Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

AgTFA as a Bifunctional Reagent for Palladium-Catalyzed Oxidative Carbonylative [4+1] Annulation of Aromatic acids

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I. General experimental details

All reagents were obtained from commercial suppliers and utilized without further purification. All work-up and purification procedures were carried out with analytical reagent solvents. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer with tetramethylsilane (TMS) as internal standard at room temperature. Chemical shifts are given in δ relative to TMS, with the coupling constants J given in Hz. High-resolution mass spectra (HRMS) were detected by a Bruker Compass-Maxis instrument (ESI or APCI). Melting points were determined using WRX-4 without correction. X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Bruker D8 Advance) equipped with Cu-Kα radiation (40 kV, 40 mA). The sample was scanned from the 2θ of 30° to 100° with a rate of 0.2 s/step. Gas chromatography (GC) were recorded on a SHIMADZU GC-2010 Plus instrument equipped with a FID detector and a DB-5 column).

II. General experimental procedure for the reaction

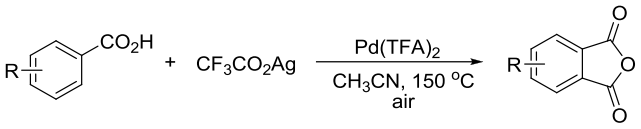
An reaction vessel was charged with aromatic acids (0.1 mmol), CF_3CO_2Ag (90.2 mg, 0.4 mmol), $Pd(TFA)_2$ (3.5 mg, 10 mol%, 0.01 mmol), CH_3CN (0.5 mL). The reaction vessel was sealed under air. Then, the mixture was stirred at 150 ℃ for 24 h. After the reaction was completed, the resulting mixture was cooled to room temperature, diluted with EtOAc, and filtered via a short silica gel pad. The solution was concentrated under vacuum, and the residue was purified by a preparative TLC to afford the desired product.

III. Procedure for the synthesis of 3a on 1 mmol scale

An 10 mL Schlenk tube was charged with 2-methylbenzoic acid (139 mg, 1 mmol), CF_3CO_2Ag (902 mg, 4 mmol), $Pd(TFA)_2$ (35 mg, 10 mol%, 0.1 mmol), CH_3CN (3 mL). The reaction vessel was sealed under air. Then, the mixture was reacted at 150 ℃ (oil bath temperature) for 15 h. After the reaction was completed, the resulting mixture was cooled to room temperature, and concentrated to give a crude product, which is purified by silica-gel column chromatography using hexane/EtOAc/HOAc (5/1/0.05) to yield compound 3a (0.099 g, 61%).

IV. The results of unactive substrates

Table S1 The results of unactive substrates[a]



Entry	Aromatic acids	Yield (%)[b]
1	4-chlorobenzoic acid	45
2	3-chlorobenzoic acid	33
3	4-bromobenzoic acid	20
4	2,4,5-trimethylbenzoic acid	46
5	2-methyl-4-methoxybenzoic acid	41
6	4-ethoxybenzoic acid	30
7	1-naphthoic acid	45
8	2-naphthoic acid	33
9	3-fluoro-2-methylbenzoic acid	42
10	4-fluoro-2-methylbenzoic acid	46
11	4-hydroxybenzoic acid	28
12	2-biphenylcarboxylic acid	49
13	2-phenoxybenzoic acid	ND
14	2-cyanobenzoic Acid	ND
15	2-nitrobenzoic acid	ND
16	4-tert-butylbenzoic acid	40
17	2-fluorobenzoic acid	23
18	2-bromobenzoic acid	ND
19	3-bromo-2-methylbenzoic acid	31
20	4-bromo-2-methylbenzoic acid	16
21	2-methyl-4-chlorobenzoic acid	45
22	3-(trifluoromethyl)benzoic acid	ND
23	3-chloro-4-methylbenzoic acid	22
24	2-acetylbenzoic acid	ND

[a] Reaction conditions: acids (0.1 mmol), CF_3CO_2Ag (0.4 mmol), $Pd(TFA)_2$ (10 mol%), CH_3CN (0.5 mL), 150 °C, 24 h, under air. [b] Determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

V. The recovery of silver

When the reaction was completed, bright silver particles shown as Figure S1A. were deposited on the bottom of the reaction tube. After the upper suspension was decanted, high purity silver can be acquired when the particles on the bottom was washed with ethyl acetate three times (Figure S1B).

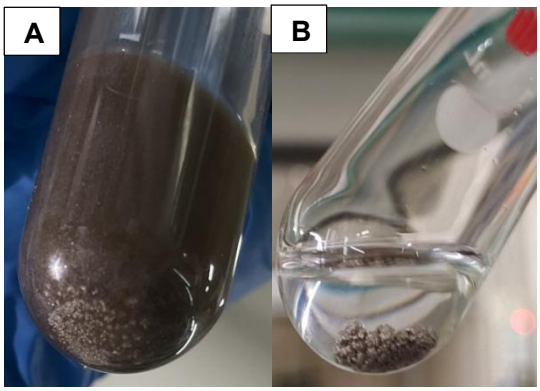
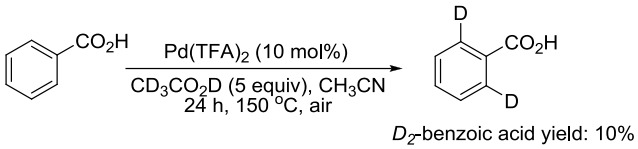


Figure S1 The picture after reaction.

VI. Mechanistic studies

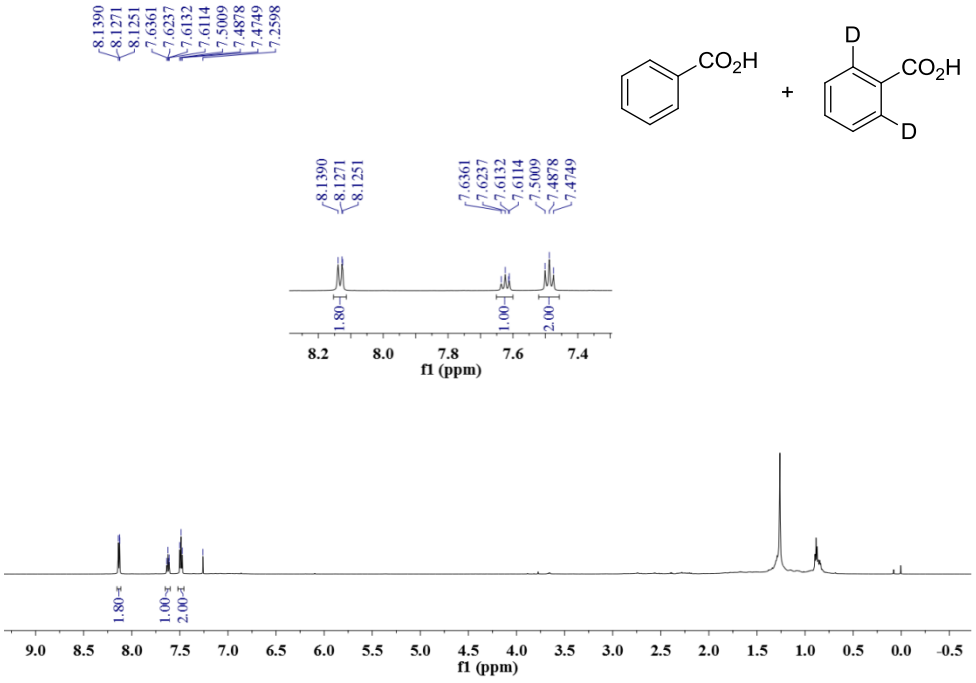
6.1 *Ortho* deuteration experiment



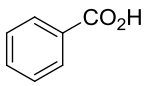
D$_2$-benzoic acid yield: 10%

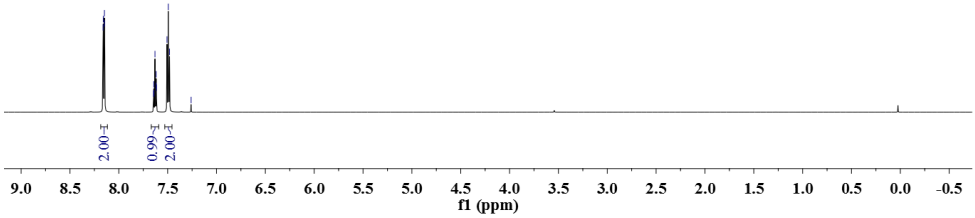
An reaction vessel was charged with benzoic acid (12.2 mg, 0.1 mmol), $Pd(TFA)_2$ (3.5 mg, 10 mol%, 0.01 mmol), CD_3CO_2D (0.5 mmol, 29 μL), CH_3CN (0.5 mL), and sealed under air. Then, the mixture was stirred at 150 ℃ (oil bath temperature) for 24 h. After the reaction was completed, the resulting mixture was cooled to room temperature, diluted with EtOAc and filtered through a short silica gel pad. The solvent was removed under reduced pressure and the amount of *ortho*-deuterated benzoic acid was determined by integral area in ^{1}H NMR.

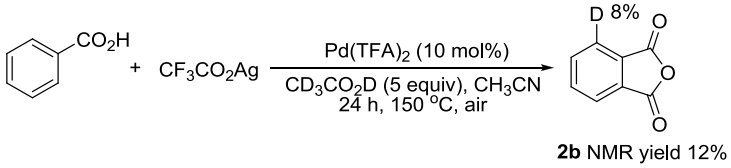
^{1}H NMR spectra of crude reaction mixture of *ortho* deuteration experiment



^{1}H NMR spectra of benzoic acid



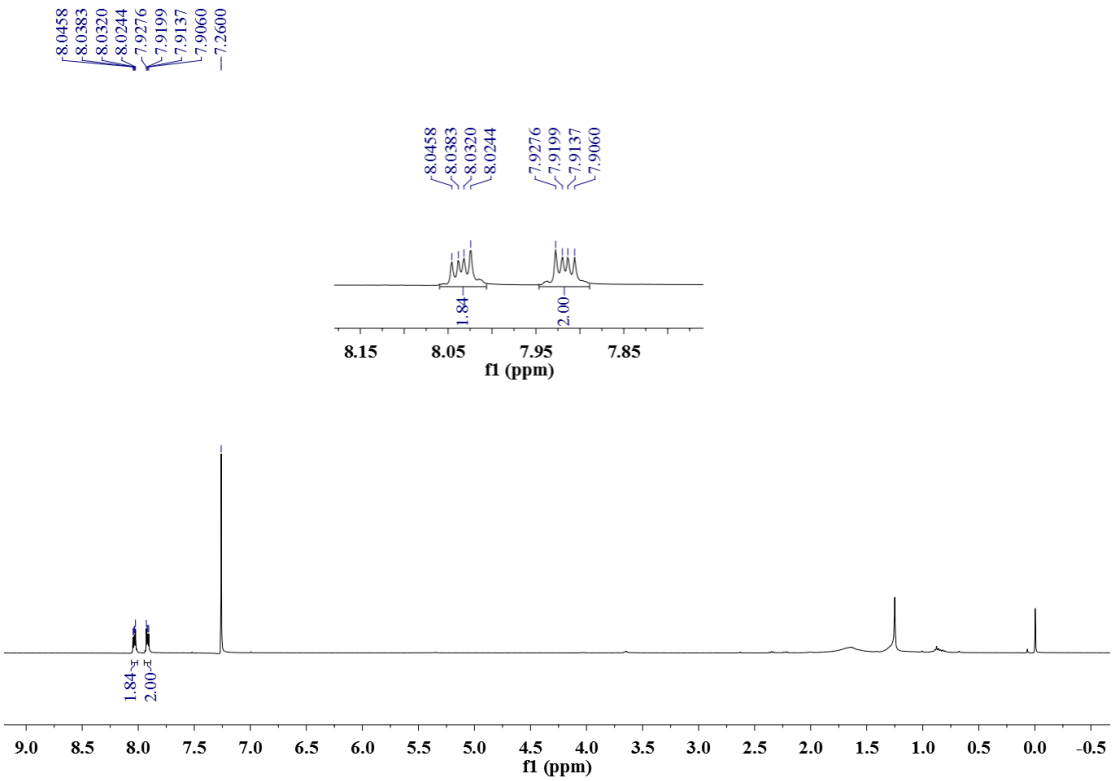




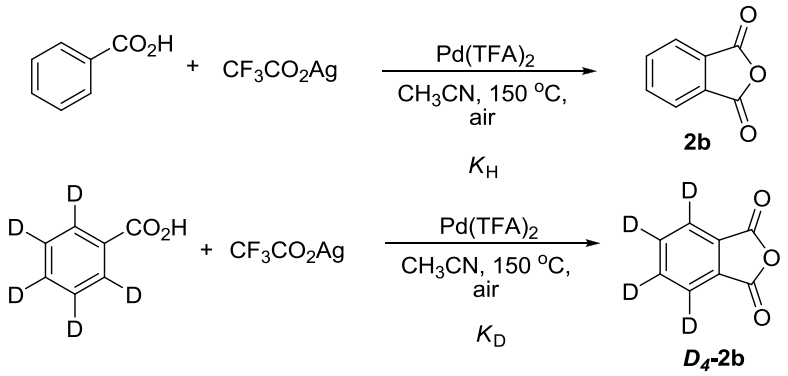
2b NMR yield 12%

An reaction vessel was charged with benzoic acid (12.2 mg, 0.1 mmol), CF_3CO_2Ag (90.2 mg, 0.4 mmol), $Pd(TFA)_2$ (3.5 mg, 10 mol%, 0.01 mmol), CD_3CO_2D (0.5 mmol, 29 μL), CH_3CN (0.5 mL), and sealed under air. The resulting mixture was stirred at 150 ℃ (oil bath temperature) for 24 h. After the reaction was completed, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a short silica gel pad. The solvent was removed under reduced pressure, the yield of product 2b was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. The product 2b was purified by a preparative TLC using hexane/EtOAc/HOAc (100/1/0.05). The amount of *ortho*-deuterated 2b was determined by integral area in ^{1}H NMR.

^{1}H NMR spectra of D_1-2b and 2b



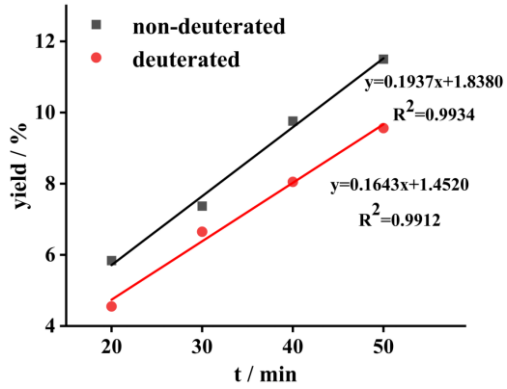
6.2 KIE experiment (parallel experiments)



$Pd(TFA)_2$ (3.5 mg, 0.01 mmol), benzoic acid (12.2 mg, 0.1 mmol), CF_3CO_2Ag (90.2 mg, 0.4 mmol), CH_3CN (0.5 mL) were successively added to a reaction vessel equipped with a stir bar. In another reaction vessel, benzoic acid was replaced by D_5-benzoic acid (13.0 mg, 0.1 mmol). The vessel was sealed under air. The two reactions were stirred at 150 ℃ (oil bath temperature) for 20 min, 30 min, 40 min, and 50 min, respectively. Then the two reaction mixtures were filtered through a short silica gel pad. The solvent was then removed under reduced pressure. The KIE was determined by GC, and the yield of phthalic anhydride was determined by external standard method. Thus the KIE was found to be 1.18.

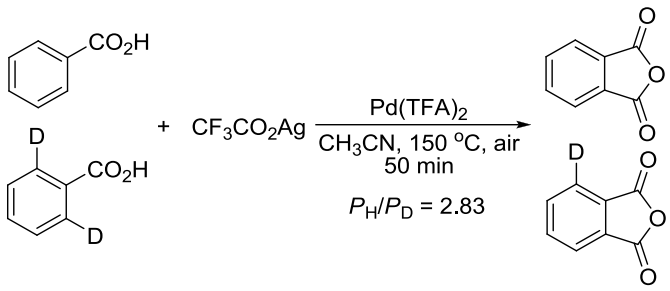
Table S2 The yields of **2b** and ***D*$_4$-2b**

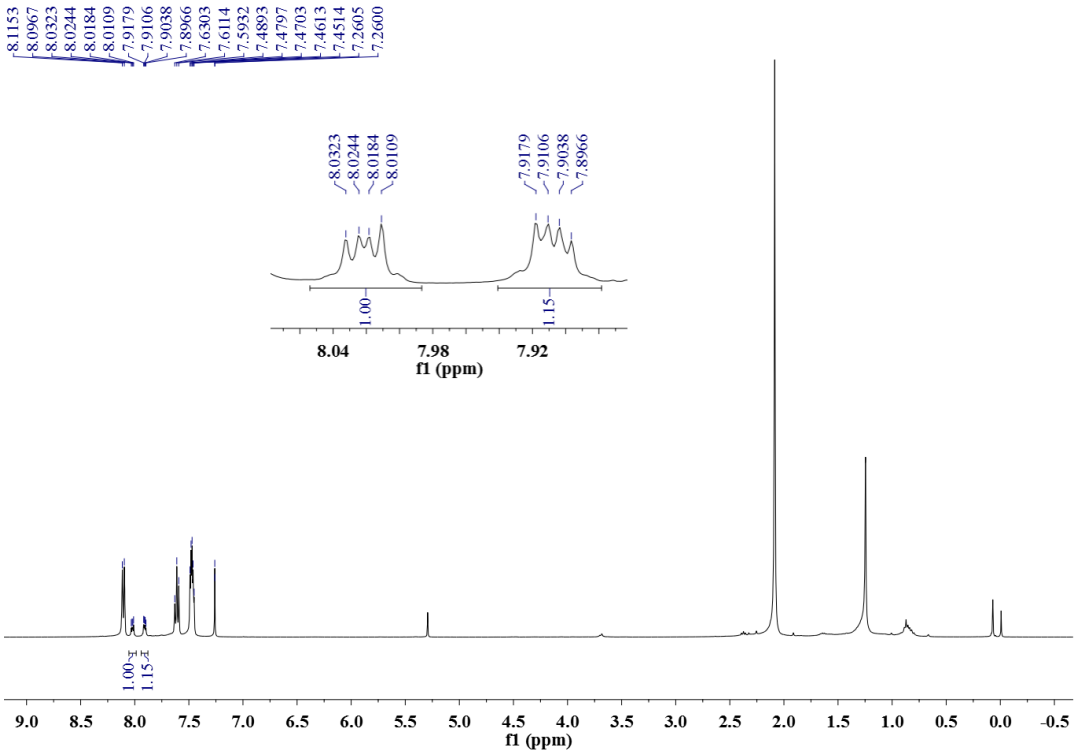
Entry	Time (min)	Yield of **2b** (%)	Yield of ***D*$_4$-2b**(%)
1	20	5.84	4.55
2	30	7.37	6.65
3	40	9.76	8.05
4	50	11.50	9.56



6.3 KIE experiment (intermolecular experiment)

$Pd(TFA)_2$ (3.5 mg, 0.01 mmol), benzoic acid (0.05 mmol, 6.1 mg), benzoic acid-2,5-d_2 (0.05 mmol, 6.2 mg), CF_3CO_2Ag (90.2 mg, 0.4 mmol), CH_3CN (0.5 mL) were successively added to a reaction vessel equipped with a stir bar. The vessel was sealed under air and stirred at 150 °C (oil bath temperature) for 6 h. Then the reaction mixture was filtered through a short column. The solvent was then removed under reduced pressure. The ratio of **2b: *D*-2b** = 2.83 was determined by ^{1}H NMR of crude reaction mixture using relative integral area.





