

**Thermal Decarboxylative Cloke-Wilson Rearrangement of Dispirocyclopropanes
Derived from *para*-Quinone Methides and Bromo-Meldrum's Acids: An
Approach to Spirobutyrolactone *para*-Dienones**

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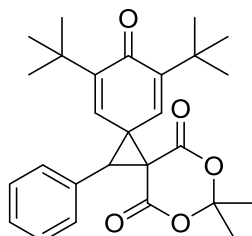
General Information

Reagents and solvents were purchased from commercial sources and used without further purification. The *para*-quinone methides and bromo-Meldrum's acids were prepared according to the known literatures.^{1,2} TLC was performed on dry silica gel plates (10-40 μm , from Yantai Dexin Biotechnology Co. Ltd.) eluting with petroleum ether (bp 60-90 $^{\circ}\text{C}$) and ethyl acetate. Flash column chromatography was performed over silica gel (200-300 mesh, from Henan Sanlian Science and Trade Co. Ltd.). Melting points were determined using a XT4A hot-stage apparatus. IR spectra were obtained using an IFS25 FT-IR spectrometer. NMR spectra (^1H and ^{13}C) were recorded on a Bruker AV400 spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) using CDCl_3 as the solvent (referenced internally to Me_4Si); J values were given in Hertz. High-resolution mass spectra were recorded on a Micromass Q-TOF mass spectrometer. X-ray crystal structure analysis was performed using a MM007HF Saturn 724+ spectrometer.

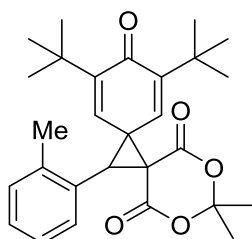
General Procedure for the Synthesis of Dispirocyclopropanes **3**

The solution of 0.1 mmol of *para*-quinone methide **1** (1 equiv.), 0.3 mmol of bromo-Meldrum's acid **2** (3 equiv.), and 0.2 mmol of DBU (2 equiv.) in 0.5 mL of DCM (0.2 *M*) was stirred at 15 °C. The reaction process was monitored by TLC analysis. After the reaction was finished, the reaction mixture was quenched with saturated ammonium chloride (2 mL). The mixture was then extracted with diethyl ether (3 × 5 mL). The combined organic phase was washed with brine (10 mL), dried using anhydrous Na₂SO₄, and then filtered. The solvent was removed under vacuum, and the crude was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 20/1) to give the desired product **3**.

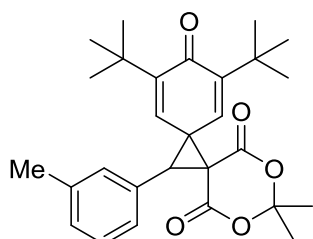
Spectroscopic Data of Dispirocyclopropanes 3



9,11-Di-tert-butyl-3,3-dimethyl-13-phenyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3aa). Yellow solid; yield: 41.9 mg (96%); mp 85-87 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.36-7.35 (m, 3H), δ = 7.17-7.16 (m, 2H), δ = 6.69 (d, J = 2.3 Hz, 1H), δ = 6.60 (d, J = 2.3 Hz, 1H), δ = 4.63 (s, 1H), δ = 1.74 (s, 3H), δ = 1.33 (s, 3H), δ = 1.26 (s, 9H), δ = 1.19 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.6, 164.5, 161.8, 153.8, 153.3, 134.5, 131.8, 130.6, 129.3, 128.0, 104.9, 46.2, 43.9, 42.3, 36.0, 35.7, 29.2, 29.2, 27.5, 26.9 ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₂₇H₃₂O₅Na 459.2142; Found 459.2143.

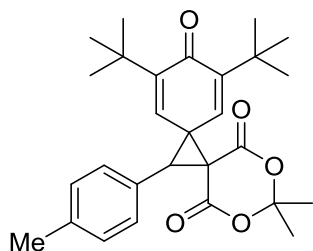


9,11-Di-tert-butyl-3,3-dimethyl-13-(o-tolyl)-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3ba). Yellow solid; yield: 40.5 mg (90%); mp 93-95 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.30-7.26 (m, 1H), δ = 7.23-7.17 (m, 2H), δ = 7.05 (d, J = 7.6 Hz, 1H), δ = 6.79 (d, J = 2.8 Hz, 1H), δ = 6.60 (s, J = 2.8 Hz, 1H), δ = 4.40 (s, 1H), δ = 2.19 (s, 3H), δ = 1.74 (s, 3H), δ = 1.33 (s, 3H), δ = 1.27 (s, 9H), δ = 1.21 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.6, 164.4, 162.0, 154.0, 153.0, 137.8, 134.7, 132.2, 130.3, 129.6, 128.7, 128.3, 125.7, 104.9, 46.2, 43.3, 36.0, 35.8, 29.3, 29.3, 27.6, 26.9, 26.8, 19.7 ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₂₈H₃₄O₅Na 473.2298; Found 473.2296.

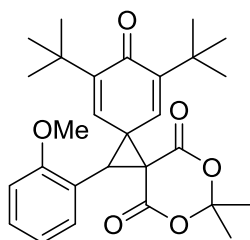


9,11-Di-tert-butyl-3,3-dimethyl-13-phenyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3ca). Yellow solid; yield: 43.2 mg (96%); mp 89-91 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.23 (d, J = 8.0 Hz, 1H), δ = 7.14 (d, J = 7.6 Hz,

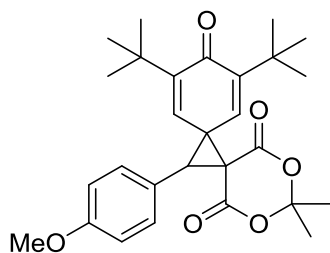
1H), $\delta = 6.96$ (d, $J = 7.4$ Hz, 2H), $\delta = 6.71$ (d, $J = 2.8$ Hz, 1H), $\delta = 6.59$ (s, $J = 2.8$ Hz, 1H), $\delta = 4.60$ (s, 1H), $\delta = 2.34$ (s, 3H), $\delta = 1.74$ (s, 3H), $\delta = 1.33$ (s, 1H), $\delta = 1.26$ (s, 9H), $\delta = 1.19$ (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100MHz, CDCl_3 , 25 °C): $\delta = 184.7$, 164.6, 161.9, 153.8, 153.2, 138.0, 134.6, 132.0, 130.6, 130.1, 128.8, 128.2, 126.4, 104.9, 46.3, 43.9, 42.3, 36.0, 35.8, 29.3, 29.3, 27.6, 26.9, 21.4 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_5\text{Na}$ 473.2298; Found 473.2299.



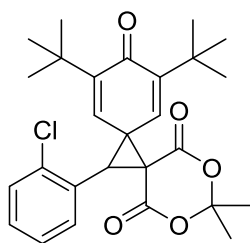
9,11-Di-tert-butyl-3,3-dimethyl-13-(p-tolyl)-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3da). Yellow solid; yield: 39.6 mg (88%); mp 87-89 °C; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): $\delta = 7.16$ (d, $J = 7.9$ Hz, 2H), $\delta = 7.04$ (d, $J = 7.8$ Hz, 2H), $\delta = 6.69$ (d, $J = 2.8$ Hz, 1H), $\delta = 6.59$ (d, $J = 2.8$ Hz, 1H), $\delta = 4.59$ (s, 1H), $\delta = 2.37$ (s, 3H), $\delta = 1.74$ (s, 3H), $\delta = 1.32$ (s, 3H), $\delta = 1.26$ (s, 9H), $\delta = 1.19$ (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100MHz, CDCl_3 , 25 °C): $\delta = 184.7$, 164.6, 161.9, 153.8, 153.3, 137.7, 134.7, 132.0, 129.3, 129.2, 129.1, 127.6, 127.3, 104.9, 46.4, 43.8, 42.4, 36.0, 35.8, 29.3, 29.3, 28.7, 27.6, 26.9, 21.3 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_5\text{Na}$ 473.2298; Found 473.2297.



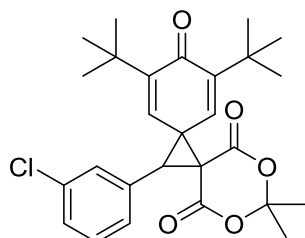
9,11-Di-tert-butyl-13-(2-methoxyphenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3ea). Yellow solid; yield: 44.7 mg (96%); mp 106-108 °C; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): $\delta = 7.35$ (m, 1H), $\delta = 7.04$ (d, $J = 8.5$ Hz, 1H), $\delta = 6.96$ -6.89 (m, 2H), $\delta = 6.76$ (d, $J = 2.8$ Hz, 1H), $\delta = 6.66$ (d, $J = 2.8$ Hz, 1H), $\delta = 4.31$ (s, 1H), $\delta = 3.78$ (s, 3H), $\delta = 1.74$ (s, 3H), $\delta = 1.33$ (s, 3H), $\delta = 1.26$ (s, 9H), $\delta = 1.19$ (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100MHz, CDCl_3 , 25 °C): $\delta = 184.9$, 164.7, 162.2, 158.2, 153.4, 152.8, 135.0, 132.4, 129.5, 129.3, 120.1, 119.7, 110.3, 104.5, 55.6, 45.9, 42.6, 40.6, 35.9, 35.7, 29.3, 27.6, 26.9, 26.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_6\text{Na}$ 489.2248; Found 489.2249.



9,11-Di-tert-butyl-13-(4-methoxyphenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3fa**). Yellow solid; yield: 41.5 mg (89%); mp 86-88 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.07 (d, *J* = 8.3 Hz, 2H), δ = 6.88(d, *J* = 8.7 Hz, 2H), δ = 6.70 (d, *J* = 2.8 Hz, 1H), δ = 6.59 (d, *J* = 2.8 Hz, 1H), δ = 4.58 (s, 1H), δ = 3.82 (s, 3H), δ = 1.74 (s, 3H), δ = 1.32 (s, 3H), δ = 1.26 (s, 9H), δ = 1.19 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.7, 164.6, 161.9, 159.2, 153.8, 153.3, 134.7, 131.9, 130.5, 128.7, 122.5, 114.1, 113.7, 104.8, 55.2, 46.5, 43.5, 42.4, 36.0, 35.7, 29.3, 29.2, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₈H₃₄O₆Na 489.2248; Found 489.2247.

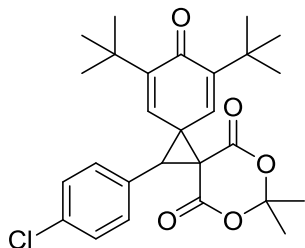


9,11-Di-tert-butyl-13-(2-chlorophenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3ga**). Yellow solid; yield: 41.4 mg (88%); mp 102-104 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.44 (d, *J* = 7.8 Hz, 2H), δ = 7.29 (m, 2H), δ = 7.16 (d, *J* = 7.4 Hz, 1H), δ = 6.74 (s, 1H), δ = 6.65 (s, 1H), δ = 4.40 (s, 1H), δ = 1.75 (s, 3H), δ = 1.34 (d, *J* = 0.8 Hz 3H), δ = 1.26 (d, *J* = 1.8 Hz 9H), δ = 1.20 (d, *J* = 1.8 Hz 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.6, 164.2, 162.1, 153.9, 153.3, 135.6, 134.4, 131.4, 130.0, 129.6, 126.5, 104.9, 45.9, 42.8, 42.6, 36.1, 35.8, 29.3, 28.8, 27.5, 27.0 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₇H₃₁ClO₅Na 493.1752; Found 493.1753.

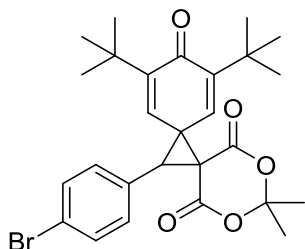


9,11-Di-tert-butyl-13-(3-chlorophenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3ha**). Yellow solid; yield: 42.3 mg (90%); mp 94-96 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.44 (d, *J* = 7.8 Hz, 2H), δ = 7.29 (m, 2H), δ = 7.32-7.27 (m, 2H), δ = 7.16 (s, 1H), δ = 7.08-7.06 (m, 1H), δ = 6.63 (d, *J* = 2.8 Hz, 1H), δ = 6.56 (d, *J* = 2.8 Hz, 1H), δ = 4.56 (s, 1H), δ = 1.75 (s, 3H), δ = 1.33 (s, 3H), δ

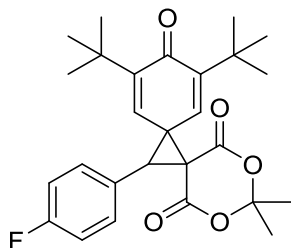
= 1.26 (s, 9H), δ = 1.20 (s, 9H) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (100MHz, CDCl_3 , 25 °C): δ = 184.5, 164.3, 161.8, 154.1, 153.8, 134.2, 134.1, 132.7, 131.2, 129.6, 129.5, 128.3, 127.7, 105.1, 45.9, 42.9, 42.2, 36.1, 35.8, 29.3, 29.3, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{31}\text{ClO}_5\text{Na}$ 493.1752; Found 493.1754.



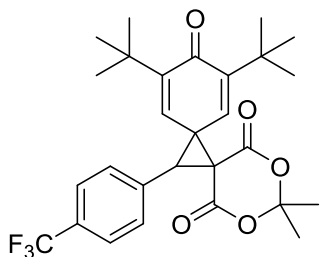
9,11-Di-tert-butyl-13-(4-chlorophenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3ia). Yellow solid; yield: 44.2 mg (94%); mp 86-89 °C; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.44 (d, J = 7.8 Hz, 2H), δ = 7.29 (m, 2H), δ = 7.32-7.27 (m, 2H), δ = 7.16 (s, 1H), δ = 7.08-7.06 (m, 1H), δ = 6.63 (d, J = 2.8 Hz, 1H), δ = 6.56 (d, J = 2.8 Hz, 1H), δ = 4.56 (s, 1H), δ = 1.75 (s, 3H), δ = 1.33 (s, 3H), δ = 1.26 (s, 9H), δ = 1.20 (s, 9H) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (100MHz, CDCl_3 , 25 °C): δ = 184.5, 164.3, 161.8, 154.1, 153.8, 134.2, 134.1, 132.7, 131.2, 129.6, 129.5, 128.3, 127.7, 105.1, 45.9, 42.9, 42.2, 36.1, 35.8, 29.3, 29.3, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{31}\text{ClO}_5\text{Na}$ 493.1752; Found 493.1753.



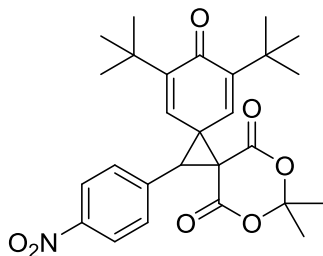
13-(4-Bromophenyl)-9,11-di-tert-butyl-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3ja). Yellow solid; yield: 49.9 mg (97%); mp 98-101 °C; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.48 (d, J = 8.4 Hz, 2H), δ = 7.04 (d, J = 7.8 Hz, 2H), δ = 6.60 (d, J = 2.9 Hz, 1H), δ = 6.56 (d, J = 2.9 Hz, 1H), δ = 4.52 (s, 1H), δ = 1.74 (s, 3H), δ = 1.32 (s, 3H), δ = 1.25 (s, 9H), δ = 1.18 (s, 9H) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (100MHz, CDCl_3 , 25 °C): δ = 184.5, 164.3, 161.8, 154.1, 153.8, 134.2, 134.1, 132.7, 131.2, 129.6, 129.5, 128.3, 127.7, 105.1, 45.9, 42.9, 42.2, 36.1, 35.8, 29.3, 29.3, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{31}\text{BrO}_5\text{Na}$ 537.1247; Found 537.1248.



9,11-Di-tert-butyl-13-(4-fluorophenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3ka**). Yellow solid; yield: 41.8 mg (92%); mp 89-93 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.15-7.12 (m, 2H), δ = 7.07-7.03 (m, 2H), δ = 6.62 (d, *J* = 2.9 Hz, 1H), δ = 6.58 (d, *J* = 2.8 Hz, 1H), δ = 4.57 (s, 1H), δ = 1.75 (s, 3H), δ = 1.33 (s, 3H), δ = 1.26 (s, 9H), δ = 1.18 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.6, 164.4, 161.9, 154.0, 153.7, 134.3, 131.4, 131.1, 131.0, 126.4, 126.4, 115.5, 115.3, 105.0, 46.3, 43.0, 42.2, 36.1, 35.8, 29.3, 29.3, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₇H₃₁FO₅Na 477.2048; Found 477.2047.

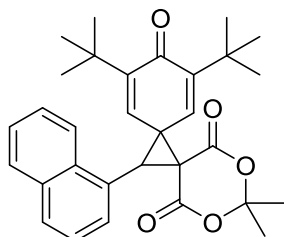


9,11-Di-tert-butyl-13-(4-trifluoromethylphenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3la**). Yellow solid; yield: 32.8 mg (65%); mp 105-107 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.62 (d, *J* = 8.0 Hz, 2H), δ = 7.30-7.27 (m, 2H), δ = 6.59 (s, 2H), δ = 4.60 (s, 1H), δ = 1.76 (s, 3H), δ = 1.33 (s, 3H), δ = 1.27 (s, 9H), δ = 1.19 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.5, 164.2, 161.9, 154.3, 154.1, 134.8, 134.0, 130.9, 129.8, 125.3, 105.2, 46.0, 43.0, 42.2, 36.1, 35.8, 29.3, 28.6, 27.6, 27.0, 26.9 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₈H₃₁F₃O₅Na 527.2016; Found 527.2015.

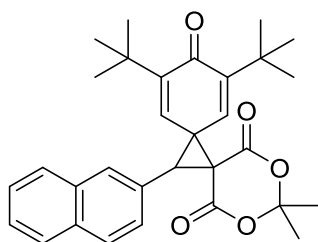


9,11-Di-tert-butyl-13-(4-nitrophenyl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3ma**). Yellow solid; yield: 39.9 mg (83%); mp 106-109 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 8.24 (d, *J* = 8.7 Hz, 2H), δ = 7.36 (d, *J* = 8.1 Hz, 2H), δ = 6.58 (d, *J* = 2.9 Hz, 1H), δ = 6.53 (d, *J* = 2.8 Hz, 1H), δ = 4.61 (s, 1H), δ = 1.77 (s, 3H), δ = 1.34 (s, 3H), δ = 1.27 (s, 9H), δ = 1.19 (s, 9H); ¹³C{¹H} NMR

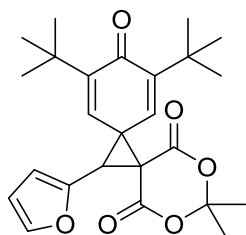
(100MHz, CDCl₃, 25 °C): δ = 184.3, 164.0, 162.0, 154.5, 154.5, 147.6, 138.2, 133.6, 130.5, 130.3, 128.7, 123.8, 123.6, 105.4, 45.8, 42.5, 42.2, 36.2, 35.9, 29.3, 28.8, 27.5, 27.0, ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₂₇H₃₁NO₇Na 504.1993; Found 504.1992..



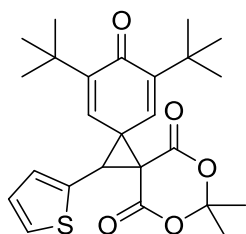
9,11-Di-tert-butyl-3,3-dimethyl-13-(naphthalen-1-yl)-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3na). Yellow solid; yield: 44.7 mg (92%); mp 108-110 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.91-7.86 (m, 2H), δ = 7.68-7.64 (m, 1H), δ = 7.53-7.49 (m, 2H), δ = 7.44 (m, 1H), δ = 7.30 (d, *J* = 7.2 Hz, 1H), δ = 6.83 (d, *J* = 2.8 Hz, 1H), δ = 6.72 (d, *J* = 2.9 Hz, 1H), δ = 4.81 (s, 1H), δ = 1.75 (s, 3H), δ = 1.36 (s, 3H), δ = 1.30 (s, 9H), δ = 1.19 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 186.1, 166.1, 163.0, 155.6, 154.6, 136.1, 134.9, 133.9, 133.8, 130.5, 130.4, 128.8, 128.3, 128.3, 127.5, 126.2, 124.3, 106.4, 47.4, 44.4, 43.7, 37.4, 37.3, 30.7, 30.6, 29.0, 28.3 ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₃₁H₃₄O₅Na 509.2298; Found 509.2297.



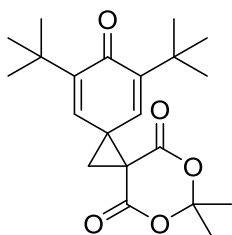
9,11-Di-tert-butyl-3,3-dimethyl-13-(naphthalen-2-yl)-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (3oa). Yellow solid; yield: 45.7 mg (94%); mp 86-88 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.87-7.83 (m, 2H), δ = 7.77-7.75 (m, 1H), δ = 7.61 (s, 1H), δ = 7.51-7.48 (m, 2H), δ = 7.28 (dd, *J* = 8.6, 1.4 Hz, 1H), δ = 6.78 (d, *J* = 2.8 Hz, 1H), δ = 6.65 (d, *J* = 2.8 Hz, 1H), δ = 4.76 (s, 1H), δ = 1.76 (s, 3H), δ = 1.35 (s, 3H), δ = 1.29 (s, 9H), δ = 1.19 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.8, 164.6, 161.9, 154.0, 153.5, 134.5, 133.1, 132.9, 131.9, 128.3, 128.3, 128.1, 127.9, 127.7, 127.2, 126.5, 126.4, 105.0, 46.4, 44.0, 42.3, 36.1, 35.8, 29.3, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₃₁H₃₄O₅Na 509.2298; Found 509.2299.



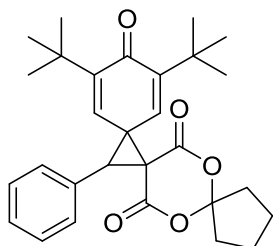
9,11-Di-tert-butyl-13-(furan-2-yl)-3,3-dimethyl-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3pa**). Yellow solid; yield: 39.6 mg (93%); mp 86-89 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.44 (t, *J* = 1.6 Hz, 1H), δ = 6.97(d, *J* = 2.9 Hz, 1H), δ = 6.54 (d, *J* = 2.8 Hz, 1H), δ = 6.42-6.41 (m, 1H), δ = 6.30 (d, *J* = 3.1 Hz, 1H), δ = 4.38 (s, 1H), δ = 1.73 (s, 3H), δ = 1.33 (s, 3H), δ = 1.24 (s, 9H), δ = 1.23 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.6, 163.9, 161.6, 154.1, 153.7, 144.7, 142.8, 133.7, 131.2, 110.7, 110.2, 105.0, 45.1, 41.9, 36.6, 36.0, 35.8, 29.3, 29.2, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₂₅H₃₀O₆Na 449.1935; Found 449.1936.



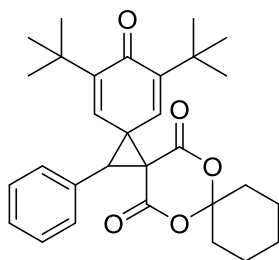
9,11-Di-tert-butyl-3,3-dimethyl-13-(thiophen-2-yl)-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3qa**). Yellow solid; yield: 41.5 mg (94%); mp 77-79 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.33 (d, *J* = 5.0 Hz, 1H), δ = 7.02-7.00 (m, 1H), δ = 6.96-6.95 (m, 2H), δ = 6.56 (d, *J* = 2.8 Hz, 1H), δ = 4.60 (s, 1H), δ = 1.74 (s, 3H), δ = 1.33 (s, 3H), δ = 1.25 (s, 9H), δ = 1.23 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.6, 164.0, 161.6, 154.0, 153.7, 133.9, 132.6, 131.1, 128.5, 126.7, 126.2, 105.0, 46.3, 42.9, 39.0, 36.1, 35.8, 29.3, 29.2, 27.6, 26.9 ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₂₅H₃₀O₅SNa 465.1706; Found 465.1705.



9,11-Di-tert-butyl-3,3-dimethyl-13-(thiophen-2-yl)-2,4-dioxadispiro[5.0.5⁷.1⁶]trideca-8,11-diene-1,5,10-trione (**3ra**). Yellow solid; yield: 22.0 mg (61%); mp 106-109 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 6.50 (s, 2H), δ = 2.84 (s, 2H), δ = 1.75 (s, 3H), δ = 1.32 (s, 3H), δ = 1.22 (s, 18H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.5, 164.1, 154.0, 133.7, 105.3, 43.9, 39.5, 35.7, 29.2, 27.6, 26.9, 26.7 ppm; HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ Calcd for C₂₁H₂₈O₄Na 361.2010; Found 361.2011.



