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Electronic Supplementary Information

Unexpected Diels-Alder reaction of [60]fullerene with electron-deficient ferrocenes as cyclopentadiene surrogates

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1. General information

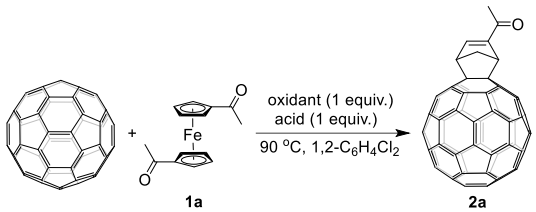
Anhydrous 1,2-dichlorobenzene (1,2-$C_6H_4Cl_2$) was freshly distilled, ferrocenes **1a**–**n** were purchased from commercial sources or synthesized by the literature procedure.[1] Other chemicals were purchased from commercial sources and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ASCEND III–400 or a Bruker ASCEND III–500 or a JEOL JNM-ECZ600R/SI spectrometer at room temperature. ^{1}H NMR chemical shifts were determined relative to TMS. ^{13}C NMR chemical shifts were determined relative to TMS or undeuterated solvent ($C_2D_2Cl_4$, δ 72.95 ppm; DMSO-d_6, δ 39.50 ppm; $CDCl_3$, δ 77.16 ppm). Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectra were obtained on a Bruker UltrafleXtreme MALDI-TOF/TOF instrument. UV-vis spectra were obtained on a SHIMADZU UV-3600PLUS instrument. IR spectra were obtained on a Thermo Scientific Nicolet 6700 instrument. All CV measurements were performed under an argon atmosphere at 25 °C using a Shanghai Chenhua CHI630D workstation.

2. Optimization of the reaction conditions

We initiated our exploration with 1,1'-diacetylferrocene (**1a**) as the model substrate to optimize the reaction conditions (Table S1). The reaction was initially performed with C_{60} (0.05 mmol), **1a** (0.05 mmol) and PTSA (0.05 mmol) in 1,2-dichlorobenzene (1,2-$C_6H_4Cl_2$, 4 mL) under an argon atmosphere at 90 °C for 3 h, giving **2a** in 11% yield (entry 1). When the reaction was conducted under an open-air atmosphere, the yield of **2a** was dramatically improved to 41% (entry 2), which demonstrated that an oxidant played an important role in the reaction. Other oxidants such as 1,4-benzoquinone (BQ), $NaIO_4$ and *m*-CPBA were also investigated in order to enhance the product yield, but they failed to give a better result (entries 3–5 *vs*. entry 2). To our delight, the yield was sharply improved to 53% upon using $K_2S_2O_8$ as the oxidant (entry 6). It was worth noting that only a trace amount of **2a** was obtained in the absence of PTSA, which indicated that an acid was indispensable for the transformation (entry 7). Replacement of PTSA with other acids, including acetic acid (AcOH), pivalic acid (PivOH), trifluoroacetic acid (TFA), trifluoromethanesulfonic acid (TfOH) and *D*-camphorsulfonic acid (*D*-CSA) could only give **2a** in no more than 28% yield (entries 8–12). Decreasing the amount of **1a** to 0.5 equiv. led to a drop of the yield to 45%, and increasing **2a** to 2 equiv. couldn't provide a better yield (entries 13 and 14). When the reaction was performed under the Pd–catalyzed conditions,[2] **2a** was obtained in 46% yield (entry 15), suggesting that the additional Pd catalyst was not beneficial to the reaction. Intriguingly, acetylferrocene exhibited a lower reactivity and gave **2a** in only 26% yield (entry 16), which was about half of the yield for **1a** (entry 6) and hinted that both acetylcyclopentadiene moieties in **1a** were involved in the reaction. The effect of reaction temperature was also investigated, and the results indicated that a temperature of 90 °C was the best (entries 17 and 18 *vs*. entry 6). Reducing the reaction time to 2 h gave a slightly lower yield of 47% (entry 19). The same yield of 53% was obtained upon prolonging the reaction time to 4 h, whereas the consumption of C_{60} was increased (entry 20). Therefore, the optimal reaction conditions were selected as follows: C_{60} (0.05 mmol), **1a** (0.05 mmol), $K_2S_2O_8$ (0.05 mmol) and PTSA (0.05 mmol) in 1,2-

$C_6H_4Cl_2$ (4 mL) at 90 ºC for 3 h under an open air atmosphere.

Table S1 Optimization of the reaction conditions[a]



1a 2a

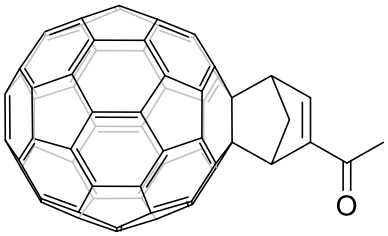
entry	oxidant	acid	yield (%)[b]
1[c]	/	PTSA	11 (92)
2	/	PTSA	41 (93)
3	BQ	PTSA	28 (87)
4	$NaIO_4$	PTSA	33 (59)
5	*m*-CPBA	PTSA	19 (78)
6	**$K_2S_2O_8$**	**PTSA**	**53 (85)**
7	$K_2S_2O_8$	/	trace
8	$K_2S_2O_8$	AcOH	trace
9	$K_2S_2O_8$	PivOH	trace
10	$K_2S_2O_8$	TFA	21 (91)
11	$K_2S_2O_8$	TfOH	11 (63)
12	$K_2S_2O_8$	*D*-CSA	28 (48)
13[d]	$K_2S_2O_8$	PTSA	45 (91)
14[e]	$K_2S_2O_8$	PTSA	52 (83)
15[f]	$K_2S_2O_8$	TfOH	46 (72)
16[g]	$K_2S_2O_8$	PTSA	26 (44)
17[h]	$K_2S_2O_8$	PTSA	48 (88)
18[i]	$K_2S_2O_8$	PTSA	53 (84)
19[j]	$K_2S_2O_8$	PTSA	47 (92)
20[k]	$K_2S_2O_8$	PTSA	53 (80)

[a]Unless otherwise noted, the reactions were performed with C_{60} (0.05 mmol), **1a** (0.05 mmol), oxidant (0.05 mmol) and acid (0.05 mmol) in anhydrous 1,2-$C_6H_4Cl_2$ (4 mL) at 90 °C under an open-air atmosphere for 3 h. [b]Isolated yield. Values in parentheses are based on the consumed C_{60}. [c]The reaction was performed under an argon atmosphere. [d]The amount of **1a** was 0.025 mmol. [e]The amount of **1a** was 0.10 mmol. [f]10 mmol% $Pd(OTf)_2(CH_3CN)_4$ was added. [g]The substrate was acetylferrocene. [h]The reaction was performed at 80 °C. [i]The reaction was performed at 100 °C. [j]The reaction time was 2 h. [k]The reaction time was 4 h.

3. Synthesis and spectral data of compounds 2a–n

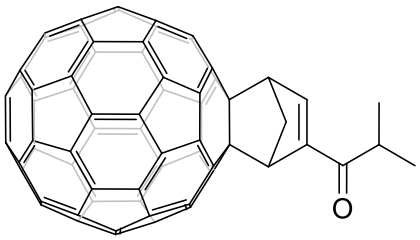
General procedure: a mixture of C_{60} (0.05 mmol), **1** (0.05 mmol), $K_2S_2O_8$ (0.05 mmol) and *p*-toluenesulfonic monohydrate (PTSA) (0.05 mmol) was dissolved in 1,2-$C_6H_4Cl_2$ (4 mL). Then, the solution was stirred at the desired temperature and stopped at the designated time. The resulting solution was evaporated in vacuo and subsequently

separated on a silica gel column (300–400 mesh) with CS_2/CH_2Cl_2 (1/1~5/1, v/v) or CS_2/EtOAc (4/1, v/v) as the eluent to give recovered C_{60} and the desired product **2**.



2a

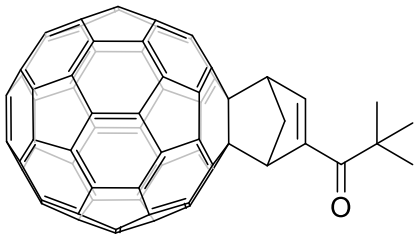
***Synthesis and spectral data of 2a*:** by following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1a** (13.5 mg, 0.05 mmol), $K_2S_2O_8$ (13.8 mg, 0.05 mmol) and PTSA (9.7 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 4/1), and afforded recovered C_{60} (13.8 mg, 38%) and **2a** (21.8 mg, 53%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) δ 7.73 (d, J = 3.2 Hz, 1H), 4.97–4.93 (m, 1H), 4.69–4.65 (m, 1H), 3.52 (d, J = 10.0 Hz, 1H), 2.67–2.62 (m, 1H), 2.57 (s, 3H); ^{13}C NMR (100.6 MHz, CS_2 with DMSO-d_6 as the external deuterium lock and containing TMS as the reference) δ 191.99 (C=O), 156.40, 155.80, 155.59, 154.19, 151.57 (C=C), 147.41, 147.29, 146.60, 146.55 (3C), 146.35 (3C), 146.31 (3C), 146.20, 145.97, 145.76, 145.69 (2C), 145.58 (6C), 145.36, 145.27, 144.90, 144.71, 144.60, 144.46, 143.23, 143.14, 142.90, 142.85, 142.83, 142.79 (2C), 142.67, 142.36 (2C), 142.16 (4C), 142.10 (3C), 141.95, 140.40, 140.30, 140.26, 140.07, 137.81, 137.64, 137.36, 136.28, 74.92 (sp^3-C of C_{60}), 74.64 (sp^3-C of C_{60}), 58.34, 55.17, 45.12, 26.26; FT-IR ν/cm^{-1} (KBr) 1668, 1586, 1508, 1424, 1360, 1260, 1182, 1013, 942, 760, 612, 558, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.17), 309 (4.66), 328 (4.62), 432 (3.68), 701 (2.87).



2b

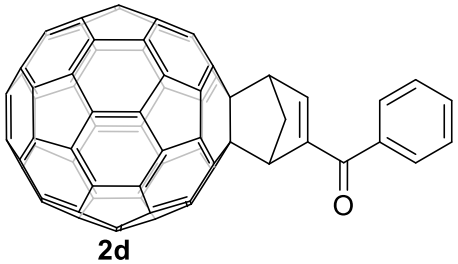
***Synthesis and spectral data of 2b*:** by following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with **1b** (16.3 mg, 0.05 mmol), $K_2S_2O_8$ (13.3 mg, 0.05 mmol) and PTSA (10.0 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 1.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 4/1), and afforded recovered C_{60} (12.1 mg, 34%) and **2b** (21.6 mg, 51%): amorphous brown solid;^{1}H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) δ 7.76 (d, J = 3.2 Hz, 1H), 4.97–4.93 (m, 1H), 4.70–4.66 (m, 1H), 3.55–3.41 (m, 2H), 2.66–2.61 (m, 1H), 1.29 (d, J = 6.9 Hz, 3H), 1.28 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, 2/1 $CS_2/CDCl_3$) δ 200.07 (C=O), 156.24, 155.48, 155.07, 154.00, 149.75 (C=C), 147.08, 146.95, 146.25,

146.22, 146.20 (2C), 146.05, 146.01, 145.99 (2C), 145.96, 145.85, 145.72, 145.40, 145.32, 145.28 (3C), 145.24, 145.23, 145.17, 145.13 (3C), 145.08, 144.55, 144.34, 144.26, 144.10, 142.88, 142.78, 142.55, 142.49 (2C), 142.45, 142.32, 142.16, 142.02, 141.99, 141.84 (3C), 141.80, 141.78 (2C), 141.71, 141.61, 139.99, 139.96, 139.93, 139.74, 137.42, 137.36, 137.01, 136.13, 74.67 (sp^3-C of C_{60}), 74.33 (sp^3-C of C_{60}), 58.01, 54.35, 44.52, 36.31, 20.15, 19.18; FT-IR ν/cm^{-1} (KBr) 2963, 1664, 1585, 1511, 1458, 1427, 1381, 1253, 1218, 1184, 1120, 1092, 986, 877, 746, 714, 672, 568, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.10), 307 (4.59), 327 (4.55), 432 (3.57), 701 (2.57).



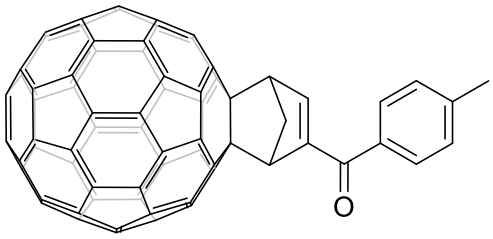
2c

***Synthesis and spectral data of 2c*:** by following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1c** (17.3 mg, 0.05 mmol), $K_2S_2O_8$ (13.4 mg, 0.05 mmol) and PTSA (9.4 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 4/1), and afforded recovered C_{60} (17.6 mg, 49%) and **2c** (13.9 mg, 32%): amorphous brown solid;^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 7.70 (d, J = 3.1 Hz, 1H), 4.98–4.94 (m, 1H), 4.72–4.68 (m, 1H), 3.50–3.44 (m, 1H), 2.57 (dt, J = 9.9, 1.8 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100.6 MHz, CS_2 with DMSO-d_6 as the external deuterium lock and the reference) δ 199.52 (C=O), 155.94, 154.95, 154.89, 153.64, 146.83 (C=C), 146.56, 146.43, 145.90, 145.73, 145.723, 145.715, 145.62, 145.50 (2C), 145.49 (2C), 145.44, 145.35, 145.29, 144.94, 144.87, 144.86, 144.80, 144.78, 144.76, 144.75, 144.74, 144.72, 144.66, 144.61, 144.08, 143.90, 143.74, 143.62, 142.39, 142.32, 142.09, 142.01, 142.00, 141.97, 141.95, 141.71, 141.58, 141.54, 141.38, 141.35 (2C), 141.34, 141.30, 141.284, 141.276, 141.16, 139.55, 139.48, 139.39, 139.28, 137.05, 136.94, 136.46, 135.45, 74.18 (sp^3-*C* of C_{60}), 73.93 (sp^3-C of C_{60}), 58.37, 55.81, 43.33 (2C), 27.74 (3C); FT-IR ν/cm^{-1} (KBr) 2969, 1650, 1579, 1511, 1424, 1319, 1269, 1198, 1138, 1118, 975, 902, 791, 758, 557, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.07), 307 (4.56), 327 (4.52), 432 (3.52), 701 (2.40).



2d

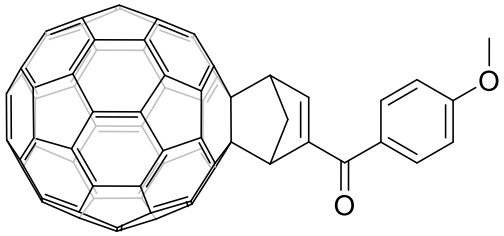
***Synthesis and spectral data of 2d*:** by following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1d** (18.8 mg, 0.05 mmol), $K_2S_2O_8$ (13.4 mg, 0.05 mmol) and PTSA (9.4 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 1.5 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 4/1), and afforded recovered C_{60} (13.7 mg, 38%) and **2d** (22.0 mg, 50%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) δ 7.99–7.94 (m, 2H), 7.61 (d, J = 3.3 Hz, 1H), 7.60–7.56 (m, 1H), 7.54–7.48 (m, 2H), 5.13–5.09 (m, 1H), 4.77–4.73 (m, 1H), 3.64–3.58 (m, 1H), 2.77 (dt, J = 10.0, 1.8 Hz, 1H); ^{13}C NMR (100.6 MHz, 2/1 $CS_2/CDCl_3$) δ 190.43 (C=O), 156.28, 155.51 (2C), 153.92, 149.64 (C=C), 148.49 (C=C), 147.17, 147.04, 146.33 (2C), 146.31, 146.29, 146.13, 146.07 (3C), 146.02, 145.93, 145.87, 145.52, 145.43 (2C), 145.37 (2C), 145.35, 145.32, 145.31, 145.28, 145.23, 145.18, 144.64, 144.46, 144.32, 144.18, 142.96, 142.86, 142.65, 142.59, 142.57, 142.53 (2C), 142.45, 142.14, 142.12, 141.93 (3C), 141.89, 141.87, 141.85, 141.82, 141.73, 140.10 (2C), 140.04, 139.78, 137.79 (aryl *C*), 137.56, 137.53, 137.09, 136.05, 132.39 (aryl C), 128.88 (aryl C, 2C), 128.54 (aryl C, 2C), 74.70 (sp^3-C of C_{60}), 74.59 (sp^3-C of C_{60}), 58.60, 56.11, 44.75; FT-IR ν/cm^{-1} (KBr) 1643, 1590, 1510, 1449, 1427, 1343, 1269, 1184, 722, 695, 666, 568, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (4.99), 308 (4.49), 328 (4.43), 432 (3.43), 701 (2.46).



2e

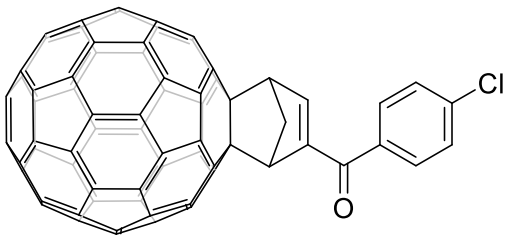
***Synthesis and spectral data of 2e*:** by following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1e** (21.1 mg, 0.05 mmol), $K_2S_2O_8$ (13.7 mg, 0.05 mmol) and PTSA (9.7 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 1.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 5/1), and afforded recovered C_{60} (13.0 mg, 36%) and **2e** (27.0 mg, 59%): amorphous brown solid; ^{1}H NMR (500 MHz, 2/1 $CS_2/CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 3.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 5.08–5.03 (m, 1H), 4.74–4.68 (m, 1H), 3.57 (d, J = 10.0 Hz, 1H), 2.76–2.70 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (125.8 MHz, 2/1 $CS_2/CDCl_3$) δ 189.14 (C=O), 155.40, 154.64 (2C), 153.03, 148.76 (C=C), 146.89 (C=C), 146.20, 146.07, 145.38, 145.35, 145.33, 145.32, 145.19, 145.10 (3C), 145.05, 144.96, 144.94, 144.54, 144.50, 144.44, 144.40, 144.39, 144.38, 144.35, 144.33, 144.29, 144.25, 144.22, 143.68, 143.50, 143.35, 143.22, 142.04 (aryl C), 141.98, 141.89, 141.68, 141.61, 141.59, 141.57, 141.55, 141.49, 141.17, 141.15, 140.97, 140.95 (2C), 140.94, 140.90, 140.88, 140.85, 140.76, 139.11 (2C), 139.06, 138.80, 136.65, 136.57, 136.12, 135.11, 134.24 (aryl C), 128.28 (aryl C, 2C), 128.15 (aryl C, 2C), 73.78 (sp^3-C of C_{60}), 73.69 (sp^3-C of C_{60}), 57.60, 55.32, 43.78, 20.81; FT-IR ν/cm^{-1} (KBr) 1638, 1604, 1510, 1459, 1426, 1341, 1270, 1178, 748, 625, 564, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.12), 308 (4.66), 329 (4.57), 432 (3.45), 700

(3.07).



2f

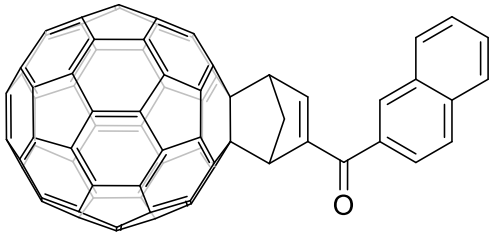
***Synthesis and spectral data of 2f*:** by following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with **1f** (22.7 mg, 0.05 mmol), $K_2S_2O_8$ (13.5 mg, 0.05 mmol) and PTSA (9.6 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 2/1), and afforded recovered C_{60} (17.6 mg, 49%) and **2f** (19.7 mg, 43%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 8.03 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 3.2 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 5.11–5.08 (m, 1H), 4.77–4.73 (m, 1H), 3.90 (s, 3H), 3.60 (d, J = 9.9 Hz, 1H), 2.79–2.73 (m, 1H); ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4$/CS_2) δ 189.08 (C=O), 162.20 (aryl C), 155.47, 154.77 (2C), 153.25, 148.47 (C=C), 147.42 (C=C), 146.11, 146.02, 145.23 (2C), 145.21, 145.19, 145.15, 145.01 (2C), 144.97, 144.95, 144.90, 144.86, 144.54, 144.38, 144.36, 144.27 (2C), 144.252, 144.245 (2C), 144.16 (2C), 144.05, 143.56, 143.34, 143.30, 143.18, 141.87, 141.77, 141.55, 141.53, 141.49, 141.48, 141.43 (2C), 141.03, 141.00, 140.92, 140.88, 140.87 (2C), 140.82, 140.75, 140.65 (2C), 138.96, 138.90 (2C), 138.66, 136.47 (2C), 136.13, 135.13, 130.20 (aryl C, 2C), 129.48 (aryl C), 112.94 (aryl C, 2C), 73.82 (sp^3-C of C_{60}), 73.78 (sp^3-C of C_{60}), 57.38, 55.37, 54.67, 43.69; FT-IR ν/cm^{-1} (KBr) 1637, 1595, 1508, 1457, 1421, 1340, 1306, 1256, 1164, 1109, 1028, 899, 838, 787, 759, 617, 558, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.02), 308 (4.64), 432 (3.42), 701 (2.52).



2g

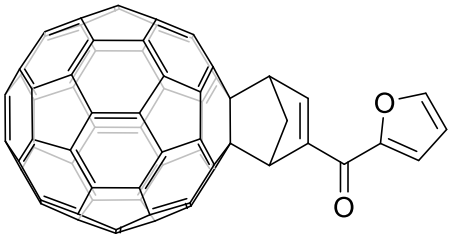
***Synthesis and spectral data of 2g*:** by following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1g** (23.2 mg, 0.05 mmol), $K_2S_2O_8$ (13.8 mg, 0.05 mmol) and PTSA (9.7 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 4/1), and afforded recovered C_{60} (13.4 mg, 37%) and **2g** (22.4 mg, 48%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 3.2 Hz, 1H), 7.50 (d, J = 8.5 Hz, 2H), 5.13–5.11 (m, 1H), 4.79–4.74 (m, 1H), 3.61 (d, J = 10.0 Hz, 1H), 2.77 (dt, J = 10.0, 1.8 Hz, 1H); ^{13}C NMR (100.6 MHz, CS_2 with DMSO-d_6 as the external deuterium lock and containing TMS as the

reference) δ 186.96 (C=O), 155.09, 154.38, 154.31, 152.71, 148.46 (C=C), 146.45 (C=C), 146.13, 146.01, 145.32, 145.30, 145.29, 145.28, 145.05 (4C), 145.00, 144.92, 144.73, 144.53, 144.46, 144.38, 144.33 (2C), 144.31, 144.29 (2C), 144.26, 144.20, 144.09, 143.61, 143.43, 143.28, 143.14, 141.94, 141.86, 141.65, 141.58, 141.55, 141.53, 141.45, 141.38, 141.11 (2C), 140.90 (2C), 140.88, 140.86 (3C), 140.81, 140.72, 139.14, 139.06, 139.03, 138.81, 138.18 (aryl C), 136.51, 136.49, 136.06, 134.86, 134.83 (aryl C), 129.29 (aryl C, 2C), 127.83 (aryl C, 2C), 73.57 (sp^3-C of C_{60}), 73.45 (sp^3-C of C_{60}), 57.70, 55.44, 43.80; FT-IR ν/cm^{-1} (KBr) 2922, 1643, 1583, 1512, 1339, 1267, 1186, 1090, 1014, 837, 750, 563, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.08), 308 (4.59), 327 (4.51), 432 (3.46), 701 (2.32).



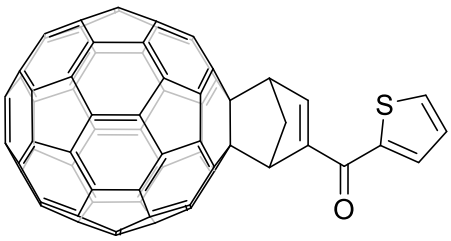
2h

***Synthesis and spectral data of 2h*:** by following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1h** (24.7 mg, 0.05 mmol), $K_2S_2O_8$ (13.4 mg, 0.05 mmol) and PTSA (9.3 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 °C in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 4/1), and afforded recovered C_{60} (17.5 mg, 49%) and **2h** (15.7 mg, 33%): amorphous brown solid;^{1}H NMR (400 MHz, 2/1 $C_2D_2Cl_4$/CS_2) δ 8.55 (s, 1H), 8.01–7.92 (m, 3H), 7.88 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 3.2 Hz, 1H), 7.63–7.50 (m, 2H), 5.15–4.08 (m, 1H), 4.79–4.72 (m, 1H), 3.62–3.53 (m, 1H), 2.83–2.75 (m, 1H); ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4$/CS_2) δ 190.51 (C=O), 155.36, 154.67, 154.64, 153.20, 148.85 (C=C), 148.54 (C=C), 146.11, 146.02, 145.25 (2C), 145.20, 145.18, 145.16, 145.03, 145.01, 144.98, 144.96, 144.87 (2C), 144.51, 144.38, 144.37, 144.34, 144.26 (4C), 144.18, 144.16, 144.12, 143.56, 143.33, 143.31, 143.17, 141.88, 141.79, 141.53, 141.52, 141.50, 141.48, 141.44, 141.38, 141.02, 141.01, 140.92, 140.88 (2C), 140.86, 140.81, 140.77, 140.67, 140.64, 139.00, 138.93 (2C), 138.72, 136.50, 136.40, 136.17, 135.15, 134.19 (aryl C), 134.08 (aryl C), 131.29 (aryl C), 129.19 (aryl C), 128.45 (aryl C), 127.72 (aryl C), 127.46 (aryl C), 126.90 (aryl C), 126.09 (aryl C), 123.93 (aryl C), 73.80 (sp^3-C of C_{60}), 73.76 (sp^3-C of C_{60}), 57.48, 55.08, 43.69; FT-IR ν/cm^{-1} (KBr) 1641, 1582, 1508, 1459, 1425, 1329, 1269, 1181, 1040, 901, 860, 821, 788, 759, 557, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (4.89), 307 (4.43), 326 (4.32), 432 (3.27).



2i

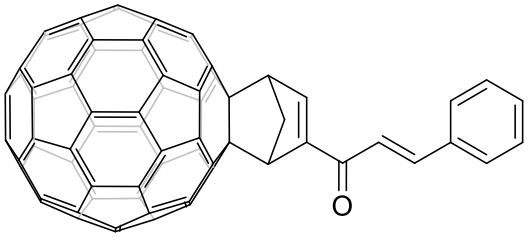
***Synthesis and spectral data of 2i*:** by following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1i** (18.4 mg, 0.05 mmol), $K_2S_2O_8$ (13.4 mg, 0.05 mmol) and PTSA (9.7 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 3/1), and afforded recovered C_{60} (15.1 mg, 42%) and **2i** (20.9 mg, 48%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 8.18 (d, J = 3.3 Hz, 1H), 7.67 (dd, J = 1.7, 0.8 Hz, 1H), 7.37 (dd, J = 3.6, 0.8 Hz, 1H), 6.62 (dd, J = 3.6, 1.7 Hz, 1H), 5.14–5.09 (m, 1H), 4.77–4.73 (m, 1H), 3.59–3.54 (m, 1H), 2.70 (dt, J = 10.0, 1.8 Hz, 1H); ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4$/CS_2) δ 175.90 (C=O), 155.28, 154.78, 154.34, 153.04, 151.80 (aryl C), 147.67 (*C*=C), 147.42 (C=C), 146.14, 146.04, 145.64 (aryl C), 145.29, 145.26, 145.21 (2C), 145.19, 145.03 (2C), 145.01, 144.99, 144.91, 144.86, 144.51, 144.41, 144.38, 144.32 (2C), 144.30, 144.28 (2C), 144.21, 144.13, 144.10, 143.58, 143.37, 143.34, 143.20, 141.91, 141.79, 141.56 (2C), 141.52 (2C), 141.47, 141.42, 141.04 (2C), 140.93, 140.91, 140.87 (2C), 140.86, 140.80, 140.73, 140.70, 138.96 (2C), 138.92, 138.72, 136.61, 136.49, 136.18, 135.46, 117.62 (aryl C), 111.58 (aryl C), 73.75 (sp^3-C of C_{60}), 73.64 (sp^3-C of C_{60}), 57.27, 55.00, 43.44; FT-IR ν/cm^{-1} (KBr) 1623, 1508, 1462, 1425, 1340, 1275, 1183, 1078, 1010, 884, 791, 752, 592, 558, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.11), 309 (4.69), 328 (4.61), 432 (3.66), 701 (2.62).



2j

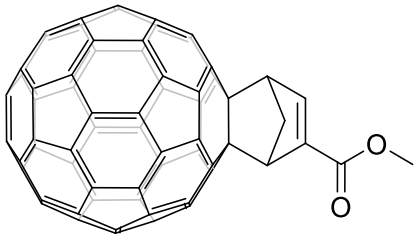
***Synthesis and spectral data of 2j*:** by following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1j** (20.7 mg, 0.05 mmol), $K_2S_2O_8$ (13.8 mg, 0.05 mmol) and PTSA (9.5 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 3/1), and afforded recovered C_{60} (17.5 mg, 49%) and **2j** (18.4 mg, 41%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 8.00 (dd, J = 3.8, 1.2 Hz, 1H), 7.87 (d, J = 3.2 Hz, 1H), 7.70 (dd, J = 4.9, 1.2 Hz, 1H), 7.22 (dd, J = 4.9, 3.8 Hz, 1H), 5.10–5.07 (m, 1H), 4.78–4.74 (m, 1H), 3.59 (d, J = 10.0 Hz, 1H), 2.76 (dt, J = 10.0, 2.3 Hz, 1H); ^{13}C NMR (100.6 MHz, CS_2 with DMSO-d_6 as the external deuterium lock and containing TMS as the reference) δ 179.16 (C=O), 155.16, 154.48,

154.24, 152.78, 148.92 (C=C, 2C), 146.13, 145.99, 145.36, 145.29, 145.27 (2C), 145.07, 145.05, 145.03, 145.01, 144.98, 144.91, 144.78, 144.52, 144.42, 144.40, 144.37, 144.33, 144.31, 144.28 (2C), 144.27, 144.25, 144.19, 144.16, 143.61, 143.47, 143.28, 143.14, 142.11, 141.92, 141.82, 141.63, 141.56, 141.53 (2C), 141.50, 141.44, 141.13, 141.11, 140.91, 140.89, 140.87 (2C), 140.86, 140.80, 140.74, 139.12, 139.04, 139.02, 138.78, 136.75, 136.53, 136.07, 135.24, 132.10 (aryl C), 130.92 (aryl C), 126.94 (aryl C), 73.60 (sp^3-C of C_{60}), 73.51 (sp^3-C of C_{60}), 57.48, 55.69, 43.76; FT-IR ν/cm^{-1} (KBr) 1619, 1584, 1509, 1458, 1412, 1355, 1329, 1269, 1234, 1184, 1043, 861, 787, 736, 717, 558, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.15), 309 (4.74), 326 (4.67), 432 (3.67), 701 (2.99).



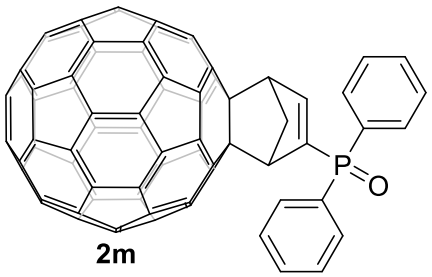
2k

***Synthesis and spectral data of 2k*:** by following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with **1k** (22.0 mg, 0.05 mmol), $K_2S_2O_8$ (40.4 mg, 0.15 mmol) and PTSA (9.4 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 °C in oil bath for 7.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 3/1), and afforded recovered C_{60} (20.8 mg, 58%) and **2k** (11.5 mg, 25%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 7.86 (d, J = 3.2 Hz, 1H), 7.77 (d, J =15.7 Hz, 1H), 7.65–7.58 (m, 2H), 7.47 (d, J = 15.7 Hz, 1H), 7.42–7.36 (m, 3H), 5.09–5.05 (m, 1H), 4.75–4.71 (m, 1H), 3.57 (d, J = 9.9 Hz, 1H), 2.73–2.67 (m, 1H); ^{13}C NMR (100.6 MHz, $C_2D_2Cl_4$) δ 184.96 (C=O), 155.29, 154.76, 154.38, 153.04, 150.86 (C=C), 146.11, 146.02, 145.72 (C=C), 145.25, 145.23, 145.17 (2C), 145.12, 145.02, 145.01, 144.96 (2C), 144.86 (2C), 144.53, 144.37, 144.35, 144.27 (2C), 144.25 (3C), 144.18, 144.15, 144.03, 143.55, 143.33, 143.30, 143.18, 142.61 (C=C), 141.88, 141.73, 141.62, 141.51, 141.48 (2C), 141.43 (2C), 141.00, 140.98, 140.92, 140.89, 140.85, 140.83 (2C), 140.76, 140.64, 140.63, 138.91, 138.89 (2C), 138.67, 136.47 (2C), 136.17, 135.36, 133.47 (aryl C), 129.79 (aryl C), 128.06 (aryl C, 2C), 127.57 (aryl C, 2C), 120.33 (C=C), 73.83 (sp^3-C of C_{60}), 73.57 (sp^3-C of C_{60}), 56.91, 54.23, 43.60; FT-IR ν/cm^{-1} (KBr) 1653, 1594, 1449, 1426, 1354, 1214, 1181, 1120, 978, 838, 758, 713, 685, 567, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.11), 321 (4.80), 432 (3.58), 701 (2.64).



