Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Access to functionalized 2-pyrones through cascade reactions of α-halothioesters involving DBU-derived ammonium ylides

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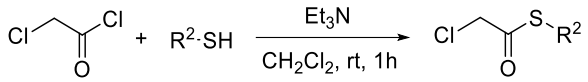
Contents

1. General information

Unless stated otherwise, reagents were used directly as obtained commercially. Reactions were monitored by TLC using silica gel GF254 plates. Flash column chromatography was performed using silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on Bruker AV III 400MHz NMR spectrometers. Chemical shifts are reported in ppm using tetramethylsilane or the residual solvent peak as a reference. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR. HRMS were recorded on a Waters Xevo G2-XS TOF mass spectrometer. *β,γ*-Unsaturated *α*-keto esters were prepared according to previously reported procedures.[1] NHC catalysts **5a** and **5b** were prepared according to previously reported procedures.[2]

2. Preparation and characterizations of α-halothioesters 1

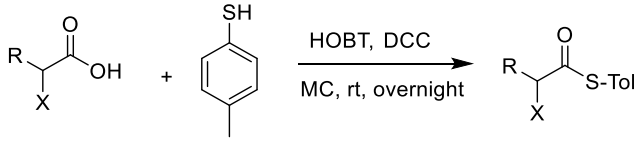
General procedure A:



1

To a solution of 2-chloroacetyl chloride (1 equiv.) in dichloromethane (5 mL/mmol based on 2-chloroacetyl chloride) were added thiol (0.8 equiv.), Et_3N (1.5 equiv.) successively at 0℃ and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (petroleum ether:ethyl acetate = 25:1) to afford the desired thioester **1**.

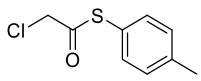
General procedure B:



1

To a solution of carboxylic acid (1 equiv.) in dichloromethane (5 mL/mmol based on carboxylic acid) was added HOBT (1.5 equiv.) and DCC (1.5 equiv.) successively at 0℃. After 30 min, *p*-toluenethiol was added and the reaction was stirred overnight at room temperature. The solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (petroleum ether:ethyl acetate = 20:1) to afford the desired thioester **1**.

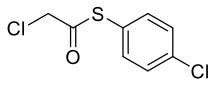
S-(p-tolyl) 2-chloroethanethioate (**1a**)



Following the general procedure A with 2-chloroacetyl chloride (22.6 mmol) and *p*-toluenethiol (18.5 mmol), **1a** was obtained as a yellow solid (2.82 g, 76% yield). R_f =0.6 (petroleum ether:ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.35 – 7.29 (m, 2H), 7.25 (m, 2H), 4.27 (s, 2H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.9, 140.4, 134.6, 130.3, 122.9, 47.9,

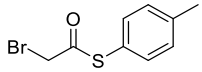
21.4; **IR** (KBr): v = 3380, 2938, 1919, 1698, 1595, 1492, 1401, 1208, 1180, 1103, 986, 814, 779, 732, 530 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_9H_{10}OSCl$ 201.0141, found 201.0145.

S-(4-chlorophenyl) 2-chloroethanethioate (**1b**)



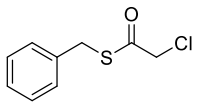
Following the general procedure A with 2-chloroacetyl chloride (4.9 mmol) and 4-chlorobenzenethiol (3.9 mmol), **1b** was obtained as a yellow liquid (0.56 g, 65% yield). R_f =0.6 (petroleum ether:ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.42 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 4.29 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 192.2, 136.5, 135.9, 129.8, 124.9, 47.9; **IR** (KBr): v = 3322, 3079, 3002, 2947, 1899, 1678, 1572, 1475, 1407, 1387, 1259, 1179, 1079, 1012, 823, 815, 793, 594 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_8H_6OSCl_2Na$ 242.9414, found 242.9418.

S-(p-tolyl) 2-bromoethanethioate (**1c**)



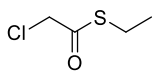
Following the general procedure B with 2-bromoacetic acid (7.2 mmol) and *p*-toluenethiol (5.8 mmol), **1c** was obtained as a yellow solid (0.99 g, 70% yield). R_f =0.7 (petroleum ether:ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.20 (m, 2H), 4.07 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.3, 140.2, 134.4, 130.2, 123.3, 33.2, 21.3; **IR** (KBr): v = 3019, 2918, 2864, 1897, 1491, 1398, 1302, 1197, 1090, 1017, 801, 718 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_9H_{10}OSBr$ 244.9636, found 244.9635.

S-benzyl 2-chloroethanethioate (**1d**)



Following the general procedure A with 2-chloroacetyl chloride (10.0 mmol) and phenylmethanethiol (8.0 mmol), **1d** was obtained as a brown yellow liquid (1.22 g, 76% yield). R_f =0.7 (petroleum ether:ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 5H), 4.20 (s, 2H), 4.18 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.6, 136.5, 129.0, 128.8, 127.6, 47.9, 34.0; **IR** (KBr): v = 3029, 2940, 1675, 1496, 1454, 1407, 1257, 1174, 1088, 1028, 736, 701, 590 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_9H_9OSClNa$ 222.9960, found 222.9964.

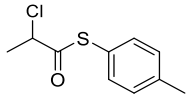
S-ethyl 2-chloroethanethioate (**1e**)



Following the general procedure A with 2-chloroacetyl chloride (30.2 mmol) and ethanethiol

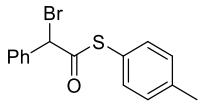
(24.2 mmol), **1e** was obtained as a yellow liquid (1.58 g, 47% yield). R_f =0.6 (petroleum ether:ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 4.18 (s, 2H), 2.96 (q, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 194.2, 48.0, 24.0, 14.3; **IR** (KBr): v = 3423, 2972, 2933, 1700, 1671, 1456, 1414, 1263, 1096, 1002, 794, 738, 589 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_4H_7OSClNa$ 160.9804, found 160.9800.

S-(p-tolyl) 2-chloropropanethioate (**1f**)



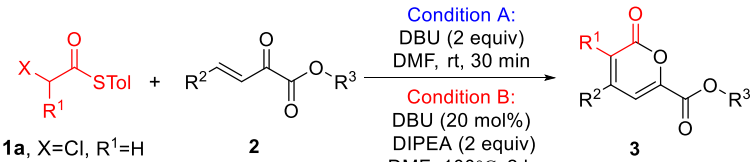
Following the general procedure B with 2-chloropropanoic acid (4.6 mmol) and *p*-toluenethiol (3.7 mmol), **1f** was obtained as a yellow liquid (0.38 g, 48% yield). R_f =0.7 (petroleum ether:ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.57 (q, *J* = 7.0 Hz, 1H), 2.37 (s, 3H), 1.75 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl3) δ 196.5, 140.1, 134.6, 130.2, 59.7, 22.2, 21.4; **IR** (KBr): v = 3393, 3069, 2976, 2621, 2362, 2245, 1885, 1622, 1517, 1453, 1327, 1190, 1121, 879, 830, 749 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{10}H_{11}ONaSCl$ 237.0117, found 237.0121.

S-(p-tolyl) 2-bromo-2-phenylethanethioate (**1g**)



Following the general procedure B with 2-bromo-2-phenylacetic acid (4.7 mmol) and *p*-toluenethiol (3.8 mmol), **1g** was obtained as a yellow solid (0.66 g, 56% yield). R_f =0.7 (petroleum ether:ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.41 – 7.34 (m, 4H), 7.28 – 7.27 (m, 1H), 7.21 – 7.19 (m, 2H), 5.57 (s, 1H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.4, 140.2, 135.4, 134.4, 130.2, 129.5, 129.0, 129.0, 123.5, 53.7, 21.3; **IR** (KBr): v = 3025, 2920, 1903, 1705, 1676, 1492, 1452, 1398, 1302, 1277, 1097, 1051, 974, 917, 805, 704, 582 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{15}H_{13}OSNaBr$ 342.9768, found 342.9772.

3. Preparation and characterizations of 2-pyrones 3



1a, X=Cl, R^1=H
1f, X=Cl, R^1=methyl
1g, X=Br, R^1=phenyl

2

3

General procedure C (condition A)

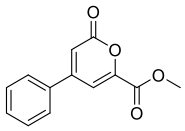
To a stirred solution of thioester **1a** (0.25 mmol, 1 equiv.) and *β,γ*-unsaturated *α*-keto ester **2** (0.50 mmol, 2 equiv.) in DMF (2 mL) was added DBU (0.50 mmol, 2 equiv.). The reaction mixture was stirred for 30 min at room temperature and then was quenched with 1 M HCl (2 mL) solution and extracted with ethyl acetate. The combined organic layer was washed with

saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo to give the crude product which was purified by column chromatography (petroleum ether:ethyl acetate = 5:1) to afford the desired product **3**.

General procedure D (condition B)

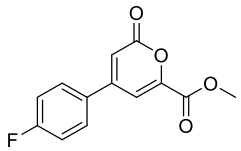
To a stirred solution of thioester **1a** (0.25 mmol, 1 equiv.) and *β,γ*-unsaturated *α*-keto ester **2** (0.50 mmol, 2 equiv.) in DMF (2 mL) was added DIPEA (0.50 mmol, 2 equiv.) and DBU (0.05 mmol, 0.02 equiv.) successively. The reaction mixture was stirred for 2 h at 100℃ and then quenched with 1 M HCl (2 mL) solution and extracted with ethyl acetate. The combined organic layer was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo to give the crude product which was purified by column chromatography (petroleum ether:ethyl acetate = 5:1) to afford the desired product **3**.

Methyl 2-oxo-4-phenyl-2H-pyran-6-carboxylate (**3a**)



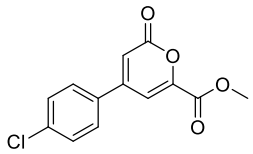
Following the general procedure C and D with **1a** and methyl (*E*)-2-oxo-4-phenylbut-3-enoate (95.1 mg, 0.50 mmol), **3a** was obtained as a yellow solid (with procedure C: 51.8 mg, 90% yield; with procedure D: 53.5 mg, 93% yield). **Gram scale**: Following the general procedure C with **1a** (1.04 g, 5.2 mmol), **3a** was obtained as a faint yellow solid (1.03 g, 86% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.55 – 7.51 (m, 3H), 7.47 (d, *J* = 1.7 Hz, 1H), 6.72 (d, *J* = 1.7 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 160.1, 153.5, 148.9, 134.5, 131.3, 129.5, 126.7, 115.0, 110.2, 53.2.

Methyl 4-(4-fluorophenyl)-2-oxo-2H-pyran-6-carboxylate (**3b**)



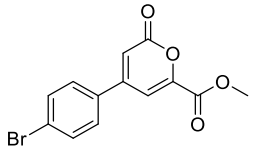
Following the general procedure C and D with **1a** and methyl (*E*)-4-(4-fluorophenyl)-2-oxobut-3-enoate (104.1 mg, 0.50 mmol), **3b** was obtained as a faint yellow solid (with procedure C: 51.5 mg, 83% yield; with procedure D: 52.1 mg, 84% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.42 (d, *J* = 1.7 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.67 (d, *J* = 1.7 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6 (d, *J* = 253.2 Hz), 160.4, 160.0, 152.4, 149.0, 130.6, 128.8 (d, *J* = 8.8 Hz), 116.7 (d, *J* = 22.2 Hz), 114.8 (d, *J* = 1.4 Hz), 109.9, 53.2.

Methyl 4-(4-chlorophenyl)-2-oxo-2H-pyran-6-carboxylate (**3c**)



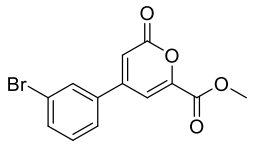
Following the general procedure C and D with **1a** and methyl (*E*)-4-(4-chlorophenyl)-2-oxobut-3-enoate (112.3 mg, 0.50 mmol), **3c** was obtained as a faint yellow solid (with procedure C: 63.5 mg, 96% yield; with procedure D: 47.6 mg, 72% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 1.7 Hz, 1H), 6.69 (d, *J* = 1.7 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3, 160.0, 152.3, 149.1, 137.8, 132.8, 129.8, 128.0, 115.1, 109.7, 53.3.

Methyl 4-(4-bromophenyl)-2-oxo-2H-pyran-6-carboxylate (**3d**)



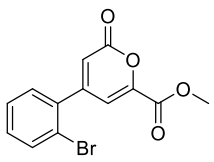
Following the general procedure C and D with **1a** and methyl (*E*)-4-(4-bromophenyl)-2-oxobut-3-enoate (134.5 mg, 0.50 mmol), **3d** was obtained as a faint yellow solid (with procedure C: 71.1 mg, 92% yield; with procedure D: 76.5 mg, 99% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.66 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 1.7 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3, 160.0, 152.4, 149.1, 133.3, 132.8, 128.2, 126.1, 115.1, 109.7, 53.3.

Methyl 4-(3-bromophenyl)-2-oxo-2H-pyran-6-carboxylate (**3e**)



Following the general procedure C and D with **1a** and methyl (*E*)-4-(3-bromophenyl)-2-oxobut-3-enoate (134.5 mg, 0.50 mmol), **3e** was obtained as a faint yellow solid (with procedure C: 73.4 mg, 95% yield; with procedure D: 54.1 mg, 70% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (t, *J* = 1.8 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.37 (m, 2H), 6.69 (d, *J* = 1.7 Hz, 1H), 3.98 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 159.9, 152.1, 149.2, 136.6, 134.2, 131.0, 129.8, 125.3, 123.6, 115.7, 109.8, 53.3.

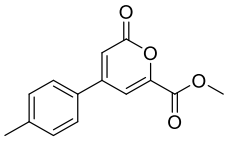
methyl 4-(2-bromophenyl)-2-oxo-2H-pyran-6-carboxylate (**3f**)



Following the general procedure C and D with **1a** and methyl (*E*)-4-(2-bromophenyl)-2-oxobut-

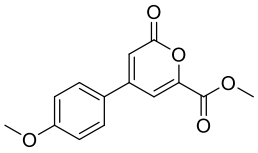
3-enoate (134.5 mg, 0.50 mmol), **3f** was obtained as a faint yellow solid (with procedure C: 59.5 mg, 77% yield; with procedure D: 7.7 mg, 10% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.38 – 7.23 (m, 3H), 6.55 (d, *J* = 1.6 Hz, 1H), 3.95 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 159.9, 154.7, 148.0, 136.8, 133.8, 131.4, 129.8, 128.1, 121.0, 119.4, 112.7, 53.2, 29.7.

Methyl 2-oxo-4-p-tolyl-2H-pyran-6-carboxylate (**3g**)



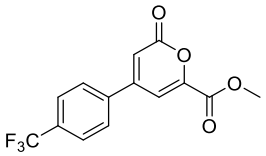
Following the general procedure C and D with **1a** and methyl (*E*)-2-oxo-4-(p-tolyl)but-3-enoate (102.1 mg, 0.50 mmol), **3g** was obtained as a faint yellow solid (with procedure C: 56.1 mg, 92% yield; with procedure D: 23.2 mg, 38% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 1.7 Hz, 1H), 3.97 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 160.2, 153.4, 148.8, 142.0, 131.5, 130.2, 126.6, 114.2, 110.2, 53.2, 21.4.

Methyl 4-(4-methoxyphenyl)-2-oxo-2H-pyran-6-carboxylate (**3h**)



Following the general procedure C and D with **1a** and methyl (*E*)-4-(4-methoxyphenyl)-2-oxobut-3-enoate (110.1 mg, 0.50 mmol), **3h** was obtained as a faint yellow solid (with procedure C: 52.0 mg, 80% yield; with procedure D: 16.9 mg, 26% yield). Analytical data are consistent with previous literature reports. [3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 1.7 Hz, 1H), 3.97 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ162.3, 160.8, 160.3, 152.3, 148.7, 128.4, 126.5, 114.9, 113.0, 110.0, 55.6, 53.2, 29.7.

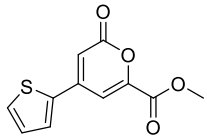
methyl 2-oxo-4-(4-(trifluoromethyl)phenyl)-2H-pyran-6-carboxylate (**3i**)



Following the general procedure C and D with **1a** and methyl (*E*)-2-oxo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (129.1 mg, 0.50 mmol), **3i** was obtained as a faint yellow solid (with procedure C: 71.6 mg, 96% yield; with procedure D: 49.9 mg, 67% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 4H), 7.43 (d, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 1.7 Hz, 1H), 3.98 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 159.9, 152.2, 149.4, 138.0, 133.0 (d, *J* = 33.1 Hz), 127.2, 126.4 (d, *J* = 3.7 Hz),

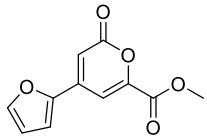
123.6 (d, *J* = 272.5 Hz), 116.4, 109.7, 53.3.

methyl 2-oxo-4-(thiophen-2-yl)-2H-pyran-6-carboxylate (**3j**)



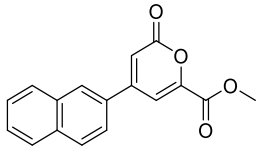
Following the general procedure C and D with **1a** and methyl (*E*)-2-oxo-4-(thiophen-2-yl)but-3-enoate (98.1 mg, 0.50 mmol), **3j** was obtained as a faint yellow solid (with procedure C: 51.4 mg, 87% yield; with procedure D: 12.4 mg, 21% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 2H), 7.42 (d, *J* = 1.7 Hz, 1H), 7.19 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 160.1, 148.8, 146.3, 137.7, 130.7, 129.0, 128.8, 111.5, 109.1, 53.2.

Methyl 4-(furan-2-yl)-2-oxo-2H-pyran-6-carboxylate (**3k**)



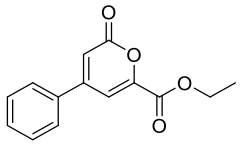
Following the general procedure C and D with **1a** and methyl (*E*)-4-(furan-2-yl)-2-oxobut-3-enoate (90.1 mg, 0.50 mmol), **3k** was obtained as a red brown solid (with procedure C: 38.0 mg, 69% yield; with procedure D: 27.5 mg, 50% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.70 (d, *J* = 1.6 Hz, 1H), 6.61 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 160.0, 149.1, 148.4, 146.5, 141.4, 114.0, 113.0, 109.5, 107.4, 53.2.

Methyl 4-(naphthalen-2-yl)-2-oxo-2H-pyran-6-carboxylate (**3l**)



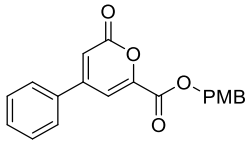
Following the general procedure C and D with **1a** and methyl (*E*)-4-(naphthalen-2-yl)-2-oxobut-3-enoate (120.1 mg, 0.50 mmol), **3l** was obtained as a faint yellow solid (with procedure C: 58.2 mg, 83% yield; with procedure D: 42.0 mg, 60% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.15 (d, *J* = 1.9 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.69 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.65 – 7.57 (m, 3H), 6.85 (d, *J* = 1.7 Hz, 1H), 4.00 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 160.2, 153.31, 148.9, 134.4, 133.1, 131.5, 129.5, 128.9, 128.1, 127.8, 127.3, 123.1, 115.1, 110.2, 53.2.

Ethyl 2-oxo-4-phenyl-2H-pyran-6-carboxylate (**3m**)



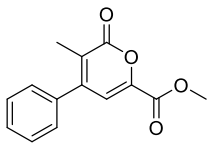
Following the general procedure C with **1a** and ethyl (*E*)-2-oxo-4-phenylbut-3-enoate (102.1 mg, 0.50 mmol), **3m** was obtained as a faint yellow solid (51.9 mg, 85% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 2H), 7.52 (dt, *J* = 5.4, 2.5 Hz, 3H), 7.45 (d, *J* = 1.7 Hz, 1H), 6.71 (d, *J* = 1.7 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 159.6, 153.6, 149.2, 134.5, 131.2, 129.4, 126.7, 114.9, 110.0, 62.7, 14.2.

4-methoxybenzyl 2-oxo-4-phenyl-2H-pyran-6-carboxylate (**3n**)



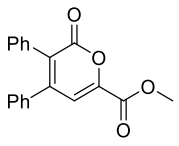
Following the general procedure C with **1a** and 4-methoxybenzyl (*E*)-2-oxo-4-phenylbut-3-enoate (148.2 mg, 0.50 mmol), **3n** was obtained as a faint yellow solid (81.5 mg, 95% yield). Analytical data are consistent with previous literature reports.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.52 – 7.50 (m, 3H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 1.7 Hz, 1H), 5.33 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 160.1, 159.6, 153.6, 149.1, 134.5, 131.2, 130.7, 129.4, 126.7, 115.0, 114.1, 110.3, 68.0, 55.3.

methyl 3-methyl-2-oxo-4-phenyl-2H-pyran-6-carboxylate (**3o**)



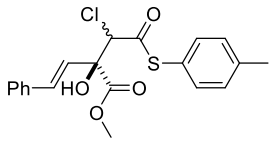
Following the general procedure C with **1f** and methyl (*E*)-2-oxo-4-phenylbut-3-enoate (95.1 mg, 0.50 mmol), **3o** was obtained as a faint yellow solid (51.9 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 3H), 7.36 – 7.31 (m, 2H), 7.14 (s, 1H), 3.93 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 160.2, 150.0, 145.3, 136.5, 129.4, 128.8, 128.0, 127.0, 113.7, 53.0, 14.8; **IR** (KBr): v = 3416, 3086, 2924, 2853, 1715, 1433, 1349, 1257, 1102, 1053, 934, 786, 766, 709, 612, 541 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{14}H_{12}O_4Na$ 267.0633, found 267.0636.

methyl 2-oxo-3,4-diphenyl-2H-pyran-6-carboxylate (**3p**)



Following the general procedure C with **1g** and methyl (*E*)-2-oxo-4-phenylbut-3-enoate (95.1 mg, 0.50 mmol), **3p** was obtained as a faint yellow solid (38.3 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.28 – 7.23 (m, 6H), 7.20 – 7.16 (m, 2H), 7.14 – 7.10 (m, 2H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 160.1, 150.4, 146.8, 136.5, 133.0, 130.6, 129.4, 129.2, 128.8, 128.6, 128.5, 128.2, 114.1, 53.1; **IR** (KBr): v = 3053, 3019, 2924, 2851, 1958, 1743, 1639, 1487, 1445, 1352, 1268, 1131, 1077, 1015, 928, 771, 698, 567 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{16}H_{15}O_4$ 307.0970, found 307.0975.

