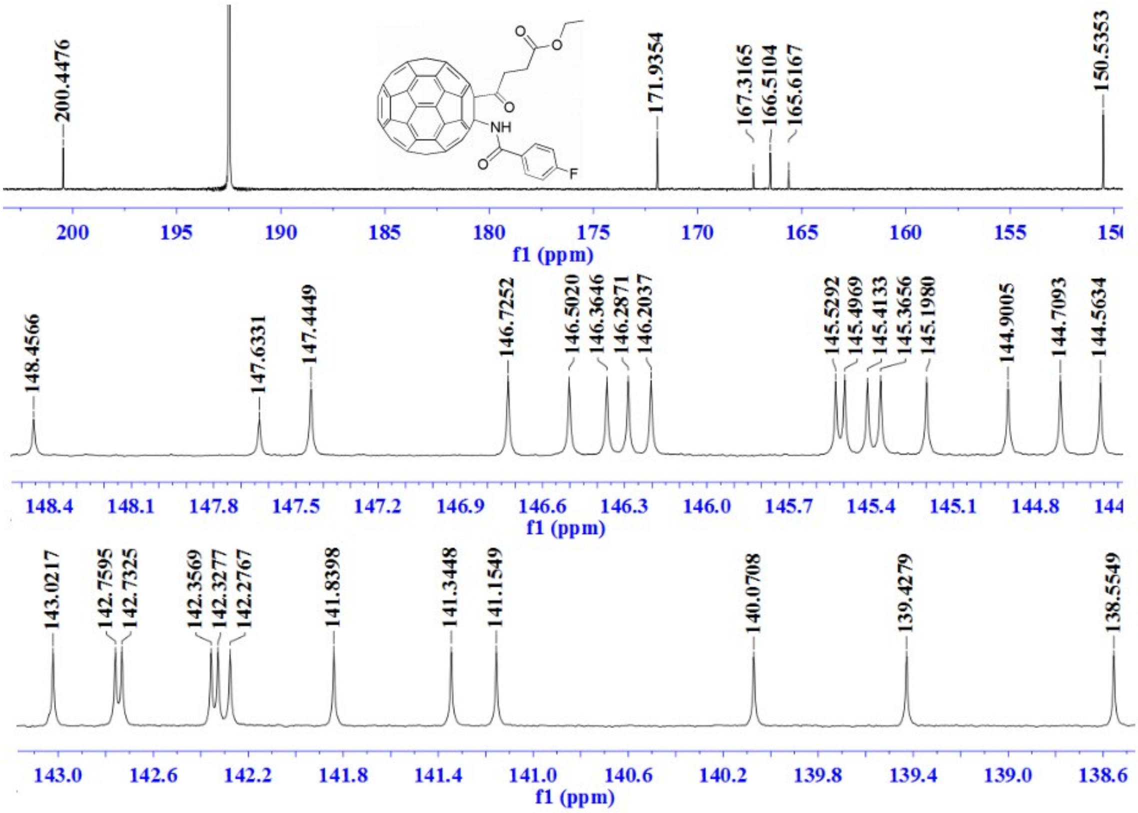


Figure S48-1. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3l

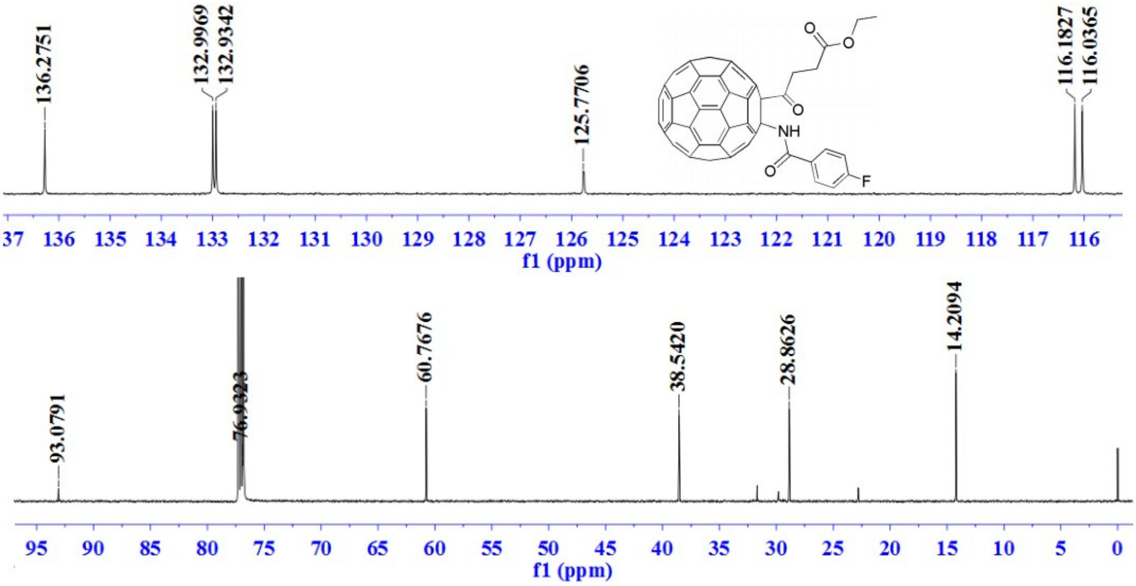


Figure S48-2. Expanded ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) of compound 3l

HPLC of photooxidation process of compounds 2a

Compounds **2a** and **3a** were seperated by EC2000 (Dalian Elite Analytical InstrumentsCo., Ltd., China) on