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Supporting Information for

Dual 1,3-dipolar cycloaddition of carbon dioxide: two C=O bonds of CO_2 react in one reaction

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Experimental Section

General

Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer using KBr optics. In situ IR spectra were recorded on a METTLER TOLEDO ReacIR-ic10 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 300 or 400 MHz (^{1}H NMR) and 75 or 100 MHz (^{13}C NMR) spectrumeter using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. High resolution mass spectra were obtained using GCT-TOF instrument with ESI source.

Typical procedure for the the synthesis of 1,6-dioxospiro[4,4]nonane-3,8-diene derivatives:

To a mixture of isocyanides 1(1.0 mmol) and dialkyl acetylenedicarboxylates 2 (1.5 mmol) and CO_2 (balloon, 1 atm) in 2.5 ml toluene at 80 ^{o}C. The mixture was stirred under room temperature for 24-48 h. After the completion (monitored by TLC), The solvent was then removed under reduced pressure and the residue was separated by column chromatography (silica gel, Merck 300–400 mesh) using Petroleum ether–Acetone (30~15 :1) as eluent.

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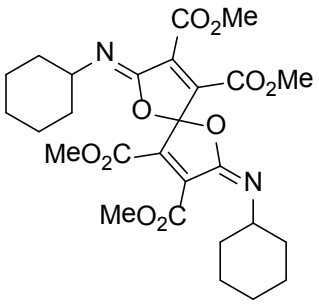
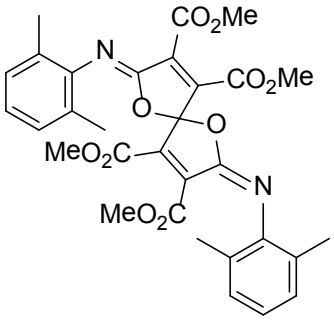
(2E,7Z)-tetramethyl
2,7-bis(cyclohexylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4a)



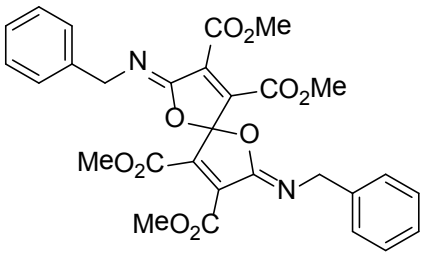
Yield 55% (80°C, 24h). White solide. mp 176-177 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 3.95 (s, 6H), 3.76 (s, 6H), 3.62-3.60 (m, 2H), 1.74-1.71 (m, 4H), 1.62-1.57 (m, 4H), 1.43-1.16 (m, 12H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 161.60, 159.83, 150.84, 139.87, 136.04, 111.49, 57.44, 53.53, 53.14, 33.45, 33.10, 25.74, 24.76, 24.66; **I.R.** (KBr) 2933, 2860, 1743, 1442, 1350, 1296, 1200, 1081, 1020 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{27}H_{34}N_2O_{10}Na^+$: 569.2111 ($[M+ Na]^+$), found: 569.2074.

(2E,7Z)-tetramethyl
2,7-bis(2,6-dimethylphenylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4b)



Yield 54% (80°C, 24h). Yellow solide. mp 185-186 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 7.01 (d, J = 7.0 Hz, 4H), 6.98-6.91 (m, 2H), 3.98 (s, 6H), 3.81 (s, 6H), 2.05 (s, 12H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 160.82, 159.36, 150.72, 142.97, 138.86, 137.27, 127.78, 127.39, 124.65, 106.98, 53.68, 53.41, 18.08; **I.R.** (KBr) 2934, 1739, 1447, 1360, 1295, 1094, 1020 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{31}H_{30}N_2O_{10}Na^+$: 613.1798 ($[M+Na]^+$), found: 613.1808.

(2Z,7Z)-tetramethyl
2,7-bis(benzylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4c)



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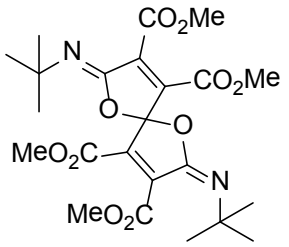
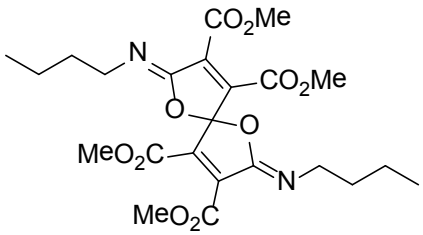
Yield 39% (80°C, 36h). Pale yellow solide. mp 45-46 °C; **^{1}H NMR (DMSO, 300 MHz)** δ 7.31-7.24 (m, 10H), 4.64 (s, 4H), 3.89 (s, 6H), 3.74 (s, 6H); **^{13}C NMR (DMSO, 75 MHz)** δ. 165.67, 164.12, 157.30, 143.54, 143.45, 141.13, 133.56, 132.76, 132.12, 116.74, 58.78, 56.76; **I.R.** (KBr) 3027, 2949, 1740, 1444, 1350, 1293, 1050 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{29}H_{26}N_2O_{10}Na^+$: 585.1485 ($[M+Na]^+$), found: 585.1486.

(2E,7Z)-tetramethyl
2,7-bis(tert-butylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4d)



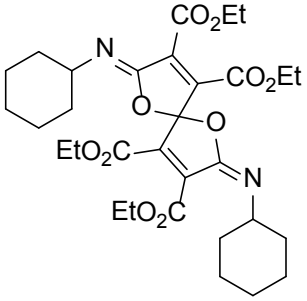
Yield 45% (80°C, 24h). Pale yellow solide. mp 78-79 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 3.96 (s, 6H), 3.78 (s, 6H), 1.28 (s, 18H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 161.88, 159.87, 148.69, 141.17, 135.08, 112.16, 55.97, 53.48, 53.12, 29.70, 29.63, 29.59; **I.R.** (KBr) 2969, 2056, 1744, 1446, 1310, 1295, 1218, 1096, 1031 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{23}H_{30}N_2O_{10}Na^+$: 517.1798 ($[M+Na]^+$), found: 517.1812.

(2Z,7Z)-tetramethyl
2,7-bis(butylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4e)



Yield 56% (80°C, 36h). Pale yellow oil; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 3.96 (s, 6H), 3.78 (s, 6H), 3.45 (t, 4H, J = 7.0 Hz), 1.58-1.52 (m, 4H), 1.35-1.28 (m, 4H), 0.89 (t, 6H, J = 7.3 Hz); **^{13}C NMR (DMSO, 75 MHz)** δ 161.03, 159.47, 151.84, 138.72, 135.95, 111.57, 53.84, 48.08, 32.07, 20.13, 13.85; **I.R.** (KBr) 2958, 2874, 1736, 1700, 1439, 1354, 1300, 1252 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{23}H_{31}N_2O_{10}^+$: 495.1979 ($[M+H]^+$), found: 495.1967.

(2E,7Z)-tetraethyl
2,7-bis(cyclohexylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4i)



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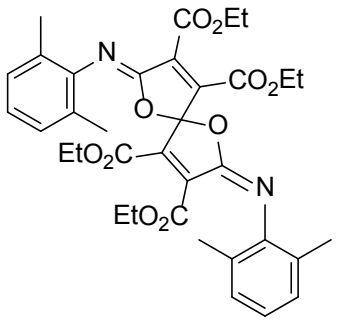
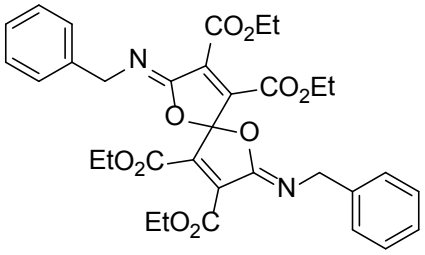
Yield 54% (80°C, 36h). White solide. mp 108-109 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 4.44 (dd, J = 14.1, 7.0 Hz, 4H), 4.21 (dd, J = 13.1, 6.1 Hz, 4H), 3.65-3.62 (m, 2H), 1.77-1.73 (m, 6H), 1.64-1.59 (m, 4H), 1.42-1.23 (m, 22H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 161.20, 159.37, 151.01, 140.33, 136.41, 111.53, 62.74, 62.39, 57.22, 33.48, 33.21, 25.79, 24.72, 24.62, 14.17, 13.84; **I.R.** (KBr) 2933, 2850, 1744, 1384, 1296, 1239, 1087, 1018 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{31}H_{42}N_2O_{10}Na^+$: 625.2737 ($[M+Na]^+$), found: 625.2701.

(2E,7Z)-tetraethyl
2,7-bis(2,6-dimethylphenylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4j)



Yield 63% (80°C, 24h). Yellow solide. mp 188-189 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 7.02 (d, J = 7.0 Hz, 4H), 6.97-6.94 (m, 2H), 4.47-4.43 (m, 4H), 4.35-4.31 (m, 2H), 4.21-4.17 (m, 2H), 2.06 (s, 12H), 1.39 (t, J = 6.0 Hz, 6H), 1.30 (t, J = 7.0 Hz, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 160.44, 158.91, 150.96, 143.10, 138.90, 137.53, 127.78, 127.47, 124.58, 62.98, 62.74, 18.16, 14.22, 13.95; **I.R.** (KBr) 2982, 2941, 2909, 1729, 1706, 1659, 1593, 1472, 1446, 1377, 1300, 1259, 1196, 1093, 1027 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{35}H_{38}N_2O_{10}Na^+$: 669.2424 ($[M+Na]^+$), found: 669.2443.

(2Z,7Z)-tetraethyl
2,7-bis(benzylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4k)



Yield 35% (80°C, 36h). Pale yellow oil; **^{1}H NMR (DMSO, 400 MHz)** δ 7.35-7.24 (m, 10H), 4.67(s, 4H), 4.40-4.35 (m, 4H), 4.24-4.17 (m, 4H),1.30 (t, J = 7.0 Hz, 6H), 1.12 (t, J = 7.0 Hz, 6H); **^{13}C NMR (DMSO, 75 MHz)** δ 165.19, 163.55, 157.43, 143.83, 143.65, 141.35, 133.50, 132.70, 132.08, 116.76, 67.84, 67.76, 56.69, 18.99, 18.49; **I.R.** (KBr) 2983, 1737, 1450, 1382, 1340, 1289, 1100, 1019 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{33}H_{34}N_2O_{10}Na^+$: 641.2111 ($[M+Na]^+$), found: 641.2097.