11,13-Di-tert-butyl-15-phenyl-6,17-dioxatrispiro[4.2.0.5⁹.1⁸.2⁵]heptadeca-10,13-diene-7,12,16-trione (3ab). Yellow solid; yield: 43.0 mg (93%); mp 81-84 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.36-7.34 (m, 3H), δ = 7.17-7.15 (m, 2H), δ = 6.63 (d, *J* = 2.9 Hz, 1H), δ = 6.54 (d, *J* = 2.9 Hz, 1H), δ = 4.60 (s, 1H), δ = 2.22-2.19 (m, 2H), δ = 1.81-1.70 (m, 4H), δ = 1.57-1.56 (m, 2H), δ = 1.27 (s, 9H), δ = 1.19 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.7, 165.1, 162.4, 153.8, 153.3, 134.7, 131.9, 130.6, 129.5, 128.3, 128.0, 114.1, 46.2, 43.6, 42.6, 38.8, 37.9, 36.0, 35.7, 29.3, 29.3, 23.9, 22.3 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + Na]⁺ Calcd for C₃₀H₃₆O₅Na 485.2298; Found 485.2297.

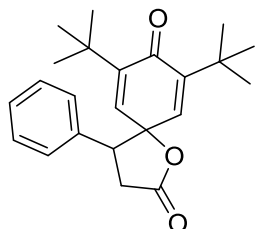


2,4-Di-tert-butyl-18-phenyl-9,16-dioxatrispiro[5.0.2.5¹⁰.2⁷.1⁶]octadeca-1,4-diene-3,8,17-trione (3ac). Yellow solid; yield: 45.2 mg (95%); mp 110-113 °C; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.34 (d, *J* = 7.3 Hz, 3H), δ = 7.17-7.15 (m, 2H), δ = 6.66 (d, *J* = 2.9 Hz, 1H), δ = 6.57 (d, *J* = 2.8 Hz, 1H), δ = 4.62 (s, 1H), δ = 1.98-1.92 (m, 2H), δ = 1.75-1.74 (d, *J* = 5.5 Hz, 2H), δ = 1.43 (s, 6H), δ = 1.26 (s, 9H), δ = 1.18 (s, 9H); ¹³C{¹H} NMR (100MHz, CDCl₃, 25 °C): δ = 184.8, 164.6, 161.9, 153.9, 153.4, 134.7, 131.9, 130.8, 129.4, 128.3, 127.9, 105.8, 46.2, 43.8, 42.7, 36.5, 36.0, 35.9, 35.7, 29.3, 29.3, 23.9, 22.6, 21.6 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₉H₃₄O₅Na 499.2455; Found 499.2454.

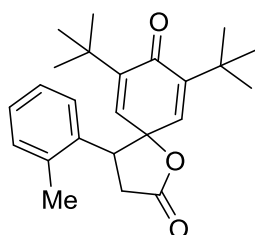
General Procedure for the Synthesis of Spirobutyrolactones **4**

The solution of 0.1 mmol dispirocyclopropane **3** in 1 mL of DMSO (0.1 *M*) was stirred at 90 °C (silicon oil bath) for 4 h. The reaction process was monitored by TLC analysis. The reaction mixture was quenched with distilled water (5 mL). The mixture was then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (3 × 10 mL), dried using anhydrous Na₂SO₄, and then filtered. The solvent was removed under vacuum, and the crude was purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 20/1) to give the desired product **4**.

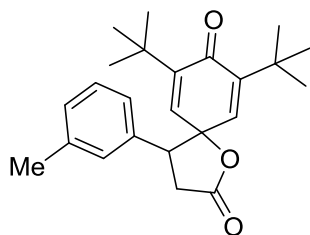
Spectroscopic Data of Spirobutyrolactones 4



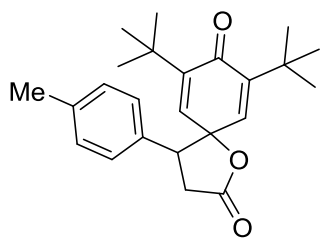
7,9-Di-tert-butyl-4-phenyl-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4a**). White solid; yield: 28.5 mg (81%); mp 152.5-153.2 °C; IR (neat): 2958, 1790, 1667, 1646, 1482, 1458, 1193, 881, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.27-7.24 (m, 3H), δ = 7.03-7.00 (m, 2H), δ = 6.66 (d, J = 3.1 Hz, 1H), δ = 6.30 (d, J = 3.2 Hz, 1H), δ = 3.83 (dd, J = 12.4, 8.4 Hz, 1H), δ = 3.27 (dd, J = 17.4, 12.4 Hz, 1H), δ = 2.99 (dd, J = 17.4, 8.3 Hz, 1H), δ = 1.25 (s, 9H), δ = 0.91 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.9, 174.7, 149.2, 149.0, 137.1, 134.4, 133.6, 128.6, 128.4, 127.5, 83.5, 50.9, 35.0, 34.7, 32.7, 29.3, 28.7 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_3\text{Na}$ 375.1931; Found 375.1935.



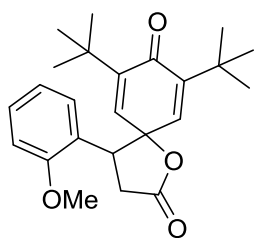
7,9-Di-tert-butyl-4-(*o*-tolyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4b**). Red solid; yield: 33.7 mg (92%); mp 118.9-119.5 °C; IR (neat): 2955, 1765, 1670, 1650, 1483, 1459, 1366, 954 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.23-7.10 (m, 4H), δ = 6.66 (d, J = 3.2 Hz, 1H), δ = 6.16 (d, J = 3.2 Hz, 1H), δ = 4.07 (dd, J = 8.8, 7.6 Hz, 1H), δ = 3.17 (dd, J = 18.0, 9.0 Hz, 1H), δ = 3.07 (dd, J = 18.0, 7.5 Hz, 1H), δ = 2.15 (s, 3H), δ = 1.23 (s, 9H), δ = 0.95 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 185.1, 175.4, 147.7, 147.5, 137.5, 136.4, 136.2, 134.6, 131.1, 128.0, 126.5, 126.4, 83.0, 45.6, 35.1, 34.9, 34.8, 29.1, 28.8, 20.3 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{31}\text{O}_3$ 367.2268; Found 367.2266.



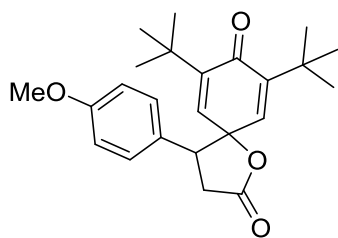
7,9-Di-*tert*-butyl-4-(*m*-tolyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4c**). Yellow solid; yield: 26.7 mg (73%); mp 110.0-110.7 °C; IR (neat): 2917, 1778, 1670, 1647, 1659, 1484, 1365, 1205, 981cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.27-7.22 (m, 1H), δ = 7.00 (d, *J* = 6.6 Hz, 1H), δ = 6.89 (t, *J* = 7.4 Hz, 1H), δ = 6.82 (d, *J* = 8.2 Hz, 1H), δ = 6.63 (d, *J* = 3.0 Hz, 1H), δ = 6.28 (d, *J* = 3.0 Hz, 1H), δ = 4.13 (t, *J* = 9.0 Hz, 1H), δ = 3.75 (s, 3H), δ = 3.24 (dd, *J* = 17.8, 8.5 Hz, 1H), δ = 3.02 (dd, *J* = 17.8, 9.5 Hz, 1H), δ = 1.22 (s, 9H), δ = 0.94 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ = 185.0, 174.8, 149.1, 148.8, 138.2, 137.2, 134.5, 133.5, 129.0, 128.5, 128.4, 124.2, 83.6, 50.7, 35.0, 34.7, 32.5, 29.3, 28.7, 21.3ppm; HRMS (ESI/Q-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₃₁O₃ 367.2268; Found 367.2269.



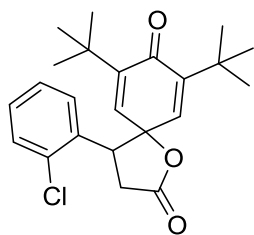
7,9-Di-*tert*-butyl-4-(*p*-tolyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4d**). Yellow solid; yield: 25.6 mg (70%); mp 160.3-160.8 °C; IR (neat): 2920, 1780, 1668, 1644, 1518, 1460, 1364, 1188, 980, 816cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.06 (d, *J* = 7.9 Hz, 2H), δ = 6.91(d, *J* = 8.0 Hz, 2H), δ = 6.63 (d, *J* = 3.1 Hz, 1H), δ = 6.26 (d, *J* = 3.1 Hz, 1H), δ = 3.77 (dd, *J* = 12.3, 8.4 Hz, 1H), δ = 3.22(dd, *J* = 17.4, 12.4 Hz, 1H), δ = 2.97 (dd, *J* = 17.4, 8.3 Hz, 1H), δ = 2.27 (s, 3H), δ = 1.25 (s, 9H), δ = 0.92 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ = 184.9, 174.8, 149.1, 148.8, 138.3, 137.2, 134.5, 130.5, 129.2, 127.3, 83.7, 50.5, 35.0, 34.7, 32.7, 29.3, 28.7, 21.0ppm; HRMS (ESI/Q-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₃₁O₃ 367.2268; Found 367.2270.



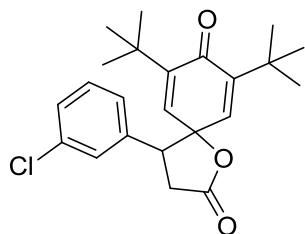
7,9-Di-*tert*-butyl-4-(2-methoxyphenyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4e**). Yellow solid; yield: 35.1 mg (92%); mp 120.7-121.3 °C; IR (neat): 2955, 1777, 1699, 1643, 1604, 1497, 1461, 1365, 978, 749cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.19-7.13 (m, 1H), δ = 7.05 (d, *J* = 7.4 Hz, 1H), δ = 6.82 (d, *J* = 9.7 Hz, 2H), δ = 6.62 (d, *J* = 3.0 Hz, 1H), δ = 6.24 (d, *J* = 3.0 Hz, 1H), δ = 3.76(dd, *J* = 12.2, 8.4 Hz, 1H), δ = 3.23 (dd, *J* = 17.4, 12.4 Hz, 1H), δ = 2.97 (dd, *J* = 17.4, 8.3 Hz, 1H), δ = 1.26 (s, 9H), δ = 0.91 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ = 185.5, 175.8, 157.1, 147.6, 147.1, 138.2, 136.0, 129.4, 129.0, 123.9, 120.5, 110.8, 83.2, 55.1, 45.4, 34.8, 34.6, 33.6, 29.3, 28.9 ppm; HRMS (ESI/Q-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₃₁O₄ 383.2217; Found 383.2215.



7,9-Di-tert-butyl-4-(4-methoxyphenyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4f). Yellow solid; yield: 28.3 mg (74%); mp 150.1-150.7 °C; IR (neat): 2959, 1779, 1667, 1640, 1515, 1453, 1250, 981, 829 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 6.93 (d, J = 8.7 Hz, 2H), δ = 6.78 (d, J = 8.7 Hz, 2H), δ = 6.61 (d, J = 3.1 Hz, 1H), δ = 6.25 (d, J = 3.2 Hz, 1H), δ = 3.77-3.72 (m, 4H), δ = 3.17 (dd, J = 17.4, 12.3 Hz, 1H), δ = 2.98 (dd, J = 17.4, 8.4 Hz, 1H), δ = 1.25 (s, 9H), δ = 0.94 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.8, 174.2, 149.4, 149.3, 136.9, 134.3, 134.0, 132.2, 128.8, 128.7, 83.3, 50.3, 35.1, 34.8, 32.7, 29.3, 28.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{31}\text{O}_4$ 383.2217; Found 383.2214.

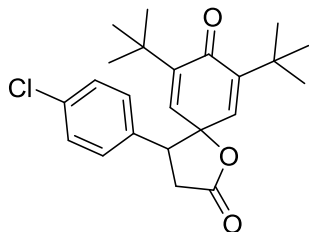


7,9-Di-tert-butyl-4-(2-chlorophenyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4g). Yellow solid; yield: 32.4 mg (84%); mp 118.3-119.0 °C; IR (neat): 2965, 1773, 1671, 1652, 1596, 1481, 1363, 948, 755 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.34-7.20 (m, 4H), δ = 6.66 (d, J = 3.2 Hz, 1H), δ = 6.18 (d, J = 3.2 Hz, 1H), δ = 4.45 (t, J = 8.8 Hz, 1H), δ = 3.19-3.06 (m, 2H), δ = 1.22 (s, 9H), δ = 0.98 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.9, 174.7, 148.6, 147.7, 137.2, 134.8, 134.7, 133.4, 130.2, 129.4, 128.3, 127.0, 83.0, 46.2, 34.9, 34.8, 34.3, 29.0, 28.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{ClO}_3$ 387.1721; Found 387.1723.

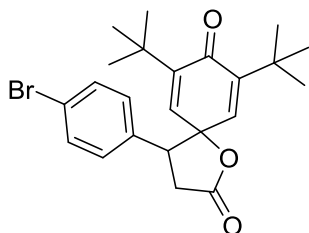


7,9-Di-tert-butyl-4-(3-chlorophenyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4h). Yellow solid; yield: 37.1 mg (96%); mp 147.3-147.9 °C; IR (neat): 2959, 1778, 1669, 1646, 1599, 1481, 1394, 981, 788 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.26-7.18 (m, 2H), δ = 7.02 (d, J = 1.8 Hz, 1H), δ = 6.91 (d, J = 7.4 Hz, 1H), δ = 6.62 (d, J = 3.2 Hz, 1H), δ = 6.27 (d, J = 3.2 Hz, 1H), δ = 3.78 (dd, J = 12.5, 8.3 Hz, 1H), δ = 3.20 (dd, J = 17.4, 12.5 Hz, 1H), δ = 2.99 (dd, J = 17.4, 8.3 Hz, 1H), δ = 1.26 (s, 9H), δ = 0.95

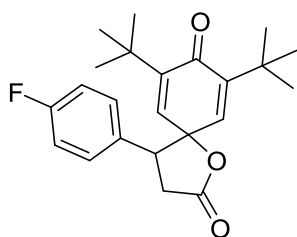
(s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.8, 174.1, 149.6, 149.4, 136.8, 135.6, 134.6, 133.9, 129.8, 128.5, 127.9, 125.7, 83.3, 50.5, 35.1, 34.8, 32.4, 29.3, 28.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{ClO}_3$ 387.1721; Found 387.1723.



7,9-Di-tert-butyl-4-(4-chlorophenyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4i**). Yellow solid; yield: 34.0 mg (88%); mp 219.3-220.1 °C; IR (neat): 2917, 1793, 1668, 1645, 1526, 1494, 1466, 1366, 1192, 980, 750 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.27-7.24 (m, 2H), δ = 6.97(d, J = 8.4 Hz, 2H), δ = 6.62 (d, J = 3.2 Hz, 1H), δ = 6.24 (d, J = 3.2 Hz, 1H), δ = 3.78 (dd, J = 12.2, 8.4 Hz, 1H), δ = 3.18 (dd, J = 17.4, 12.3 Hz, 1H), δ = 3.00 (dd, J = 17.4, 8.4 Hz, 1H), δ = 1.25 (s, 9H), δ = 0.94 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.8, 174.2, 149.4, 149.3, 136.9, 134.3, 134.0, 132.2, 128.8, 128.7, 83.3, 50.3, 35.1, 34.8, 32.7, 29.3, 28.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{ClO}_3$ 387.1721; Found 387.1720.

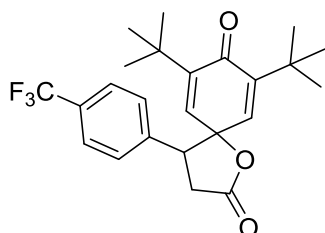


4-(4-Bromophenyl)-7,9-di-tert-butyl-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4j**). Yellow solid; yield: 31.0 mg (72%); mp 209.6-210.1 °C; IR (neat): 2966, 1793, 1668, 1645, 1490, 1451, 1391, 1127, 979, 604 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.40 (d, J = 8.5 Hz, 2H), δ = 6.90 (d, J = 8.4 Hz, 2H), δ = 6.61 (d, J = 3.2 Hz, 1H), δ = 6.22 (d, J = 3.2 Hz, 1H), δ = 3.76 (dd, J = 12.2, 8.4 Hz, 1H), δ = 3.17 (dd, J = 17.4, 12.2 Hz, 1H), δ = 3.00 (dd, J = 17.4, 8.4 Hz, 1H), δ = 1.25 (s, 9H), δ = 0.94 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.8, 174.2, 149.5, 149.4, 136.9, 133.9, 132.7, 131.7, 129.0, 122.4, 83.2, 50.3, 35.1, 34.8, 32.6, 29.3, 28.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{BrO}_3$ 431.1216; Found 431.1212.

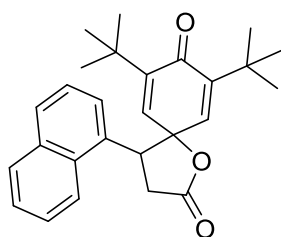


7,9-Di-tert-butyl-4-(4-fluorophenyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (**4k**).

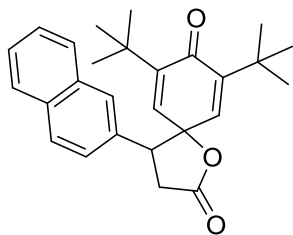
Yellow solid; yield: 32.9 mg (89%); mp 204.4-205.2 °C; IR (neat): 2918, 1794, 1667, 1645, 1513, 1451, 1366, 1189, 1161, 981 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.03-6.94 (m, 4H), δ = 6.62 (d, J = 3.2 Hz, 1H), δ = 6.26 (d, J = 3.1 Hz, 1H), δ = 3.79 (dd, J = 12.3, 8.4 Hz, 1H), δ = 3.18 (dd, J = 17.4, 12.4 Hz, 1H), δ = 3.00 (dd, J = 17.4, 8.3 Hz, 1H), δ = 1.25 (s, 9H), δ = 0.95 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.8, 174.3, 163.7, 161.3, 149.4, 149.3, 136.9, 134.1, 129.4, 129.3, 129.2, 129.1, 115.6, 115.4, 83.5, 83.4, 50.2, 35.0, 34.8, 32.9, 29.3, 28.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{FO}_3$ 371.2017; Found 371.2019.



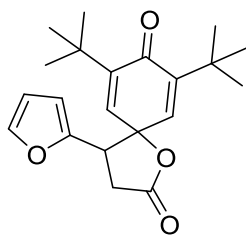
7,9-Di-tert-butyl-4-(4-(trifluoromethyl)phenyl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4l). White solid; yield: 35.3 mg (84%); mp 161.3-161.9 °C; IR (neat): 2959, 1779, 1670, 1645, 1622, 1486, 1461, 1326, 1119, 1072, 980 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.54 (d, J = 8.2 Hz, 2H), δ = 7.17 (d, J = 8.2 Hz, 2H), δ = 6.65 (d, J = 3.2 Hz, 1H), δ = 6.23 (d, J = 3.2 Hz, 1H), δ = 3.88 (dd, J = 12.2, 8.4 Hz, 1H), δ = 3.26 (dd, J = 17.4, 12.3 Hz, 1H), δ = 3.04 (dd, J = 17.4, 8.4 Hz, 1H), δ = 1.26 (s, 9H), δ = 0.90 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.7, 174.0, 149.6, 149.5, 137.8, 136.8, 133.8, 130.8 (q, $J_{\text{F-C}}$ = 33.1), 127.9, 125.5 (q, $J_{\text{F-C}}$ = 3.6), 123.7 (q, $J_{\text{F-C}}$ = 270.3), 83.1, 50.4, 35.1, 34.8, 32.4, 29.2, 28.7 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_3\text{O}_3$ 421.1985; Found 421.1987.



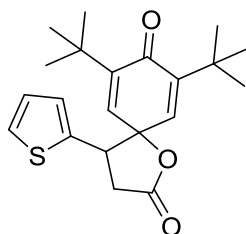
7,9-Di-tert-butyl-4-(naphthalen-1-yl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4n). Yellow solid; yield: 36.2 mg (90%); mp 169.3-169.9 °C; IR (neat): 2955, 1776, 1668, 1644, 1512, 1456, 1346, 1049, 814 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ = 7.83-7.77 (m, 2H), δ = 7.71-6.68 (m, 1H), δ = 7.48-7.36 (m, 4H), δ = 6.78 (d, J = 2.7 Hz, 1H), δ = 6.02 (t, J = 3.0 Hz, 1H), δ = 4.72 (t, J = 8.2 Hz, 1H), δ = 3.30 (d, J = 8.1 Hz, 1H), δ = 1.18 (s, 9H), δ = 0.65 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ = 184.9, 173.7, 149.8, 149.4, 136.9, 136.5, 133.7, 127.1, 125.4, 125.1, 83.2, 46.2, 35.1, 34.8, 34.3, 29.3, 28.8 ppm; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{31}\text{O}_3$ 403.2268; Found 403.2269.



7,9-Di-tert-butyl-4-(naphthalen-2-yl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4o). Yellow solid; yield: 31.0 mg (77%); mp 162.5-163.3 °C; IR (neat): 2958, 1777, 1670, 1648, 1510, 1483, 1459, 1182, 814cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.78-7.70 (m, 3H), δ = 7.49-7.43 (m, 3H), δ = 7.11 (dd, *J* = 8.5, 1.5 Hz, 1H), δ = 6.29 (d, *J* = 3.1 Hz, 1H), δ = 3.96 (dd, *J* = 12.0, 8.4 Hz, 1H), δ = 3.37 (dd, *J* = 17.4, 12.1 Hz, 1H), δ = 3.09 (dd, *J* = 17.4, 8.3 Hz, 1H), δ = 1.27 (s, 9H), δ = 0.76 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ = 184.8, 174.7, 149.2, 148.9, 137.3, 134.5, 132.9, 131.1, 128.4, 127.6, 126.7, 126.6, 126.5, 125.0, 83.7, 50.9, 35.0, 34.6, 32.8, 29.3, 28.6 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + H]⁺ Calcd for C₂₇H₃₁O₃ 403.2268; Found 403.2267.



7,9-Di-tert-butyl-4-(furan-2-yl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4p). Red solid; yield: 20.5 mg (60%); mp 117.3-118.3 °C; IR (neat): 2954, 1775, 1667, 1643, 1511, 1455, 1199, 1083, 973cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.28 (d, *J* = 1.1 Hz, 1H), δ = 6.55 (d, *J* = 3.1 Hz, 1H), δ = 6.32 (d, *J* = 3.2 Hz, 1H), δ = 6.26 (dd, *J* = 3.1, 1.9 Hz, 1H), δ = 6.02 (d, *J* = 3.2 Hz, 1H), δ = 3.25 (dd, *J* = 17.6, 11.8 Hz, 1H), δ = 3.00 (dd, *J* = 17.6, 8.7 Hz, 1H), δ = 1.26 (s, 9H), δ = 1.03 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ = 185.1, 174.1, 149.0, 148.8, 148.0, 142.6, 136.7, 134.1, 110.7, 108.4, 82.9, 44.9, 35.0, 34.7, 32.0, 29.3, 28.9 ppm; HRMS (ESI/Q-TOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₇O₄ 343.1904; Found 343.1906.



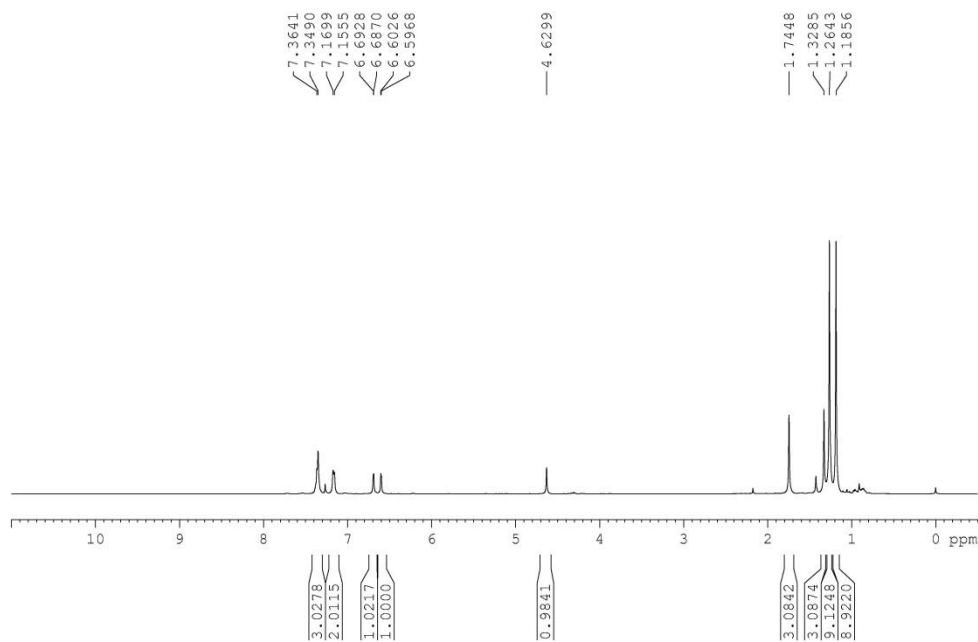
7,9-Di-tert-butyl-4-(thiophen-2-yl)-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (4q). Yellow solid; yield: 22.9 mg (64%); mp 156.6-157.3 °C; IR (neat): 2957, 1779, 1670, 1648, 1485, 1459, 980, 833cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ = 7.17 (d, *J* = 5.1 Hz, 1H), δ = 6.91 (t, *J* = 3.7 Hz, 1H), δ = 6.74 (d, *J* = 3.5 Hz, 1H), δ = 6.58 (d, *J* = 3.2 Hz, 1H), δ = 6.27 (d, *J* = 3.2 Hz, 1H), δ = 4.03 (dd, *J* = 12.2, 8.9 Hz, 1H), δ =

3.21-3.07 (m, 2H), $\delta = 1.28$ (s, 9H), $\delta = 0.96$ (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): $\delta = 184.9, 173.7, 149.8, 149.4, 136.9, 136.5, 133.7, 127.04, 125.4, 125.1, 83.2, 46.2, 35.1, 34.8, 34.3, 29.3, 28.8$ ppm; HRMS (ESI/Q-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{27}\text{O}_3\text{S}$ 359.1675; Found 359.1674.