a supersil SiO_2 column (Dalian Elite Analytical InstrumentsCo., Ltd., China). The mobile phase was toluene with a flow rate of 1 mL/min. The detection wavelength was at 330 nm. The retention time for **2a** is about 5 min and **3a** is about 7 min.

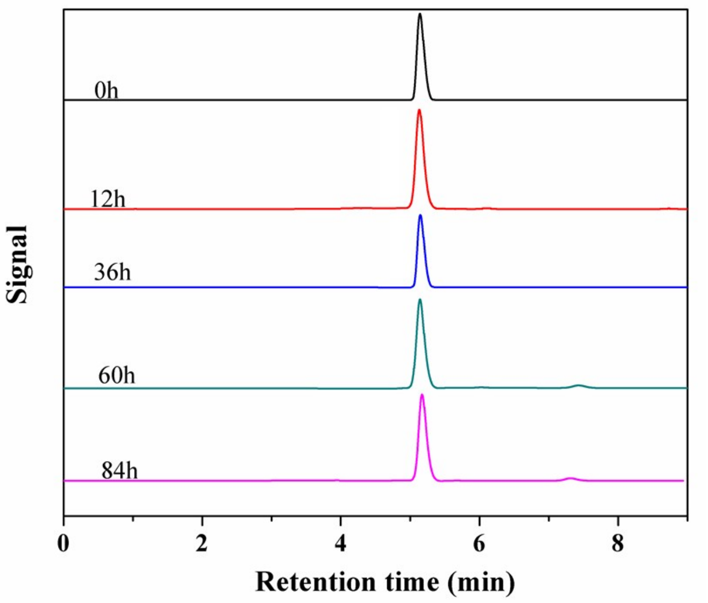


Figure S49. High Performance Liquid Chromatography of photo-oxidation process of 2a in chlorobenzene 25 °C