(2E,7Z)-tetraethyl

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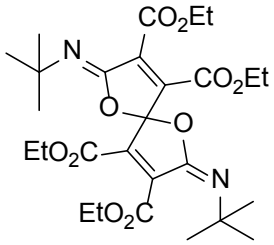
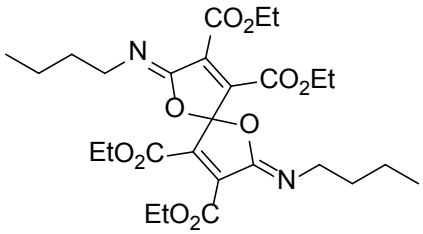
2,7-bis(tert-butylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4l)



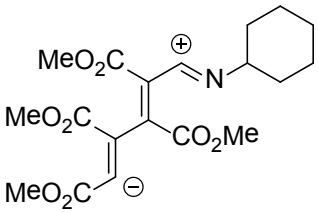
Yield 54% (80°C, 36h). Pale yellow solide. mp 58-59 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 4.57 (q, J_1 = 7.1 Hz, J_2 =12 Hz, 4H), 4.37-4.33 (m, 4H), 1.52(t, J = 7.1 Hz, 6H), 1.42-1.38 (m, 24H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ161.43, 159.39, 148.81, 141.45, 135.39, 112.20, 62.56, 62.26, 55.75, 29.78, 29.58, 14.27, 14.09, 13.97; **I.R.** (KBr) 2976, 2936, 1733, 1699, 1466, 1375, 1336, 1296, 1242, 1212, 1095, 1037 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{27}H_{38}N_2O_{10}Na^+$: 573.2424 ($[M+Na]^+$), found: 573.2406.

(2Z,7Z)-tetraethyl
2,7-bis(butylimino)-1,6-dioxaspiro[4.4]nona-3,8-diene-3,4,8,9-tetracarboxylate(4m)



Yield 55% (80°C, 36h). Pale yellow oil; **^{1}H NMR (DMSO, 400 MHz)** δ 4.36-4.33 (m, 4H), 4.21-4.18 (m, 4H), 3.41(t, J = 6.7 Hz, 4H), 1.52-1.45(m, 4H), 1.30-1.23 (m, 10H), 1.16 (t, J = 7.0 Hz, 6H), 0.85(t, J = 7.2 Hz, 6H); **^{13}C NMR (DMSO, 75 MHz)** δ 160.54, 158.91, 151.94, 139.05, 136.18, 111.58, 62.91, 62.82, 48.03, 32.15, 20.16, 14.18, 13.88, 13.77; **I.R.** (KBr) 2935, 2874, 1733, 1702, 1578, 1466, 1375, 1338, 1299, 1249, 1095, 1018 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{27}H_{38}N_2O_{10}Na^+$: 573.2424 ($[M+ Na]^+$), found: 573.2456.

N-((2E,4Z)-6-methoxy-2,3,4-tris(methoxycarbonyl)-6-oxohexa-2,4-dienylidyne)cyclohexanaminium(5a)



Yield 2% (80°C, 24h). Pale yellow oil; **^{1}H NMR (DMSO, 400 MHz)** δ 3.87 (s, 3H) , 3.84 (s, 3H) , 3.78 (s, 3H) , 3.48 (s, 3H) , 1.70-1.65 (m, 4H) , 1.59-1.56 (m, 1H) , 1.30-1.16 (m, 6H); **^{13}C NMR (DMSO, 101 MHz)** δ 166.30, 164.49, 157.67, 156.12, 143.99, 143.30, 106.68, 84.30, 81.88, 62.18, 59.31, 59.24, 59.20, 58.88, 38.64, 38.49, 30.77, 29.70, 29.60; **I.R.** (KBr) 2934, 2856, 1727, 1692, 1437, 1350, 1264, 1134, 1092, 1032 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{19}H_{23}NO_8^-$: 393.1424 ($[M-H]^-$), found: 393.1412.

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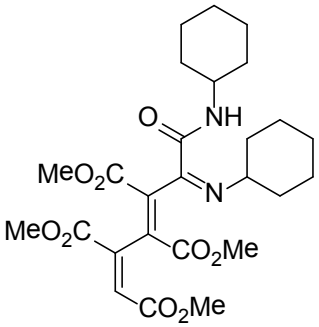
(1E,3E,5Z)-tetramethyl
6-(cyclohexylamino)-5-(cyclohexylimino)-6-oxohexa-1,3-diene-1,2,3,4-tetracarboxylate(7a)



Yield 3% (80°C, 24h). Pale yellow solide. mp 162-163 °C; **^{1}H NMR (DMSO, 400 MHz)** δ 7.71 (d, 1H, $^{3}J_{HH}$ = 17.6 Hz), 6.69 (s, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.53-3.51(m, 1H), 3.37 (s, 3H), 2.42-2.34 (m, 1H), 1.93-1.69(m, 8H), 1.54-1.29 (m, 8H), 1.16-1.06 (m, 4H); **^{13}C NMR (DMSO, 101 MHz)** δ 173.62, 172.35, 171.90, 170.20, 167.50, 150.80, 150.78, 144.11, 131.32, 115.03, 61.99, 58.93, 58.84, 57.88, 55.99, 38.37, 37.98, 37.01, 35.96, 34.71, 33.89, 31.75, 31.37, 30.75, 30.42, 30.07; **I.R.** (KBr) 2924, 2853, 1753, 1675, 1618, 1461, 1322, 1265, 1218, 1101, 1031 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{26}H_{35}N_2O_9^-$: 519.2343 ([M-H]$^-$), found: 519.2328.

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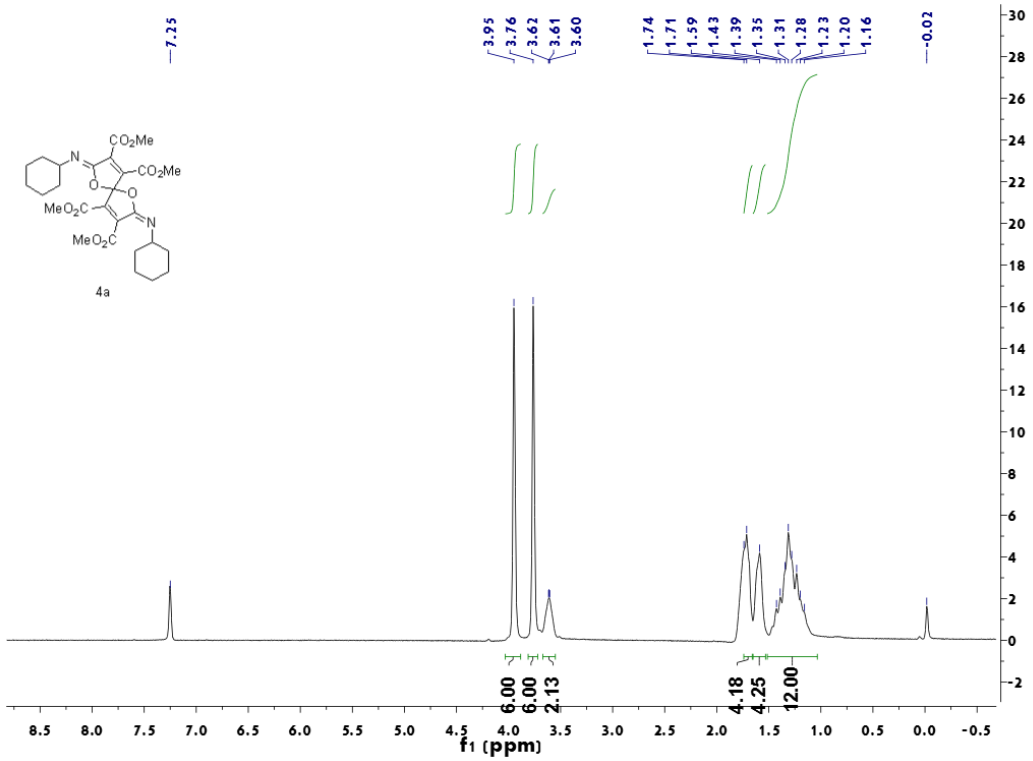