2l

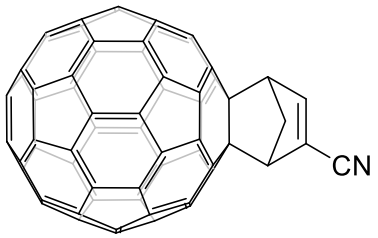
***Synthesis and spectral data of 2l*:** by following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1l** (29.8 mg, 0.10 mmol), $K_2S_2O_8$ (13.7 mg, 0.05 mmol) and PTSA (9.9 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 100 ºC in oil bath for 3.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 2/1), and afforded recovered C_{60} (18.9 mg, 52%) and **2l** (13.8 mg, 33%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 7.82 (d, J = 3.2 Hz, 1H), 4.87–4.84 (m, 1H), 4.65–4.61 (m, 1H), 3.84 (s, 3H), 3.55–3.50 (m, 1H), 2.67 (dt, J = 9.9, 1.8 Hz, 1H); ^{13}C NMR (100.6 MHz, CS_2 with DMSO-d_6 as the external deuterium lock and the reference) δ 162.25 (C=O), 155.63, 155.30, 154.23, 153.32, 146.61, 146.53, 145.80 (2C), 145.74, 145.70, 145.57 (6C), 145.52, 145.45, 145.19, 144.98, 144.93 (3C), 144.83 (2C), 144.77 (2C), 144.74, 144.67, 144.06, 143.88 (2C), 143.75, 142.45, 142.39, 142.36, 142.13, 142.07 (2C), 142.01 (2C), 141.92, 141.54 (2C), 141.41 (3C), 141.37 (2C), 141.32 (2C), 141.27, 139.59, 139.54, 139.41, 139.32, 137.14, 136.95, 136.71, 136.20, 74.09 (sp^3-C of C_{60}), 74.03 (sp^3-C of C_{60}), 57.26, 55.63, 50.95, 44.91; FT-IR ν/cm^{-1} (KBr) 1715, 1601, 1509, 1429, 1344, 1265, 1234, 1186, 1155, 1089, 788, 753, 712, 568, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.22), 308 (4.70), 327 (4.67), 432 (3.69), 701 (2.65).



2m

***Synthesis and spectral data of 2m*:** by following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1m** (19.8 mg, 0.05 mmol), $K_2S_2O_8$ (13.5 mg, 0.05 mmol) and PTSA (10.0 mg, 0.05 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 ºC in oil bath for 1.5 h. The reaction mixture was purified by silica gel column chromatography (CS_2/EtOAc = 4/1), and afforded recovered C_{60} (19.8 mg, 55%) and **2m** (11.0 mg, 22%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 $C_2D_2Cl_4$/CS_2) δ 7.79–7.73 (m, 4H), 7.64 (dd, J = 9.5, 3.2 Hz, 1H), 7.57–7.39 (m, 6H), 4.82–4.77 (m, 1H), 4.67–4.63 (m, 1H), 3.58 (d, J = 10.0 Hz, 1H), 2.86–2.78 (m, 1H); ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4$/CS_2) δ 155.75, 155.48, 154.50, 153.60, 151.23 (C=C, d, J = 7.3 Hz), 146.62, 146.57, 145.74 (2C), 145.72, 145.71 (C=C, d, J = 102.2 Hz), 145.68, 145.54, 145.51, 145.46, 145.45, 145.40, 145.28, 144.98, 144.88, 144.85, 144.83 (2C), 144.80, 144.77 (3C), 144.69 (2C), 144.67, 143.94, 143.90 (2C), 143.73, 142.34, 142.33, 142.01, 141.99,

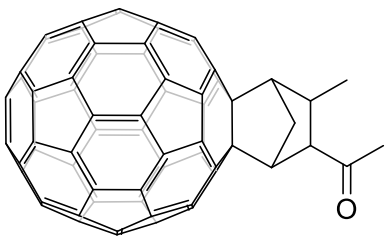
141.93, 141.92, 141.89, 141.78, 141.45, 141.43, 141.39, 141.34, 141.27, 141.22 (3C), 141.15, 141.12, 139.39, 139.26, 139.20, 139.19, 137.09, 136.78, 136.72, 136.60, 132.48 (aryl C, d, J = 106.5 Hz), 131.83 (aryl C, 2C), 131.53 (aryl C, 2C, d, J = 9.6 Hz), 131.07 (aryl C, 2C, J = 10.1 Hz), 130.54 (aryl C, d, J = 106.3 Hz), 128.32 (aryl C, 2C, d, J = 5.4 Hz), 128.20 (aryl C, 2C, d, J = 5.3 Hz), 74.21 (2C, sp^3-C of C_{60}), 57.28, 57.27 (d, J = 21.1 Hz), 46.47 (d, J = 4.4 Hz); ^{31}P NMR (243.0 MHz, $C_2D_2Cl_4$) δ 21.81; FT-IR ν/cm^{-1} (KBr) 1561, 1461, 1434, 1290, 1204, 1116, 1102, 1065, 746, 722, 699, 601, 558, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.09), 309 (4.60), 326 (4.56), 432 (3.55), 701 (2.52).



2n

***Synthesis and spectral data of 2n*:** by following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1n** (23.5 mg, 0.10 mmol), $K_2S_2O_8$ (27.2 mg, 0.10 mmol) and PTSA (19.0 mg, 0.10 mmol) was performed in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 °C in oil bath for 4.0 h. The reaction mixture was purified by silica gel column chromatography (CS_2/CH_2Cl_2 = 4/1), and afforded recovered C_{60} (15.0 mg, 42%) and **2n** (9.6 mg, 24%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) δ 7.81 (d, J = 3.2 Hz, 1H), 4.72–4.69 (m, 1H), 4.69–4.65 (m, 1H), 3.61–3.56 (m, 1H), 2.74 (dd, J = 10.2, 1.8 Hz, 1H); ^{13}C NMR (150.9 MHz, CS_2 with DMSO-d_6 as the external deuterium lock and reference) δ 154.47, 154.41, 152.44, 152.13, 150.61 (C=C), 146.72, 146.64, 145.89 (3C), 145.77, 145.63 (3C), 145.54, 145.34, 145.23, 145.16 (2C), 145.05, 145.02, 144.97, 144.94, 144.83 (3C), 144.724, 144.718, 144.68, 144.04, 143.92 (2C), 143.75, 142.50, 142.43, 142.21, 142.16 (2C), 142.13, 141.94, 141.91, 141.62, 141.56, 141.50 (2C), 141.44, 141.40 (2C), 141.35, 141.28, 141.23, 139.66 (3C), 139.48, 137.20, 137.10, 136.87, 136.83, 121.94 (C=C), 113.83 (CN), 73.56 (sp^3-C of C_{60}), 73.53 (sp^3-C of C_{60}), 58.37, 56.68, 44.98; FT-IR ν/cm^{-1} (KBr) 2217, 1511, 1460, 1426, 1298, 1186, 1042, 1013, 850, 763, 719, 563, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.09), 311 (4.58), 326 (4.55), 431 (3.52), 698 (2.53).

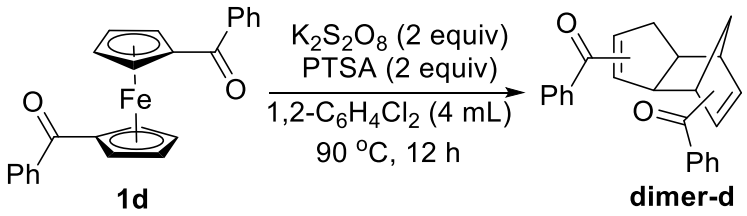
4. Synthesis and spectral data of compound 5a



5a

***Synthesis and spectral data of 5a*: 2a** (32.8 mg, 0.04 mmol) was dissolved in freshly distilled dry 1,2-$C_6H_4Cl_2$ (4 mL), followed by the addition of CuCl (19.7 mg, 0.20 mmol). After the mixture was deoxygenated with N_2 for 10 min, CH_3MgBr (67 μL, 3.00 M in THF, 0.20 mmol) was added dropwise at room temperature. Then the mixture was stirred at room temperature for 15 min and was quenched with the saturated aqueous solution of NH_4Cl (20 mL). The resulting mixture was then extracted with CS_2 and dried with anhydrous Na_2SO_4. After the solvent was removed in vacuo, the residue was separated on a silica gel column with CS_2/CH_2Cl_2 = 4/1 as the eluent to afford **5a** (29.7 mg, 89%): amorphous brown solid; ^{1}H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) δ 4.30–4.26 (m, 1H), 3.94–3.85 (m, 1H), 3.66–3.59 (m, 1H), 3.53–3.49 (m, 1H), 3.06 (dd, J = 6.5, 3.7 Hz, 1H), 2.73–2.67 (m, 1H), 2.39 (s, 3H), 1.55 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125.8 MHz, 2/1 $C_2D_2Cl_4/CS_2$) δ 205.25 (C=O), 154.50, 154.11, 152.38, 150.66, 146.00, 145.97, 145.39, 145.07, 145.01, 144.99, 144.98, 144.85 (3C), 144.83, 144.80, 144.49, 144.15, 144.13, 144.12, 144.11, 144.07, 144.05 (2C), 144.02, 144.01, 143.98, 143.82, 143.35, 143.31, 143.28, 143.06, 141.87, 141.85, 141.44, 141.41, 141.37 (2C), 140.97, 140.94, 140.77 (2C), 140.75, 140.71, 140.704, 140.699, 140.68, 140.65, 140.34, 140.04, 139.04, 138.96, 138.84, 138.53, 137.86, 137.39, 134.98, 134.94, 73.78 (sp^3-C of C_{60}), 71.06 (sp^3-C of C_{60}), 66.42, 56.00, 51.93, 34.80, 34.69, 28.89, 21.22; FT-IR ν/cm^{-1} (KBr) 2951, 1707, 1515, 1463, 1425, 1350, 1268, 1188, 1081, 765, 604, 563, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.02), 310 (4.53), 327 (4.49), 432 (3.49), 700 (2.36); MALDI-TOF MS *m/z* calcd for $C_{68}H_{12}O$ $[M]^-$ 844.0894, found 844.0885.

5. Control experiments



A mixture of **1d** (19.5 mg, 0.05 mmol), $K_2S_2O_8$ (26.9 mg, 0.10 mmol) and PTSA (19.7 mg, 0.10 mmol) was dissolved in 1,2-$C_6H_4Cl_2$ (4 mL) at 90 °C for 12 h. The resulting solution was filtered through a short silica gel column to remove the residue, and the dimer of the in-situ generated cyclopentadienes was successfully detected by ESI-MS (Figure S1).

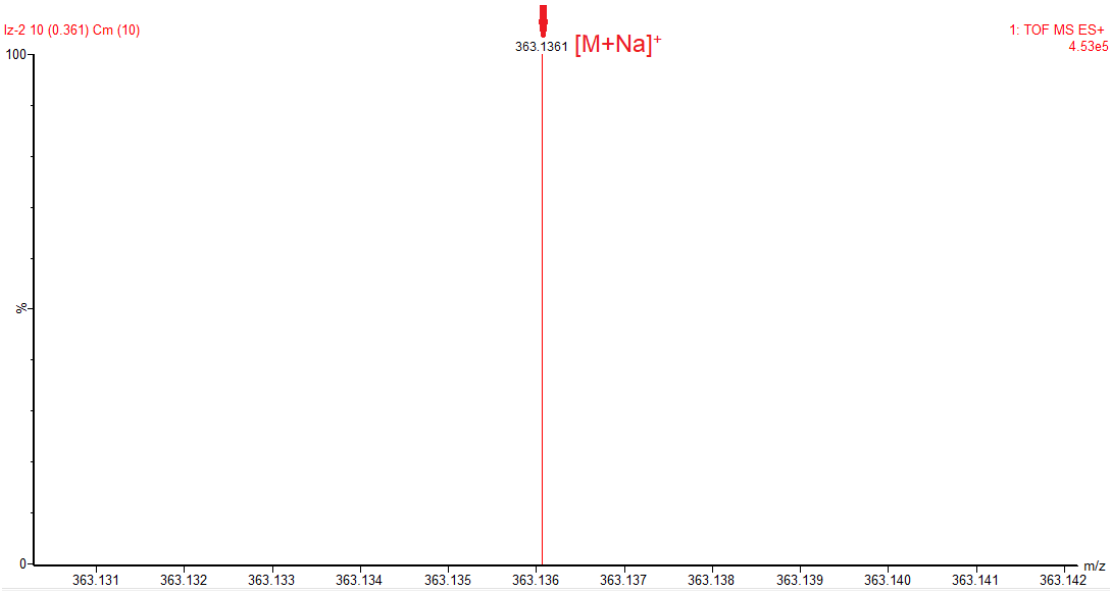
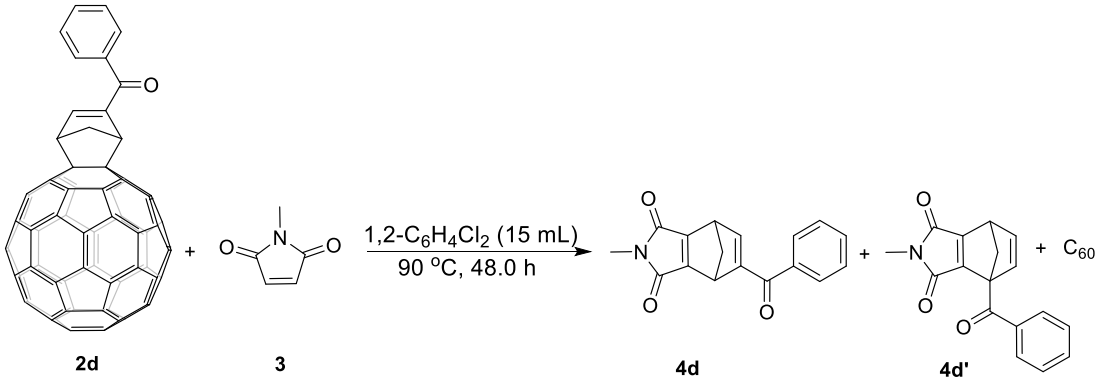
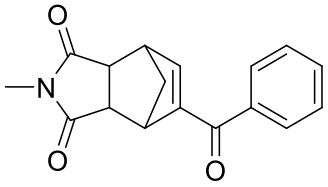


Figure S1. HRMS of **dimer-d**



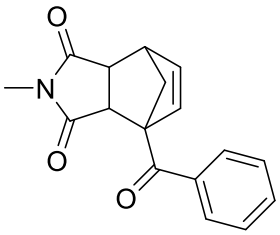
A mixture of **2d** (138.0 mg, 0.15 mmol) and *N*-methyl maleimide (**3**, 16.7 mg, 0.15 mmol) was dissolved in 1,2-$C_6H_4Cl_2$ (15 mL) at 90 °C for 48.0 h. The reaction mixture was purified by silica gel column chromatography with CS_2 as the eluent to afford C_{60} (100.6 mg, 93%) and then with petroleum ether/ethyl acetate = 5/1 as the eluent to afford **4d** (20.5 mg, 48%) and **4d'** (8.2 mg, 19%) as white powders.

Synthesis of 4d and 4d': *N*-methylmaleimide (**3**, 110.9 mg, 1.00 mmol), **1d** (0.50 mmol, 196.9 mg,), $K_2S_2O_8$ (270.3 mg, 1.00 mmol) and PTSA (192.3 mg, 1.00 mmol) were dissolved in freshly distilled dry 1,2-$C_6H_4Cl_2$ (40 mL) and performed at 90 °C in oil bath for 24.0 h. The reaction mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate = 5/1 as the eluent, and afforded **4d** (112.0 mg, 40%) and **4d'** (56.8 mg, 20%) as white powders.



4d

Spectral data of 4d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.47 (m, 2H), 7.47–7.40 (m, 1H), 7.35–7.30 (m, 2H), 7.67 (d, J = 3.2 Hz, 1H), 3.94–3.90 (m, 1H), 3.57–3.53 (m, 1H), 3.44 (dd, J = 7.7, 4.7 Hz, 1H), 3.39 (dd, J = 7.7, 4.4 Hz, 1H), 2.68 (s, 3H), 1.95–1.90 (m, 1H), 1.70–1.65 (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.2, 176.9, 175.9, 146.6, 146.0, 137.3, 132.3, 128.4 (4C), 52.1, 46.5, 46.4, 45.5, 45.2, 24.3; HRMS (ESI) Calcd for $C_{17}H_{15}NNaO_3$ $[M+Na]^+$ 304.0944; found 304.0950.



4d'

Spectral data of 4d': ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.4 Hz , 1H), 7.37 (t, J = 7.6 Hz, 2H), 6.31 (d, J = 5.6 Hz, 1H), 6.22–6.14 (m, 1H), 4.19 (d, J = 7.7 Hz, 1H), 3.57–3.48 (m, 1H), 3.38 (dd, J = 7.7, 4.5 Hz, 1H), 2.74 (s, 3H), 2.31 (dt, J = 9.0, 1.8 Hz, 1H), 1.92 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 197.5, 176.9, 176.2, 136.0, 135.6, 133.6, 133.1, 129.2 (2C), 128.5 (2C), 66.7, 58.4, 47.5, 46.2, 45.7, 24.4; HRMS (ESI) Calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$ 282.1125; found 282.1134.

6. X-Ray data of compounds 2b, 4d and 4d'

Black block crystals of **2b** were obtained by slow evaporation of a saturated solution in toluene and methanol (1:2) at room temperature. Single-crystal X-ray diffraction data were collected on a diffractometer (Gemini S Ultra, Agilent Technologies) equipped with a CCD area detector using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) in the scan range 8.14° < 2θ < 142.76°. The structure was solved with the SHELXT structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2096386.

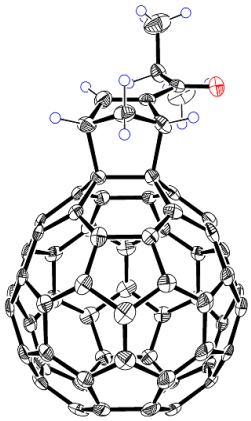


Figure S2. ORTEP diagram of **2b** with 30% thermal ellipsoids

Table S2. Crystal data for **2b**.

Identification code	2096386
Empirical formula	$C_{69}H_{12}O$
Formula weight	856.79
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.2005(2)
b/Å	14.0514(14)
c/Å	33.8218(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	6748.70(16)
Z	8
ρ_{calc}g/cm^3	1.687
μ/mm^{-1}	0.772
F(000)	3472.0
Crystal size/mm^3	0.24 × 0.22 × 0.21
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.14 to 142.76
Index ranges	-17 ≤ h ≤ 16, -16 ≤ k ≤ 17, -30 ≤ l ≤ 41
Reflections collected	17425
Independent reflections	6425 [R_{int} = 0.0354, R_{sigma} = 0.0339]
Data/restraints/parameters	6425/0/633
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0860, wR_2 = 0.1954
Final R indexes [all data]	R_1 = 0.0916, wR_2= 0.1991
Largest diff. peak/hole / e Å^{-3}	0.98/-0.35

Black block crystals of **4d** were obtained by slow evaporation of a saturated solution in dichloromethane at 4 ºC. Single-crystal X-ray diffraction data were collected on a diffractometer (Gemini S Ultra, Agilent Technologies) equipped with a CCD area detector using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) in the scan range 6.9° < 2θ < 140.06°. The structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimisation. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2096387.

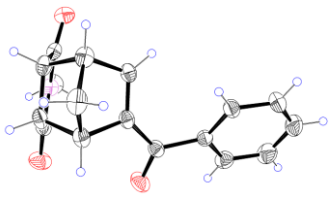


Figure S3. ORTEP diagram of **4d** with 30% thermal ellipsoids

Table S3. Crystal data for **4d**.

Identification code	2096387
Empirical formula	$C_{17}H_{15}NO_3$
Formula weight	281.30
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.19847(17)
b/Å	8.86563(12)
c/Å	25.6419(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2773.10(7)
Z	8
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.757
F(000)	1184.0
Crystal size/mm^3	0.24 × 0.22 × 0.20
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.9 to 140.06
Index ranges	-14 ≤ h ≤ 10, -10 ≤ k ≤ 8, -25≤ l ≤ 30
Reflections collected	9315
Independent reflections	2594 [R_{int} = 0.0242, R_{sigma} = 0.0195]
Data/restraints/parameters	2594/0/192
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1209
Final R indexes [all data]	R_1 = 0.0466, wR_2= 0.1242
Largest diff. peak/hole / e Å^{-3}	0.23/-0.20

Black block crystals of **4d'** were obtained by slow evaporation of a saturated solution in dichloromethane at 4 °C. Single-crystal X-ray diffraction data were collected on a diffractometer (Gemini S Ultra, Agilent Technologies) equipped with a CCD area detector using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) in the scan range 10.24° < 2θ < 140.22°. The structure was solved with the SHELXT structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2096393.

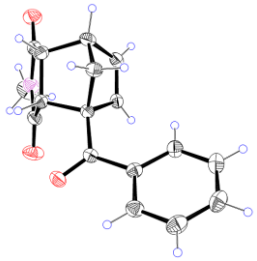


Figure S4. ORTEP diagram of **4d'** with 30% thermal ellipsoids

Table S4. Crystal data for **4d'**.

Identification code	2096393
Empirical formula	$C_{17}H_{15}NO_3$
Formula weight	281.30
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.91306(11)
b/Å	10.84345(15)
c/Å	14.26741(17)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	1378.92(3)
Z	4
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	0.761
F(000)	592.0
Crystal size/mm^3	0.24 × 0.22 × 0.20
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	10.24 to 140.22
Index ranges	$-10 \le h \le 7$, $-12 \le k \le 12$, $-17 \le l \le 4$
Reflections collected	4471
Independent reflections	2529 [R_{int} = 0.0189, R_{sigma} = 0.0203]
Data/restraints/parameters	2529/0/192
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0875
Final R indexes [all data]	R_1 = 0.0342, wR_2= 0.0879
Largest diff. peak/hole / e Å^{-3}	0.21/-0.18
Flack parameter	0.0(2)

7. CV of compounds 2a–n and 5a

A conventional three-electrode cell was used for CV measurements and consisted of a 2 mm diameter platinum disc working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE). Compound **2a–n**, **5a**, C_{60} and PCBM (1.0 mM) dissolved in anhydrous 1,2-$C_6H_4Cl_2$ containing 0.1 M TBAP was added into an electrochemical cell under an argon atmosphere at room temperature. CV measurement was then undertaken at a scan rate of 50 mV s^{-1}.

Table S5 Half-wave reduction potentials (V) of C_{60}, PCBM, products **2a**–**n** and **5a**[a]

Compound	E_1	E_2	E_3
C_{60}	–1.08	–1.46	–1.93
PCBM	–1.16	–1.54	–2.05
2a	–1.18	–1.58	–2.12
2b	–1.19	–1.58	–2.12
2c	–1.19	–1.58	–2.12
2d	–1.18	–1.58	–2.13
2e	–1.19	–1.59	–2.13
2f	–1.17	–1.54	–2.07
2g	–1.18	–1.56	–2.04
2h	–1.15	–1.52	–2.04
2i	–1.19	–1.58	/
2j	–1.18	–1.56	/
2k	–1.21	–1.59	/
2l	–1.18	–1.57	–2.11
2m	–1.18	–1.57	–2.11
2n	–1.17	–1.58	–2.12
5a	–1.18	–1.57	–2.11

[a]Versus ferrocenium/ferrocene. Experimental conditions: 2 mM of a compound and 0.1 M of *n*-Bu_4NClO_4 in anhydrous 1,2-$C_6H_4Cl_2$; reference electrode: SCE; working electrode: Pt disc; auxiliary electrode: Pt wire; scanning rate: 50 mV s^{-1}.

8. References

1) B. Gao, B. Yang, T. Li and B. Zhang, *Synth. Commun.*, 2009, **39**, 2973.
2) D.-B. Zhou and G.-W. Wang, *Adv. Synth. Catal.*, 2016, **358**, 1548.

9. NMR spectra of compounds 2a–n, 5a, 4d and 4d'

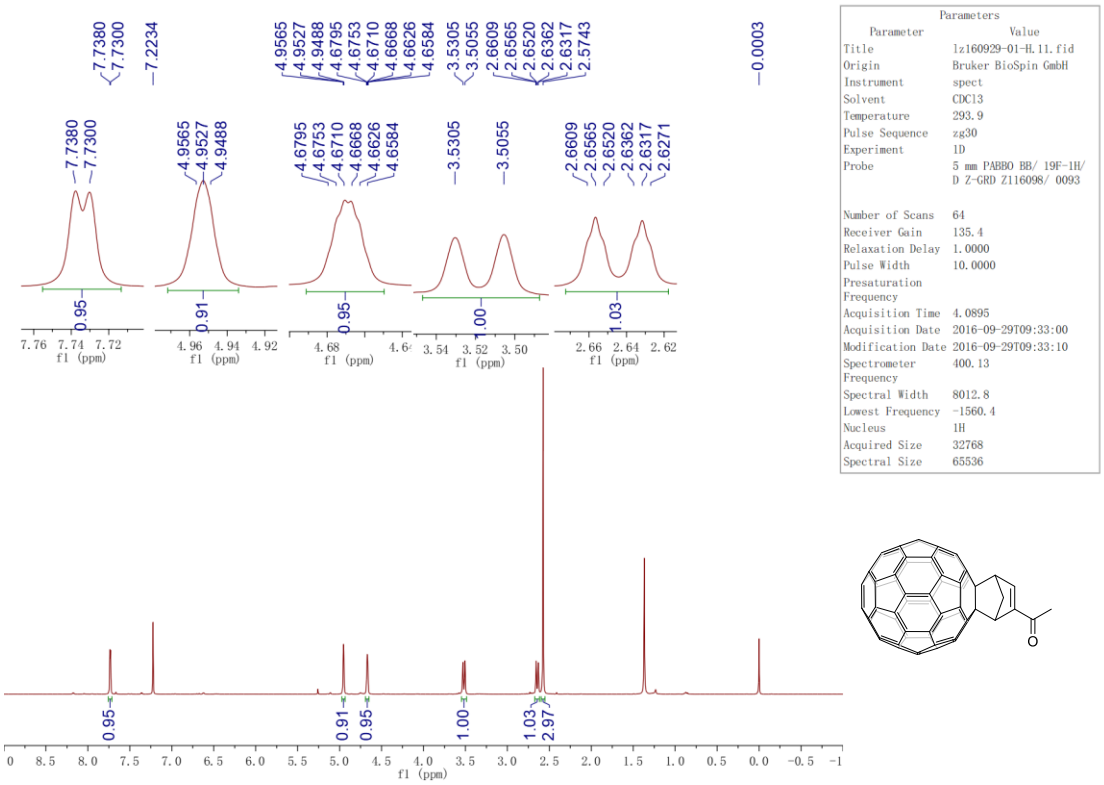


Figure S5. ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **2a**

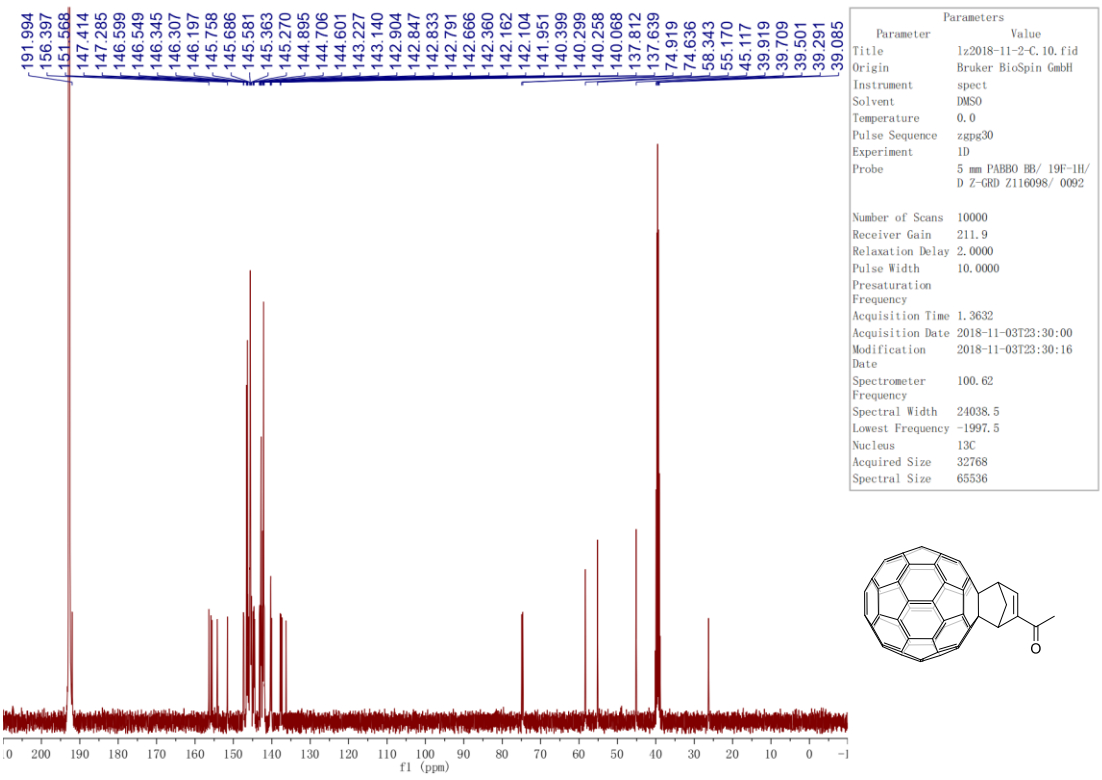


Figure S6. ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2a**

Figure S7. Expanded ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2a**

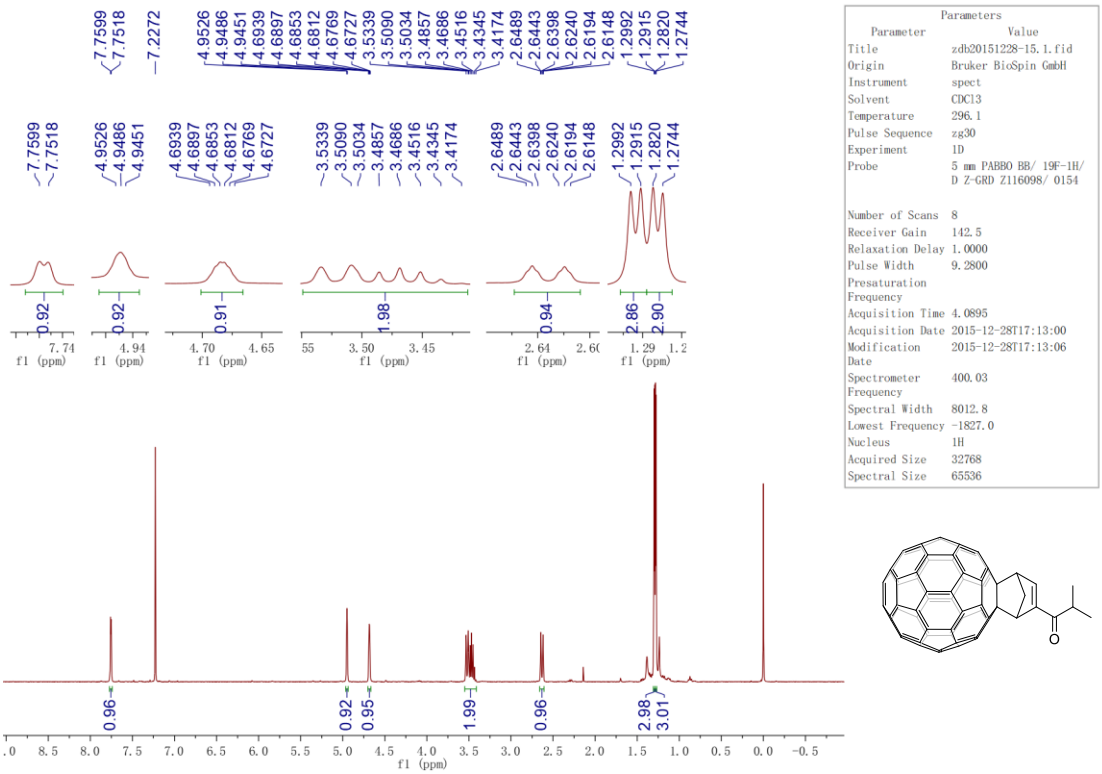


Figure S8. ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **2b**

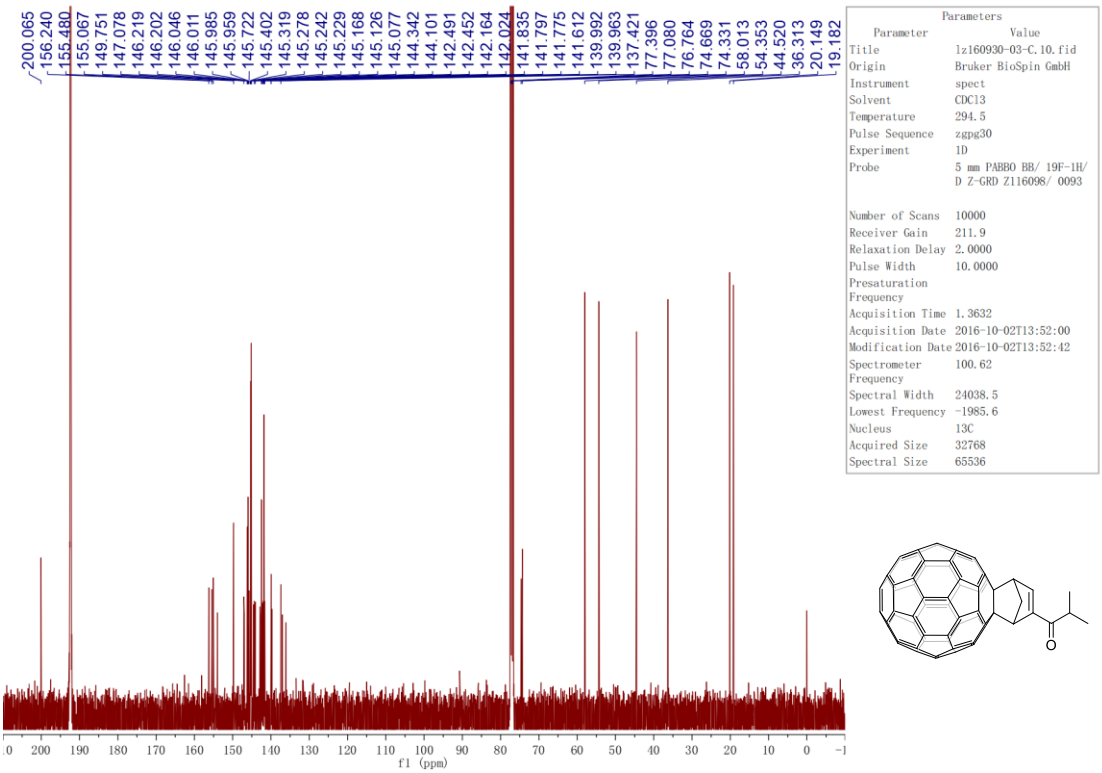


Figure S9. ^{13}C NMR (100.6 MHz, 2/1 $CS_2/CDCl_3$) of compound **2b**

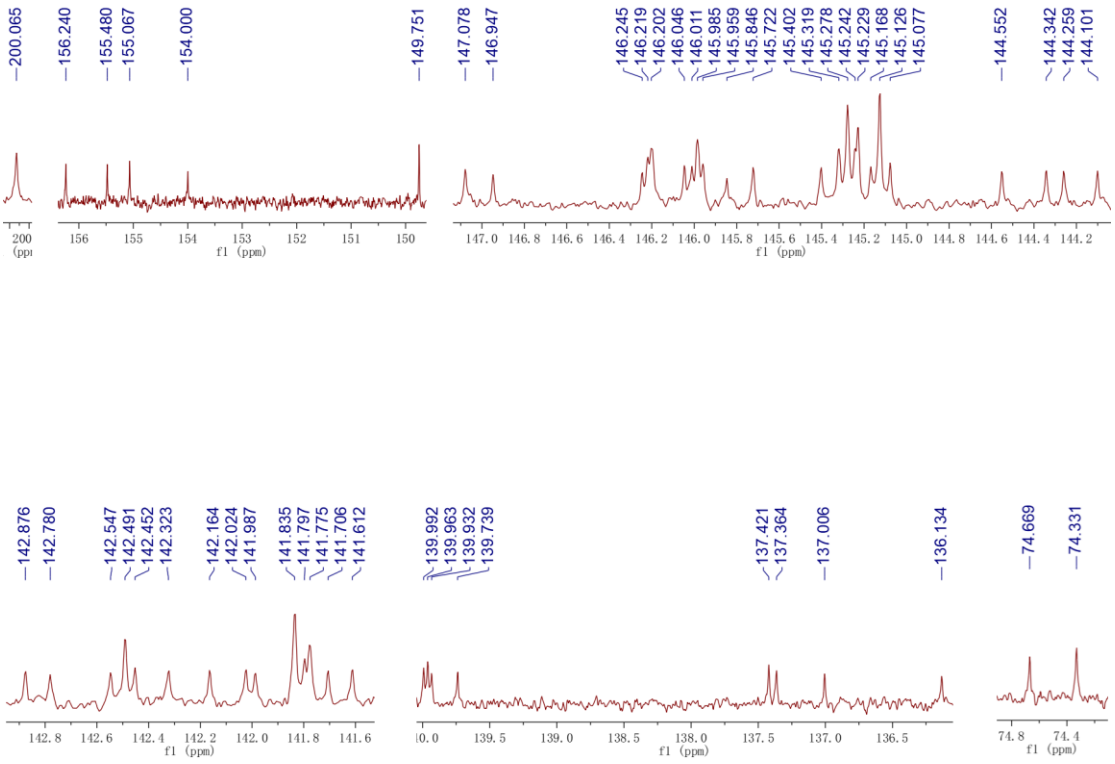


Figure S10. Expanded ^{13}C NMR (100.6 MHz, 2/1 $CS_2/CDCl_3$) of compound **2b**