6.4 TG analysis of AgTFA

The stability of AgTFA was investigated by thermogravimetric analysis on a Q1000DSC+LNCS+FACS Q600SDT thermal analyzer (USA). The detection was taken from 40 ℃ to 390 ℃ at a ramp of 10 ℃ min^{-1} under a constant flow of air.

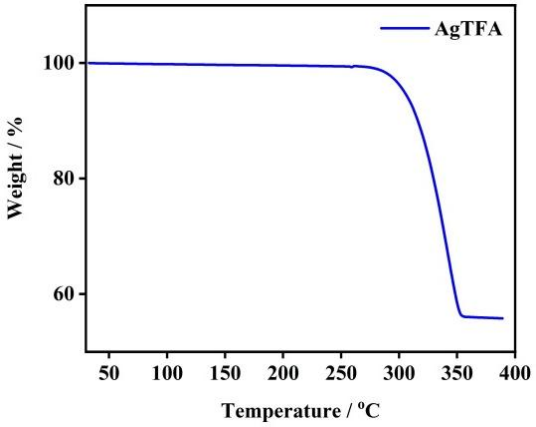


Figure S2 TG analysis of AgTFA.

6.5 Gas detection results of control experiments

The gas mixture was analyzed by gas chromatography (GC-7920, China Education Au-Light Technology Co., Ltd.) equipped with FID and TDX-01 column (injector temperature: 100 ℃, column furnace temperature: 60 ℃, FID temperature: 160 ℃, Ar as carrier gas).

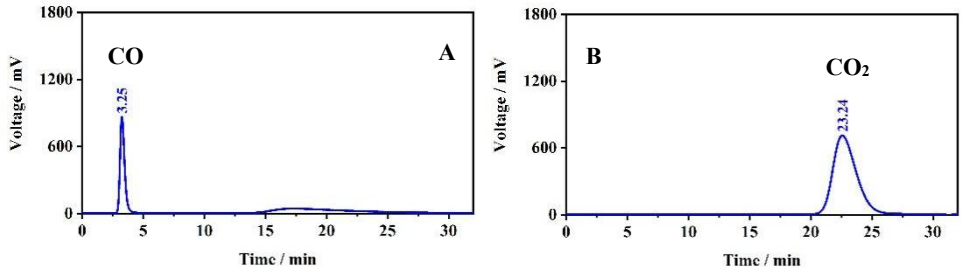


Figure S3 Retention time of CO (A) and CO_2 (B).

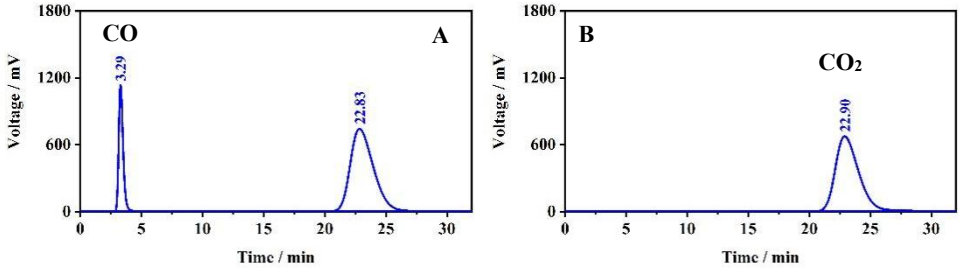


Figure S4 Gas analysis after reaction, reaction conditions: (A) CF_3CO_2Ag (0.4 mmol), $Pd(TFA)_2$ (0.01 mmol), CH_3CN (0.5 mL), 150 °C, 24 h, under Ar; (B) 2-methylbenzoic acid (0.1 m mol), CF_3CO_2Ag (0.4 mmol), $Pd(TFA)_2$ (0.01 mmol), CH_3CN (0.5 mL), 150 °C, 24 h, under Ar.

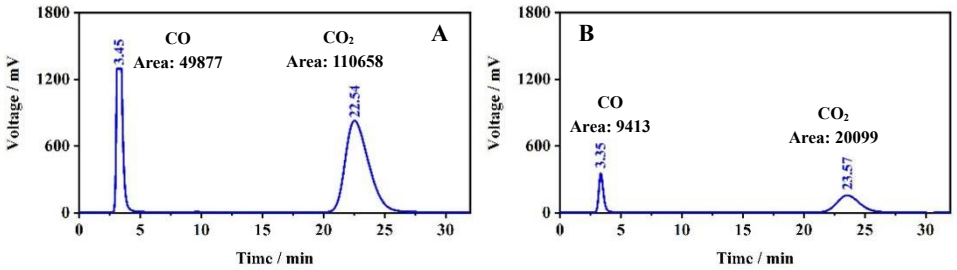
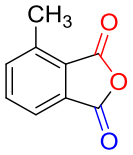


Figure S5 Gas analysis after reaction**,** reaction conditions: (A) CF_3CO_2Ag (0.4 mmol), CH_3CN (0.5 mL), 150 °C, 24 h, under Ar; (B) 2,2,6,6-tetramethylpiperidine-*N*-oxyl (0.2 mmol), CF_3CO_2Ag (0.4 mmol), CH_3CN (0.5 mL), 150 °C, 24 h, under Ar.

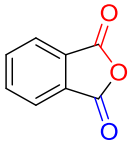
VII. Experimental characterization data for compounds

4-methylisobenzofuran-1,3-dione (2a)[1]



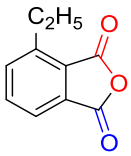
11.3 mg, 70% (isolated yield), white solid, mp 129.9-130.9 °C, R_f = 0.40 (hexane/EtOAc/HOAc = 5/1/0.05). ^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.84 (d, J = 7.4 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 2.74 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.1, 162.9, 140.5, 137.9, 135.7, 131.6, 128.5, 123.3, 17.7. HRMS (ESI) m/z calculated for $C_9H_7O_3$ $[M+H]^+$ 163.0390, found: 163.0389.

isobenzofuran-1,3-dione (2b)[2]



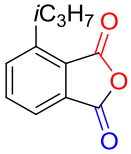
8.9 mg, 60% (isolated yield), white solid, mp 130.3-131.9 °C, R_f = 0.07 (hexane/EtOAc/HOAc = 100/1/0.05). ^{1}H NMR (600 MHz, D_6-DMSO): δ [ppm] = 8.09 (dd, J = 5.6, 3.1 Hz, 2H), 8.01 (dd, J = 5.6, 3.0 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, D_6-DMSO): δ [ppm] = 163.3, 136.2, 131.2, 125.4. HRMS (ESI) m/z calculated for $C_8H_5O_3$ $[M+H]^+$ 149.0233, found: 149.0238.

4-ethylisobenzofuran-1,3-dione (2c)[3]



11.1 mg, 63% (isolated yield), white solid, mp 99.1-100.0 °C, R_f = 0.03 (hexane/EtOAc/HOAc = 50/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.85 (d, J = 7.4 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 3.14 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 163.0, 162.9, 146.8, 136.3, 135.9, 131.8, 127.9, 123.3, 24.7, 14.6. HRMS (ESI) m/z calculated for $C_{10}H_9O_3$ $[M+H]^+$ 177.0546, found: 177.0546.

4-isopropylisobenzofuran-1,3-dione (2d)[4]

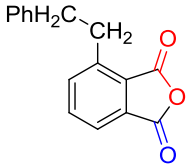


12.5 mg, 66% (isolated yield), white solid, mp 68.7-69.0 °C, R_f = 0.54 (hexane/EtOAc/HOAc = 4/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.86 – 7.78 (m, 3H), 4.10 – 3.84 (m, 1H), 1.34 (s, 3H), 1.33 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 163.0, 162.9, 151.6, 136.2, 133.3, 131.6, 127.1, 123.1, 28.5, 22.7. HRMS (ESI) m/z calculated for $C_{11}H_{11}O_3$ $[M+H]^+$ 191.0703, found: 191.0699.

4-benzylisobenzofuran-1,3-dione (2e)[5]

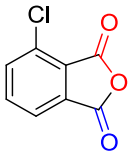
16.7 mg, 70% (isolated yield), white solid, mp 176.5-177.0 °C, R_f = 0.17 (hexane/EtOAc/HOAc = 100/1/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.86 (d, J = 7.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 18.3 Hz, 3H), 4.49 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 163.1, 162.8, 143.5, 138.2, 137.3, 136.0, 131.7, 129.1, 128.9, 128.0, 126.9, 123.7, 36.7. HRMS (APCI) m/z calculated for $C_{15}H_{11}O_3$ $[M+H]^+$ 239.0703, found: 239.0704.

4-phenethylisobenzofuran-1,3-dione (2f)[6]



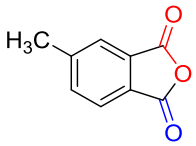
14.1 mg, 56% (isolated yield), white solid, mp 175.3-176.2 °C, R_f = 0.17 (hexane/EtOAc/HOAc = 100/1/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.86 (d, J = 7.4 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.24 – 7.17 (m, 3H), 3.40 (t, 2H), 2.98 (t, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 162.9, 162.8, 144.1, 140.2, 137.2, 135.7, 131.8, 128.5, 128.5, 128.2, 126.4, 123.6, 36.8, 33.6. HRMS (APCI) m/z calculated for $C_{16}H_{13}O_3$ $[M+H]^+$ 253.0859, found: 253.0858.

4-chloroisobenzofuran-1,3-dione (2g)[7]



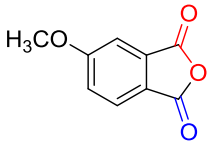
9.1 mg, 50% (isolated yield), yellow solid, mp 145.9-146.3 °C, R_f = 0.14 (hexane/EtOAc/HOAc = 30/1/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.94 (t, J = 4.2 Hz, 1H), 7.84 (d, J = 4.1 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 161.3, 159.8, 137.4, 137.0, 133.7, 133.2, 127.6, 124.1. HRMS (APCI) m/z calculated for $C_8H_4ClO_3$ $[M+H]^+$ 182.9843, found: 182.9845.

5-methylisobenzofuran-1,3-dione (2h)[8]



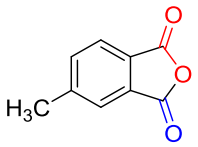
8.1 mg, 50% (isolated yield), white solid, mp 109.7-110.4 °C, R_f = 0.19 (hexane/EtOAc/HOAc = 10/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.88 (d, J = 7.1 Hz, 1H), 7.79 (s, 1H), 7.70 (d, J = 6.8 Hz, 1H), 2.58 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 162.9, 162.7, 148.0, 136.9, 131.7, 128.6, 125.9, 125.5, 22.1. HRMS (ESI) m/z calculated for $C_9H_7O_3$ $[M+H]^+$ 163.0390, found: 163.0398.

5-methoxyisobenzofuran-1,3-dione (2i)[9]



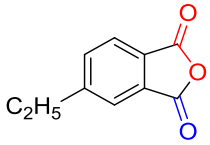
10.0 mg, 56% (isolated yield), white solid, mp 99.9-100.7 °C, R_f = 0.31 (hexane/EtOAc/HOAc = 5/1/0.05). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.90 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 1.9 Hz, 1H), 7.35 (dd, J = 8.4, 2.0 Hz, 1H), 3.98 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 166.1, 163.0, 162.4, 134.1, 127.3, 123.2, 122.9, 108.9, 56.4. HRMS (ESI) m/z calculated for $C_9H_7O_4$ $[M+H]^+$ 179.0339, found: 179.0336.

5-methylisobenzofuran-1,3-dione (2j)[8]



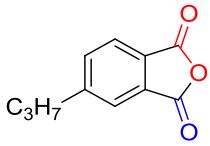
8.9 mg, 55% (isolated yield), white solid, mp 109.7-110.4 °C, R_f = 0.19 (hexane/EtOAc/HOAc = 10/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.88 (d, J = 7.1 Hz, 1H), 7.79 (s, 1H), 7.70 (d, J = 6.8 Hz, 1H), 2.58 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ [ppm] = 162.9, 162.7, 147.9, 136.9, 131.7, 128.6, 125.9, 125.5, 22.1. HRMS (ESI) m/z calculated for $C_9H_7O_3$ $[M+H]^+$ 163.0390, found: 163.0398.

5-ethylisobenzofuran-1,3-dione (2k)[10]



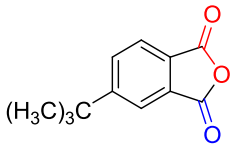
10.7 mg, 61% (isolated yield), white solid, mp 83.5-84.2 °C, R_f = 0.20 (hexane/EtOAc/HOAc = 10/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.91 (d, J = 7.8 Hz, 1H), 7.83 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 2.87 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ [ppm] = 163.1, 162.8, 154.1, 135.9, 131.8, 128.9, 125.6, 124.8, 29.3, 15.0. HRMS (ESI) m/z calculated for $C_{10}H_9O_3$ $[M+H]^+$ 177.0546, found: 177.0546.

5-propylisobenzofuran-1,3-dione (2l)



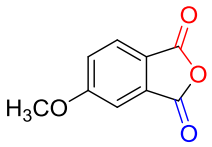
11.4 mg, 60% (isolated yield), white solid, mp 129.8-130.5 °C, R_f = 0.06 (hexane/EtOAc/HOAc = 4/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.91 (d, J = 7.8 Hz, 1H), 7.81 (s, 1H), 7.69 (d, J = 7.8 Hz, 1H), 2.80 (t, J = 7.6 Hz, 2H), 1.77 – 1.67 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ [ppm] = 163.1, 162.8, 152.6, 136.4, 131.7, 128.9, 125.6, 125.3, 38.2, 24.2, 13.6. HRMS (ESI) m/z calculated for $C_{11}H_{11}O_3$ $[M+H]^+$ 191.0703, found: 191.0700.

5-(*tert*-butyl)isobenzofuran-1,3-dione (2m)[11]



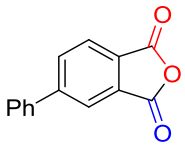
12.9 mg, 63% (isolated yield), colourless liquid, R_f = 0.06 (hexane/EtOAc/HOAc = 4/1/0.05). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.02 (s, 1H), 7.93 (s, 2H), 1.40 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = δ 163.4, 162.8, 161.2, 133.5, 131.5, 128.5, 125.4, 122.6, 36.0, 31.0.

5-methoxyisobenzofuran-1,3-dione (2n)[9]



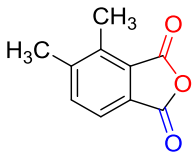
9.1 mg, 51% (isolated yield), white solid, mp 99.9-100.7 °C, R_f = 0.31 (hexane/EtOAc/HOAc = 5/1/0.05). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.90 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 1.9 Hz, 1H), 7.35 (dd, J = 8.4, 2.0 Hz, 1H), 3.98 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 166.1, 163.0, 162.4, 134.1, 127.3, 123.2, 122.9, 108.9, 56.4. HRMS (ESI) m/z calculated for $C_9H_7O_4$ $[M+H]^+$ 179.0339, found: 179.0336.

5-phenylisobenzofuran-1,3-dione (2o)[12]



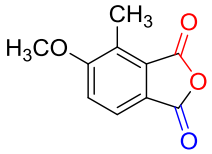
12.1 mg, 54% (isolated yield), white solid, mp 161.9-162.6 °C, R_f = 0.34 (hexane/CH_2Cl_2/HOAc = 2/1/0.05). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.20 (s, 1H), 8.09 (q, J = 7.9 Hz, 2H), 7.65 (d, J = 7.1 Hz, 2H), 7.58 – 7.46 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 162.9, 162.7, 149.7, 138.1, 134.7, 132.2, 129.6, 129.5, 129.4, 127.5, 126.1, 124.0. HRMS (ESI) m/z calculated for $C_{14}H_9O_3$ $[M+H]^+$ 225.0546, found: 225.0547.

4,5-dimethylisobenzofuran-1,3-dione (2p)[13]



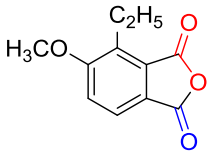
12.3 mg, 70% (isolated yield), white solid, mp 119.7-120.5 °C, R_f = 0.16 (hexane/EtOAc/HOAc = 50/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.73 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 2.66 (s, 3H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.6, 162.9, 147.2, 139.3, 136.9, 129.2, 128.6, 122.9, 20.1, 14.2. HRMS (ESI) m/z calculated for $C_{10}H_9O_3$ $[M+H]^+$ 177.0546, found: 177.0550.

5-methoxy-4-methylisobenzofuran-1,3-dione (2q)[14]



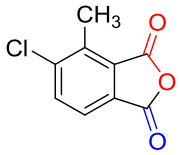
11.3 mg, 59% (isolated yield), white solid, mp 128.2-129.0 °C, R_f = 0.06 (hexane/EtOAc/HOAc = 100/1/0. 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.82 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 3.99 (s, 3H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 164.1, 163.3, 162.7, 129.9, 129.6, 125.1, 122.2, 115.8, 56.6, 10.8. HRMS (ESI) m/z calculated for $C_{10}H_9O_4$ $[M+H]^+$ 193.0495, found: 193.0496.

4-ethyl-5-methoxyisobenzofuran-1,3-dione (2r)



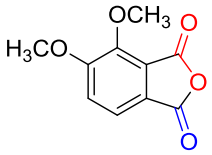
12.8 mg, 62% (isolated yield), yellow solid, mp 118.2-119.0 °C, R_f = 0.09 (hexane/EtOAc/HOAc = 100/1/0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.82 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 3.99 (s, 3H), 3.09 (q, J = 7.5 Hz, 2H), 1.18 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.7, 163.0, 162.7, 135.7, 129.4, 125.2, 122.4, 116.3, 56.6, 18.4, 13.7. HRMS (APCI) m/z calculated for $C_{11}H_{11}O_4$ $[M+H]^+$ 207.0652, found: 207.0649.