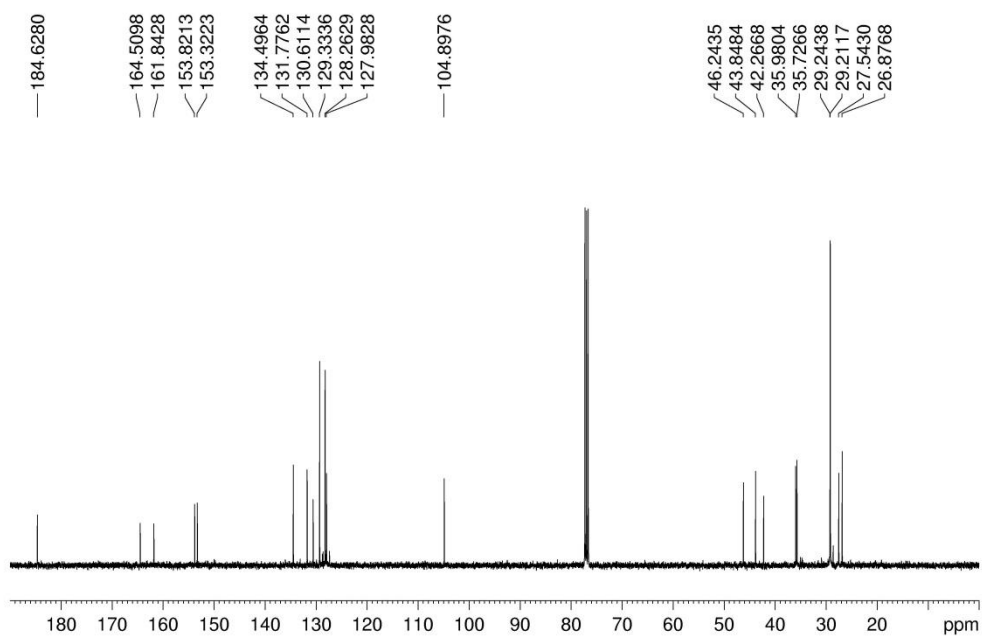
References

- (1) (a) Ge, L.; Lu, X.; Cheng, C.; Chen, J.; Cao, W.; Wu, X.; Zhao, G. *J. Org. Chem.* **2016**, *81*, 9315-9325; (b) Baik, W.; Lee, H. J.; Jang, J. M.; Koo, S.; Kim, B. H. *J. Org. Chem.* **2000**, *65*, 108-115.
- (2) Kayukova, O. V.; Kayukov, Y. S.; Nikolaev, A. N.; Nasakin, O. E. *Russ. J. Org. Chem.* **2004**, *40*, 1382-1383.