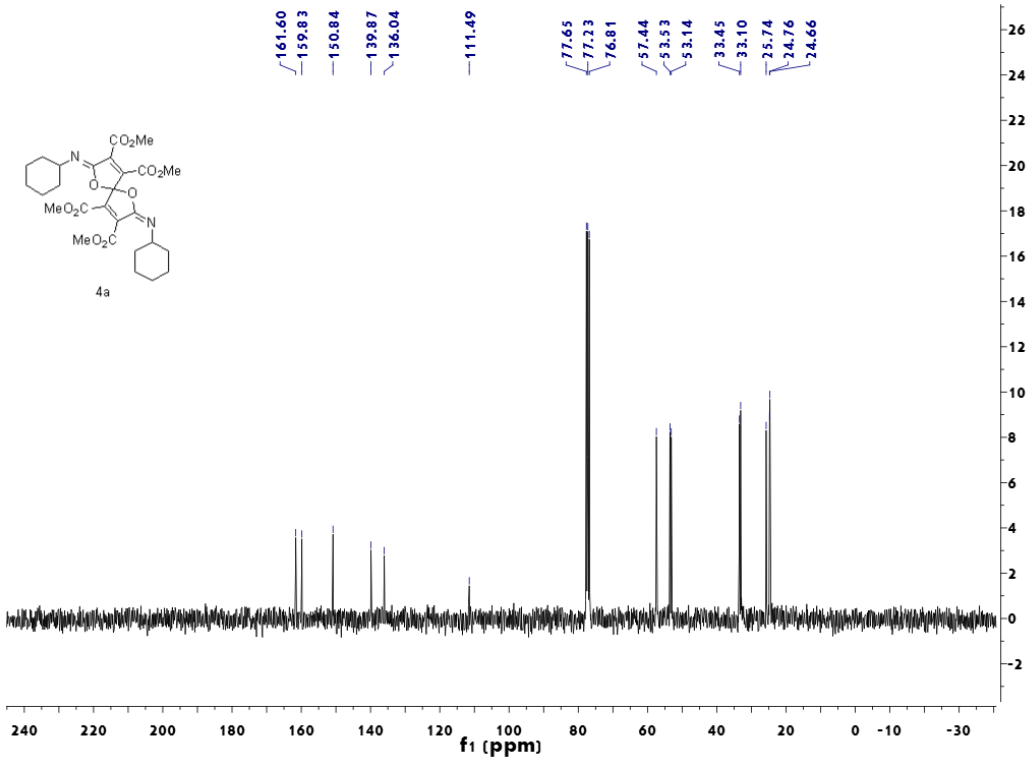

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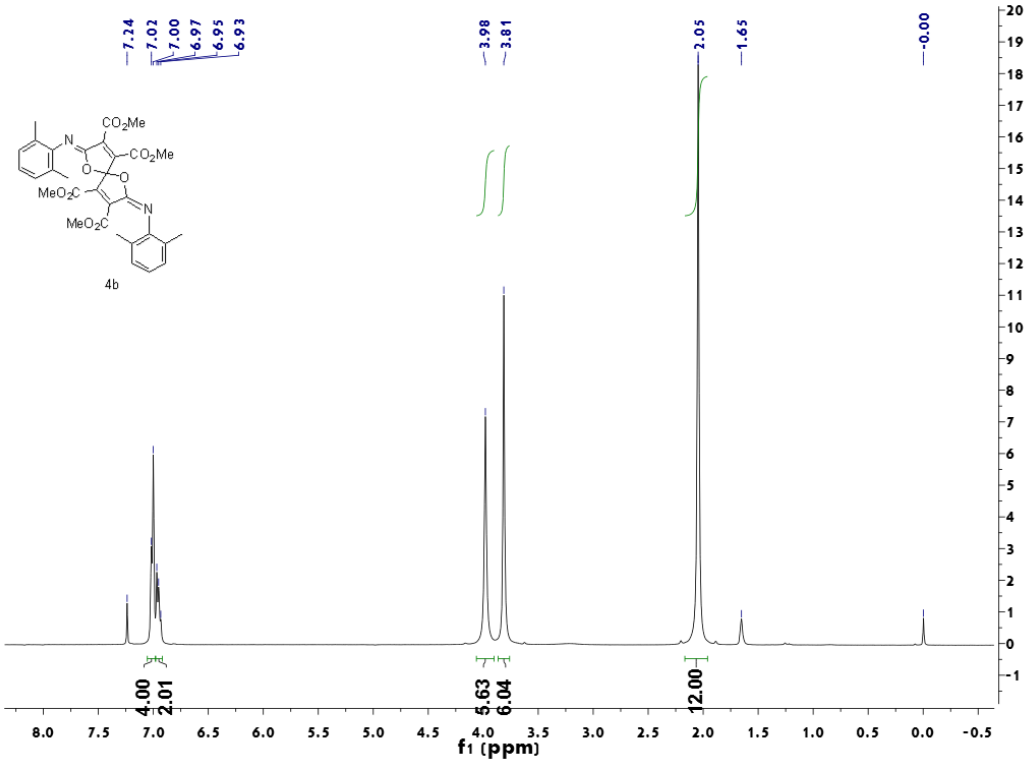

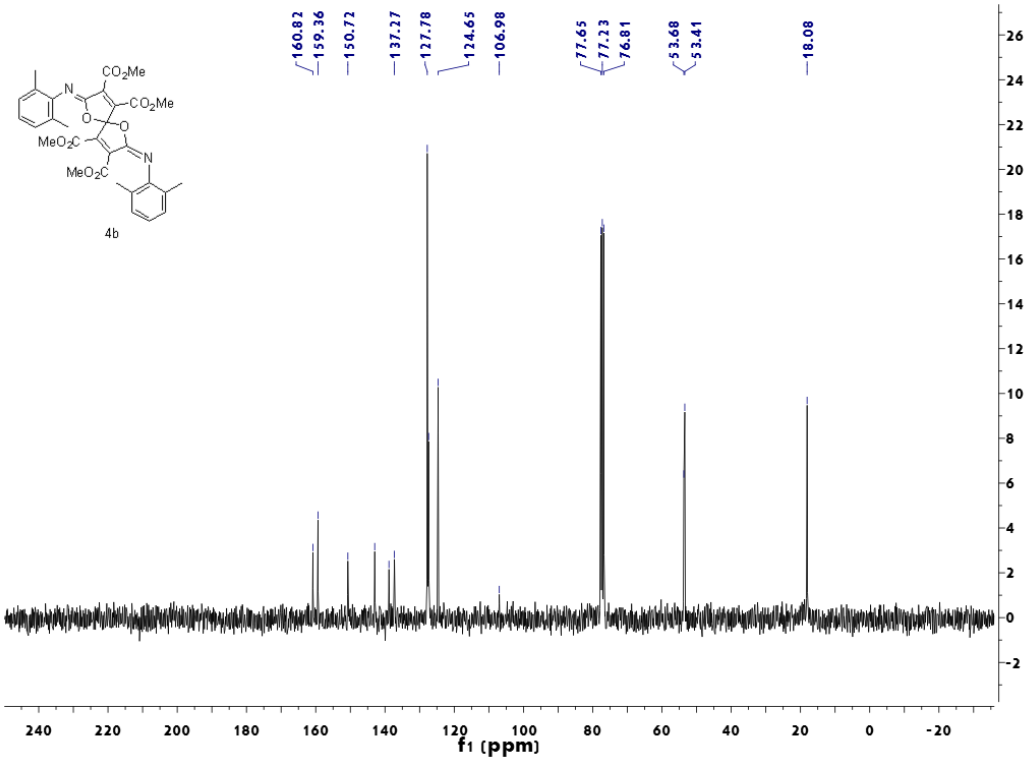

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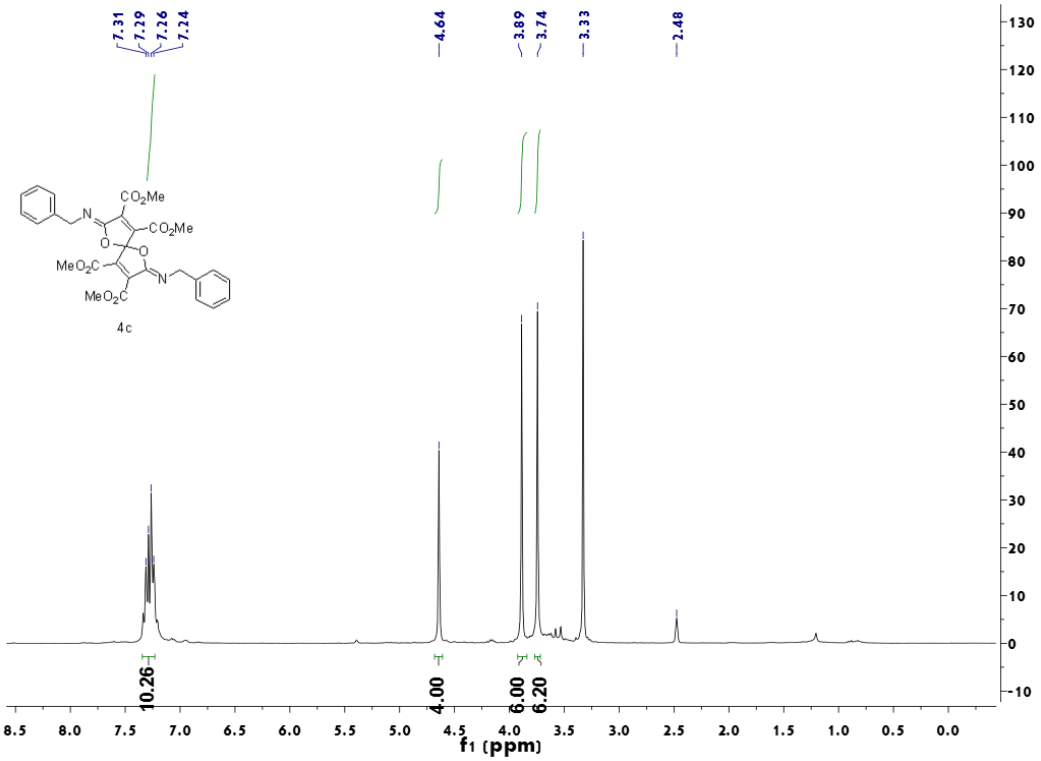