5-chloro-4-methylisobenzofuran-1,3-dione (2s)



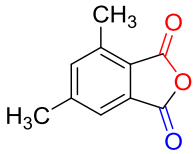
12.9 mg, 66% (isolated yield), white solid, mp 129.7-130.4 °C, R_f = 0.46 (hexane/CH_2Cl_2/HOAc = 2/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.85 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 2.78 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 162.2, 161.8, 143.8, 138.8, 136.4, 130.0, 129.6, 123.8, 14.8. HRMS (APCI) m/z calculated for $C_9H_6ClO_3$ $[M+H]^+$ 197.0000, found: 197.0001.

4,5-dimethoxyisobenzofuran-1,3-dione (2t)[15]



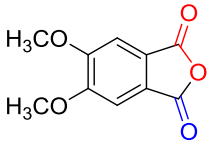
11.4 mg, 55% (isolated yield), yellow solid, mp 170.0-170.9 °C, R_f = 0.09 (hexane/EtOAc/HOAc = 50/1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.68 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 4.22 (s, 3H), 4.00 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ [ppm] = 162.4, 160.7, 158.6, 148.6, 123.1, 121.5, 120.5, 118.2, 62.7, 56.9. HRMS (ESI) m/z calculated for $C_{10}H_9O_5$ $[M+H]^+$ 209.0444, found: 209.0449.

4,6-dimethylisobenzofuran-1,3-dione (2u)[16]



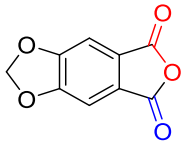
9.7 mg, 55% (isolated yield), white solid, mp 129.8-130.6 °C, R_f = 0.19 (hexane/EtOAc/HOAc = 50/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.61 (s, 1H), 7.44 (s, 1H), 2.67 (s, 3H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.3, 163.1, 147.5, 140.1, 138.6, 132.0, 125.9, 123.7, 22.0, 17.6. HRMS (ESI) m/z calculated for $C_{10}H_9O_3$ $[M+H]^+$ 177.0546, found: 177.0542.

5,6-dimethoxyisobenzofuran-1,3-dione (2v)[15]



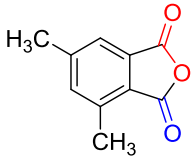
12.3 mg, 59% (isolated yield), white solid, mp 193.3-194.5 °C, R_f = 0.07 (hexane/EtOAc/HOAc = 50/1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.36 (s, 2H), 4.03 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.1, 155.8, 124.9, 106.1, 56.9. HRMS (ESI) m/z calculated for $C_{10}H_9O_5$ $[M+H]^+$ 209.0444, found: 209.0444.

[1,3]dioxolo[4,5-f]isobenzofuran-5,7-dione (2w)[17]



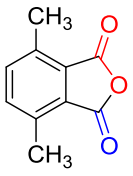
15.4 mg, 80% (isolated yield), white solid, mp 186.3-187.1 °C, R_f = 0.12 (hexane/EtOAc/HOAc = 50/1/0.5). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.28 (s, 2H), 6.26 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ [ppm] = 162.3, 154.7, 127.1, 104.7, 103.9. HRMS (ESI) m/z calculated for $C_9H_5O_5$ $[M+H]^+$ 193.0131, found: 193.0126.

4,6-dimethylisobenzofuran-1,3-dione (2x)[16]



9.9 mg, 56% (isolated yield), white solid, mp 129.8-130.6 °C, R_f = 0.19 (hexane/EtOAc/HOAc = 50/1/0.05). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.61 (s, 1H), 7.44 (s, 1H), 2.67 (s, 3H), 2.52 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.3, 163.1, 147.5, 140.1, 138.6, 131.9, 125.9, 123.7, 22.0, 17.6. HRMS (ESI) m/z calculated for $C_{10}H_9O_3$ $[M+H]^+$ 177.0546, found: 177.0542.

4,7-dimethylisobenzofuran-1,3-dione (2y)[18]



10.2 mg, 58% (isolated yield), white solid, mp 163.6-164.4 °C, R_f = 0.23 (hexane/EtOAc/HOAc = 50/1/0.05). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.50 (s, 2H), 2.67 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.3, 137.8, 137.7, 128.5, 17.4. HRMS (ESI) m/z calculated for $C_{10}H_9O_3$ $[M+H]^+$ 177.0546, found: 177.0548.

VIII. References

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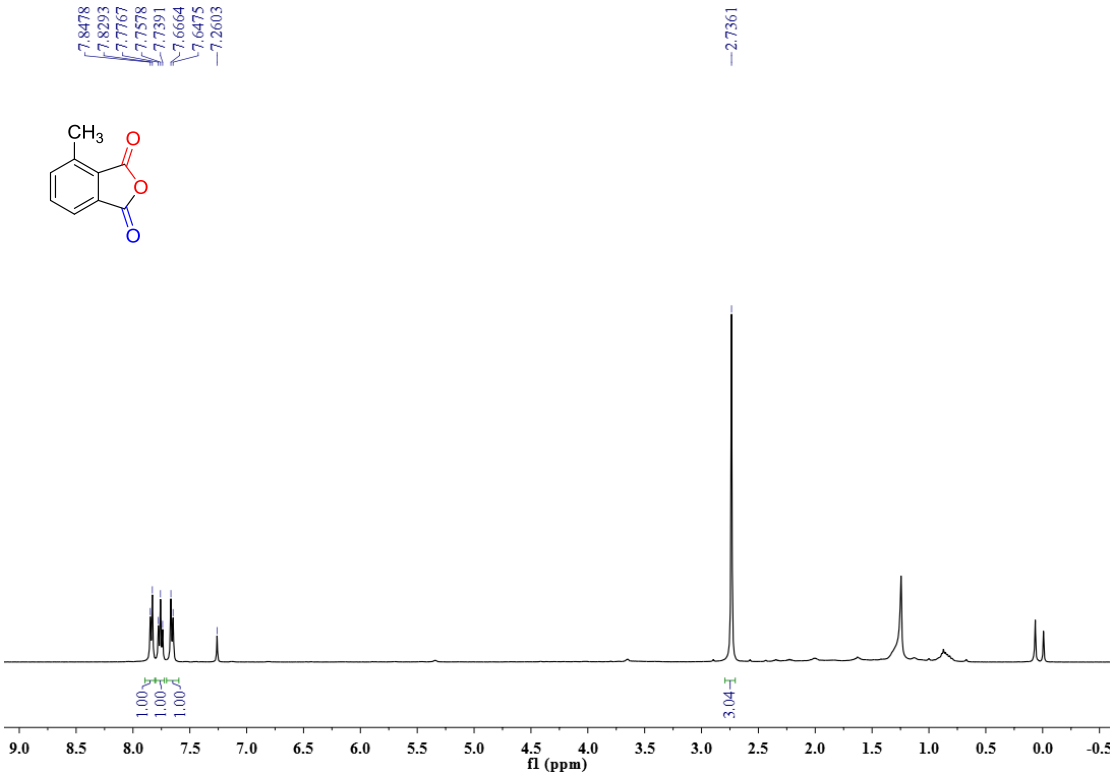
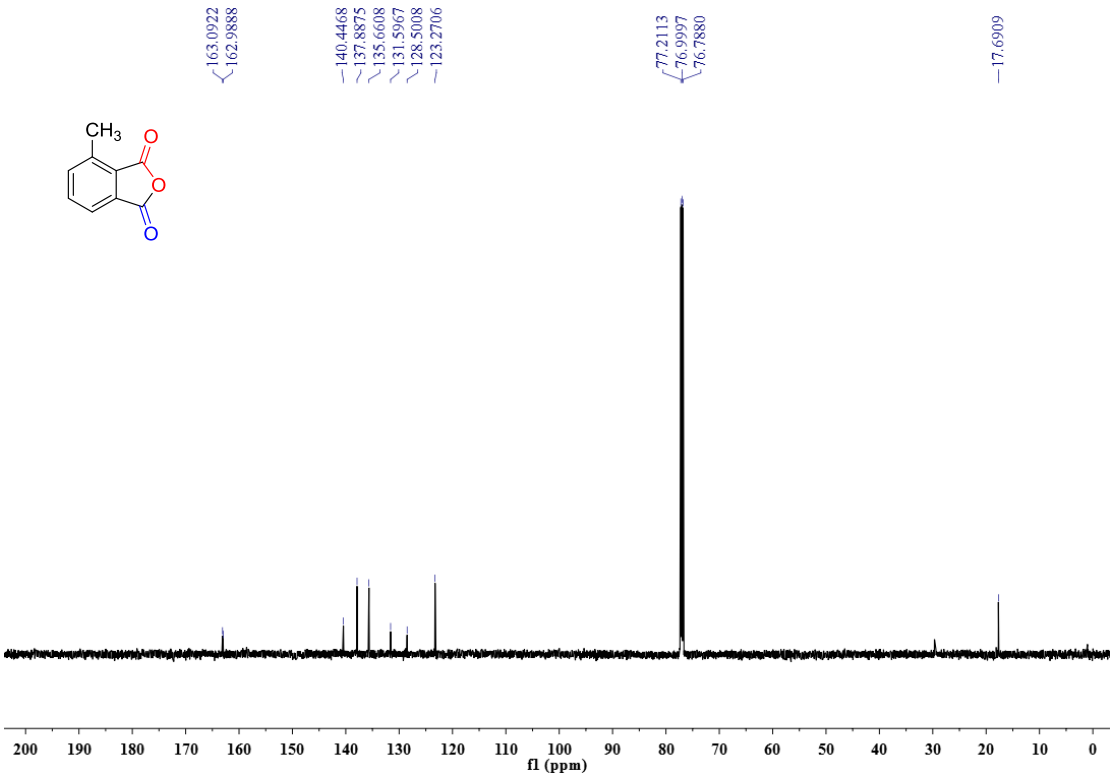
IX. Copies of NMR spectra