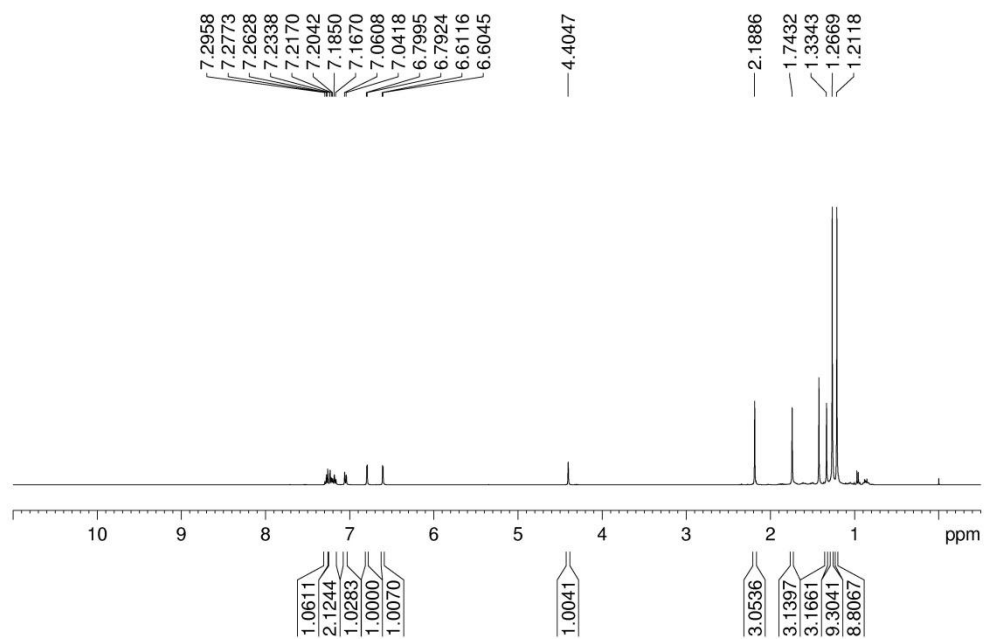
NMR Spectra of Dispirocyclopropanes 3



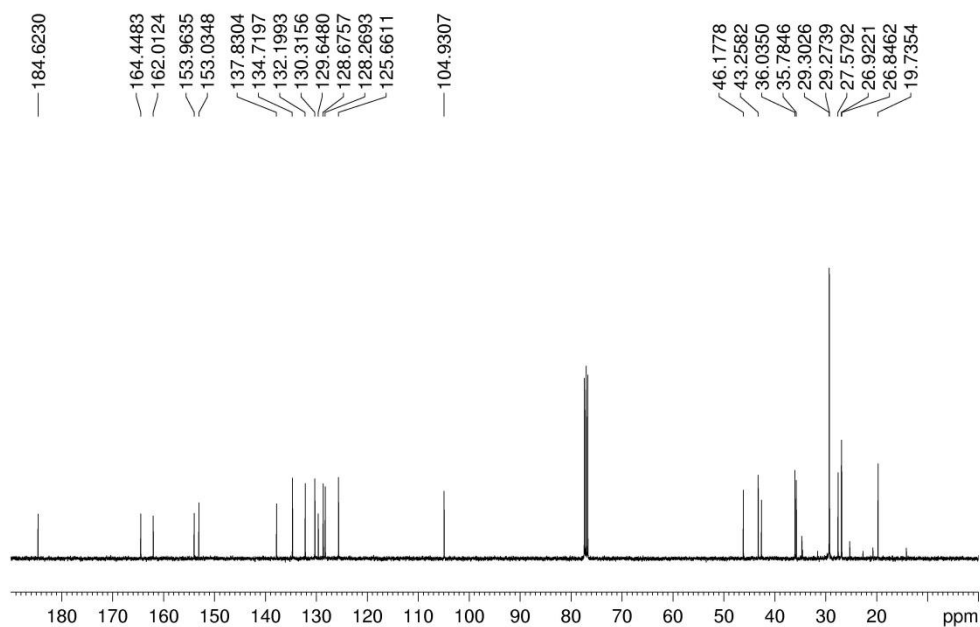
¹H NMR Spectra of Product 3aa



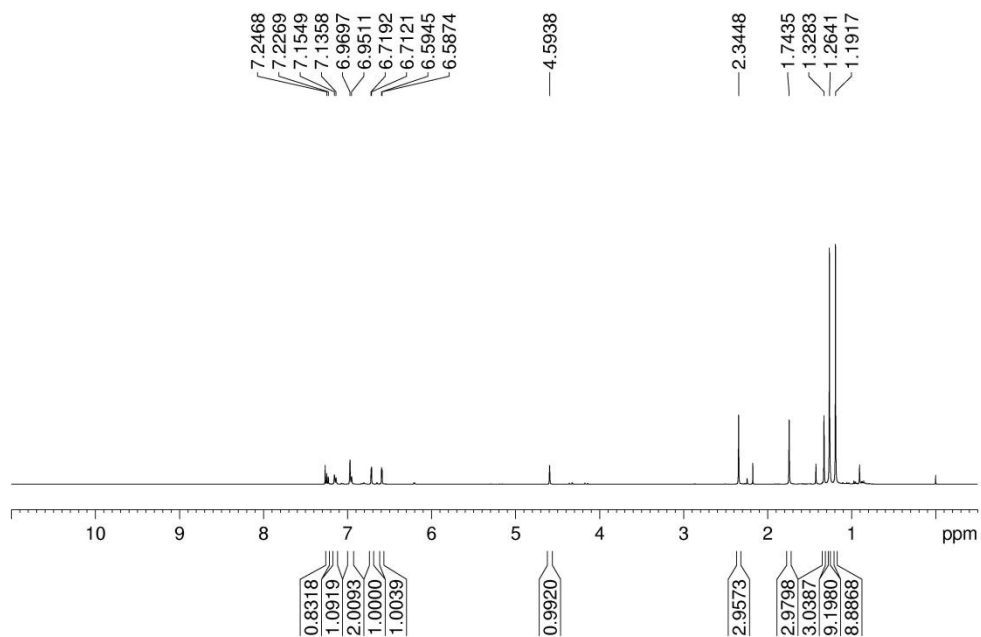
¹³C NMR Spectra of Product 3aa



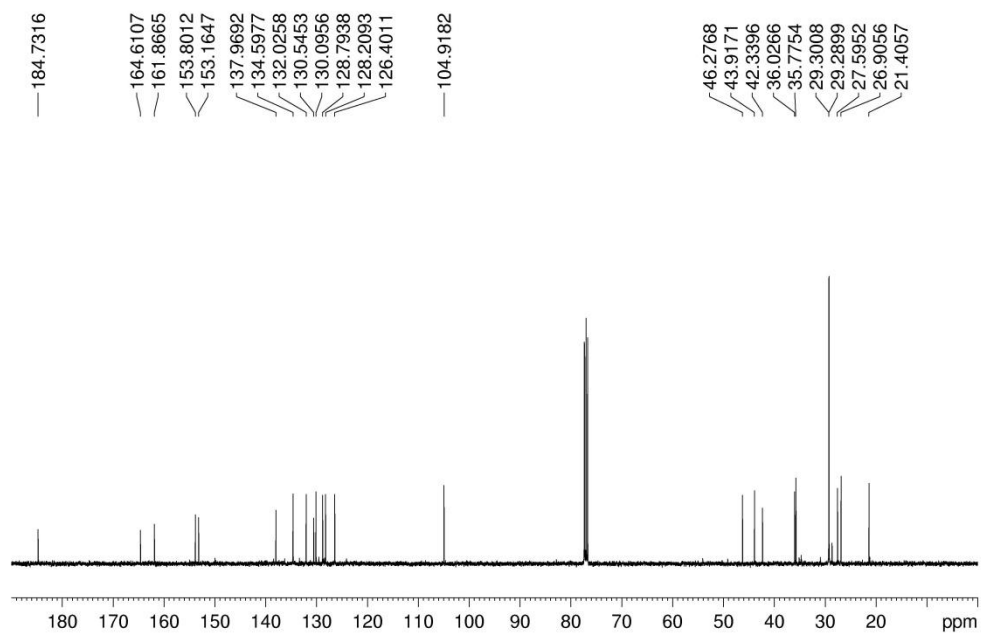
¹H NMR Spectra of Product **3ba**



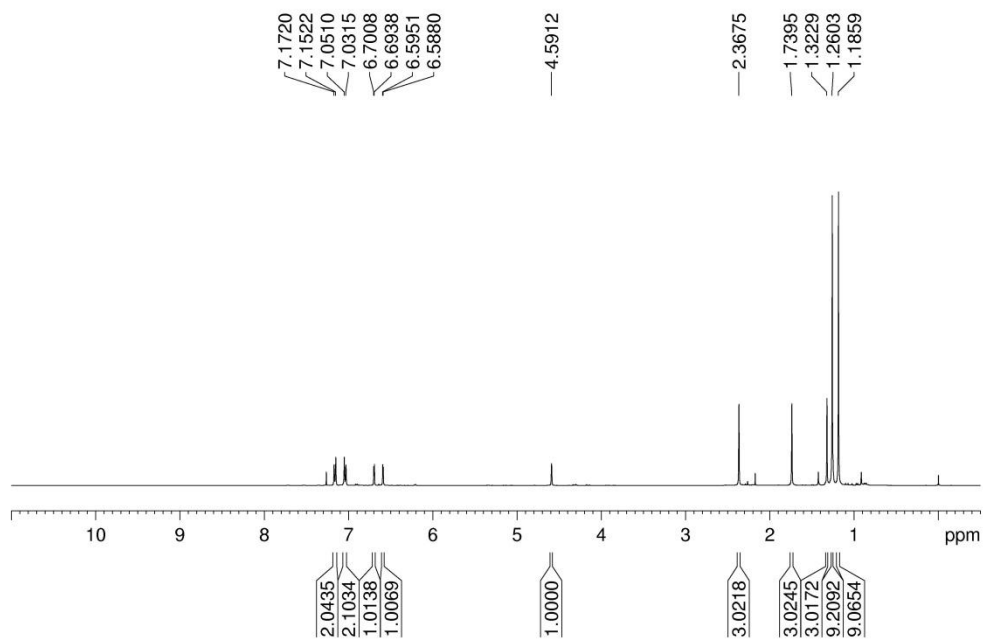
¹³C NMR Spectra of Product **3ba**



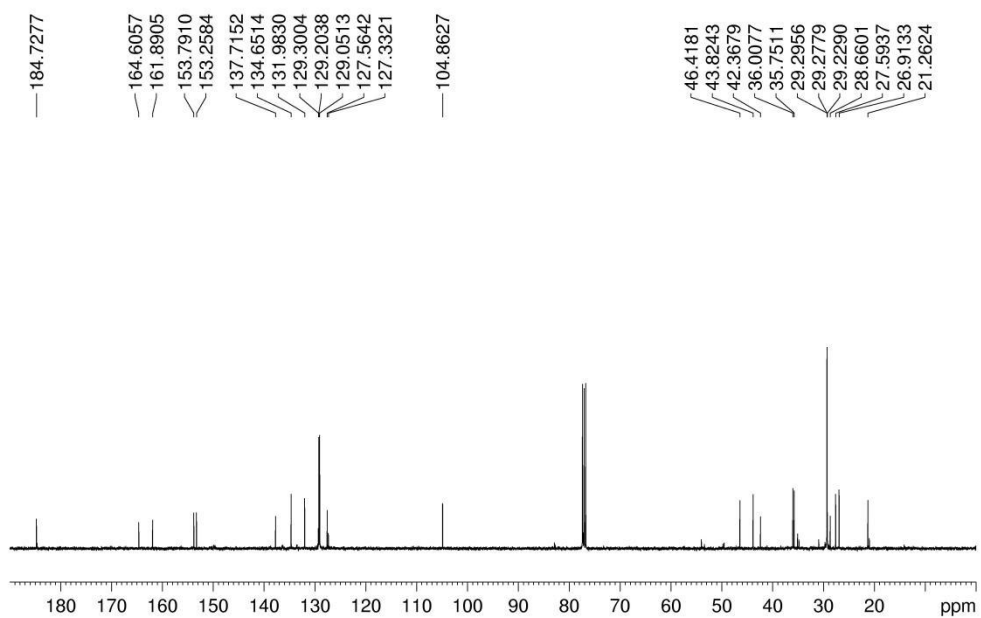
^1H NMR Spectra of Product **3ca**



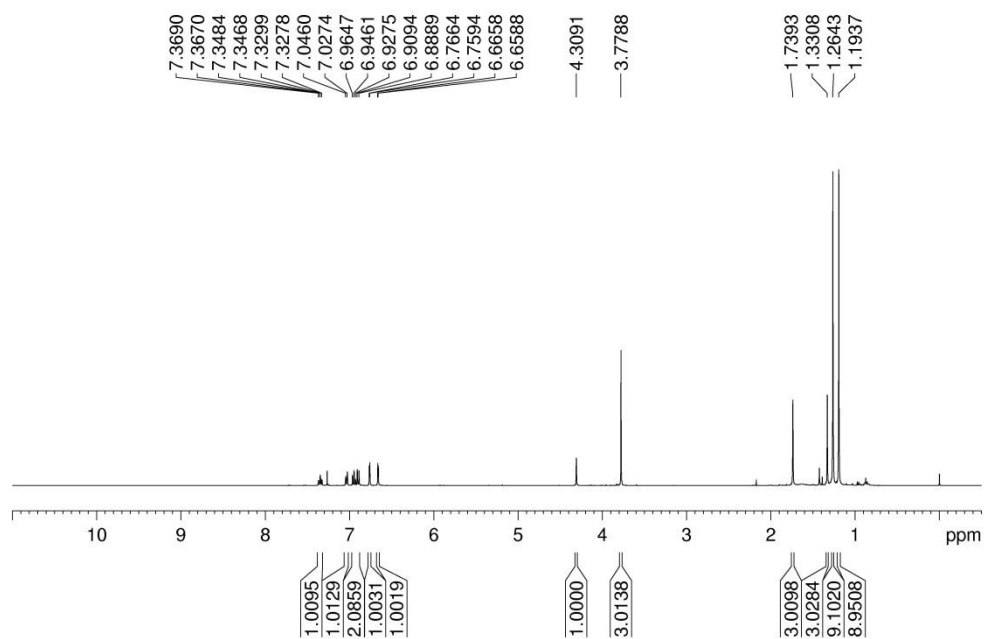
^{13}C NMR Spectra of Product **3ca**



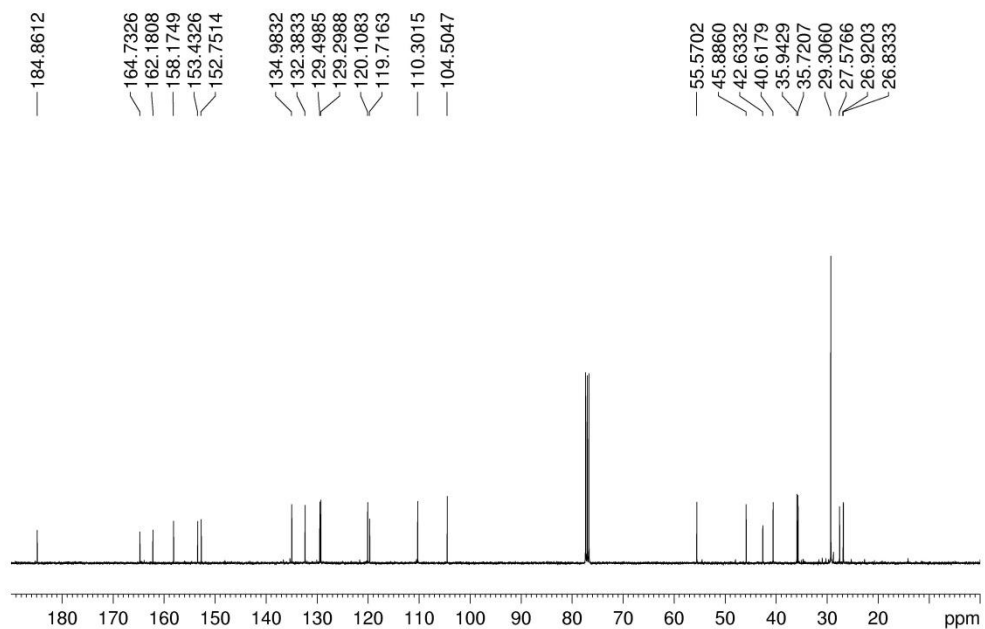
^1H NMR Spectra of Product **3da**



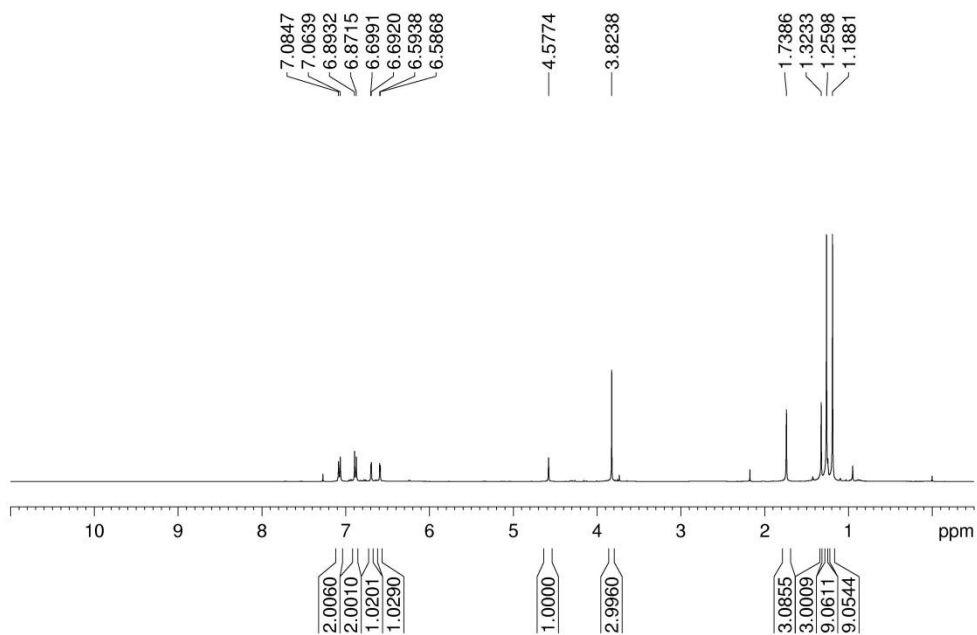
^{13}C NMR Spectra of Product **3da**



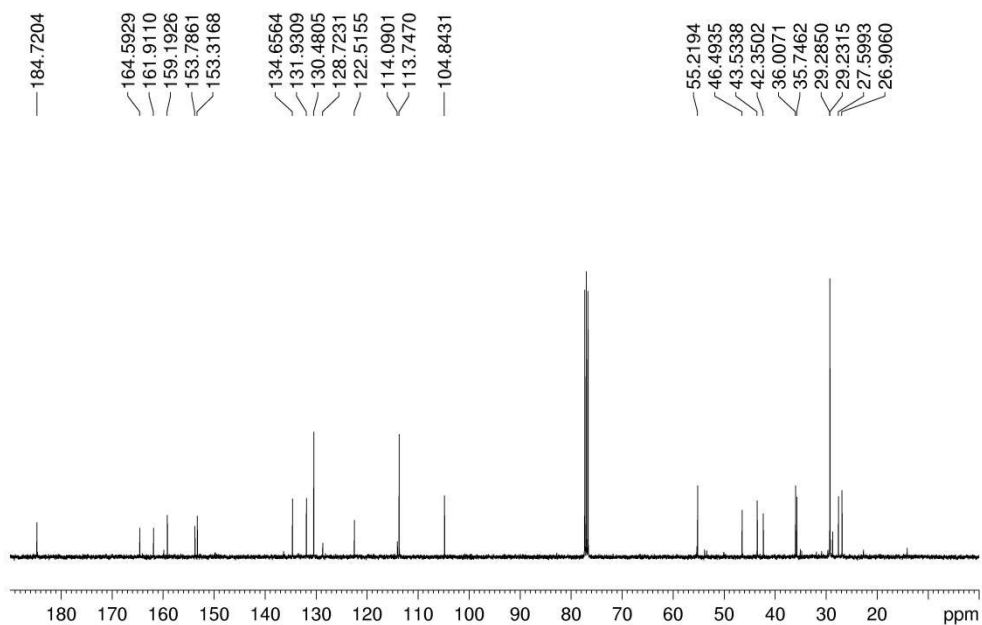
^1H NMR Spectra of Product **3ea**



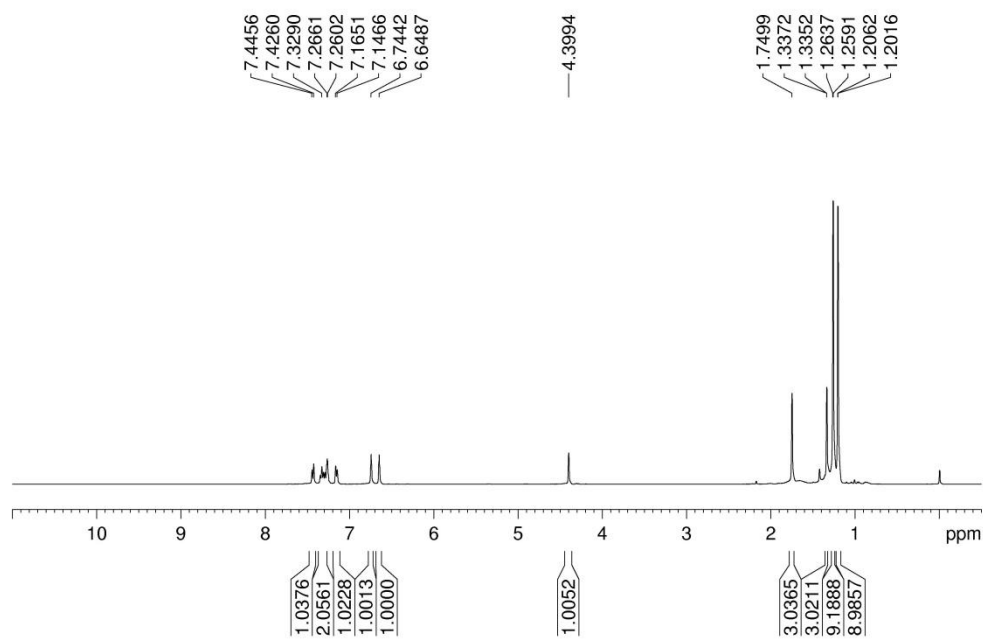
^{13}C NMR Spectra of Product **3ea**



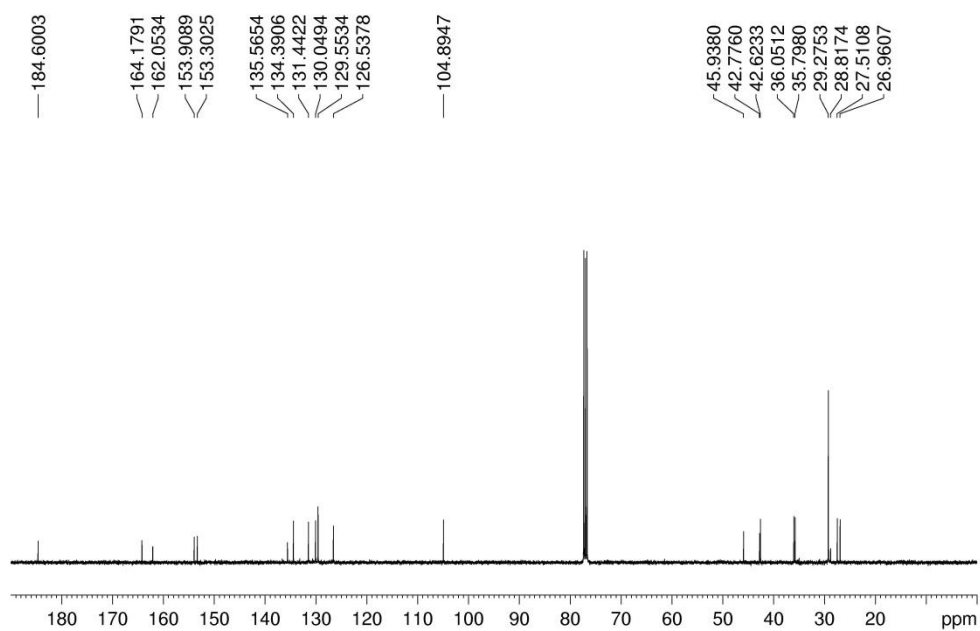
^1H NMR Spectra of Product **3fa**



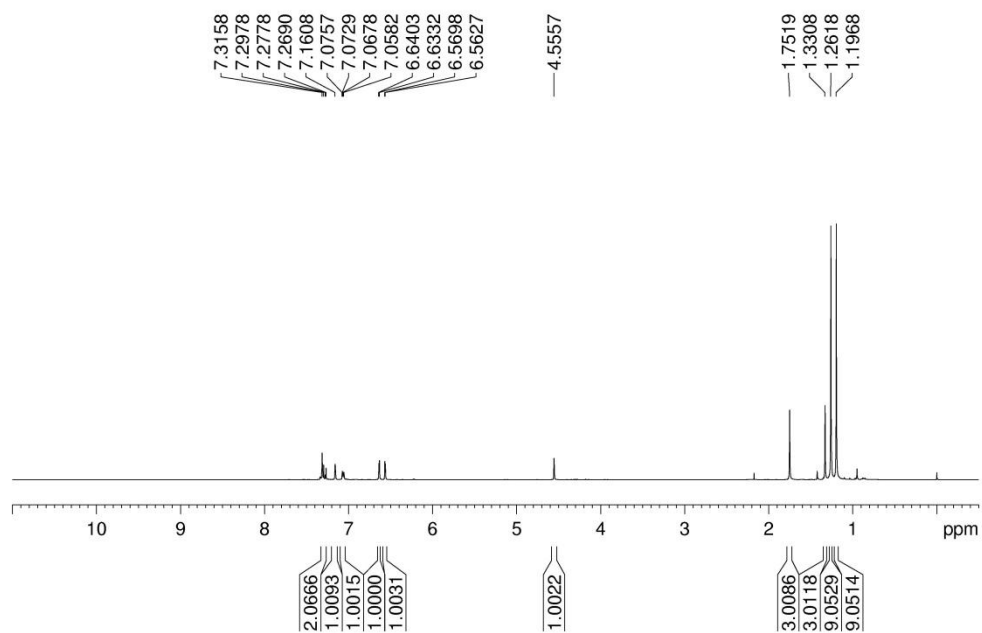
^{13}C NMR Spectra of Product **3fa**



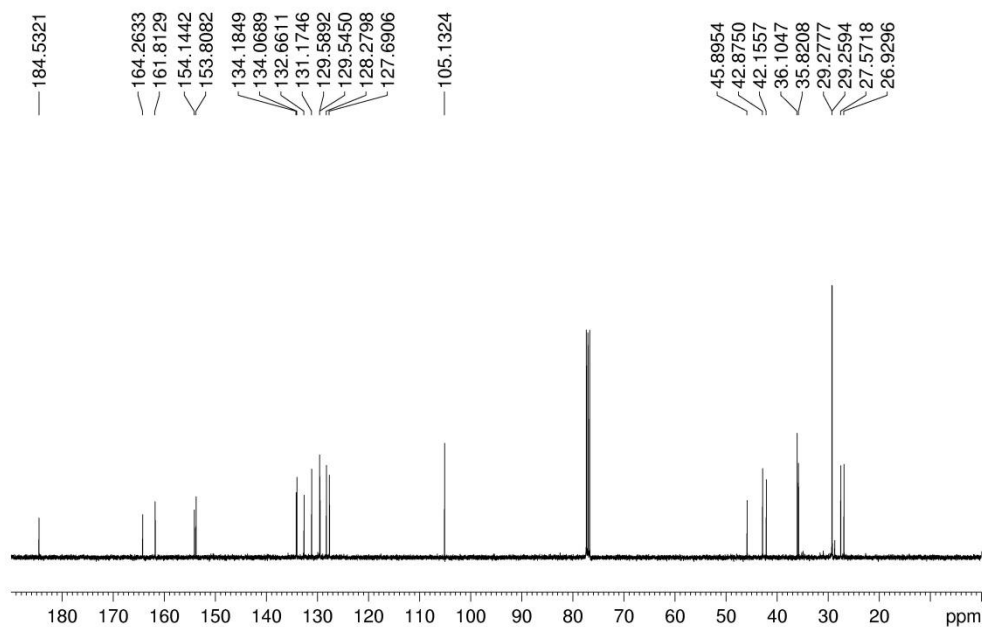
¹H NMR Spectra of Product **3ga**



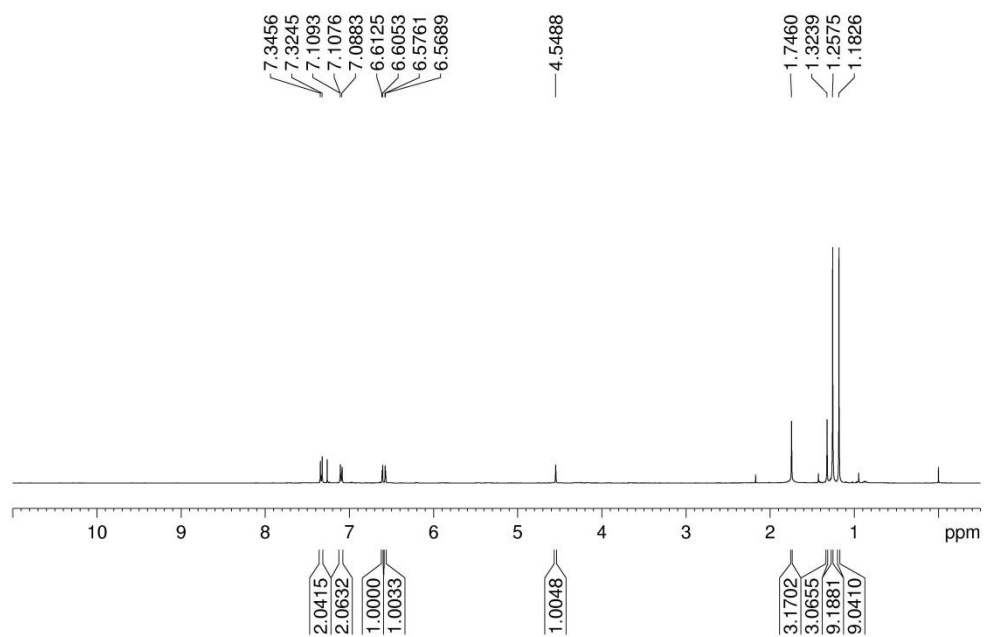
¹³C NMR Spectra of Product **3ga**



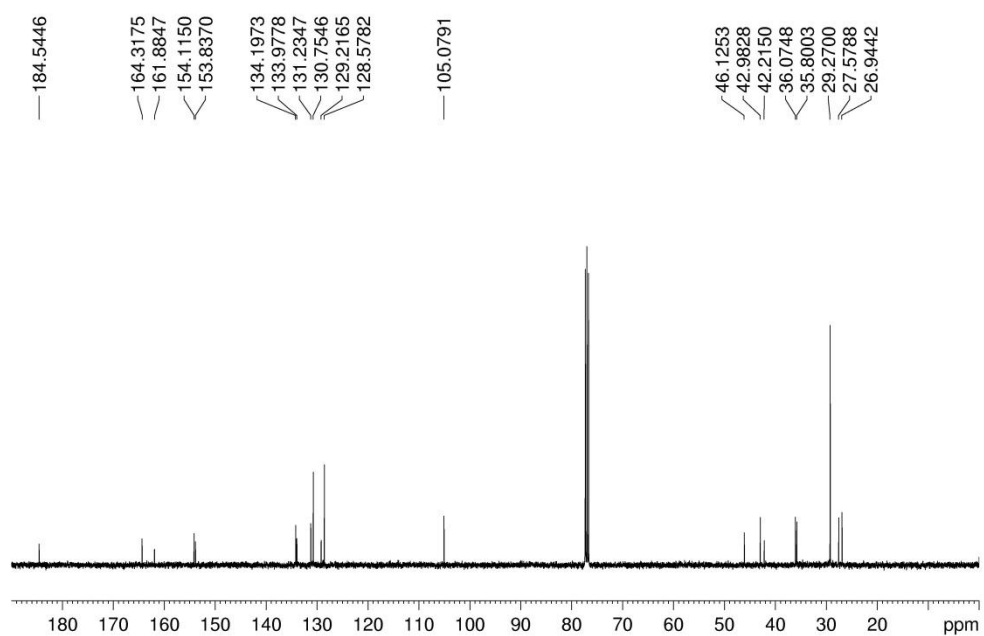
^1H NMR Spectra of Product **3ha**



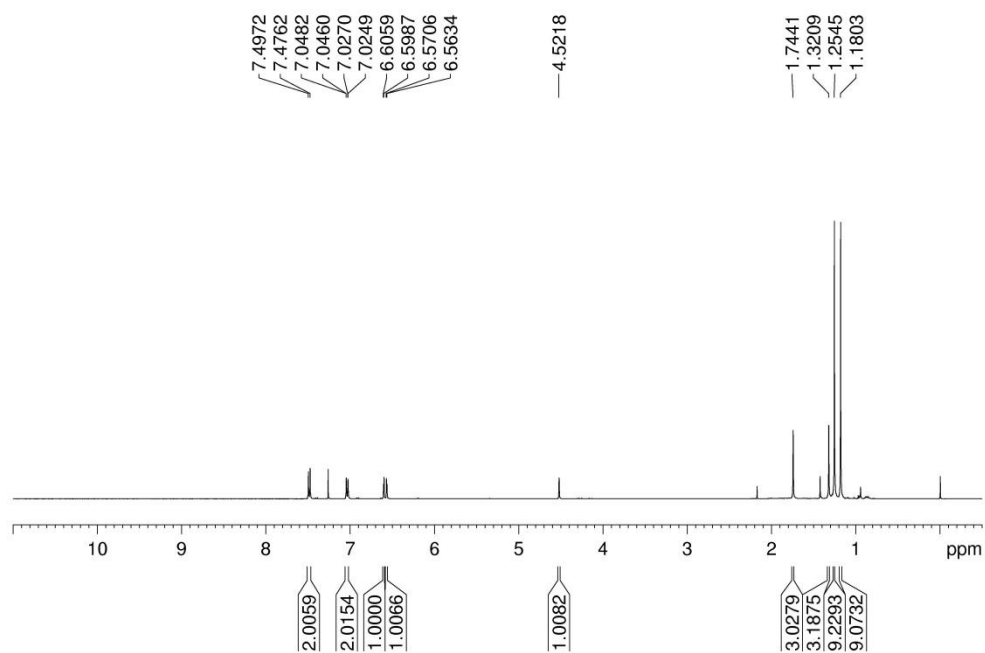
^{13}C NMR Spectra of Product **3ha**



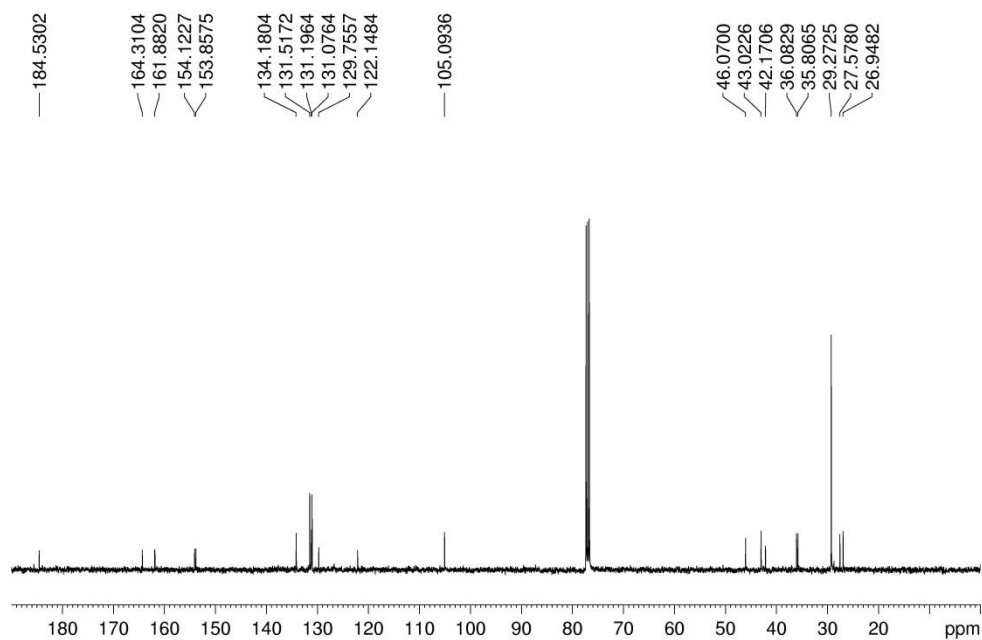
^1H NMR Spectra of Product **3ia**



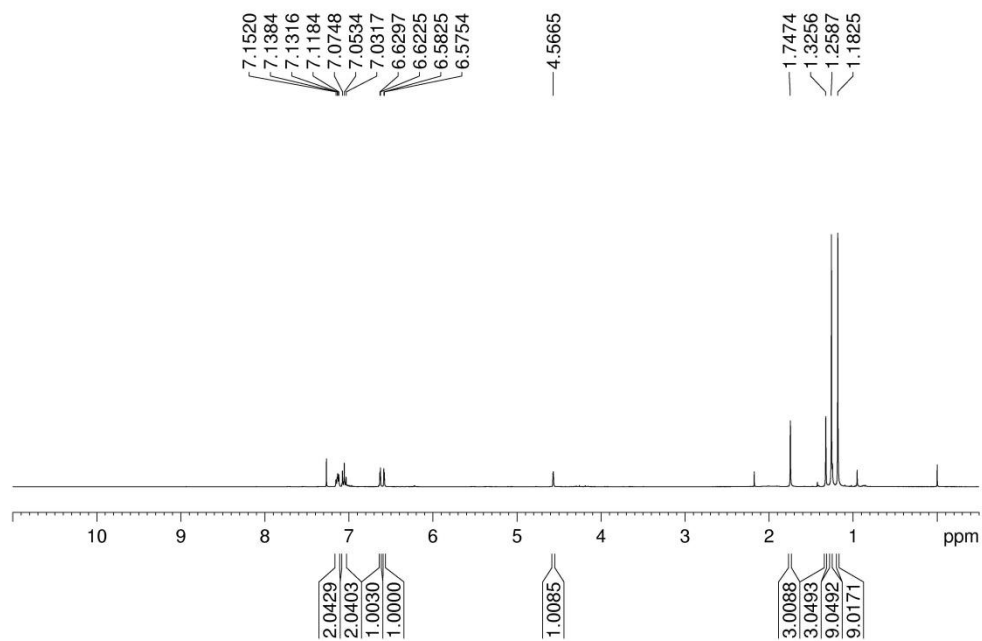
^{13}C NMR Spectra of Product **3ia**



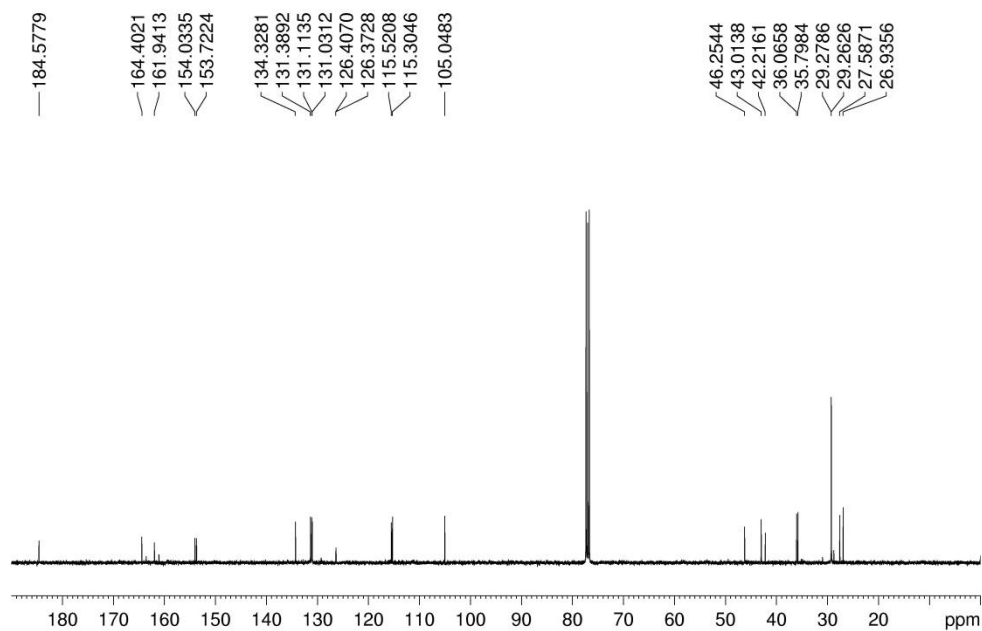
^1H NMR Spectra of Product **3ja**



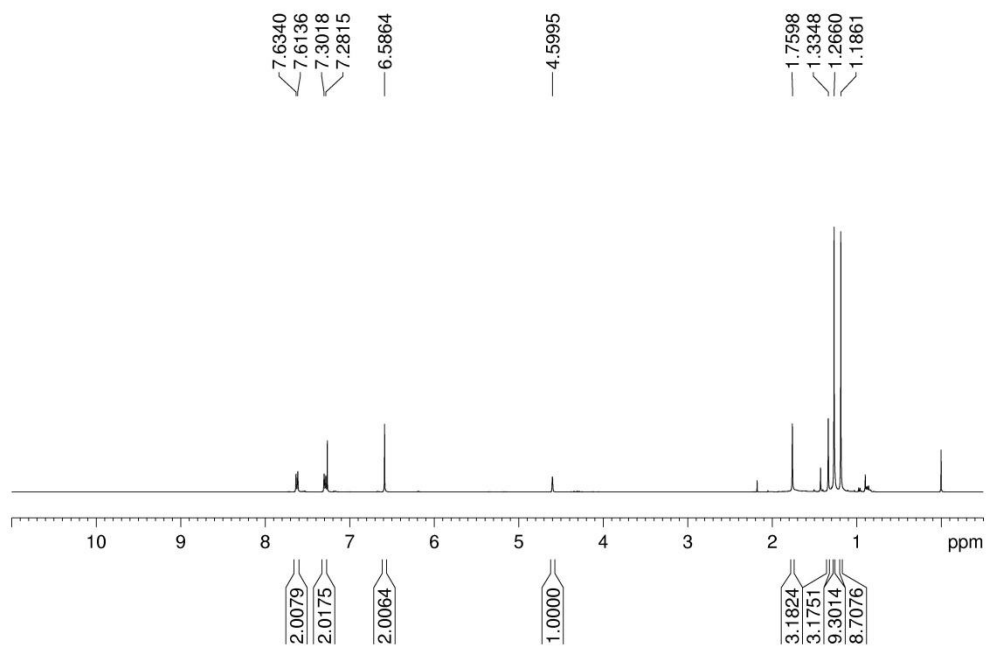
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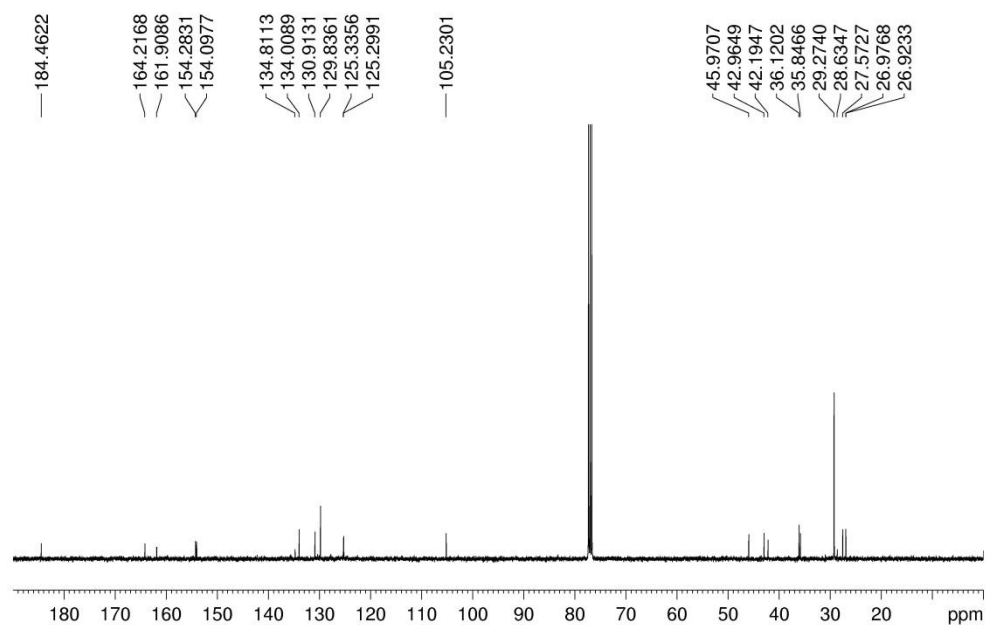
^1H NMR Spectra of Product **3ka**