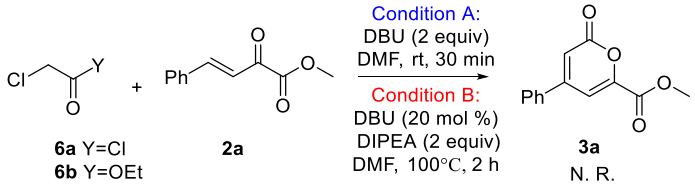
methyl (R,E)-2-((R)-1-chloro-2-oxo-2-(p-tolylthio)ethyl)-2-hydroxy-4-phenylbut-3-enoate (**4a**)



To a stirred solution of *α*-chlorothioester **1a** (0.25 mmol, 1 equiv.) and methyl (*E*)-2-oxo-4-phenylbut-3-enoate (95.1 mg, 0.50 mmol) in THF (2 mL) was added *i*-Pr_2NEt (0.50 mmol, 2 equiv.). The reaction mixture was stirred overnight at room temperature and then was quenched with 1 M HCl (2 mL) solution and extracted with ethyl acetate. The combined organic layer was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo to give the crude product which was purified by column chromatography (petroleum ether:ethyl acetate = 5:1) to afford the desired product **4a** (24.43 mg, 25% yield) as a mixture of diastereomer (dr = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.13 (m, 9H), 6.99 (d, *J* = 15.6 Hz, 0.75H), 6.98 (d, *J* = 15.6Hz, 0.25H), 6.37 (d, *J* = 15.7 Hz, 0.25H), 6.18 (d, *J* = 15.7 Hz, 0.75H), 5.10 (s, 0.75H), 4.95 (s, 0.25H), 3.89 (s, 0.75H), 3.83 (s, 2.25H), 2.83 (s, 2.25H), 2.33 (s, 0.74H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.0, 192.4, 171.9, 171.3, 140.4, 135.7, 134.6, 134.5, 133.5, 133.0, 130.3, 130.2, 128.7, 128.6, 128.5, 128.4, 127.1, 127.0, 125.5, 124.3, 123.5, 79.3, 79.0, 69.0, 66.8, 56.0, 53.8, 21.4, 21.3; **IR** (KBr): v = 3496, 2923, 2853, 1742, 1679, 1491, 1448, 1242, 1134, 1072, 976, 810, 754, 622, 547 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{20}H_{19}O4NaS$ 413.0590, found 413.0590.

4. Control Experiments

4.1 Reaction between 6 and 2a



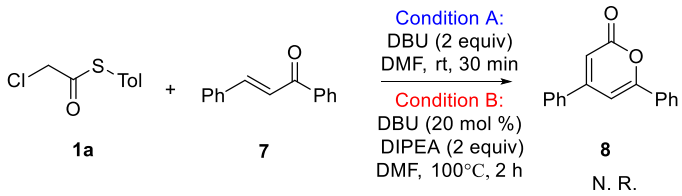
6a Y=Cl
6b Y=OEt

2a

3a
N. R.

Following the general procedure C and D with 2-chloroacetyl chloride **6a** (19 μL, 0.25 mmol) or ethyl 2-chloroacetate **6b** (26 μL, 0.25 mmol) instead of *α*-halothioester **1**, no desired product **3a** was obtained.

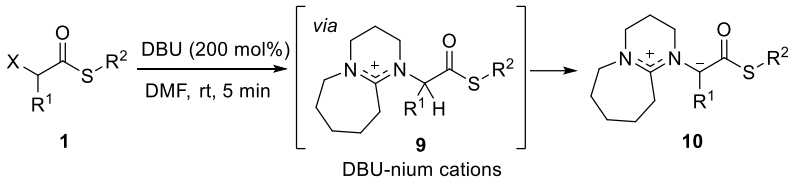
4.2 Reaction between chalcone 7 and *α*-chlorothioester 1a



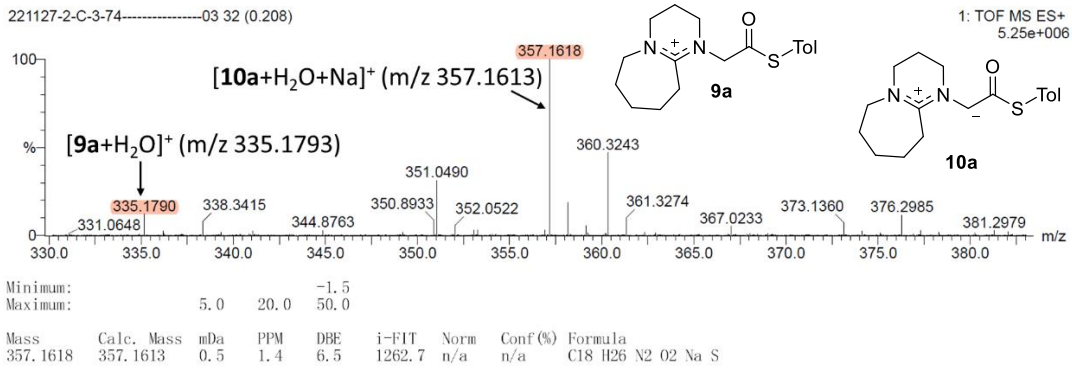
Following the general procedure C and D with (*E*)-chalcone **7** (104.1 mg, 0.50 mmol) instead of **2a**, no desired product **8** was obtained.

5. Determination of DBU-derived ammonium ylides or their precursors by HRMS

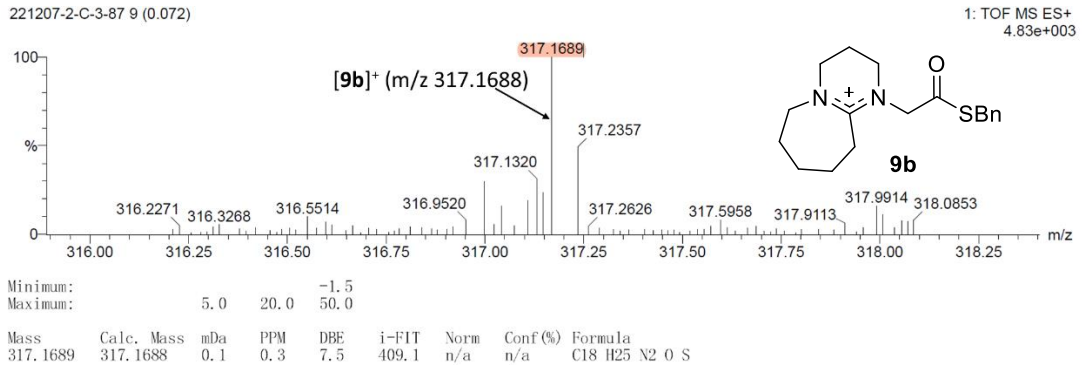
To a solution of *α*-halothioester **1** (0.05 mmol 1 equiv.) in DMF (0.1 mL) was added DBU (0.1 mmol, 2 equiv.) at room temperature. The obtained mixtures were then analyzed with high-resolution mass spectrometry (HRMS).



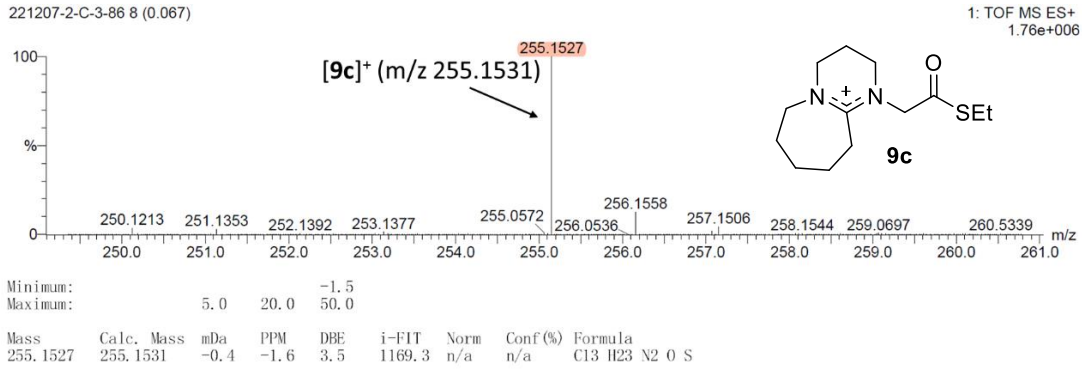
HRMS conditions: electrospray ionization source operating in the positive ion mode, capillary voltage: 3.5 kv, ion source temperature: 110℃, desolvation temperature: 400℃, nitrogen flow rate: 800L/h.



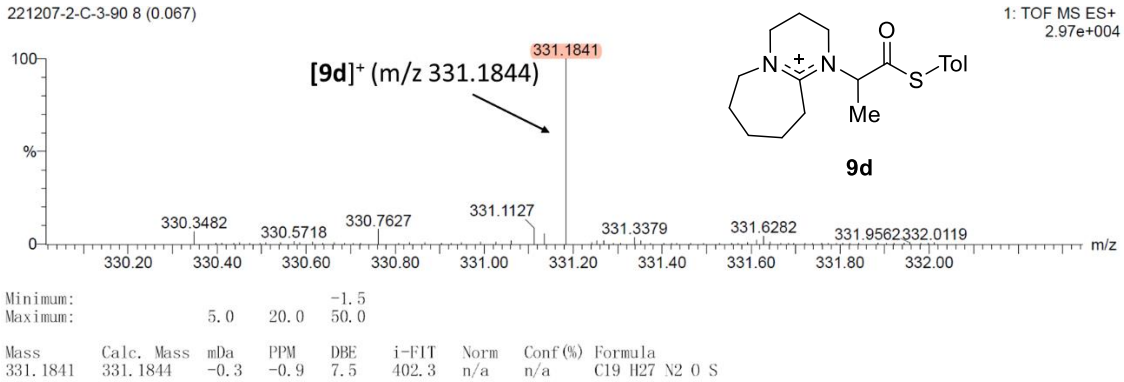
HRMS spectrum of **9a** and **10a**



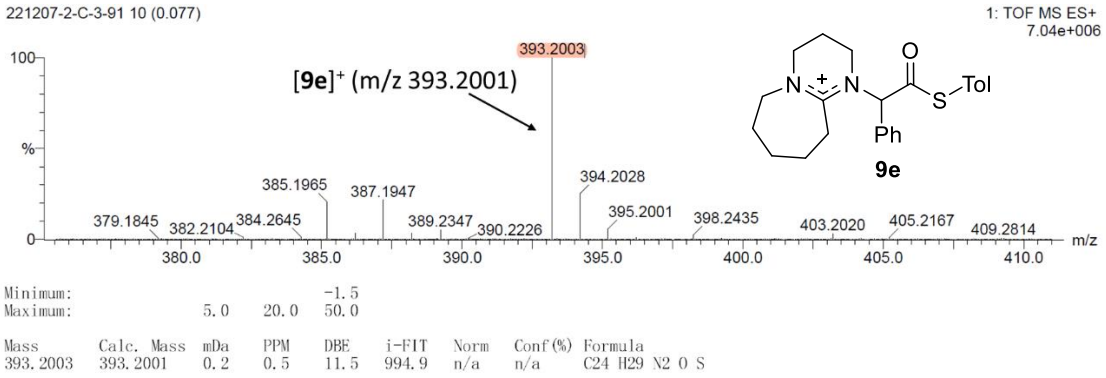
HRMS spectrum of **9b**



HRMS spectrum of **9c**



HRMS spectrum of **9d**

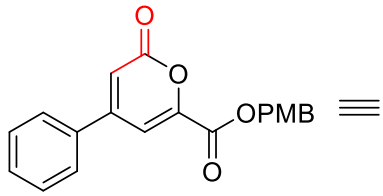


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
393.2003	393.2001	0.2	0.5	11.5	994.9	n/a	n/a	C24 H29 N2 O S

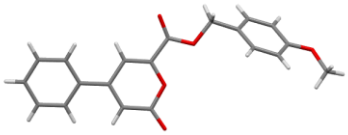
HRMS spectrum of **9e**

6. X-ray crystal structures

6.1 X-ray crystal structure of 3n (CDCC 2221791)

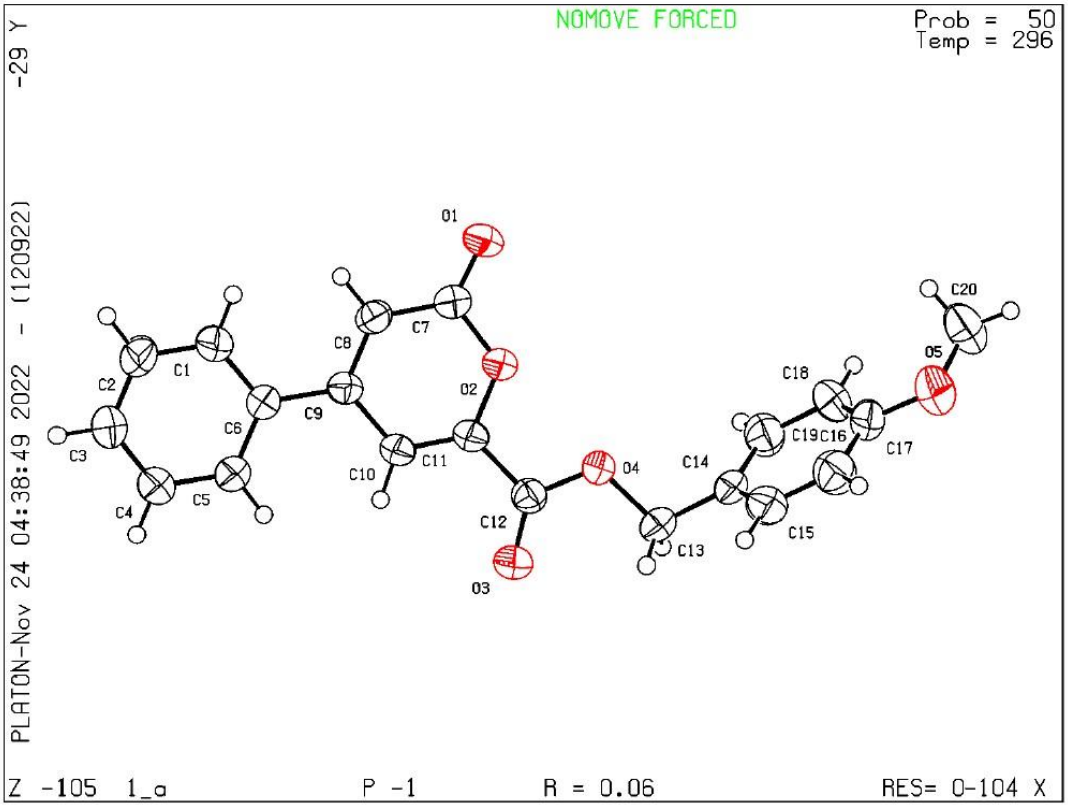


3n



x-ray structure of **3n**
(CCDC 2221791**)**

X-ray crystal structure of **3n**



Bond precision:	C-C = 0.0043 A	Wavelength=0.71073	
Cell:	a=5.588(9)	b=8.349(13)	c=17.87(3)
alpha=77.93(4)	beta=87.12(4)	gamma=85.92(4)	
Temperature:	296 K		
Calculated	Reported		
Volume	813(2)	813(2)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C20 H16 O5		
Sum formula	C20 H16 O5	C20 H16 O5	
Mr	336.33	336.33	
Dx,g cm-3	1.374	1.374	

Z	2	2
Mu (mm-1)	0.099	0.099
F000	352.0	352.0
F000’	352.20	
h, k, lmax	6,9,21	6,9,21
N ref	2899	2874
Tmin, Tmax	0.980,0.980	0.864,0.864
Tmin’	0.980	

Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864

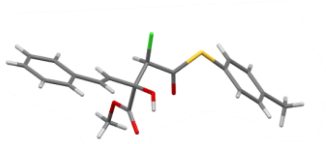
AbsCorr = MULTI - SCAN

Data completeness= 0.991 Theta(max)= 25.107

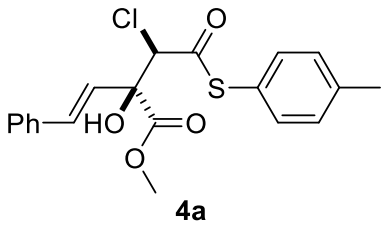
R(reflections)= 0.0587(1749) wR2(reflections)=0.1632(2874)

S = 1.047 Npar= 227

6.2 X-ray crystal structure of 4a (CDCC 2221792)

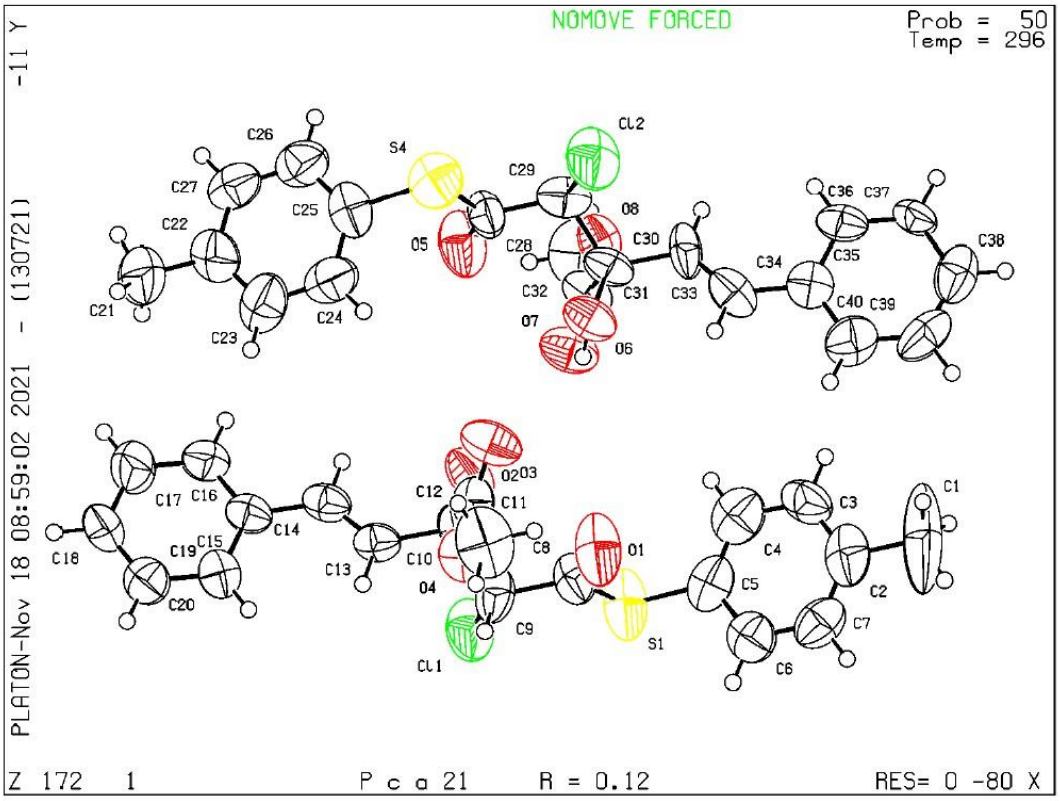


x-ray structure
(CCDC 2221792)



4a

X-ray crystal structure of **4a**



Bond precision: C-C = 0.0188 A Wavelength=0.71073

Cell:	a=23.313(13)	b=7.937(4)	c=21.274(12)
alpha=90	beta=90	gamma=90	
Temperature:	296 K		
Calculated	Reported		
Volume	3936(4)	3936(4)	
Space group	P c a 21	P c a 21	
Hall group	P 2c -2ac	P 2c -2ac	
Moiety formula	C20 H19 Cl O4 S		
Sum formula	C20 H19 Cl O4 S	C20 H19 Cl O4 S	
Mr	390.86	390.86	
Dx,g cm-3	1.319	1.319	
Z	8	8	
Mu (mm-1)	0.322	0.321	
F000	1632.0	1632.0	
F000’	1634.90		
h,k,lmax	27,9,25	27,9,25	
Nref	6937[3574]	6731	
Tmin,Tmax	0.938,0.938	0.864,0.864	
Tmin’	0.938		

Correction method = # Reported T Limits: T min = 0.864 T max = 0.864

AbsCorr = MULTI - SCAN

Data completeness= 1.88/0.97 Theta(max)= 24.994

R(reflections) = 0.1163 (2775)

wR2(reflections) = 0.2261(6731)

S = 1.047 Npar= 422

7. Copies of ^{1}H and ^{13}C NMR spectra

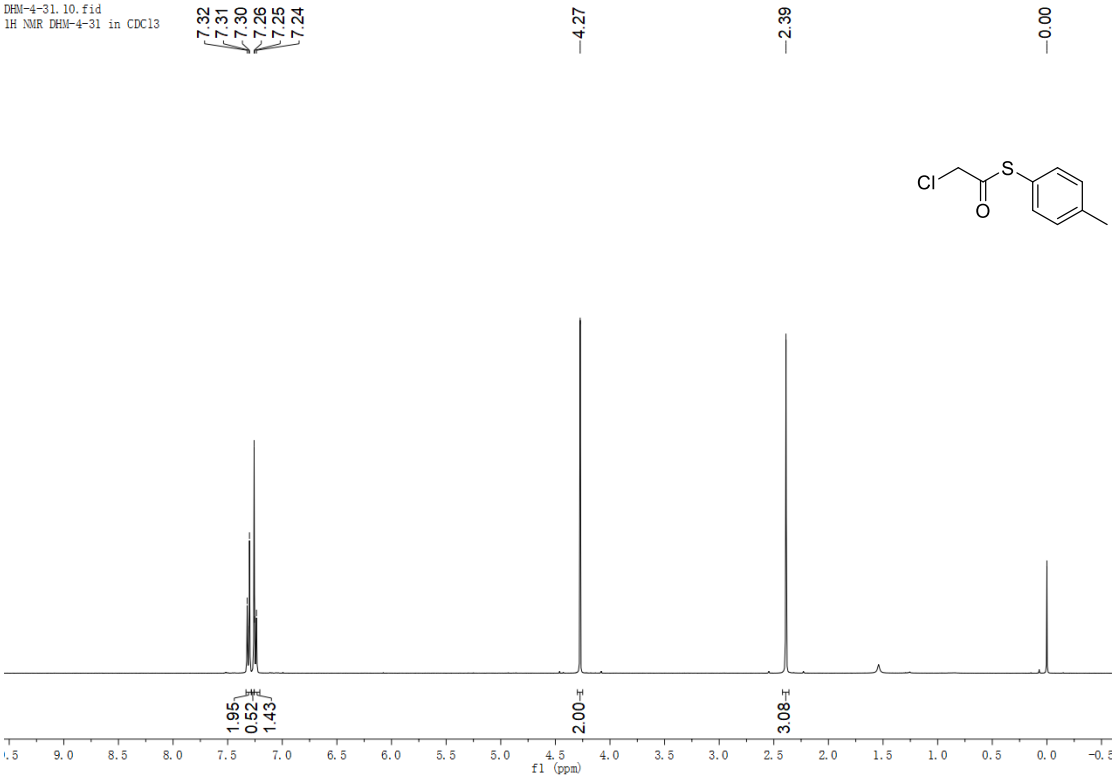


Figure 7.1 ^{1}H NMR spectrum of compound **1a** (400 MHz, $CDCl_3$)