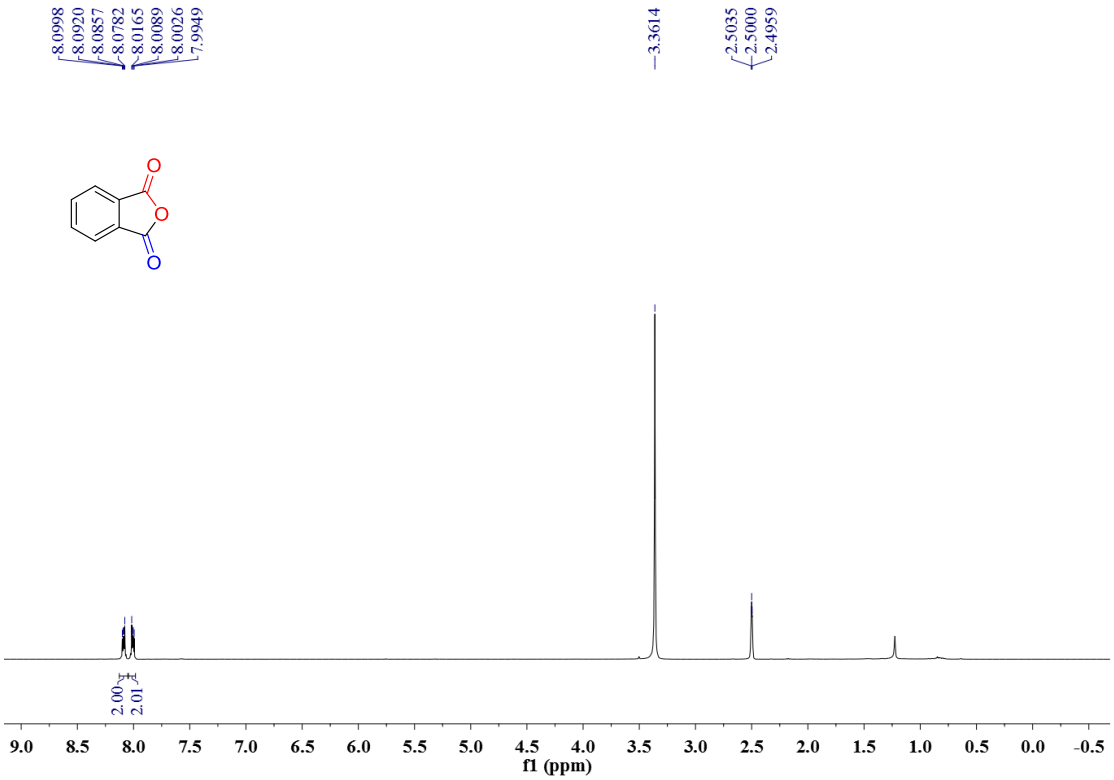
^{1}H NMR spectra of compound 2a



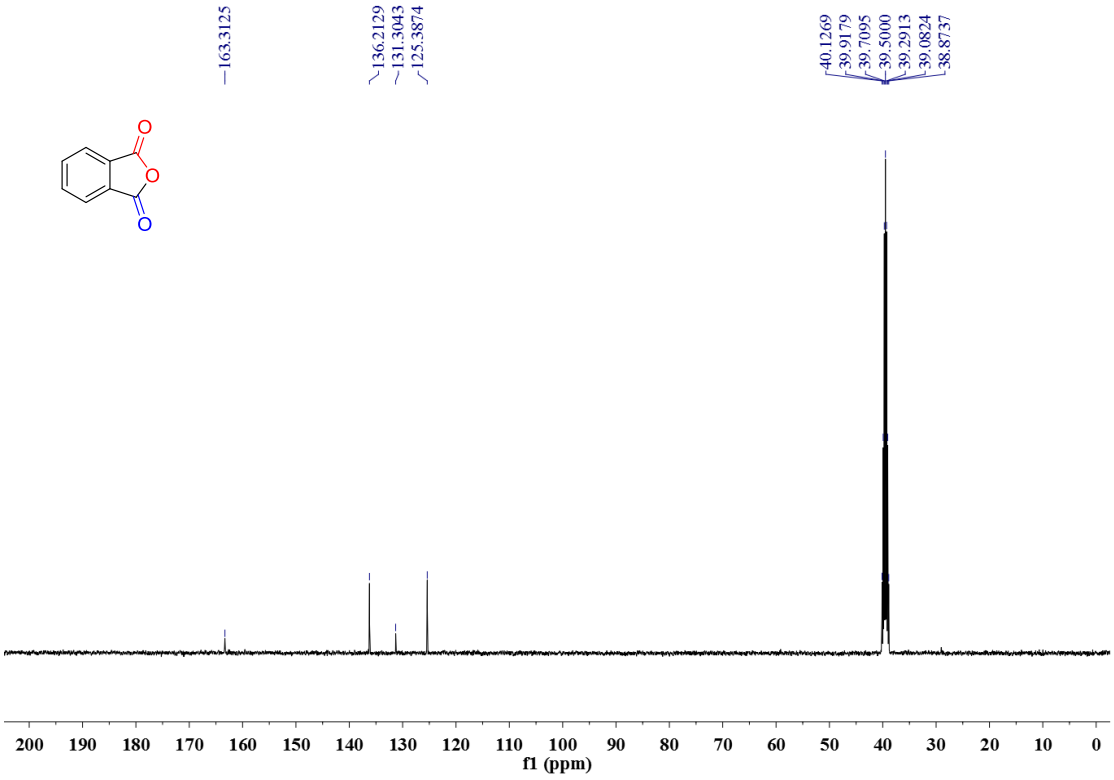
^{13}C NMR spectra of compound 2a



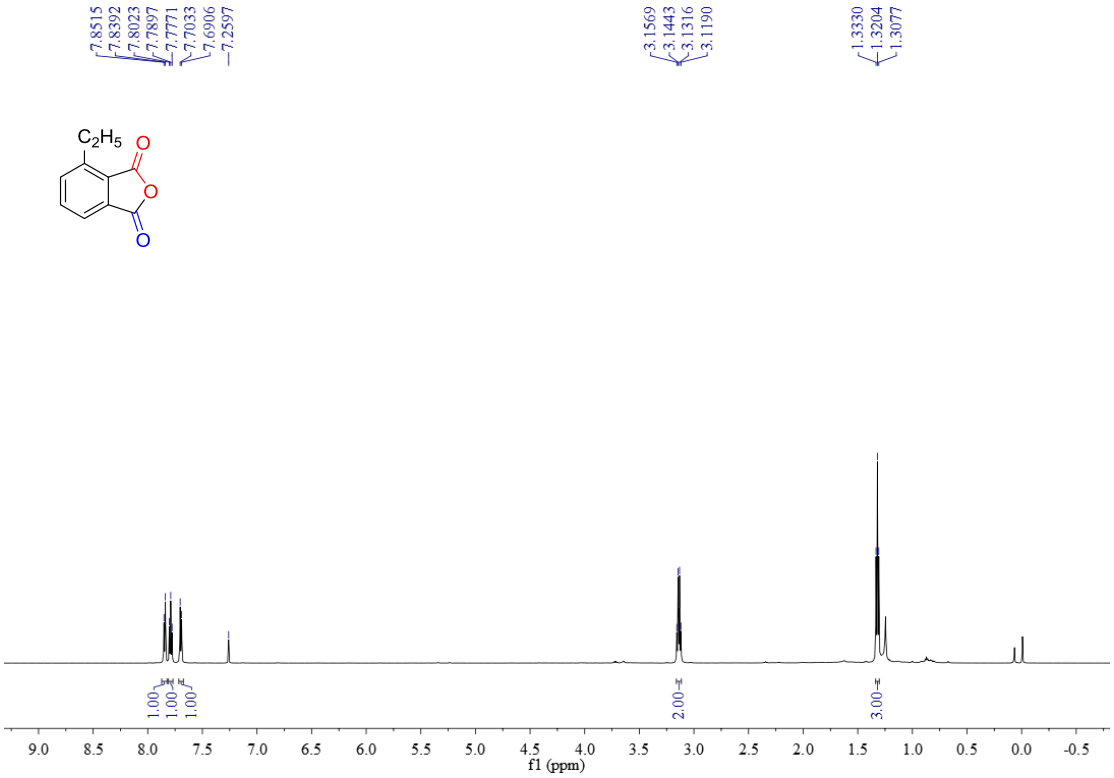
^{1}H NMR spectra of compound 2b



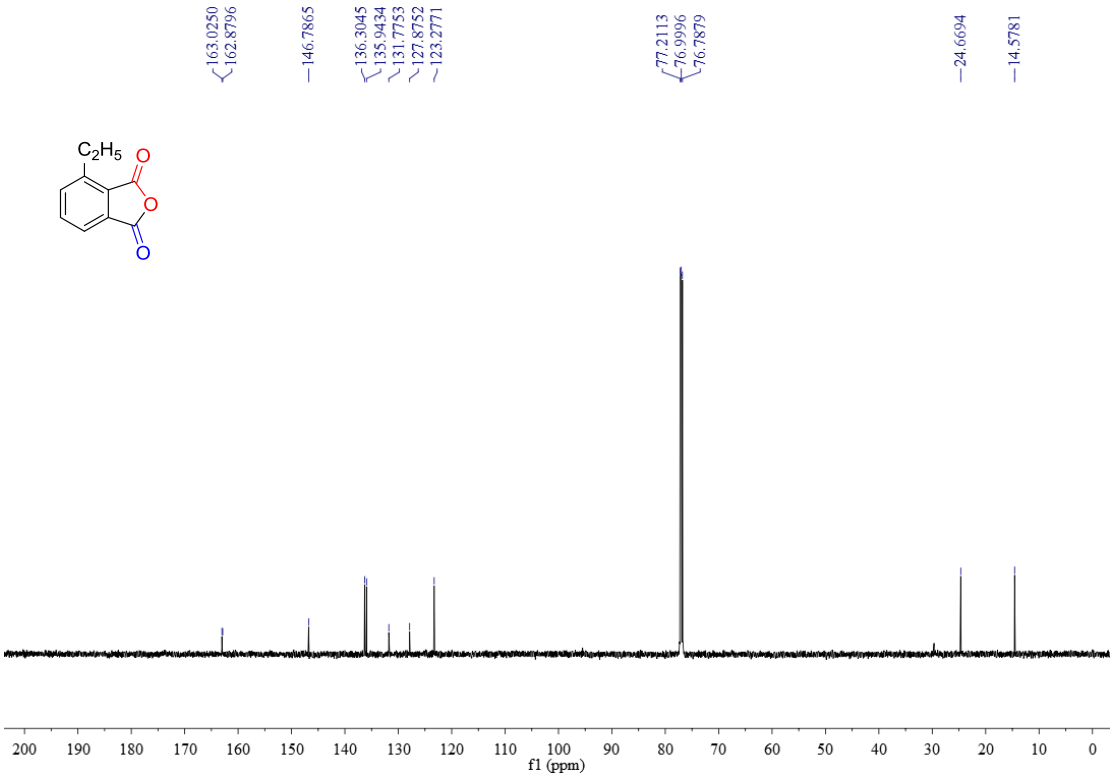
^{13}C NMR spectra of compound 2b



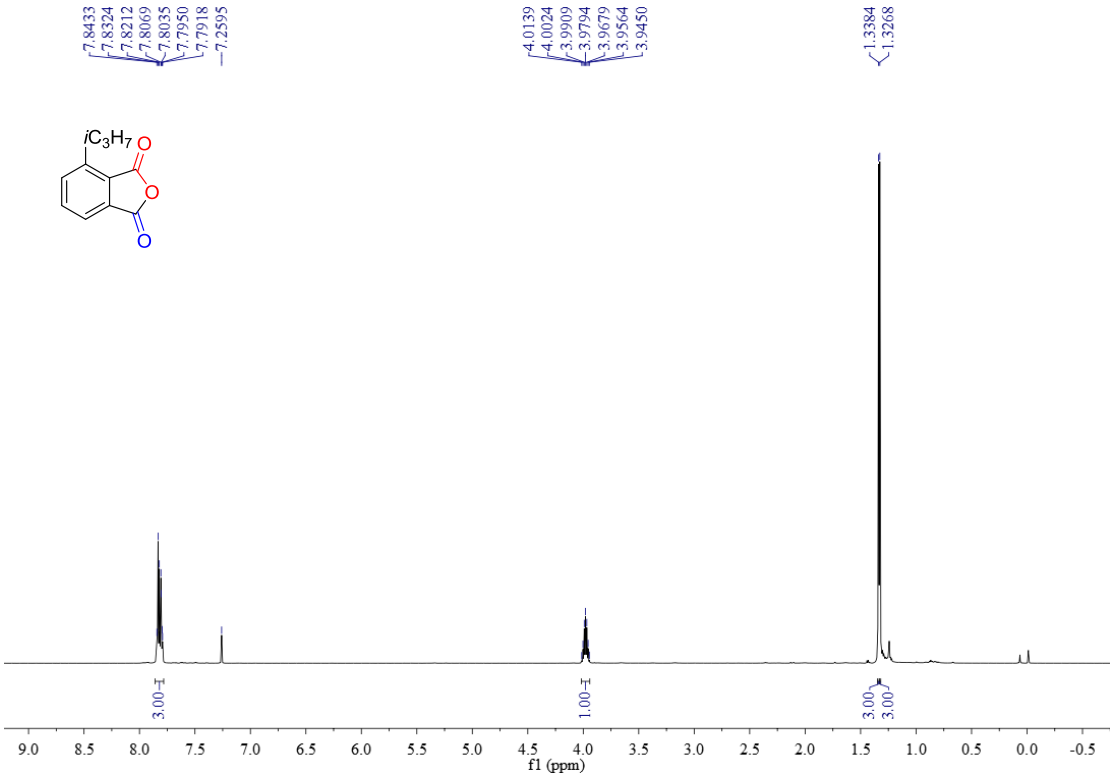
^{1}H NMR spectra of compound 2c



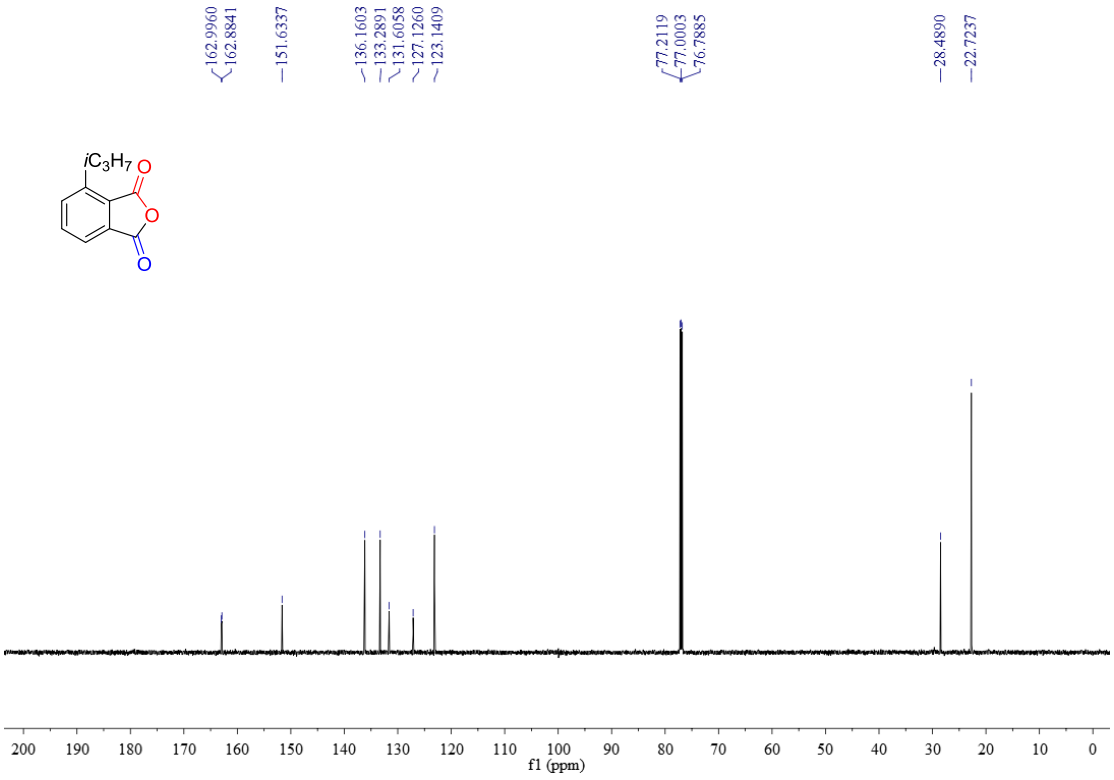
^{13}C NMR spectra of compound 2c



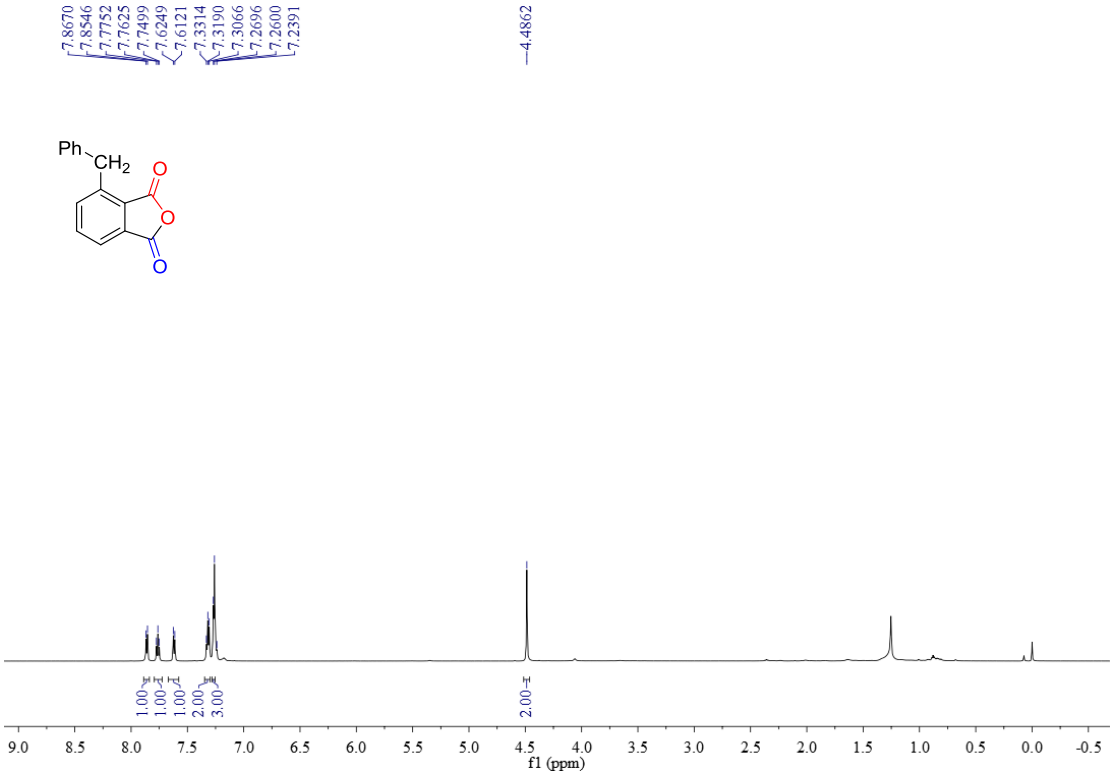
^{1}H NMR spectra of compound 2d



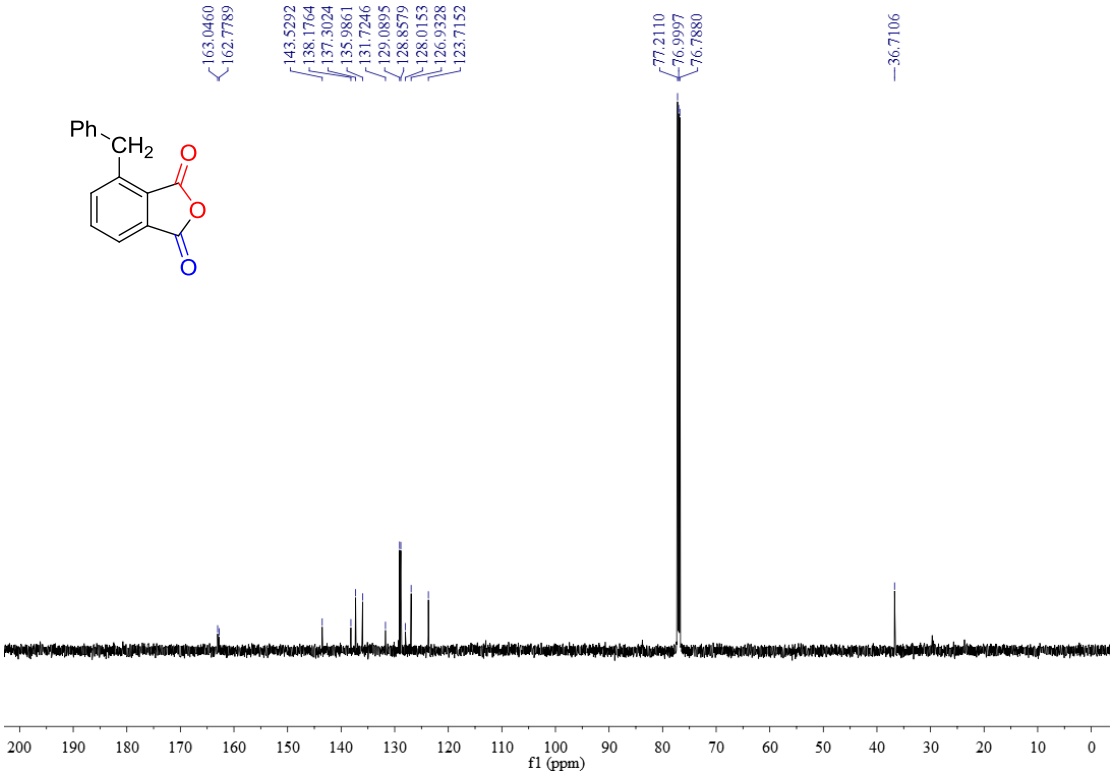