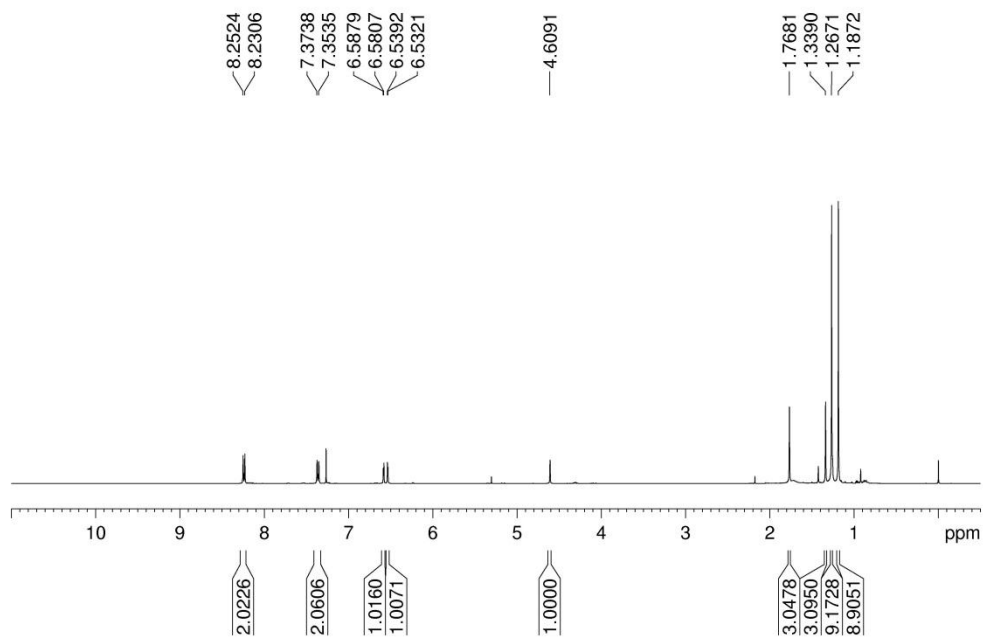
^{13}C NMR Spectra of Product **3ka**



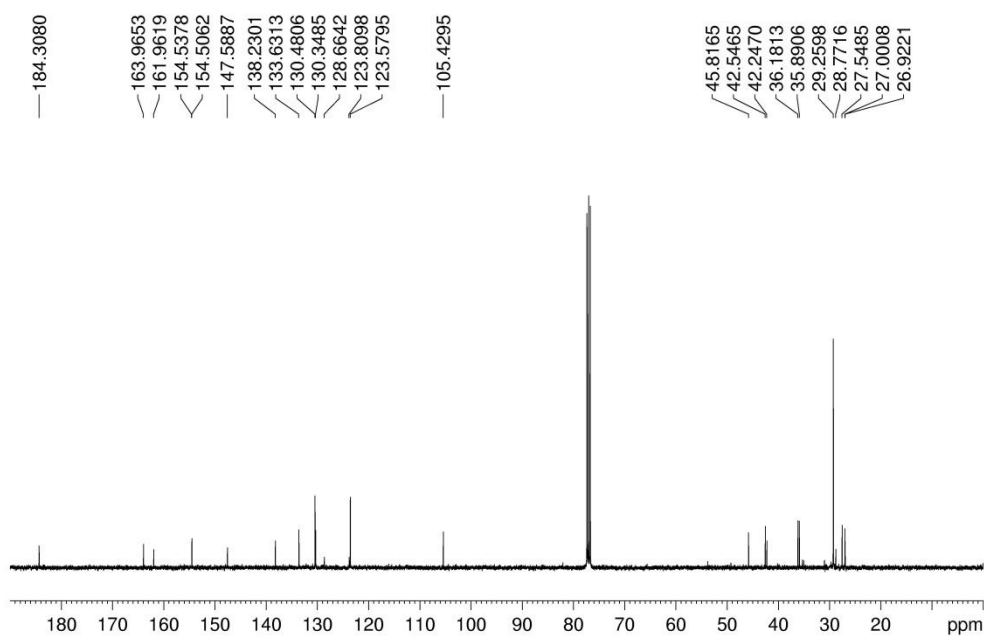
¹H NMR Spectra of Product **3la**



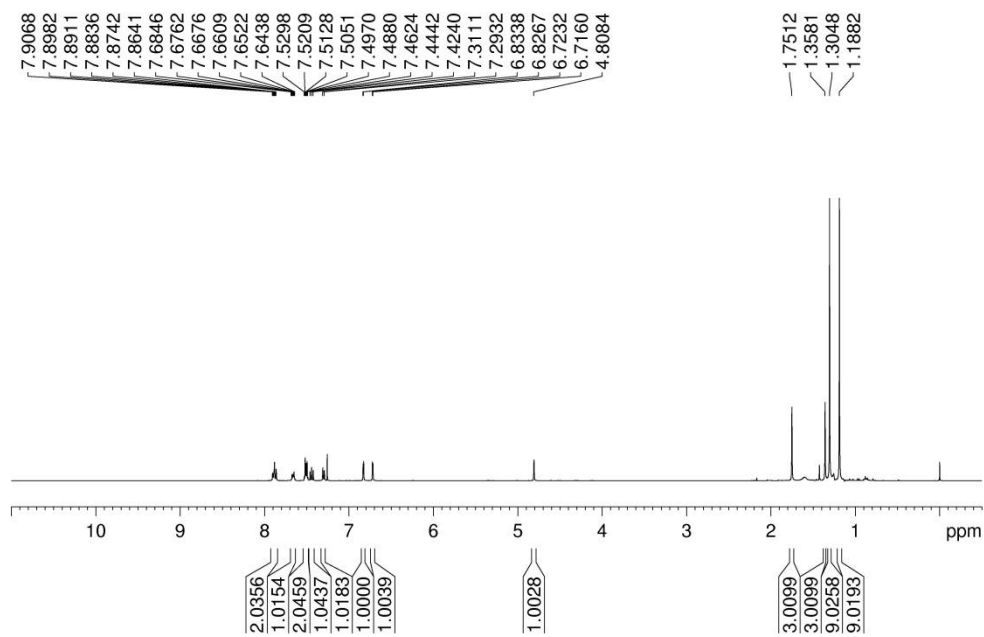
¹³C NMR Spectra of Product **3la**



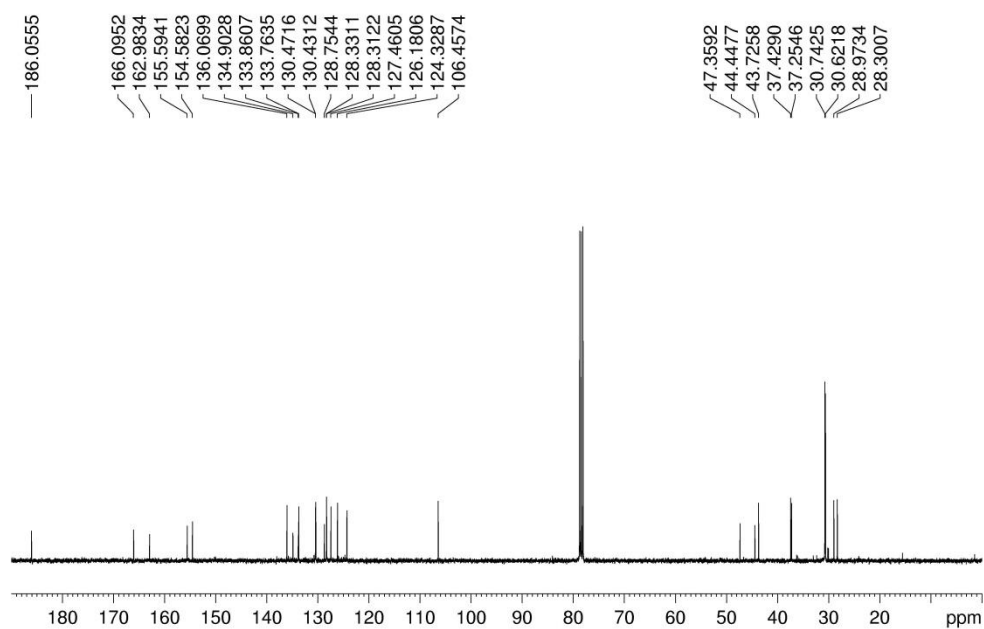
^1H NMR Spectra of Product **3ma**



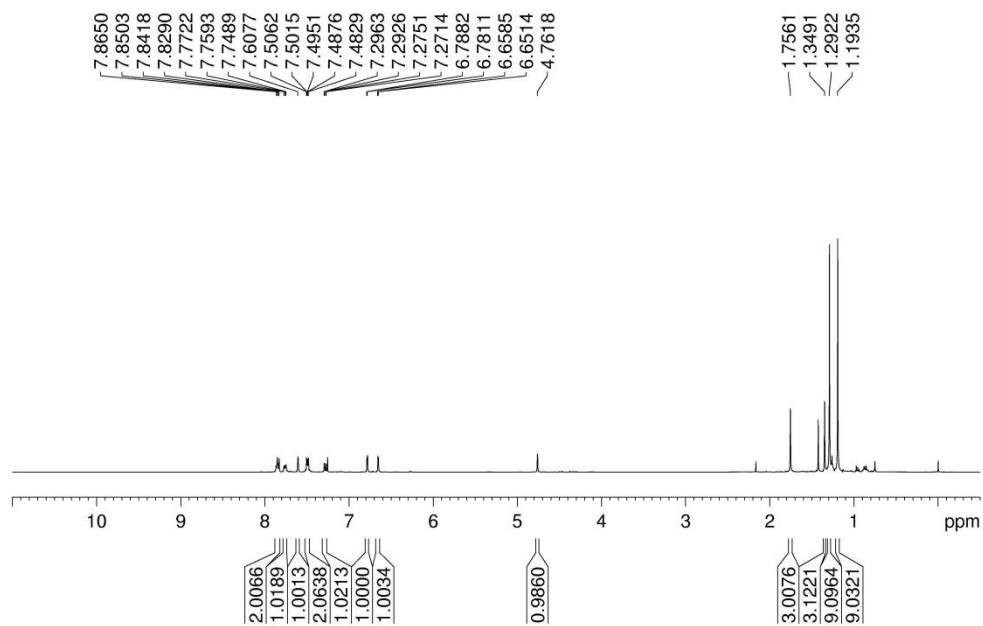
^{13}C NMR Spectra of Product **3ma**



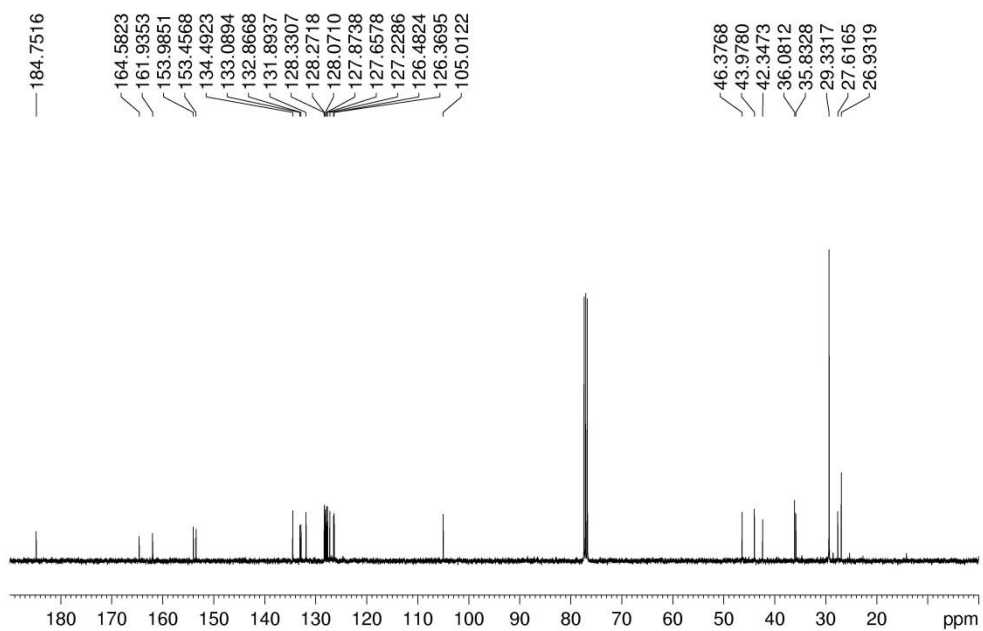
¹H NMR Spectra of Product **3na**



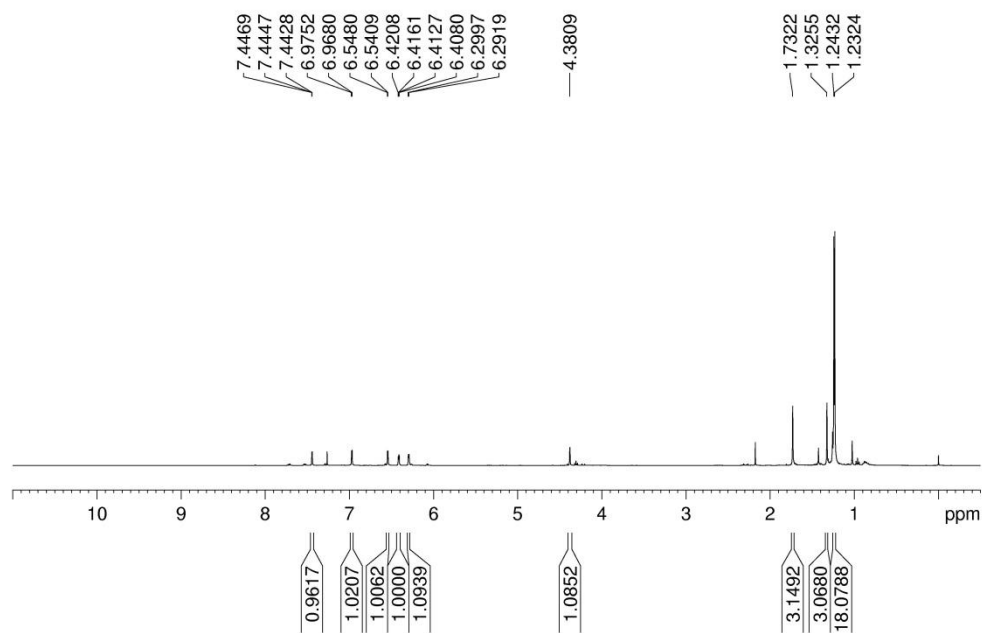
¹³C NMR Spectra of Product **3na**



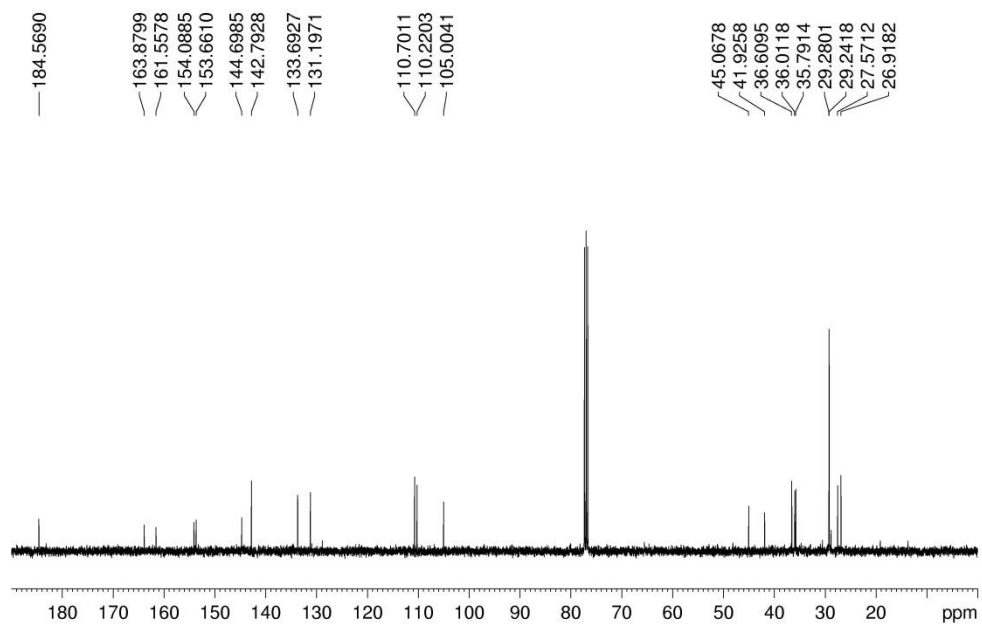
¹H NMR Spectra of Product 30a



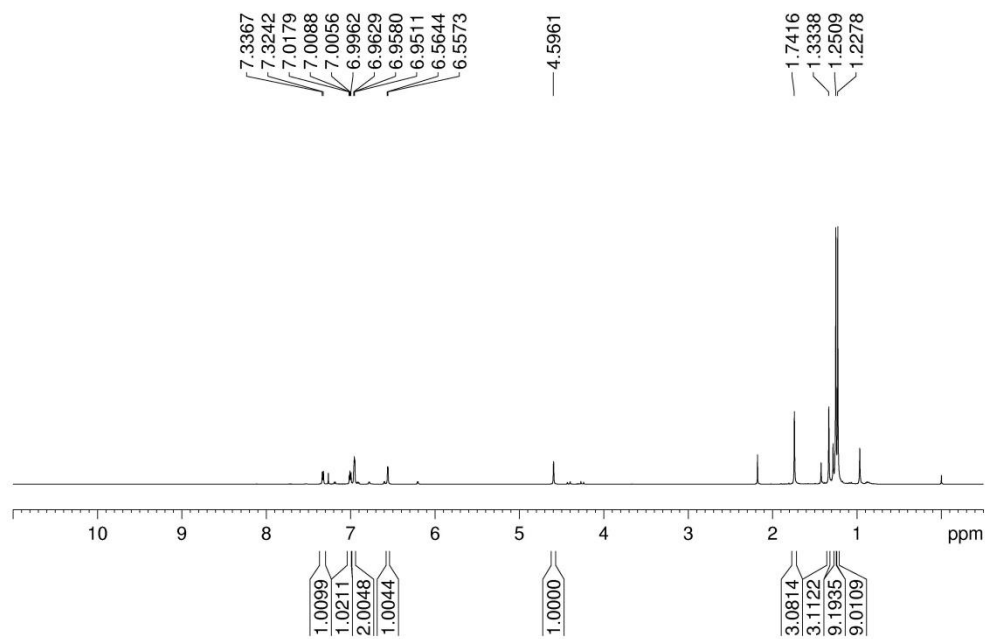
¹³C NMR Spectra of Product 30a



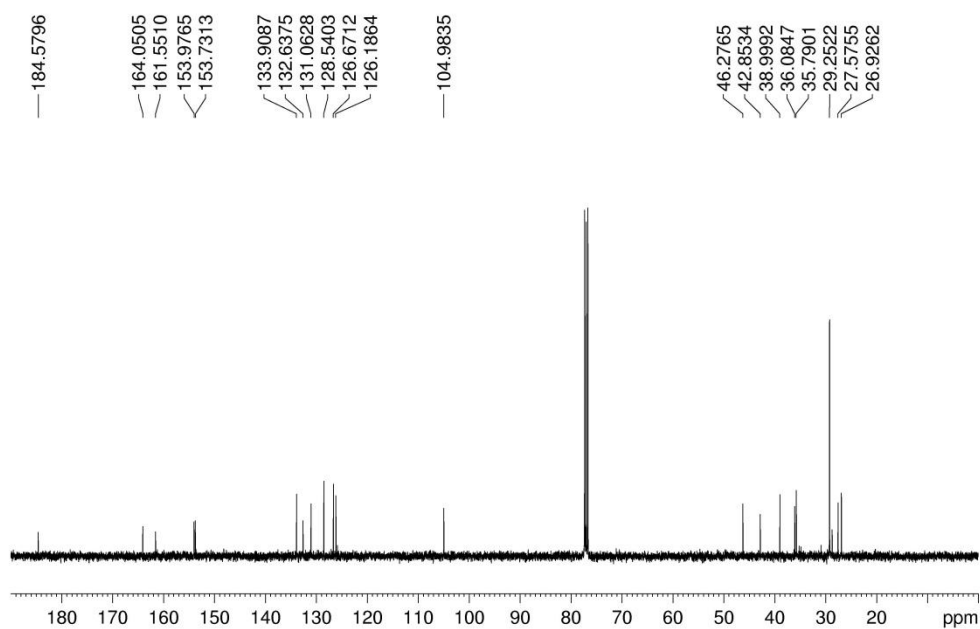
¹H NMR Spectra of Product **3pa**



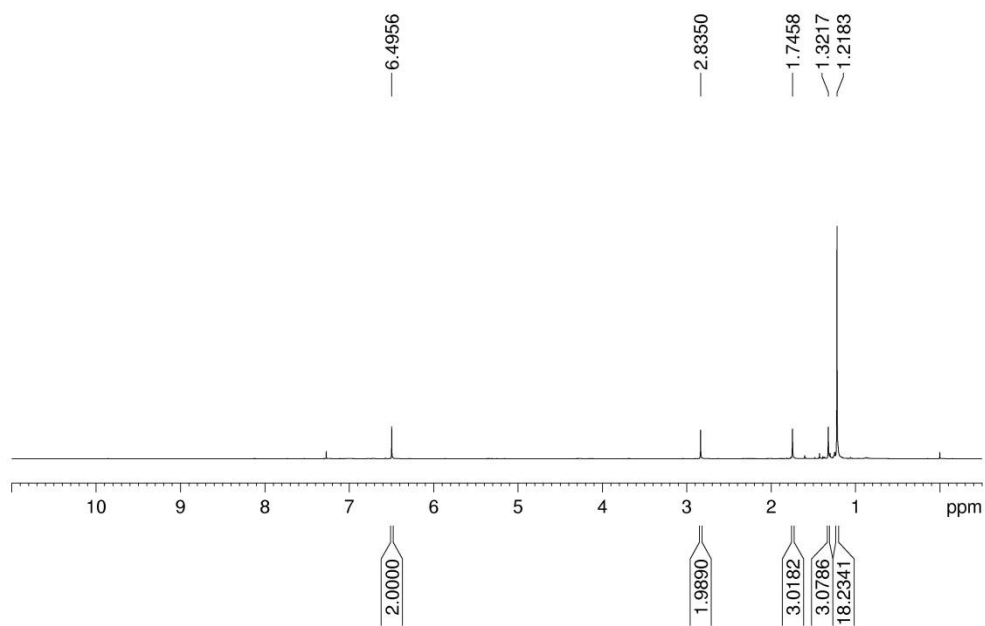
¹³C NMR Spectra of Product **3pa**



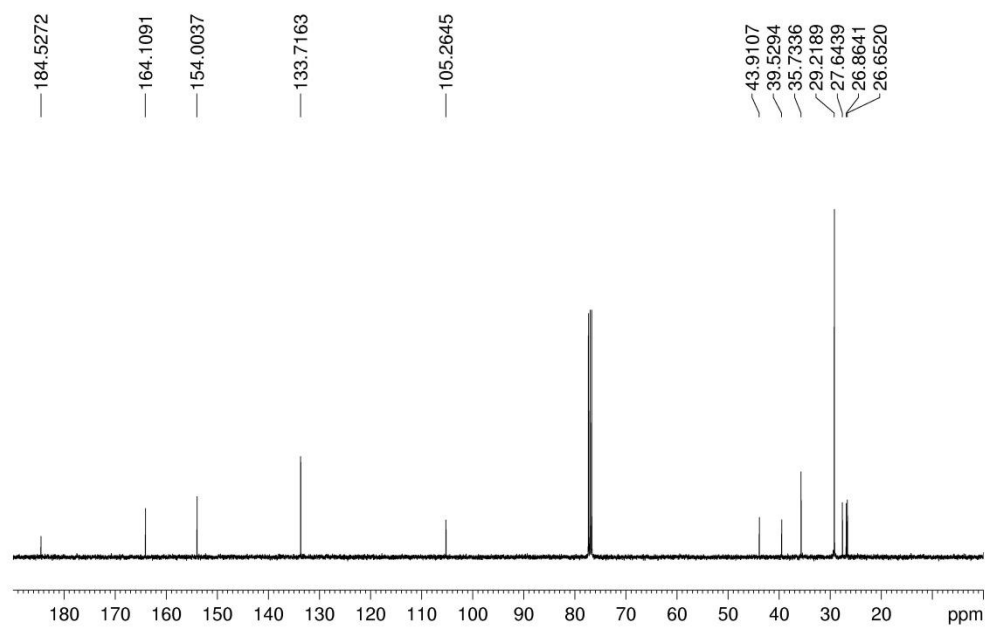
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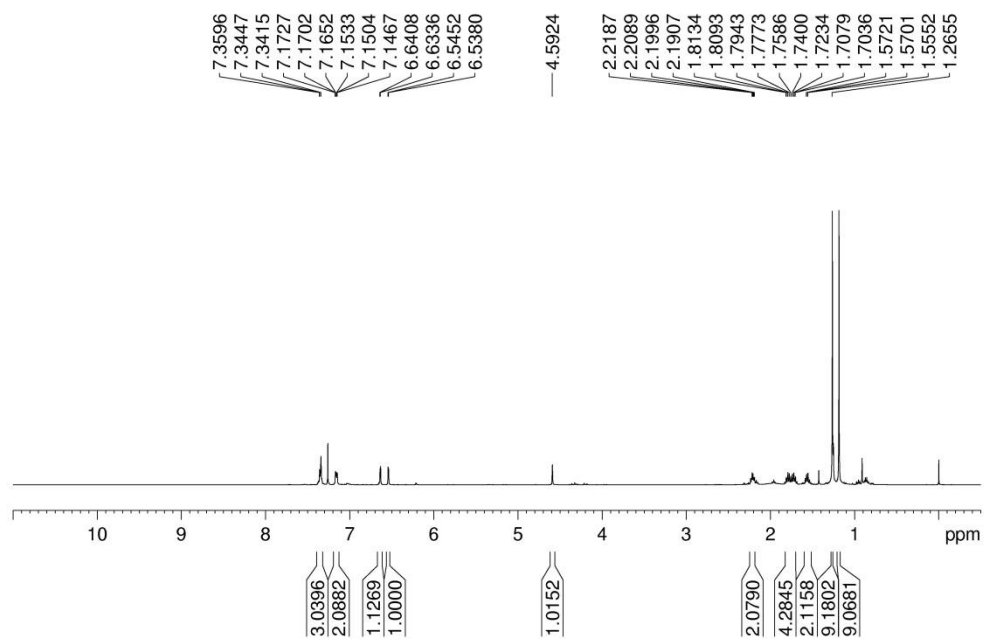
^{13}C NMR Spectra of Product **3qa**