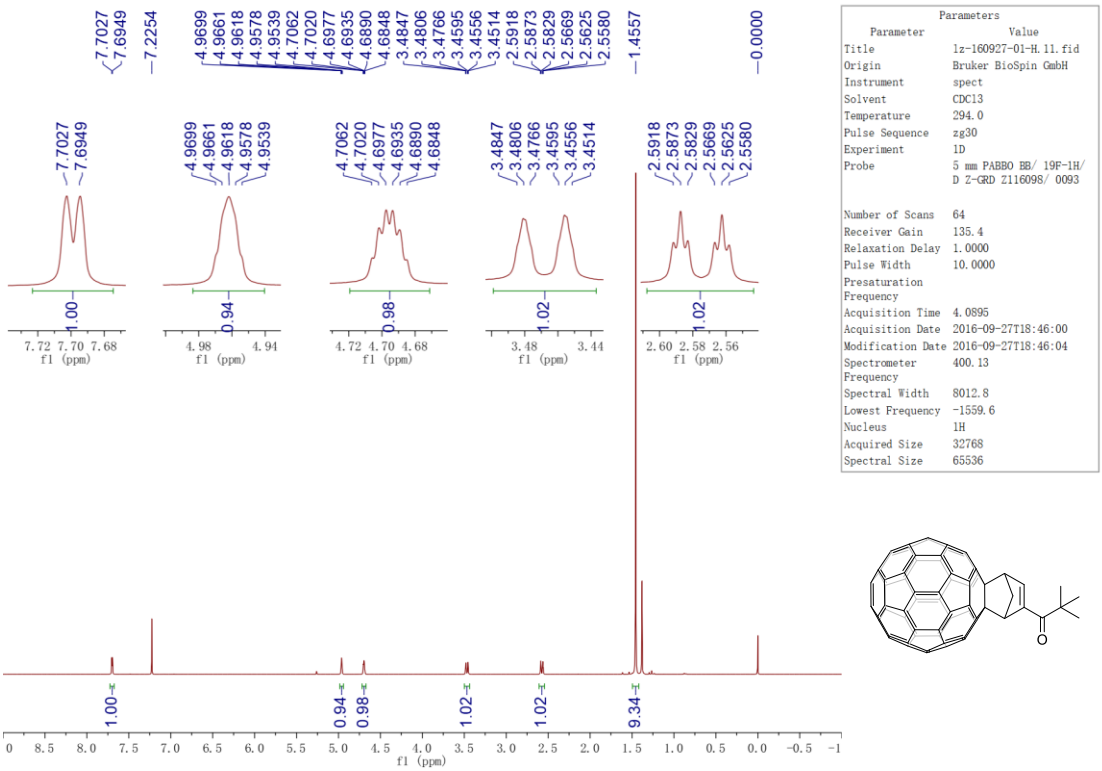


Figure S11. ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **2c**

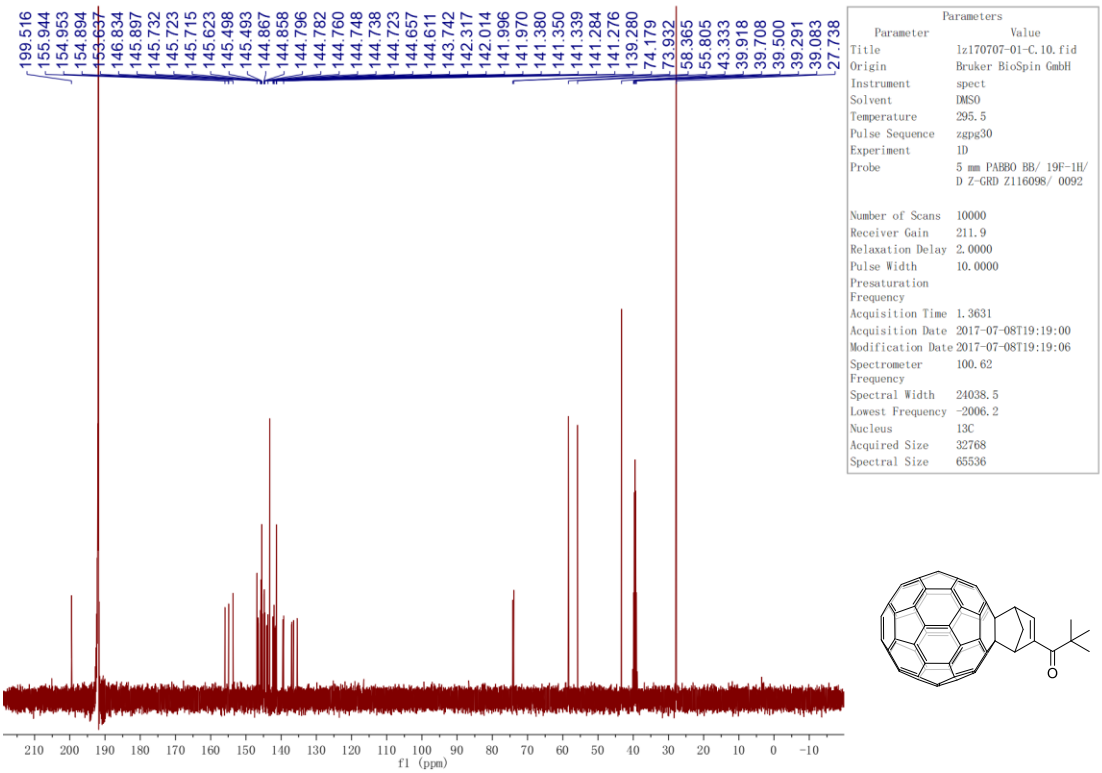


Figure S12. ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2c**

Figure S13. Expanded ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2c**

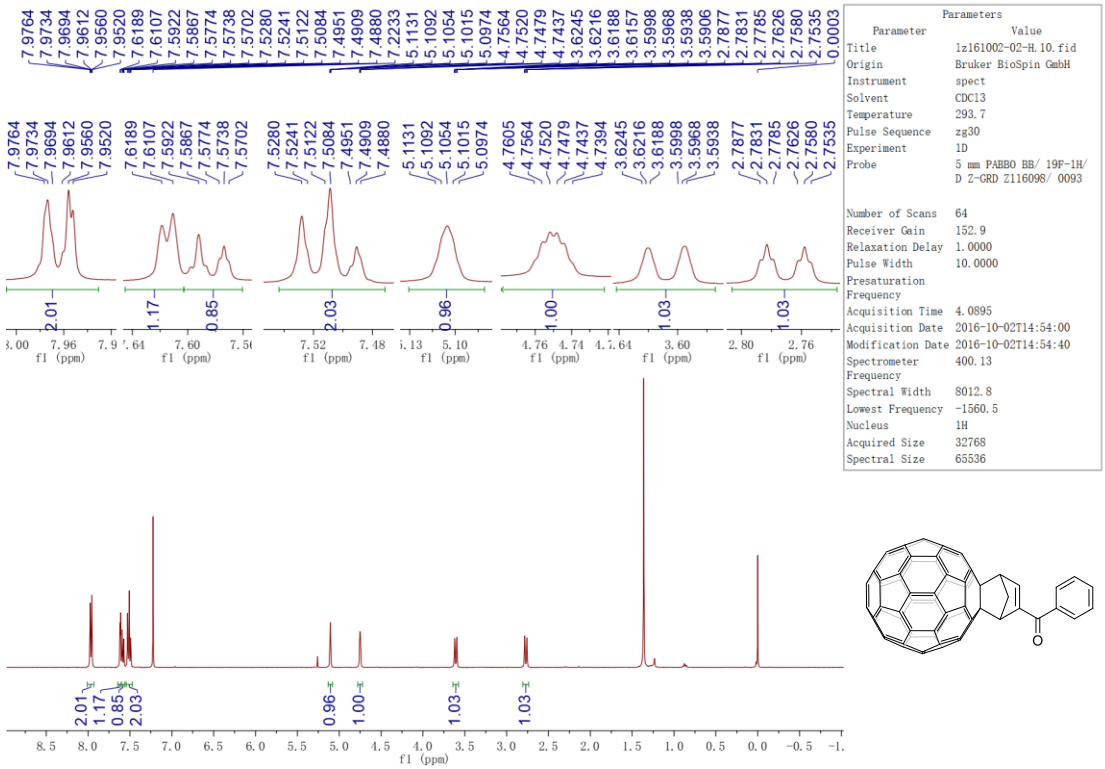


Figure S14. ^1H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **2d**

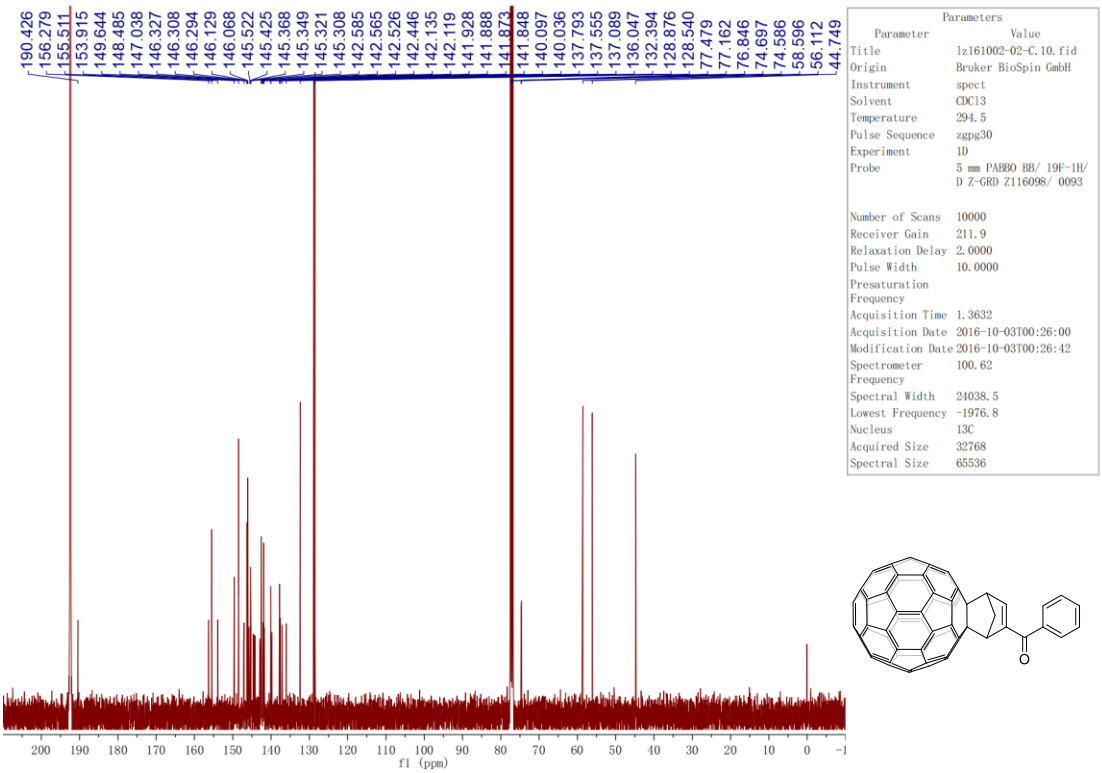


Figure S15. ^{13}C NMR (100.6 MHz, 2/1 CS_2/$CDCl_3$) of compound **2d**

Figure S16. Expanded ^{13}C NMR (100.6 MHz, 2/1 CS_2/$CDCl_3$) of compound **2d**

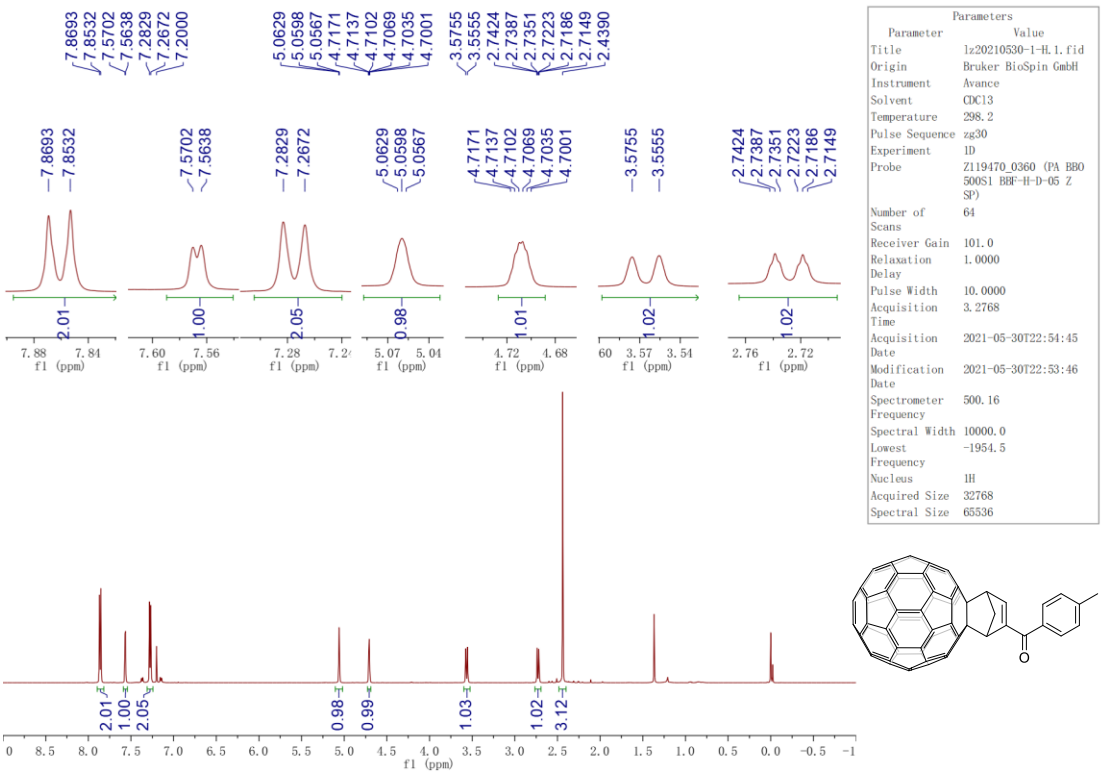


Figure S17. ^{1}H NMR (500 MHz, 2/1 CS_2/$CDCl_3$) of compound **2e**

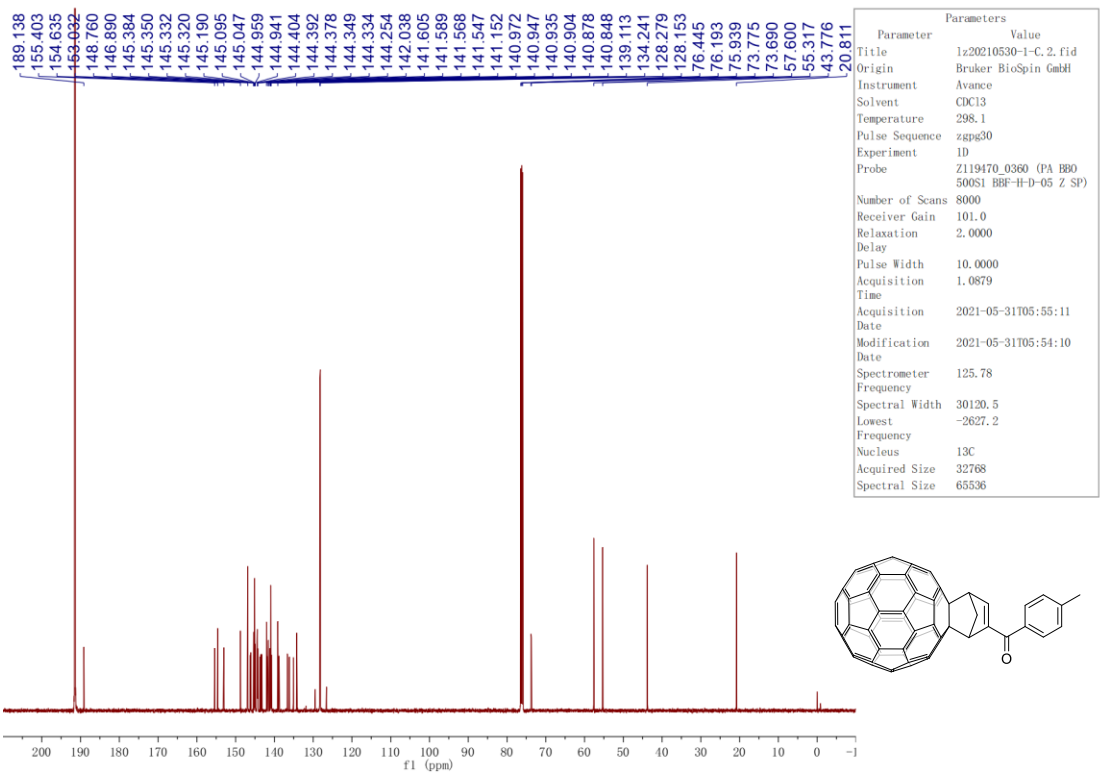


Figure S18. ^{13}C NMR (125.8 MHz, 2/1 CS_2/$CDCl_3$) of compound **2e**

Figure S19. Expanded ^{13}C NMR (125.8 MHz, 2/1 $CS_2/CDCl_3$) of compound **2e**

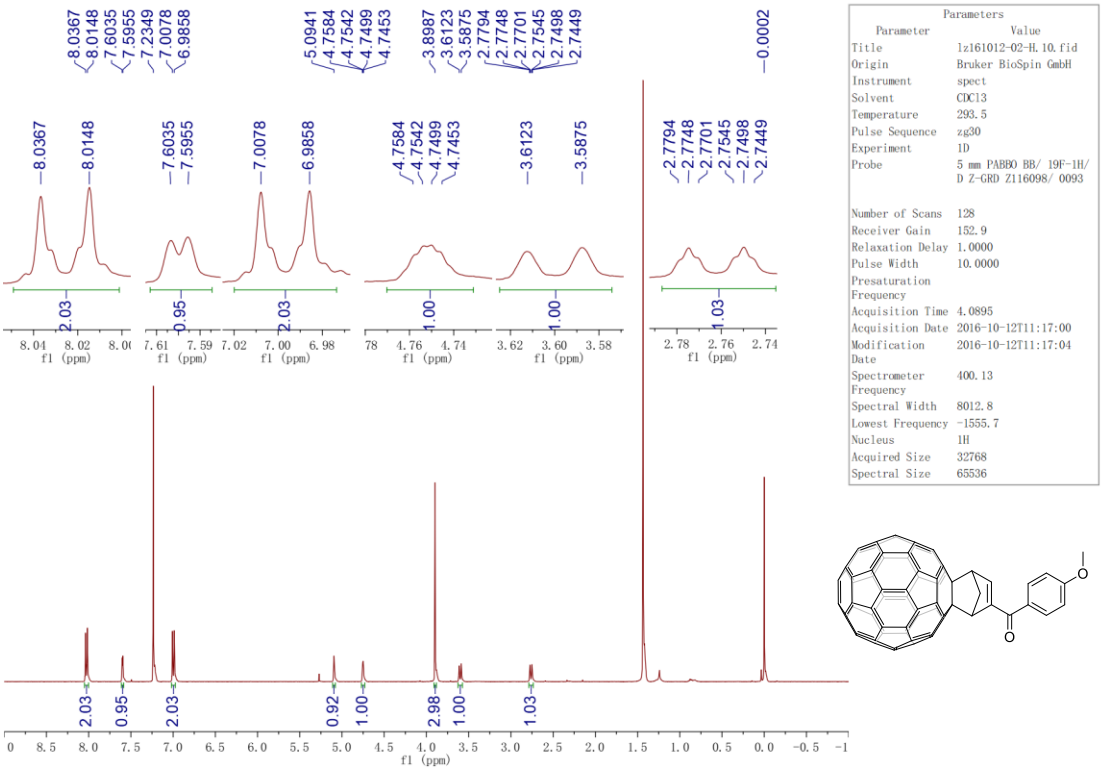


Figure S20 ^{1}H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) of compound **2f**