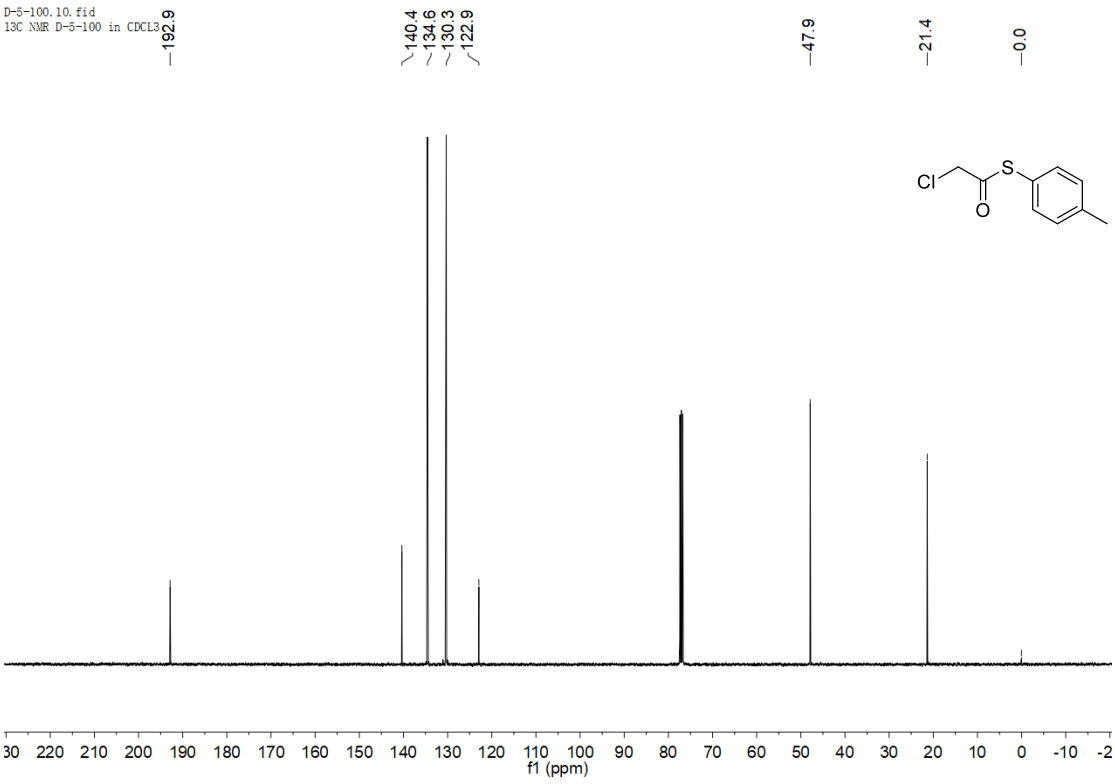


Figure 7.2 ^{13}C NMR spectrum of compound **1a** (101 MHz, $CDCl_3$)

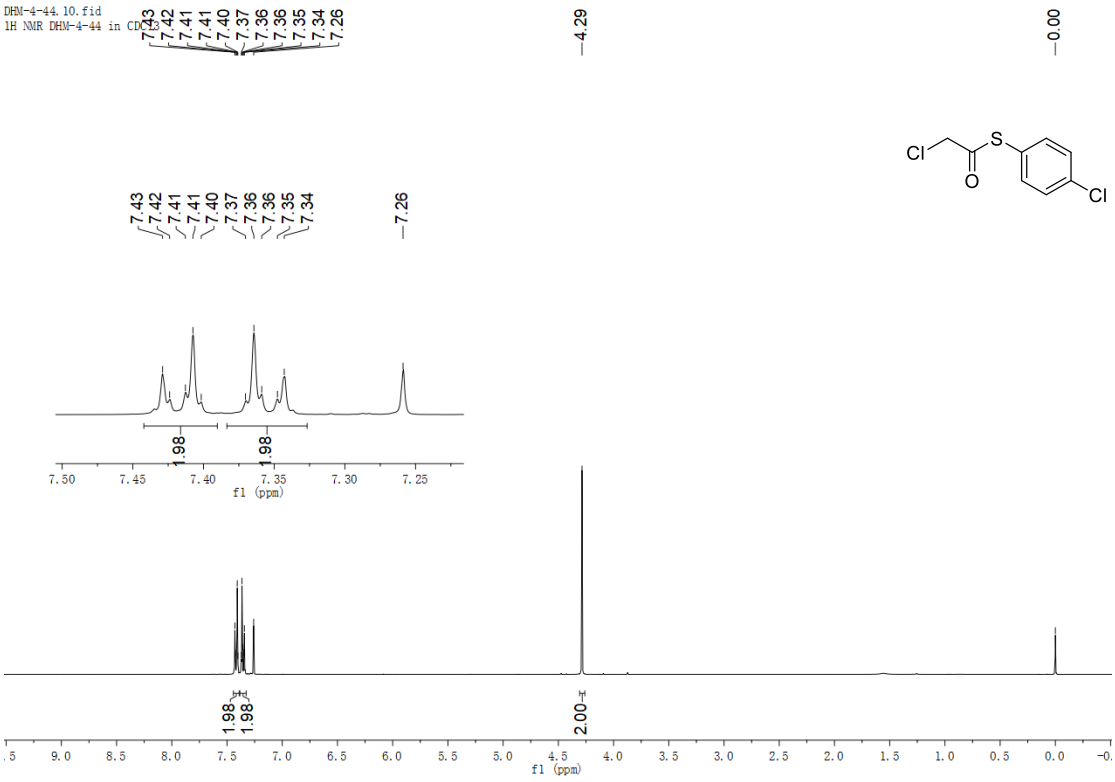


Figure 7.3 ^{1}H NMR spectrum of compound **1b** (400 MHz, $CDCl_3$)

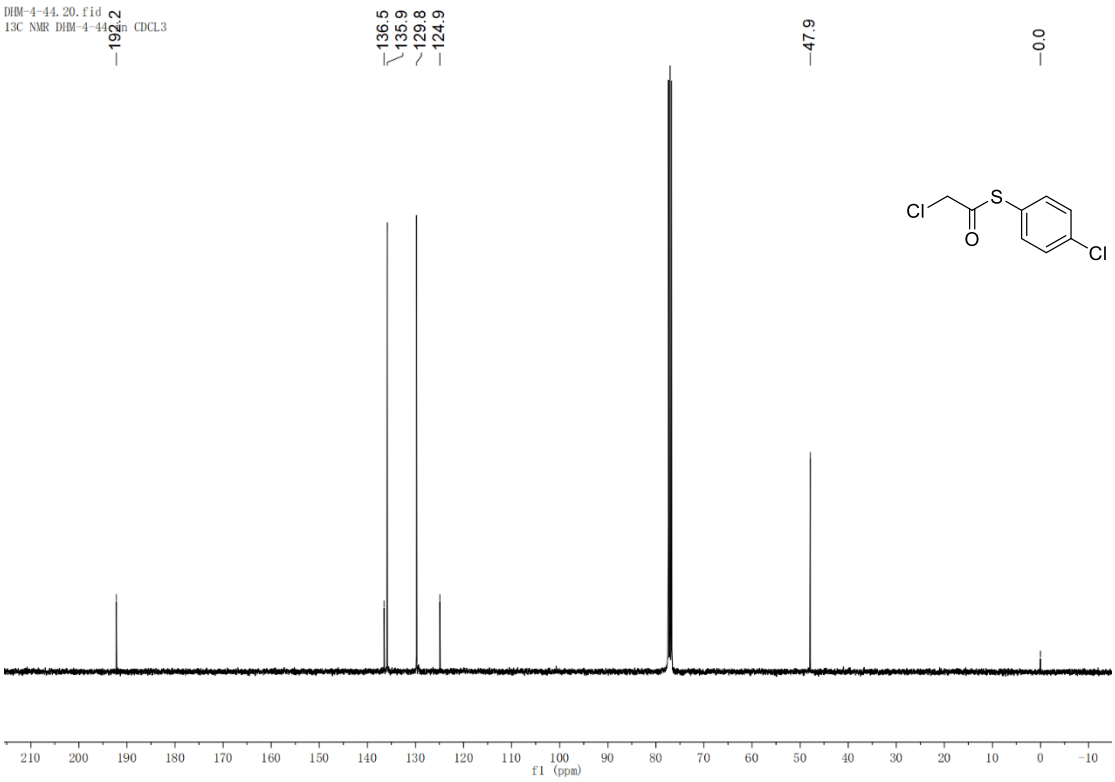


Figure 7.4 ^{13}C NMR spectrum of compound **1b** (101 MHz, $CDCl_3$)

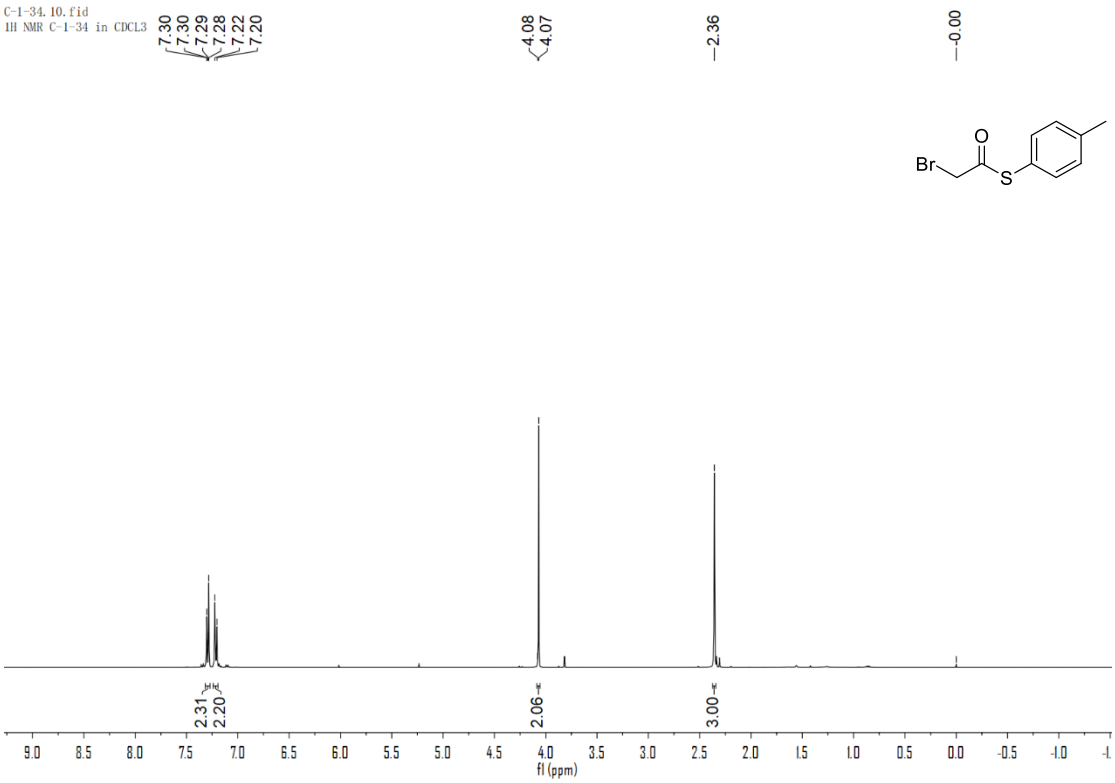


Figure 7.5 ^{1}H NMR spectrum of compound **1c** (400 MHz, $CDCl_3$)

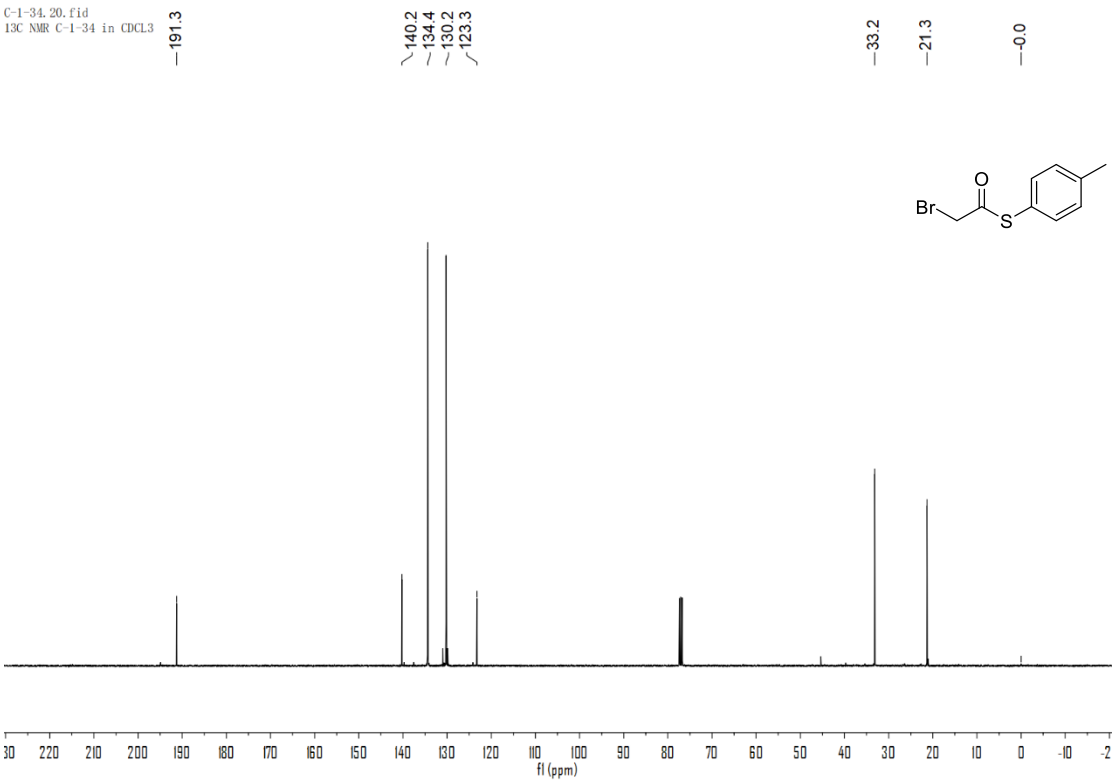


Figure 7.6 ^{13}C NMR spectrum of compound **1c** (101 MHz, $CDCl_3$)

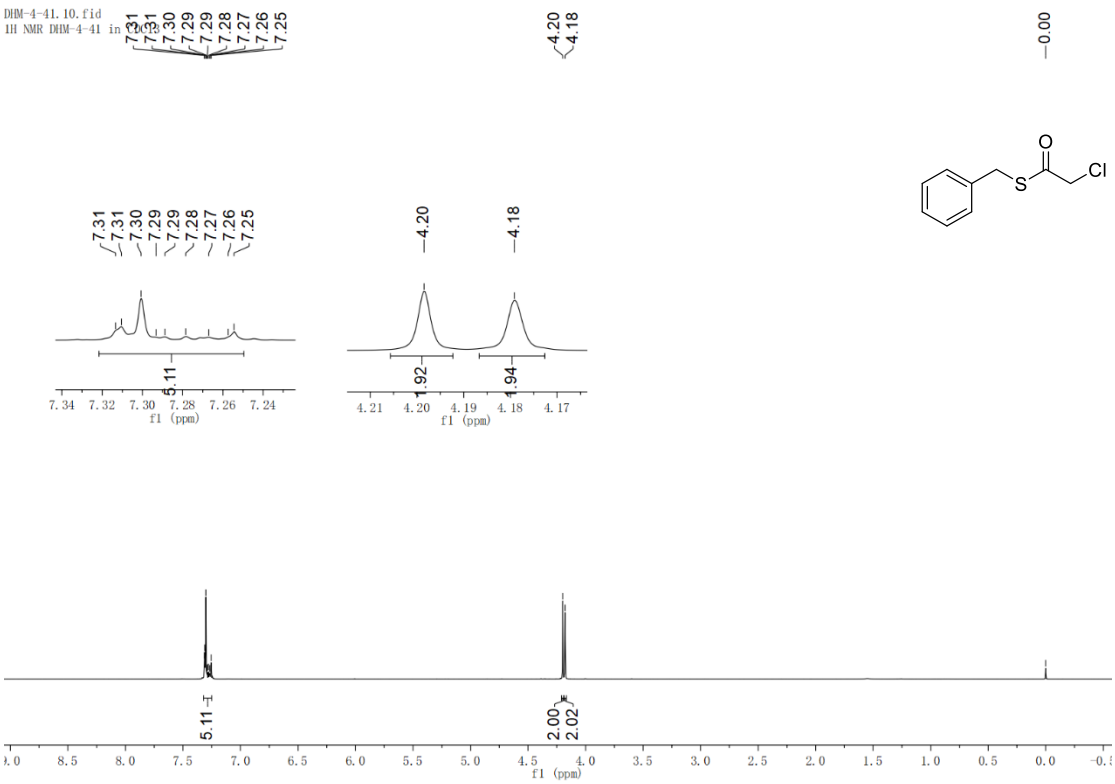


Figure 7.7 ^{1}H NMR spectrum of compound **1d** (400 MHz, $CDCl_3$)

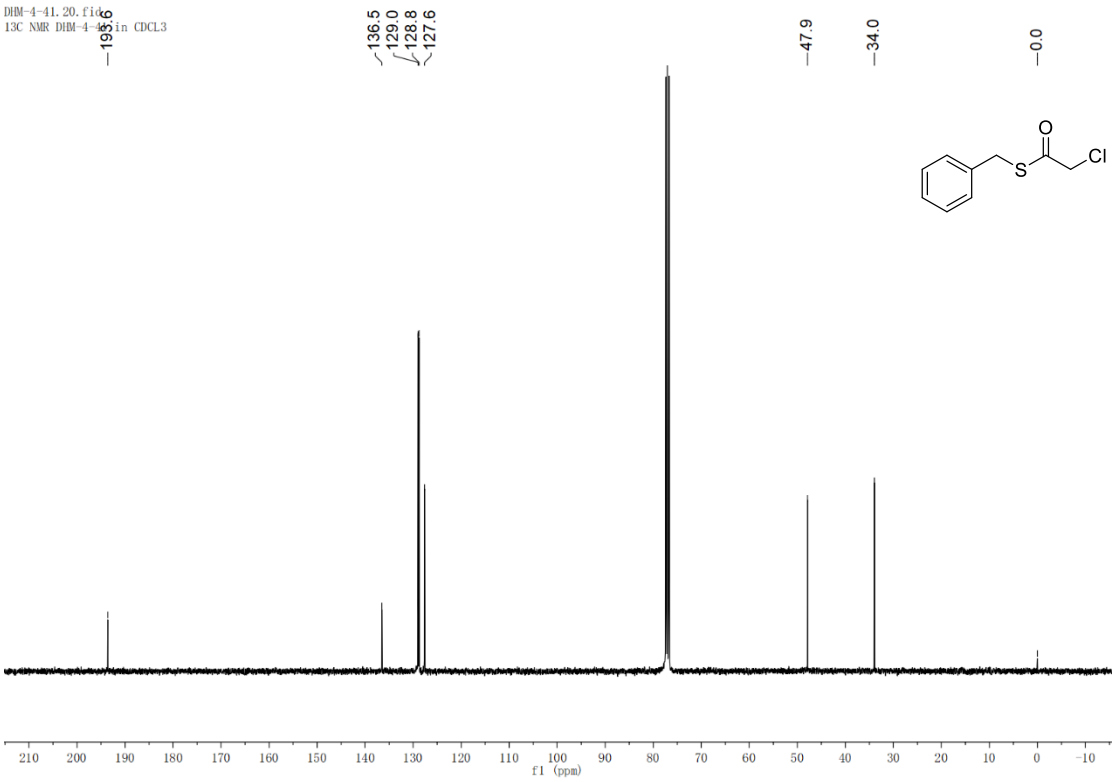


Figure 7.8 ^{13}C NMR spectrum of compound **1d** (101 MHz, $CDCl_3$)

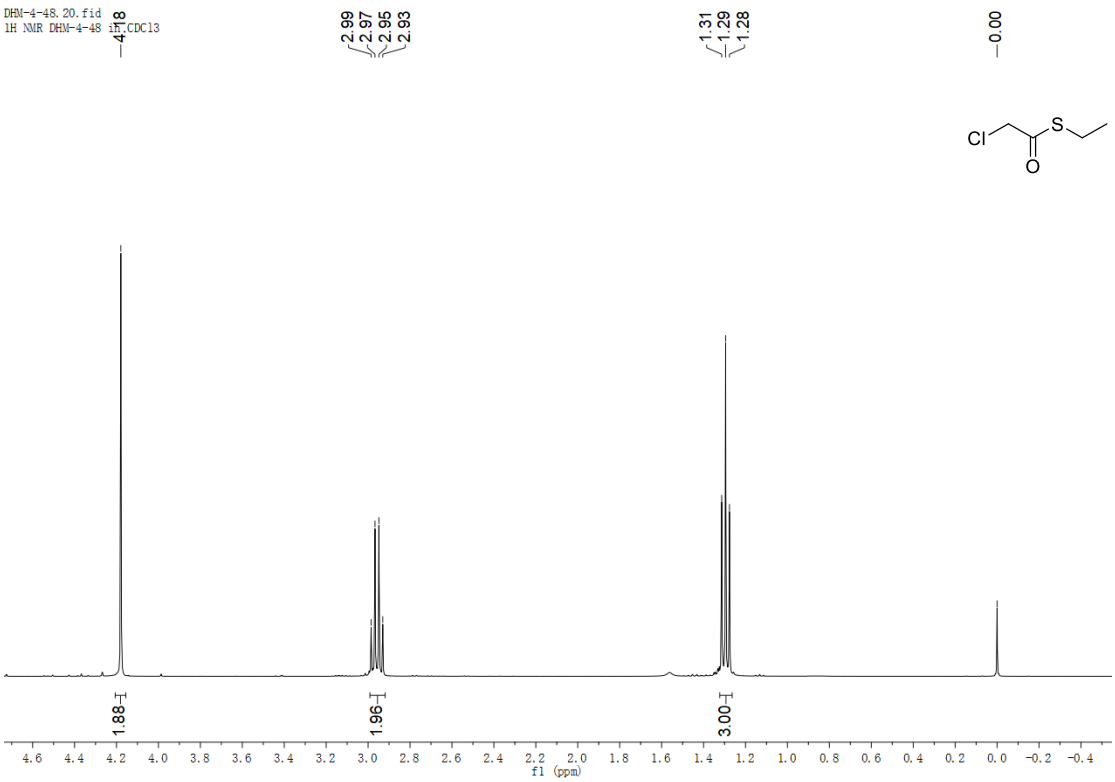


Figure 7.9 ^{1}H NMR spectrum of compound **1e** (400 MHz, $CDCl_3$)