^{13}C NMR spectra of compound 2d



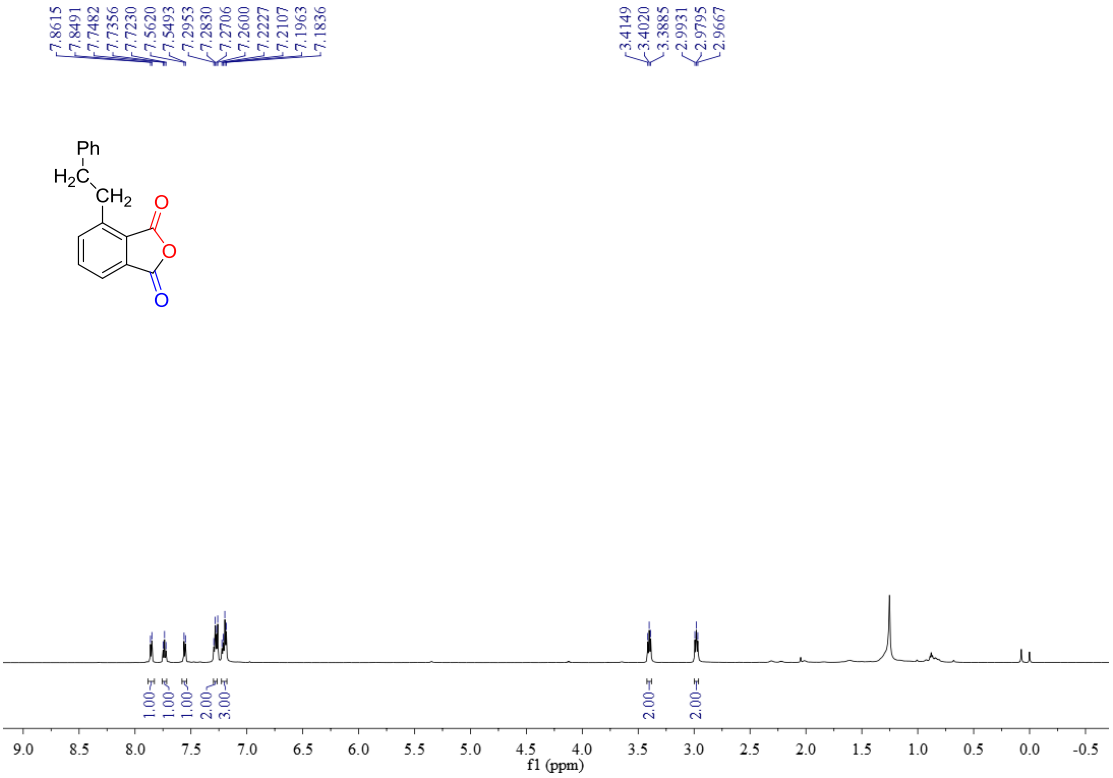
^{1}H NMR spectra of compound 2e



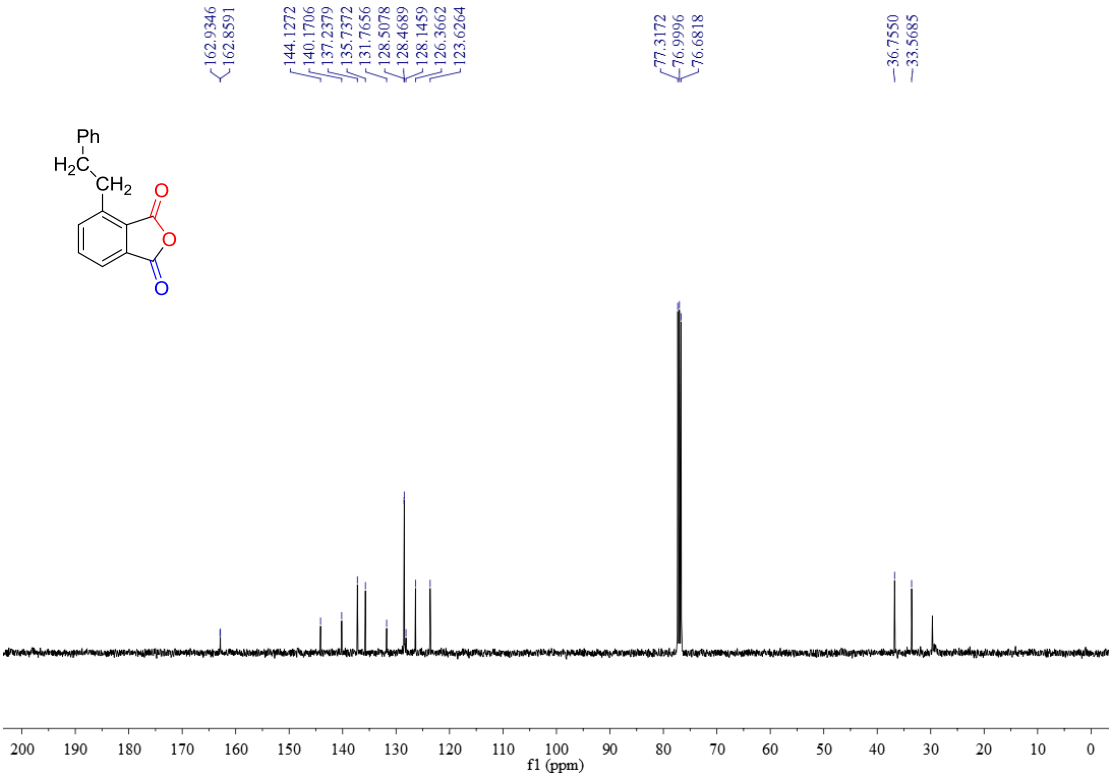
^{13}C NMR spectra of compound 2e



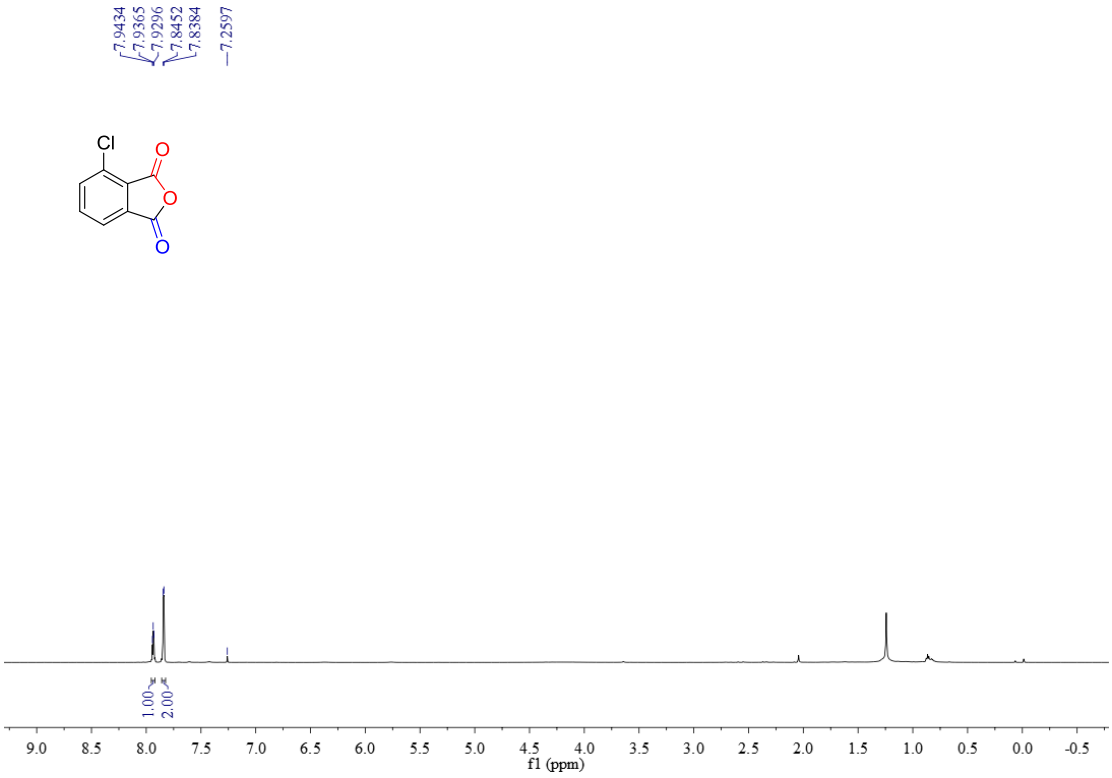
^{1}H NMR spectra of compound 2f



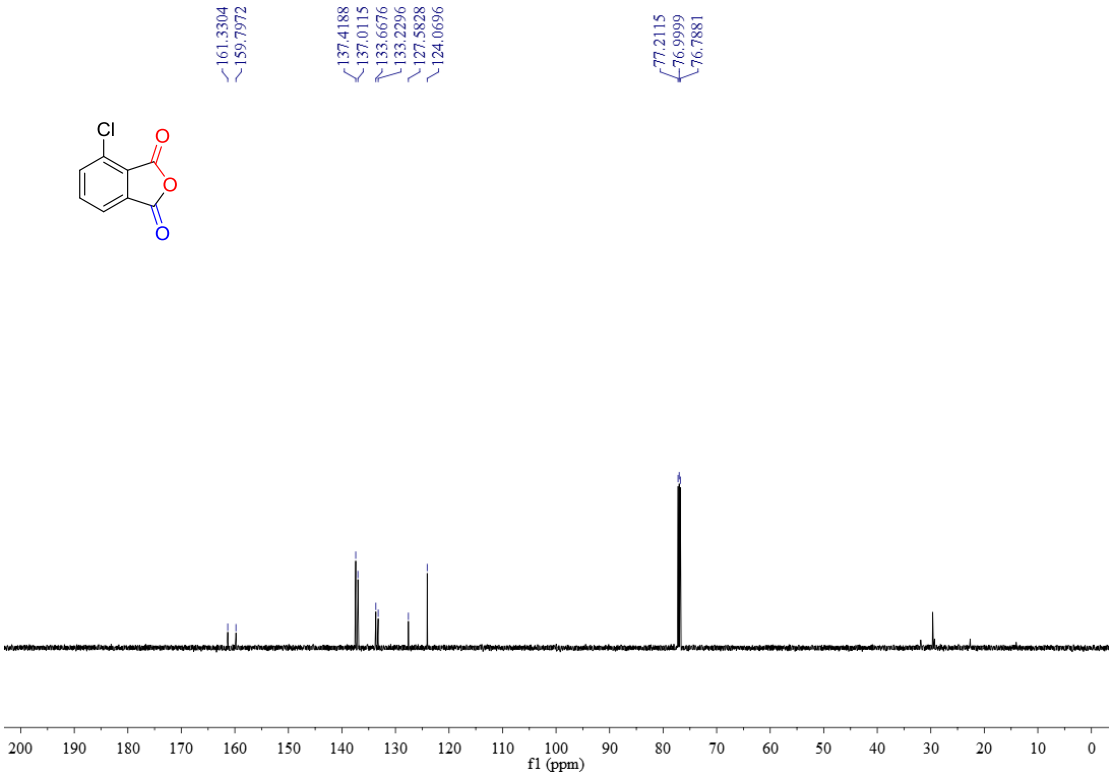
^{13}C NMR spectra of compound 2f



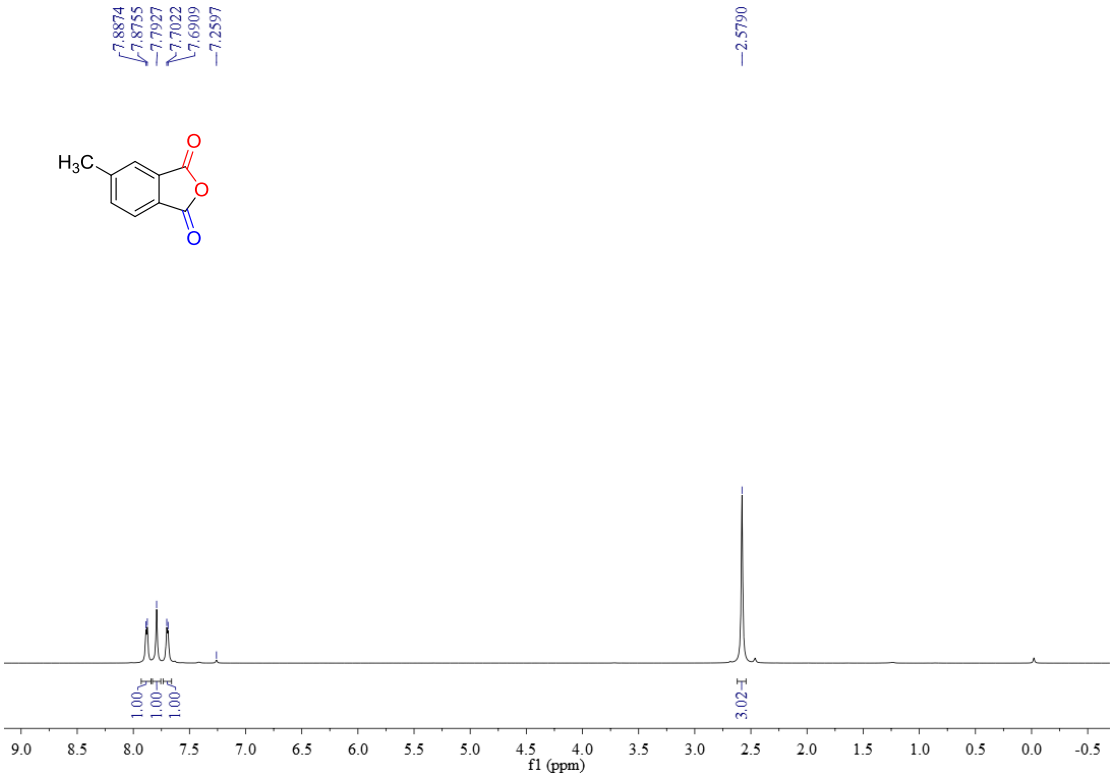
^{1}H NMR spectra of compound 2g



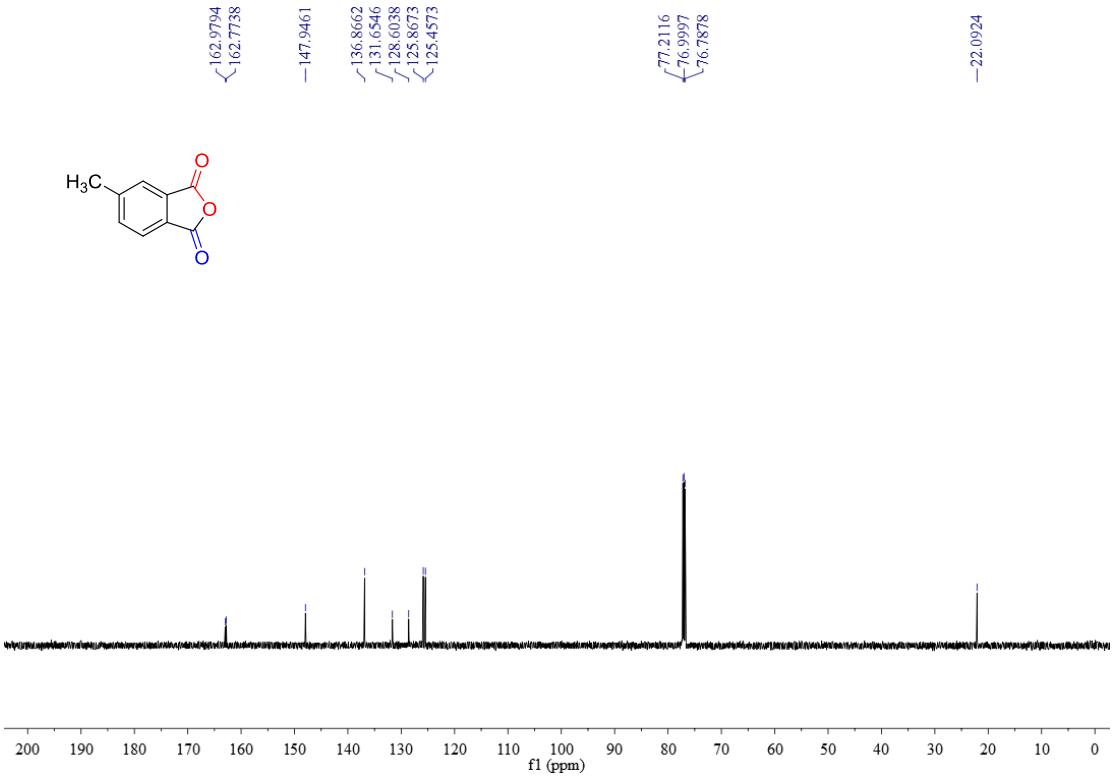
^{13}C NMR spectra of compound 2g



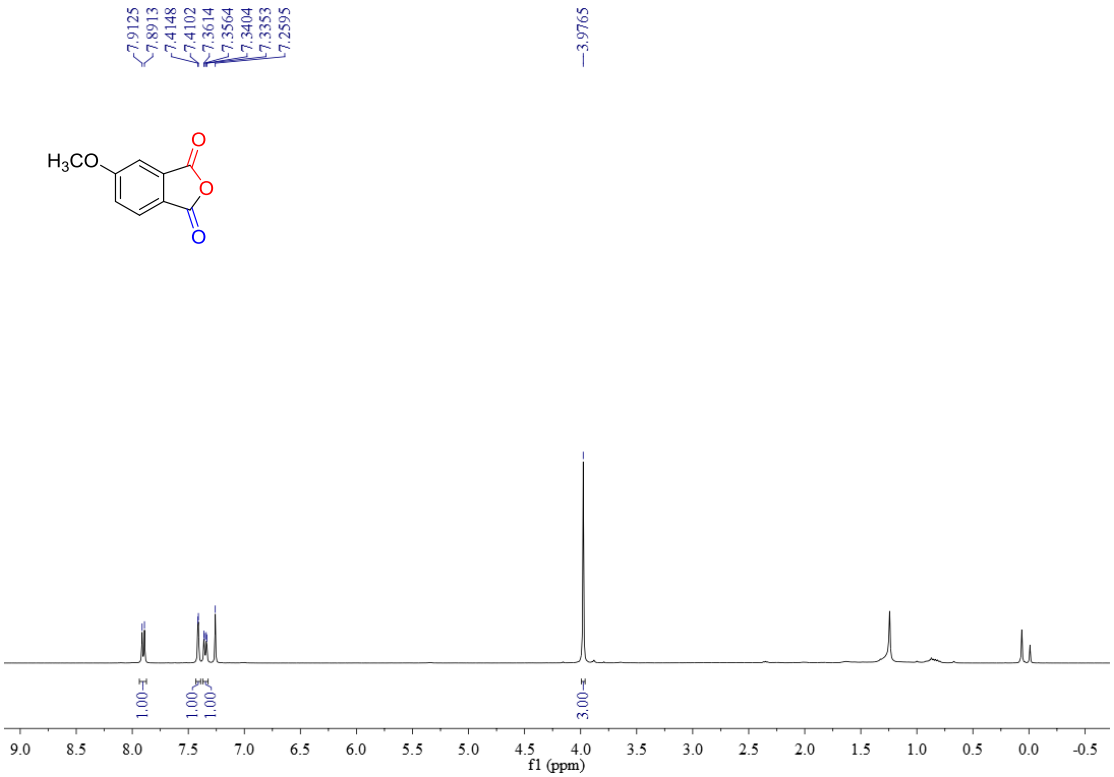
^{1}H NMR spectra of compound 2h