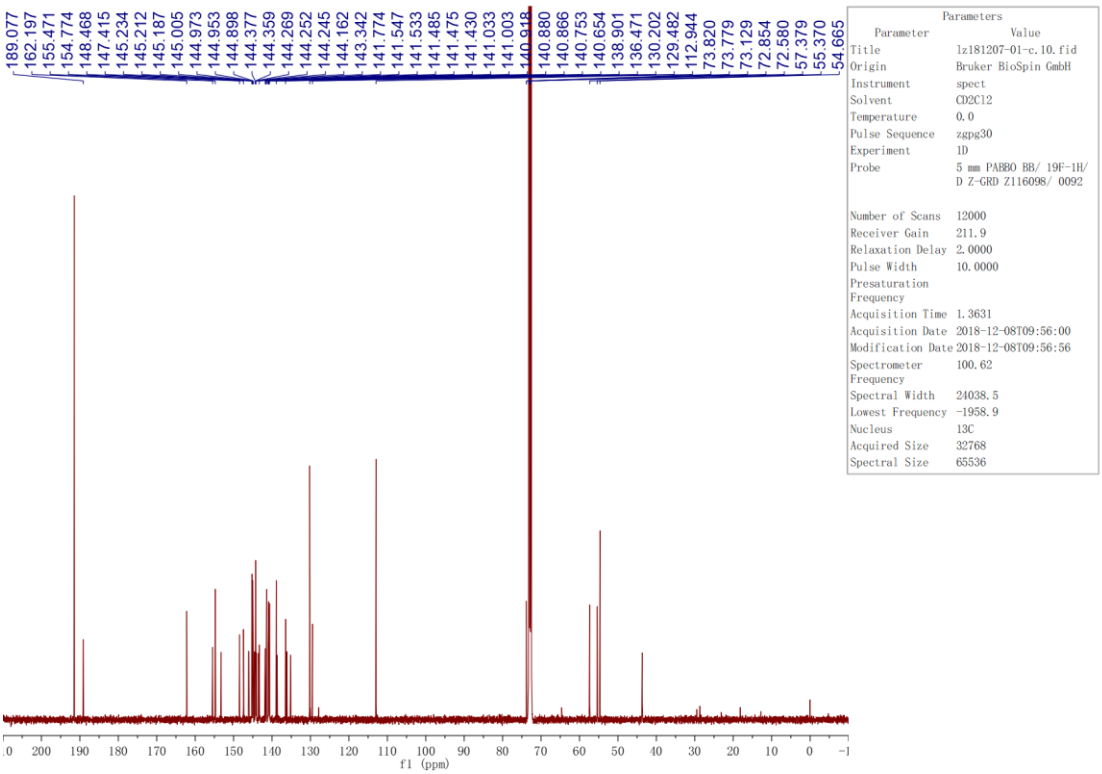


Figure S21. ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2f**

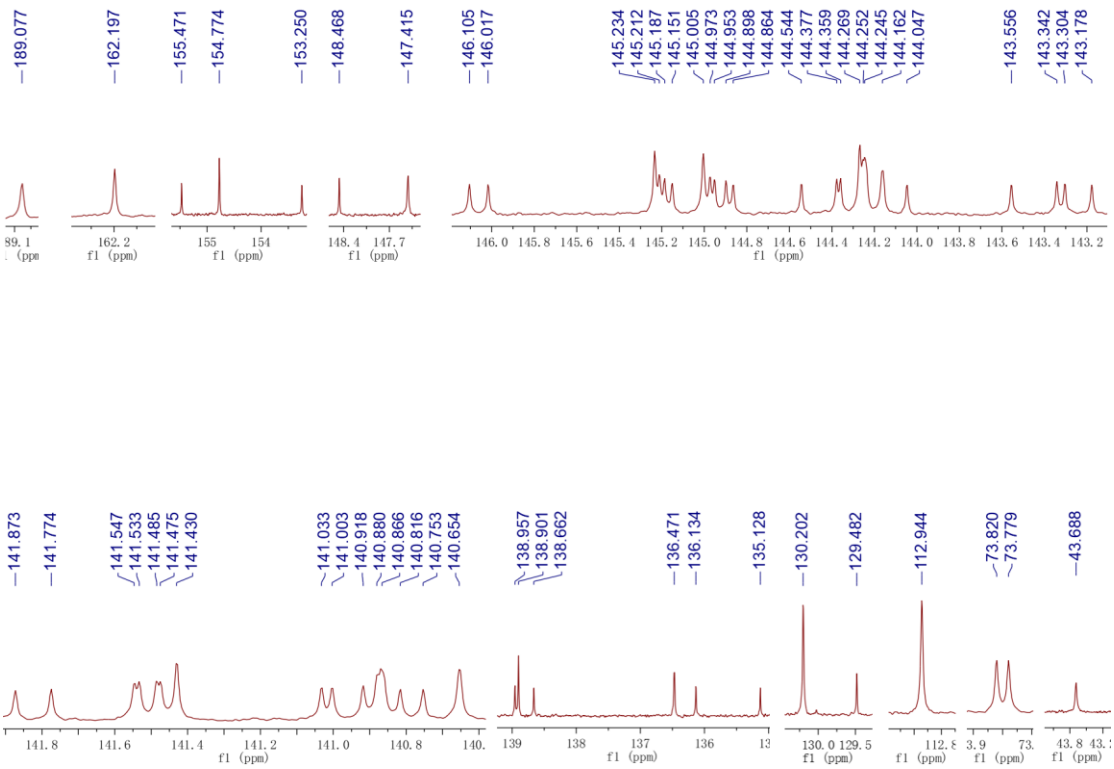


Figure S22. Expanded ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2f**

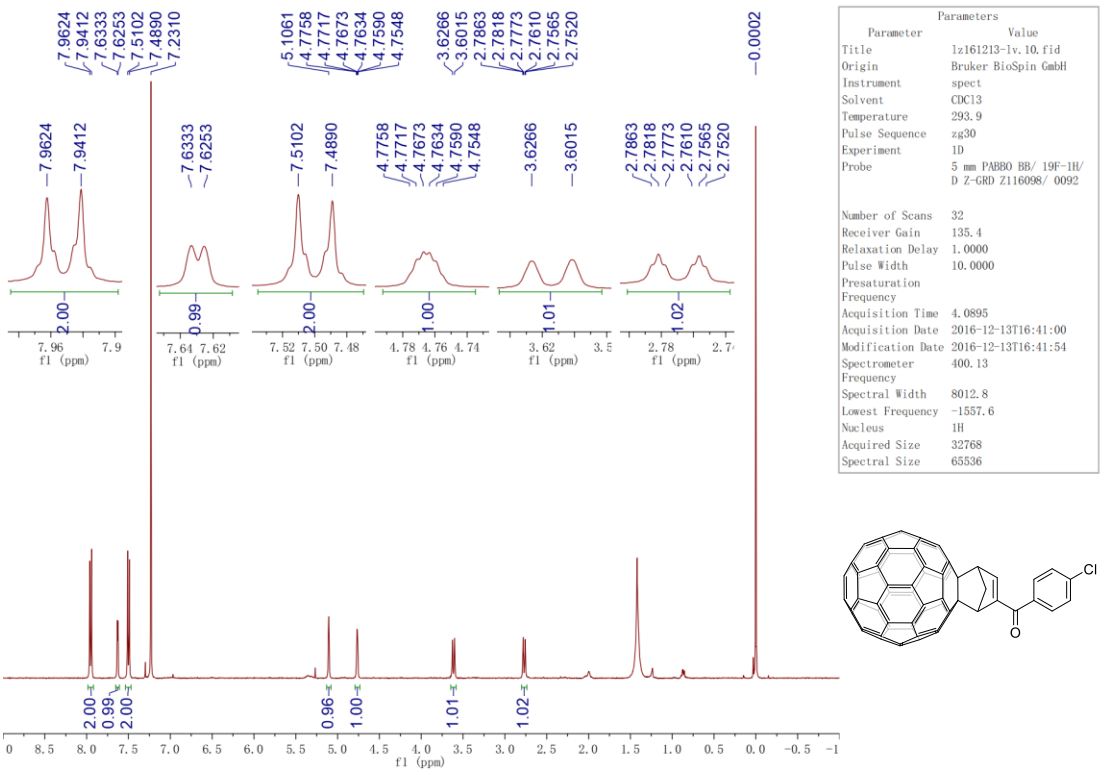


Figure S23. ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **2g**

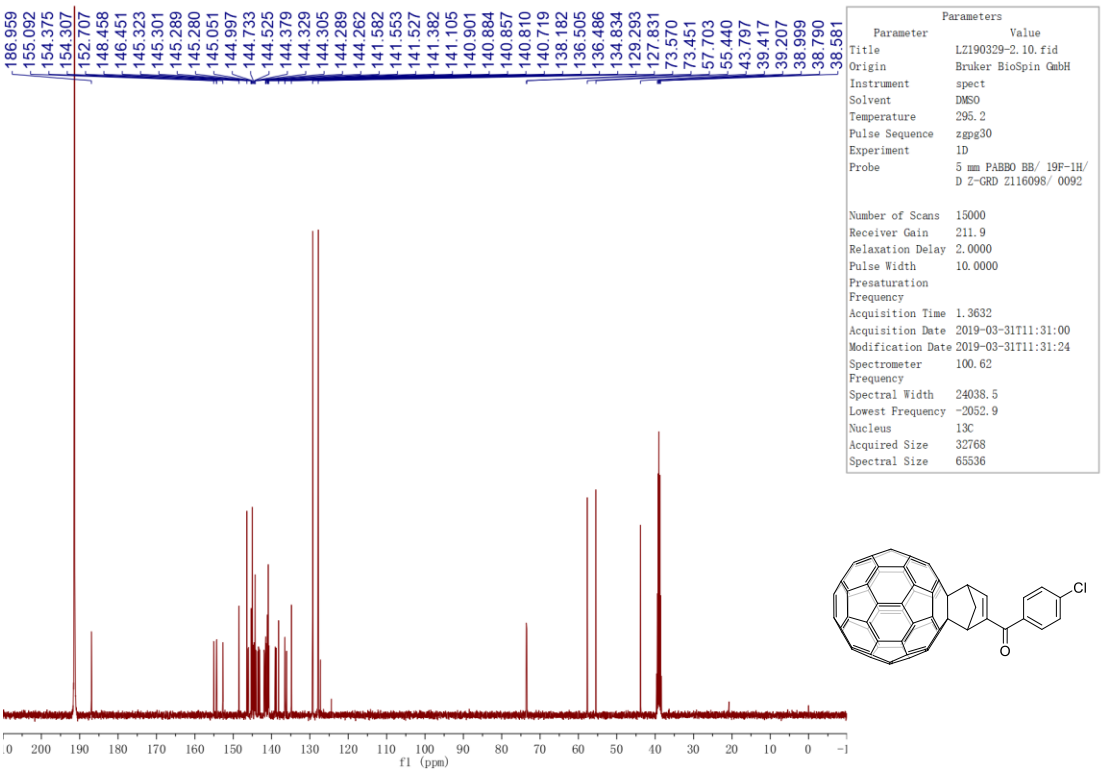


Figure S24. ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2g**

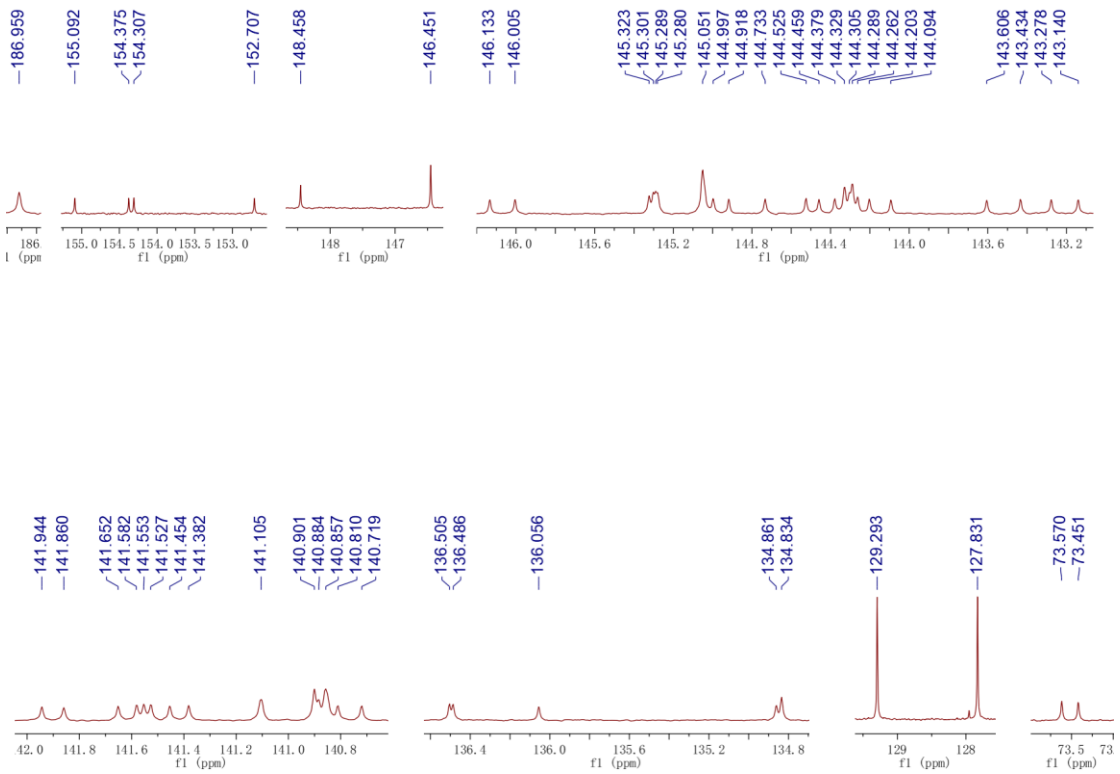


Figure S25. Expanded ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2g**

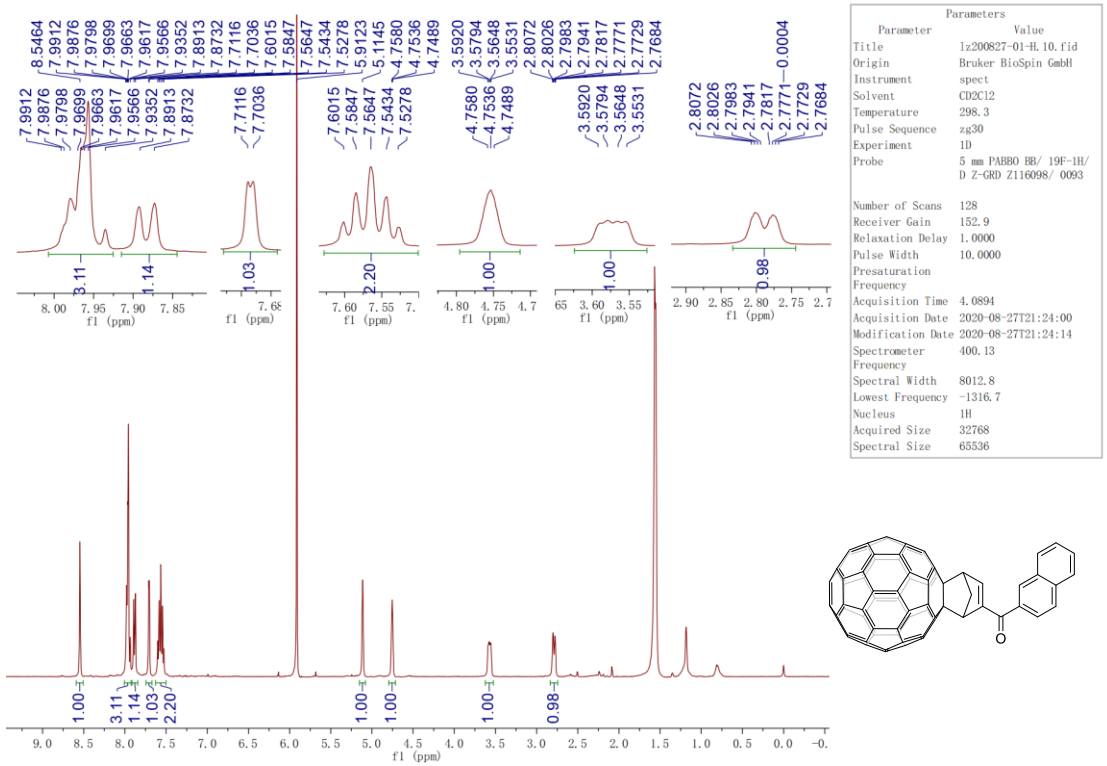


Figure S26. ^{1}H NMR (400 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2h**

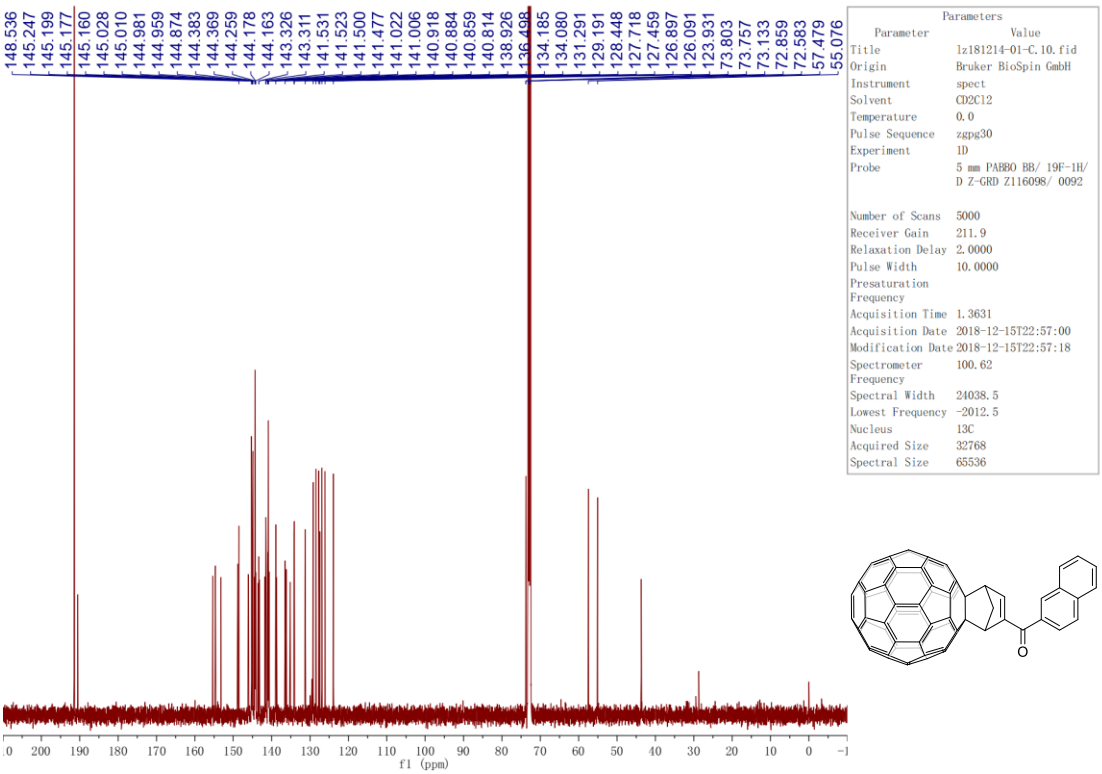
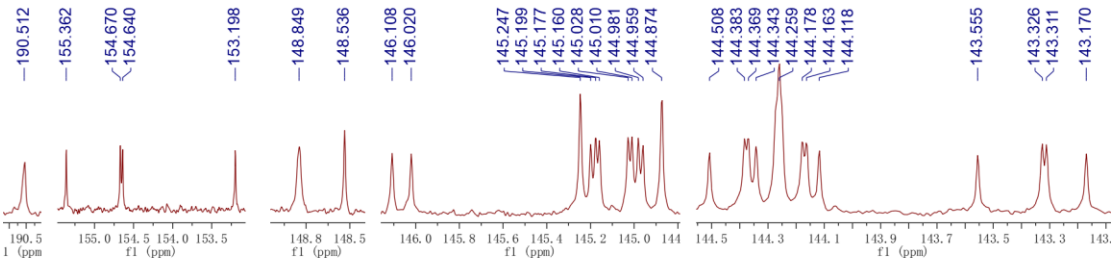


Figure S27. ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2h**



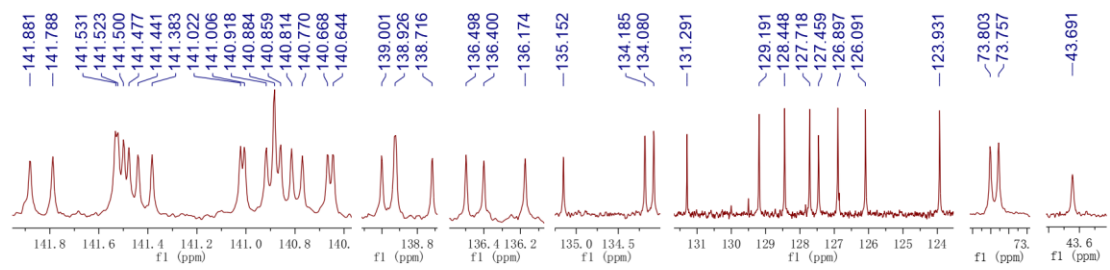


Figure S28. Expanded ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2h**

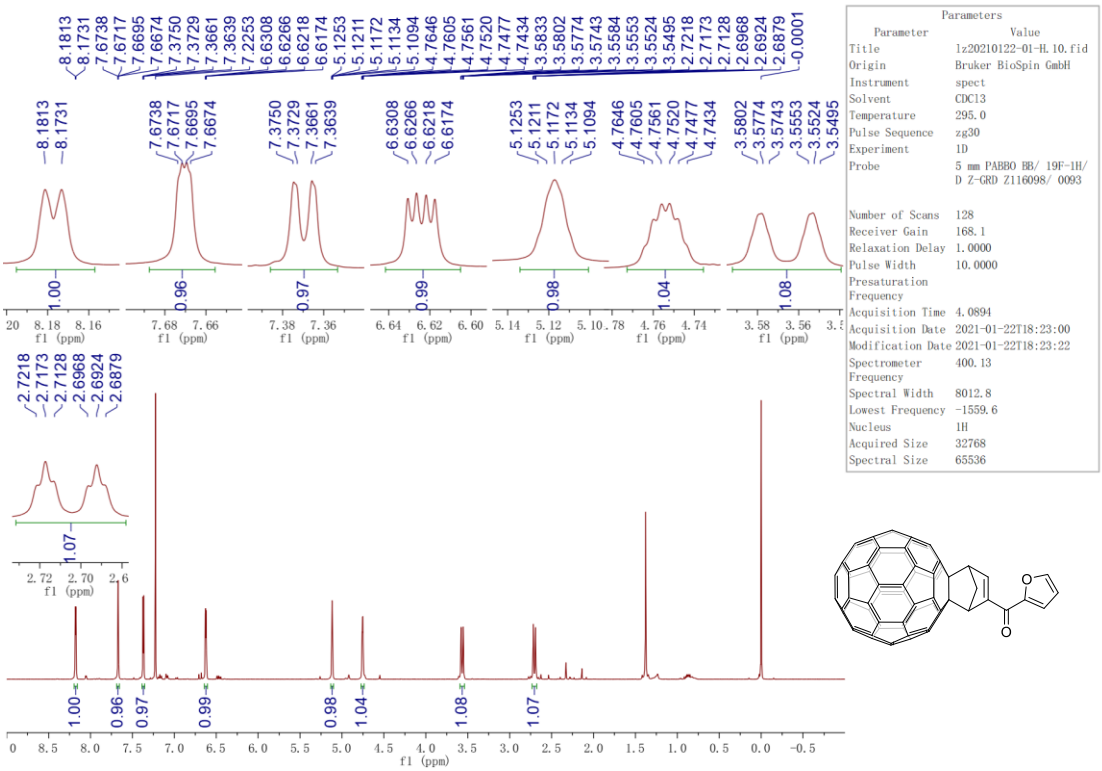


Figure S29. ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **2i**

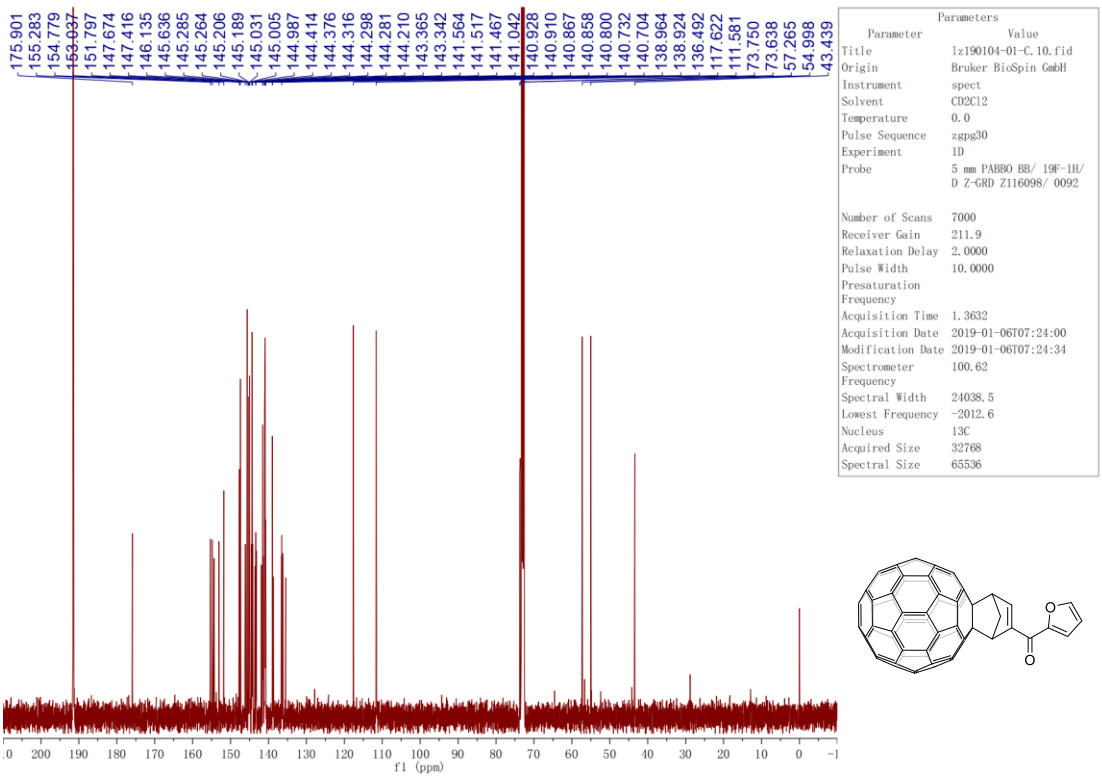


Figure S30. ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4$/CS_2) of compound **2i**

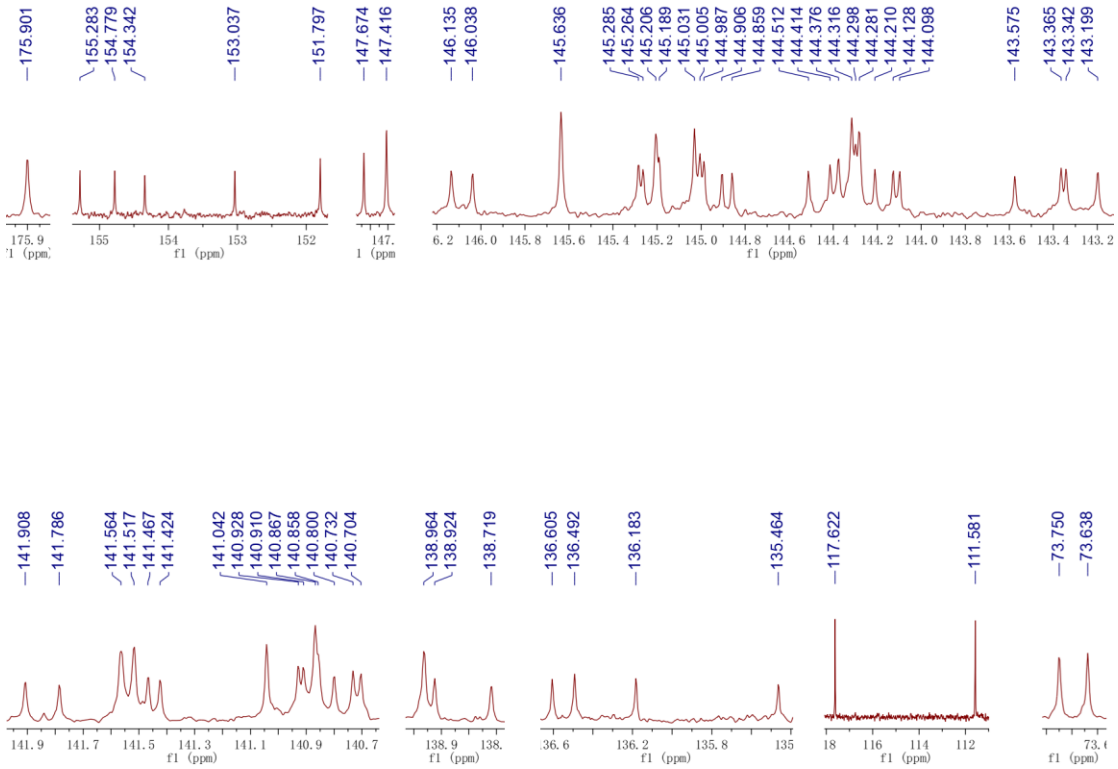


Figure S31. Expanded ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2i**

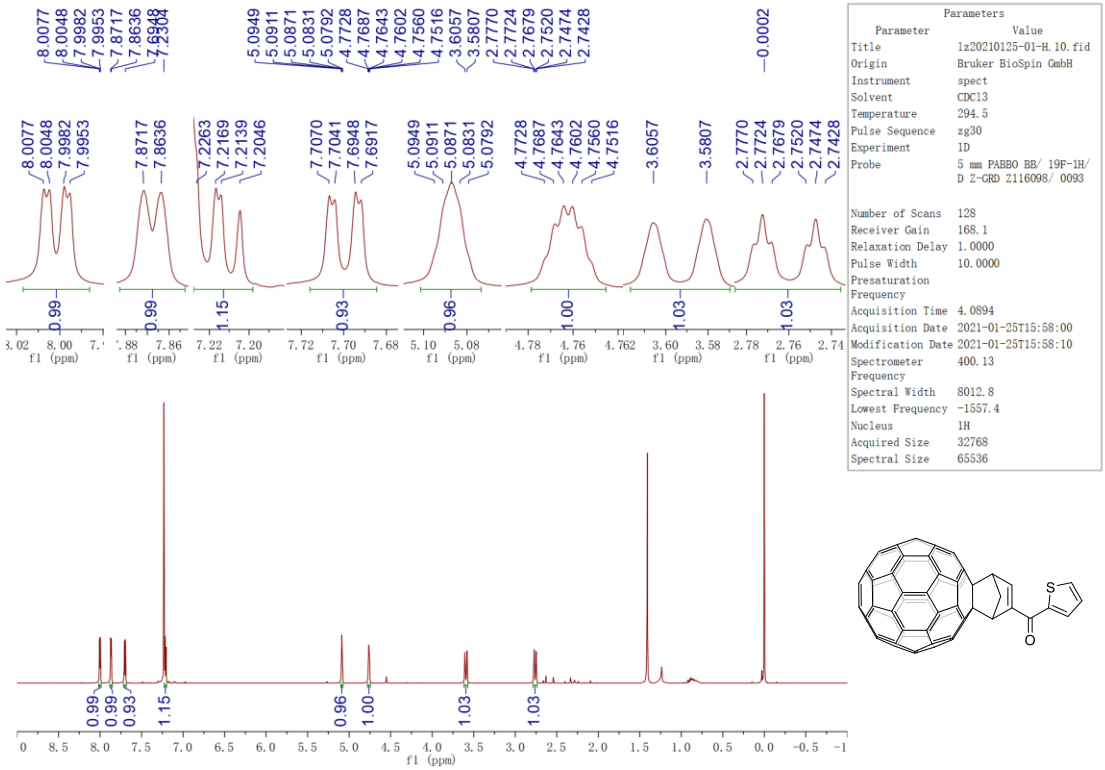


Figure S32. ^{1}H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) of compound **2j**

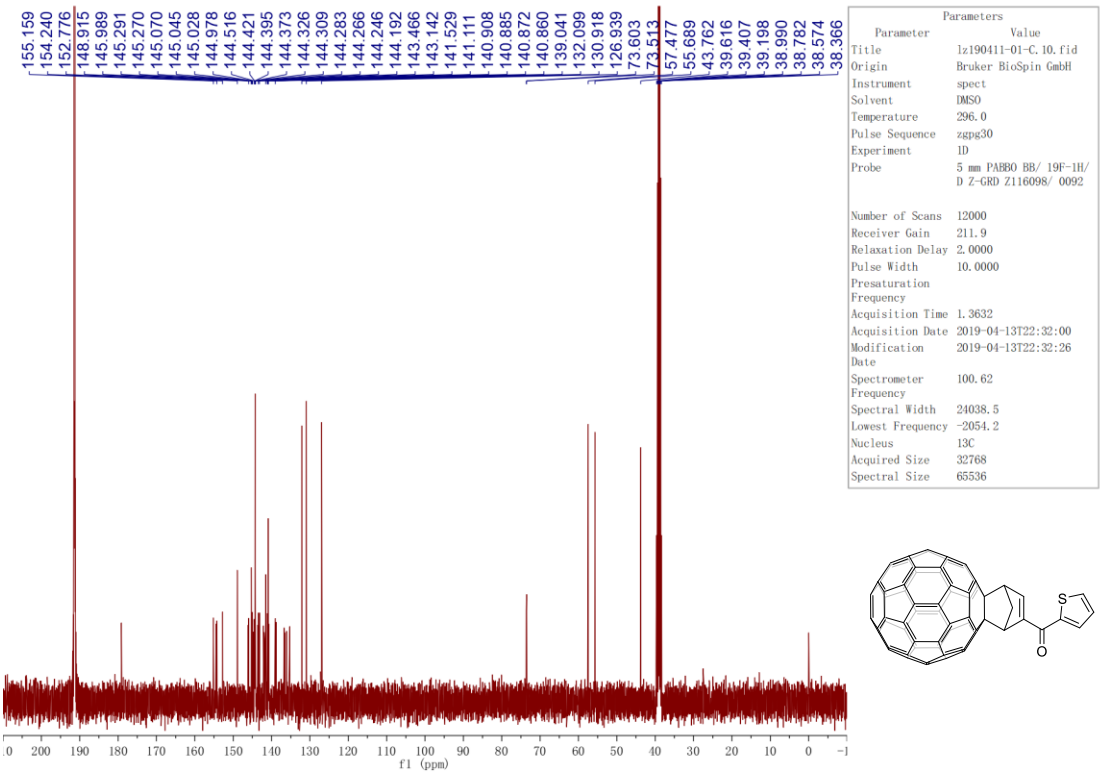


Figure S33. ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2j**

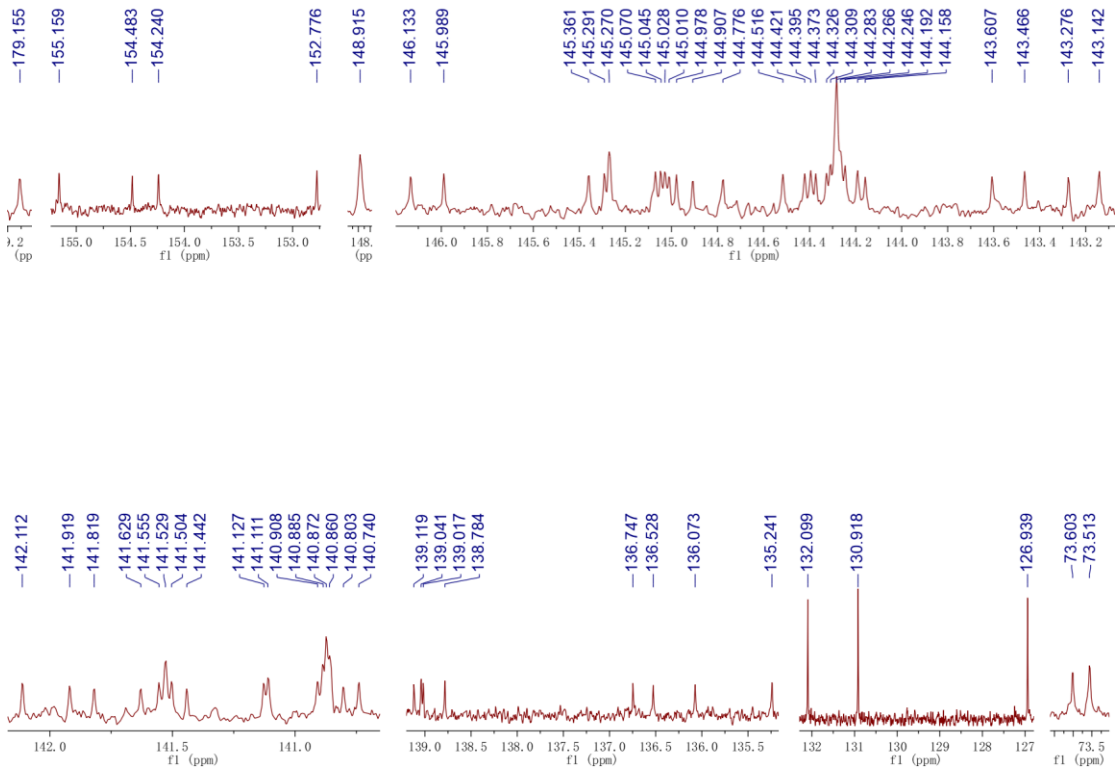


Figure S34. Expanded ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2j**

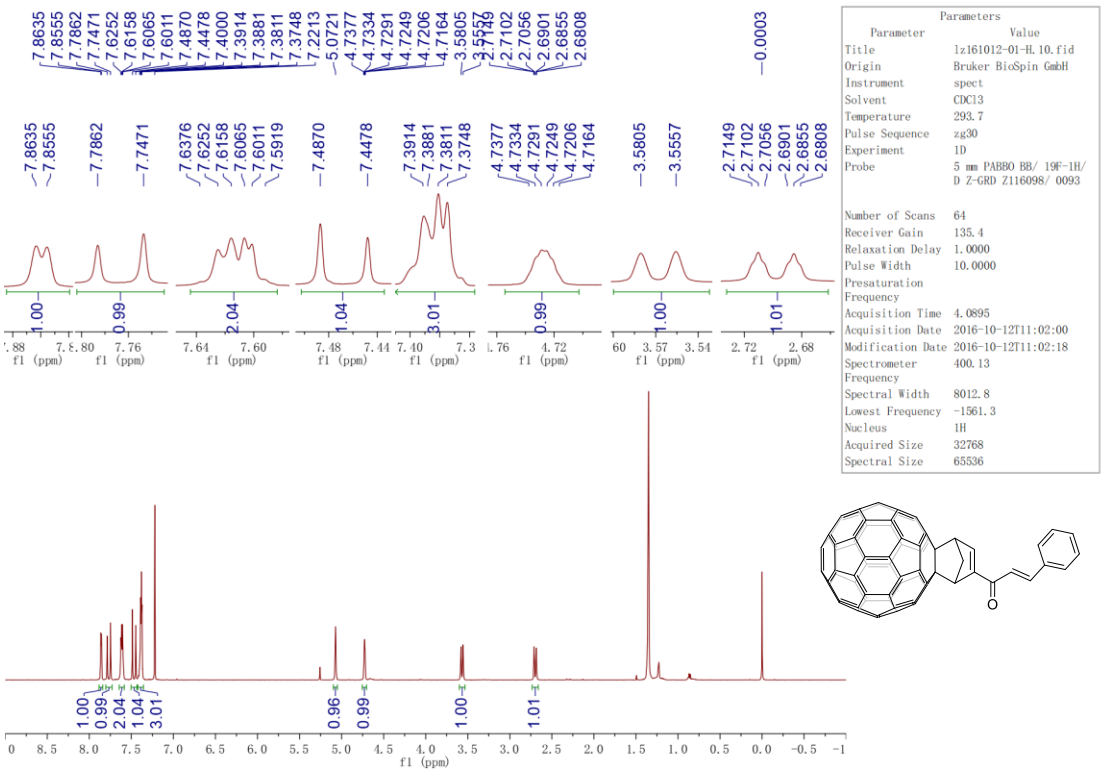


Figure S35. ^{1}H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) of compound **2k**