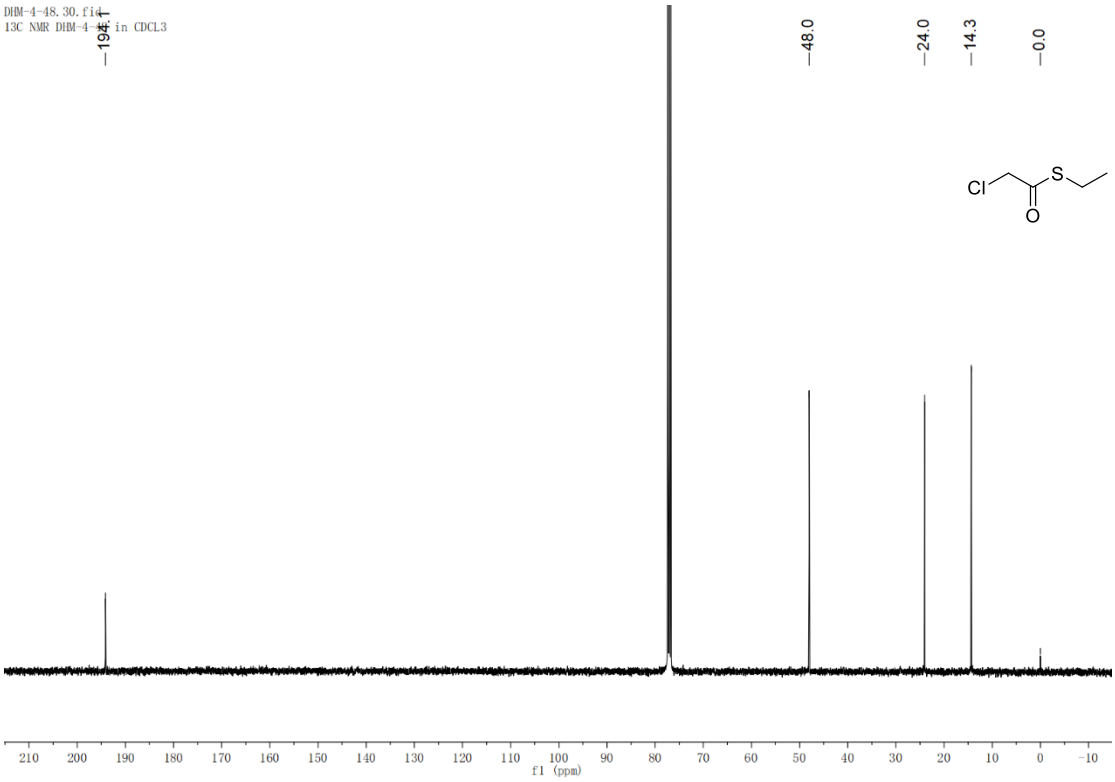


Figure 7.10 ^{13}C NMR spectrum of compound **1e** (101 MHz, $CDCl_3$)

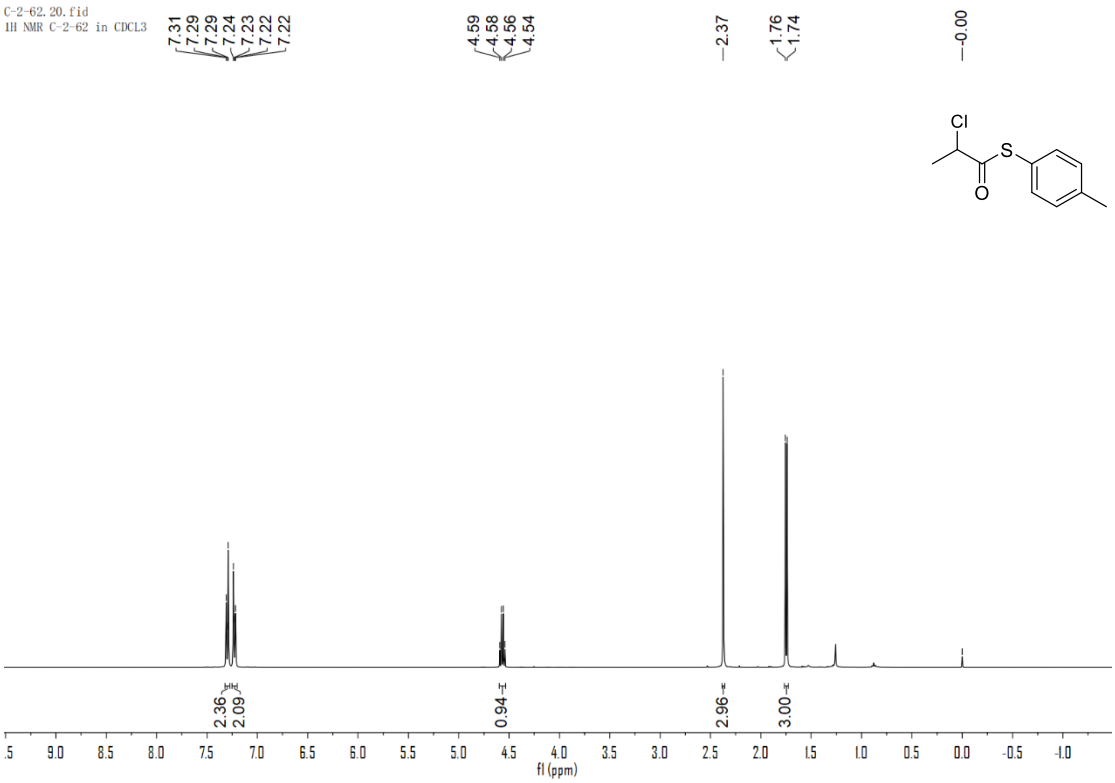


Figure 7.11 ^{1}H NMR spectrum of compound **1f** (101 MHz, $CDCl_3$)

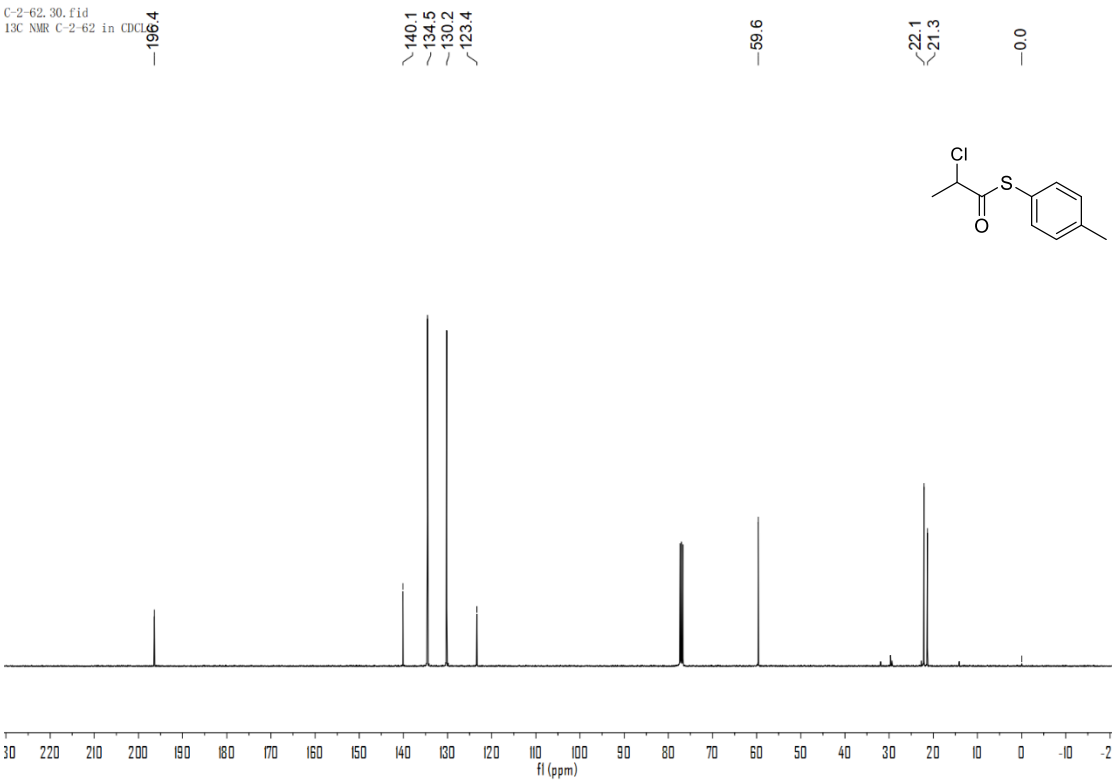


Figure 7.12 ^{13}C NMR spectrum of compound **1f** (101 MHz, $CDCl_3$)

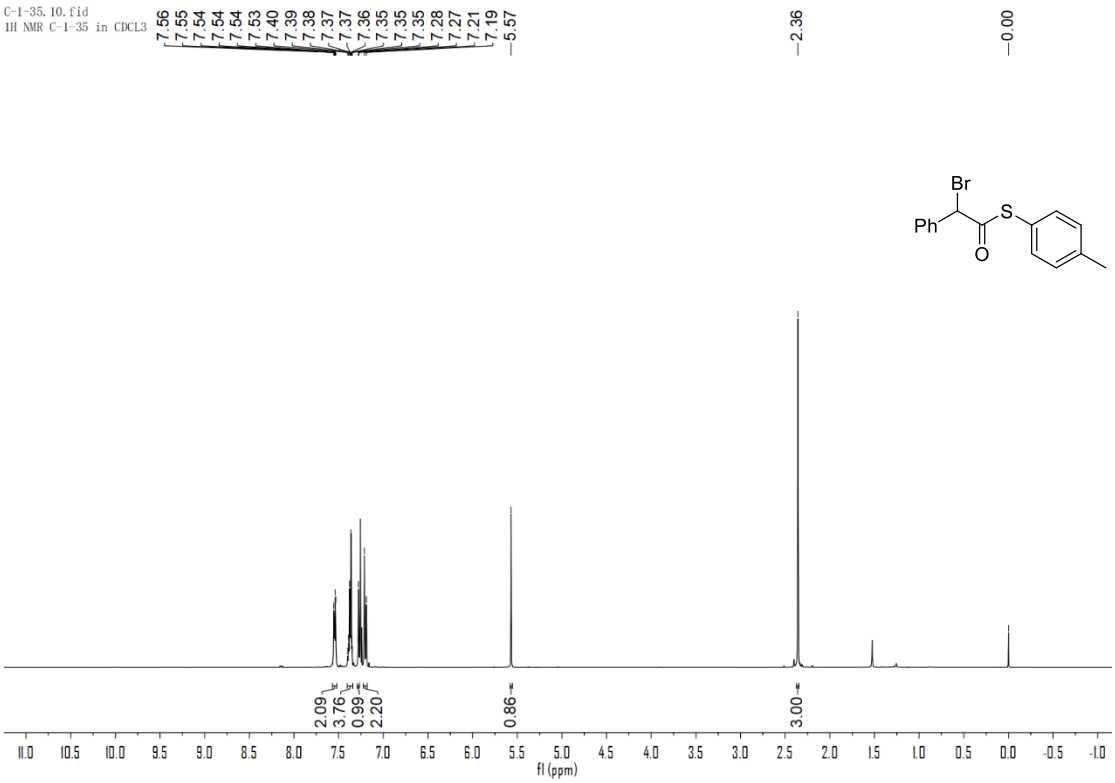


Figure 7.13 ^{1}H NMR spectrum of compound **1g** (400 MHz, $CDCl_3$)

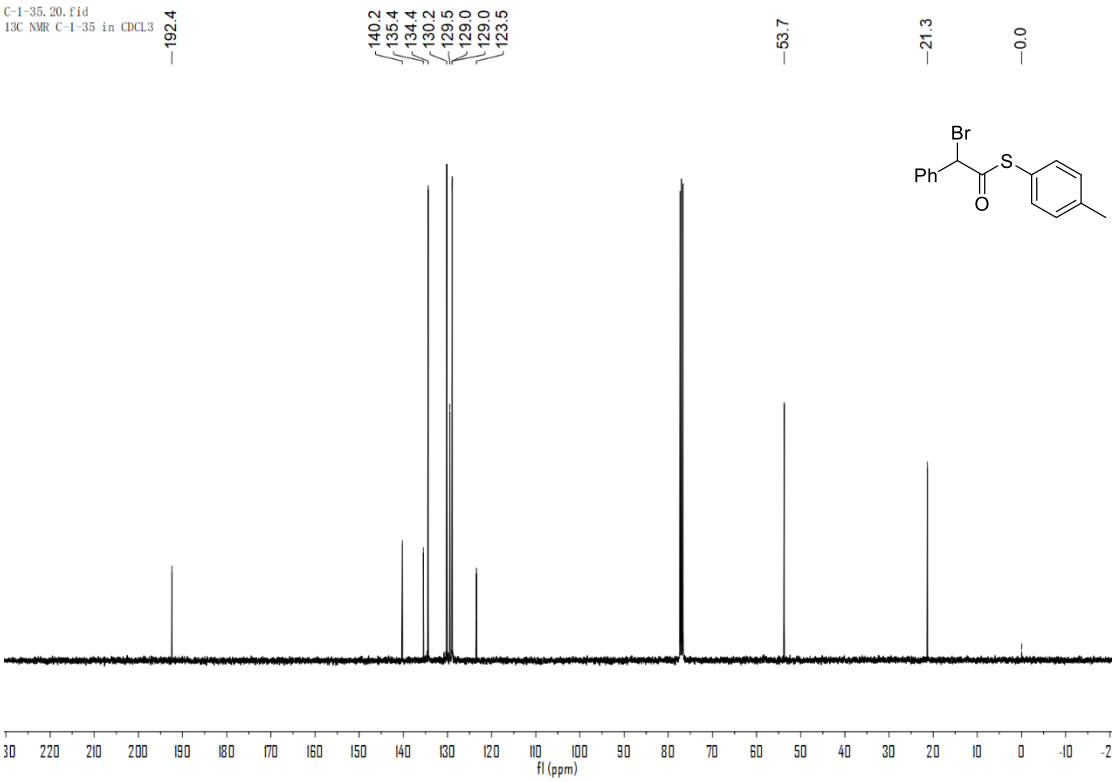


Figure 7.14 ^{13}C NMR spectrum of compound **1g** (101 MHz, $CDCl_3$)

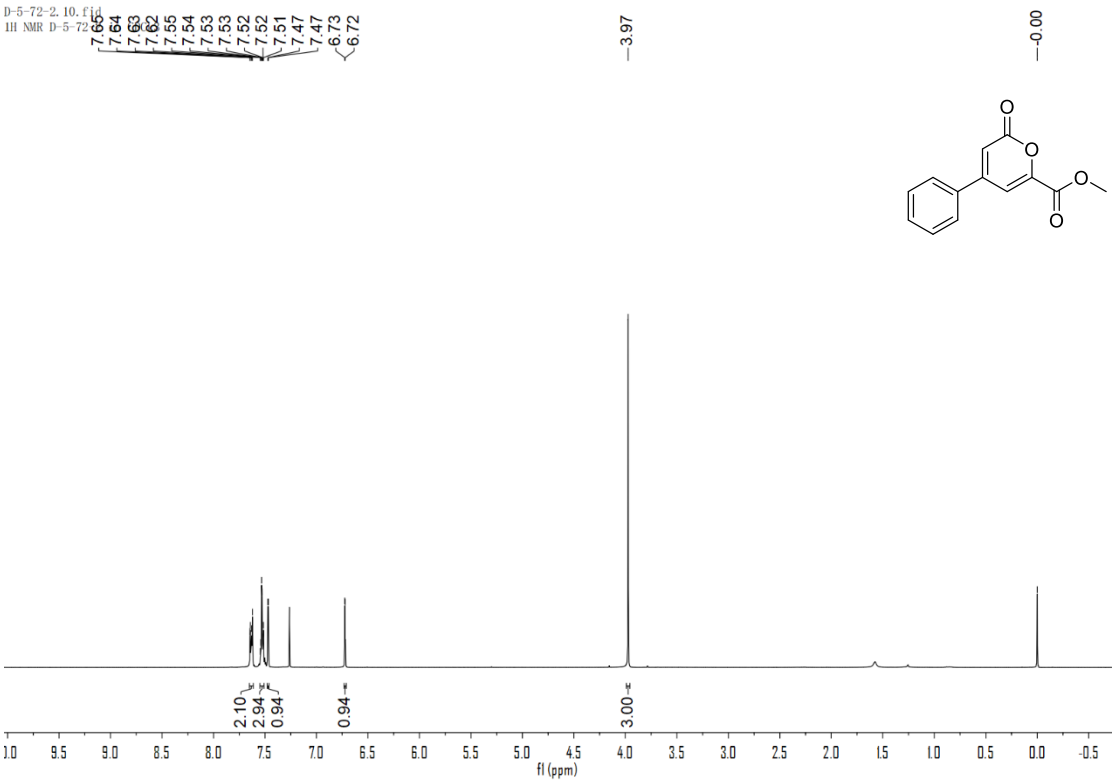


Figure 7.15 ^{1}H NMR spectrum of compound **3a** (400 MHz, $CDCl_3$)

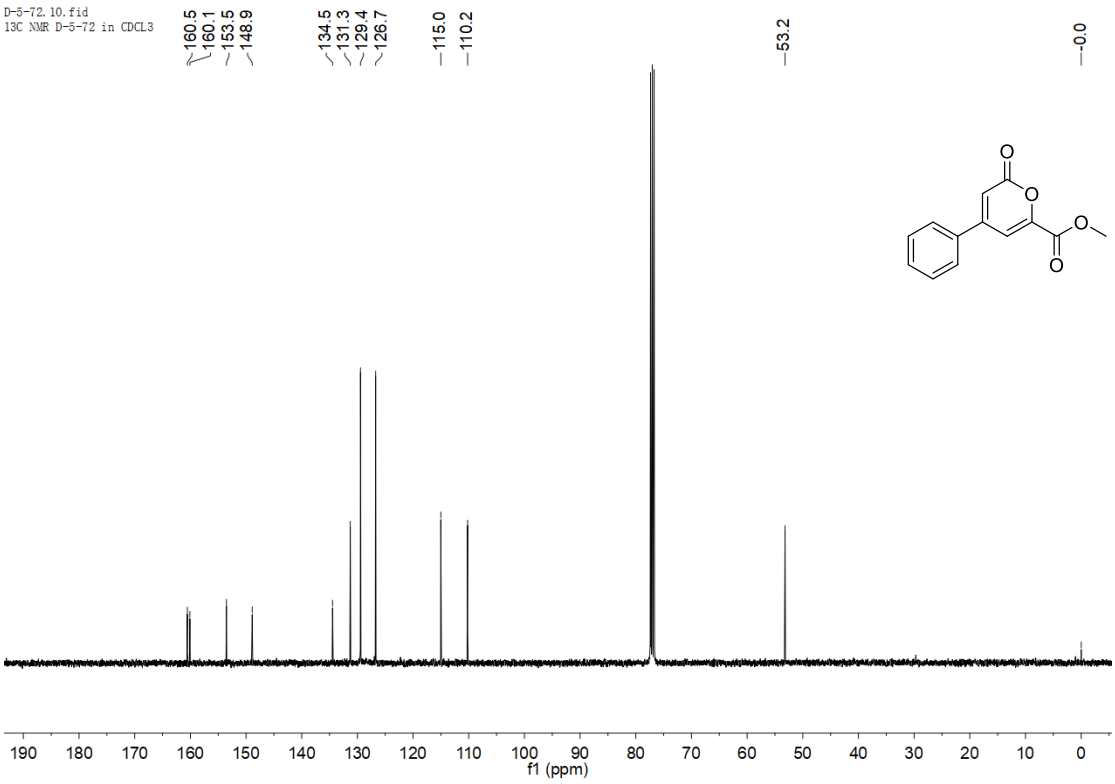


Figure 7.16 ^{13}C NMR spectrum of compound **3a** (101 MHz, $CDCl_3$)

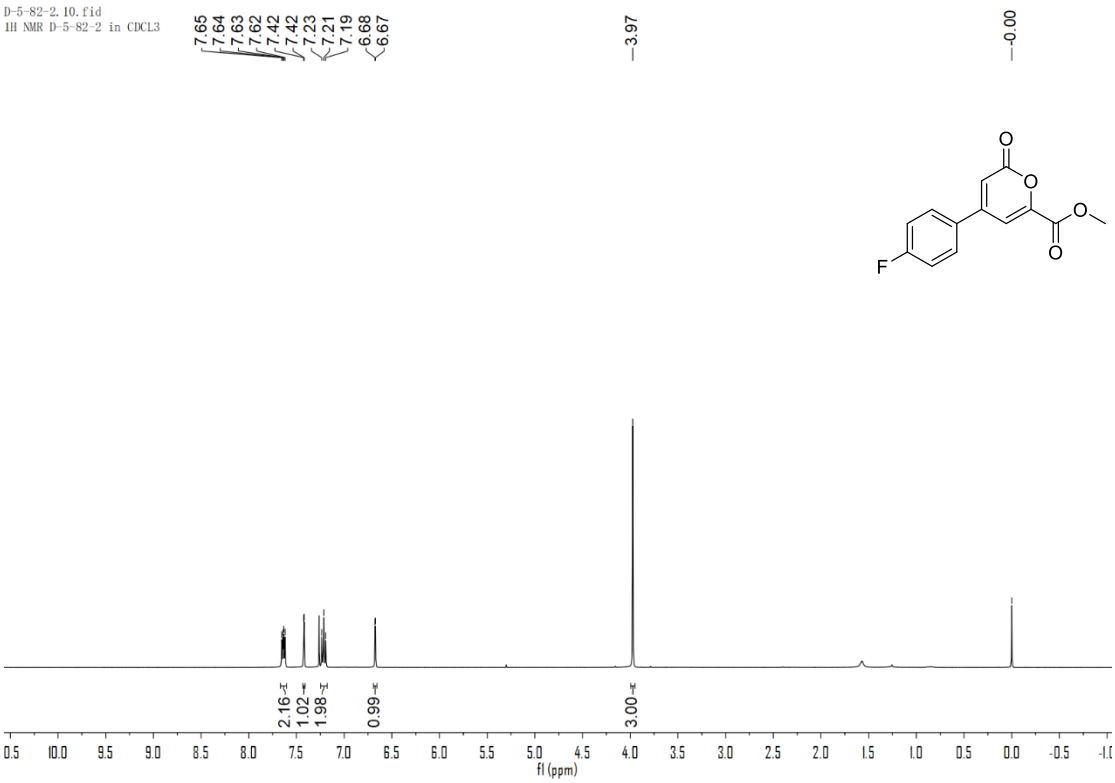


Figure 7.17 ^{1}H NMR spectrum of compound **3b** (400 MHz, $CDCl_3$)