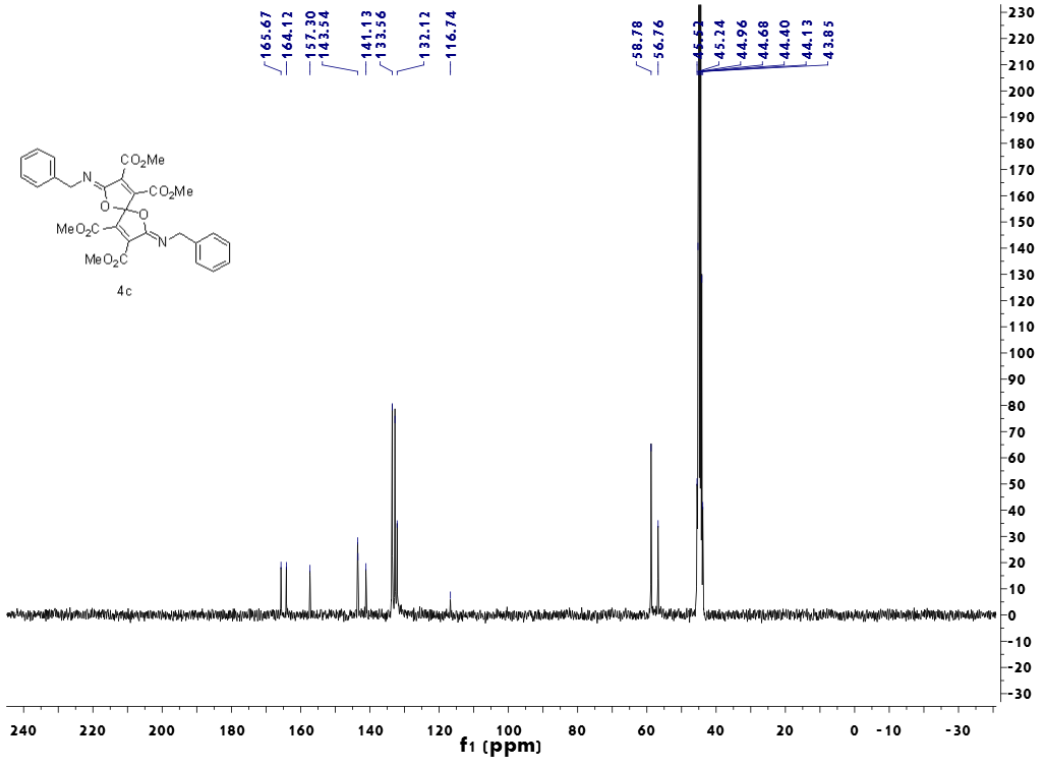

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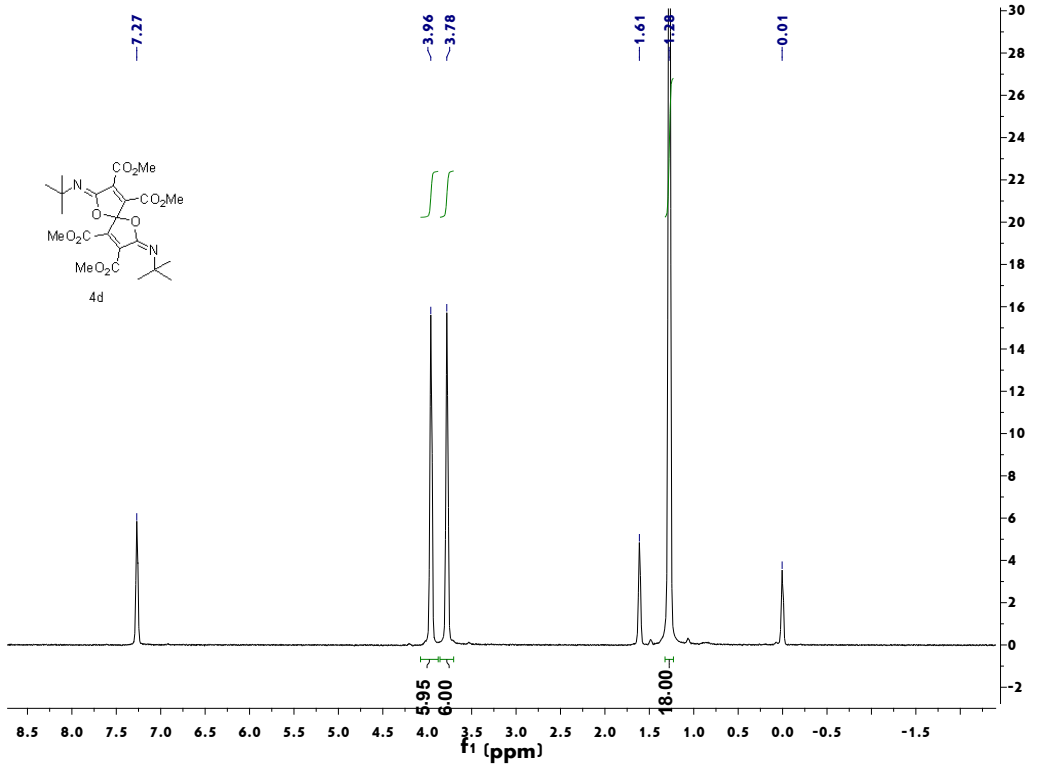

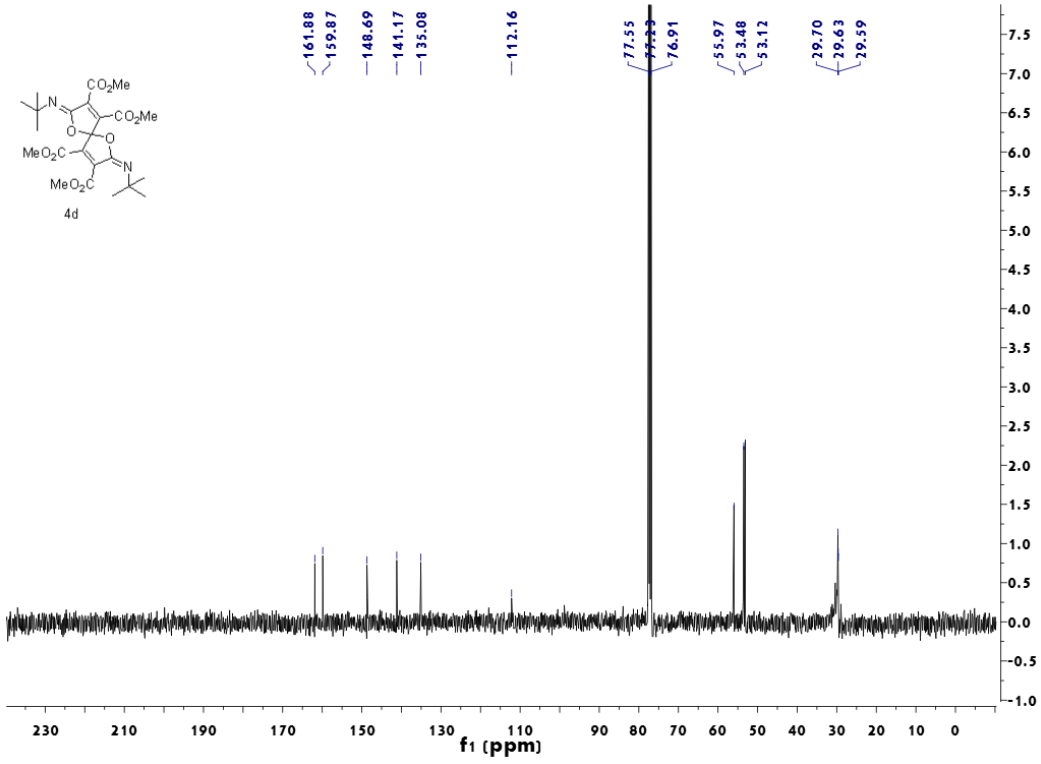

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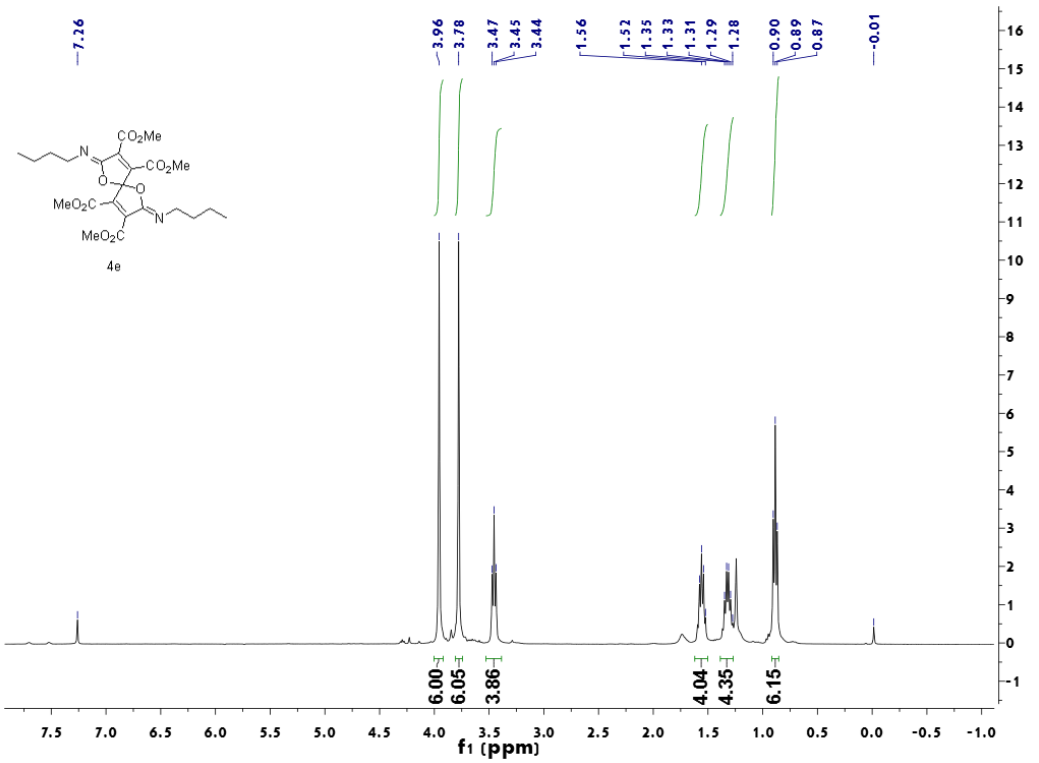