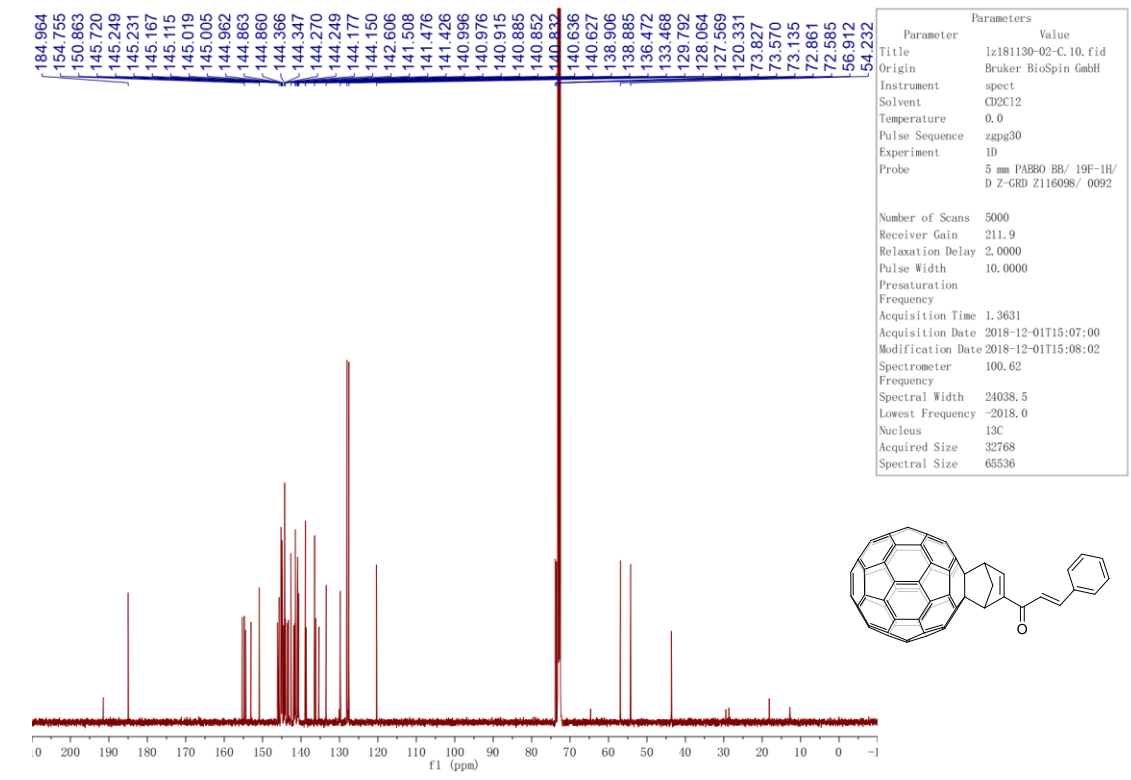


Figure S36. ^{13}C NMR (100.6 MHz, $C_2D_2Cl_4$) of compound **2k**

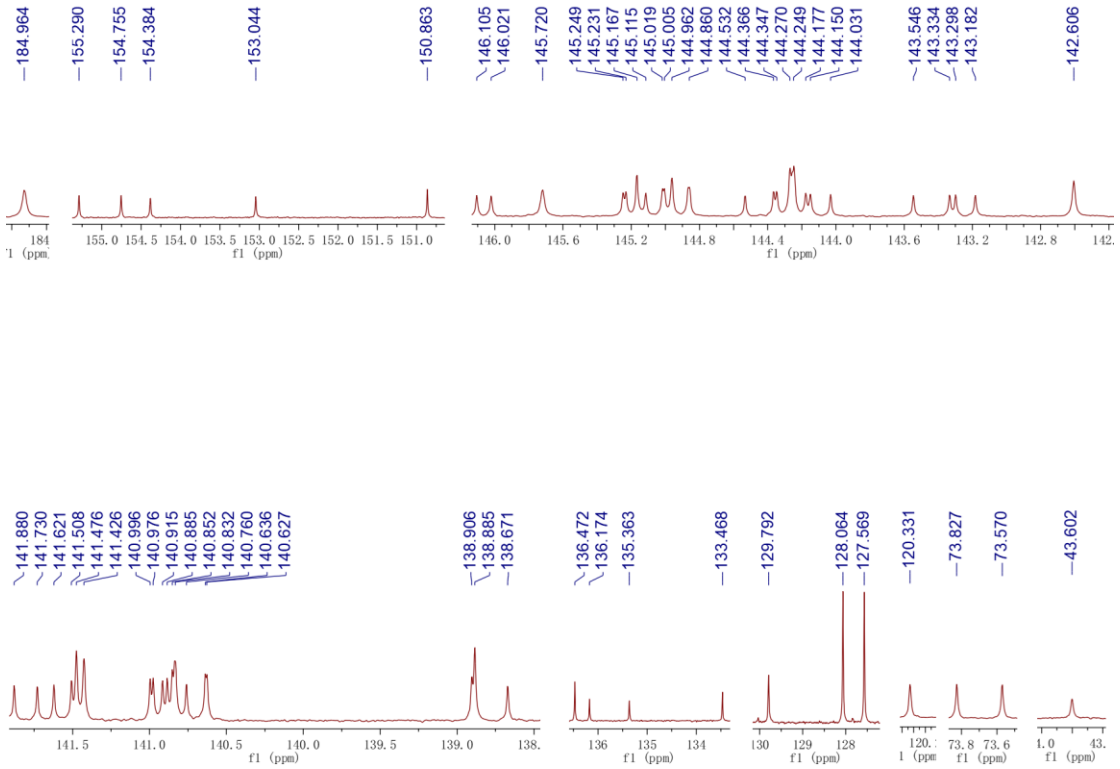


Figure S37. Expanded ^{13}C NMR (100.6 MHz, $C_2D_2Cl_4$) of compound **2k**

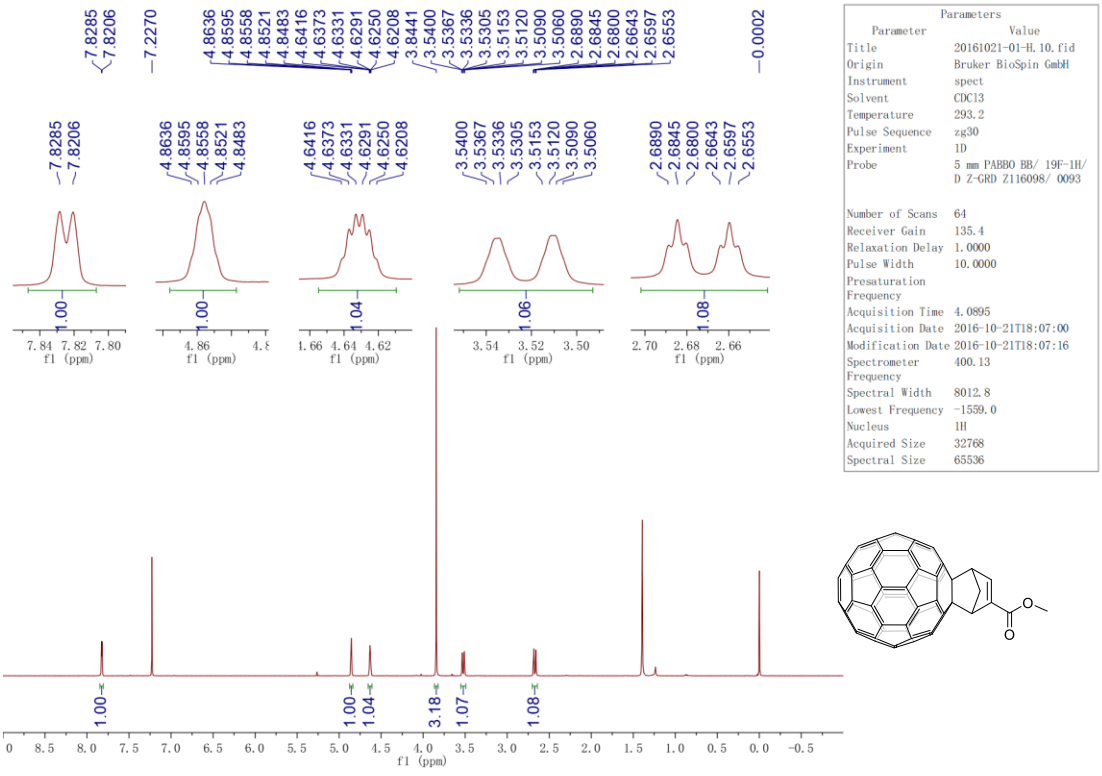


Figure S38. ^1H NMR (400 MHz, 2/1 $CS_2/CDCl_3$) of compound **2l**

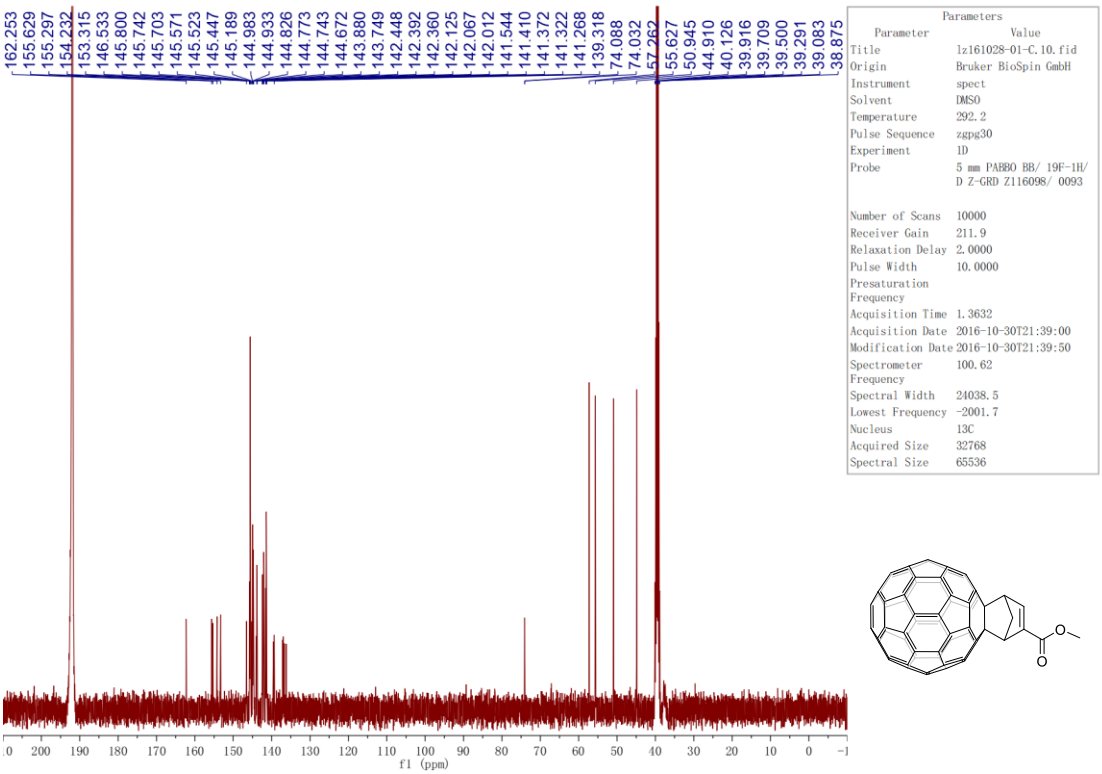


Figure S39. ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2l**

Figure S40. Expanded ^{13}C NMR (100.6 MHz, CS_2/DMSO-d_6) of compound **2l**

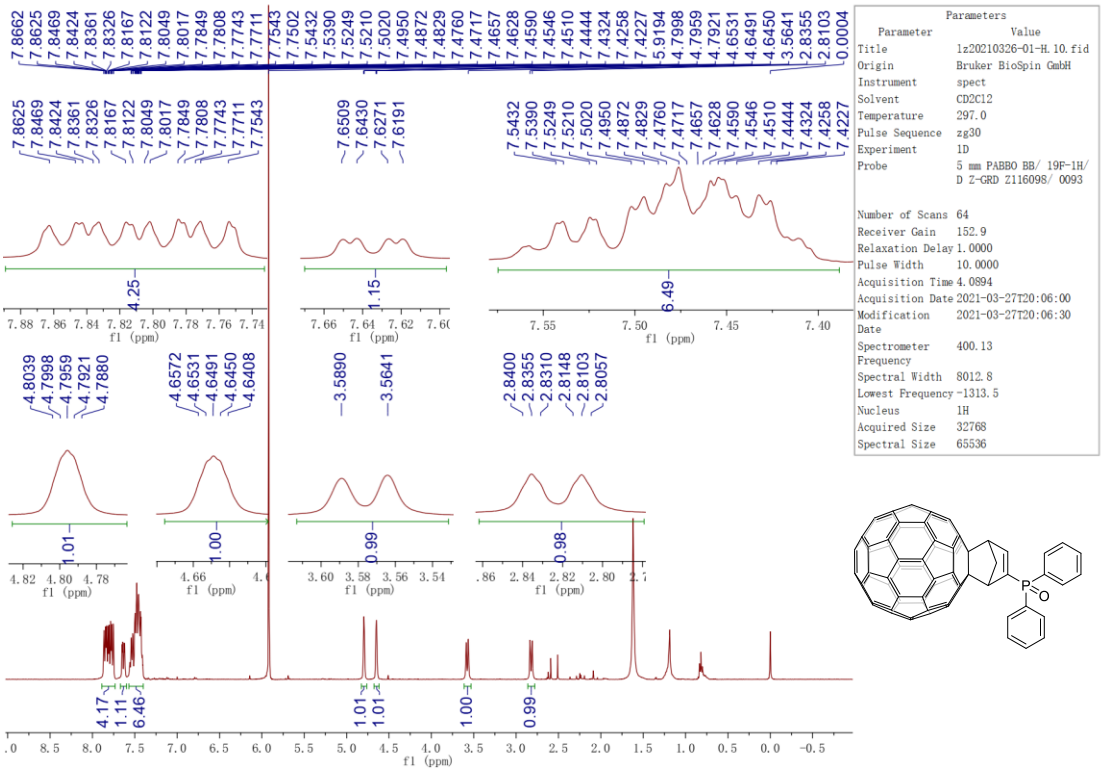


Figure S41. ^{1}H NMR (400 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2m**

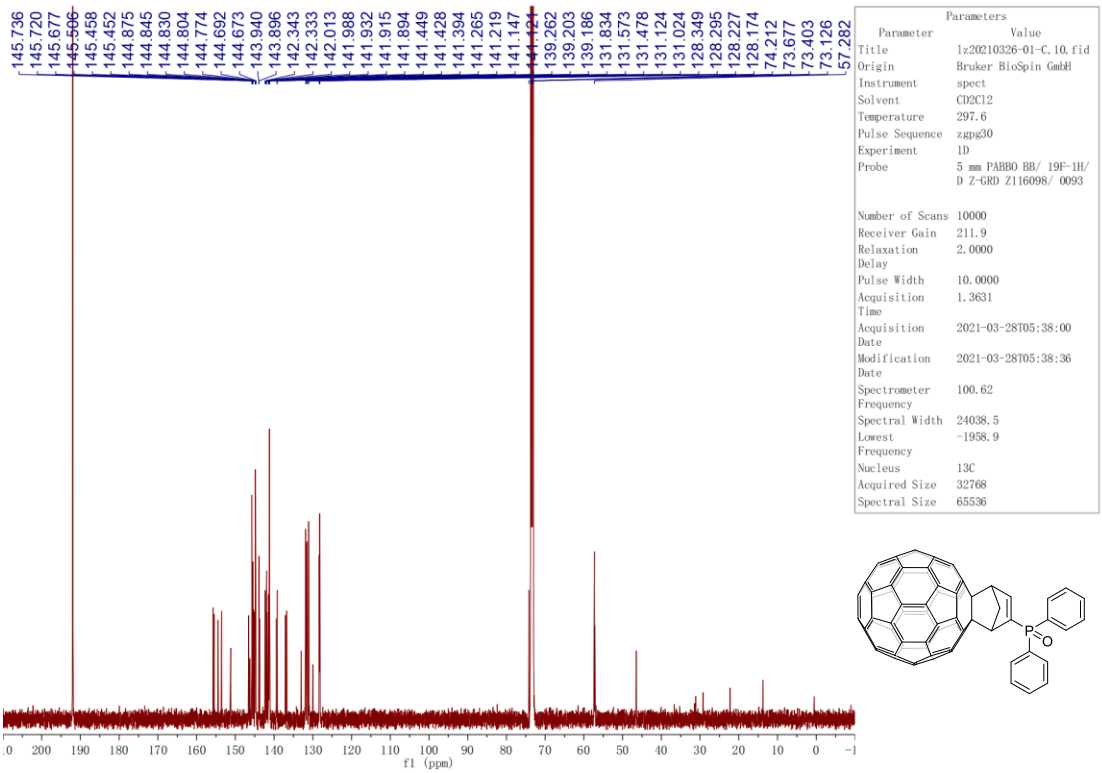


Figure S42. ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2m**

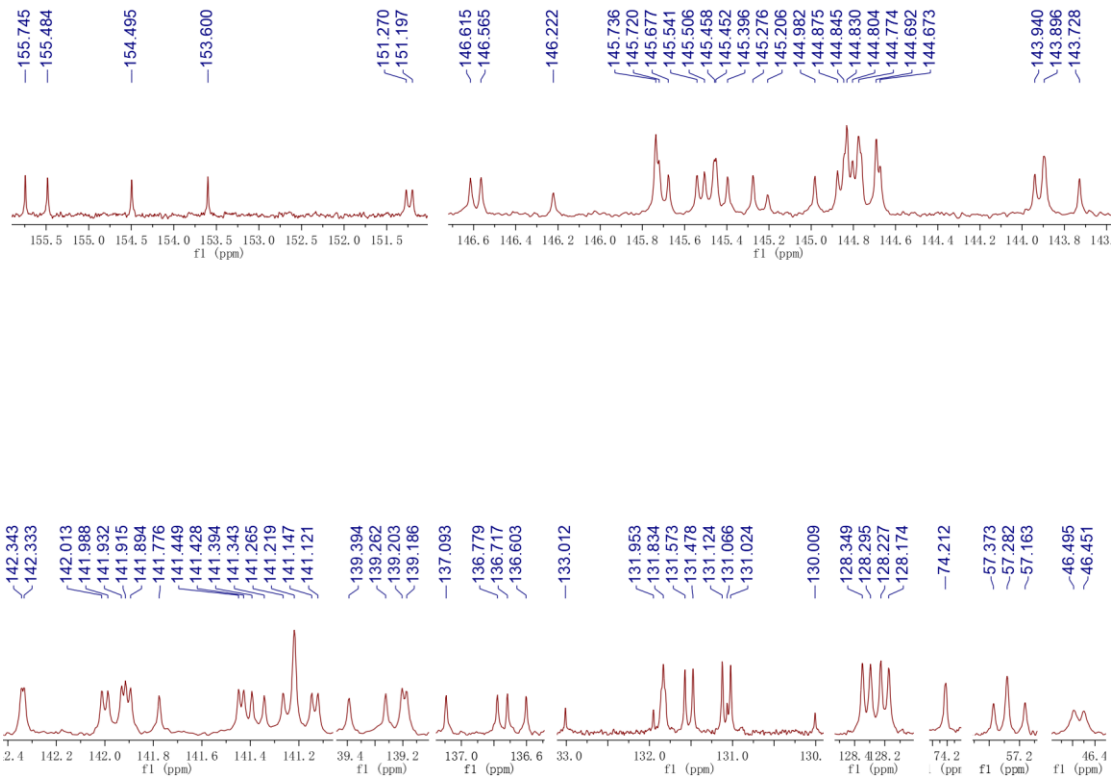


Figure S43. Expanded ^{13}C NMR (100.6 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2m**

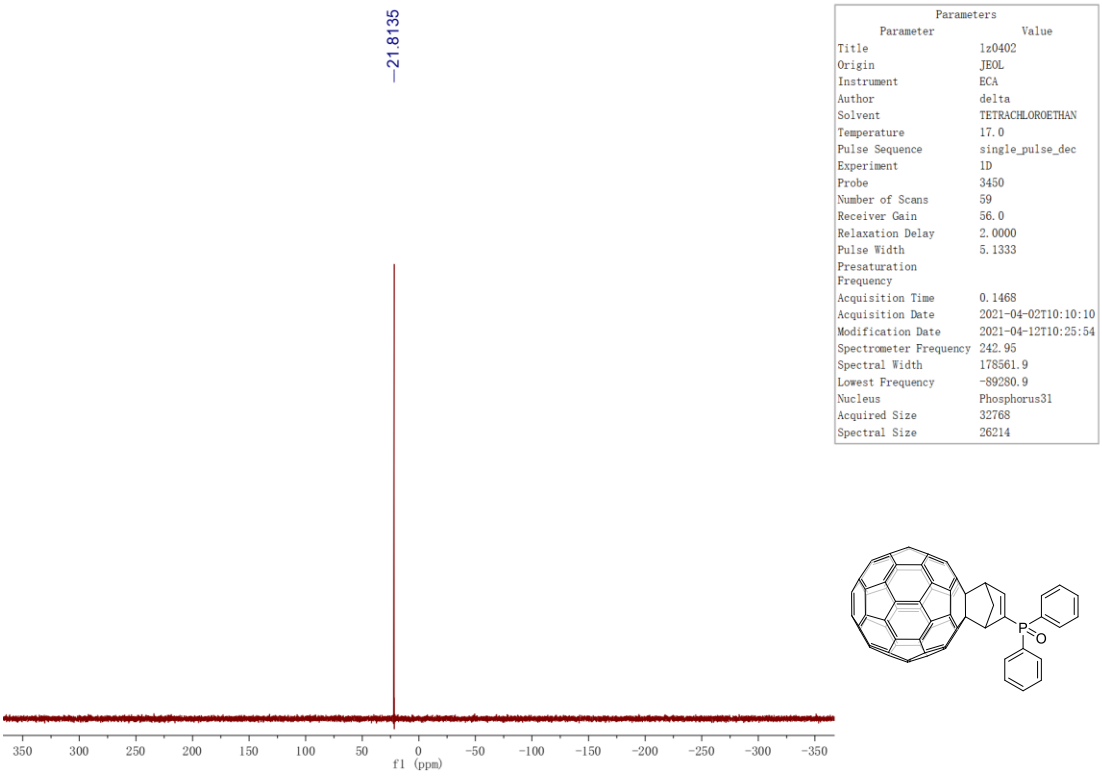


Figure S44. ^{31}P NMR (243.0 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **2m**

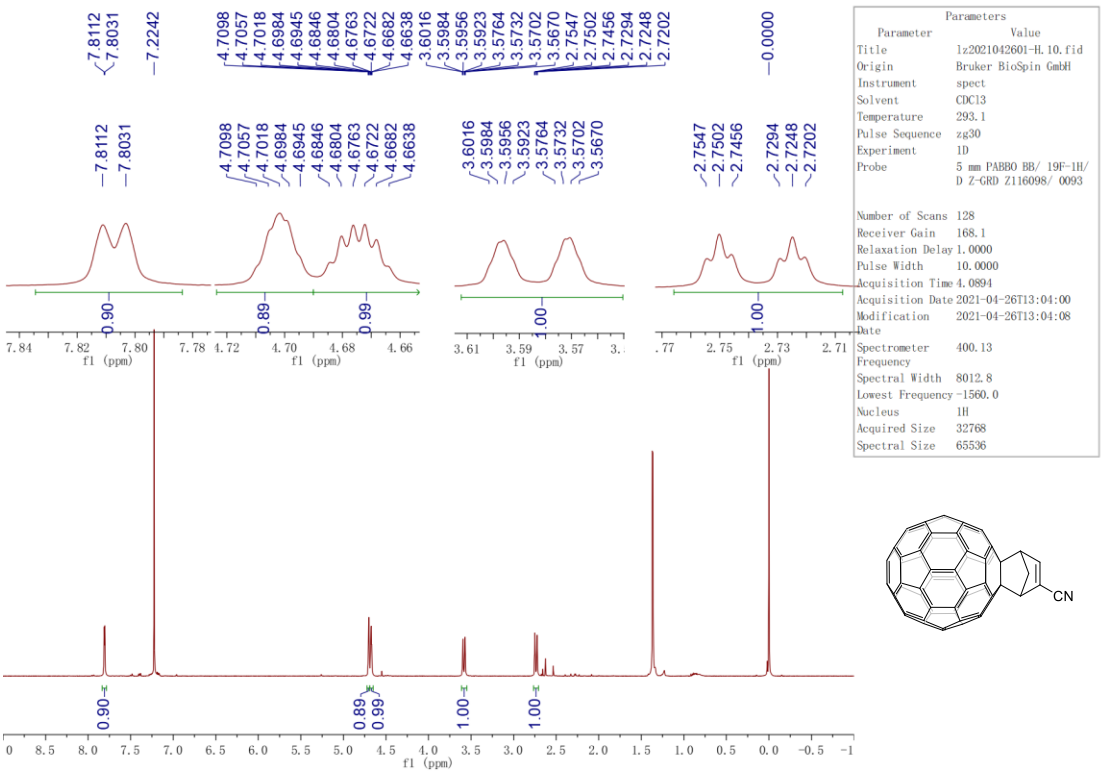


Figure S45. ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **2n**

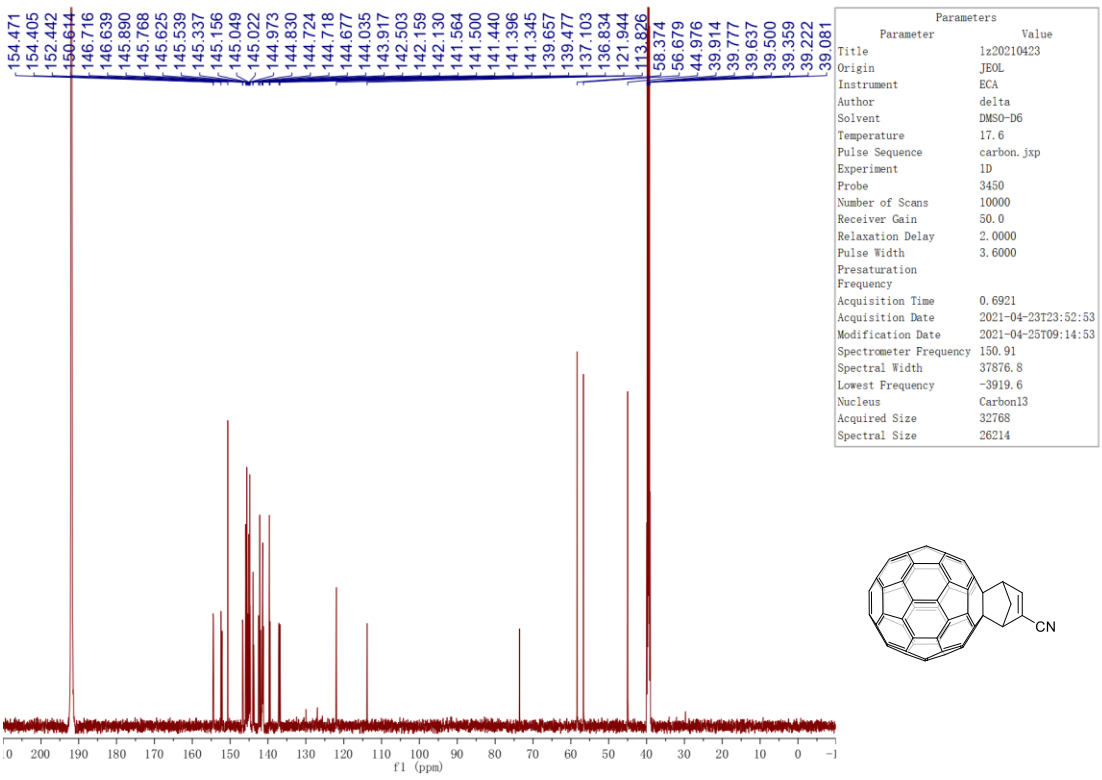


Figure S46. ^{13}C NMR (150.9 MHz, CS_2/DMSO-d_6) of compound **2n**

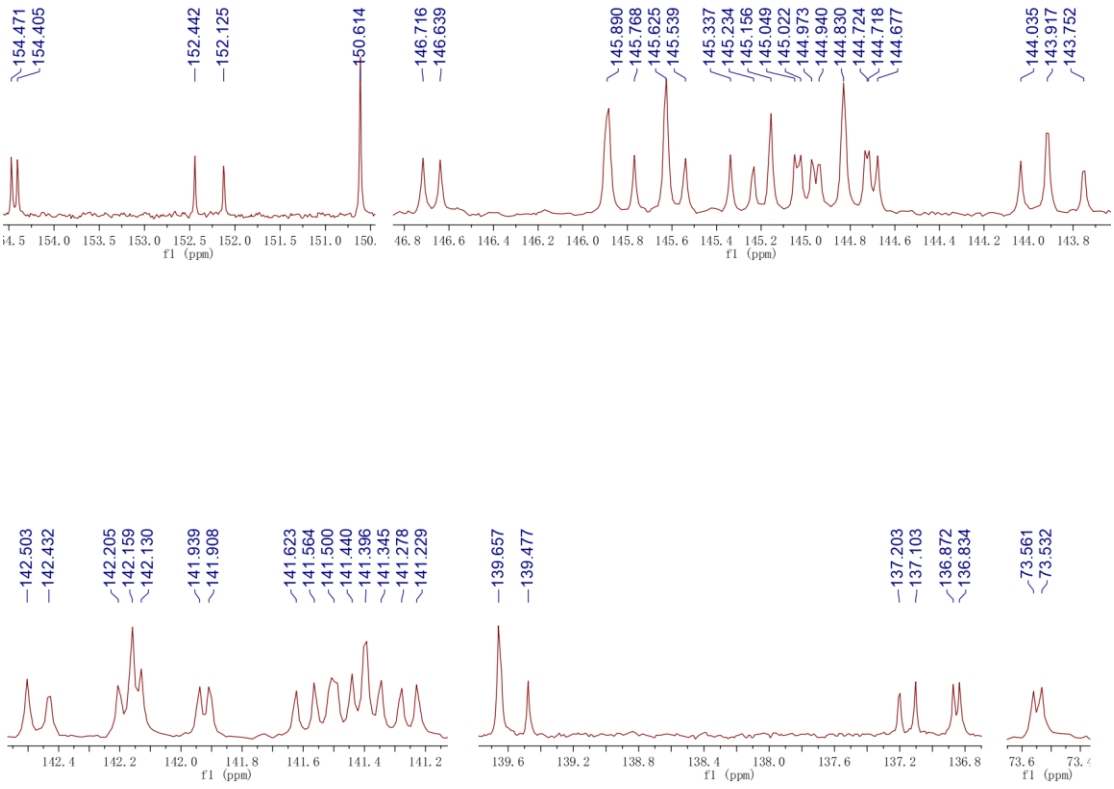


Figure S47. Expanded ^{13}C NMR (150.9 MHz, CS_2/DMSO-d_6) of compound **2n**

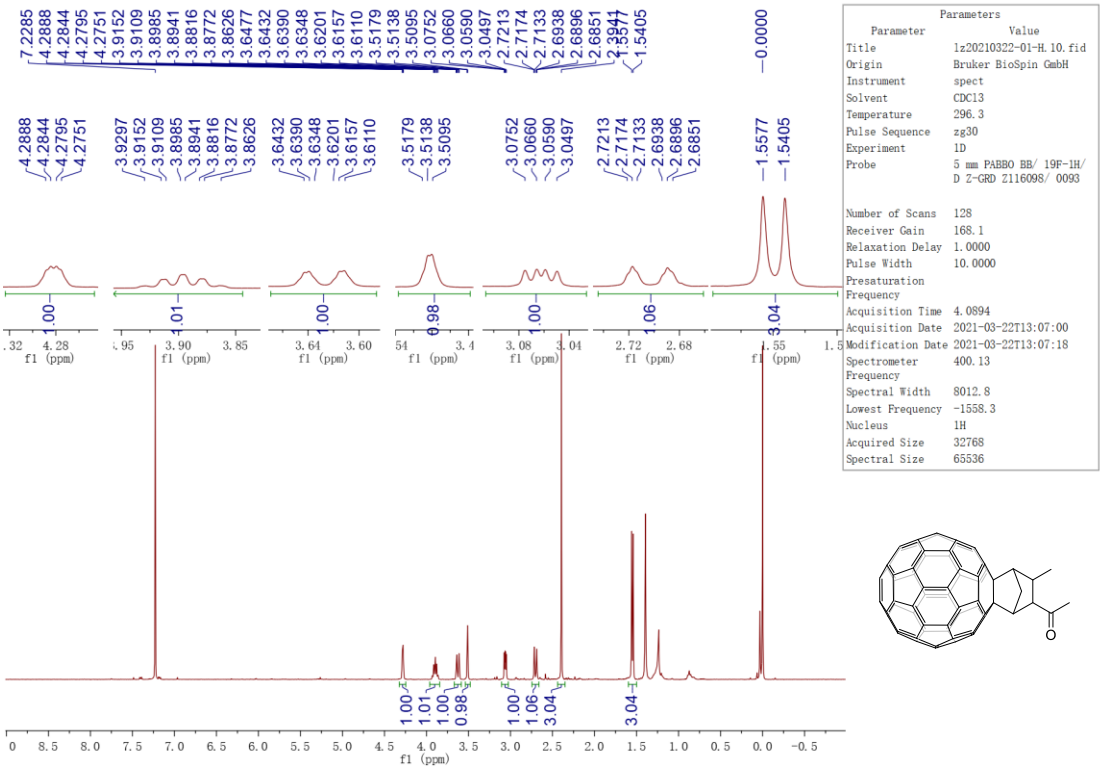


Figure S48. ^{1}H NMR (400 MHz, 2/1 CS_2/$CDCl_3$) of compound **5a**

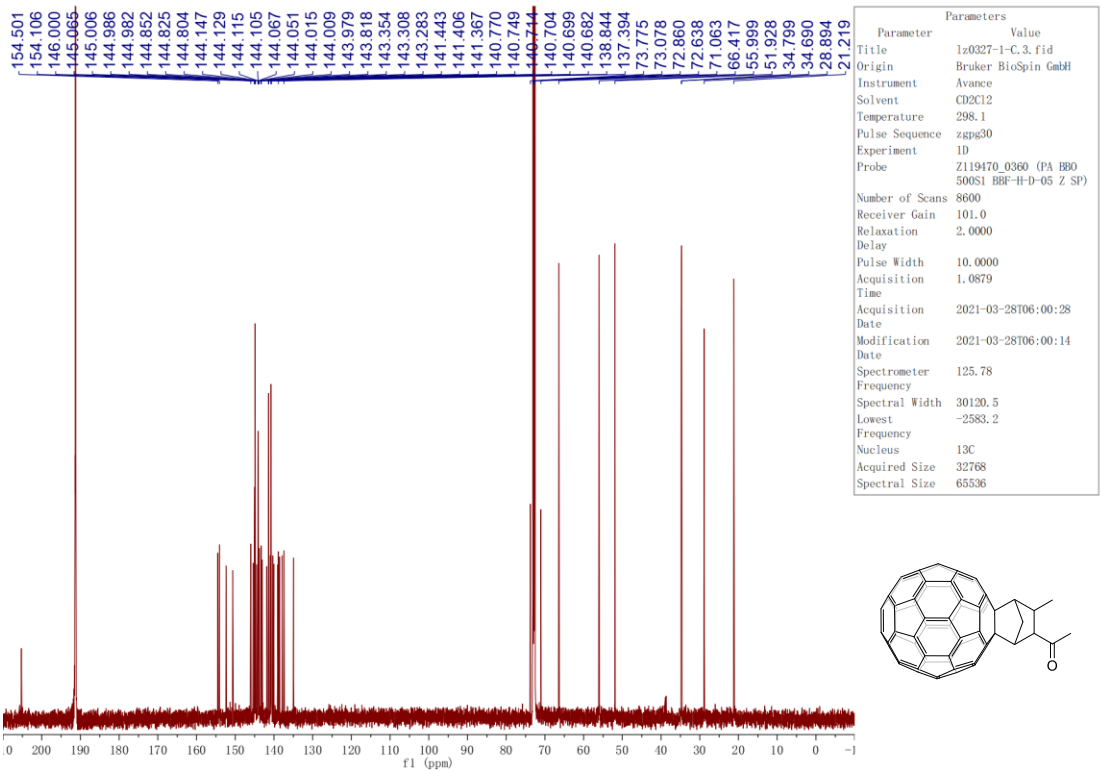


Figure S49. ^{13}C NMR (125.8 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **5a**