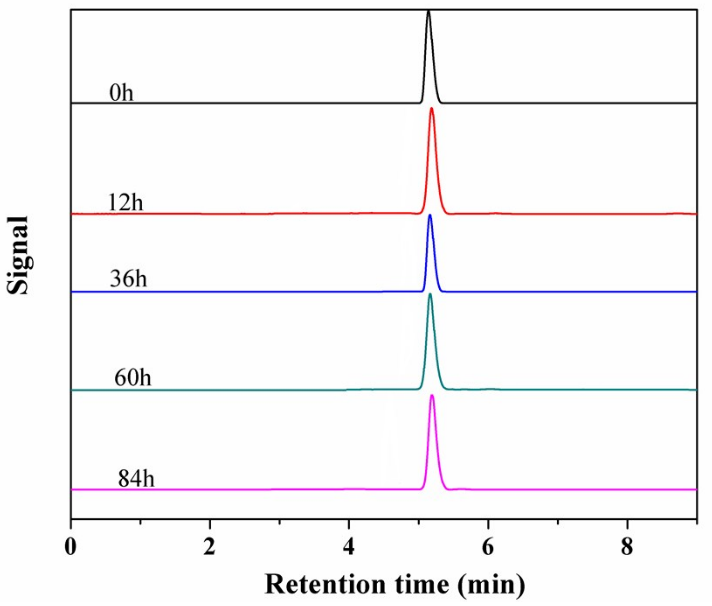


Figure S50. High Performance Liquid Chromatography of photo-oxidation process of 2a in toluene 25 °C

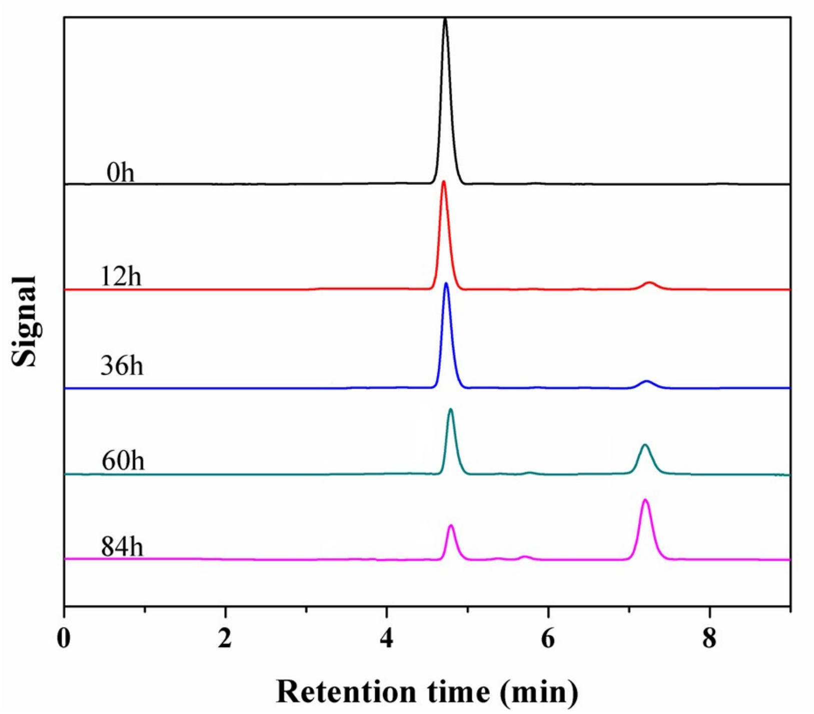


Figure S51. High Performance Liquid Chromatography of photo-oxidation process of 2a in carbon disulfide 25 ^{o}C