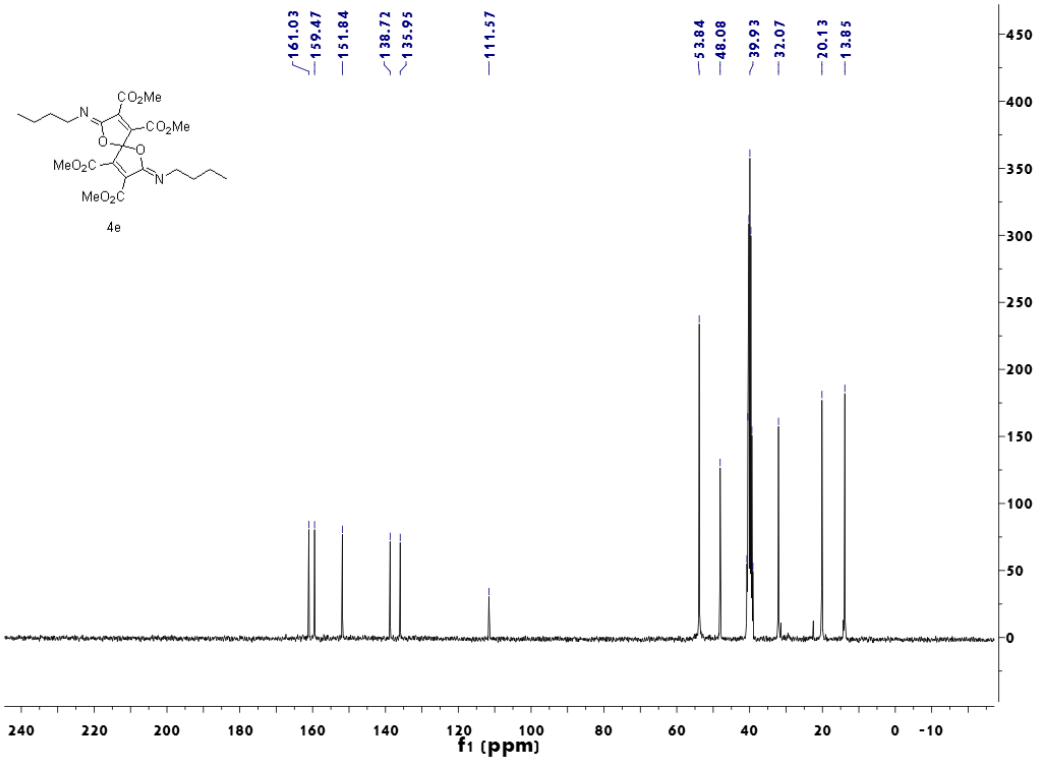

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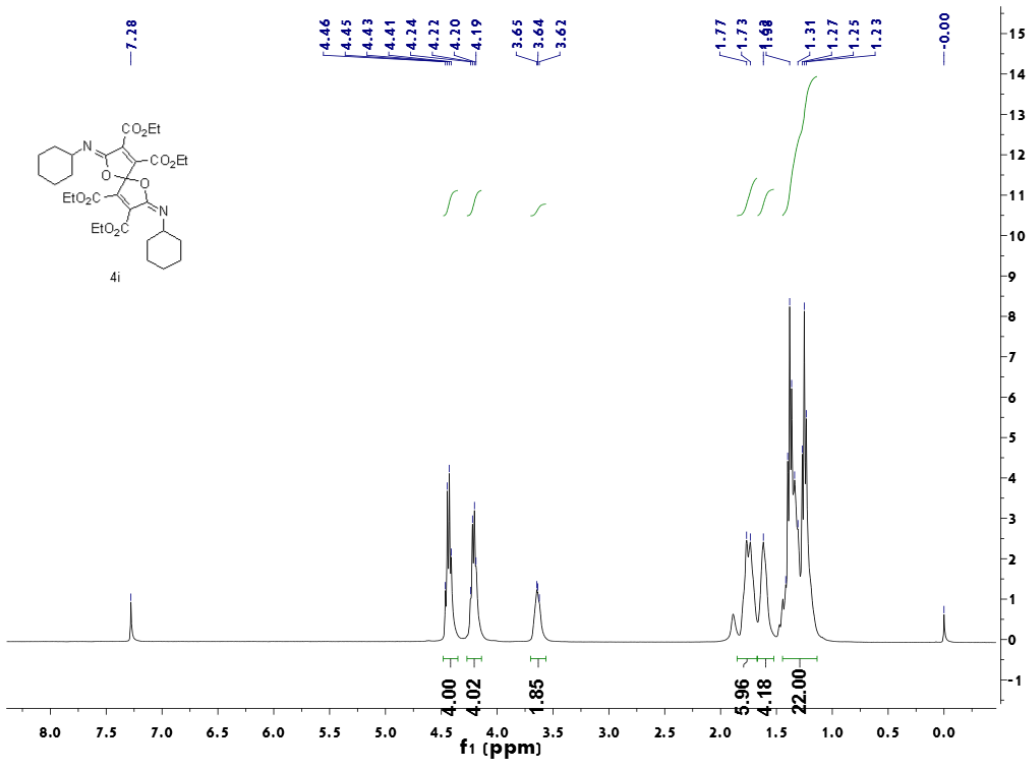

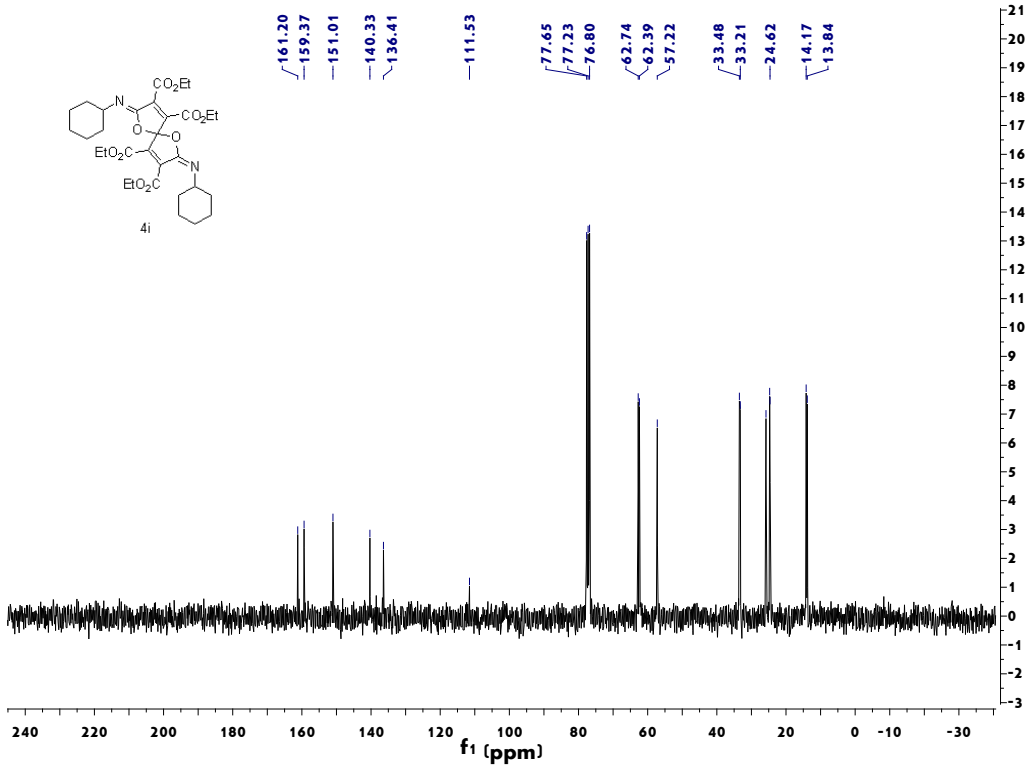

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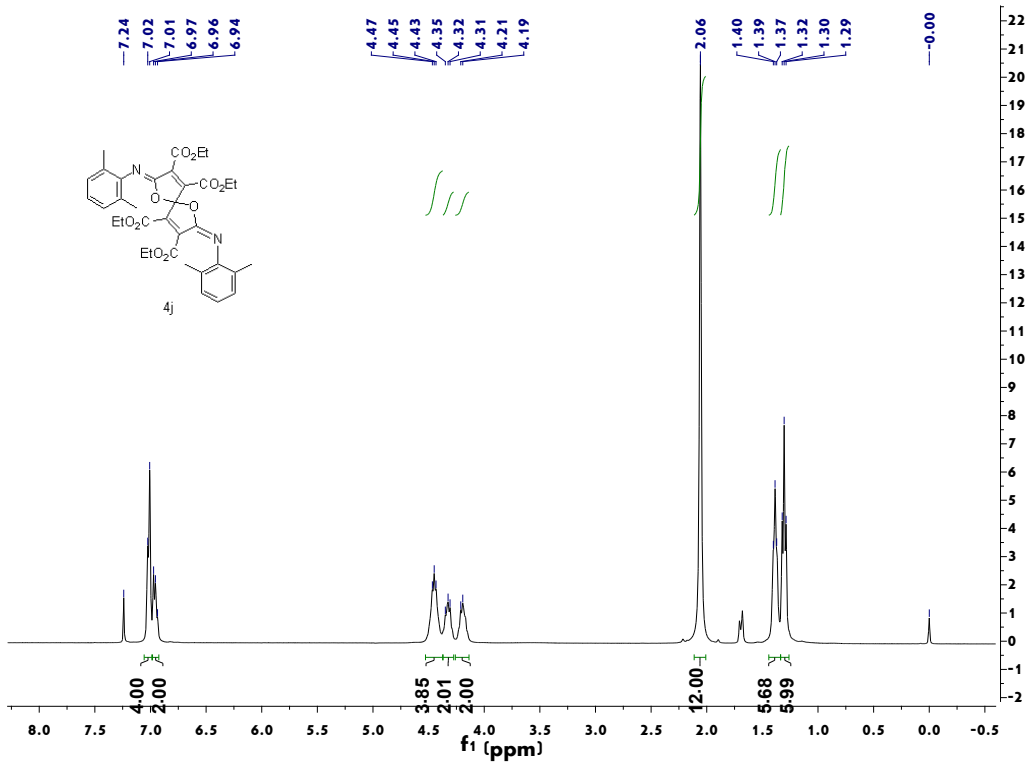