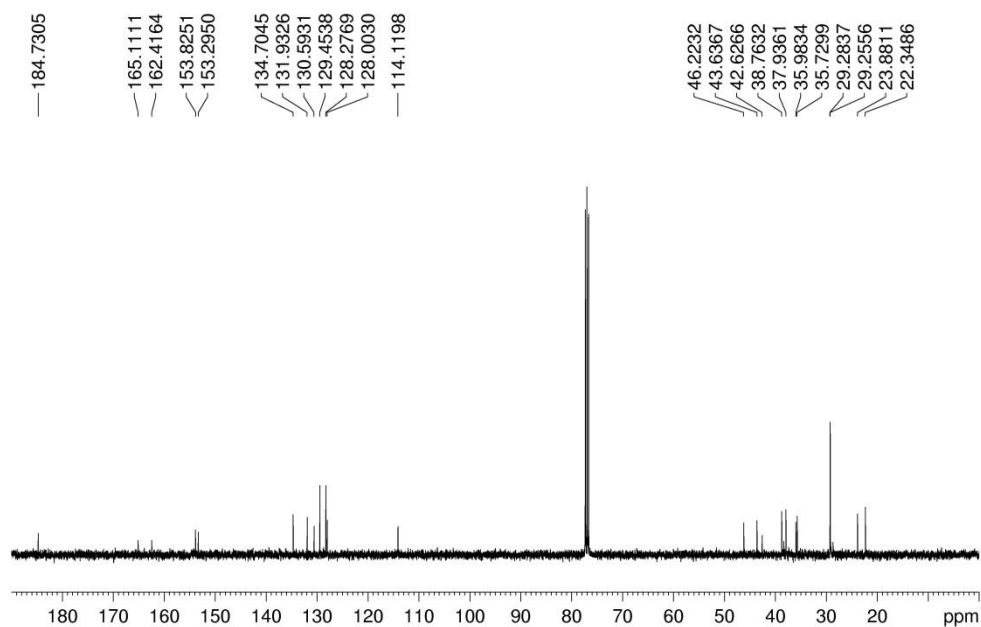
¹H NMR Spectra of Product **3ra**



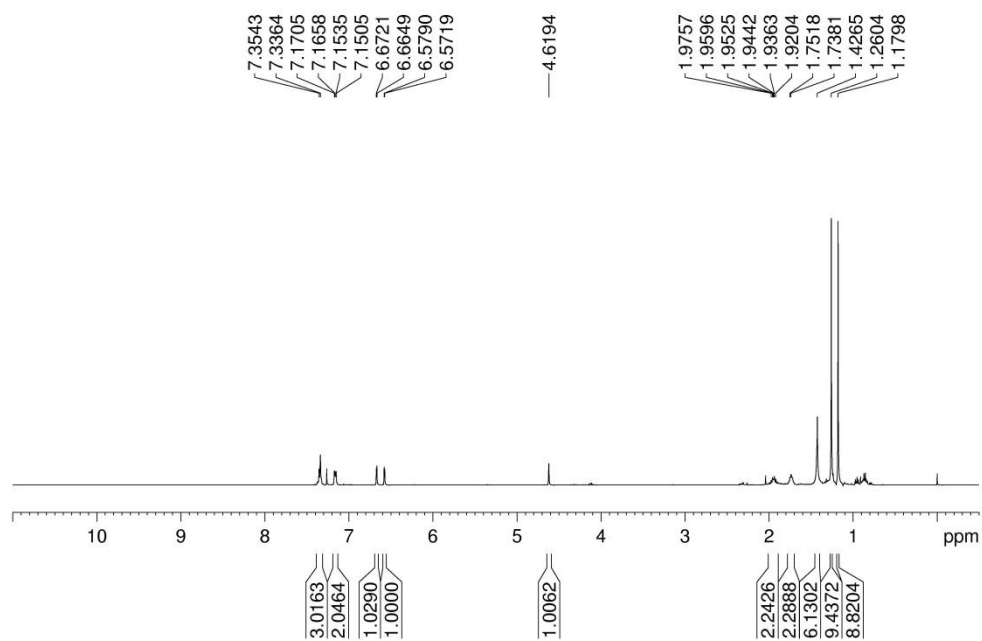
¹³C NMR Spectra of Product **3ra**



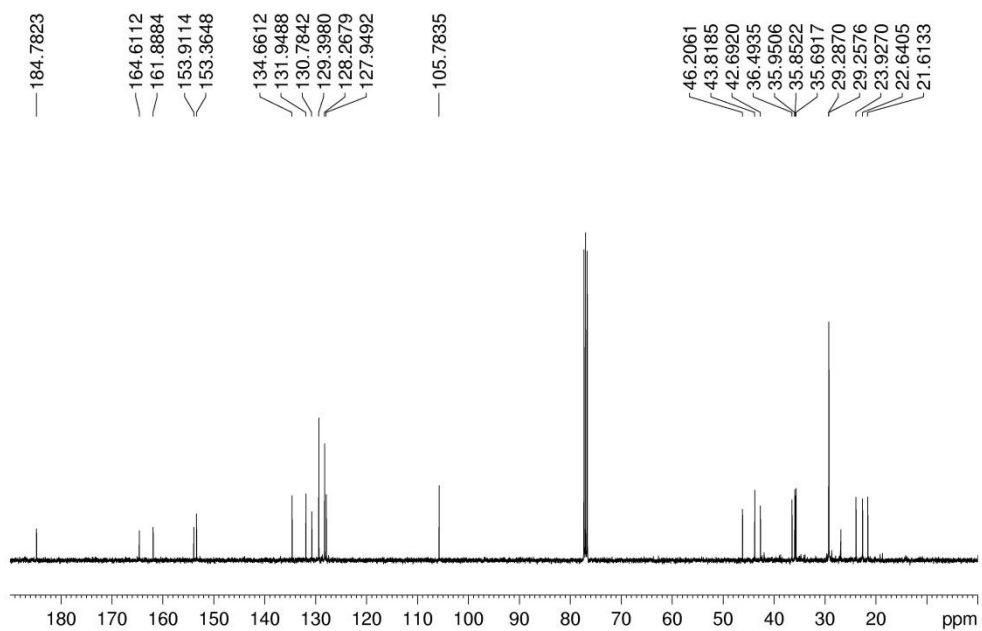
^1H NMR Spectra of Product **3ab**



^{13}C NMR Spectra of Product **3ab**

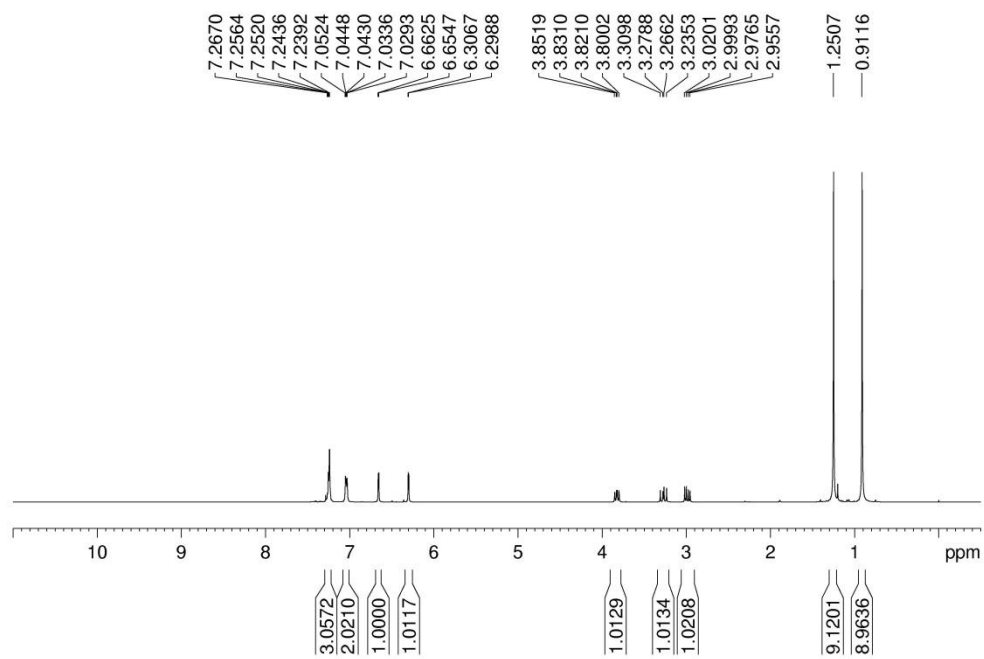


¹H NMR Spectra of Product **3ac**

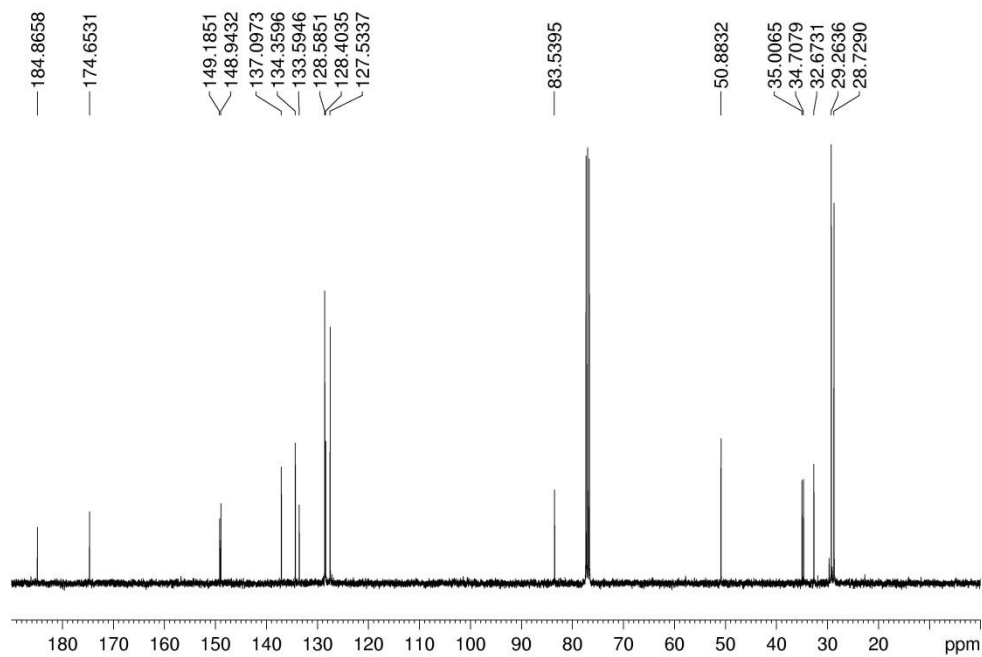


¹³C NMR Spectra of Product **3ac**

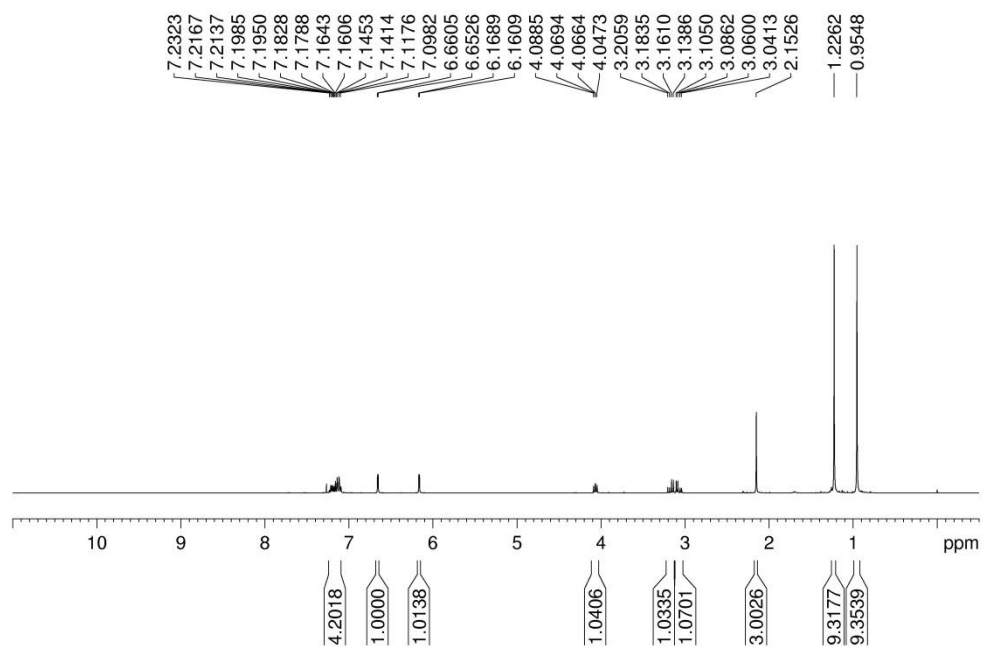
NMR Spectra of Spirobutyrolactones 4



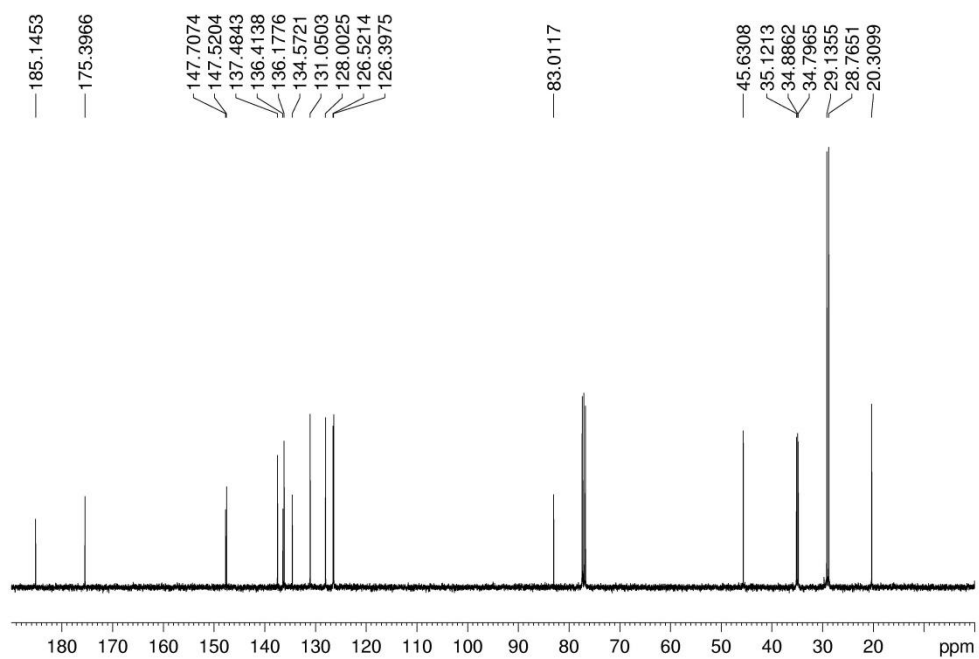
¹H NMR Spectra of Product 4a



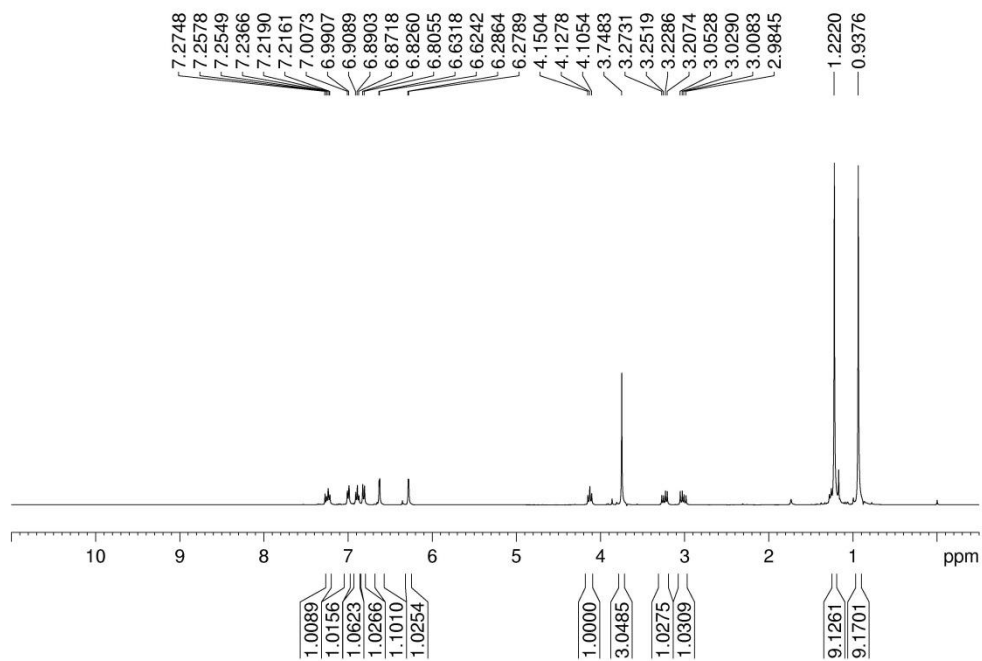
¹³C NMR Spectra of Product 4a



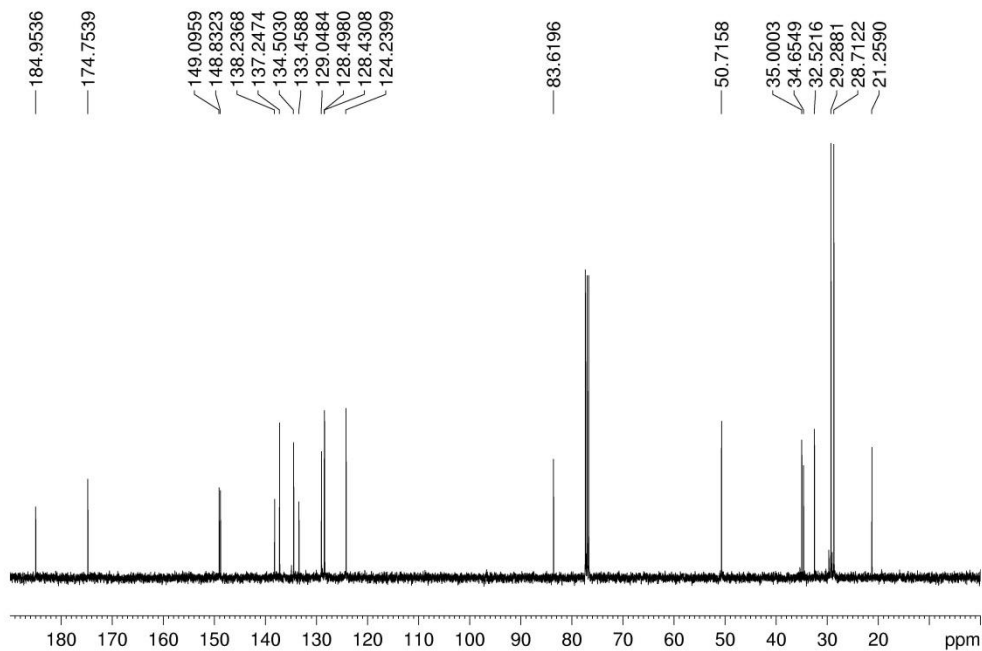
¹H NMR Spectra of Product **4b**



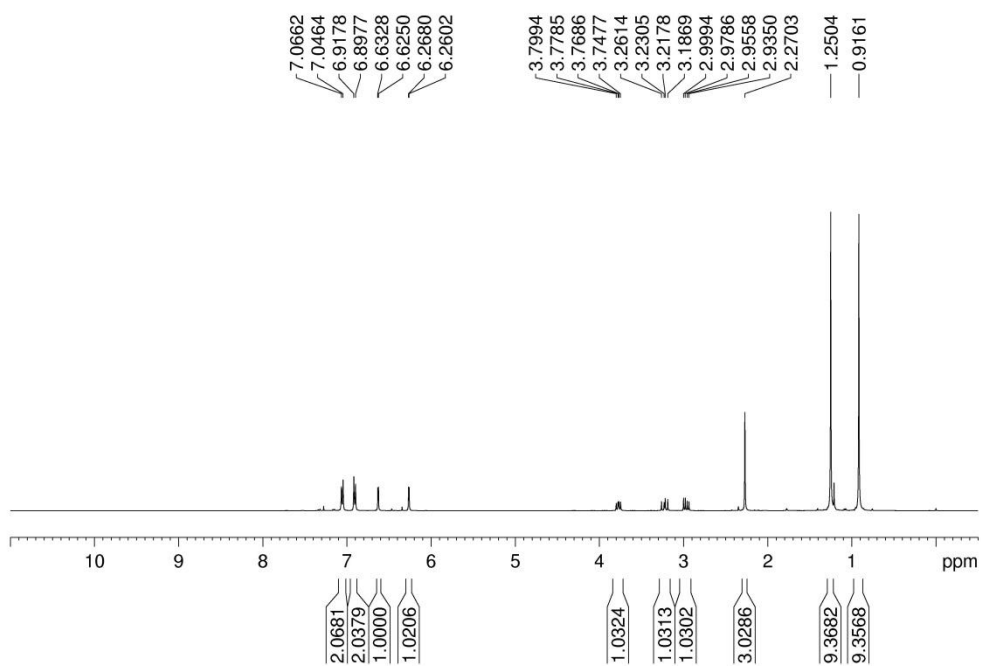
¹³C NMR Spectra of Product **4b**



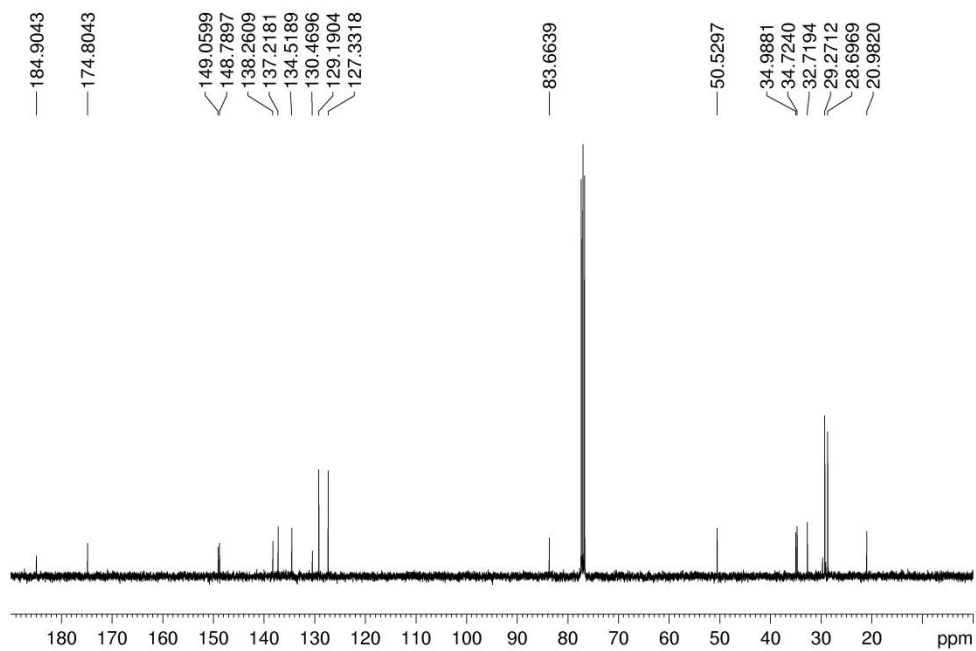
¹H NMR Spectra of Product 4c



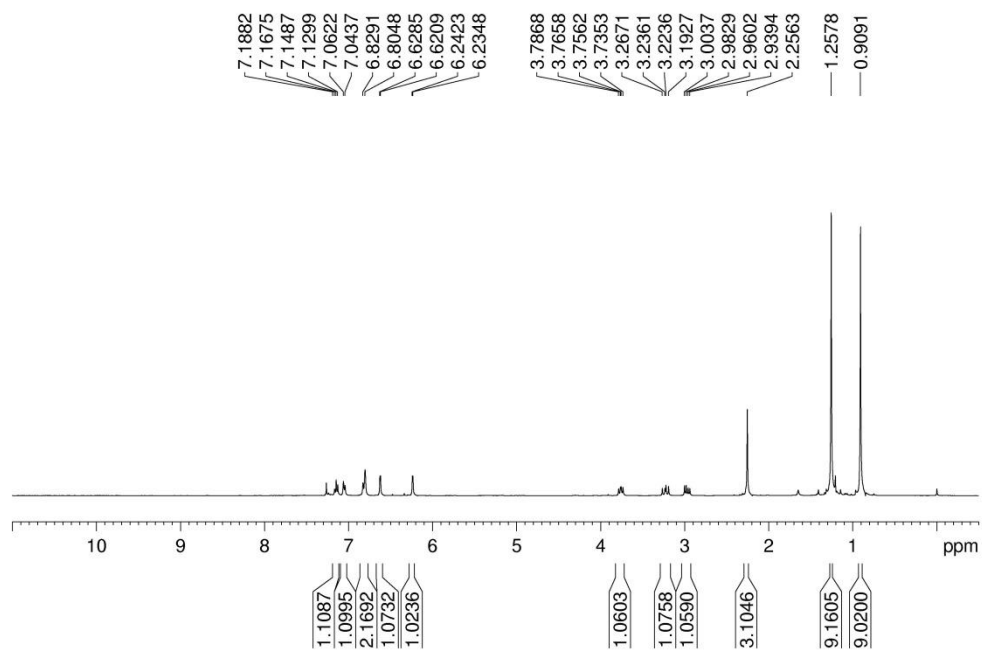
¹³C NMR Spectra of Product 4c