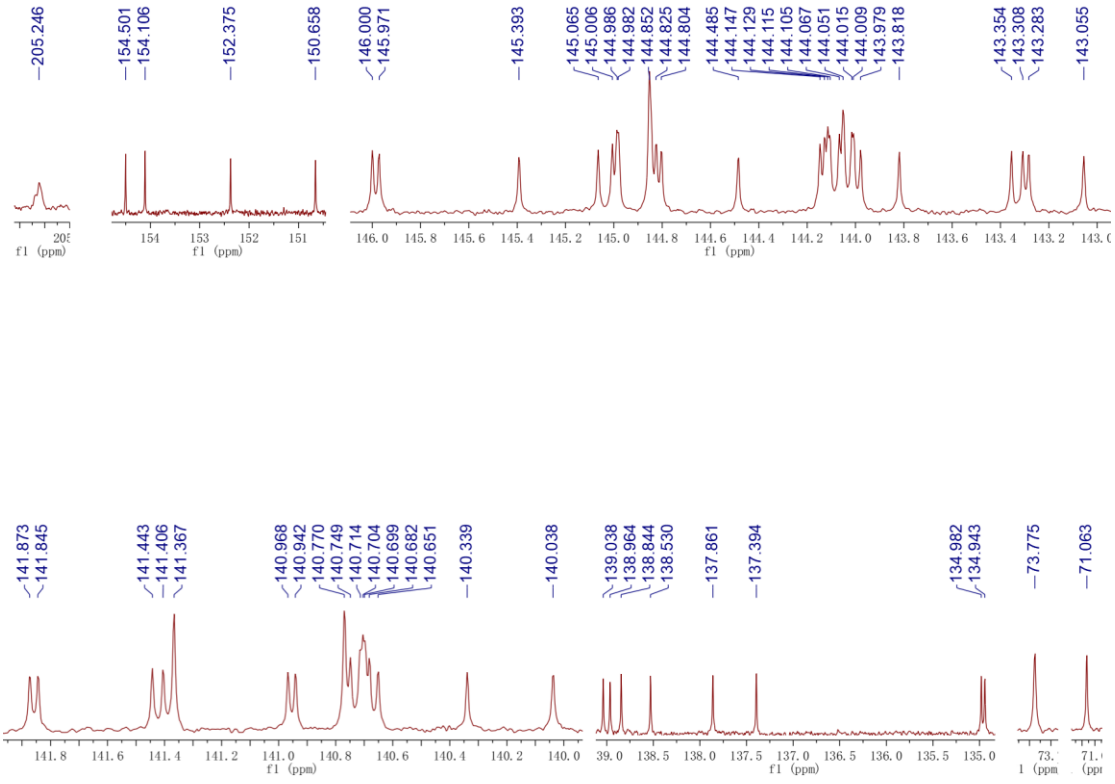


Figure S50. Expanded ^{13}C NMR (125.8 MHz, 2/1 $C_2D_2Cl_4/CS_2$) of compound **5a**

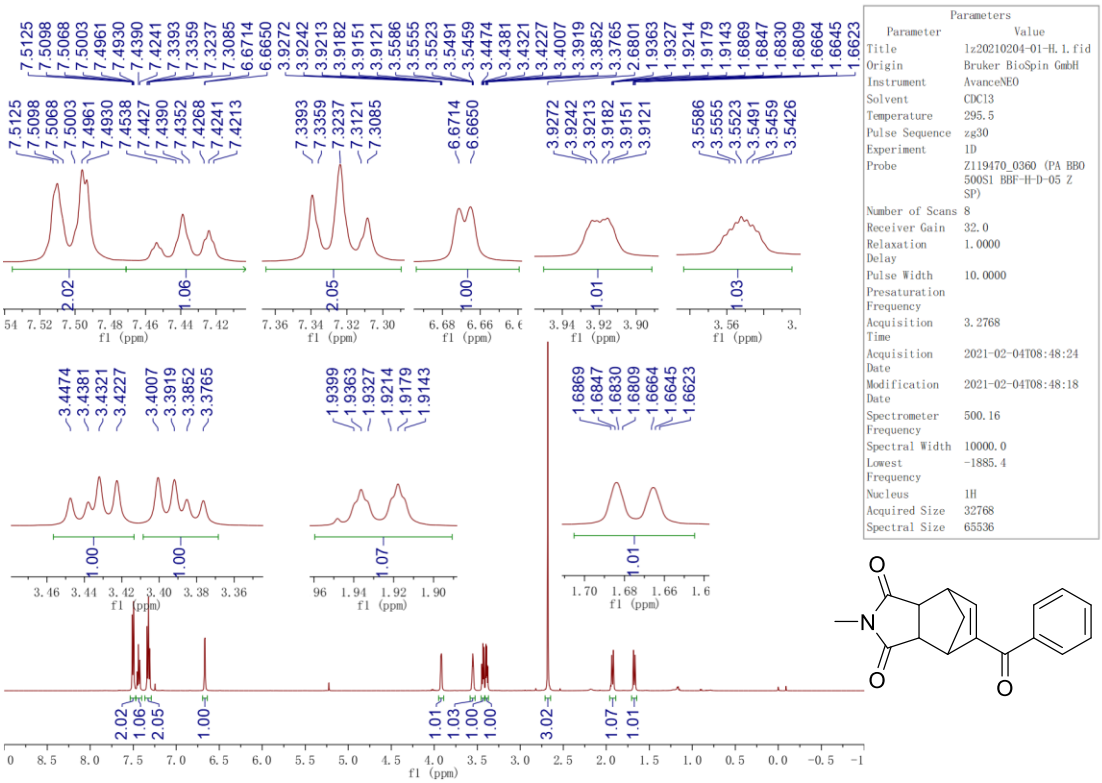


Figure S51. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **4d**

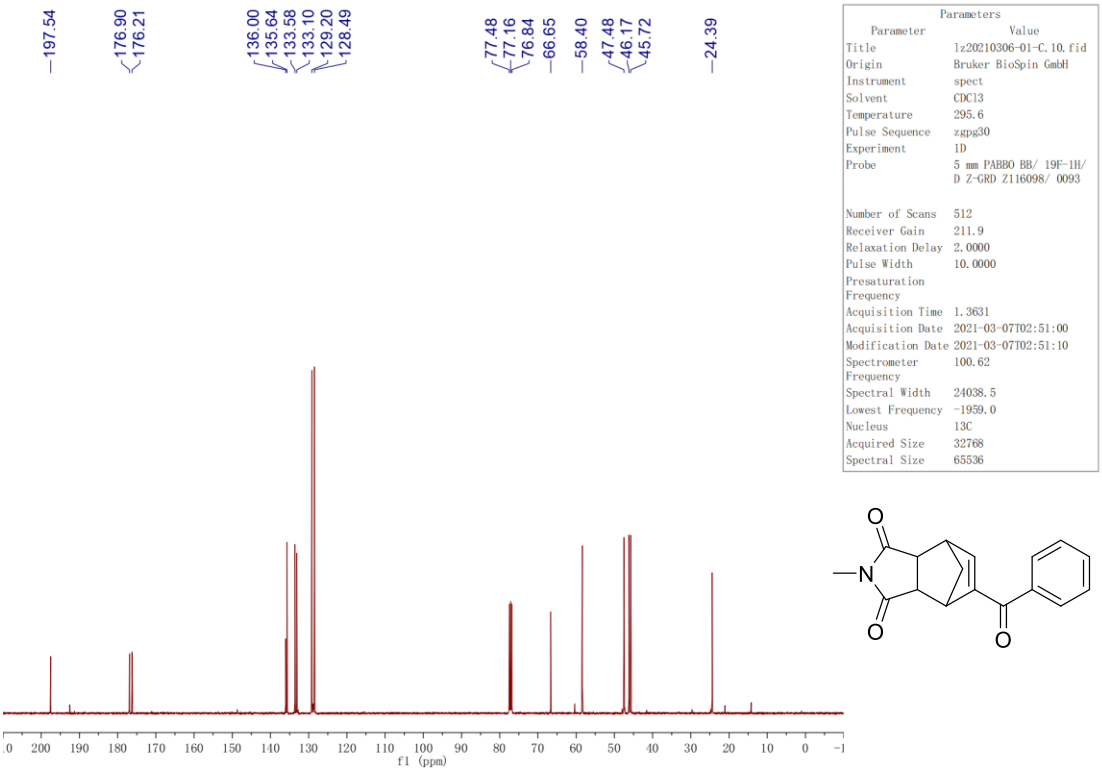


Figure S52. ^{13}C NMR (100.6 MHz, $CDCl_3$) of compound **4d**

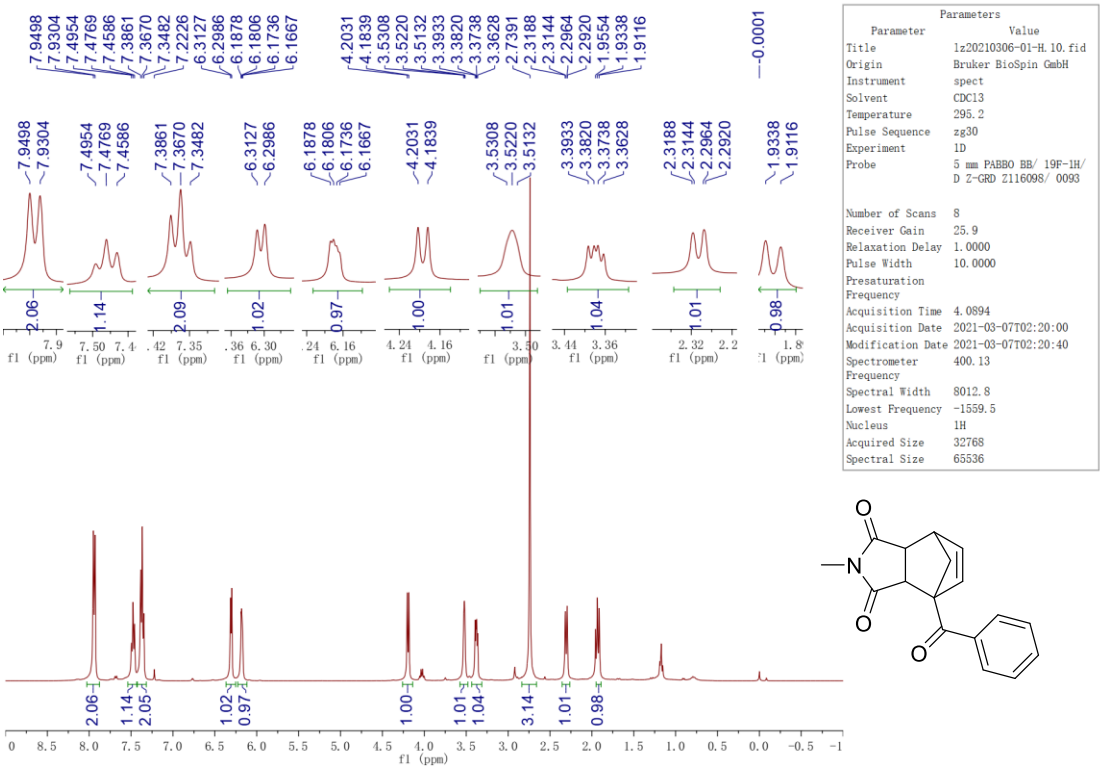


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d'**

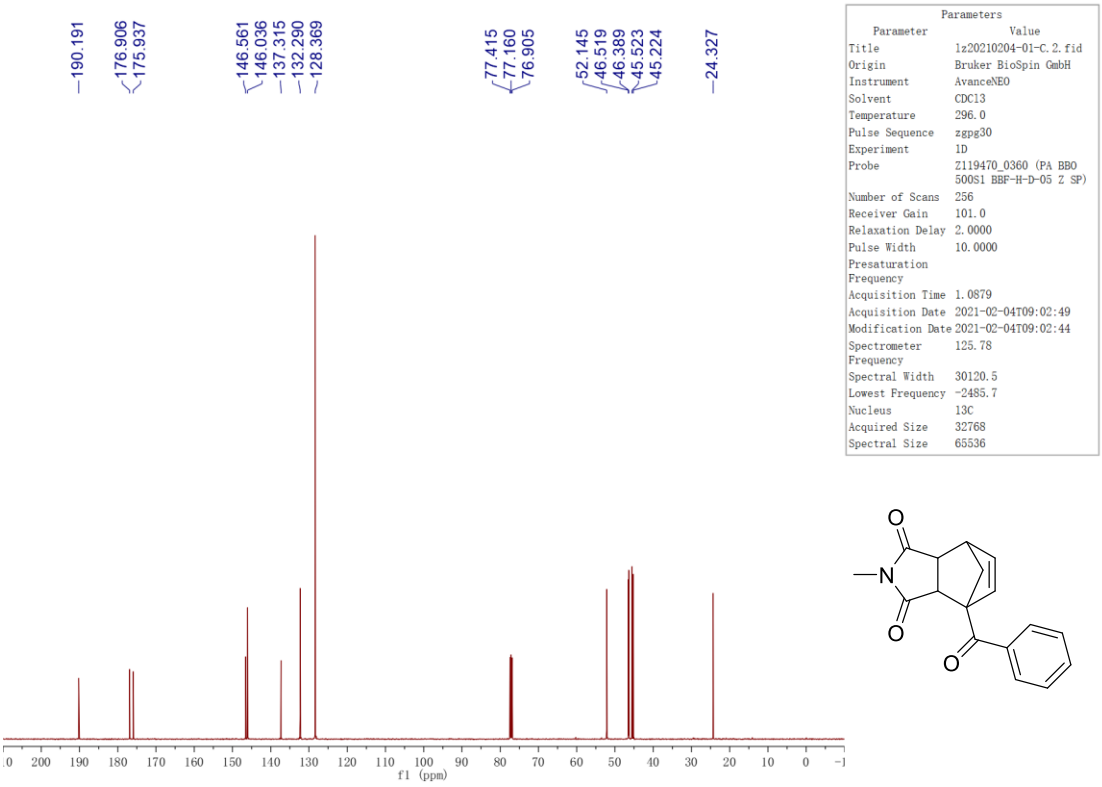


Figure S54. ^{13}C NMR (125.8 MHz, $CDCl_3$) of compound **4d'**

10. UV-vis spectra of compounds 2a–n and 5a

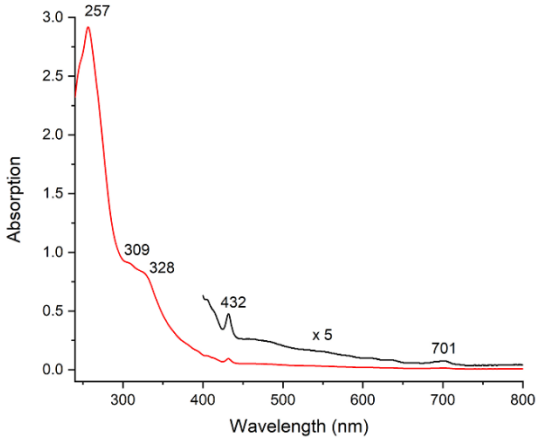


Figure S55. UV-vis absorption of compound **2a**

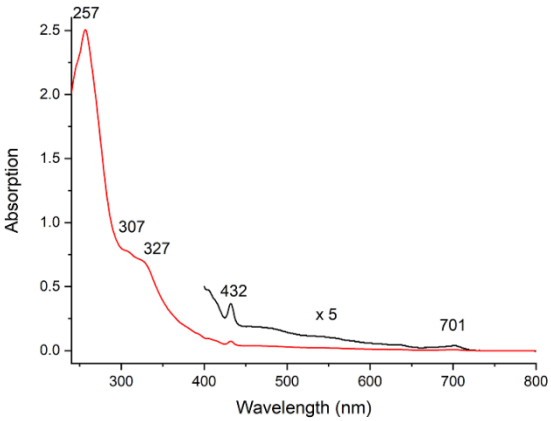


Figure S56. UV-vis absorption of compound **2b**

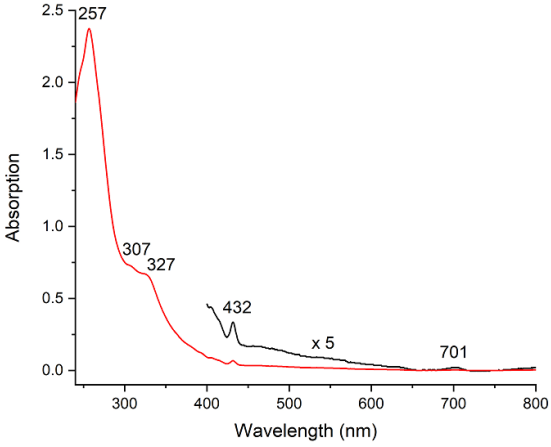
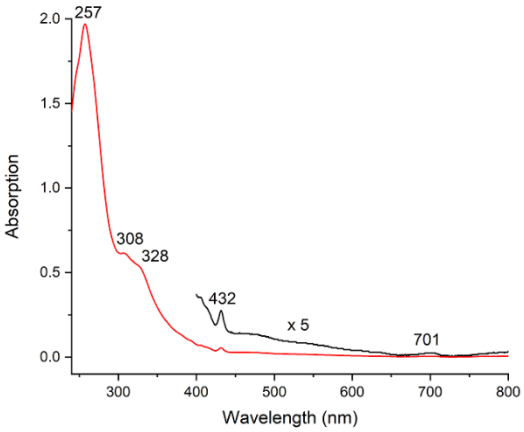


Figure S57. UV-vis absorption of compound **2c**



lFigure S58. UV-vis absorption of compound **2d**

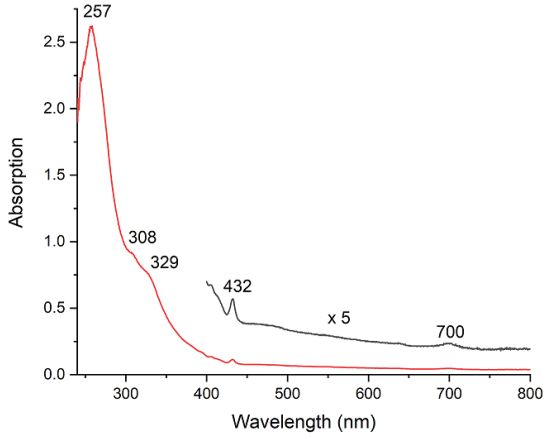


Figure S59. UV-vis absorption of compound **2e**

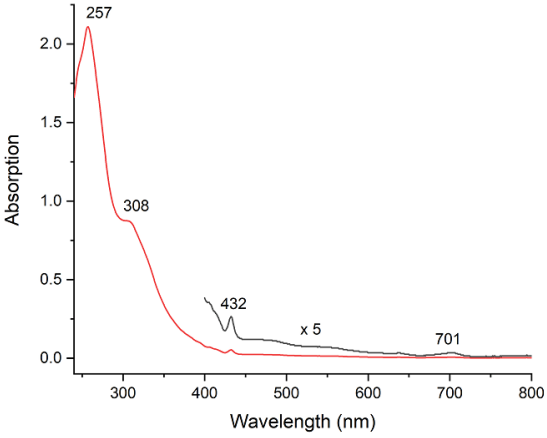


Figure S60. UV-vis absorption of compound **2f**

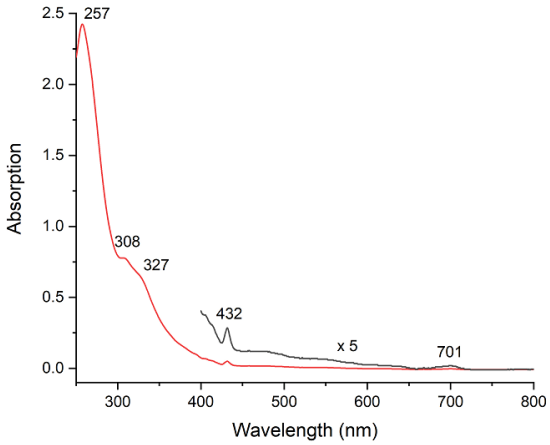


Figure S61. UV-vis absorption of compound **2g**

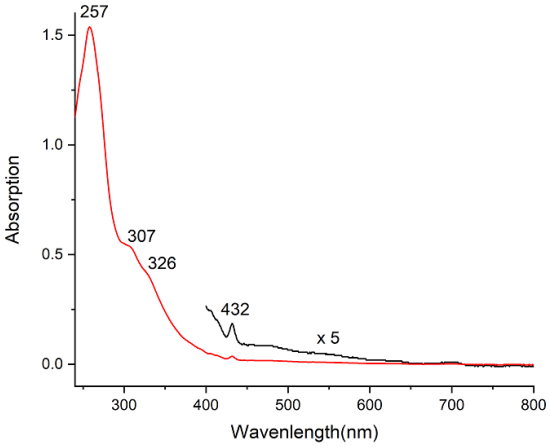


Figure S62. UV-vis absorption of compound **2h**

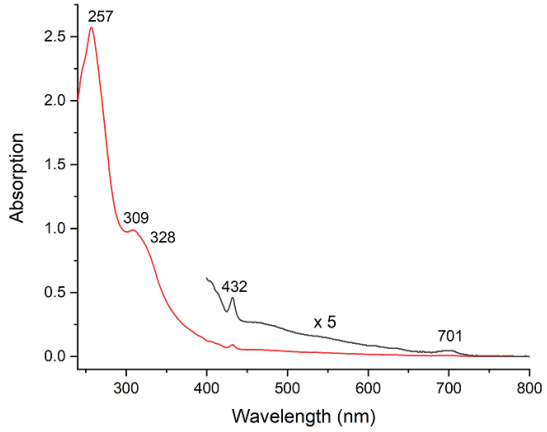


Figure S63. UV-vis absorption of compound **2i**

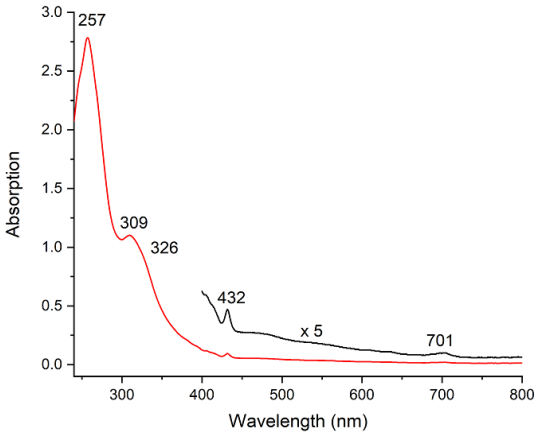


Figure S64. UV-vis absorption of compound **2j**

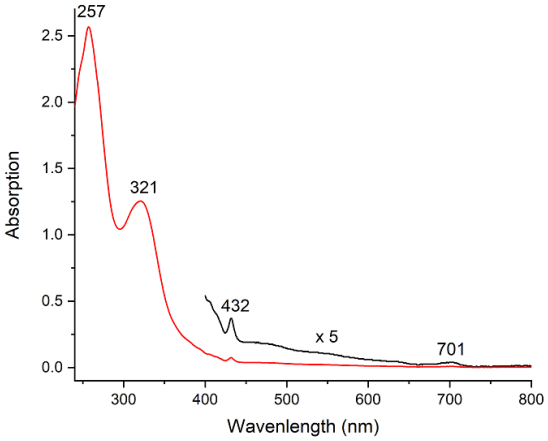


Figure S65. UV-vis absorption of compound **2k**

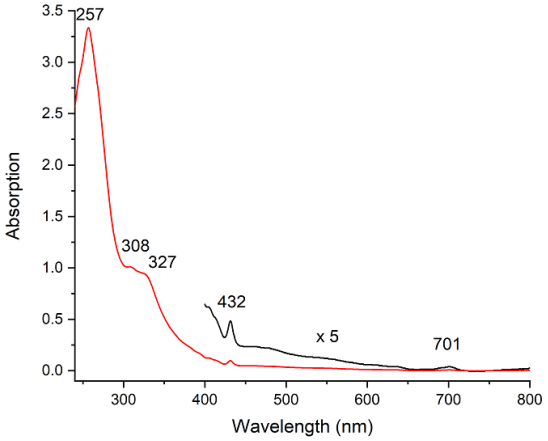


Figure S66. UV-vis absorption of compound **2l**

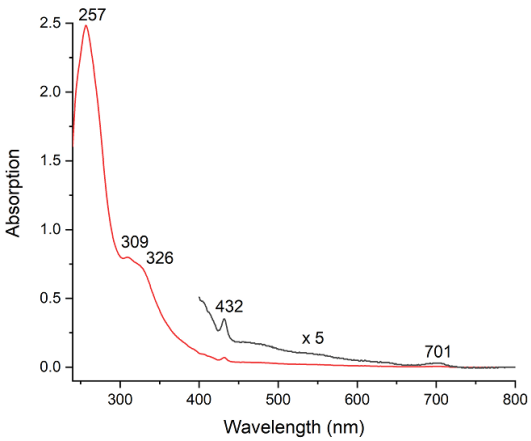


Figure S67. UV-vis absorption of compound **2m**

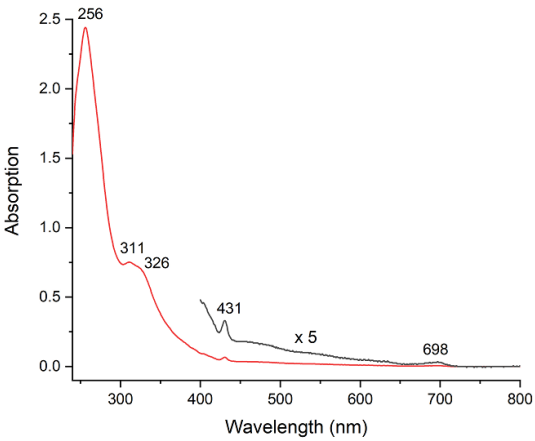


Figure S68. UV-vis absorption of compound **2n**

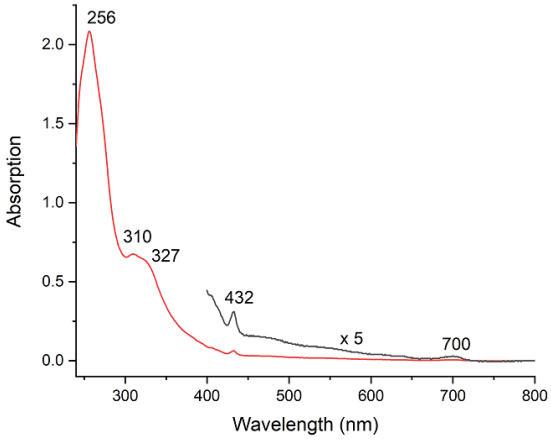


Figure S69. UV-vis absorption of compound **5a**

11. CV curves of compounds 2a–n and 5a

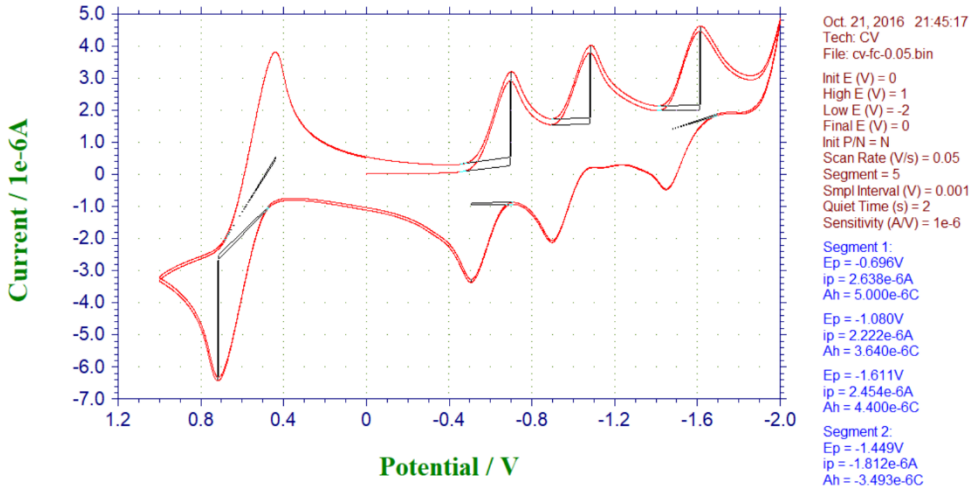


Figure S70. Cyclic voltammogram of compound **2a** (scanning rate: 50 mV s^{-1})

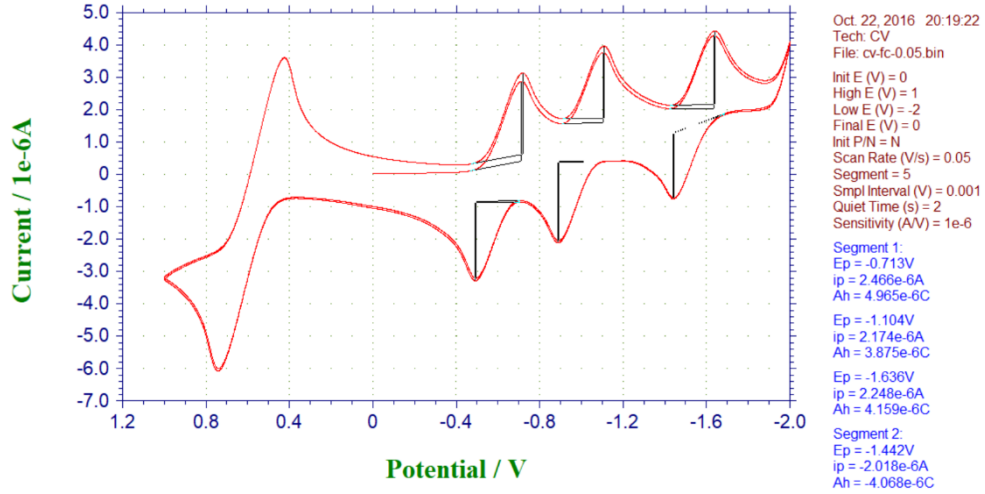


Figure S71. Cyclic voltammogram of compound **2b** (scanning rate: 50 mV s^{-1})

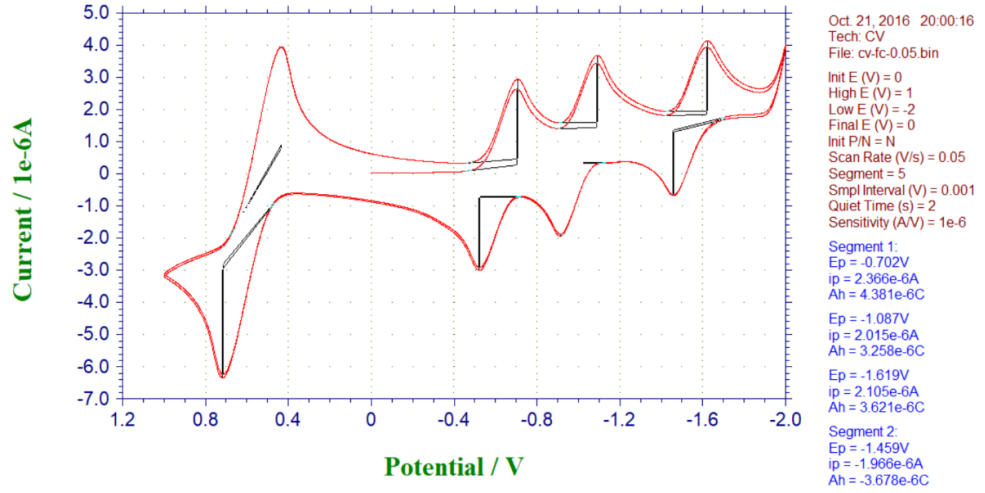


Figure S72. Cyclic voltammogram of compound **2c** (scanning rate: 50 mV s^{-1})