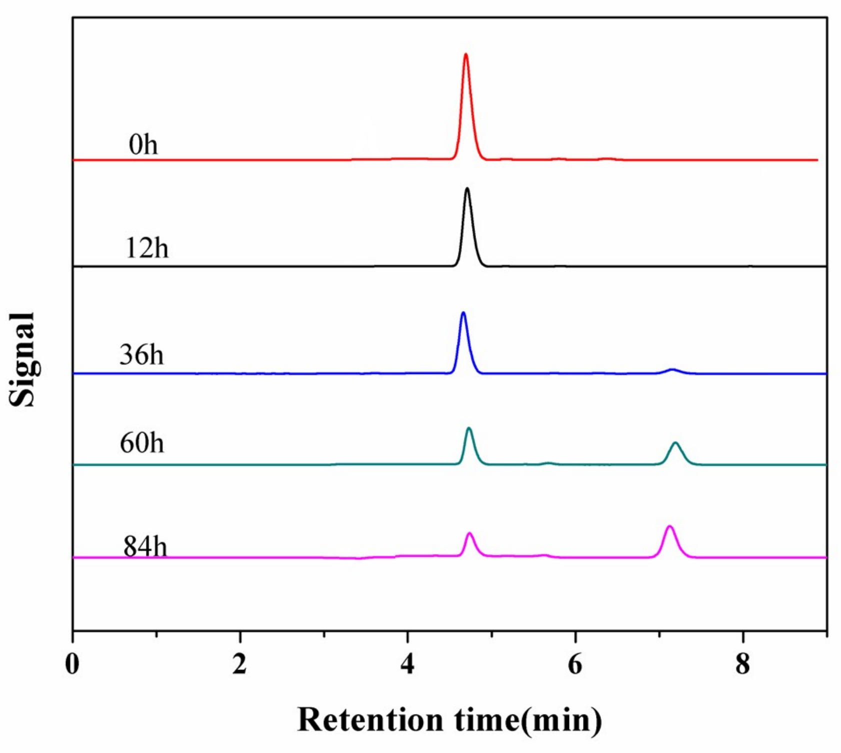


Figure S52. High Performance Liquid Chromatography of photo-oxidation process of 2a in carbon disulfide at 15 ^{o}C

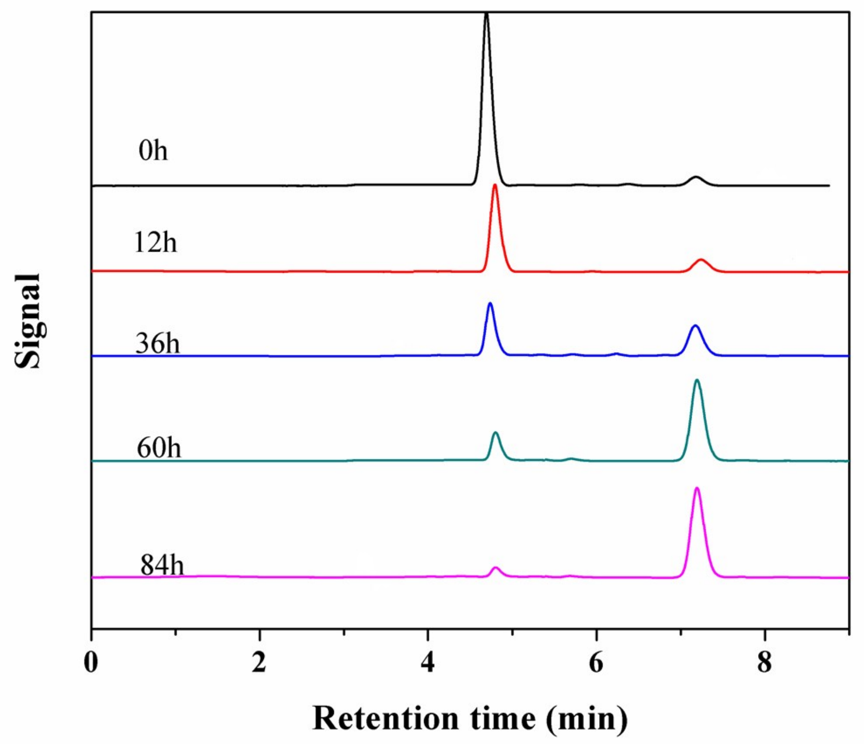


Figure S53. High Performance Liquid Chromatography of photo-oxidation process compound 2a in carbon disulfide at 35 ^{o}C