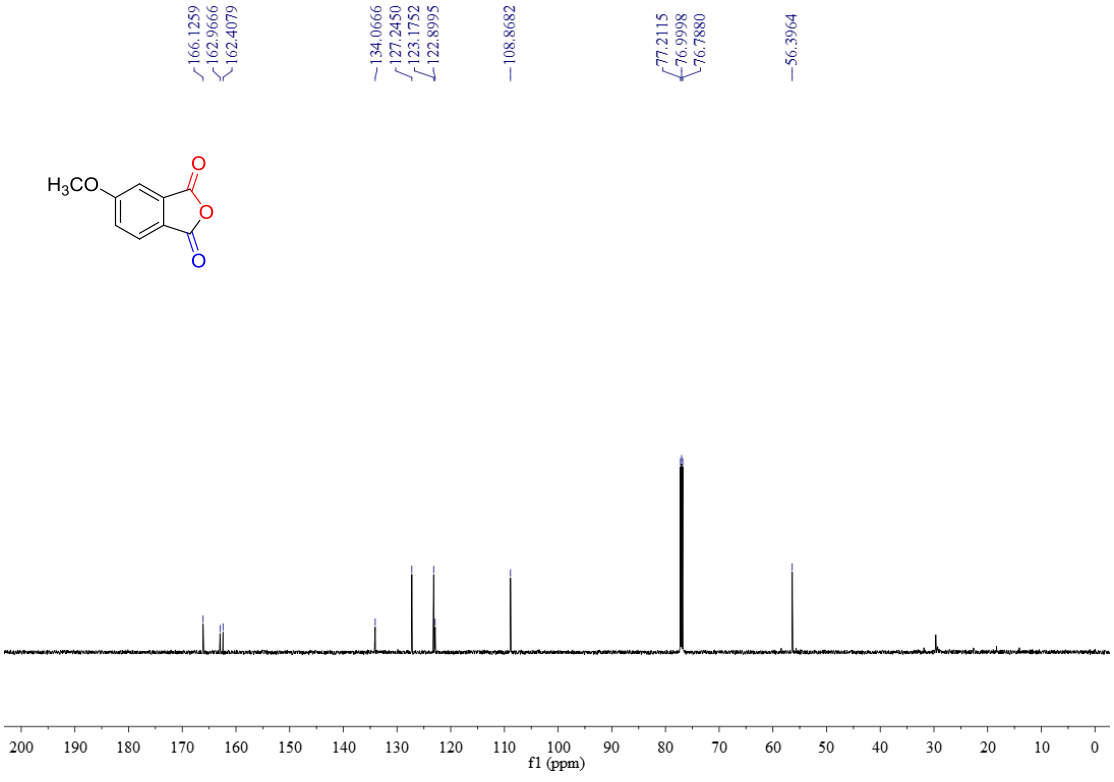
^{13}C NMR spectra of compound 2h



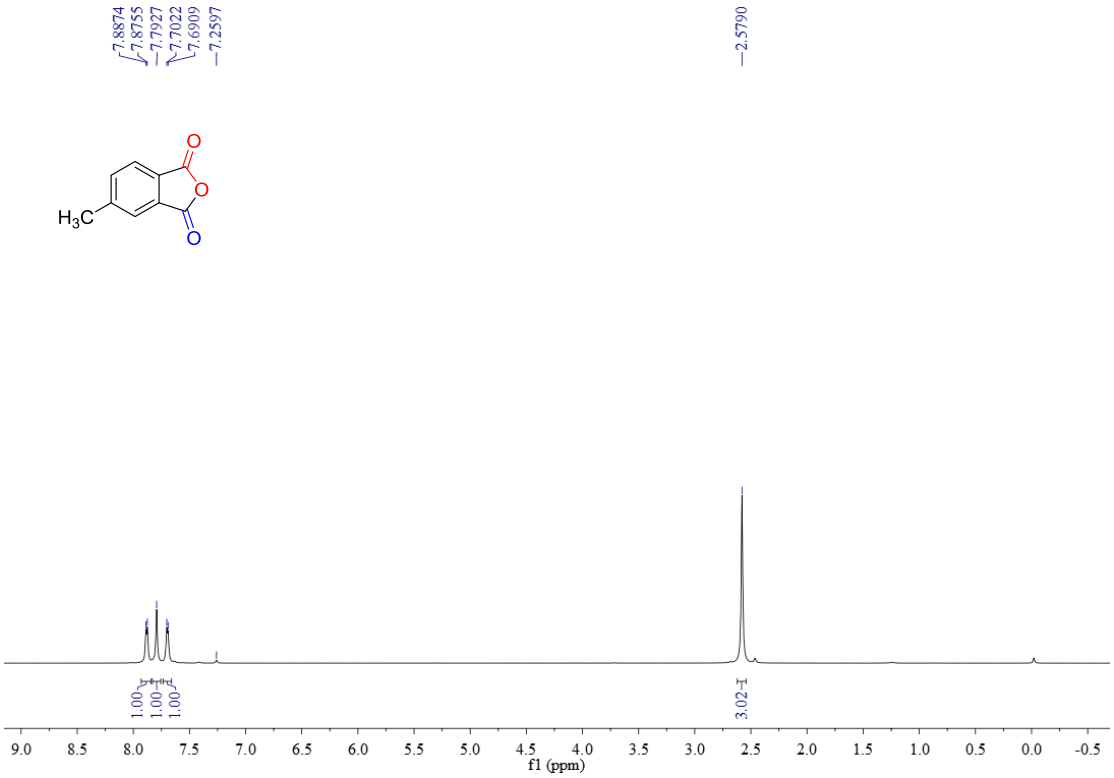
^{1}H NMR spectra of compound 2i



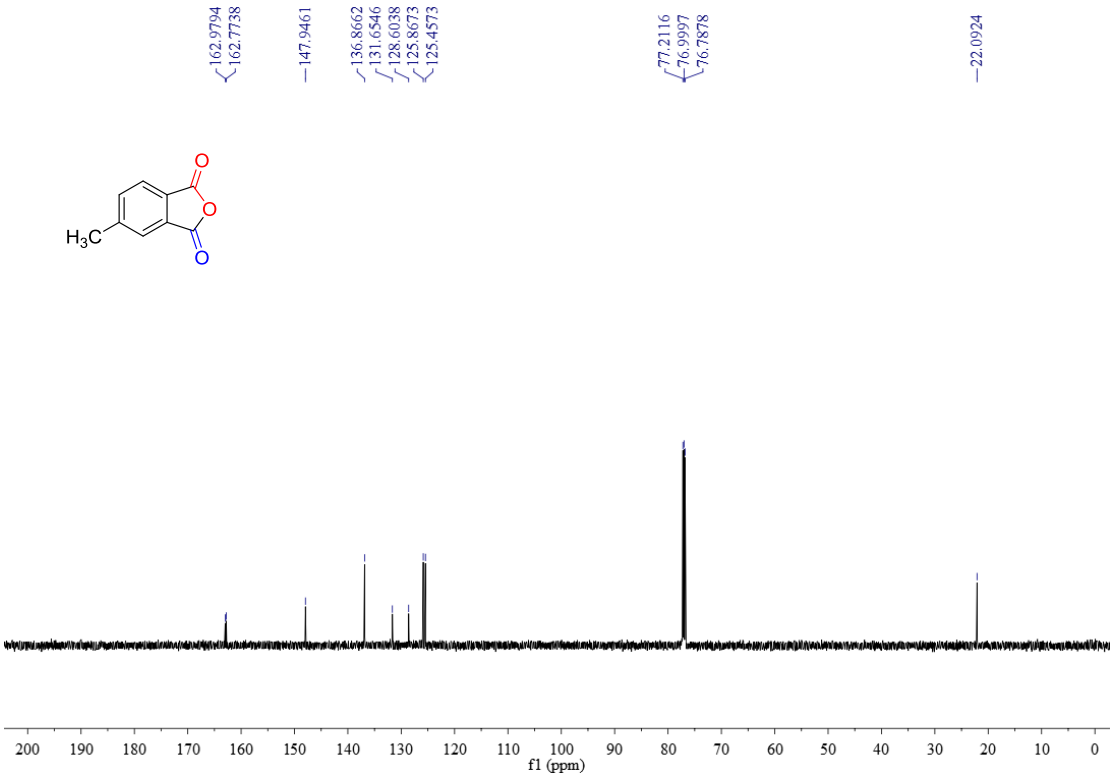
^{13}C NMR spectra of compound 2i



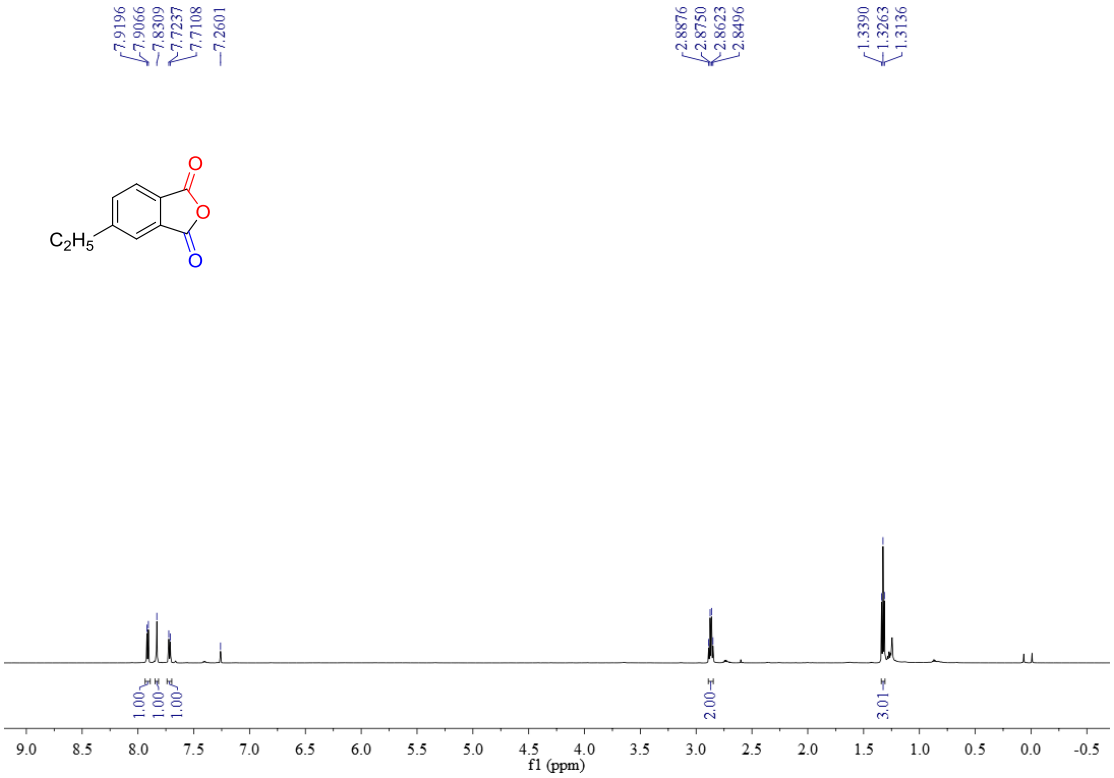
^{1}H NMR spectra of compound 2j



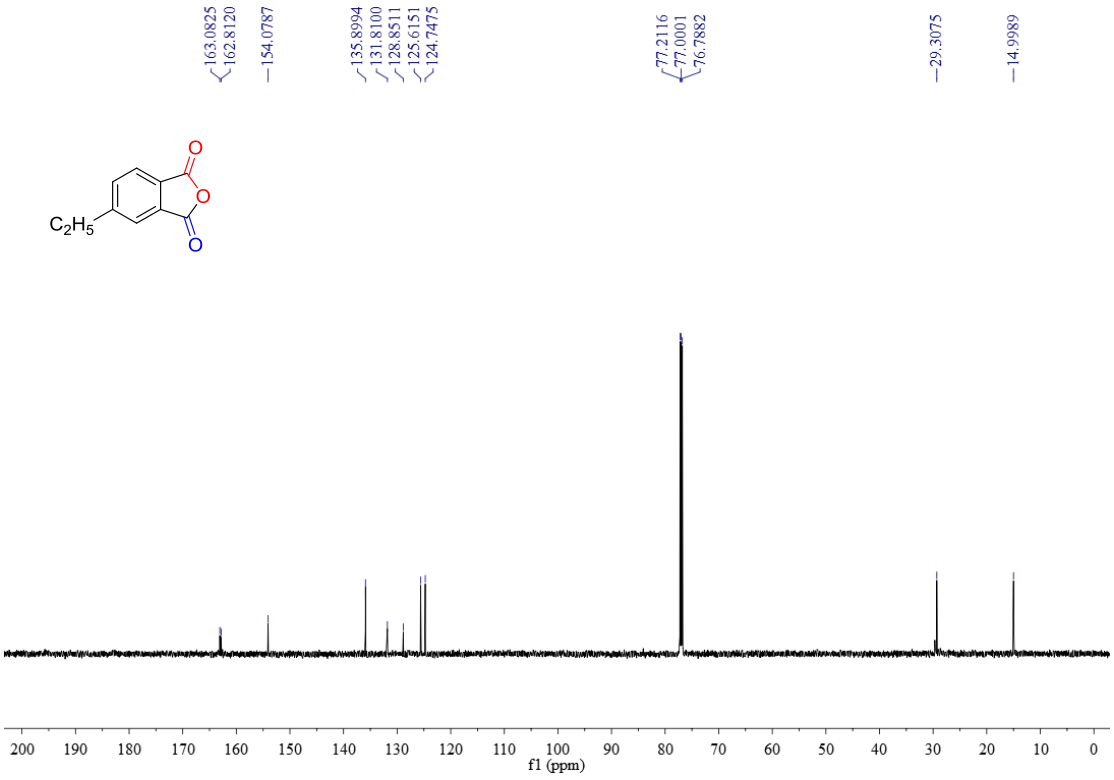
^{13}C NMR spectra of compound 2j



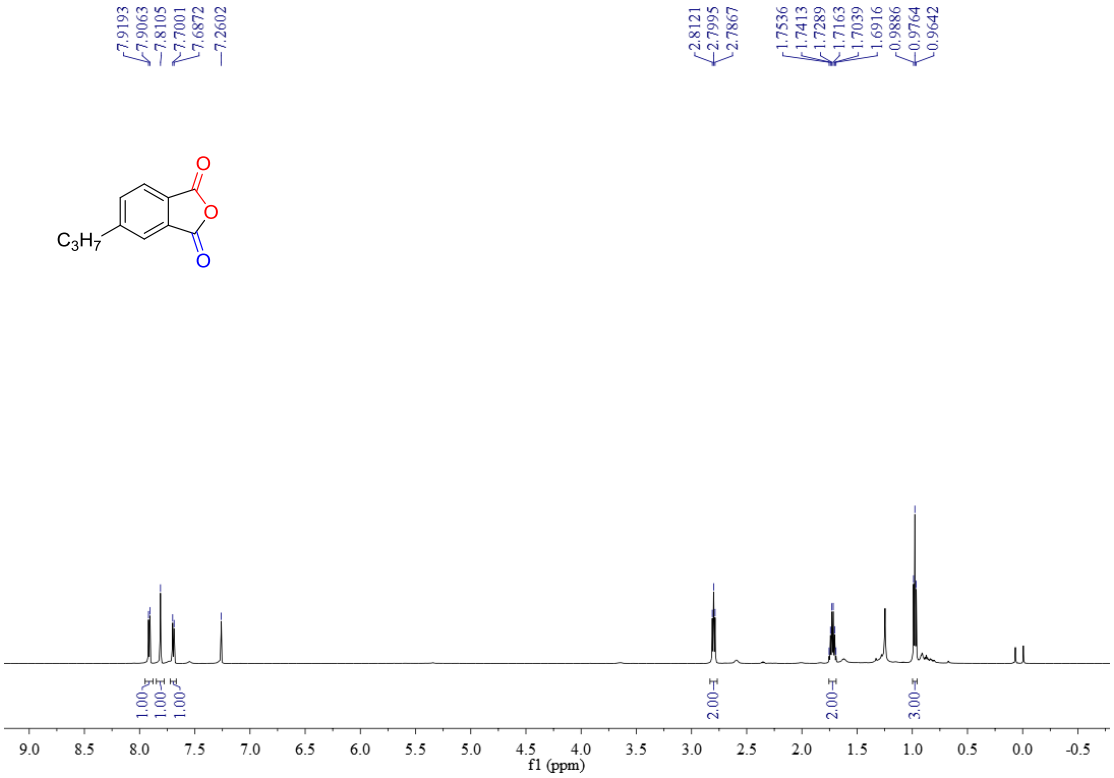
^{1}H NMR spectra of compound 2k



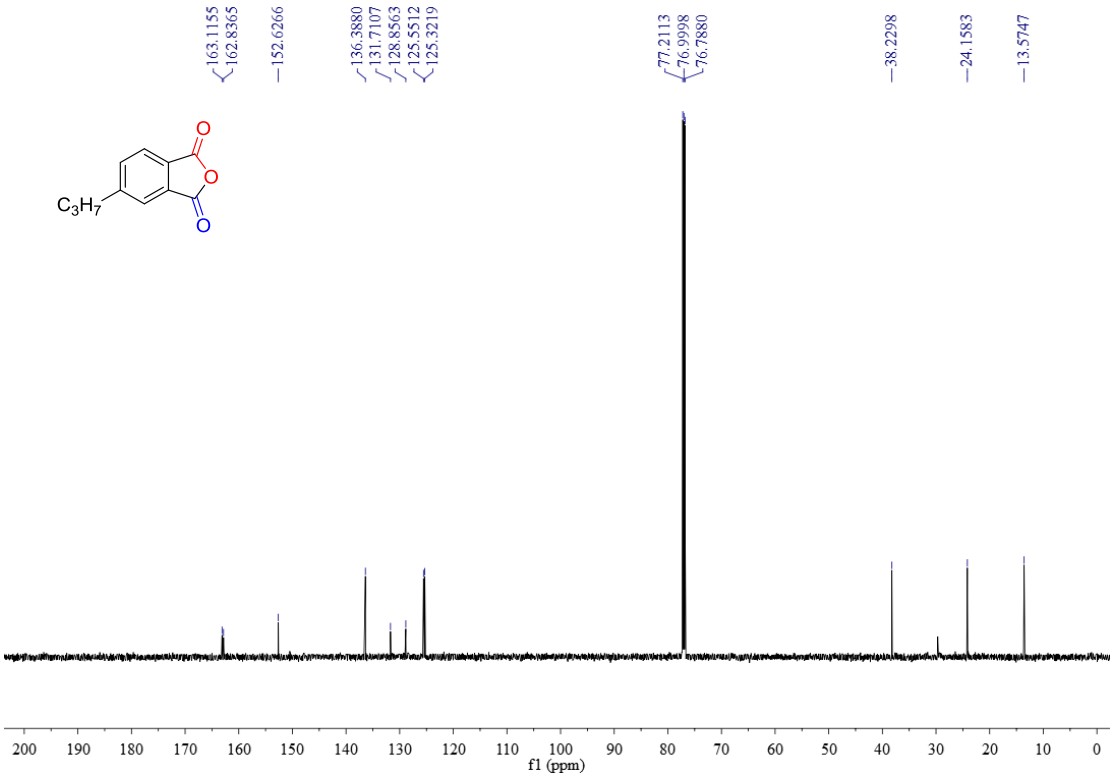
^{13}C NMR spectra of compound 2k