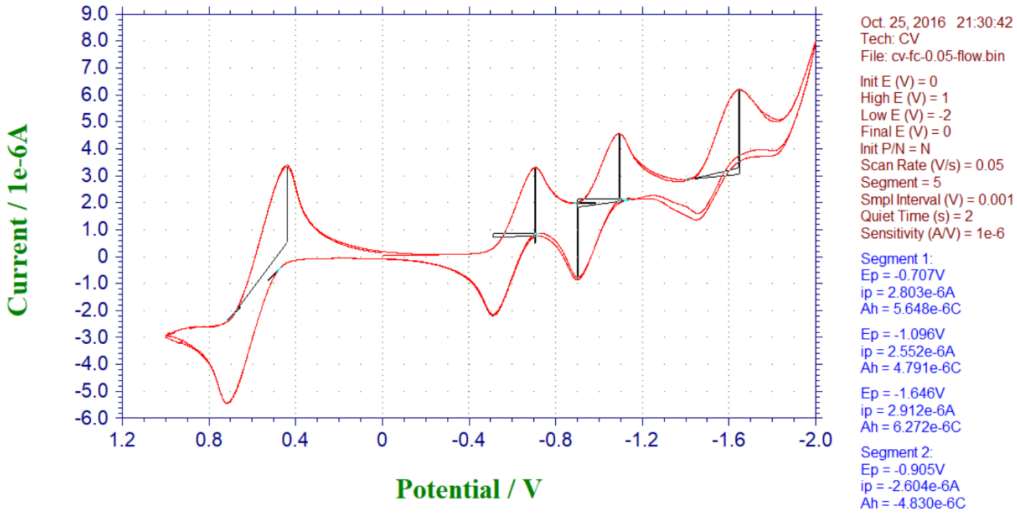


Figure S73. Cyclic voltammogram of compound **2d** (scanning rate: 50 mV s^{-1})

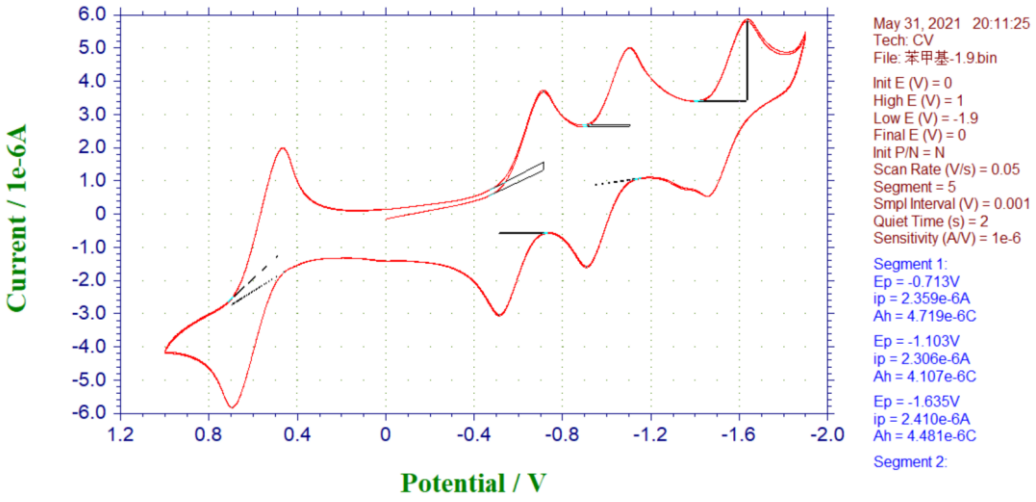


Figure S74. Cyclic voltammogram of compound **2e** (scanning rate: 50 mV s^{-1})

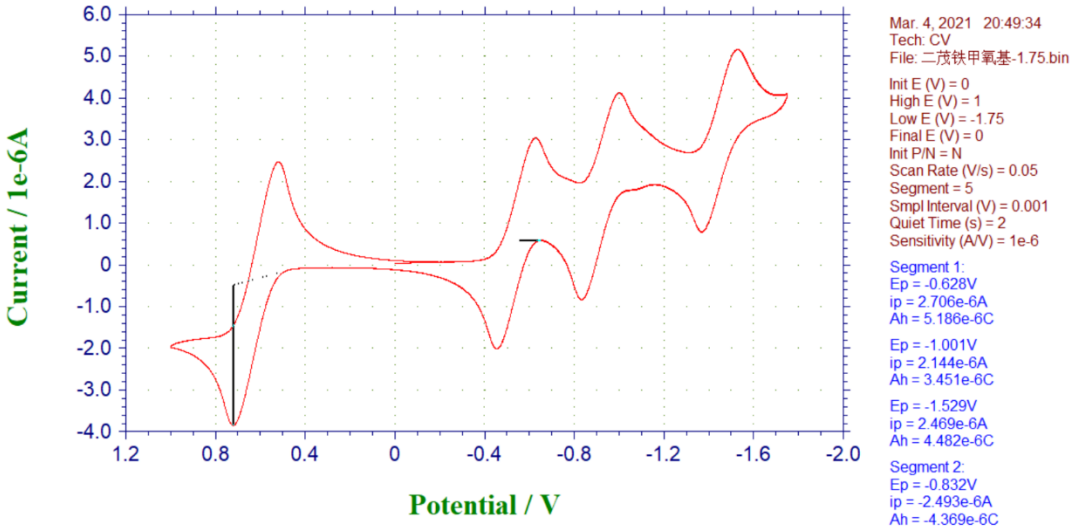


Figure S75. Cyclic voltammogram of compound **2f** (scanning rate: 50 mV s^{-1})

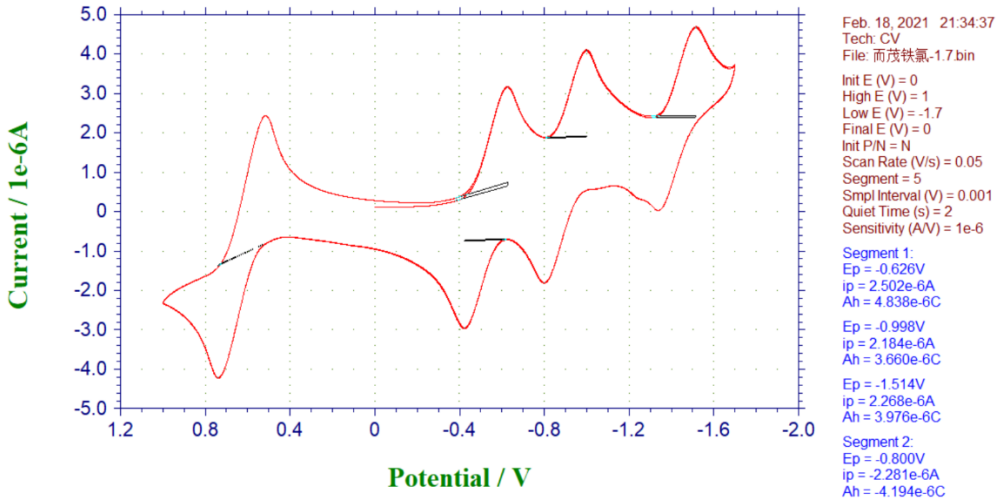


Figure S76. Cyclic voltammogram of compound **2g** (scanning rate: 50 mV s^{-1})

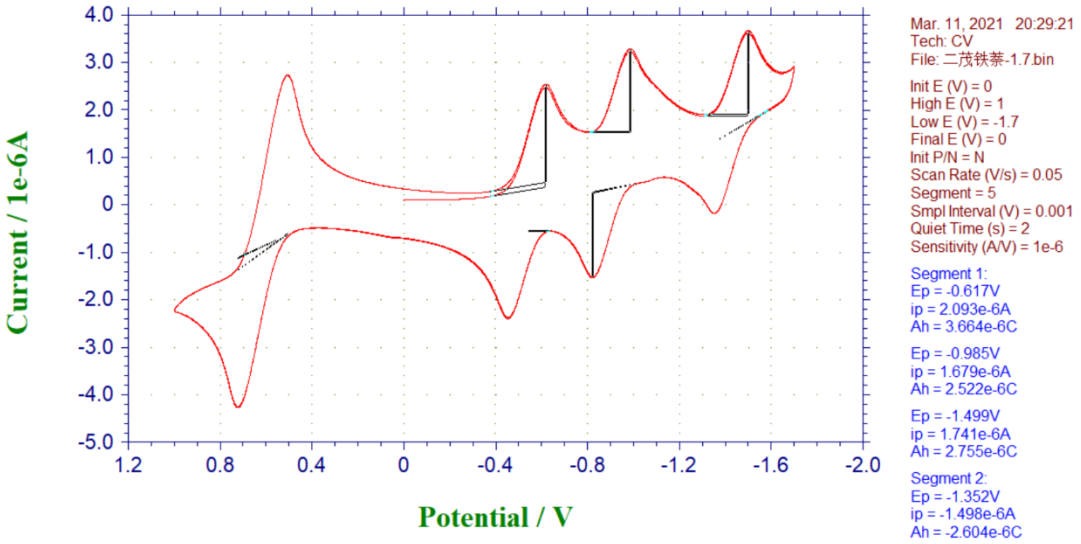


Figure S77. Cyclic voltammogram of compound **2h** (scanning rate: 50 mV s^{-1})

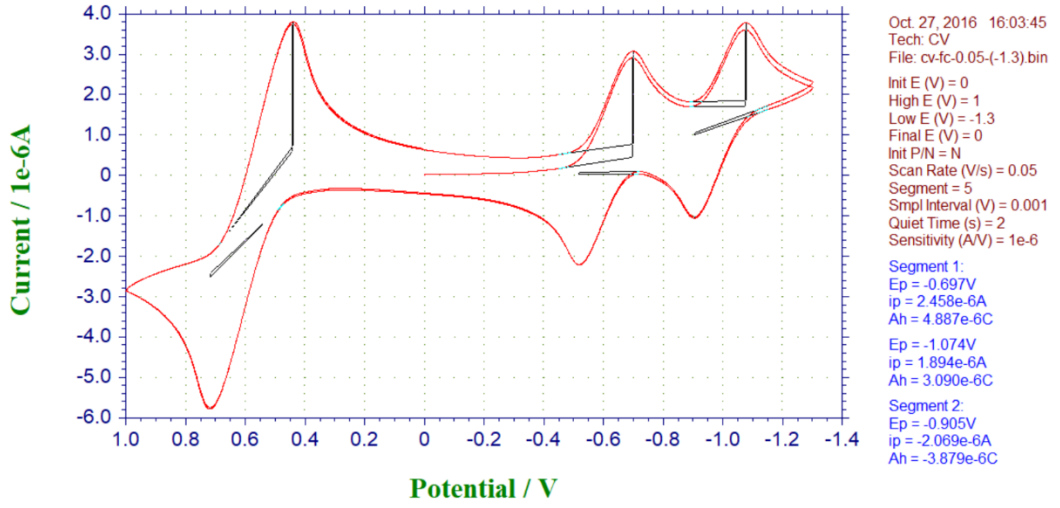


Figure S78. Cyclic voltammogram of compound **2i** (scanning rate: 50 mV s^{-1})

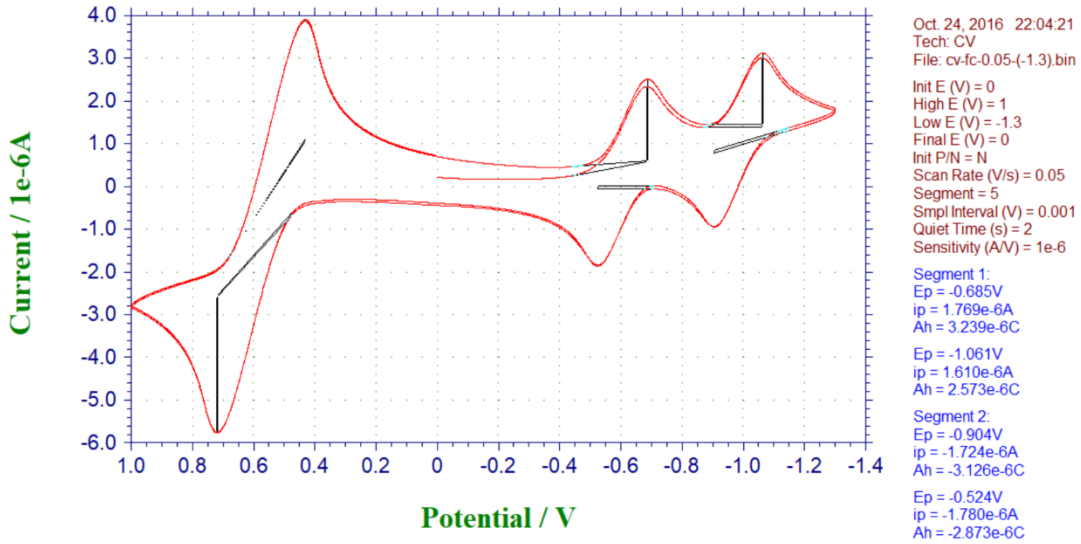


Figure S79. Cyclic voltammogram of compound **2j** (scanning rate: 50 mV s^{-1})

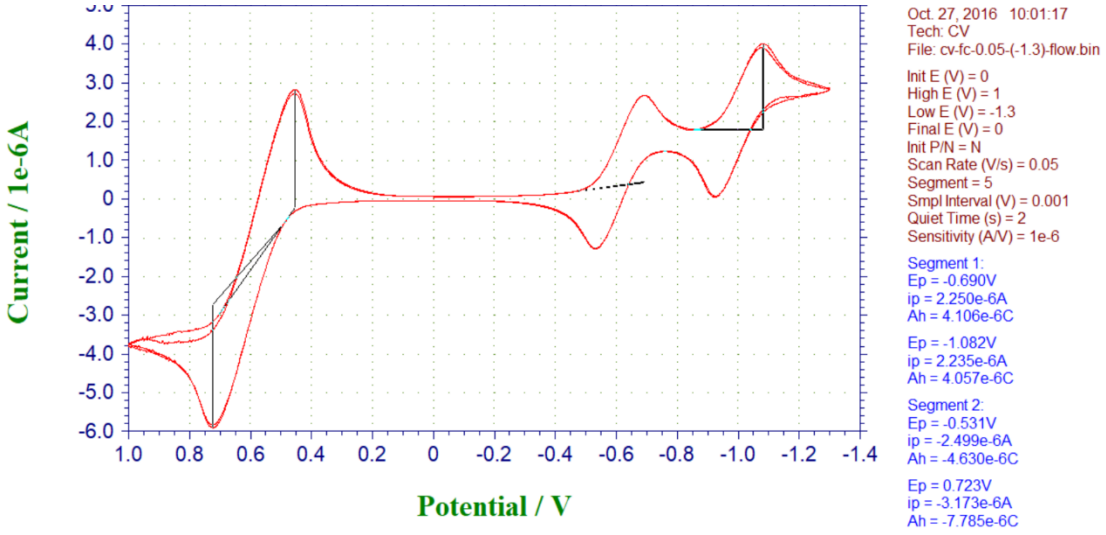


Figure S80. Cyclic voltammogram of compound **2k** (scanning rate: 50 mV s^{-1})

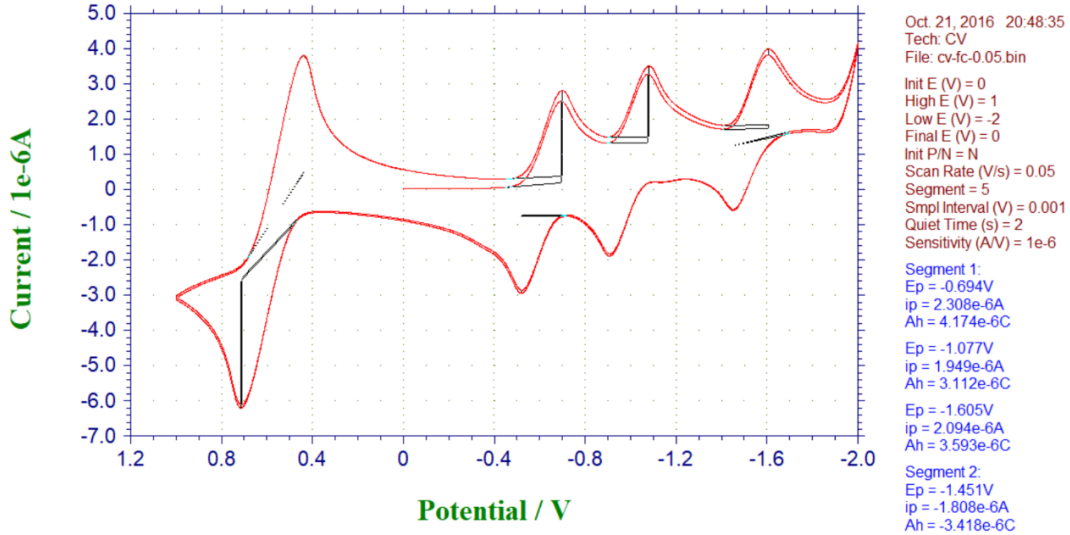


Figure S81. Cyclic voltammogram of compound **2l** (scanning rate: 50 mV s^{-1})

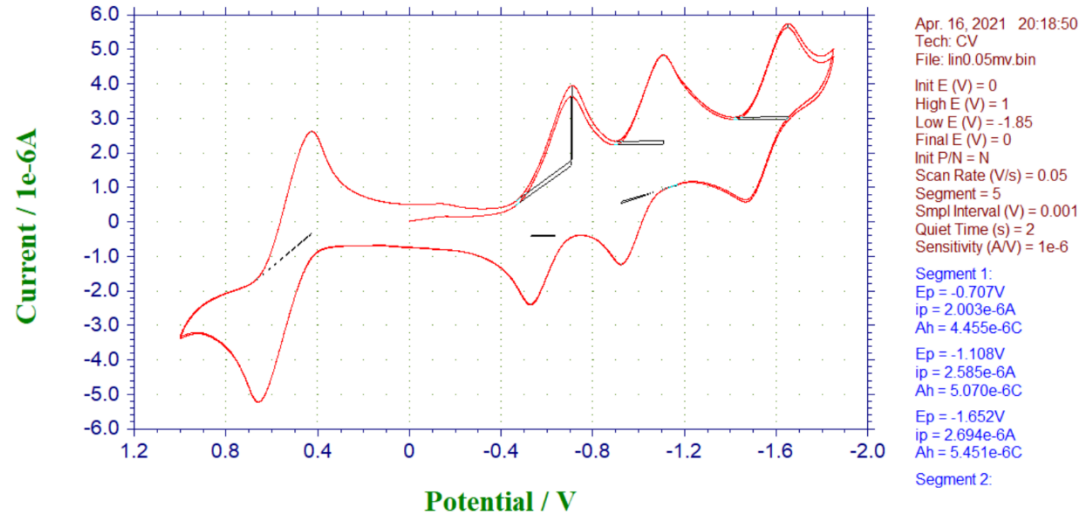


Figure S82. Cyclic voltammogram of compound **2m** (scanning rate: 50 mV s^{-1})

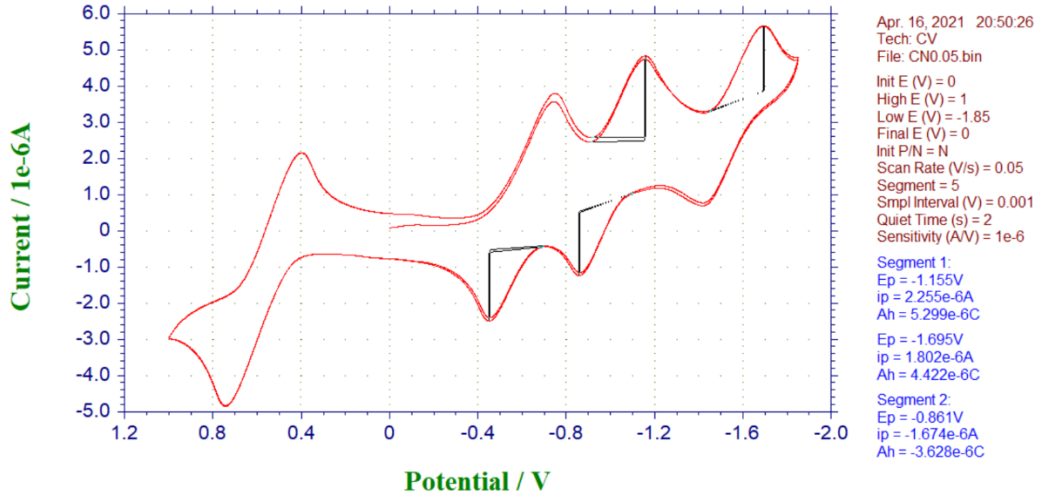


Figure S83. Cyclic voltammogram of compound **2n** (scanning rate: 50 mV s^{-1})

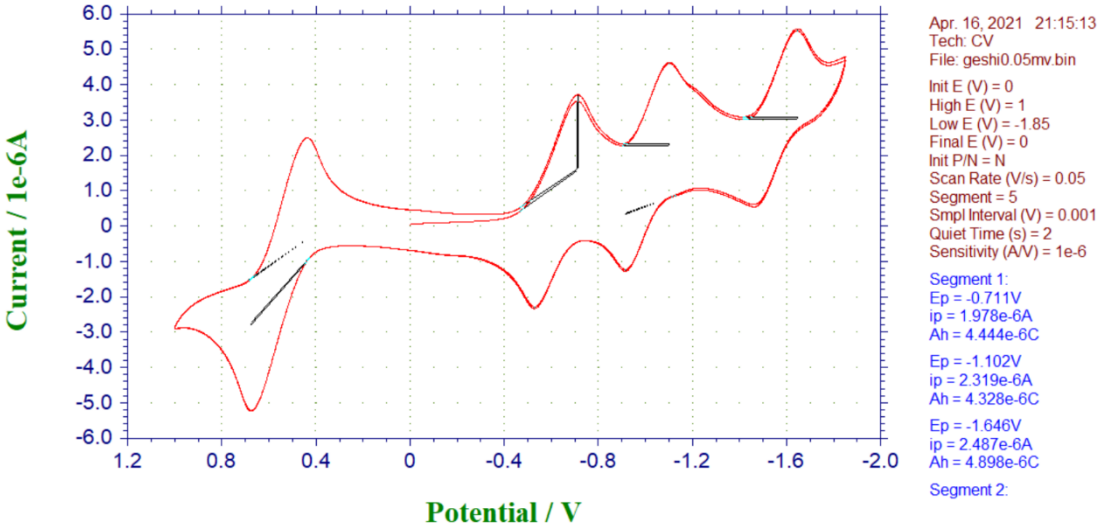
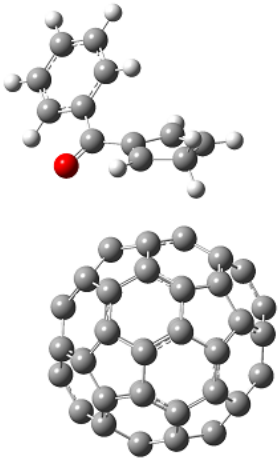
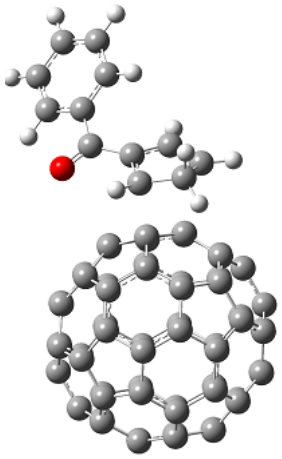


Figure S84. Cyclic voltammogram of compound **5a** (scanning rate: 50 mV s^{-1})

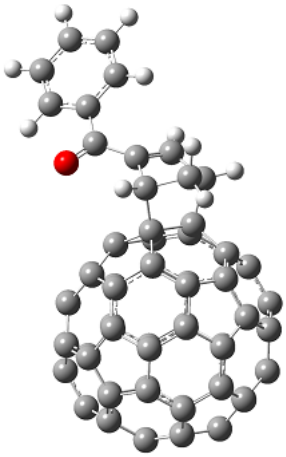
12. Calculated structures and relative energies for optimized C_{60}, A, B, TS1, TS2, 2d, 2d', 3, TS3, TS4, 4d and 4d'



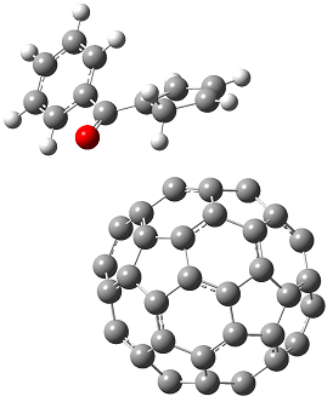
C_{60} and **A**
0.0 kcal mol^{-1}



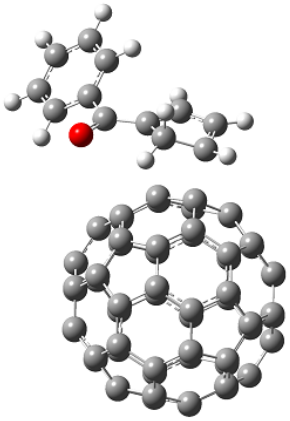
TS1
+15.4 kcal mol^{-1}



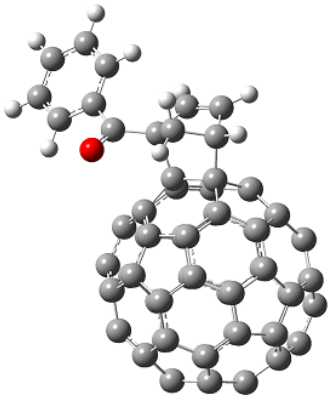
2d
-11.7 kcal $^{-1}$



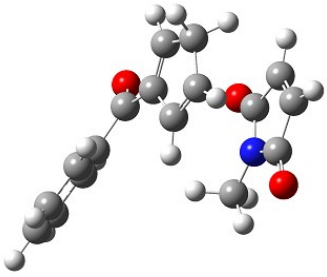
C_{60} and **B**
-3.7 kcal mol^{-1}



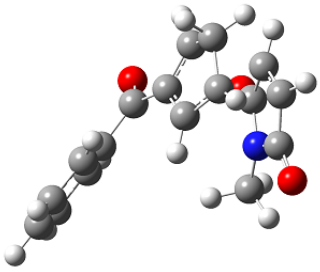
TS2
+17.4 kcal mol^{-1}



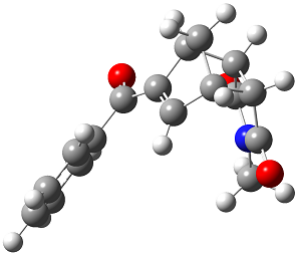
2d'
-1.3 kcal mol^{-1}



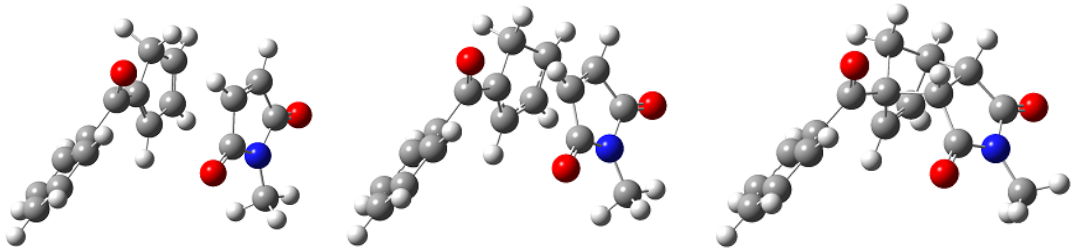
3 and **A**
0.0 kcal mol^{-1}



TS3
+14.3 kcal mol^{-1}



4d
-25.0 kcal mol^{-1}



3 and **B**
-3.7 kcal mol^{-1}

TS4
+13.5 kcal mol^{-1}

4d'
-19.9 kcal mol^{-1}

Figure S85. Relative energies (kcal mol^{-1}) for optimized C_{60}, **A**, **B**, **TS1**, **TS2**, **2d**, **2d'**, **3**, **TS3**, **TS4, 4d** and **4d'** at the B3LYP/6-31G(d) level

13. The intrinsic reaction coordinate (IRC) of TS1, TS2, TS3 and TS4

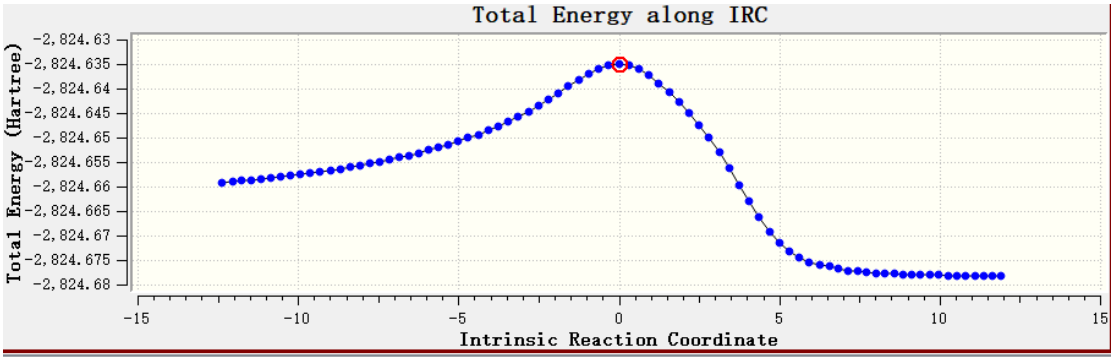


Figure S86. The intrinsic reaction coordinate (IRC) of **TS1**

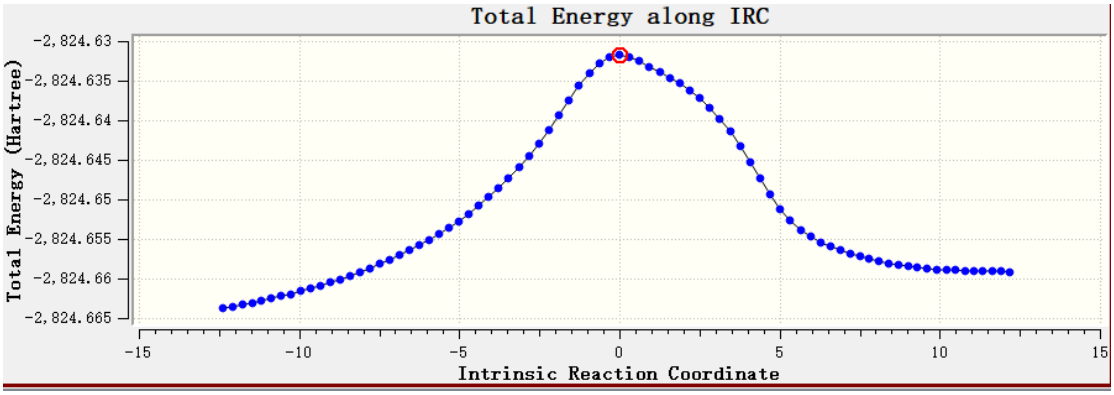


Figure S87. The intrinsic reaction coordinate (IRC) of **TS2**

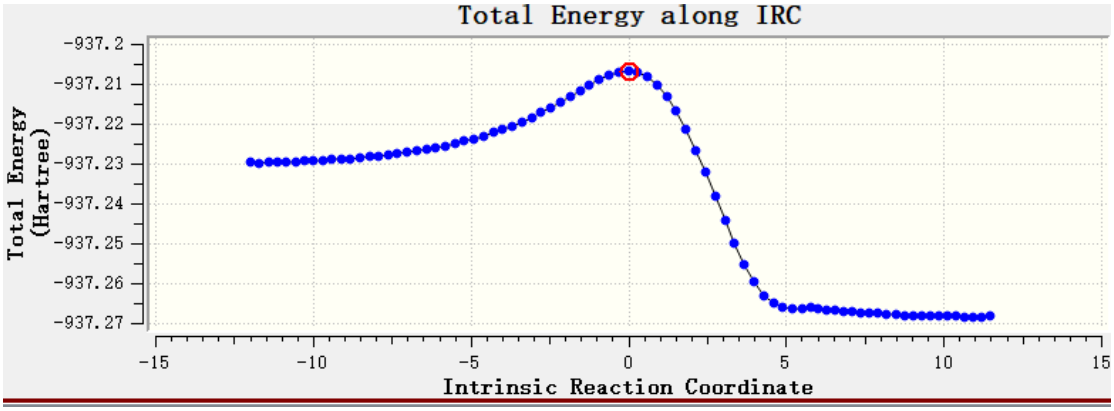


Figure S88. The intrinsic reaction coordinate (IRC) of **TS3**

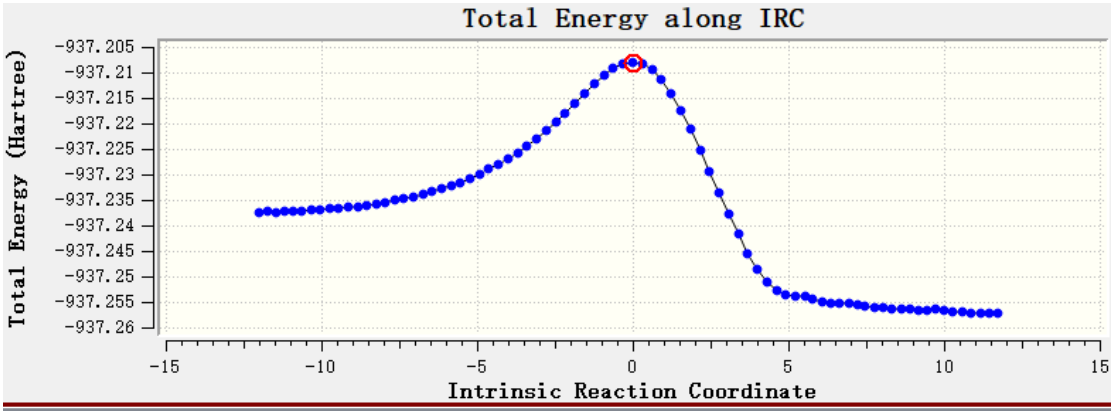


Figure S89. The intrinsic reaction coordinate (IRC) of **TS4**

14. Optimized xyz coordinates of C_{60}, A, B, TS1, TS2, 2d, 2d', 3, TS3, TS4, 4d and 4d'

The xyz coordinates for the lowest energy structure of C_{60}

0 1

C	-0.88158700	0.67024300	3.37263400
C	0.55213100	0.45528200	3.47640500
C	1.43849100	1.38640700	2.93371100
C	0.92822300	2.57142900	2.26453700
C	-0.44832900	2.77766500	2.16457400
C	-1.37149300	1.80780100	2.72970400
C	-1.51403900	-0.61925700	3.15040700
C	-0.47119100	-1.63097900	3.11734900
C	0.80577300	-0.96700400	3.31905000
C	1.93576100	-1.40165700	2.62486200
C	2.61537500	0.93387100	2.21117000
C	1.78983100	2.85126000	1.12796100
C	1.24004800	3.32576500	-0.06374200

C	-0.19356100	3.54023700	-0.16787900
C	-1.02068700	3.27205000	0.92359000
C	-2.29782400	2.60822200	0.72182900
C	-2.51414900	1.70278500	1.83791100
C	-3.12152500	0.46465200	1.62476900
C	-2.61168700	-0.72007900	2.29455900
C	-0.56723100	-2.70330500	2.22951300
C	-1.71033300	-2.80838800	1.33796300
C	-2.71150200	-1.83677900	1.36954900
C	-3.28399300	-1.34218500	0.12854500
C	-3.53763300	0.08019900	0.28636600
C	-3.32937700	0.94925400	-0.78543700
C	-2.69716600	2.23902900	-0.56341400
C	-1.83572100	2.51849800	-1.70023400
C	-0.60939200	3.15573500	-1.50632500
C	2.83217300	1.83889300	1.09480600
C	1.51404000	0.61925600	-3.15040700
C	2.61168600	0.72007700	-2.29455800
C	3.12152400	-0.46465200	-1.62476900
C	2.51414900	-1.70278500	-1.83791300
C	1.37149400	-1.80780200	-2.72970400
C	-0.55213100	-0.45528300	-3.47640500
C	-0.80577200	0.96700500	-3.31905000
C	0.47118900	1.63098000	-3.11735000
C	0.56723000	2.70330500	-2.22951300
C	1.71033400	2.80838800	-1.33796200
C	2.71150200	1.83677800	-1.36954700
C	3.53763200	-0.08020000	-0.28636600
C	3.32937600	-0.94925300	0.78543600
C	2.69716500	-2.23902900	0.56341500
C	2.29782400	-2.60822300	-0.72183000
C	1.02068900	-3.27205100	-0.92359000
C	0.44832900	-2.77766600	-2.16457400
C	-0.92822200	-2.57142900	-2.26453600
C	-1.43849100	-1.38640600	-2.93371000
C	-1.93576100	1.40165800	-2.62486200
C	-2.85875400	0.43190300	-2.05952200
C	-2.61537500	-0.93387100	-2.21116900
C	-2.83217200	-1.83889100	-1.09480600
C	-1.78983000	-2.85125900	-1.12796000
C	-1.24004700	-3.32576400	0.06374100
C	0.19356100	-3.54023800	0.16788000
C	0.60939200	-3.15573500	1.50632400
C	1.83572100	-2.51849800	1.70023300

C	3.28399200	1.34218500	-0.12854500
C	2.85875300	-0.43190200	2.05952200
C	0.88158800	-0.67024300	-3.37263500

Energy = -2286.174239 a.u.