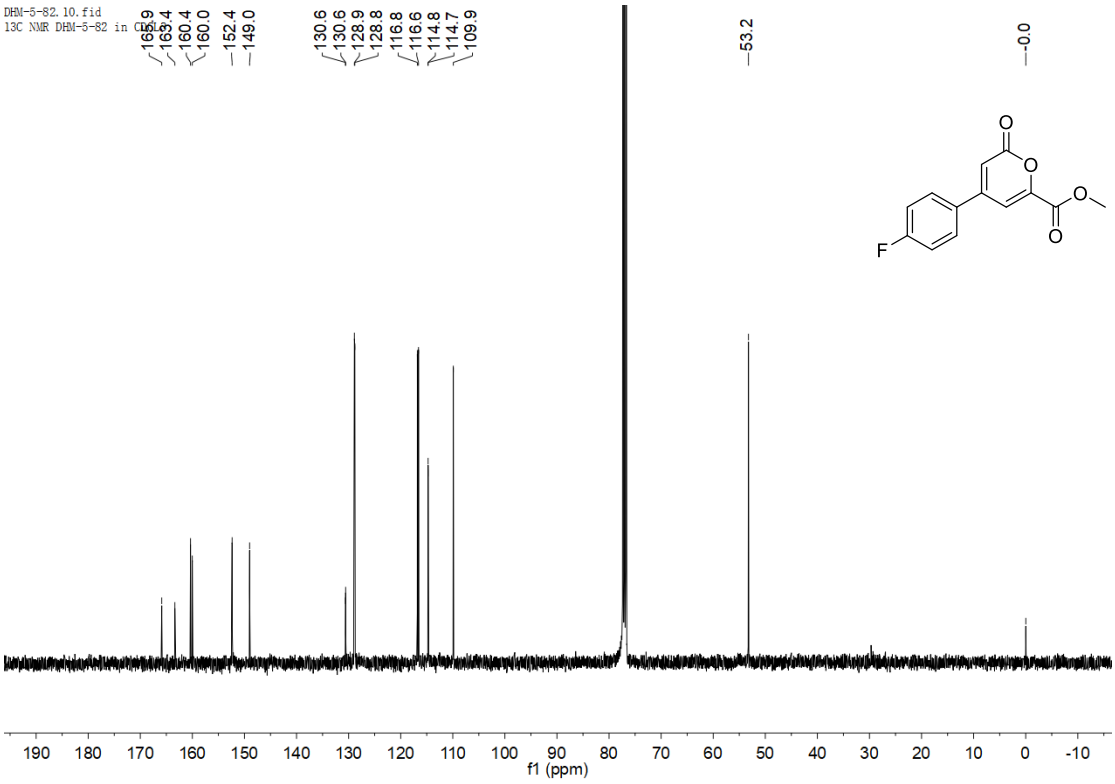


Figure 7.18 ^{13}C NMR spectrum of compound **3b** (101 MHz, $CDCl_3$)

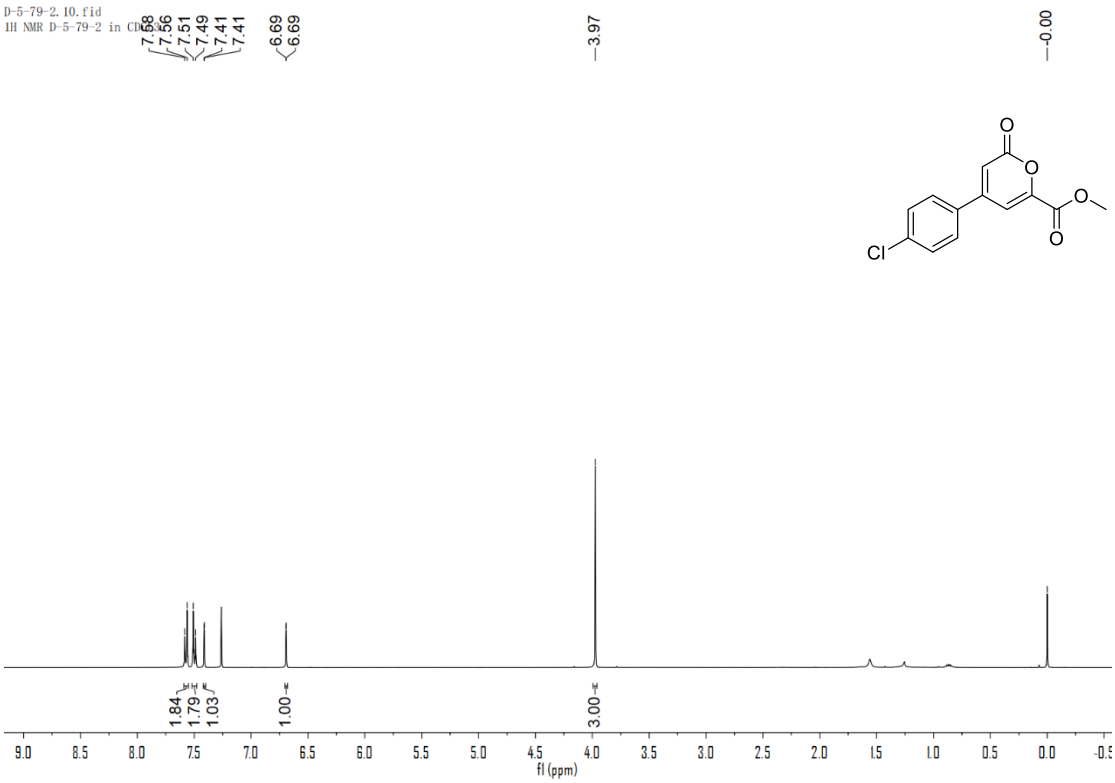


Figure 7.19 ^{1}H NMR spectrum of compound **3c** (400 MHz, $CDCl_3$)

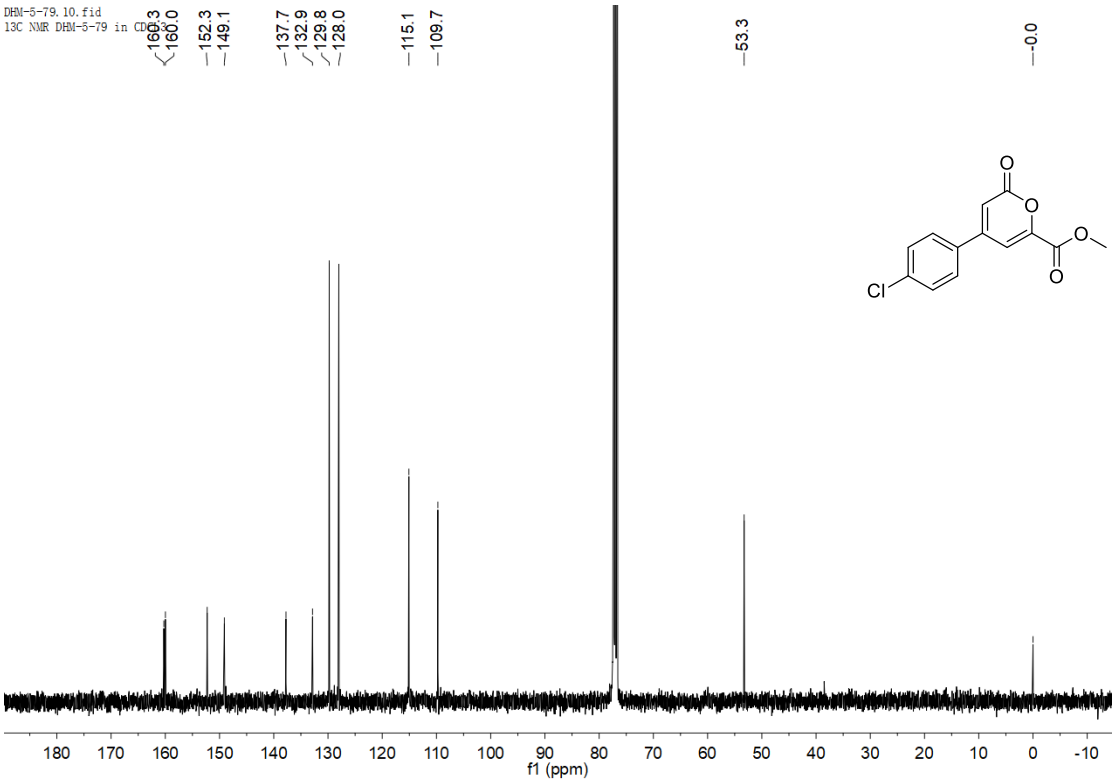


Figure 7.20 ^{13}C NMR spectrum of compound **3c** (101 MHz, $CDCl_3$)

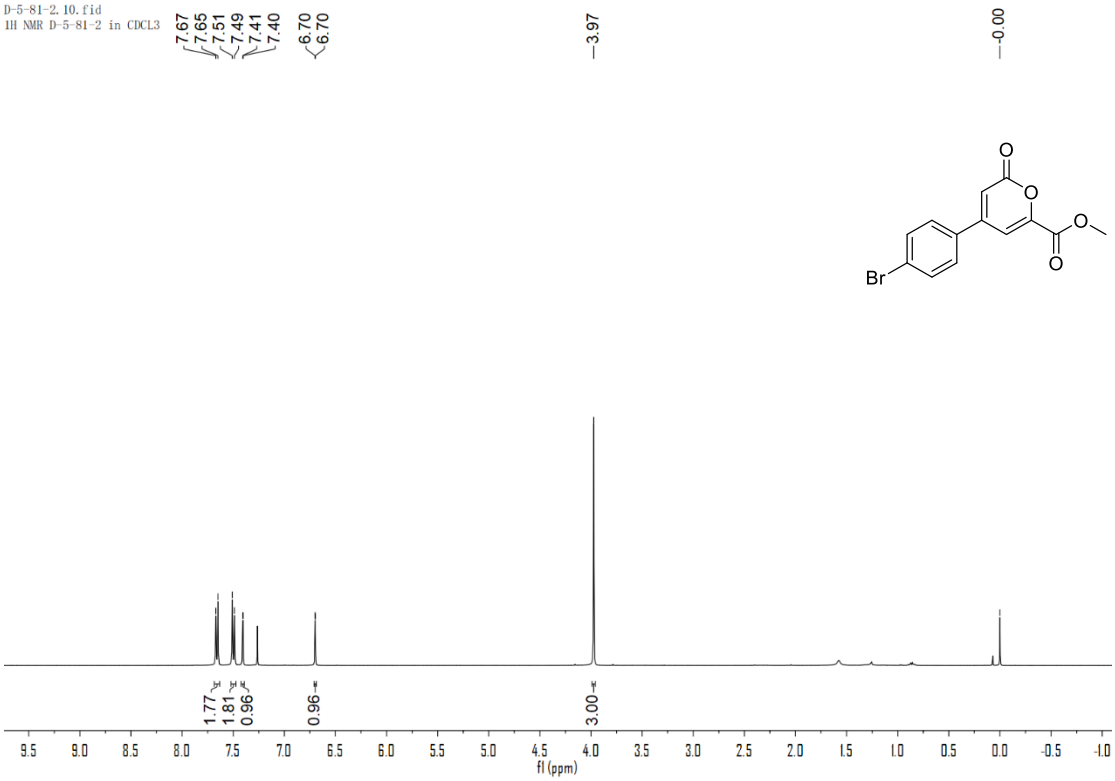


Figure 7.21 ^{1}H NMR spectrum of compound **3d** (400 MHz, $CDCl_3$)

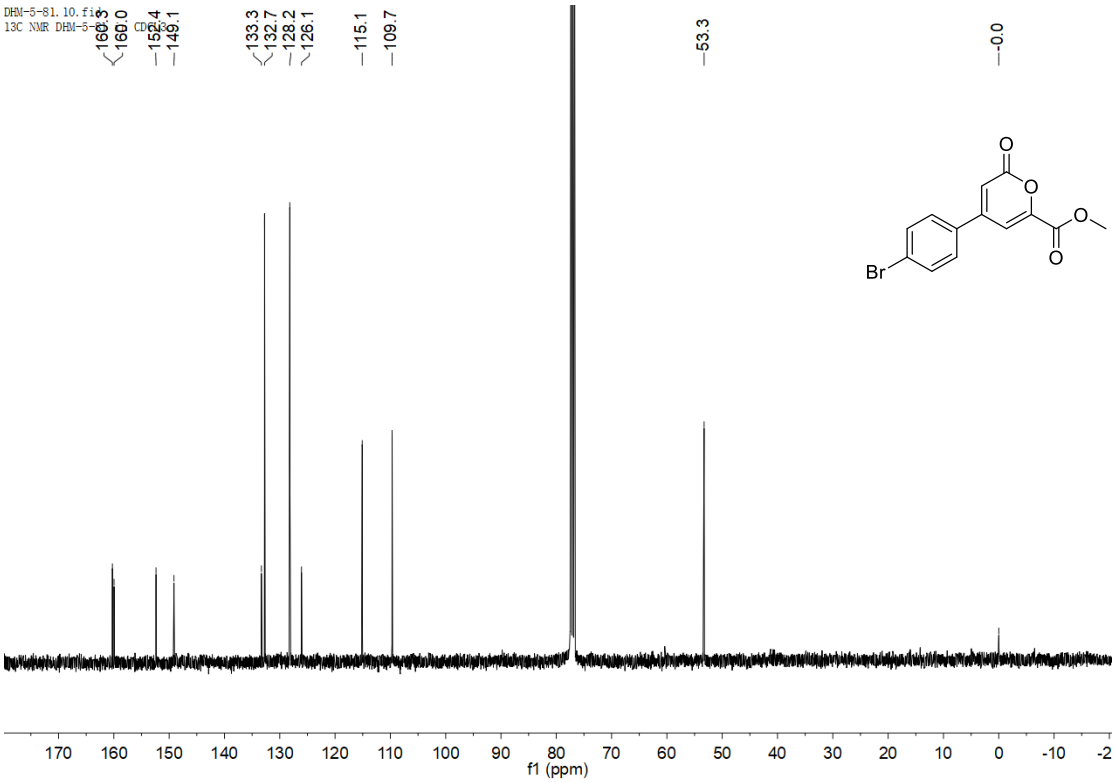


Figure 7.22 ^{13}C NMR spectrum of compound **3d** (101 MHz, $CDCl_3$)

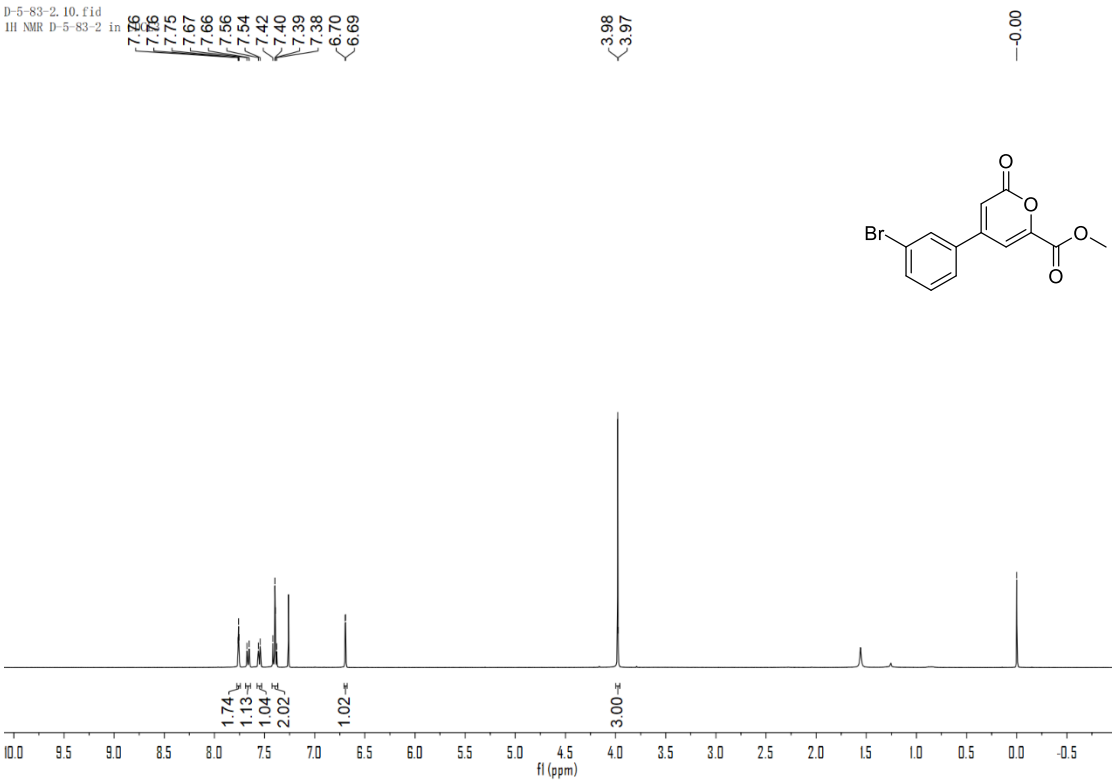


Figure 7.23 ^{1}H NMR spectrum of compound **3e** (400 MHz, $CDCl_3$)

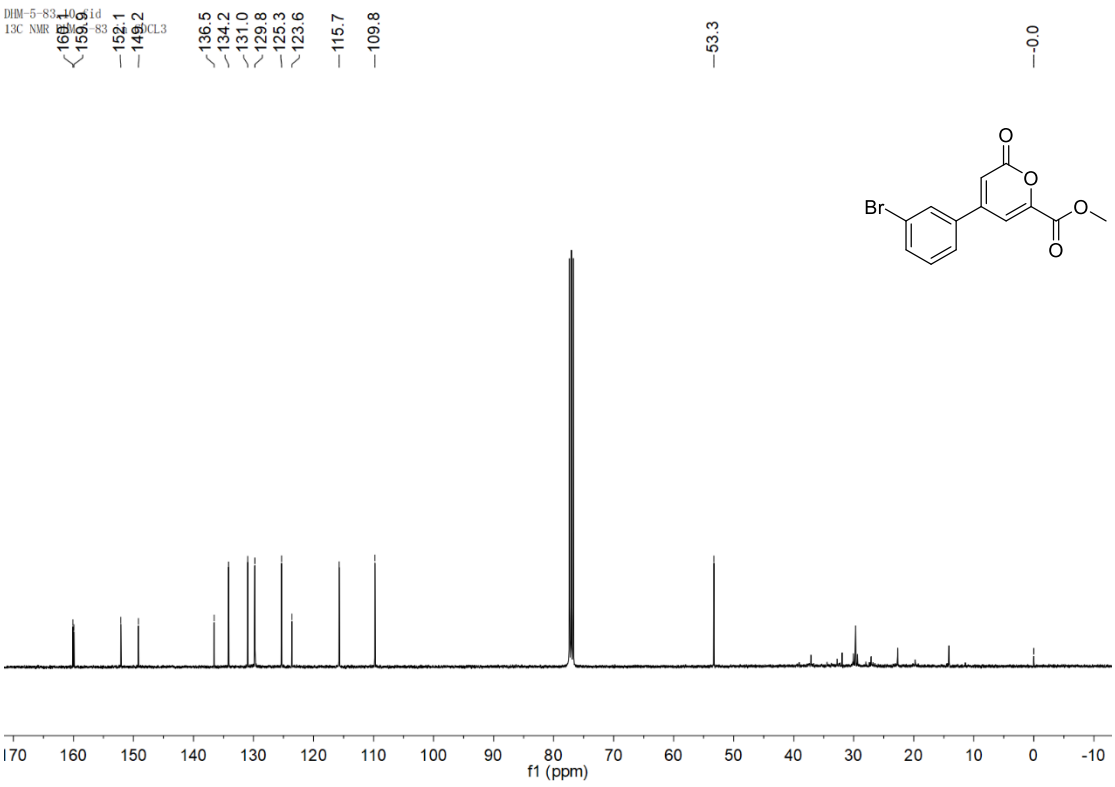


Figure 7.24 ^{13}C NMR spectrum of compound **3e** (101 MHz, $CDCl_3$)

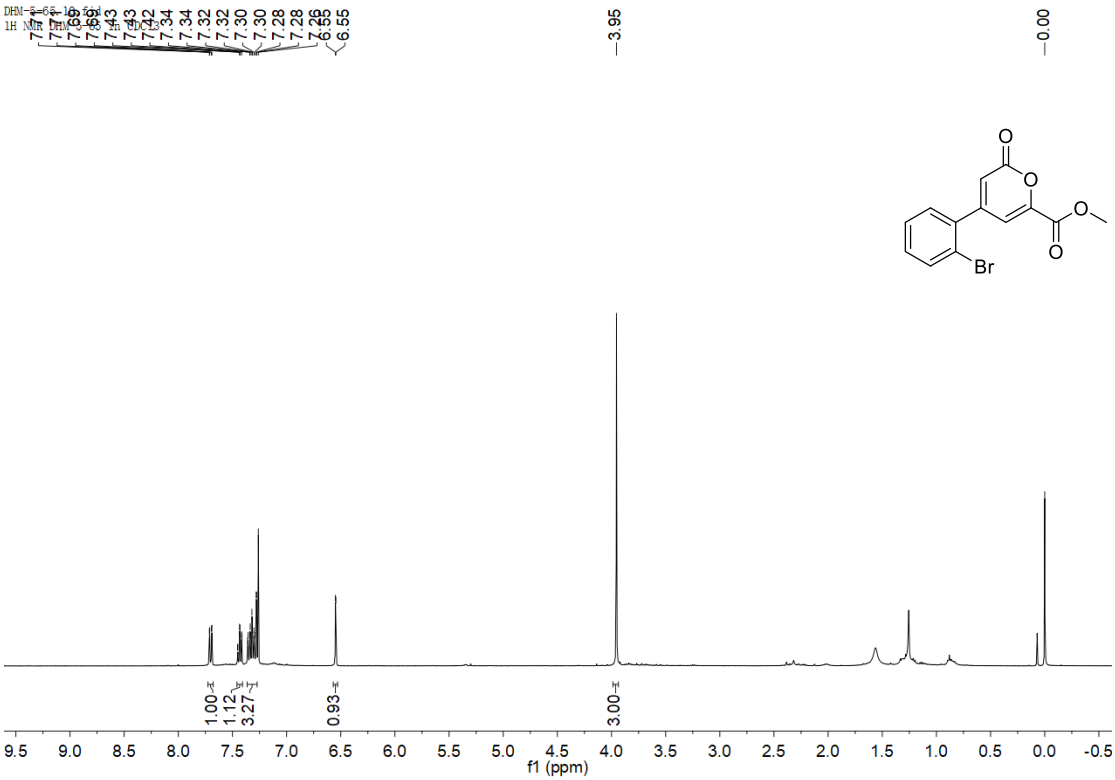


Figure 7.25 ^{1}H NMR spectrum of compound **3f** (400 MHz, $CDCl_3$)