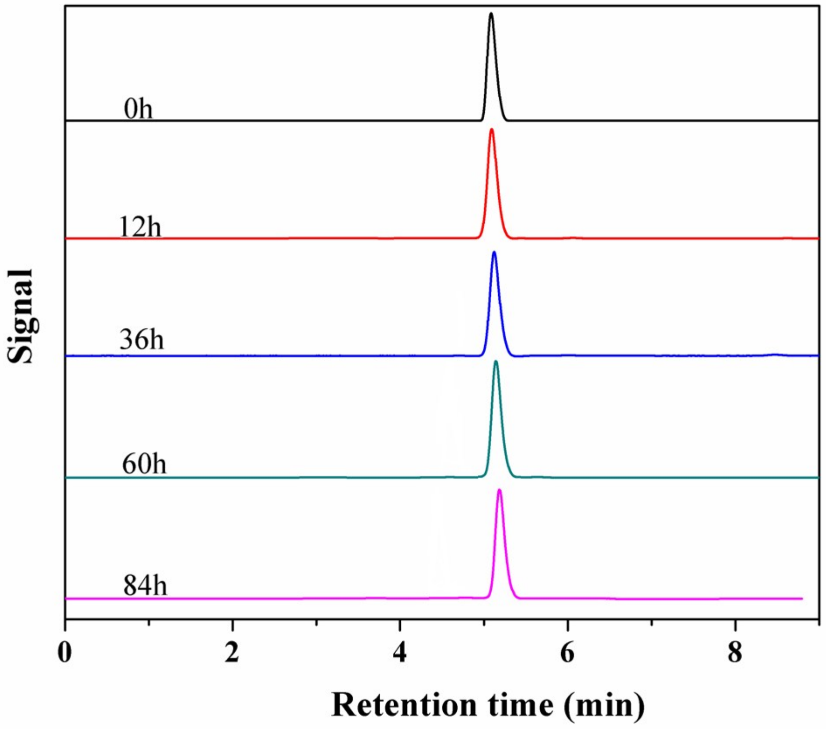


Figure S54. High Performance Liquid Chromatography of photo-oxidation process compound 2a in carbon disulfide at 25 ^{o}C in dark

The standard curve of 2a and reaction rate curves

The rate constant was derived from the first-order reaction equation as follows:

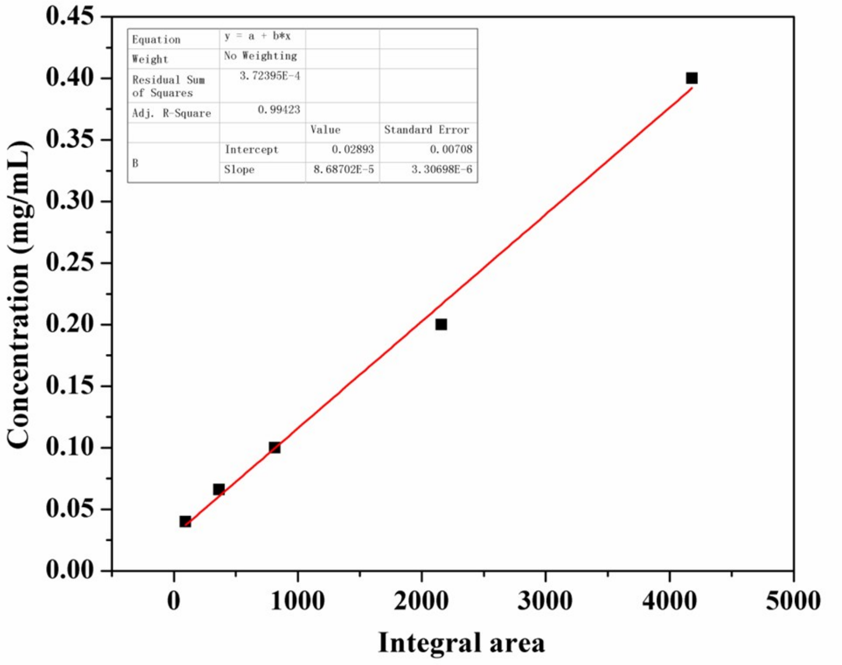
$$\ln c_A = -k_A t + \ln c_{A,0} \qquad (1)$$

Where t is the reaction time (min), c_A is the concentration at time t, and $c_{A,0}$ is initial concentration. When $\ln c_A/c_{A,0}$ was plotted against t, a straight line was obtained through a linear fitting, which as shown in Fig. S55. It can be demonstrate that this reaction is a first-order reaction. The rate constants (k_A) at different temperatures are 2.19E^{-4} min^{-1} (35℃), 2.12E^{-4} min^{-1} (25℃), and 2.11E^{-4} min^{-1} (15℃) (see ESI, Fig. S56-S58) respectively, which means that the rate of this photo-oxidation reaction is accelerating as the temperature increases.