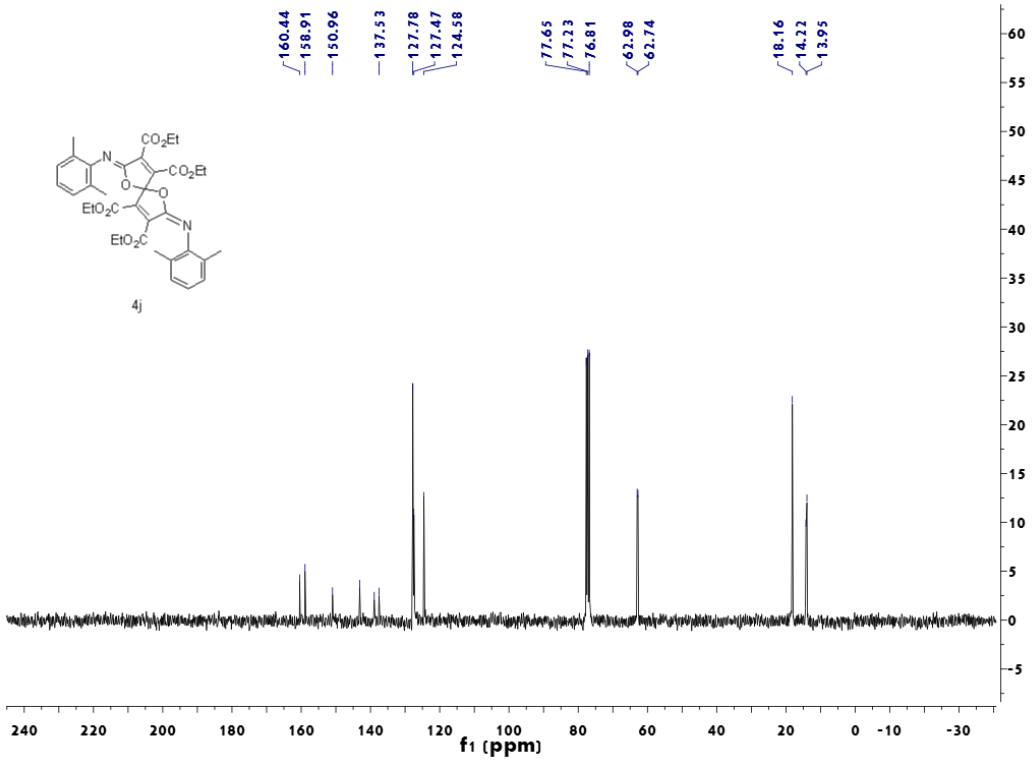

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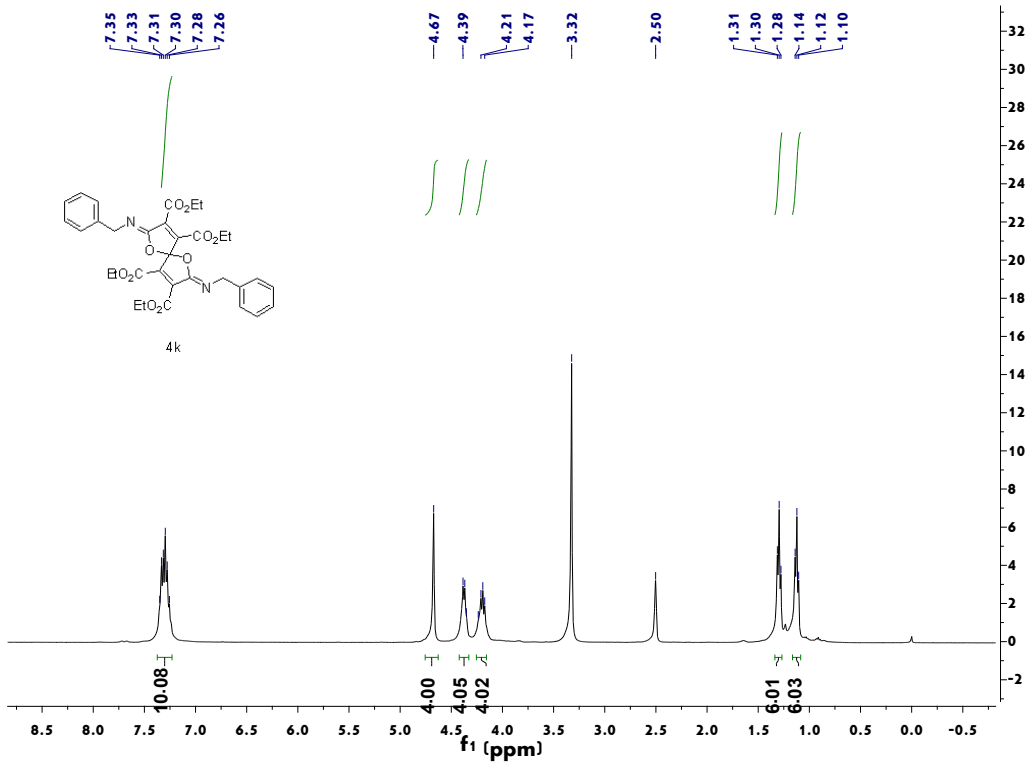

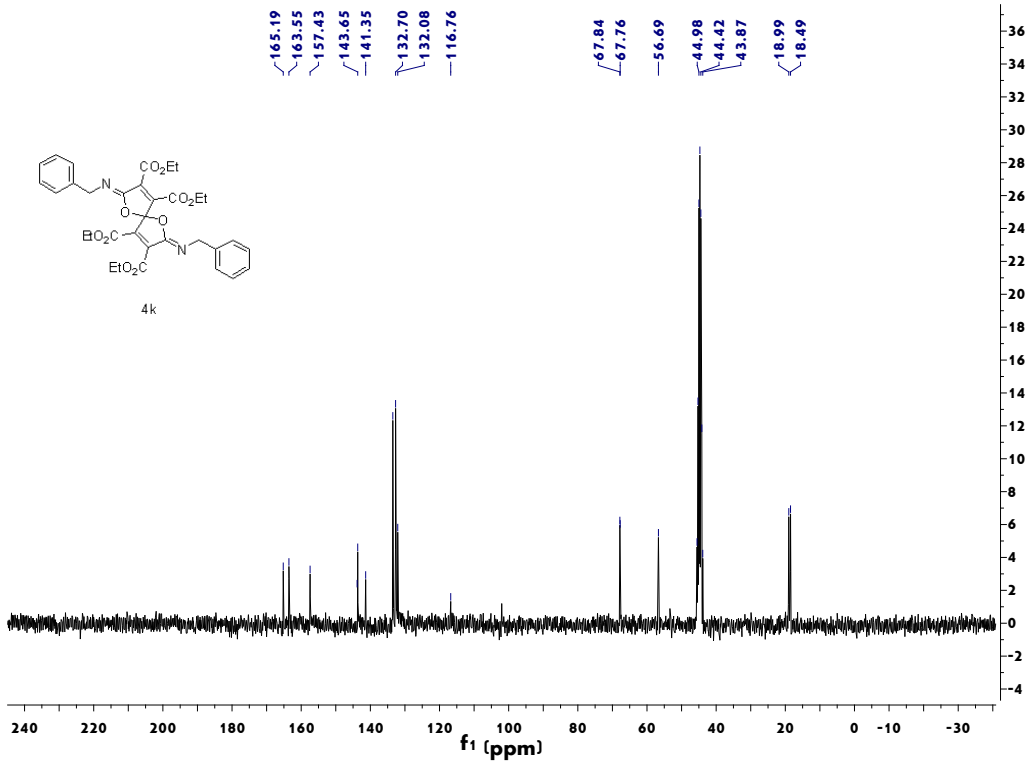

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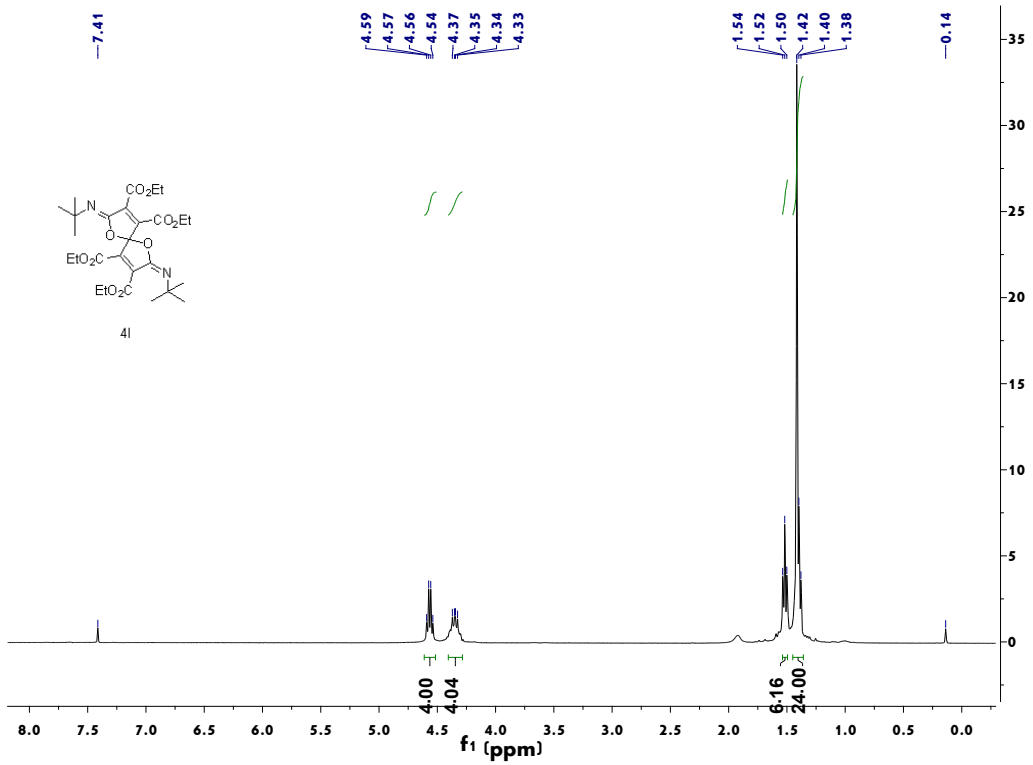