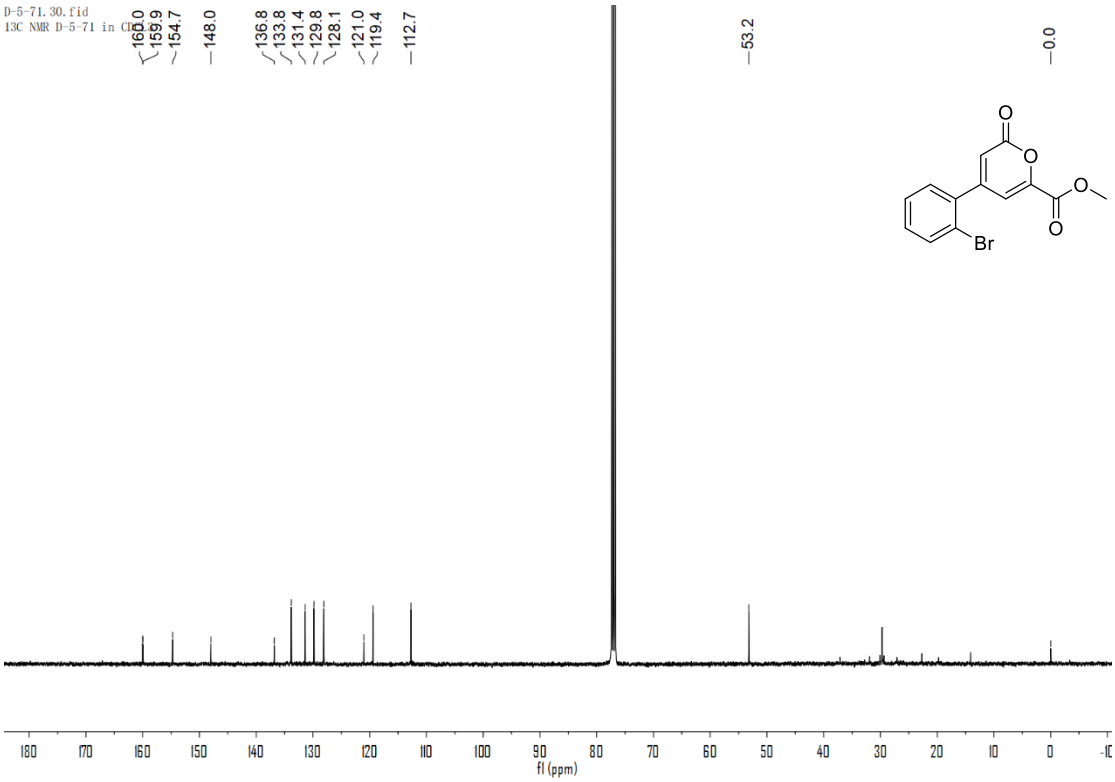


Figure 7.26 ^{13}C NMR spectrum of compound **3f** (101 MHz, $CDCl_3$)

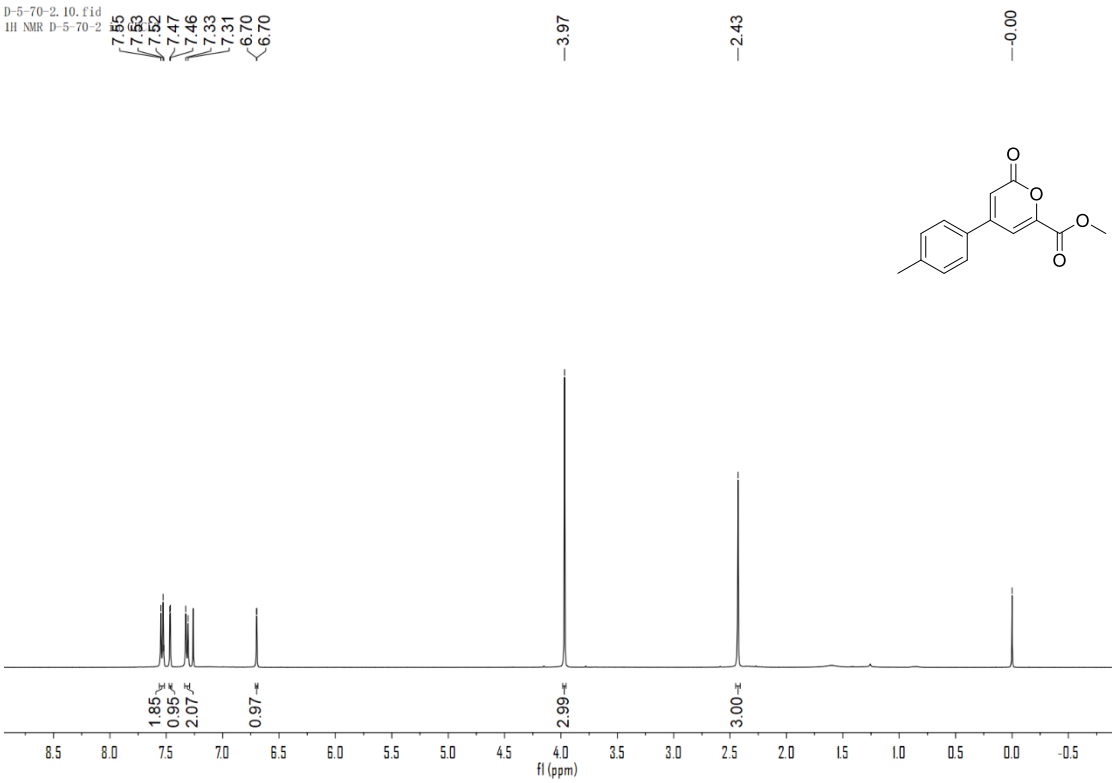


Figure 7.27 ^{1}H NMR spectrum of compound **3g** (400 MHz, $CDCl_3$)

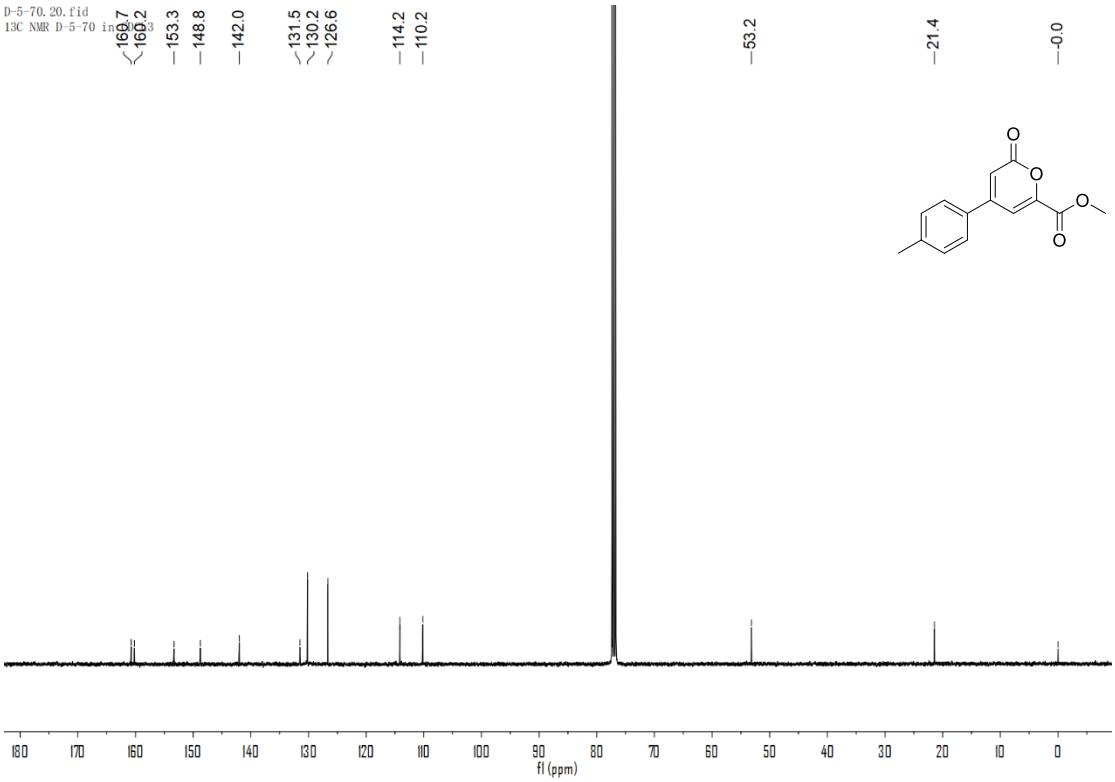


Figure 7.28 ^{13}C NMR spectrum of compound **3g** (101 MHz, $CDCl_3$)

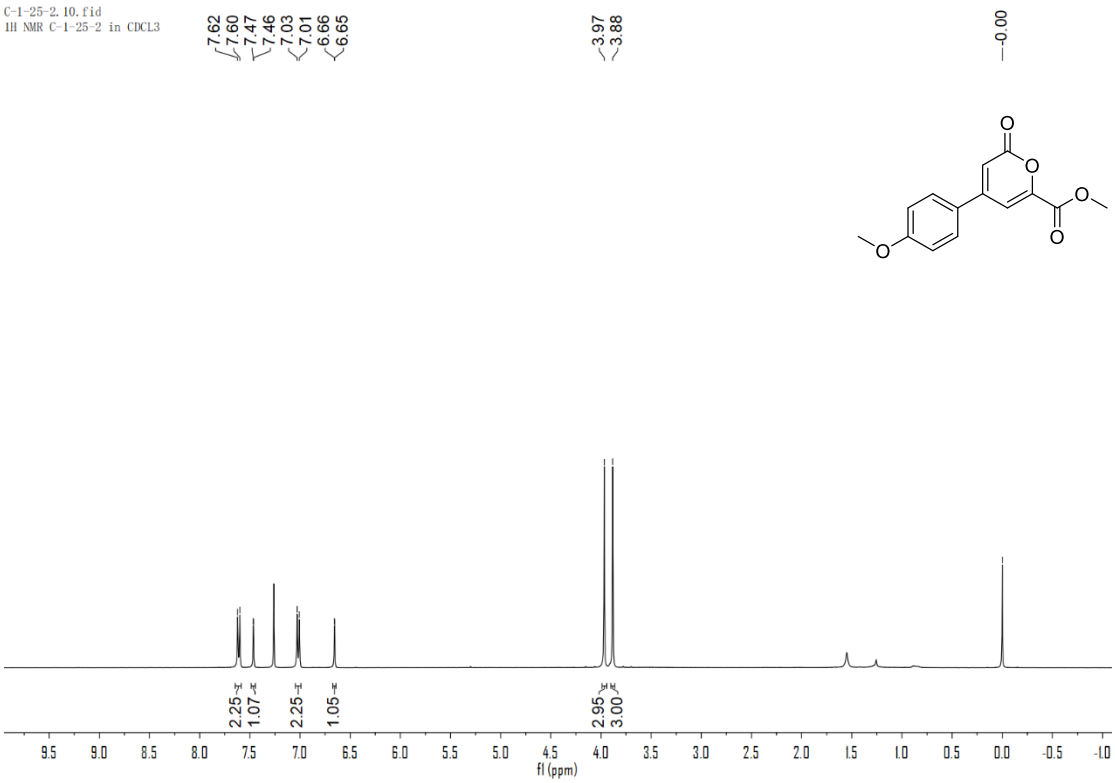


Figure 7.29 ^{1}H NMR spectrum of compound **3h** (400 MHz, $CDCl_3$)

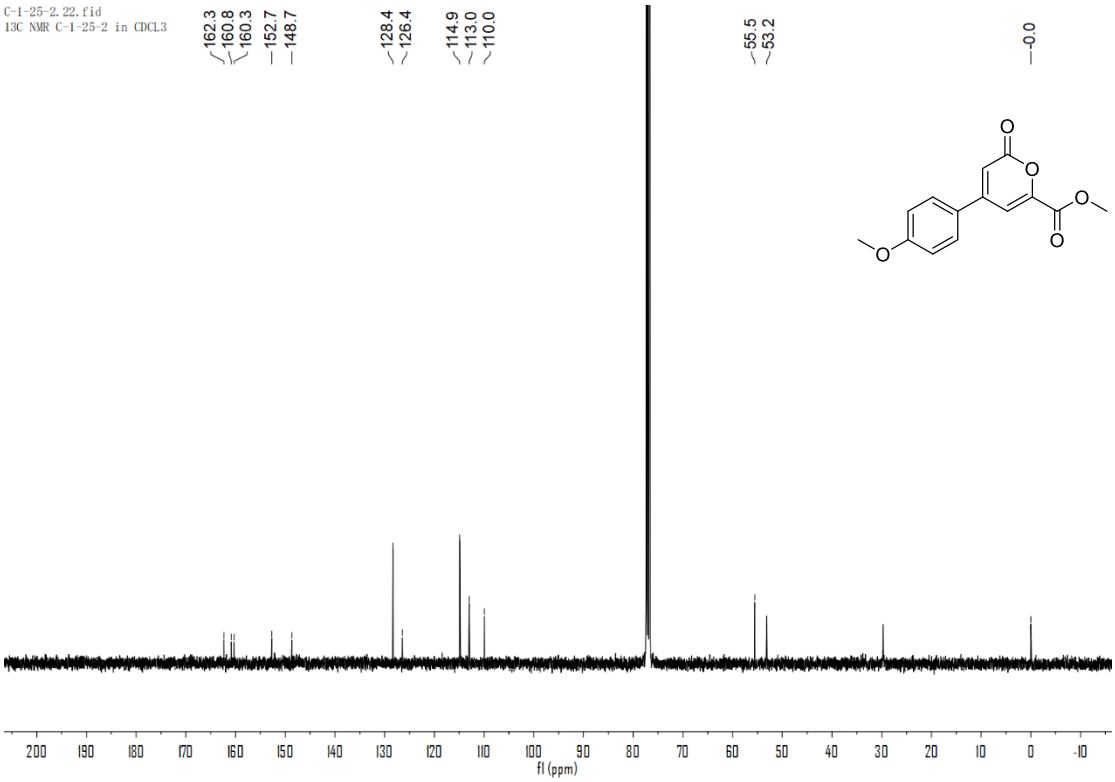


Figure 7.30 ^{13}C NMR spectrum of compound **3h** (101 MHz, $CDCl_3$)

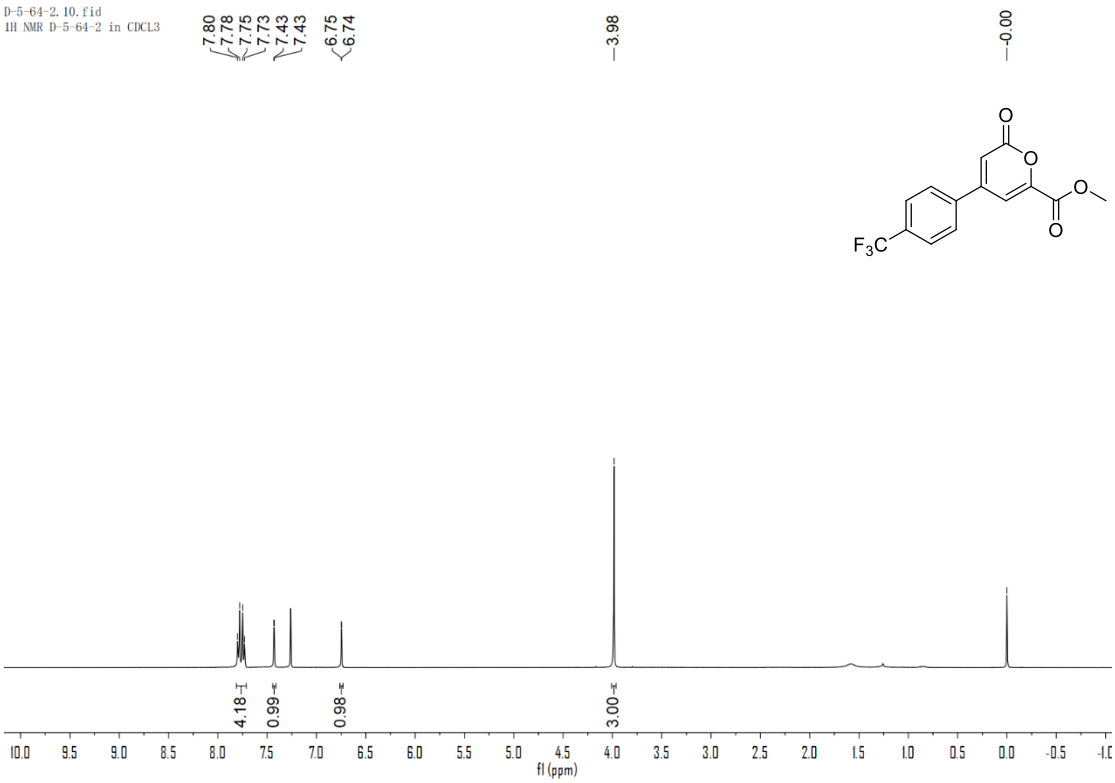


Figure 7.31 ^{1}H NMR spectrum of compound **3i** (400 MHz, $CDCl_3$)

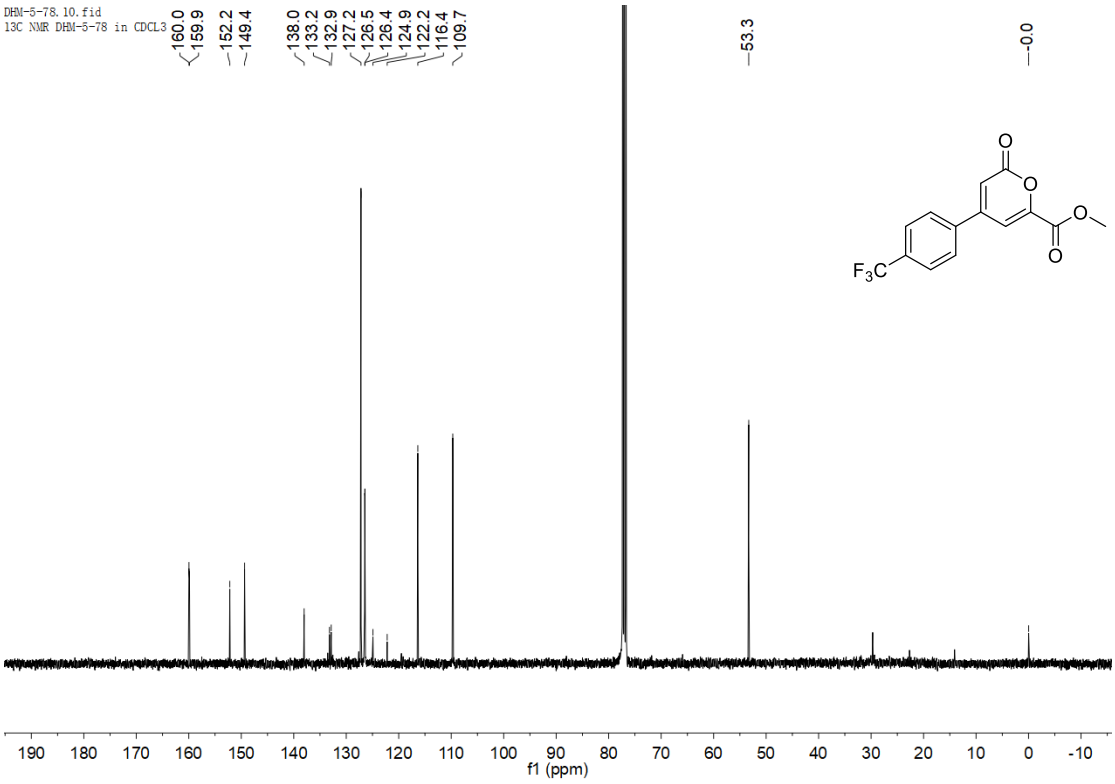


Figure 7.32 ^{13}C NMR spectrum of compound **3i** (101 MHz, $CDCl_3$)

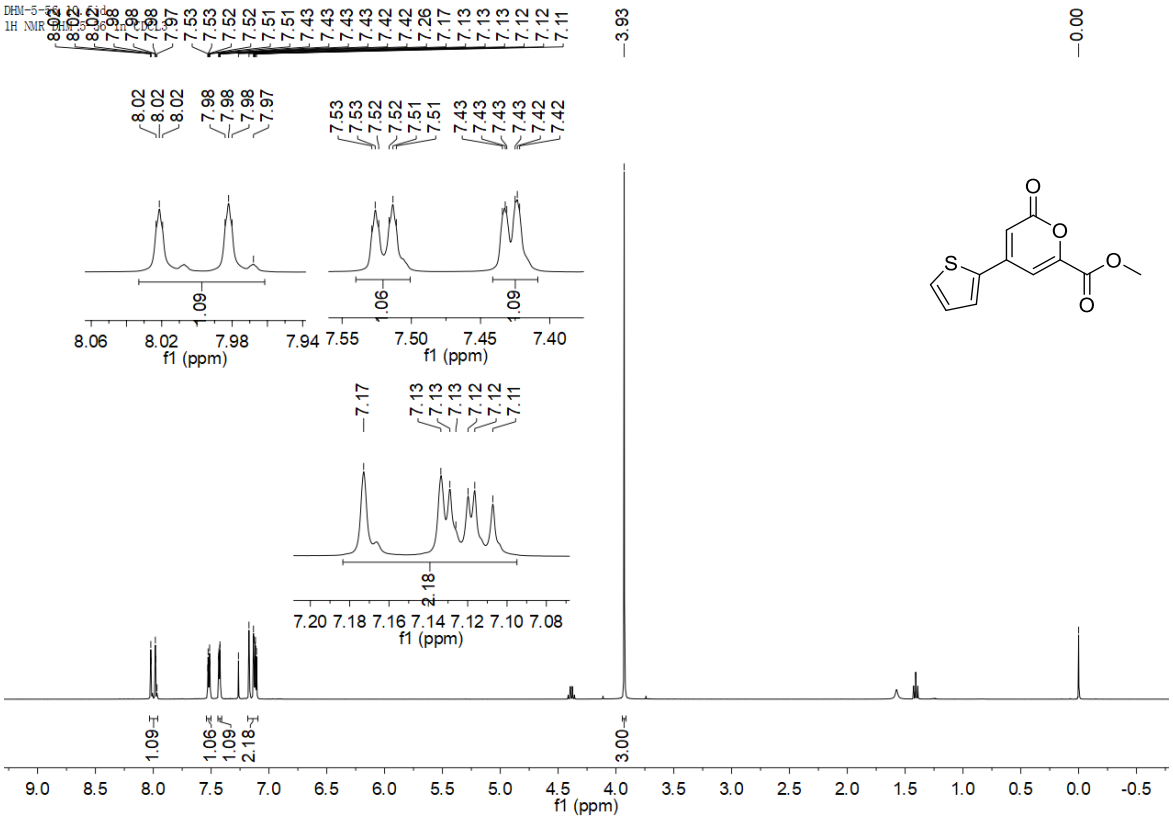


Figure 7.33 ^{1}H NMR spectrum of compound **3j** (400 MHz, $CDCl_3$)