The thermokinetic parameters activation energy (E_a) was derived from the Arrhenius equation as Eq. (2)

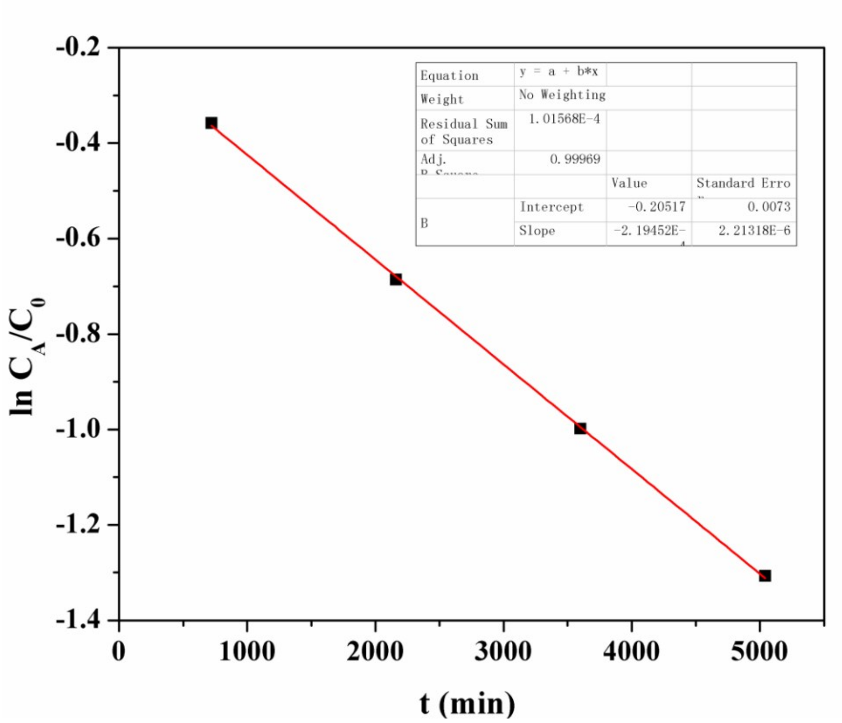
$$ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (2)$$

where k is the rate constant (min^{-1}) , R is the gas constant (8.31 J K^{-1} mol^{-1}) and T is reaction temperature. When the reaction temperature is 298.15k and 308.15k, the rate constants k_1 and k_2 are 2.12E^{-4} min^{-1} and 2.19E^{-4} min^{-1} respectively, k_2/k_1 is 0.037, and E_a is 2.79 kJ/mol.