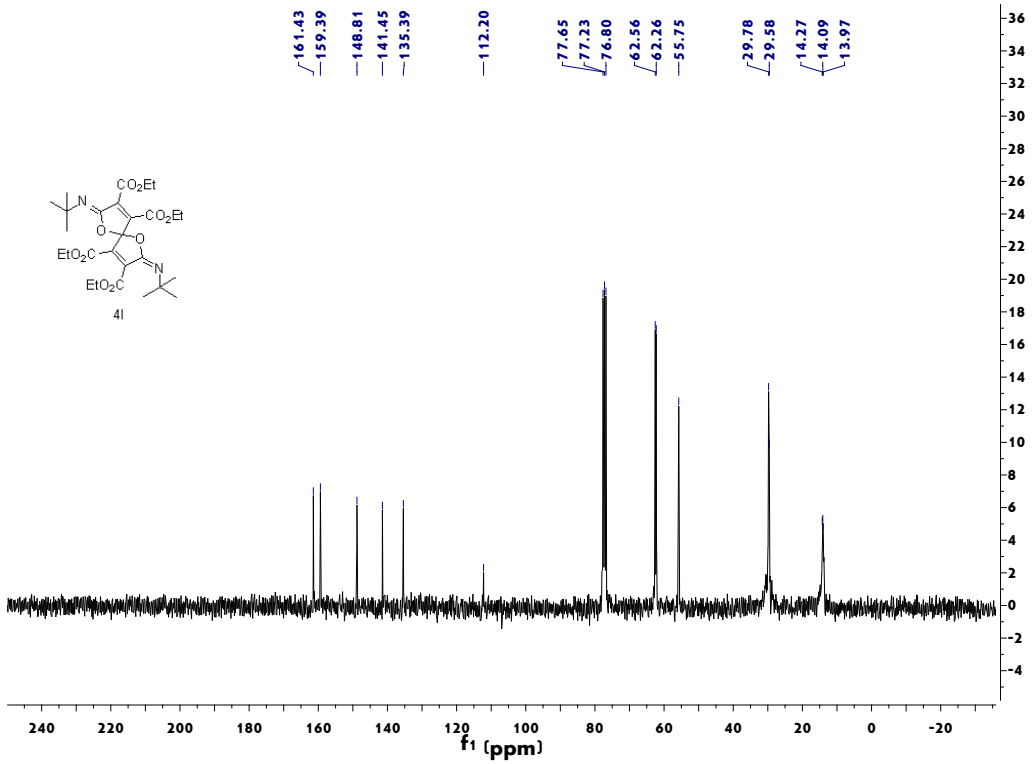

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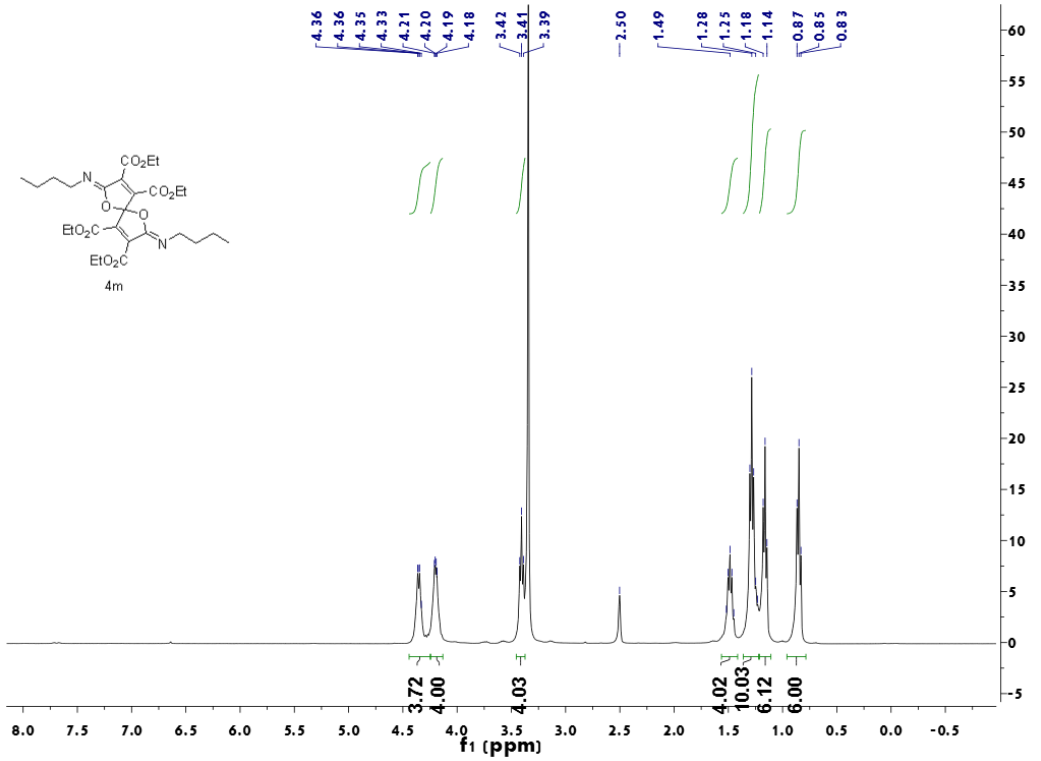

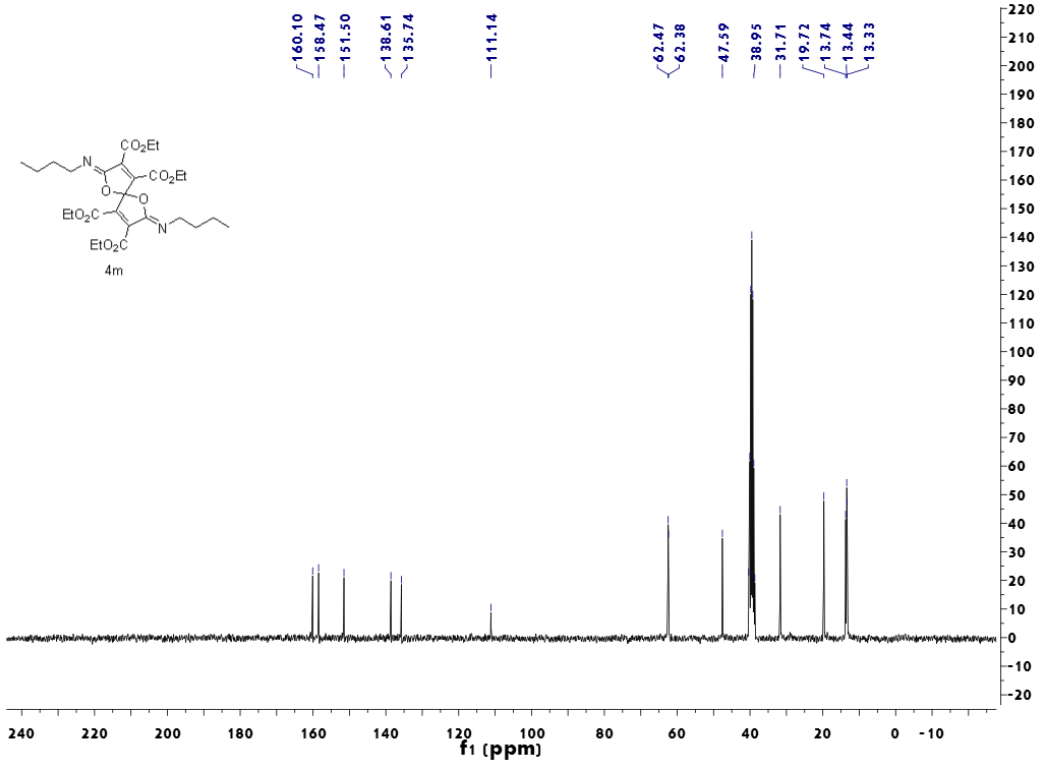

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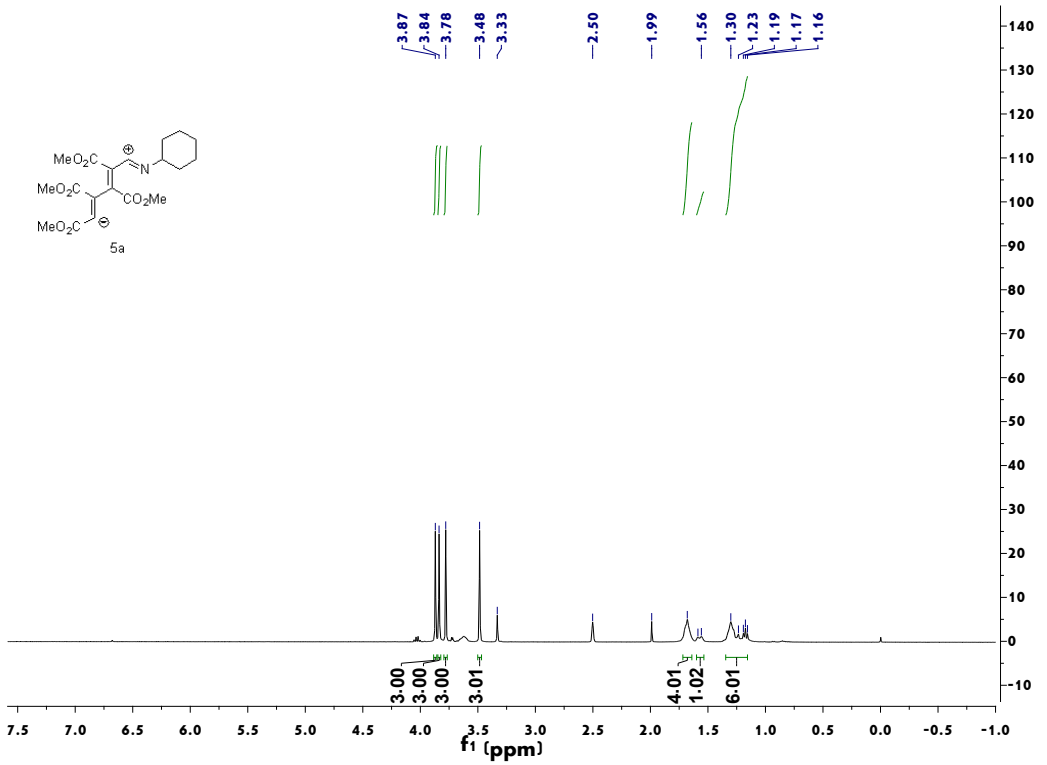