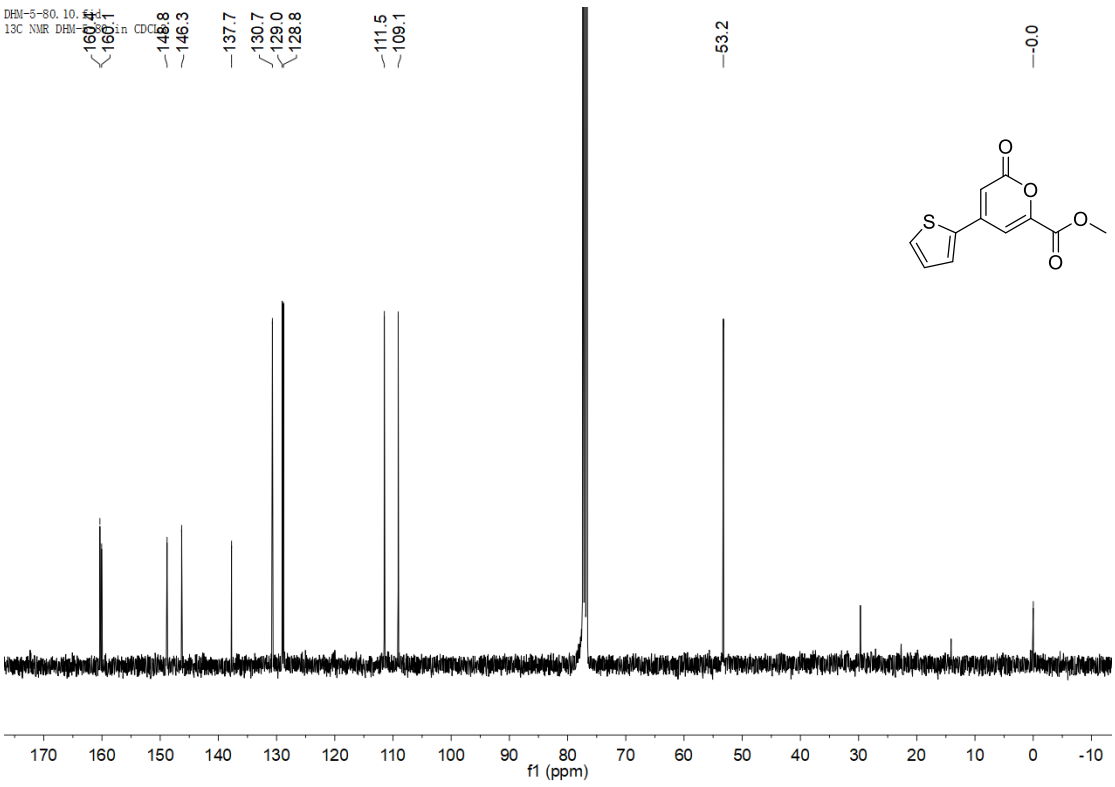


Figure 7.34 ^{13}C NMR spectrum of compound **3j** (101 MHz, $CDCl_3$)

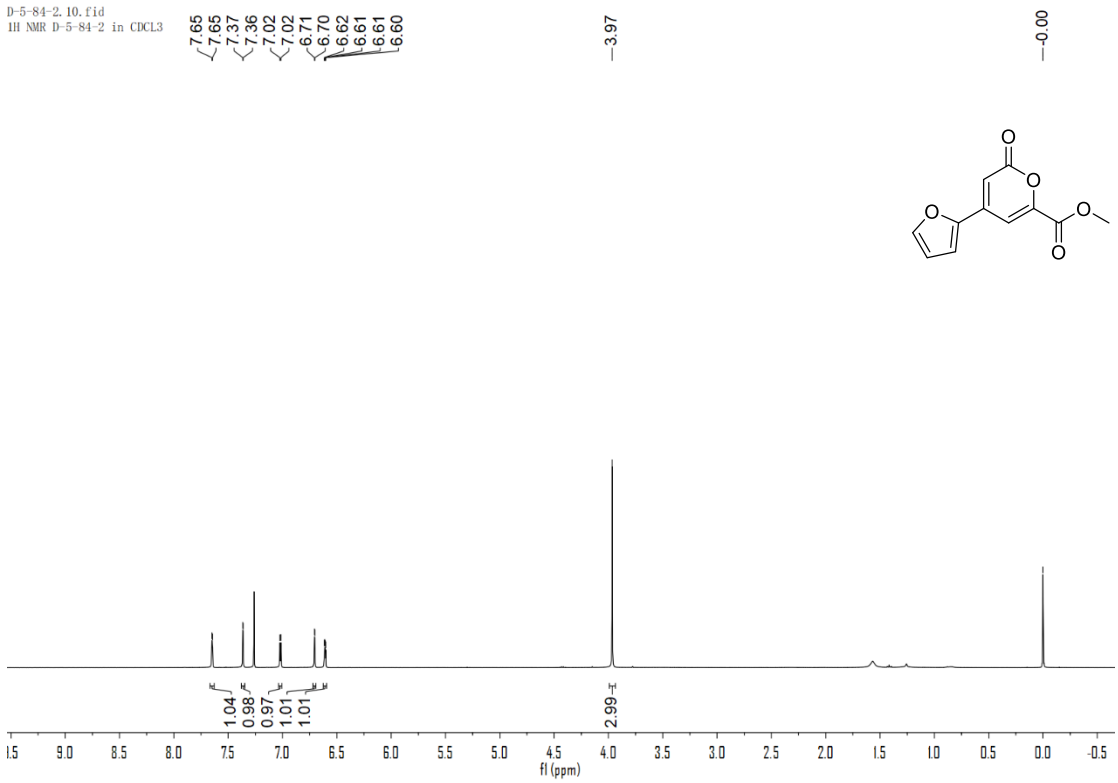


Figure 7.35 ^{1}H NMR spectrum of compound **3k** (400 MHz, $CDCl_3$)

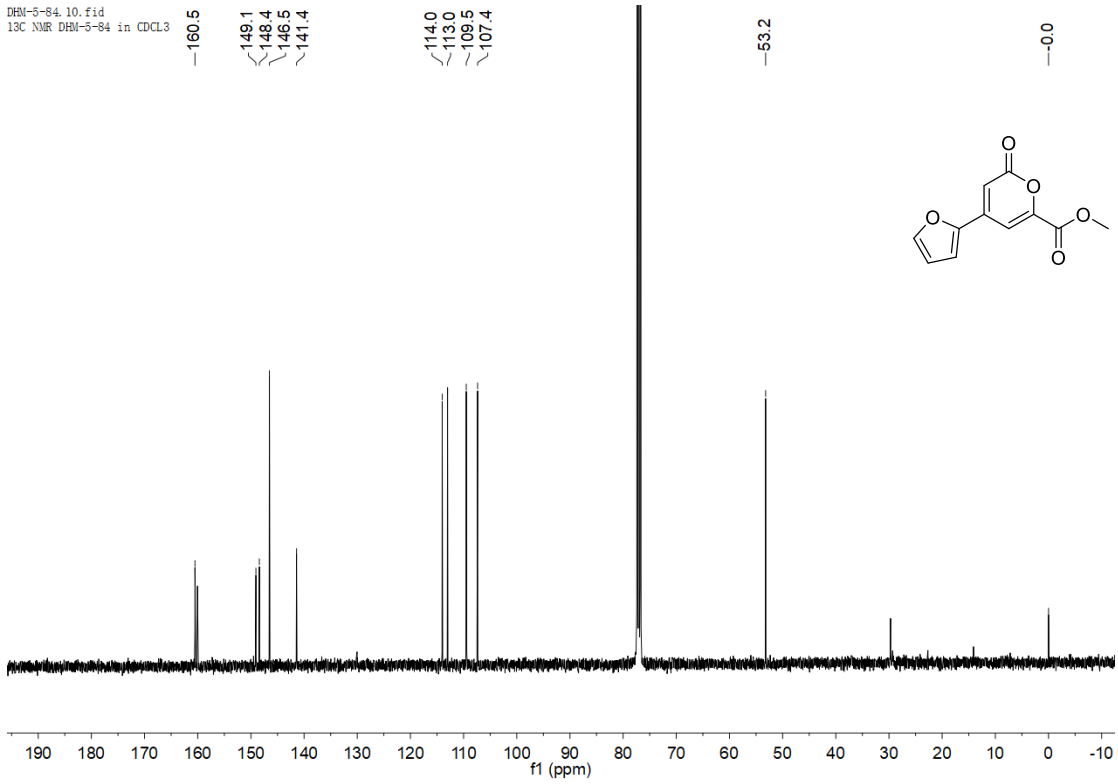


Figure 7.36 ^{13}C NMR spectrum of compound **3k** (101 MHz, $CDCl_3$)

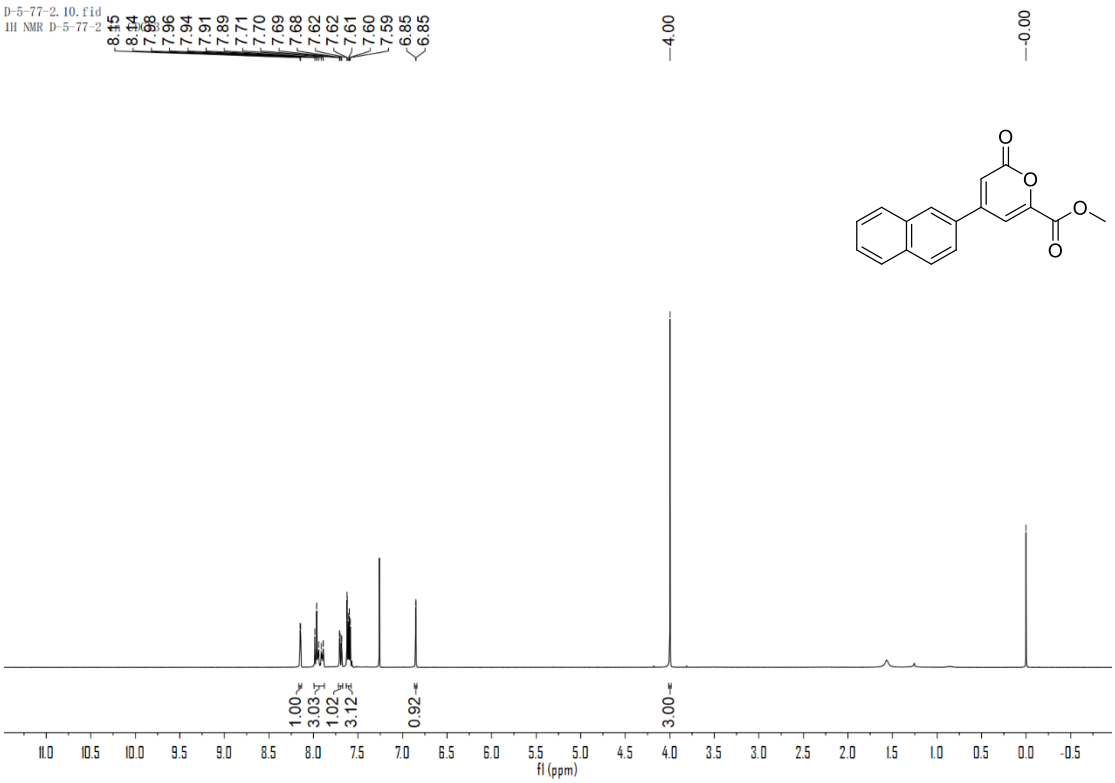


Figure 7.37 ^{1}H NMR spectrum of compound **3l** (400 MHz, $CDCl_3$)

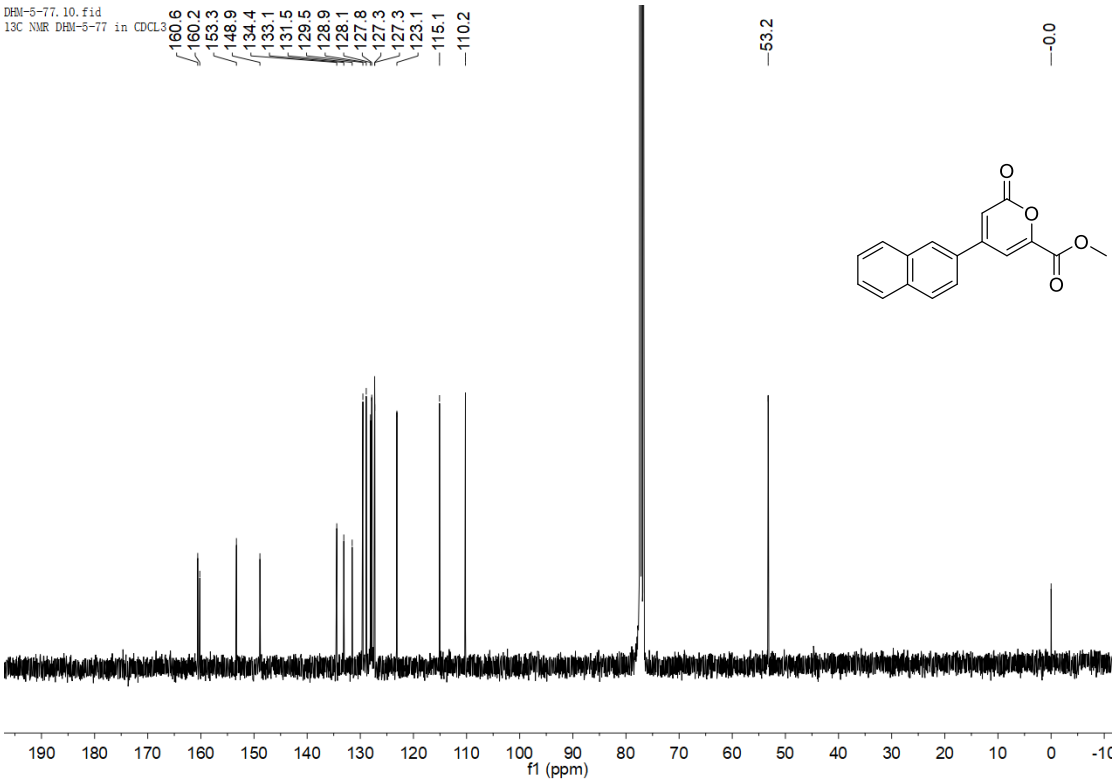


Figure 7.38 ^{13}C NMR spectrum of compound **3l** (101 MHz, $CDCl_3$)

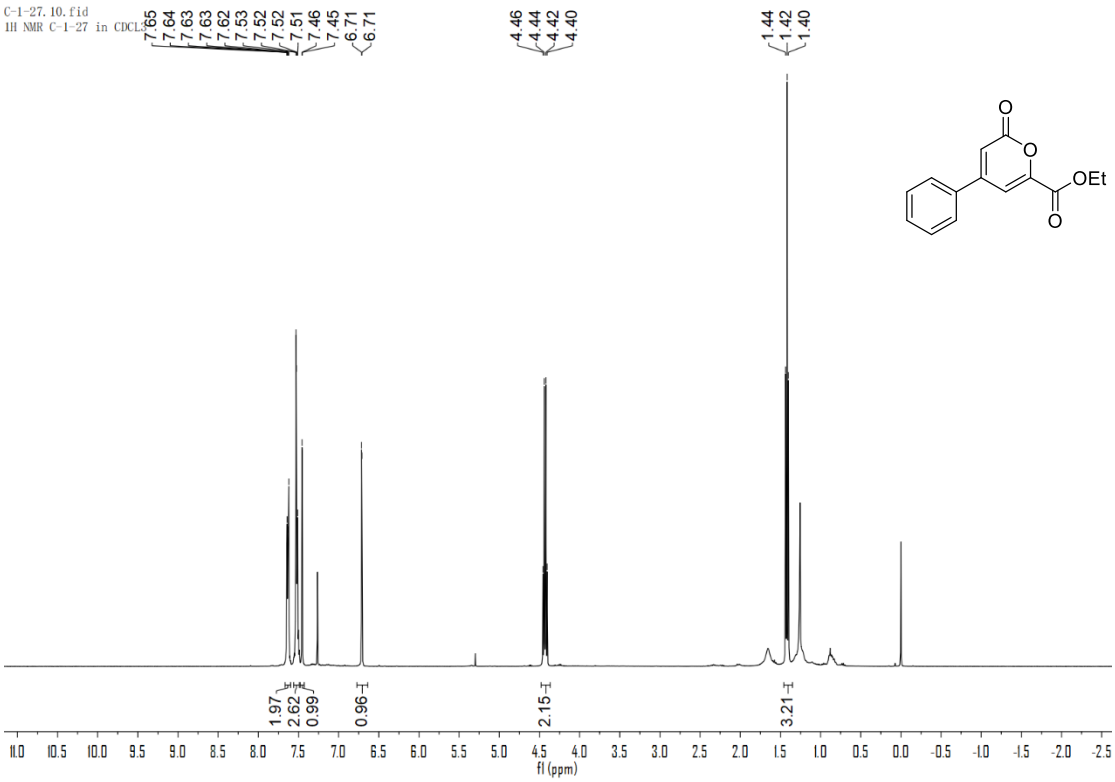


Figure 7.39 ^{1}H NMR spectrum of compound **3m** (400 MHz, $CDCl_3$)

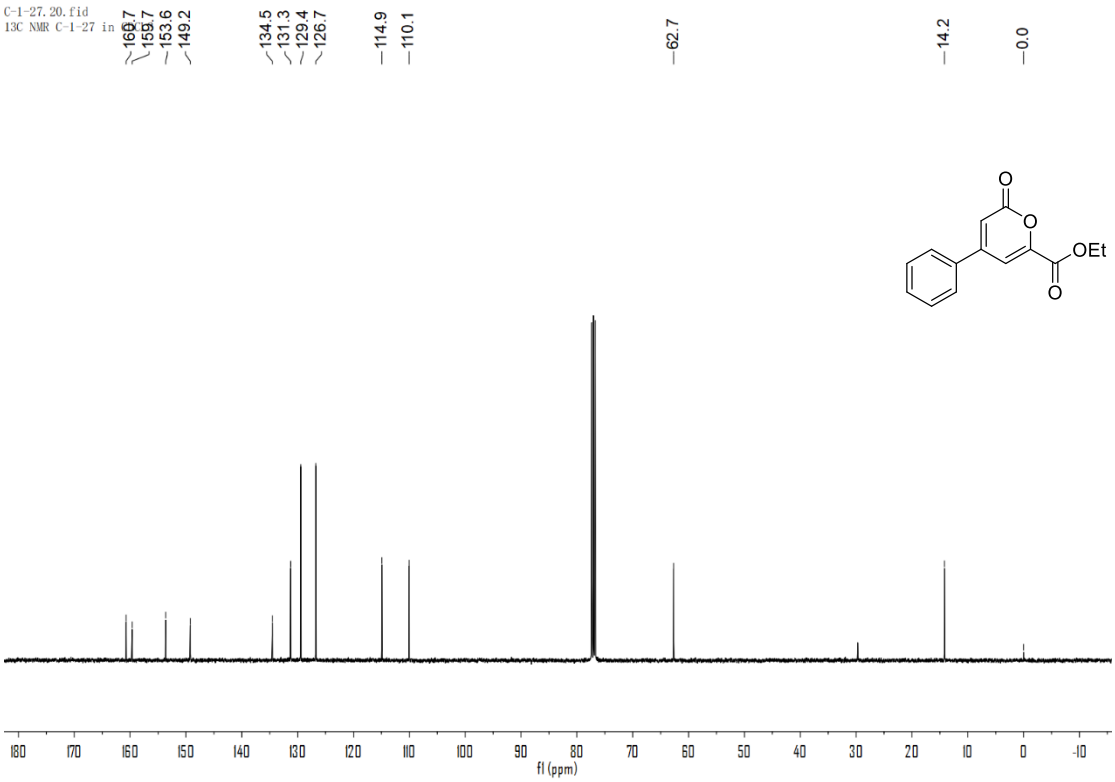


Figure 7.40 ^{13}C NMR spectrum of compound **3m** (101 MHz, $CDCl_3$)