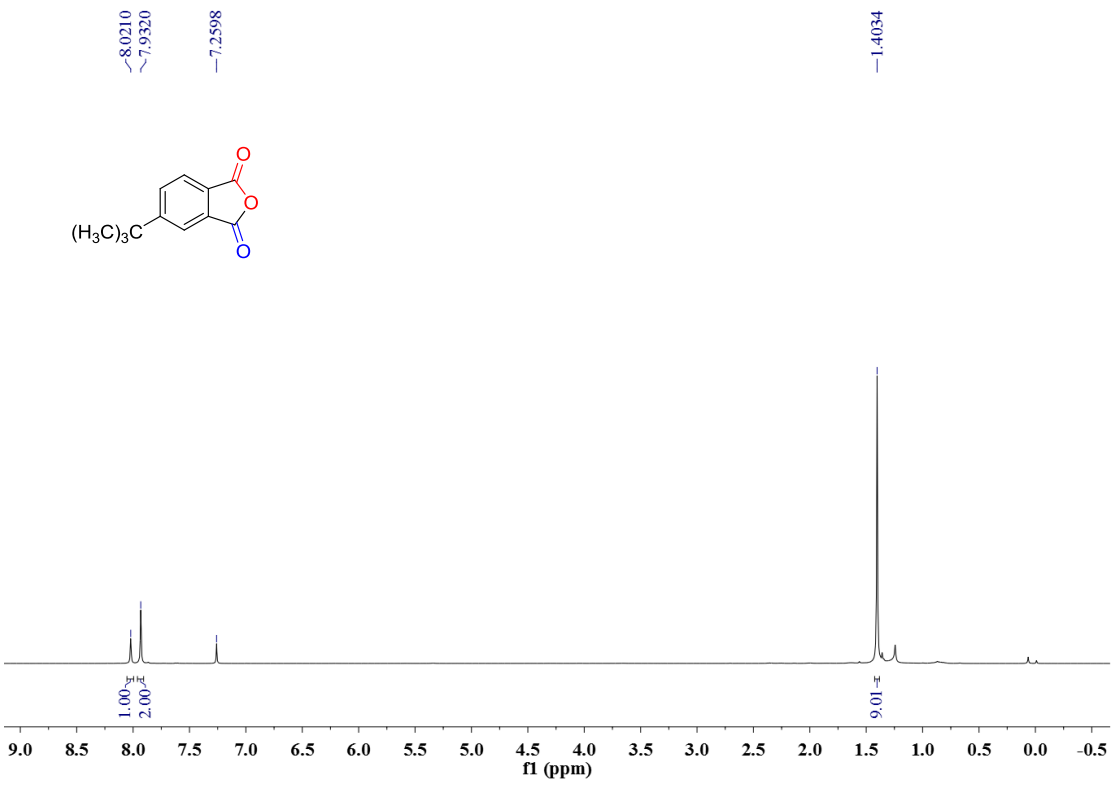
^{1}H NMR spectra of compound 2l



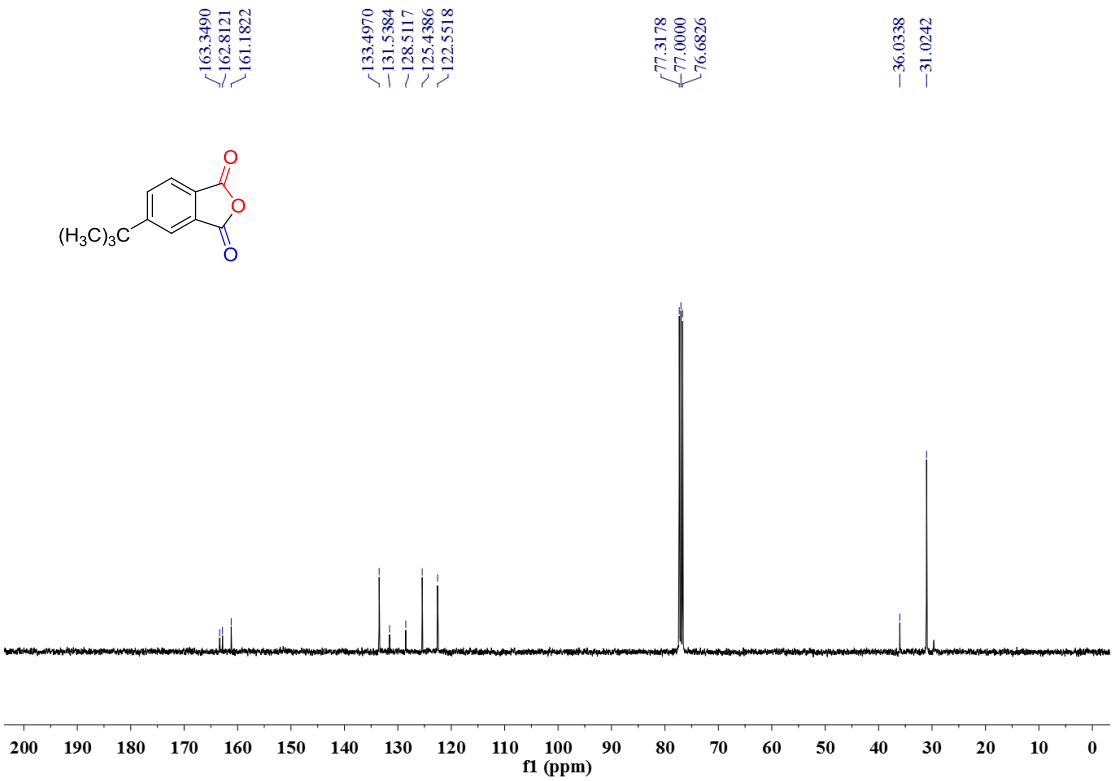
^{13}C NMR spectra of compound 2l



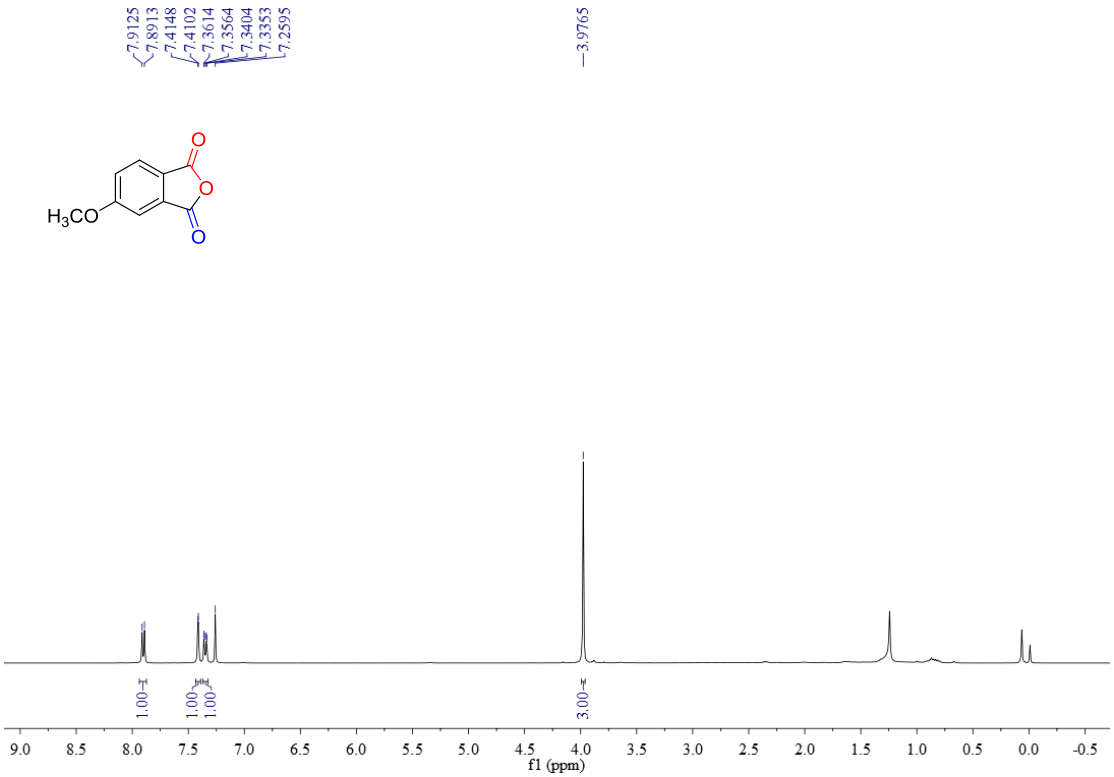
^{1}H NMR spectra of compound 2m



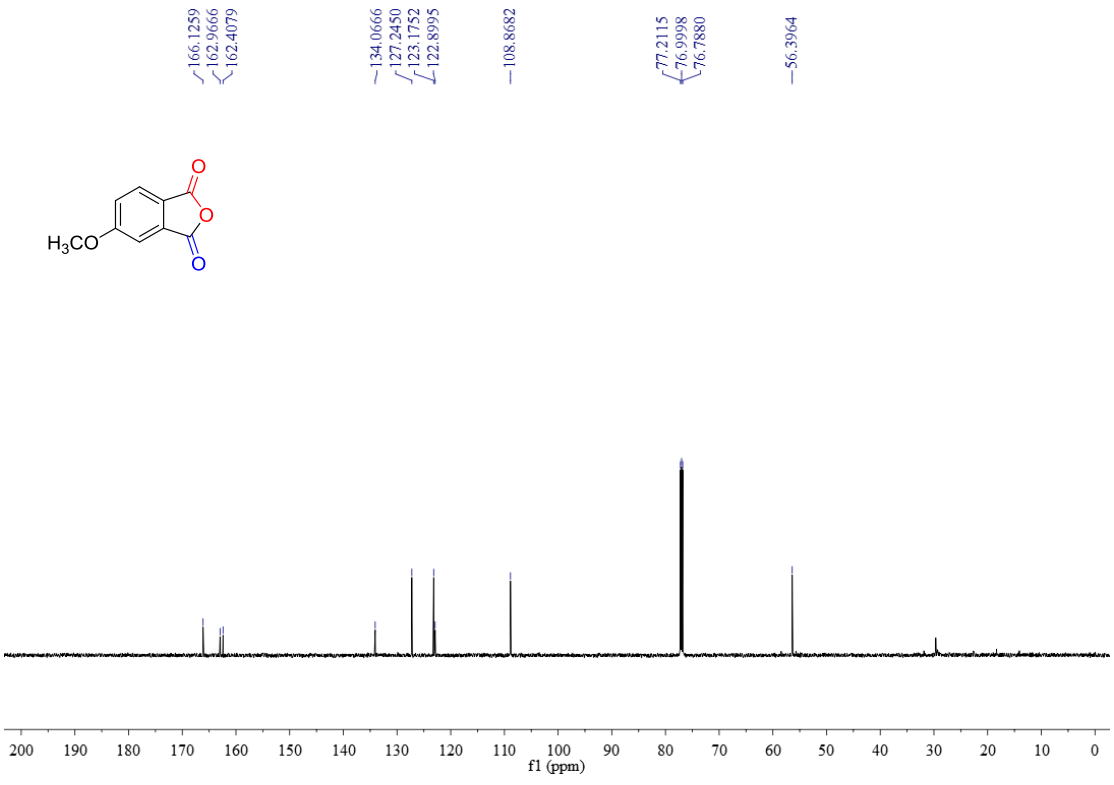
^{13}C NMR spectra of compound 2m



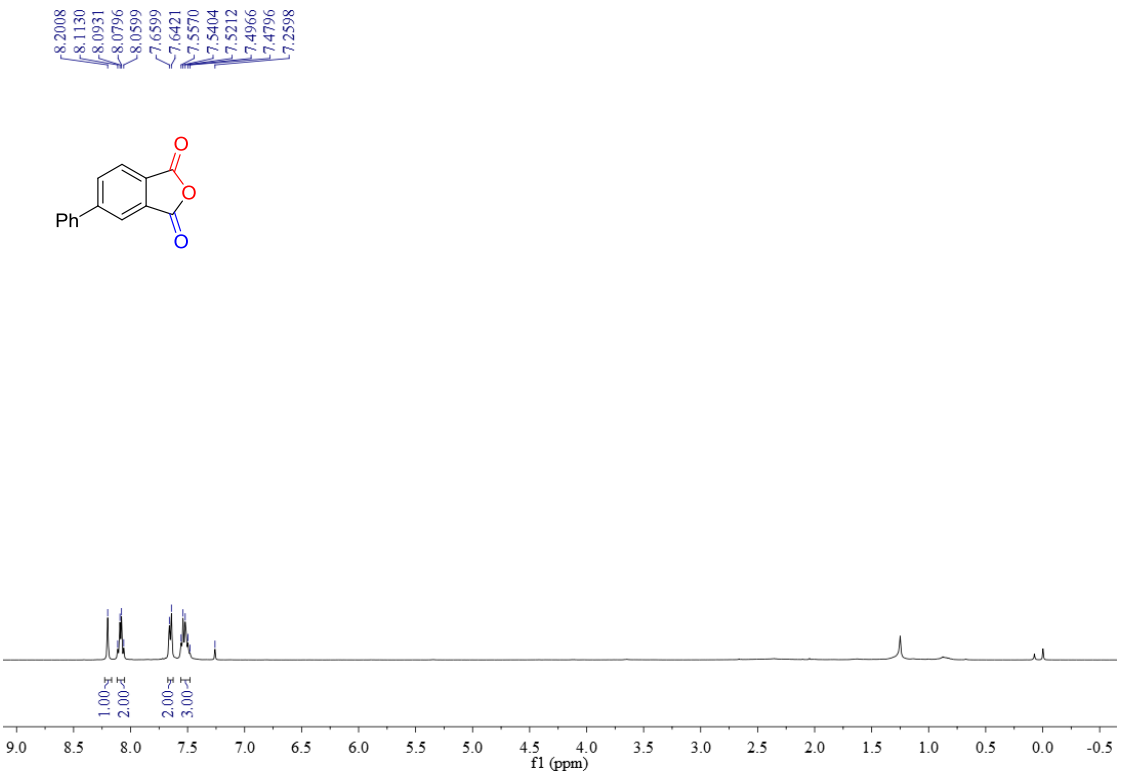
^{1}H NMR spectra of compound 2n



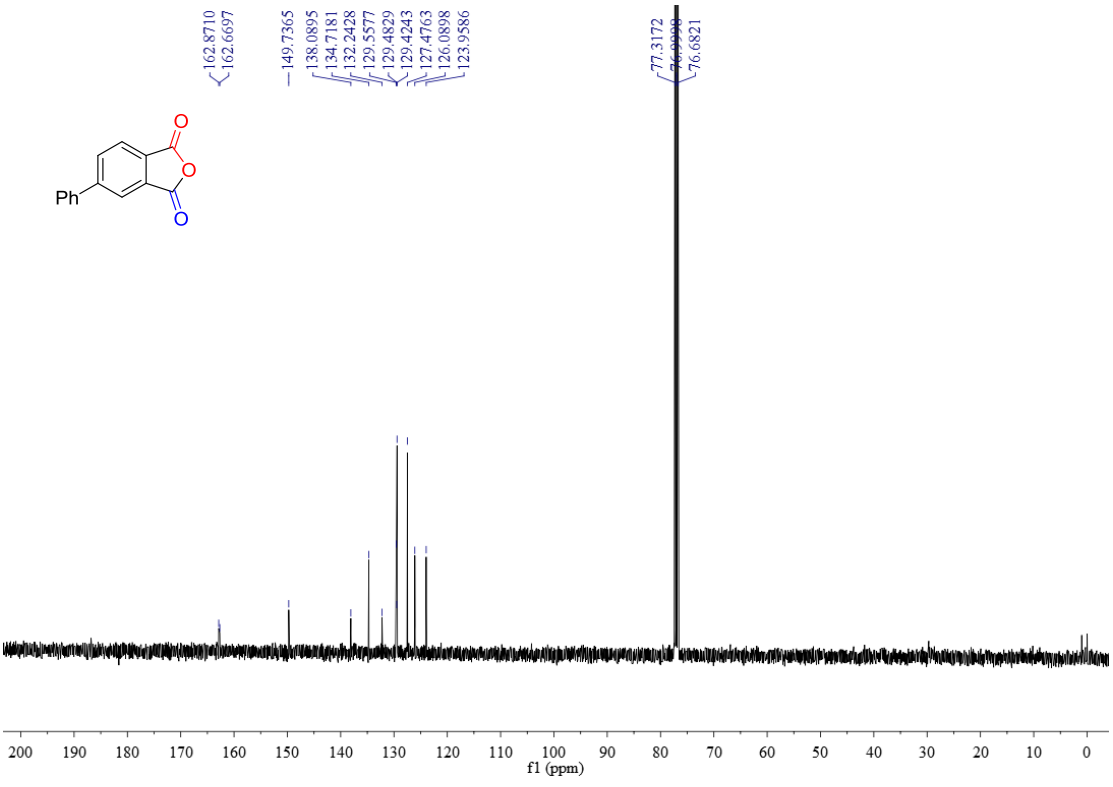
^{13}C NMR spectra of compound 2n



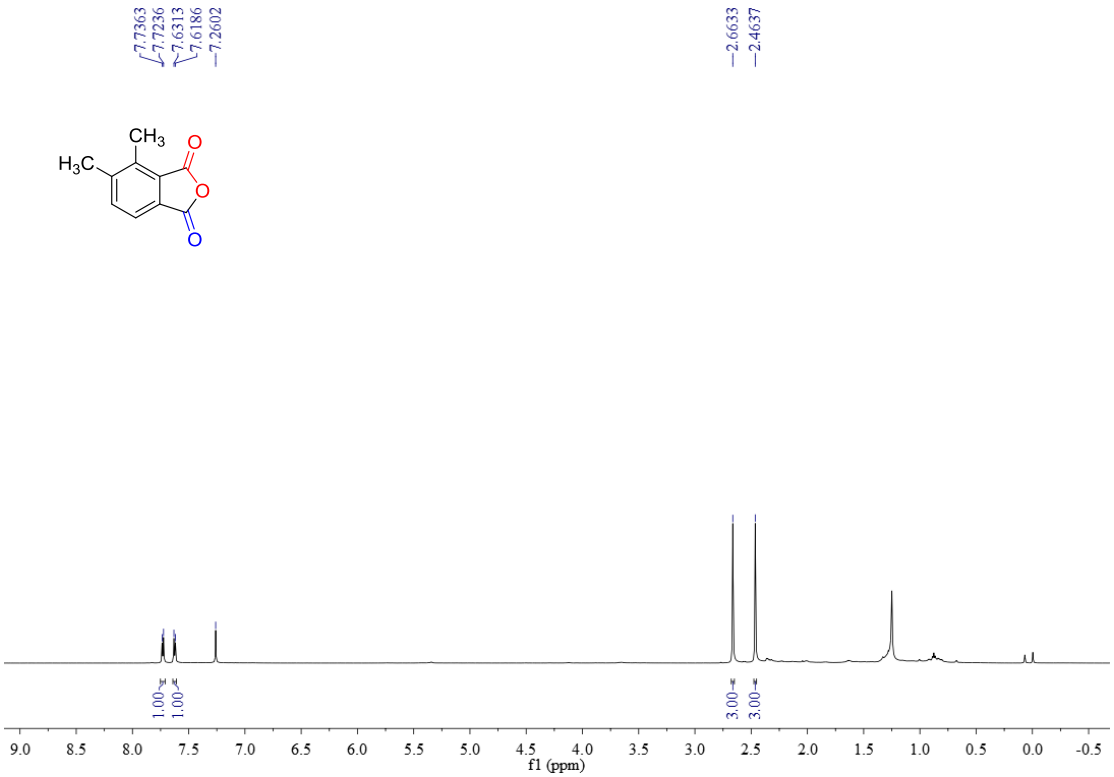
^{1}H NMR spectra of compound 2o



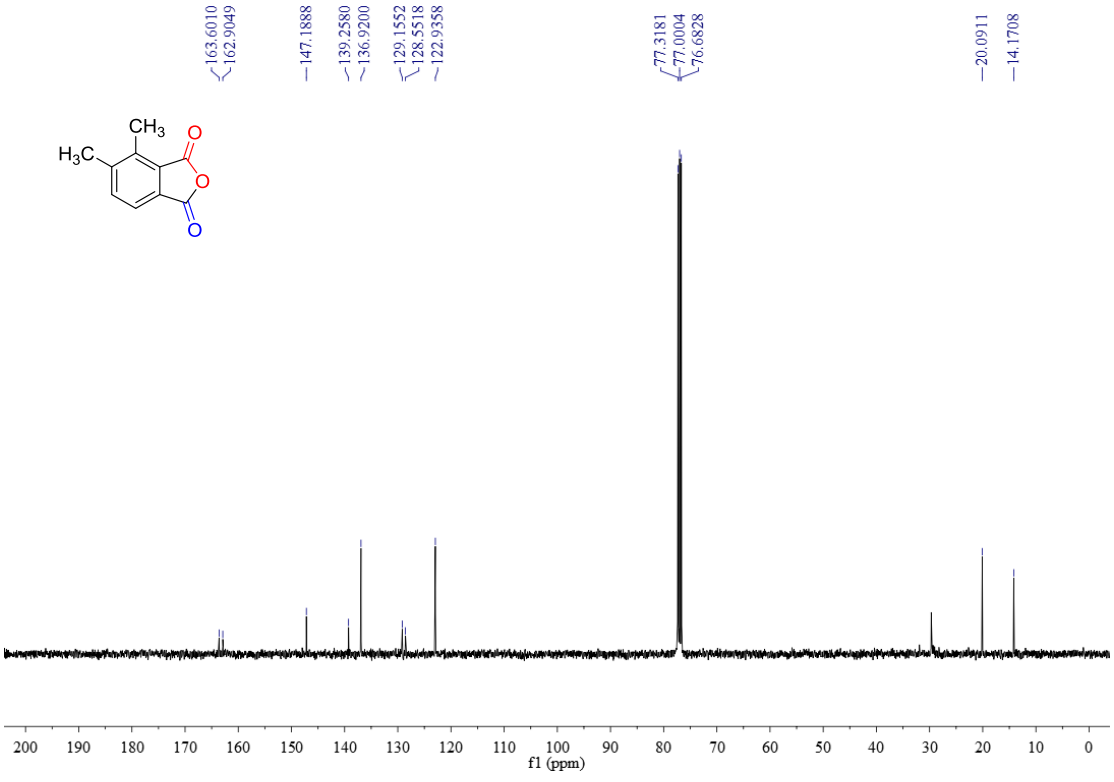