The xyz coordinates for the lowest energy structure of **A**

0 1

C	2.71105000	0.73869100	-0.46175400
H	2.84536000	1.69089300	-0.96000900
C	1.53600200	0.26895100	0.02604000
C	3.08089900	-1.37616200	0.50854000
H	3.56563900	-2.27543000	0.87092400
C	1.77825100	-1.05611200	0.63612800
H	1.01883300	-1.64827700	1.13338300
C	3.79778600	-0.26517000	-0.21256000
H	4.26795100	-0.60361600	-1.14896900
H	4.61426000	0.16245100	0.39031200
C	0.26536700	1.04746000	-0.04139100
O	0.30140900	2.27225100	-0.10942600
C	-1.05605100	0.33716200	-0.03108900
C	-1.21411300	-0.98559900	-0.47140500
C	-2.18750300	1.06096900	0.37782900
C	-2.47855400	-1.57537700	-0.49118100
H	-0.35495400	-1.54732700	-0.82423800
C	-3.44529100	0.46608800	0.37515900
H	-2.05377400	2.09097600	0.69232100
C	-3.59323700	-0.85481600	-0.05960000
H	-2.59292000	-2.59617400	-0.84577400
H	-4.31305800	1.03043500	0.70591400
H	-4.57623600	-1.31845700	-0.06674900

Energy = - 538.485281 a.u.

The xyz coordinates for the lowest energy structure of **TS1**

0 1

C	-5.00870500	-0.82083500	0.00482100
C	-4.84045100	-0.34195800	1.36793900
C	-4.67231600	1.02223000	1.61263100
C	-4.66350500	1.96366700	0.50528800
C	-4.82455100	1.50393300	-0.80276500
C	-5.00170700	0.08422200	-1.05779400
C	-4.31102200	-2.08867100	-0.11604800
C	-3.70714400	-2.39186800	1.17111400
C	-4.03774500	-1.31330400	2.08845800
C	-3.09970000	-0.88449800	3.02911700

C	-3.69591000	1.47004800	2.59050900
C	-3.68057200	2.99293700	0.79861500
C	-2.89461600	3.52043000	-0.22790800
C	-3.06263100	3.04145900	-1.59117100
C	-4.00922500	2.05459700	-1.87213900
C	-3.68310400	0.97550100	-2.78908400
C	-4.29652900	-0.24257100	-2.28549100
C	-3.62777100	-1.46163800	-2.40377300
C	-3.63333600	-2.40356000	-1.29564200
C	-2.44927300	-2.99430400	1.22743900
C	-1.74417200	-3.32510500	0.00021900
C	-2.32863100	-3.03677800	-1.23775300
C	-1.51566500	-2.48423900	-2.30306200
C	-2.31682900	-1.51196000	-3.02863100
C	-1.72744500	-0.34294800	-3.51072200
C	-2.42432500	0.92633900	-3.38950000
C	-1.43738600	1.95310600	-3.09547700
C	-1.75183300	2.98915000	-2.21378100
C	-3.08239200	2.68804400	2.08698500
C	1.07789100	2.51281800	0.11496700
C	0.40114700	2.83962200	1.29308400
C	0.39040000	1.89960000	2.39254100
C	1.05429000	0.67664200	2.26125100
C	1.77599700	0.35204700	1.05594000
C	1.61104900	0.76811700	-1.37403700
C	0.80834000	1.73908500	-2.09051500
C	0.47867400	2.81703200	-1.17296500
C	-0.77292300	3.43207100	-1.23477700
C	-1.48015300	3.76410700	-0.00866600
C	-0.90445100	3.47259000	1.22915900
C	-0.92113700	1.94879600	3.01852100
C	-1.50955700	0.78071100	3.50226300
C	-0.81275000	-0.48977900	3.37838000
C	0.44187400	-0.53887200	2.76307500
C	0.78158400	-1.61745600	1.86507700
C	1.43717700	-0.59121400	-1.61297800
C	-0.13293900	1.31907600	-3.03651700
C	-0.31149900	-0.09614000	-3.29003300
C	0.45451300	-1.02718600	-2.58600500
C	-0.15826200	-2.24122700	-2.08516000
C	0.44718900	-2.54590000	-0.80344200
C	-0.33191400	-3.08479900	0.21553700
C	-0.16097900	-2.59681100	1.58682700
C	-1.47188700	-2.54679900	2.20482800

C	-1.79260400	-1.51487800	3.09042100
C	-1.72282800	2.92285800	2.29810900
C	-2.92489600	0.53594400	3.28453800
C	1.77837800	1.24925700	0.00014200
C	1.75370100	-1.12697700	0.83838700
C	1.50129500	-1.57008500	-0.52909000
C	3.53913500	-1.92056700	1.34054300
H	3.54974300	-1.78660100	2.41706300
C	4.47276700	-1.23725200	0.50932100
C	3.58662800	-2.93023800	-0.74762200
H	3.37589900	-3.58637700	-1.58387300
C	4.42803700	-1.83027200	-0.77713200
H	4.89285900	-1.42097000	-1.66645200
C	3.31369500	-3.27137100	0.68979000
H	4.10106600	-3.95379800	1.05270400
H	2.35386700	-3.74991100	0.89360500
C	5.14269500	0.00568500	0.94276900
O	4.68763400	0.62778500	1.90385700
C	6.35274400	0.51079300	0.21933100
C	7.23074300	-0.32891300	-0.48332700
C	6.63910100	1.88301600	0.30257400
C	8.36417800	0.19763200	-1.10347700
H	7.04719400	-1.39802900	-0.52009100
C	7.76105300	2.40904600	-0.33022200
H	5.96494100	2.51700700	0.86923300
C	8.62611800	1.56687700	-1.03583400
H	9.04460600	-0.46227300	-1.63474800
H	7.96657400	3.47439500	-0.27150800
H	9.50559700	1.97676300	-1.52529200

Energy = -2824.634969 a.u.
Imaginary frequency = -380.02

The xyz coordinates for the lowest energy structure of **2d**

0 1

C	-4.84042300	-1.00249400	-0.02444300
C	-4.68446500	-0.50619800	1.33535400
C	-4.54158900	0.86373900	1.56616700
C	-4.54274500	1.79214700	0.44804100
C	-4.69278900	1.31656300	-0.85565200
C	-4.84673600	-0.10821000	-1.09703500
C	-4.12098200	-2.25710000	-0.13047900
C	-3.51321100	-2.53407700	1.16159900
C	-3.86873700	-1.45442100	2.06842600
C	-2.94297800	-1.00036600	3.01029000

C	-3.57849700	1.33885700	2.54376500
C	-3.57848600	2.84073800	0.73449600
C	-2.79561600	3.36849800	-0.29471800
C	-2.95159200	2.87225000	-1.65463800
C	-3.88356000	1.86880900	-1.92897300
C	-3.53984700	0.78667000	-2.83449400
C	-4.13522400	-0.43594000	-2.31984400
C	-3.44611500	-1.64583900	-2.42439700
C	-3.43790400	-2.57530500	-1.30618000
C	-2.24142600	-3.10422500	1.22407000
C	-1.52832500	-3.43482000	0.00355600
C	-2.12100800	-3.18158100	-1.23848900
C	-1.31821600	-2.63132100	-2.30352200
C	-2.13262500	-1.68070300	-3.04400900
C	-1.56156700	-0.50842000	-3.53681900
C	-2.27846100	0.75065600	-3.43205100
C	-1.30779600	1.79438600	-3.14460300
C	-1.63979400	2.83214100	-2.27122400
C	-2.98236000	2.56140900	2.02901400
C	1.18482200	2.41330600	0.07812700
C	0.50056900	2.75535600	1.24966600
C	0.49946800	1.83343400	2.35913800
C	1.18332300	0.61918500	2.23959600
C	1.92682500	0.29143900	1.05347200
C	1.74728500	0.65853700	-1.39762700
C	0.93164000	1.61178700	-2.11848800
C	0.58417400	2.69239200	-1.21387000
C	-0.67090900	3.29692700	-1.29098900
C	-1.38768900	3.63562000	-0.07227500
C	-0.81227400	3.36889400	1.17197500
C	-0.81462600	1.86917600	2.98087400
C	-1.38605400	0.69741200	3.47469800
C	-0.66879000	-0.56285400	3.36591400
C	0.58771600	-0.60061000	2.75133400
C	0.95959400	-1.68250900	1.87867800
C	1.61703500	-0.69237200	-1.64325300
C	0.00432100	1.17775300	-3.07256100
C	-0.15066400	-0.23587100	-3.31295900
C	0.63035900	-1.14259300	-2.58774700
C	0.03556500	-2.36253800	-2.07280300
C	0.65323500	-2.66511400	-0.80866100
C	-0.12082500	-3.17270900	0.21336400
C	0.03796700	-2.66857500	1.59759400
C	-1.27645600	-2.63346200	2.20138800

C	-1.62562400	-1.60490600	3.08339300
C	-1.62769500	2.82107800	2.24449400
C	-2.79561800	0.42580700	3.25282800
C	1.90861700	1.16357400	-0.01428900
C	2.05689600	-1.22496900	0.91288400
C	1.88168100	-1.77462200	-0.59615800
C	3.48571000	-1.81338300	1.30572500
H	3.66474800	-1.78082700	2.38007200
C	4.52499900	-1.10034500	0.45137300
C	3.24973800	-2.57297600	-0.80115000
H	3.20660700	-3.24921800	-1.65685400
C	4.36468900	-1.54995600	-0.81194400
H	4.84670700	-1.17070000	-1.70588200
C	3.43897400	-3.18394200	0.60414600
H	4.37912800	-3.73549200	0.69876700
H	2.60857700	-3.82113700	0.92304200
C	5.34074800	0.02082400	0.97244900
O	4.97352300	0.59227300	1.99692000
C	6.57752400	0.46191500	0.25333600
C	7.34131600	-0.39501800	-0.55412000
C	7.00728000	1.78501300	0.44557600
C	8.50378900	0.06926600	-1.17019300
H	7.04471100	-1.43154400	-0.67503300
C	8.15849500	2.25036200	-0.18195100
H	6.41960100	2.43018700	1.09056000
C	8.90908100	1.39290600	-0.99258900
H	9.09546800	-0.60455300	-1.78382700
H	8.47581200	3.27950400	-0.03784800
H	9.81162200	1.75468300	-1.47794600

Energy = -2824.678209 a.u.

The xyz coordinates for the lowest energy structure of **B**

0 1

C	-1.52552100	0.16672500	0.02285700
C	-1.71858200	-1.07744000	-0.49948500
C	-3.82965400	-0.35413000	0.01731800
H	-4.90282800	-0.29508500	0.16051500
C	-3.14158000	-1.39903900	-0.49727800
H	-3.55877600	-2.33320900	-0.85801000
C	-2.87392500	0.74435500	0.37857600
H	-2.93870400	1.02993700	1.43867900
H	-3.06172600	1.66958900	-0.18400300
H	-0.94658300	-1.72739100	-0.89542600
C	-0.29554500	0.97103000	0.12127000

C	1.05405400	0.31401200	0.06641900
C	2.12562600	1.06608400	-0.44022200
C	1.29901800	-0.97902900	0.55256300
C	3.40667100	0.52477900	-0.49359400
H	1.92892200	2.07575500	-0.78632800
C	2.58721200	-1.51468300	0.51435400
H	0.48930400	-1.55361700	0.99039900
C	3.64029000	-0.76877900	-0.01691800
H	4.22615600	1.11105000	-0.90071100
H	2.76862000	-2.51232300	0.90535800
H	4.64176600	-1.18961300	-0.05195300
O	-0.37681700	2.19520000	0.22829100

Energy = - 538.4912298 a.u.

The xyz coordinates for the lowest energy structure of **TS2**

0 1

C	-5.01959400	-0.76803300	0.05044700
C	-4.83695500	-0.20704100	1.38002800
C	-4.65962300	1.16862100	1.53813100
C	-4.65390800	2.03899400	0.37440100
C	-4.83062800	1.50100000	-0.90165200
C	-5.01769100	0.06907300	-1.06680000
C	-4.32928100	-2.04407400	0.00281000
C	-3.71689700	-2.27118800	1.30215900
C	-4.03467300	-1.13716900	2.15362700
C	-3.08482400	-0.65676800	3.05798400
C	-3.67170500	1.66985800	2.47870800
C	-3.66274700	3.07837600	0.59512700
C	-2.88252700	3.53570100	-0.46837900
C	-3.06564800	2.97443900	-1.79789400
C	-4.02123800	1.97856700	-2.00985200
C	-3.70971200	0.84313900	-2.86068500
C	-4.32531500	-0.33731700	-2.27750900
C	-3.66242500	-1.56522200	-2.32391600
C	-3.66541000	-2.43664800	-1.16046300
C	-2.46203300	-2.87585100	1.38524500
C	-1.76920600	-3.28253700	0.17502200
C	-2.36153000	-3.07110600	-1.07248400
C	-1.55402000	-2.59270800	-2.17299100
C	-2.35582100	-1.66150000	-2.95186000
C	-1.76619300	-0.52906100	-3.51276300
C	-2.45605200	0.74867300	-3.46751100
C	-1.46150400	1.78616600	-3.24676500

C	-1.76122500	2.87475100	-2.42631700
C	-3.05526400	2.85092700	1.89557000
C	1.09121500	2.52931000	-0.09578700
C	0.42237300	2.93227200	1.06610600
C	0.41410600	2.06340100	2.22631300
C	1.06896800	0.83228400	2.17340000
C	1.76554700	0.41865400	0.96939400
C	1.59167200	0.68829500	-1.47946800
C	0.78938700	1.61908200	-2.24574100
C	0.47793500	2.75429900	-1.39475700
C	-0.77072600	3.37111400	-1.48398600
C	-1.46504800	3.78408600	-0.27632800
C	-0.87946400	3.56549400	0.97278900
C	-0.89196800	2.16075600	2.85857700
C	-1.48341700	1.02752100	3.41804800
C	-0.79490300	-0.25220100	3.36919000
C	0.45405800	-0.34441600	2.75405400
C	0.77270700	-1.47416500	1.90215800
C	1.41604900	-0.67608400	-1.63801300
C	-0.15972400	1.14771600	-3.15810100
C	-0.34725200	-0.27613500	-3.31907400
C	0.42036800	-1.16305100	-2.55625200
C	-0.19190900	-2.34429200	-1.97412800
C	0.42716000	-2.58859300	-0.69334900
C	-0.35245200	-3.03614100	0.36287900
C	-0.17104800	-2.47665400	1.70477300
C	-1.47345500	-2.37907900	2.32795100
C	-1.78306700	-1.29043500	3.15091100
C	-1.69303900	3.09042400	2.08124200
C	-2.90129700	0.77653000	3.22392300
C	1.78464300	1.25814700	-0.13945900
C	1.65067000	-1.02937500	0.83157200
C	1.58232200	-1.64400400	-0.49896600
C	3.93629300	-2.06687500	1.39932300
C	4.60849400	-1.27034800	0.45307300
C	3.20134700	-2.64352200	-0.73759400
H	2.96243500	-3.28177700	-1.58486900
C	4.23776200	-1.65902500	-0.83005900
H	4.54837400	-1.16796700	-1.74536800
C	3.33268000	-3.23001900	0.65870000
H	4.07077200	-4.04772500	0.61535100
H	2.42663200	-3.63464500	1.10960500
H	5.23706800	-0.41926300	0.68377700
C	3.92436500	-1.99732600	2.87338300

C	4.78084100	-1.00641800	3.60629500
C	4.24821000	-0.41598600	4.76328900
C	6.09960900	-0.70661700	3.23324100
C	5.00322200	0.48654400	5.50712000
H	3.23768100	-0.67676600	5.06112100
C	6.86298100	0.18093700	3.99246400
H	6.54572500	-1.19553900	2.37272100
C	6.31283300	0.78794700	5.12254400
H	4.57489200	0.95085500	6.39124800
H	7.88866600	0.39404700	3.70376300
H	6.90501000	1.48682100	5.70725200
O	3.16169300	-2.73001300	3.50542900

Energy = -2824.631722 a.u.
Imaginary frequency = -367.46

The xyz coordinates for the lowest energy structure of **2d'**
0 1

C	-2.79621700	3.07532700	-1.25316400
C	-3.37739500	2.06043400	-2.12051300
C	-4.29626000	1.14452500	-1.60391700
C	-4.66747000	1.20154300	-0.20007800
C	-4.11074800	2.17453000	0.63147800
C	-3.15830800	3.13238100	0.09473200
C	-1.41075100	3.25634800	-1.63990600
C	-1.13163600	2.34924500	-2.74176400
C	-2.35050300	1.61563400	-3.04273600
C	-2.28215400	0.27289700	-3.42067600
C	-4.22654500	-0.25284700	-1.99388800
C	-4.82477200	-0.16149800	0.27822000
C	-4.41273300	-0.49991900	1.56910200
C	-3.83127500	0.51477000	2.43619800
C	-3.68670200	1.82587000	1.97699400
C	-2.47402800	2.56814400	2.27213400
C	-2.14745800	3.37681000	1.10856000
C	-0.81355300	3.55533700	0.73576900
C	-0.43711100	3.49322700	-0.66729400
C	0.10414100	1.70610000	-2.81708100
C	1.11757700	1.94863400	-1.80628100
C	0.85292300	2.83372000	-0.75548900
C	1.27067200	2.48563300	0.58054400
C	0.24567900	2.93257700	1.51015700
C	-0.06753100	2.15764300	2.62575300
C	-1.45419200	1.97168900	3.01608400
C	-1.60445600	0.60612800	3.49261200

C	-2.77077200	-0.10634900	3.20570500
C	-4.55319700	-1.06031600	-0.82944700
C	-1.17071700	-3.02465000	1.59806600
C	-2.16032800	-3.27140600	0.63969600
C	-1.79381100	-3.32673800	-0.75395300
C	-0.45641500	-3.13211000	-1.11684200
C	0.56476100	-2.92566300	-0.12630700
C	0.80474200	-1.82269500	2.08577400
C	-0.23013100	-1.38570500	2.99835400
C	-1.44495700	-2.12343600	2.70226100
C	-2.68981800	-1.50303900	2.80994900
C	-3.71079000	-1.74682600	1.80328800
C	-3.45108000	-2.61466200	0.74058300
C	-2.85452300	-2.70536800	-1.53068000
C	-2.54092500	-1.93143900	-2.64722400
C	-1.15159000	-1.74227100	-3.03454300
C	-0.12940200	-2.32432000	-2.27714200
C	1.09391800	-1.61782700	-2.00268300
C	1.72311800	-0.91908600	1.59245300
C	-0.31178900	-0.04645700	3.39563400
C	0.63204600	0.90475100	2.86196200
C	1.60680400	0.46660900	1.96026400
C	1.93111900	1.27174000	0.79829300
C	2.24403700	0.38422900	-0.29083200
C	1.82626600	0.71093200	-1.56411700
C	1.23485700	-0.32041700	-2.44675600
C	0.17846600	0.31032900	-3.20857100
C	-0.99443700	-0.38999600	-3.51184700
C	-3.88121800	-2.26302200	-0.60333300
C	-3.24061200	-0.68089300	-2.88508500
C	0.21083600	-2.85415200	1.20409900
C	1.74769900	-2.17315300	-0.73413200
C	2.39600500	-1.05006200	0.22754000
C	3.00347800	-3.10084800	-1.05078700
H	2.83338000	-3.74002100	-1.91925700
C	3.38556000	-3.79241800	0.24183800
C	3.95245700	-1.54455700	0.29284700
C	3.93014100	-2.87024800	1.04338300
H	4.22787500	-2.96068800	2.08025700
C	4.11986800	-2.04761500	-1.16111500
H	5.09570400	-2.51112200	-1.33345300
H	3.92454600	-1.29026200	-1.92561500
H	3.14069700	-4.81864600	0.49215100
C	4.81555500	-0.48690100	0.98586400

O	4.73444600	-0.44234900	2.20813900
C	5.66585500	0.52108500	0.27208000
C	6.16110000	0.37878300	-1.03374700
C	6.01489700	1.67197600	1.00370800
C	6.97684300	1.36326900	-1.59251700
H	5.94058400	-0.50435700	-1.61738500
C	6.81503900	2.65901500	0.44008100
H	5.64176400	1.76797300	2.01745100
C	7.29962100	2.50707900	-0.86250800
H	7.36029300	1.23347300	-2.60075300
H	7.06478400	3.54652000	1.01491500
H	7.92818400	3.27576000	-1.30406400

Energy = -2824.661649 a.u.

The xyz coordinates for the lowest energy structure of **3**

0 1

C	-0.64900400	-1.63530900	0.00000700
H	-1.32823000	-2.47821300	-0.00001300
C	0.68706800	-1.61943700	-0.00000500
C	-1.14680000	-0.21607800	-0.00000600
H	1.38650400	-2.44564600	0.00003600
C	1.15276100	-0.18966300	-0.00000900
O	-2.29404600	0.18053000	0.00000700
N	-0.00750500	0.59179300	-0.00003000
O	2.29268500	0.22733000	0.00000900
C	-0.02956600	2.04305100	0.00001100
H	-0.54341400	2.41873400	-0.88962100
H	1.00641200	2.38569400	0.00068800
H	-0.54460100	2.41861200	0.88899800

Energy = - 398.7442624 a.u.

The xyz coordinates for the lowest energy structure of **TS3**

O	2.27167100	-0.16293200	2.73123900
C	2.30220200	-0.20543400	1.51518800
N	1.77739000	-1.24019300	0.72835900
C	2.88740500	0.77705000	0.55686200
C	2.13480400	-1.08998600	-0.62273300
C	1.14029100	-2.42837400	1.26521400
C	2.74716700	0.27026800	-0.73410600
H	3.62196300	1.49362500	0.89959400
C	1.29488800	2.43761100	0.56678900
O	1.98281400	-1.93685800	-1.47788400
H	1.33283900	-2.45430000	2.33927400

H	1.55753700	-3.31372600	0.77919000
H	0.05924100	-2.40781100	1.09019900
C	1.08619800	1.51766600	-1.54728600
H	3.38021000	0.49863400	-1.58205100
C	0.15637200	1.63759500	0.53913400
H	1.60180800	3.04065300	1.41388400
C	1.67669800	2.72687300	-0.86462400
C	0.00283200	1.08847600	-0.75771500
H	1.14962300	1.31953500	-2.61069800
H	-0.43627800	1.37259000	1.40610400
H	2.73529200	2.91774800	-1.05171400
H	1.11668200	3.61542800	-1.20370900
C	-0.99096400	0.09366200	-1.24885200
O	-0.75469200	-0.53821400	-2.27285600
C	-2.26477500	-0.14387100	-0.49426700
C	-2.91195300	0.84909800	0.25682000
C	-2.85818600	-1.41182700	-0.60770100
H	-2.48966500	1.84705800	0.31765600
C	-4.12266400	0.57364900	0.89336500
H	-2.36240300	-2.16147200	-1.21619700
C	-4.05542200	-1.69067300	0.04499500
H	-4.62343600	1.35309600	1.46109600
C	-4.69019500	-0.69788500	0.79754800
H	-4.49957100	-2.67894000	-0.03705500
H	-5.62848600	-0.91358600	1.30161000

Energy = -937.2068337 a.u.
Imaginary frequency = -421.39

The xyz coordinates for the lowest energy structure of **4d**

0 1

O	2.50447700	-0.35944100	2.59575100
C	2.46102900	-0.30373200	1.38240100
N	2.22538900	-1.38894300	0.54024600
C	2.64661800	0.92960600	0.50699300
C	2.22097200	-1.06754100	-0.82394900
C	2.02353000	-2.74691300	1.01895600
C	2.41215800	0.43856200	-0.94318700
H	3.64600800	1.34170300	0.67831800
C	1.55916500	2.05597900	0.69171000
O	2.11006500	-1.88585100	-1.70996500
H	2.19310100	-2.74698800	2.09637100
H	2.72342200	-3.42190400	0.51975700
H	1.00413300	-3.07866100	0.80052600
C	1.17318100	1.29749900	-1.40806200

H	3.25301300	0.63244700	-1.61548800
C	0.20797300	1.36884300	0.69797600
H	1.76167400	2.72699400	1.52734100
C	1.55518600	2.64437400	-0.74382200
C	-0.03552800	0.92016800	-0.55270900
H	1.00502700	1.27248300	-2.48385700
H	-0.37876300	1.17429700	1.58867100
H	2.53153600	3.02988600	-1.06014000
H	0.79422900	3.41856000	-0.88272000
C	-1.12647700	0.05361400	-1.05856600
O	-0.92982700	-0.62240200	-2.06458500
C	-2.44344600	-0.01120800	-0.34460100
C	-2.95568300	1.04324500	0.42682900
C	-3.21487500	-1.17260400	-0.51243000
H	-2.39172800	1.96448600	0.52749000
C	-4.20750400	0.92899700	1.03265600
H	-2.81834200	-1.96970500	-1.13307500
C	-4.45638100	-1.29059900	0.10451500
H	-4.60055400	1.75540600	1.61861500
C	-4.95508400	-0.23950800	0.88039300
H	-5.03989100	-2.19855300	-0.02154700
H	-5.92730400	-0.32899500	1.35780500

Energy = -937.2693075 a.u.

The xyz coordinates for the lowest energy structure of **TS4**

O	-1.51171000	-0.16311700	-2.43652600
C	-1.41648300	-0.38384400	-1.23086500
C	-2.48241400	0.09279500	-0.29361700
C	-0.20992700	-1.09005200	-0.71872300
C	-2.90086700	-0.64448700	0.82439400
C	-3.13332700	1.29760500	-0.60251000
C	0.20521600	-1.30782200	0.60960600
C	0.57453800	-2.05037200	-1.58419300
C	1.45362000	0.47588000	-1.33301800
H	-2.43738900	-1.59979200	1.05061200
C	-3.94389900	-0.17815100	1.62488100
H	-2.81414500	1.85087200	-1.47944600
C	-4.15741200	1.77285400	0.21091700
C	1.40364500	-2.02349900	0.60728000
H	-0.25825600	-0.87243300	1.48646500
H	0.03827400	-3.01358100	-1.61501300
H	0.72459800	-1.72431700	-2.61303600
C	1.81334600	-2.22447200	-0.73162300
H	0.86438400	0.71787100	-2.20635500

C	2.57156500	-0.36802900	-1.26915700
C	1.47517700	1.37372700	-0.15214800
H	-4.27229000	-0.76375500	2.47924600
C	-4.56539300	1.03529100	1.32623500
H	-4.64162600	2.71648000	-0.02467800
H	2.00244800	-2.24893700	1.48258300
H	2.62373100	-2.89458000	-1.00185300
H	3.09987200	-0.75351500	-2.13362400
C	3.37358700	0.03944500	-0.06530600
O	0.71370000	2.27139800	0.15701100
N	2.60352800	0.99762400	0.60080100
H	-5.36975700	1.40365800	1.95737300
O	4.45942000	-0.37009600	0.29744700
C	2.99745600	1.64865900	1.83567900
H	2.97079400	2.73420500	1.70776700
H	4.01084600	1.32106600	2.07371500
H	2.32091500	1.37873600	2.65305000

Energy = -937.207976 a.u.
Imaginary frequency = -447.03

The xyz coordinates for the lowest energy structure of **4d'**
0 1

O	-1.23239400	1.29502300	-1.75644100
C	-1.31484000	0.46891300	-0.85785800
C	-2.63930400	0.21128300	-0.20204700
C	-0.06903800	-0.32399100	-0.46516800
C	-2.90472600	-0.88909900	0.62886900
C	-3.67537200	1.12166600	-0.47465400
C	0.17575700	-0.75665500	0.97952200
C	0.09968000	-1.70511700	-1.18435100
C	1.27104000	0.36278400	-0.94427200
H	-2.12589100	-1.60962100	0.85252500
C	-4.17611200	-1.07161400	1.17370300
H	-3.46080900	1.96264400	-1.12534000
C	-4.93861100	0.94483100	0.07905800
C	1.06745000	-1.75814000	0.96109300
H	-0.20949200	-0.23327000	1.84765100
H	-0.69622200	-2.41231200	-0.93376000
H	0.17393100	-1.60502000	-2.27299500
C	1.44029100	-2.03087600	-0.48839600
H	1.09367500	0.86207300	-1.89924500
C	2.28638000	-0.80258600	-0.99717200
C	1.86750100	1.35569200	0.04467800
H	-4.37049800	-1.93080000	1.80979500
C	-5.19287400	-0.15470000	0.90463900

H	-5.72764500	1.66130600	-0.13236400
H	1.54700000	-2.22057700	1.81739100
H	1.89727500	-2.99864900	-0.70040600
H	2.67379700	-1.00705900	-1.99993100
C	3.43643800	-0.37990600	-0.09572300
O	1.38146100	2.38611200	0.46319100
N	3.12073600	0.87335100	0.43250500
H	-6.18049800	-0.29552900	1.33583000
O	4.45288400	-0.99918800	0.14795600
C	3.96547100	1.57613800	1.38408400
H	4.16929300	2.58793800	1.02420200
H	4.89393800	1.01198000	1.48005100
H	3.46659400	1.64611900	2.35537700

Energy = -937.2612898 a.u.