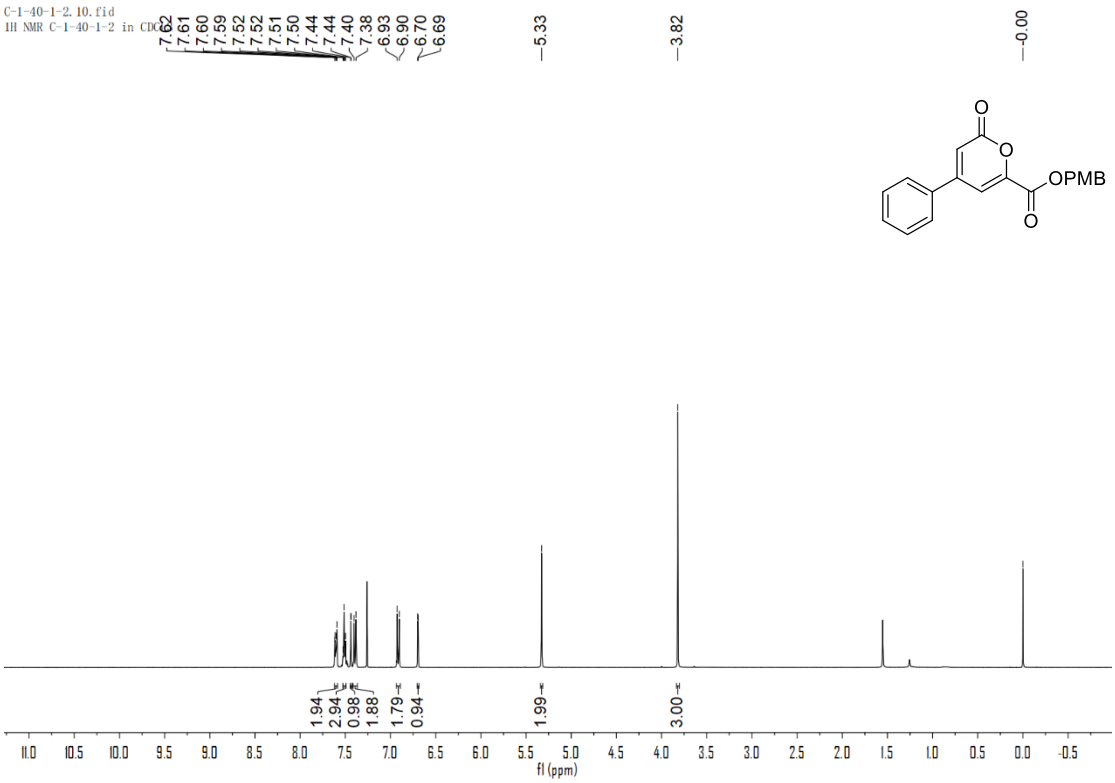


Figure 7.41 ^{1}H NMR spectrum of compound **3n** (400 MHz, $CDCl_3$)

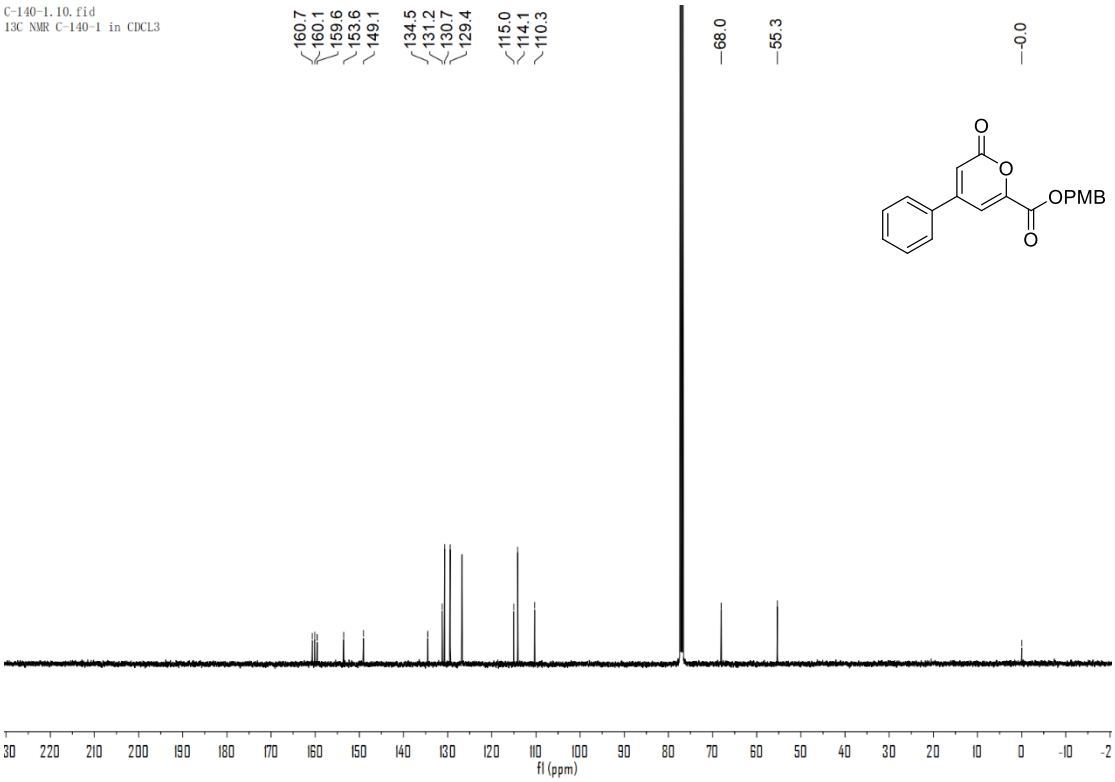


Figure 7.42 ^{13}C NMR spectrum of compound **3n** (101 MHz, $CDCl_3$)

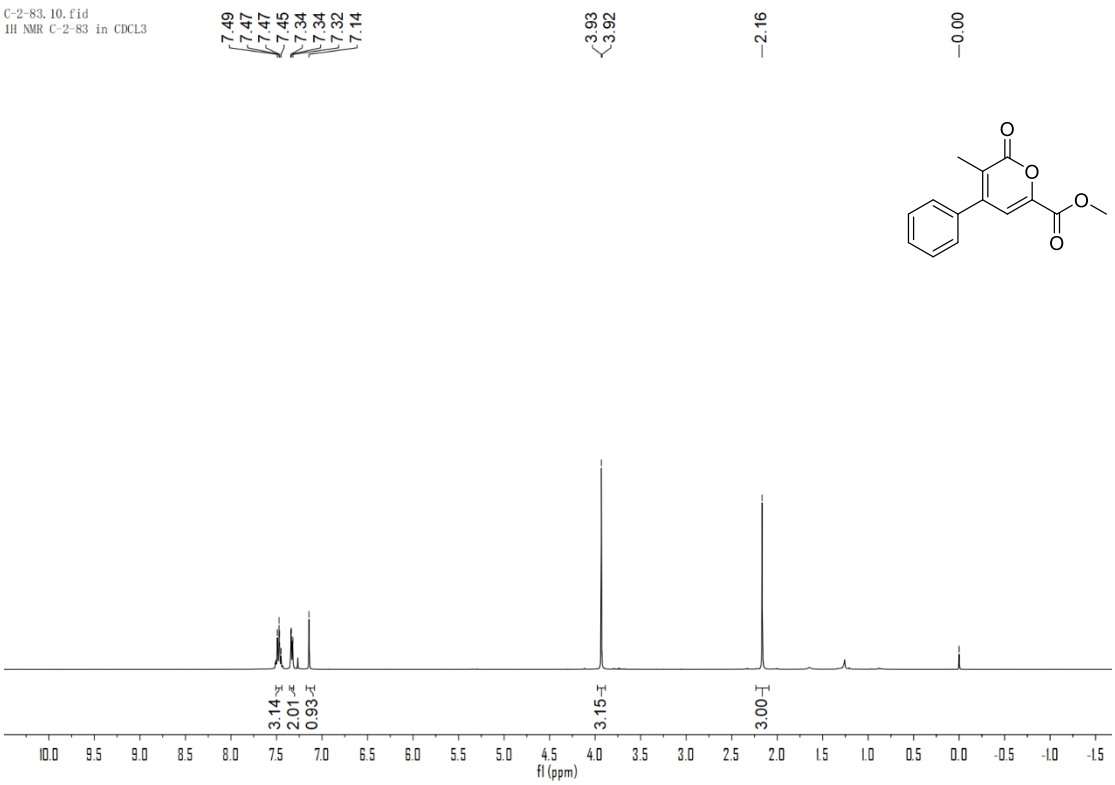


Figure 7.43 ^{1}H NMR spectrum of compound **3o** (400 MHz, $CDCl_3$)

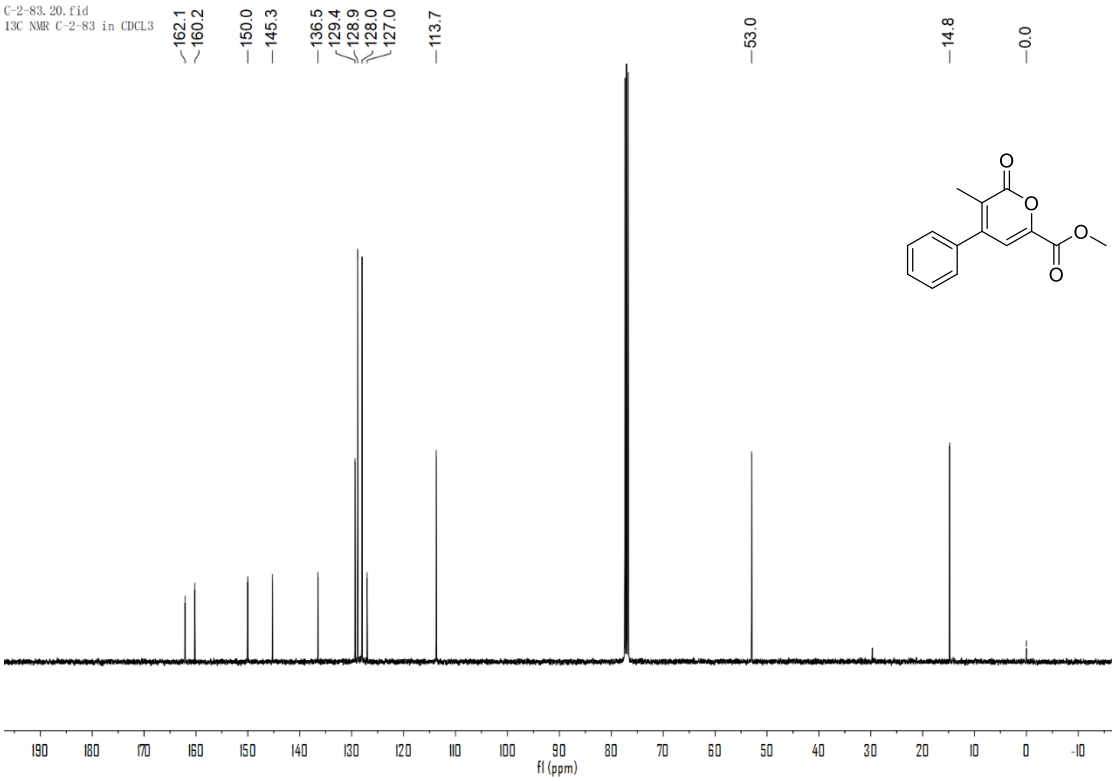


Figure 7.44 ^{13}C NMR spectrum of compound **3o** (101 MHz, $CDCl_3$)

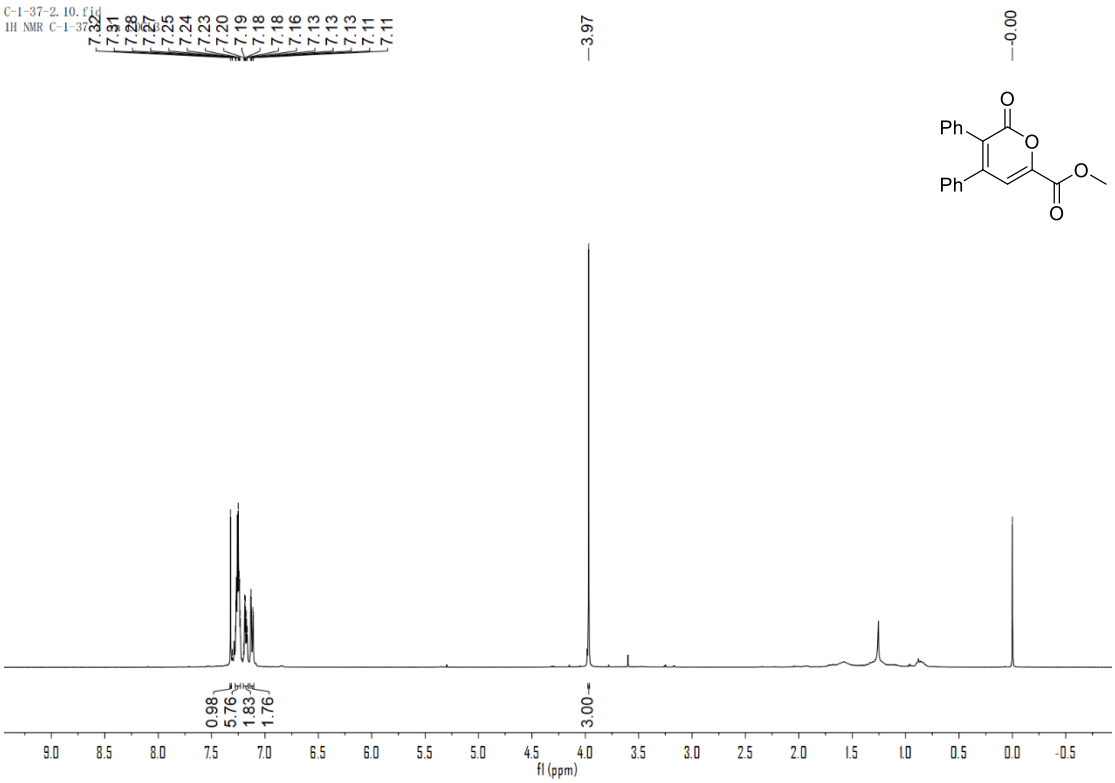


Figure 7.45 ^{1}H NMR spectrum of compound **3p** (400 MHz, $CDCl_3$)

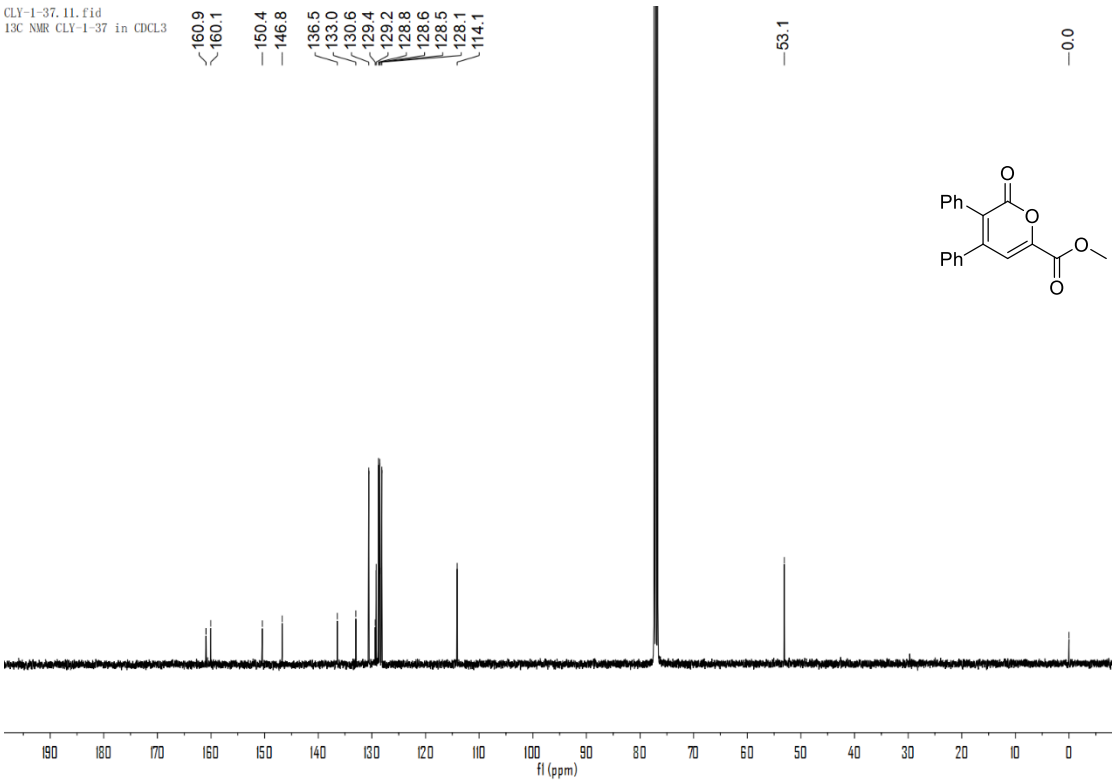


Figure 7.46 ^{13}C NMR spectrum of compound **3p** (101 MHz, $CDCl_3$)

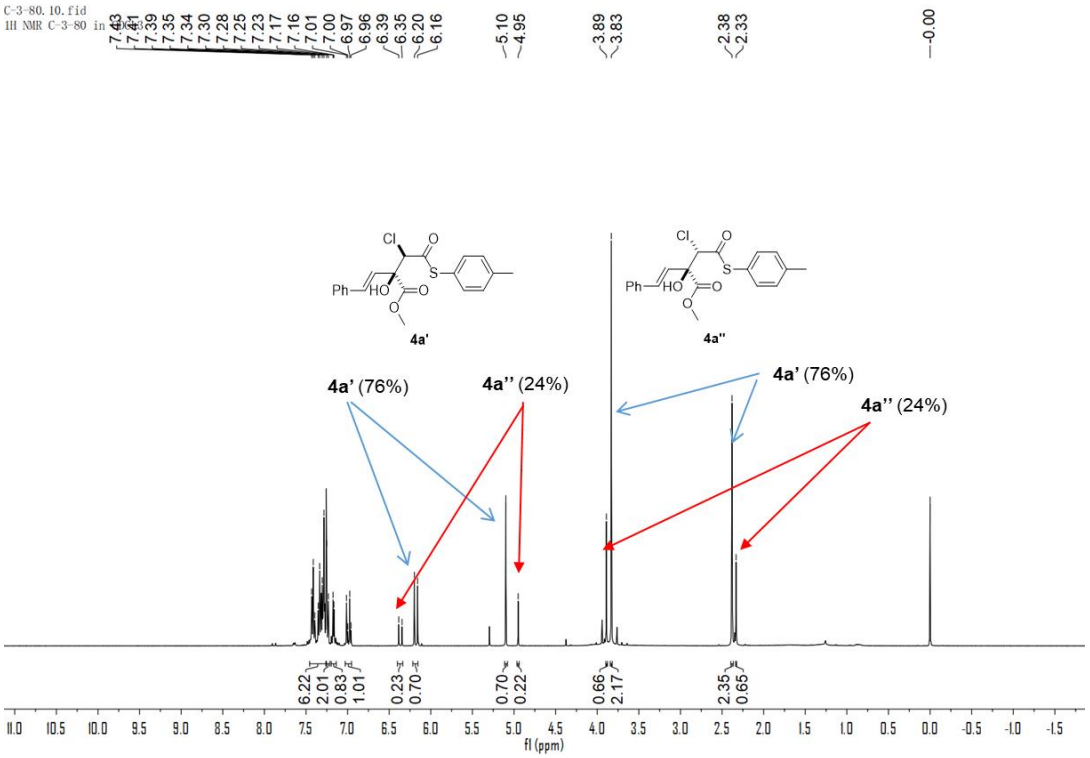


Figure 7.47 ^{1}H NMR spectrum of compound **4a** (400 MHz, $CDCl_3$)

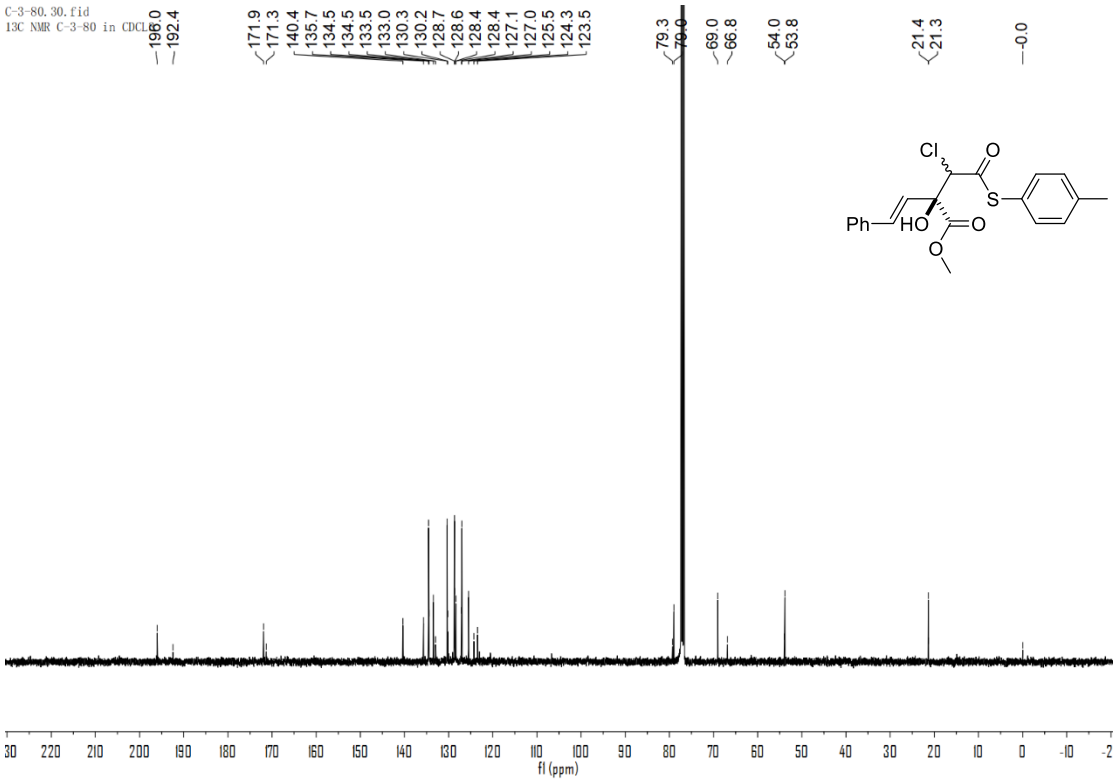


Figure 7.48 ^{13}C NMR spectrum of compound **4a** (101 MHz, $CDCl_3$)

8. References

[1] (a) C. Allais, F. Liéby-Muller, T. Constantieux, J. Rodriguez, *Adv. Synth. Catal.*, 2012, **354**, 2537; (b) Y. Z. Hua, M. M. Liu, P. J. Huang, X. Song, M. C. Wang, J. B. Chang, *Chem. Eur. J.*, 2015, **21**, 11994; (c) V. Juste-Navarro, E. Marqués-López, R. P. Herrera, *Asian J. Org. Chem.*, 2015, **4**, 884; (d) M. Espinosa, A. García-Ortiz, G. Blay, L. Cardona, M. C. Muñoz, J. R. Pedro, *RSC. Advances*, 2016, **6**, 15655.

[2] (a) J. E. Thomson, C. D. Campbell, C. Concellón, N. Duguet, K. Rix, A. M. Z. Slawin and A. D. Smith, *J. Org. Chem.,* 2008, **73**, 2784-2791; (b) N. T. Reynolds, J. R. Alaniz and T. Rovis, *J. Am. Chem. Soc.,* 2004, **126**, 9518; (c) H. Stetter, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 639–647.

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