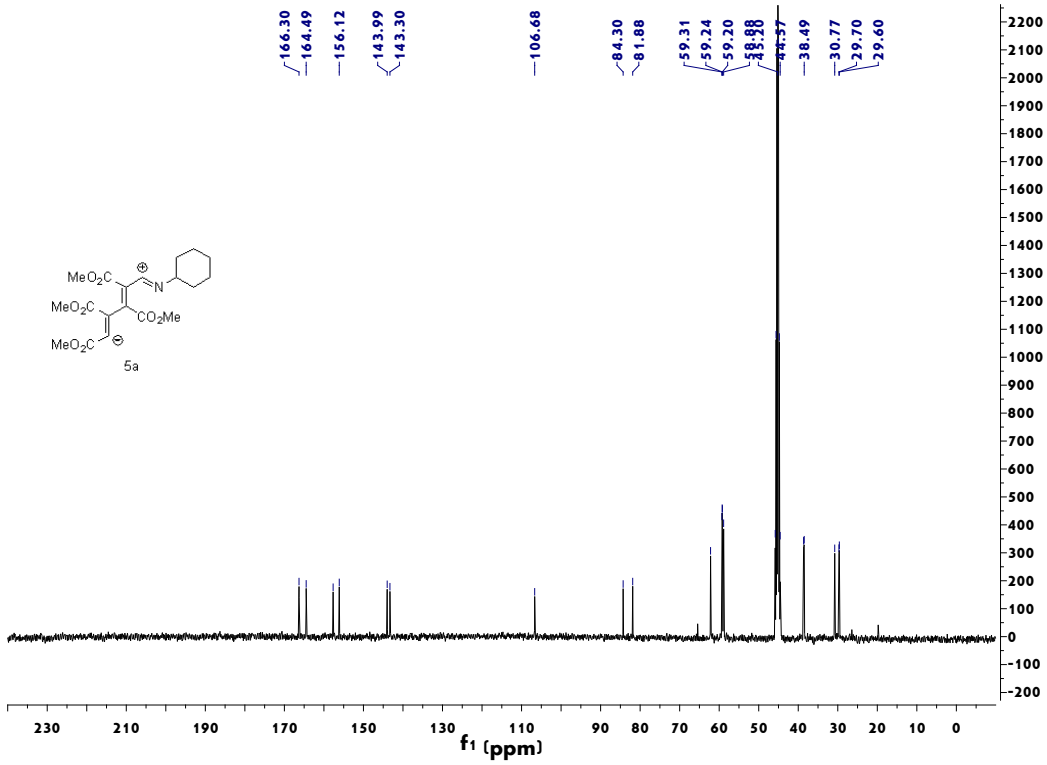

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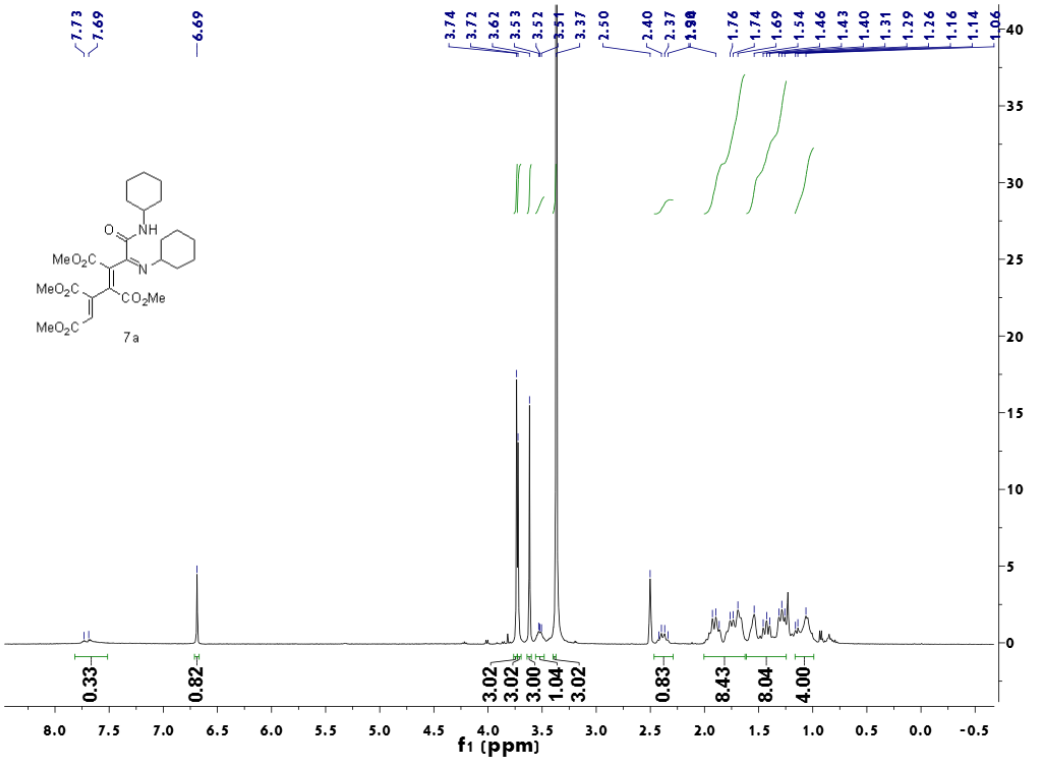

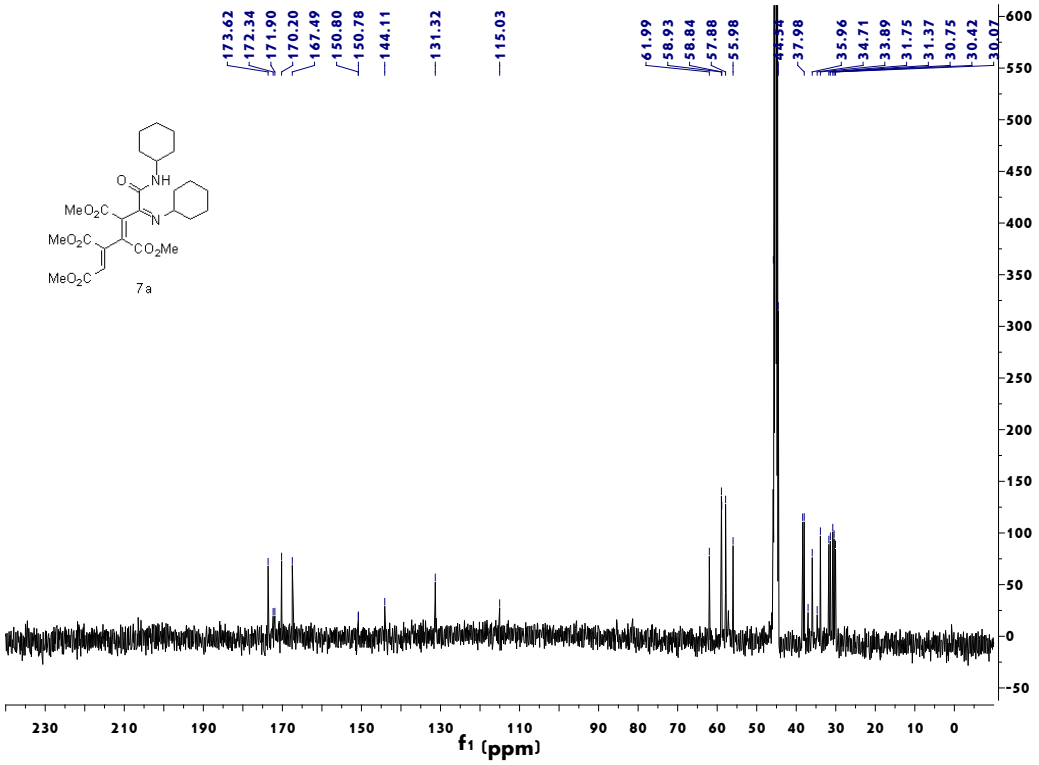

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In situ IR experiments

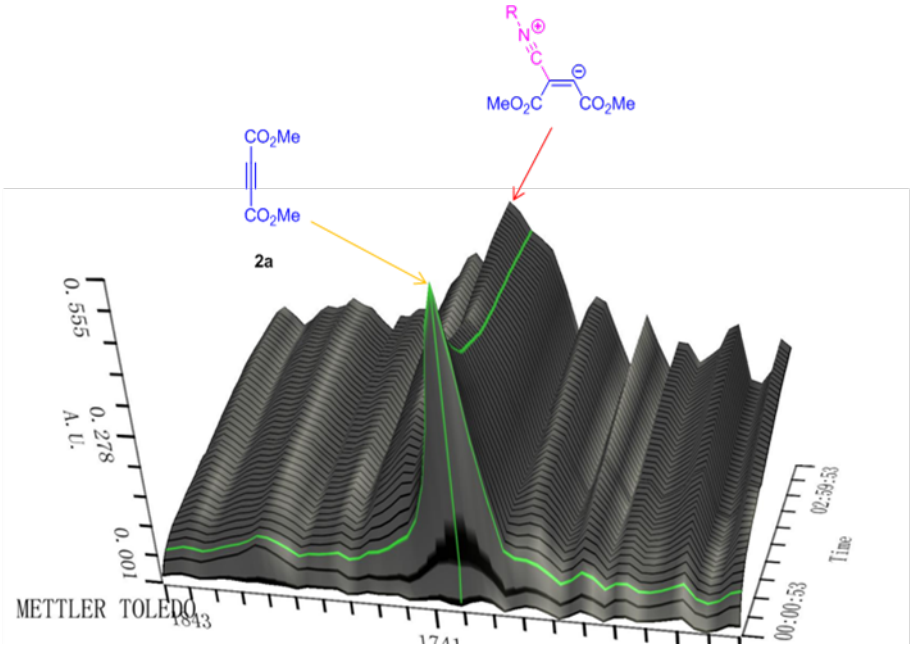

Figure 1. In situ IR experiment of **1a** with **2a** in toluene without CO_2.

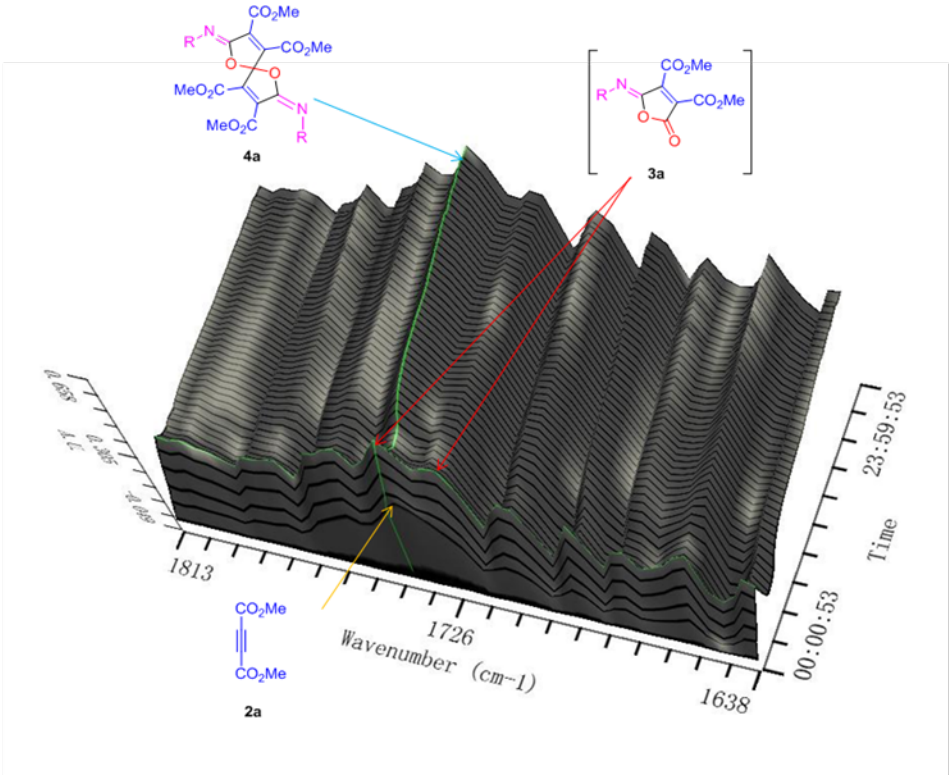

Figure 2. In situ IR experiment of **1a** with **2a** and CO_2 (1 atm) .