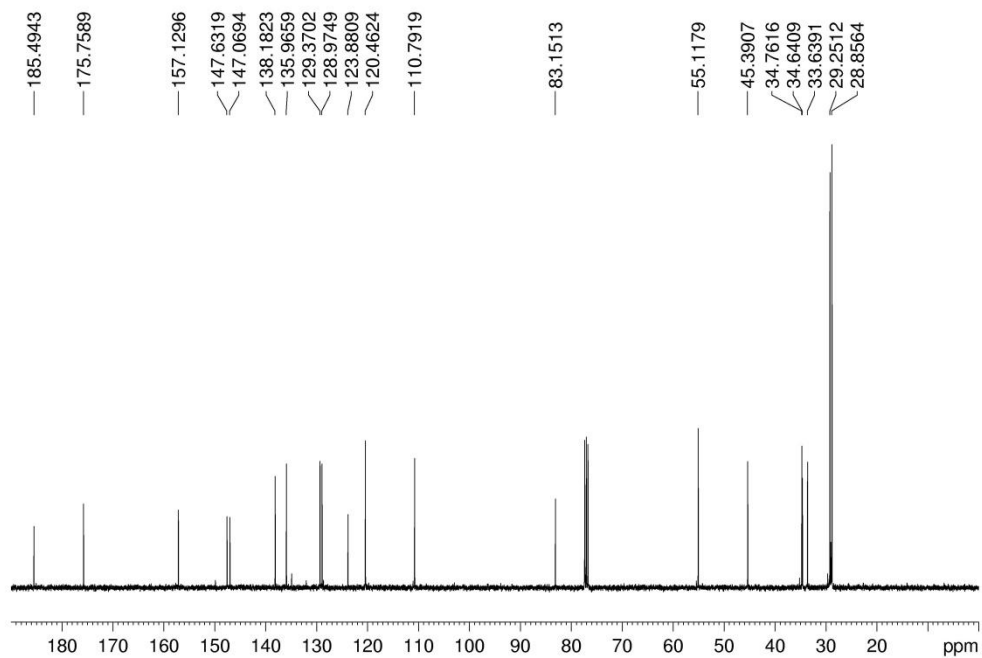
^1H NMR Spectra of Product **4d**



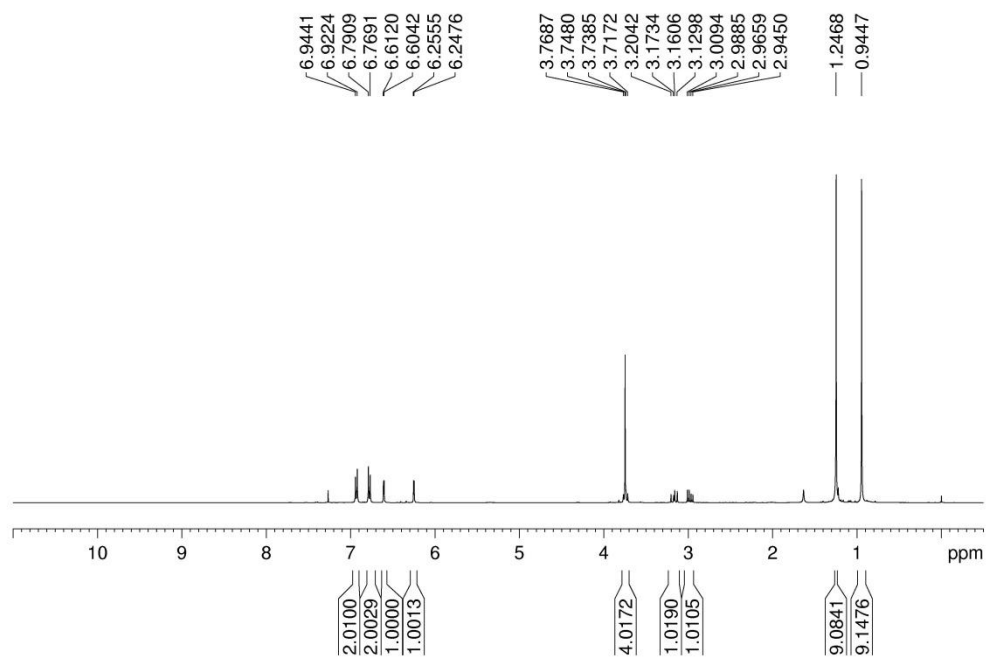
^{13}C NMR Spectra of Product **4d**



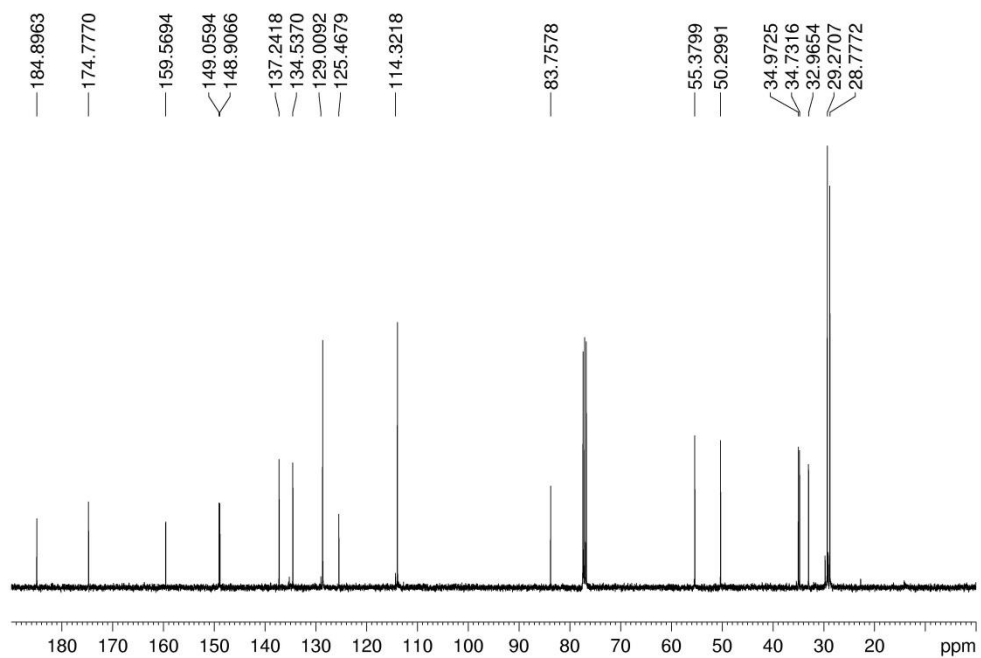
¹H NMR Spectra of Product 4e



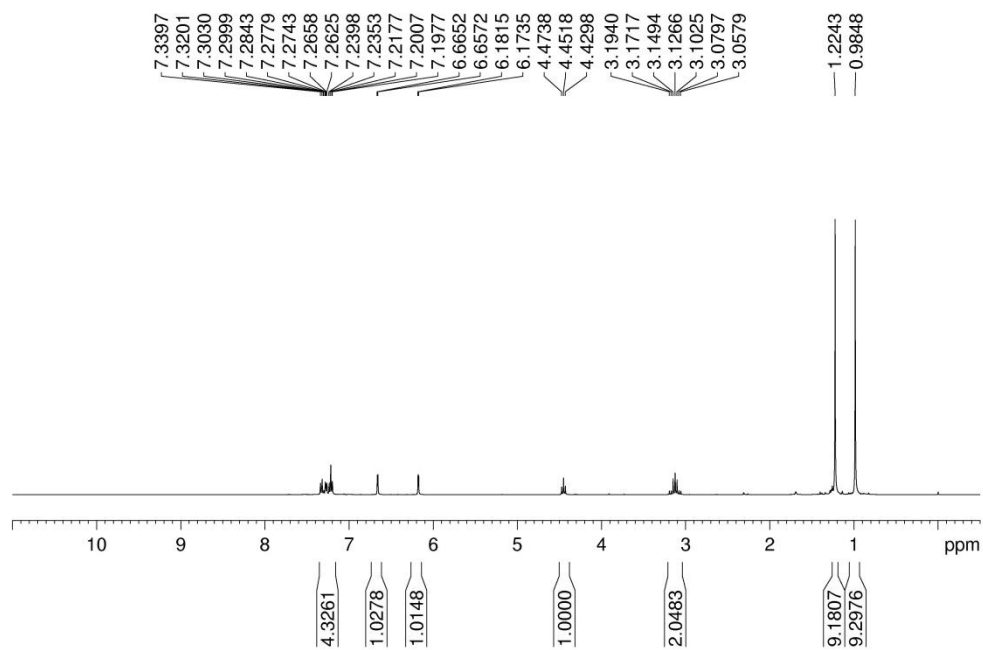
¹³C NMR Spectra of Product 4e



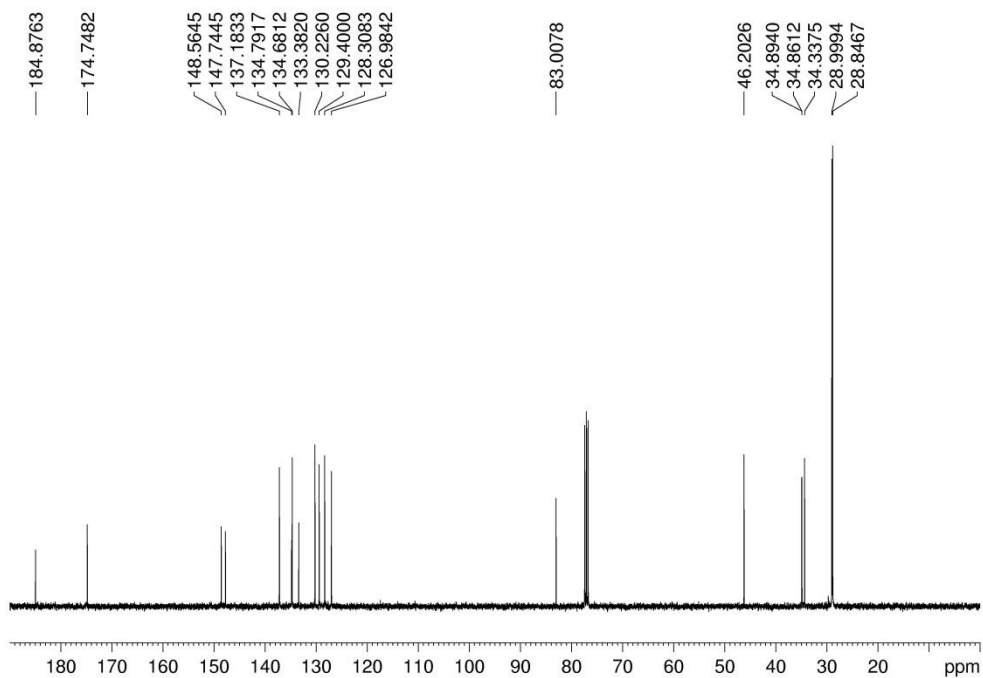
^1H NMR Spectra of Product **4f**



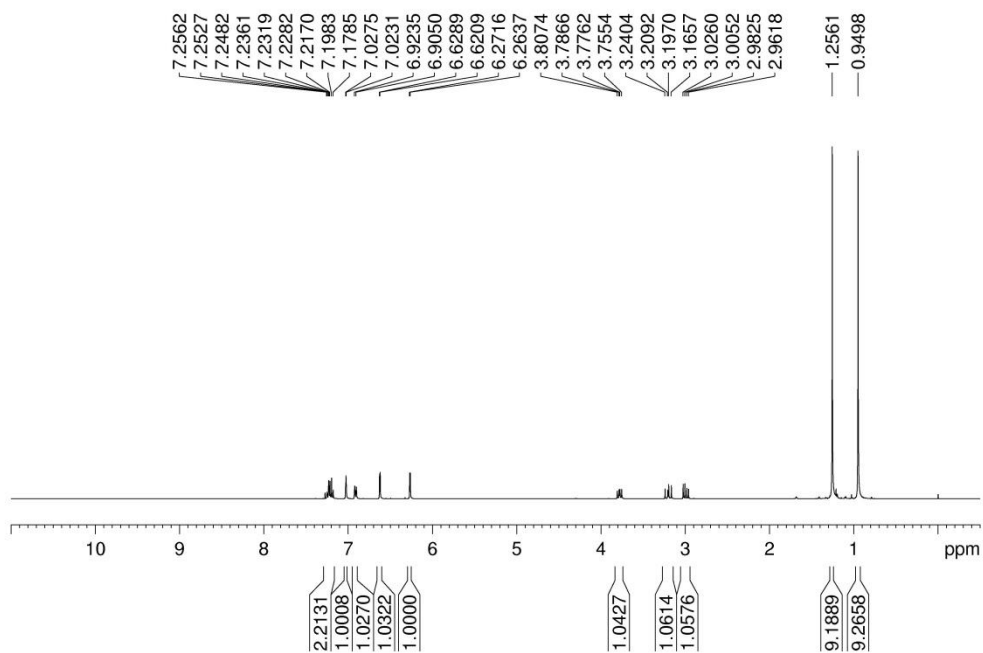
^{13}C NMR Spectra of Product **4f**



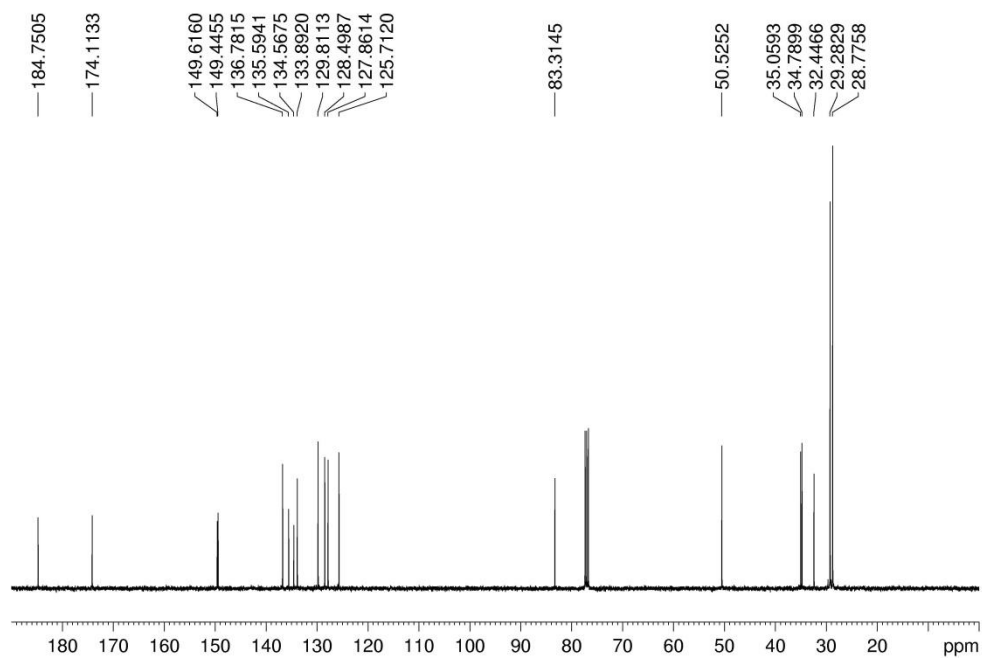
¹H NMR Spectra of Product **4g**



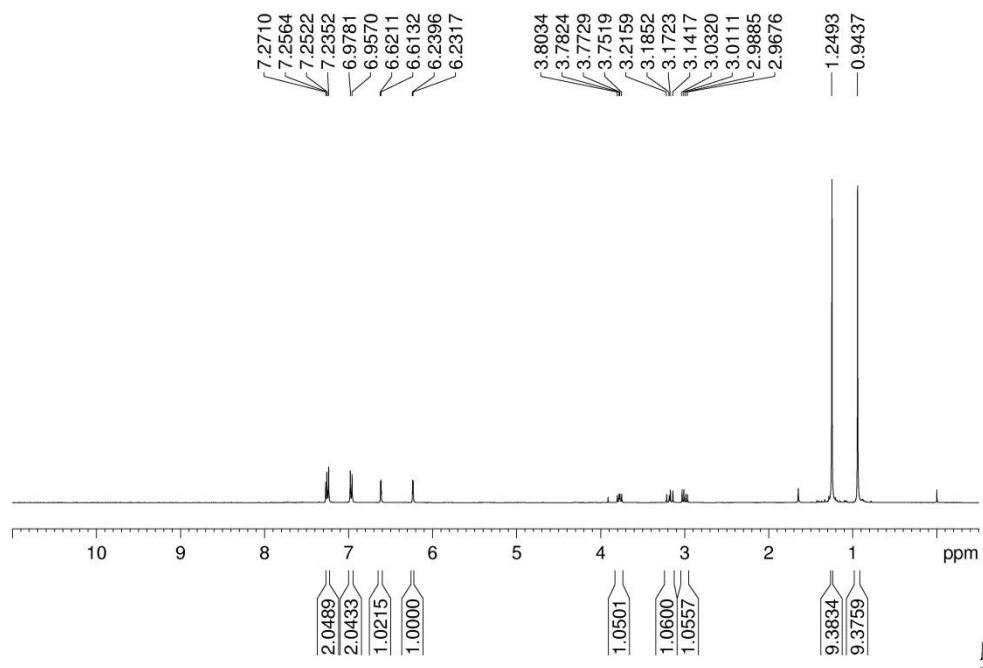
¹³C NMR Spectra of Product **4g**



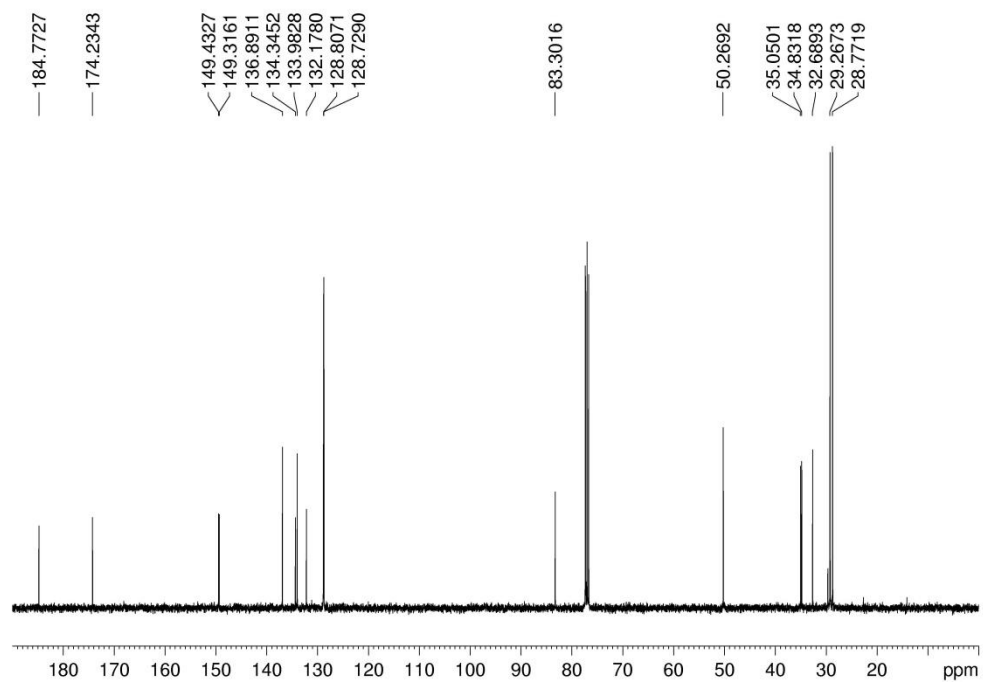
¹H NMR Spectra of Product **4h**



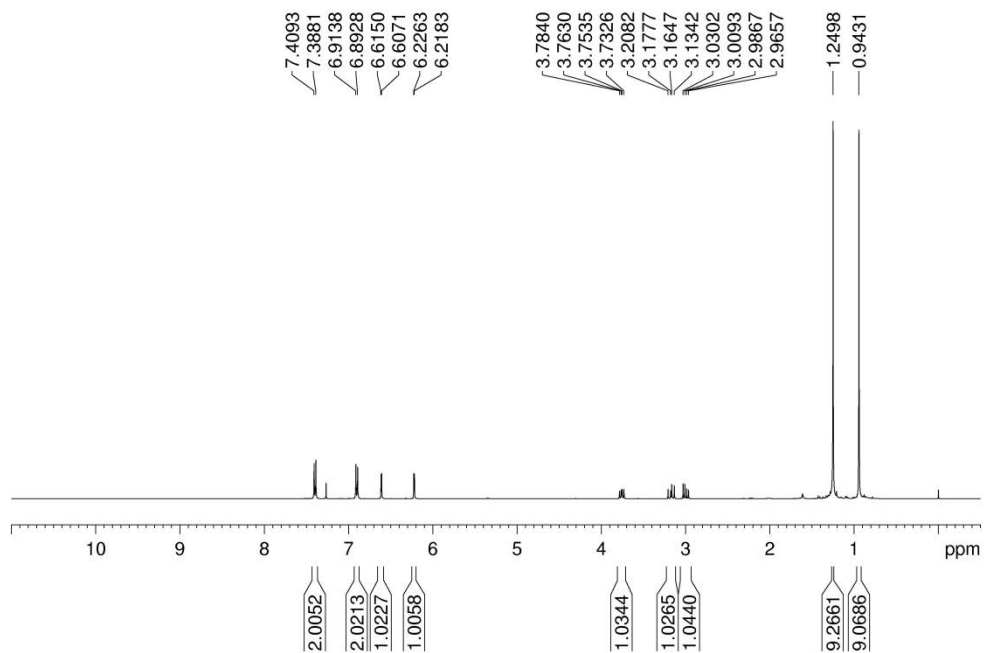
¹³C NMR Spectra of Product **4h**



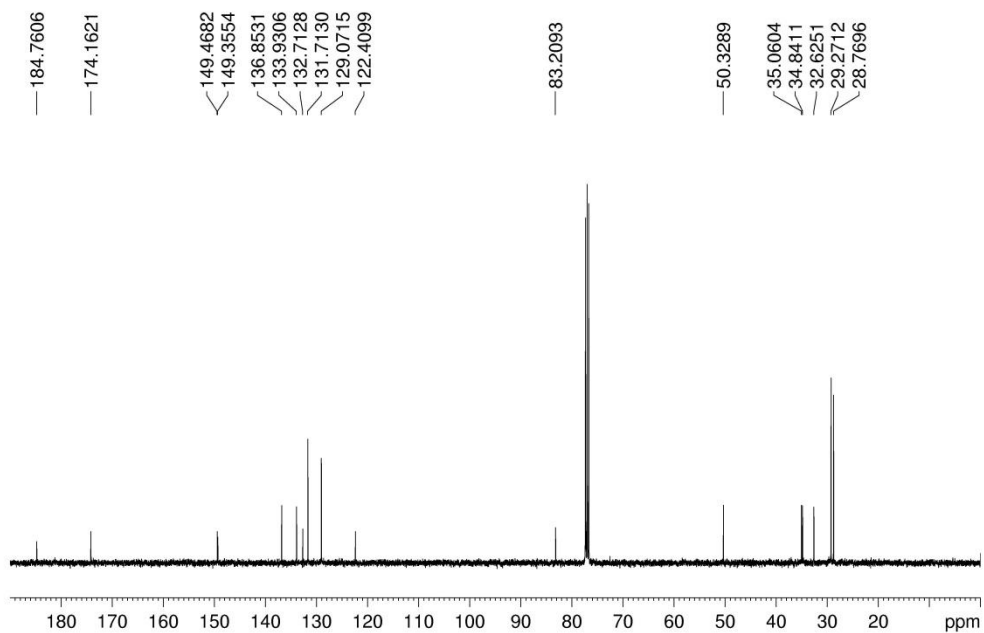
¹H NMR Spectra of Product **4i**



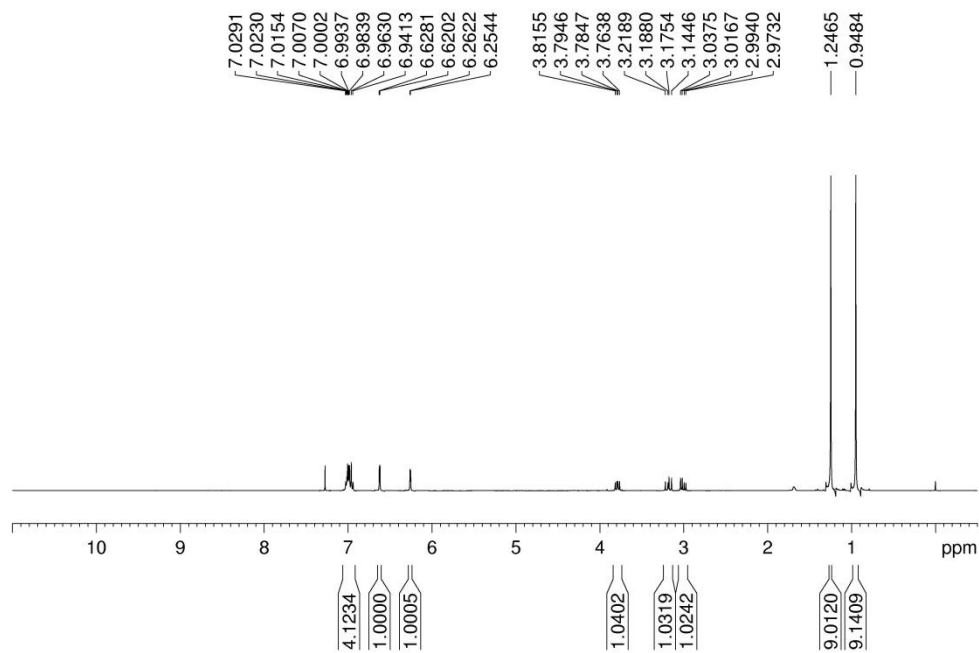
¹³C NMR Spectra of Product **4i**