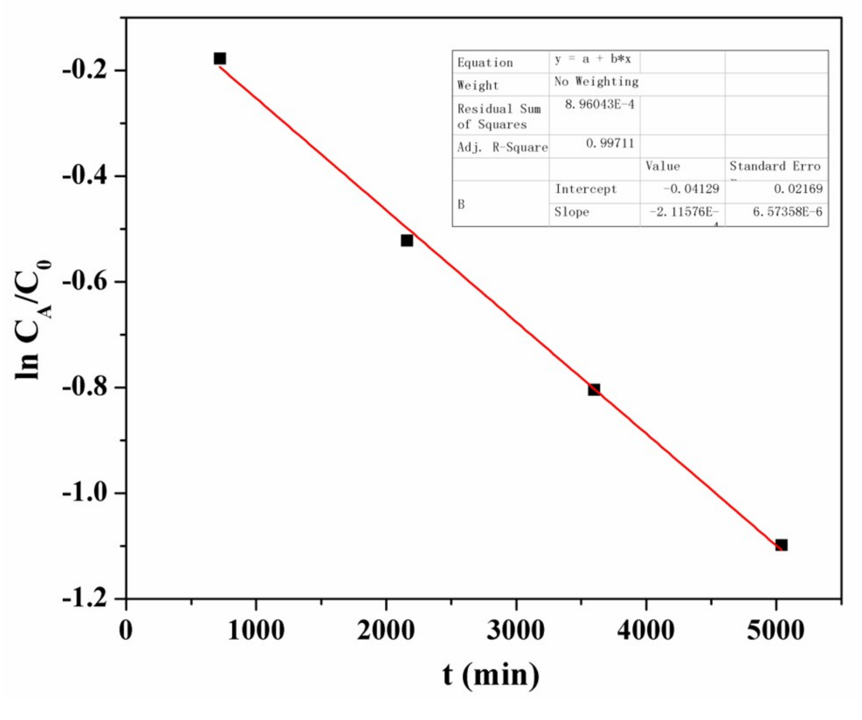
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	3.72395E-4		
Adj. R-Square	0.99423		
		Value	Standard Error
B	Intercept	0.02893	0.00708
	Slope	8.68702E-5	3.30698E-6

Figure S55. The standard curve of 2a



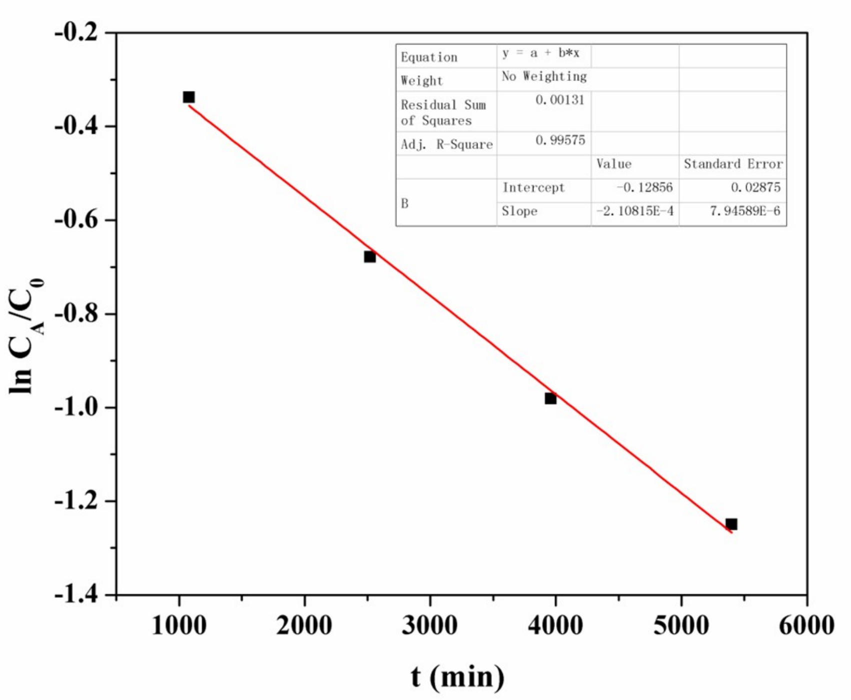
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.01568E-4		
Adj. R-Square	0.99969		
		Value	Standard Erro
B	Intercept	-0.20517	0.0073
	Slope	-2.19452E-4	2.21318E-6

Figure S56. The reaction rate curves at 35℃



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	8.96043E-4		
Adj. R-Square	0.99711		
		Value	Standard Erro
B	Intercept	-0.04129	0.02169
	Slope	-2.11576E-4	6.57358E-6

Figure S57. The reaction rate curves at 25℃



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00131		
Adj. R-Square	0.99575		
		Value	Standard Error
B	Intercept	-0.12856	0.02875
	Slope	-2.10815E-4	7.94589E-6

Figure S58 The reaction rate curves at 15℃