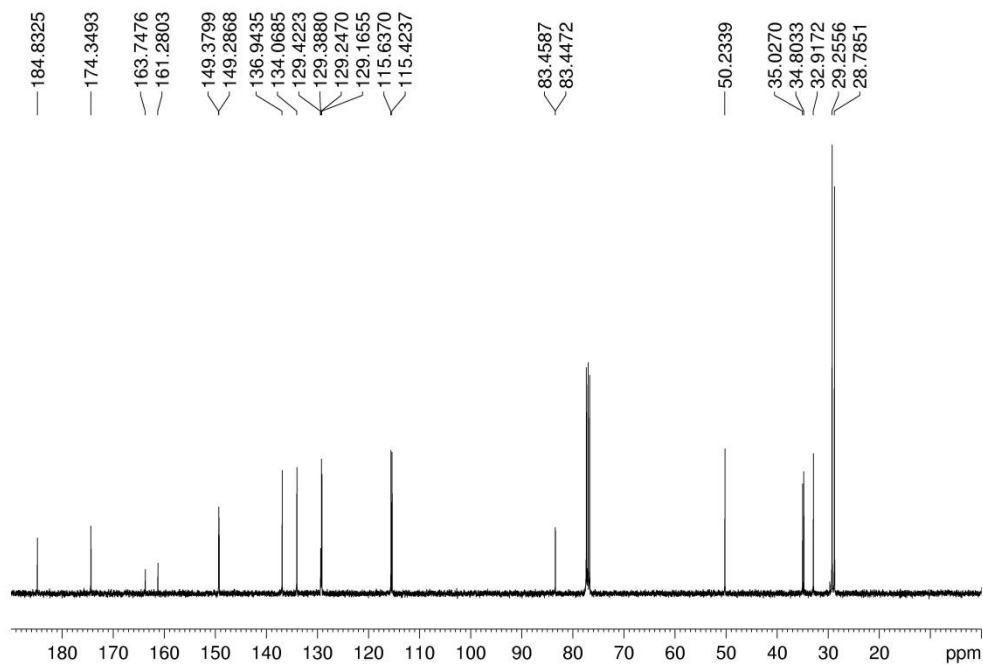
¹H NMR Spectra of Product 4j



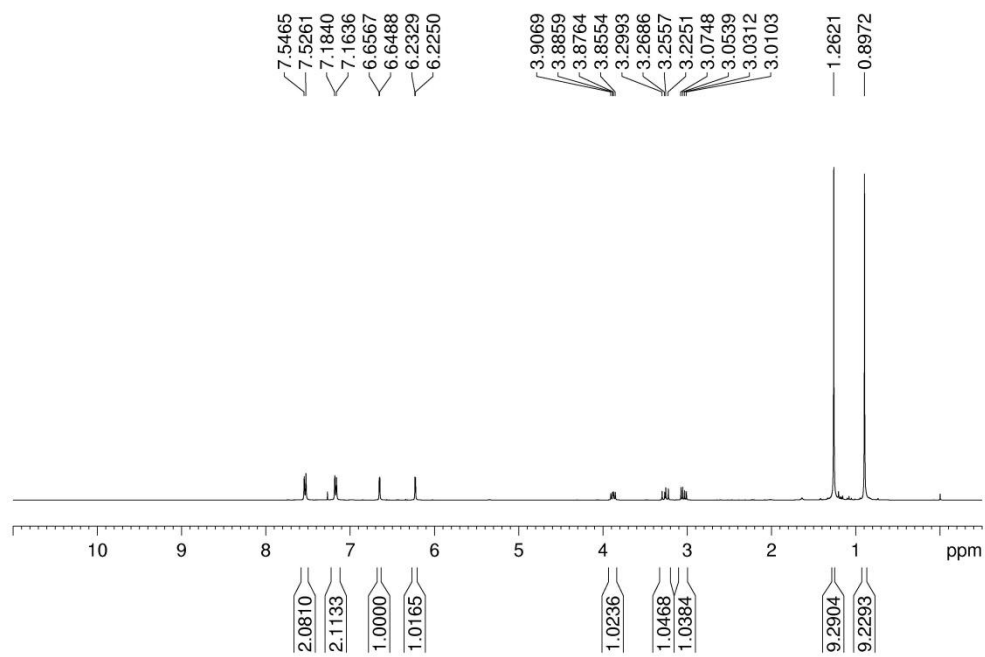
¹³C NMR Spectra of Product 4j



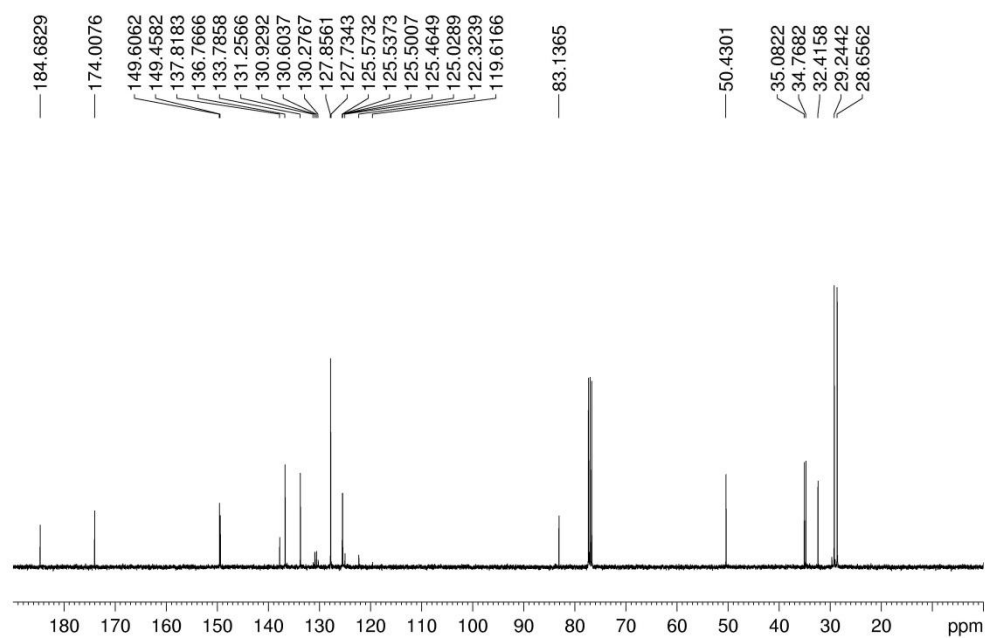
¹H NMR Spectra of Product **4k**



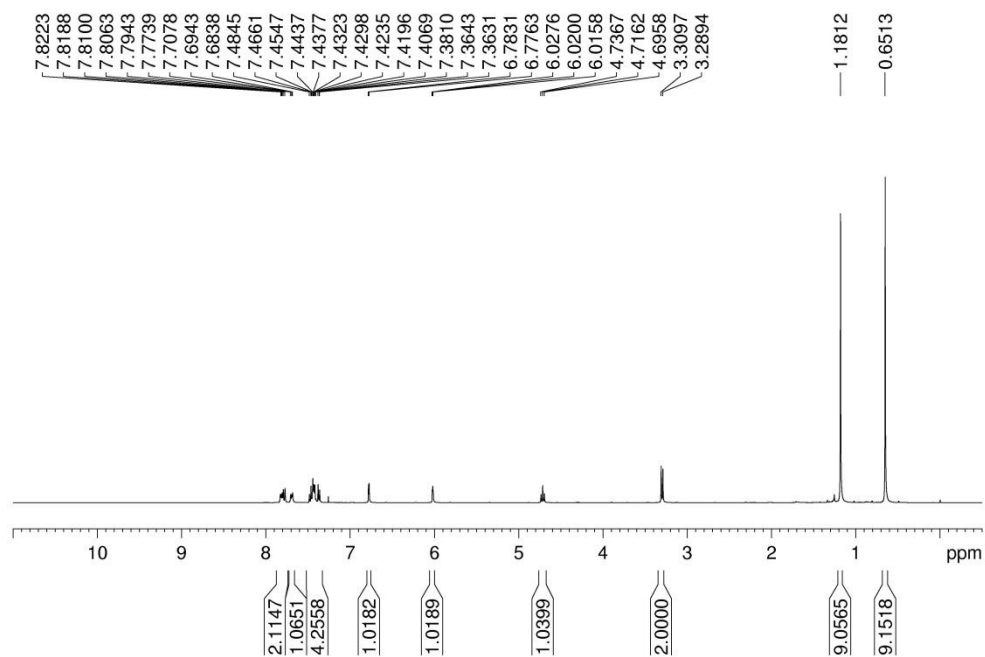
¹³C NMR Spectra of Product **4k**



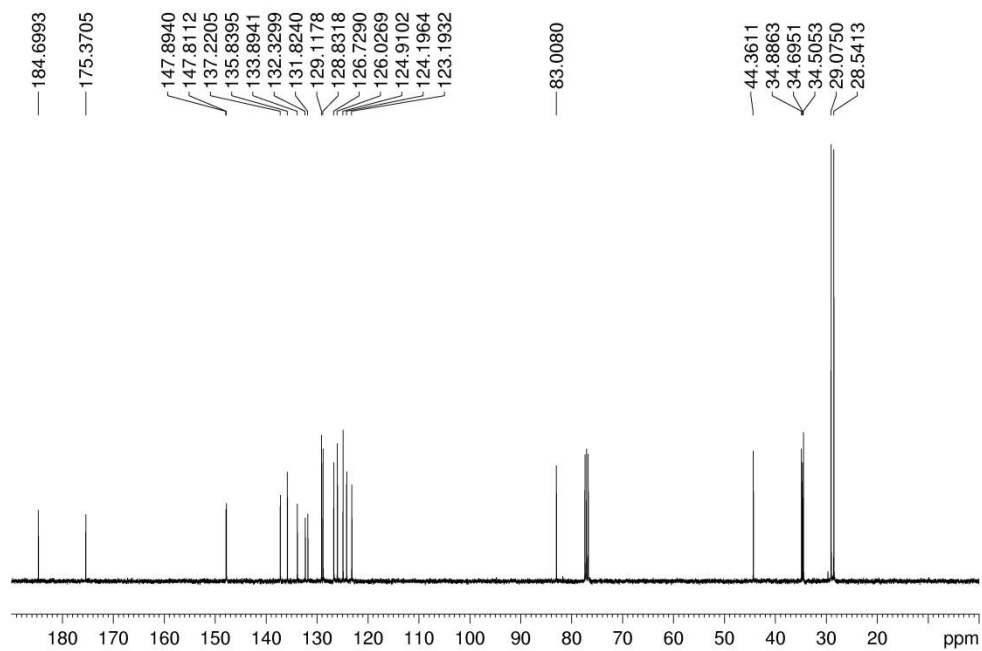
¹H NMR Spectra of Product 4I



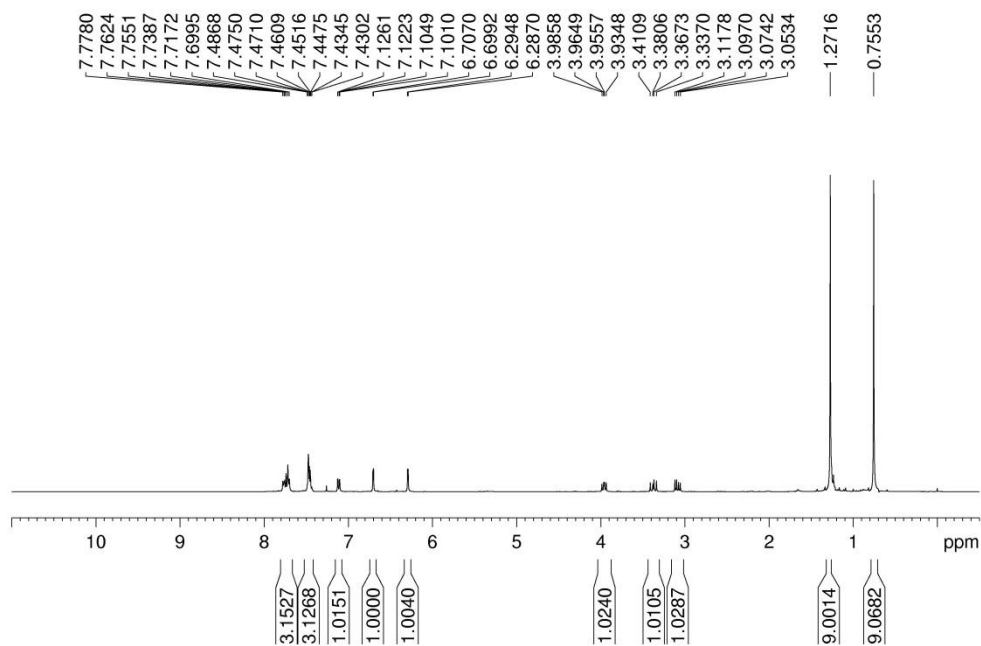
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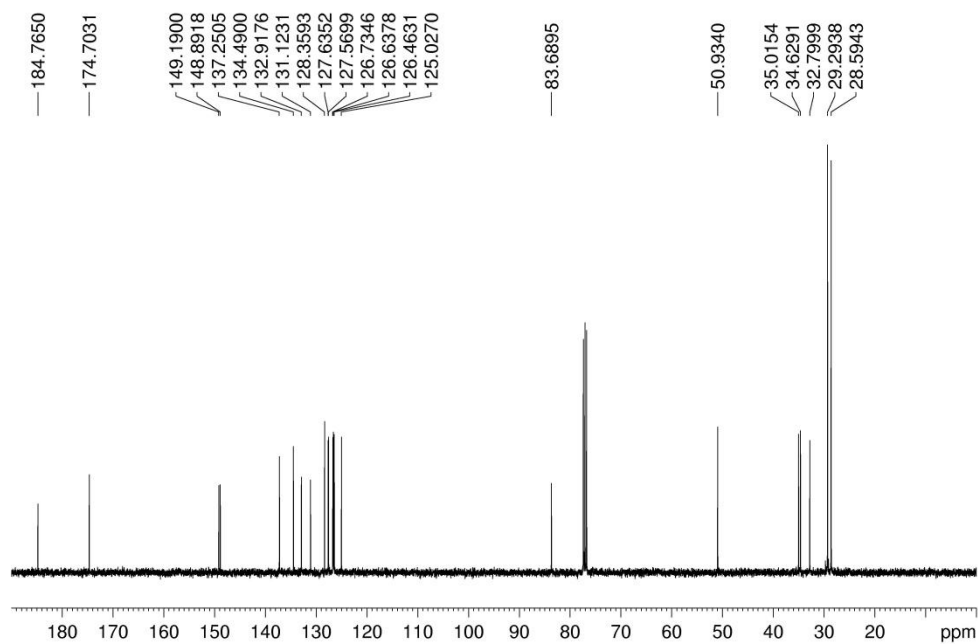
¹H NMR Spectra of Product **4n**



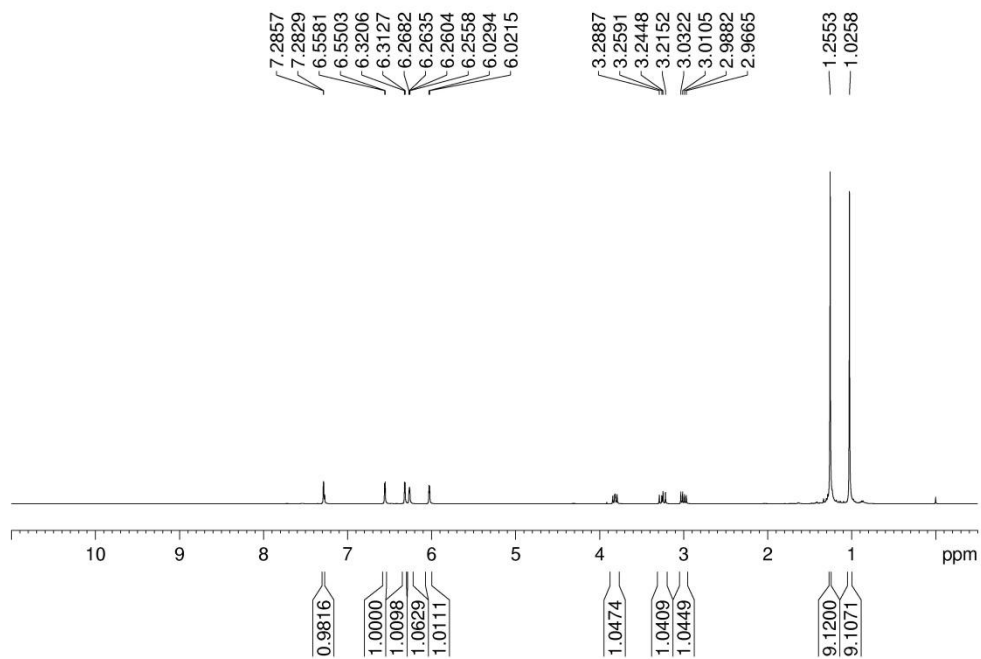
¹³C NMR Spectra of Product **4n**



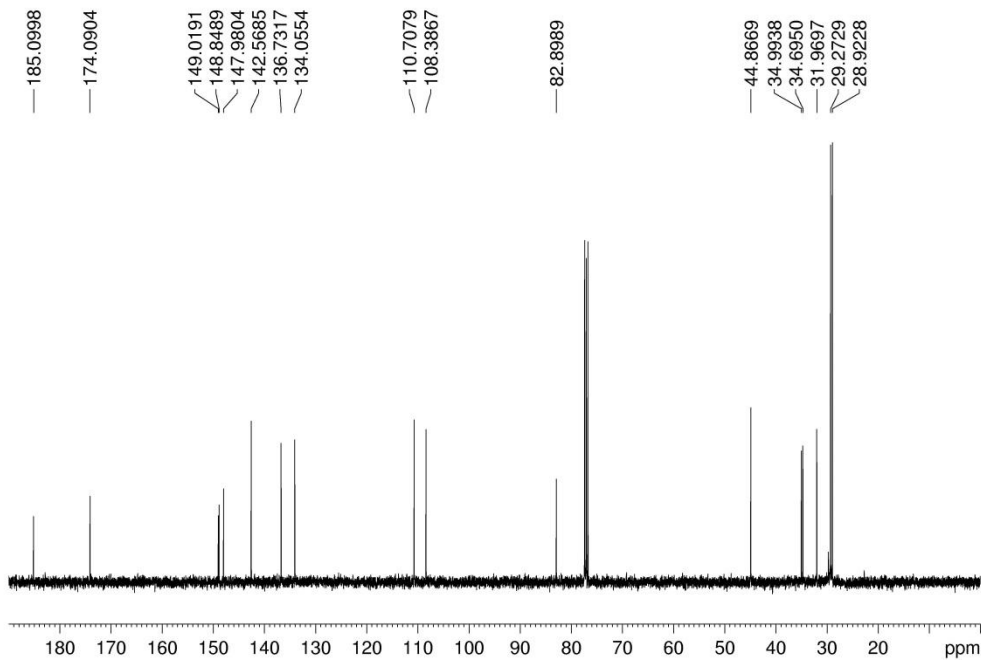
¹H NMR Spectra of Product **4o**



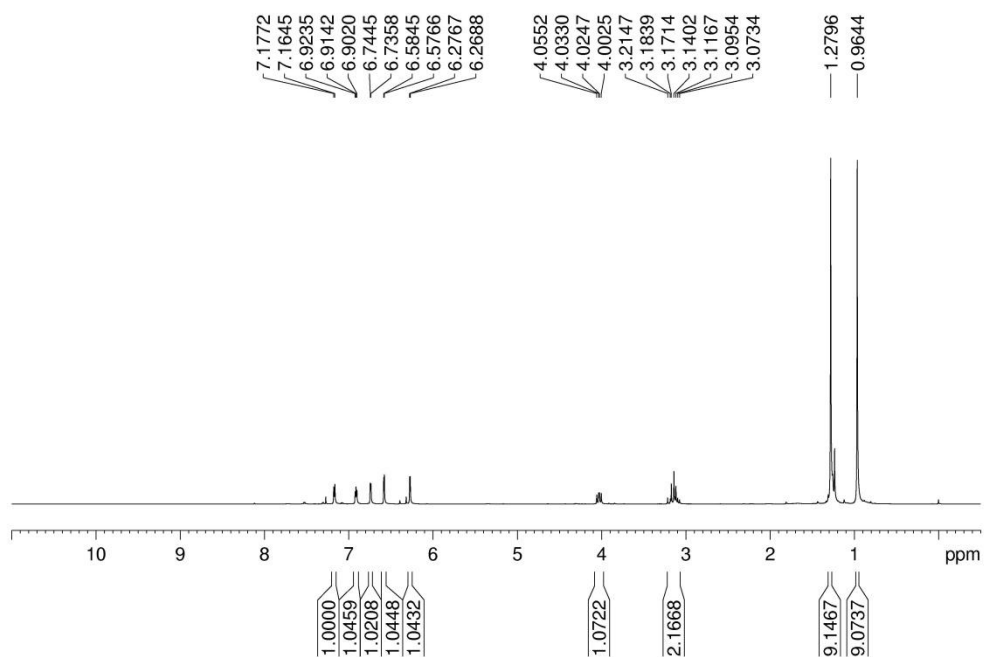
¹³C NMR Spectra of Product **4o**



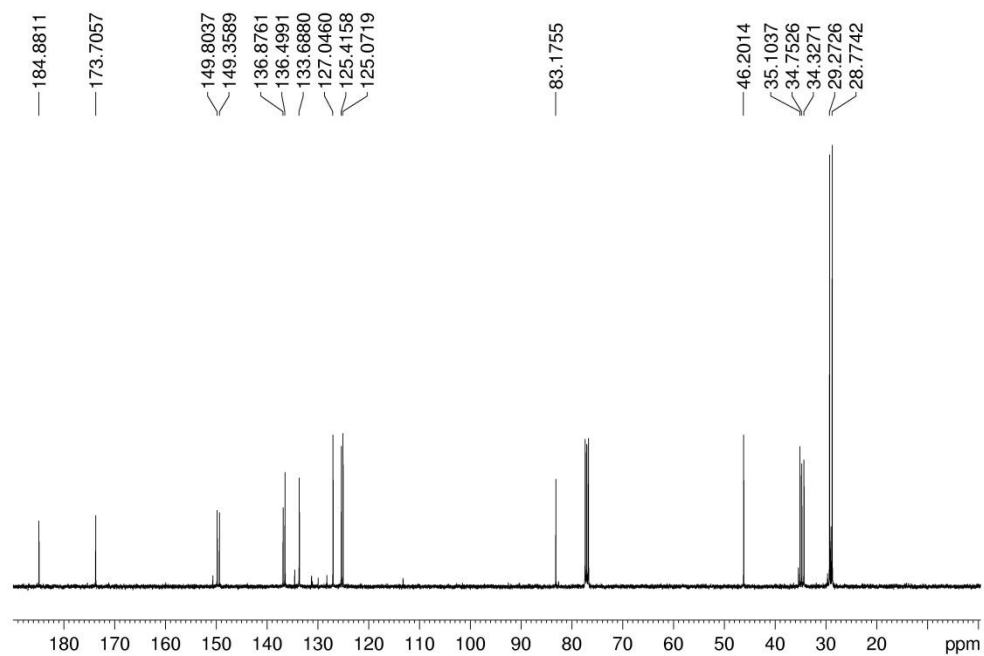
¹H NMR Spectra of Product **4p**



¹³C NMR Spectra of Product **4p**



¹H NMR Spectra of Product **4q**



¹³C NMR Spectra of Product **4q**