^{13}C NMR spectra of compound 2o



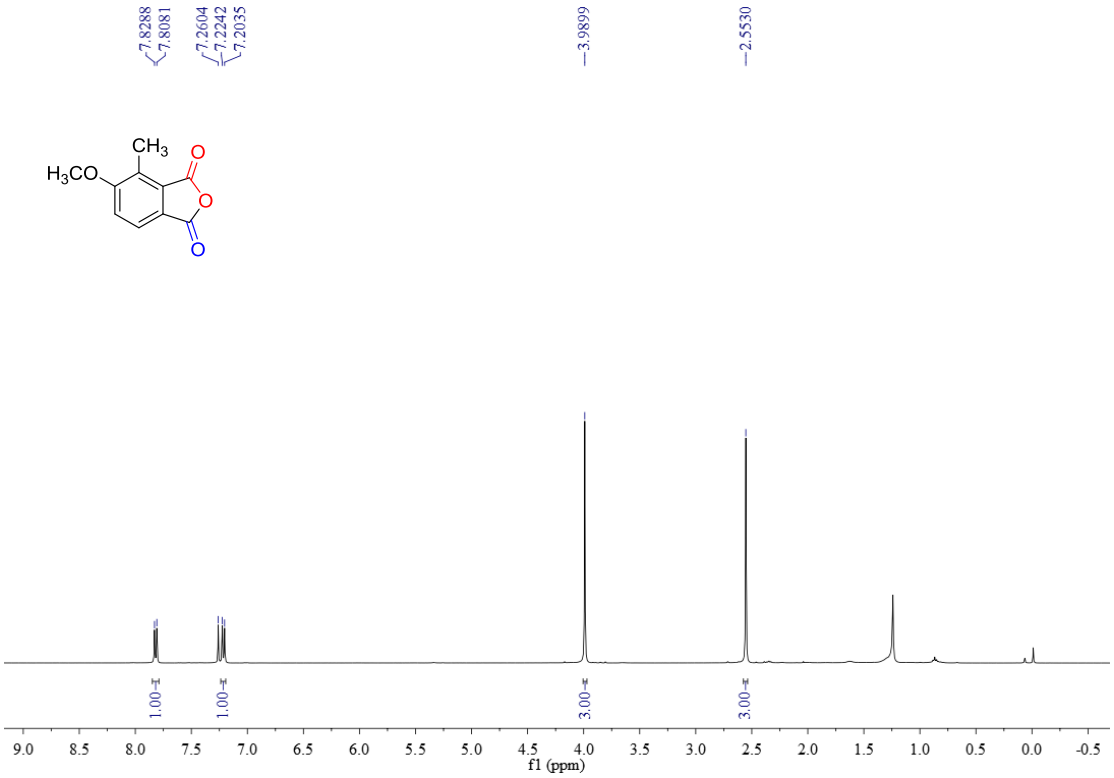
^{1}H NMR spectra of compound 2p



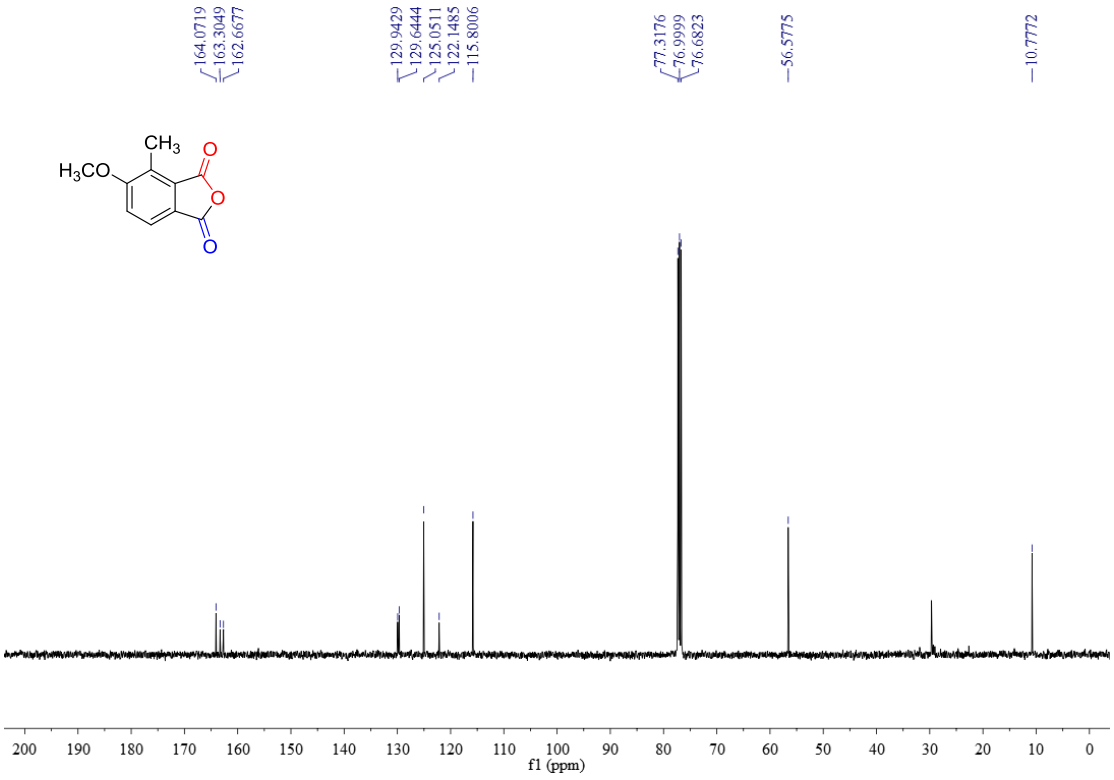
^{13}C NMR spectra of compound 2p



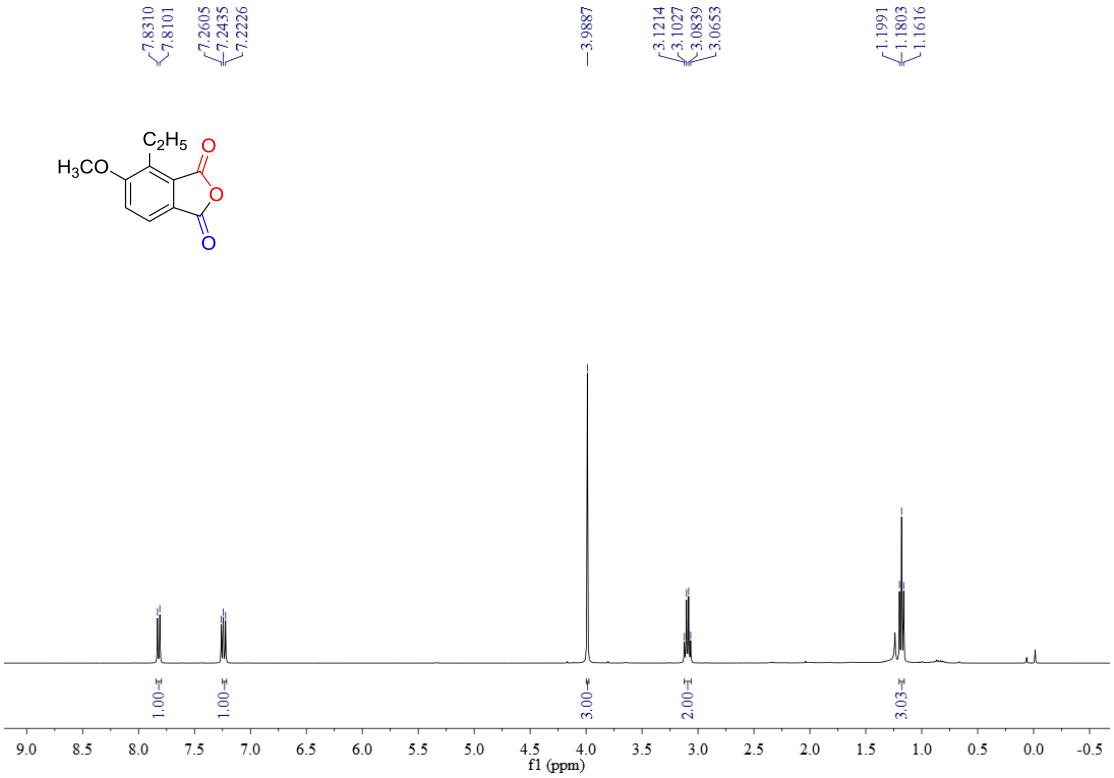
^{1}H NMR spectra of compound 2q



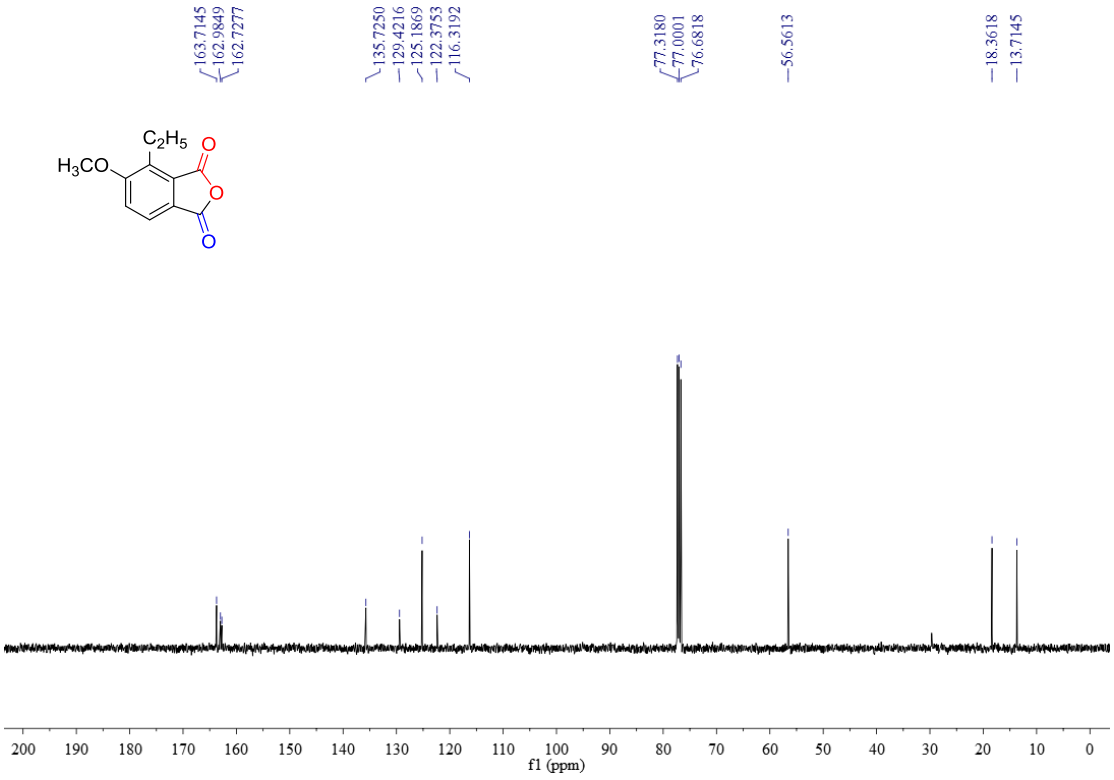
^{13}C NMR spectra of compound 2q



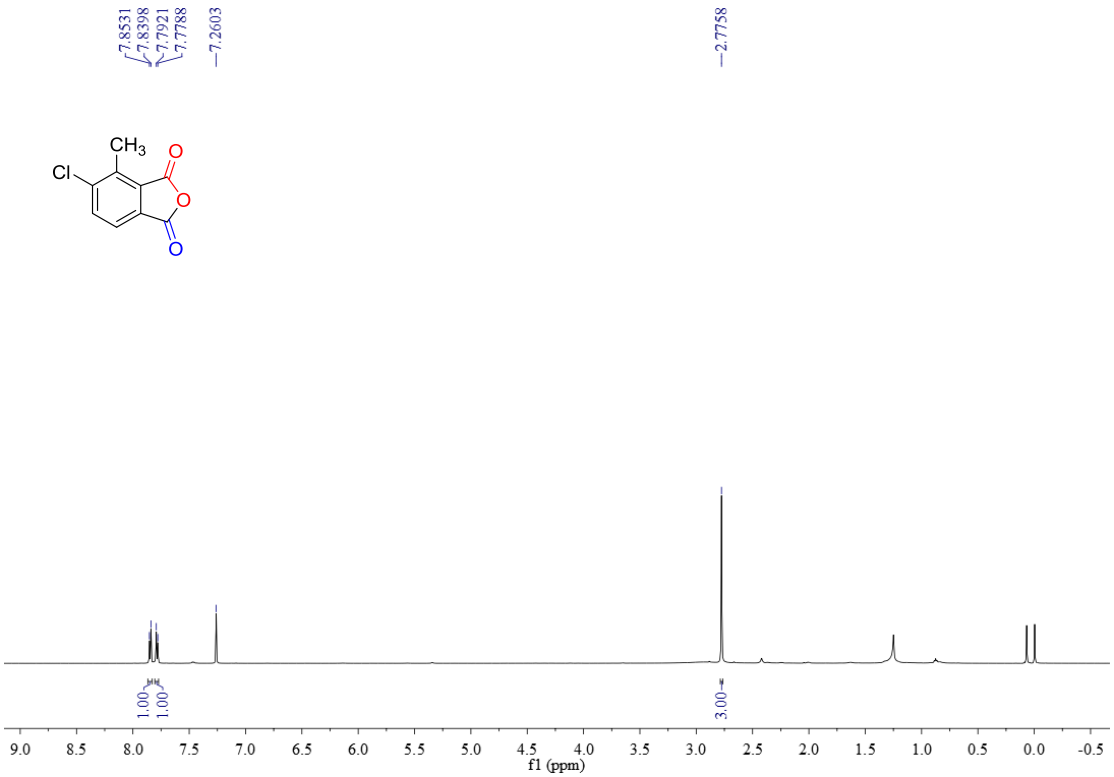
^{1}H NMR spectra of compound 2r



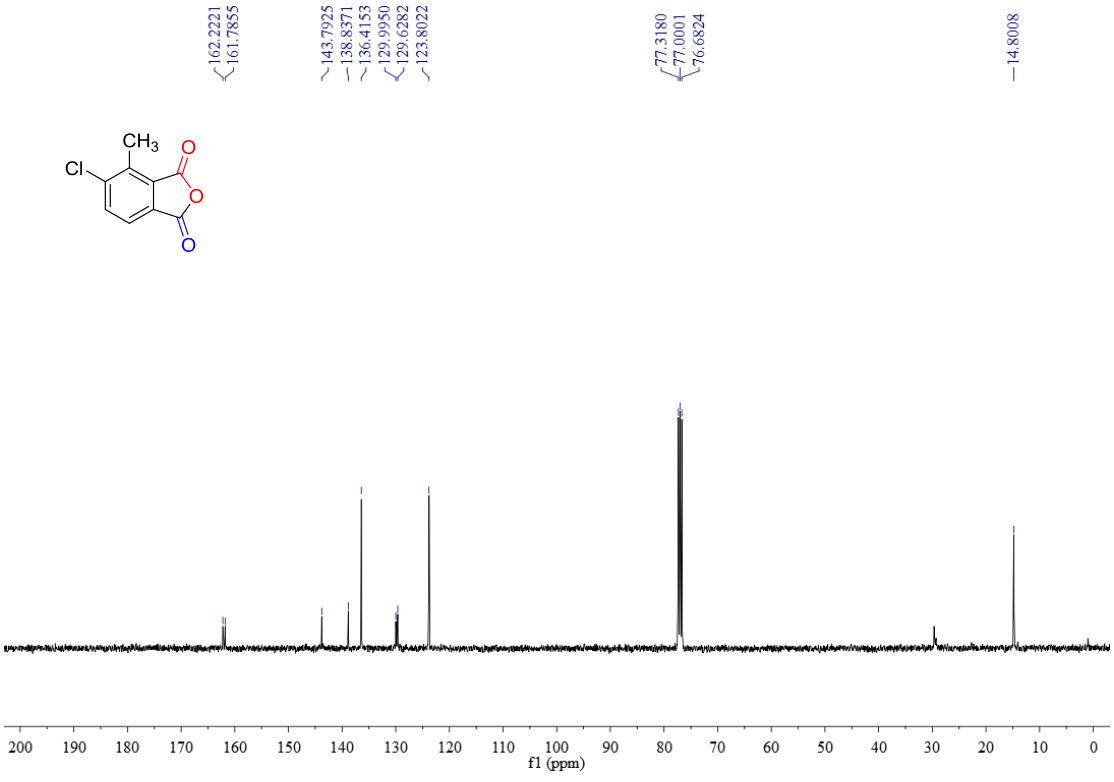
^{13}C NMR spectra of compound 2r



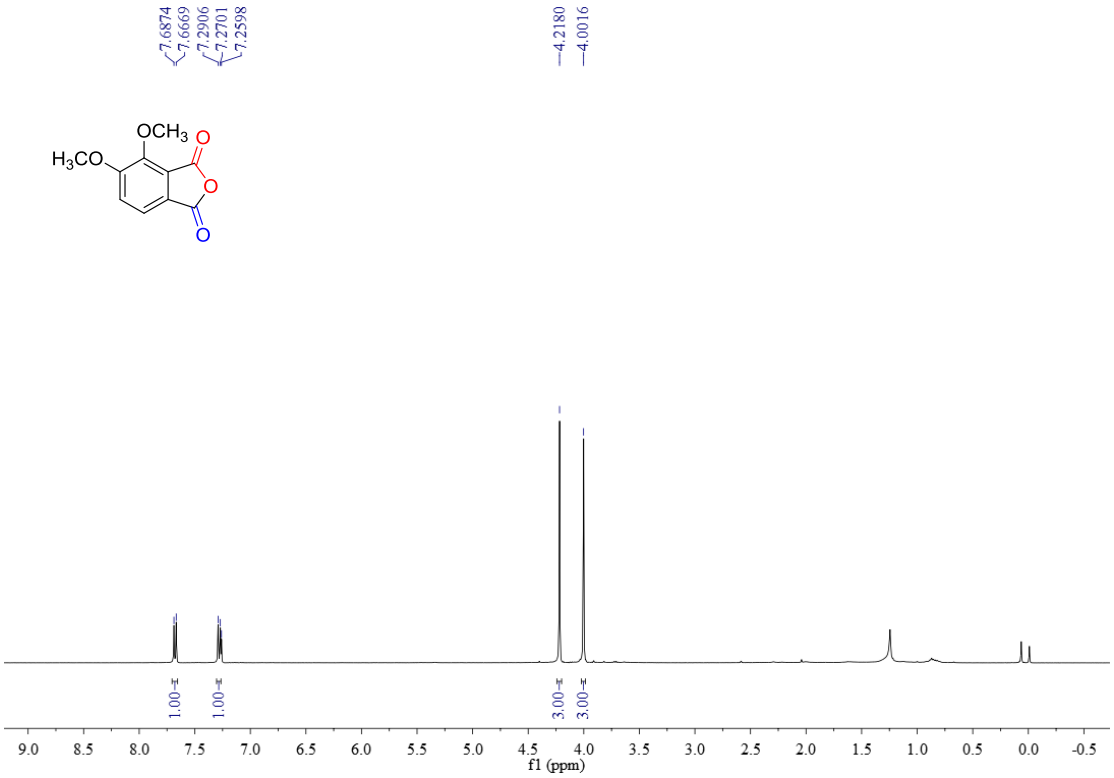
^{1}H NMR spectra of compound 2s



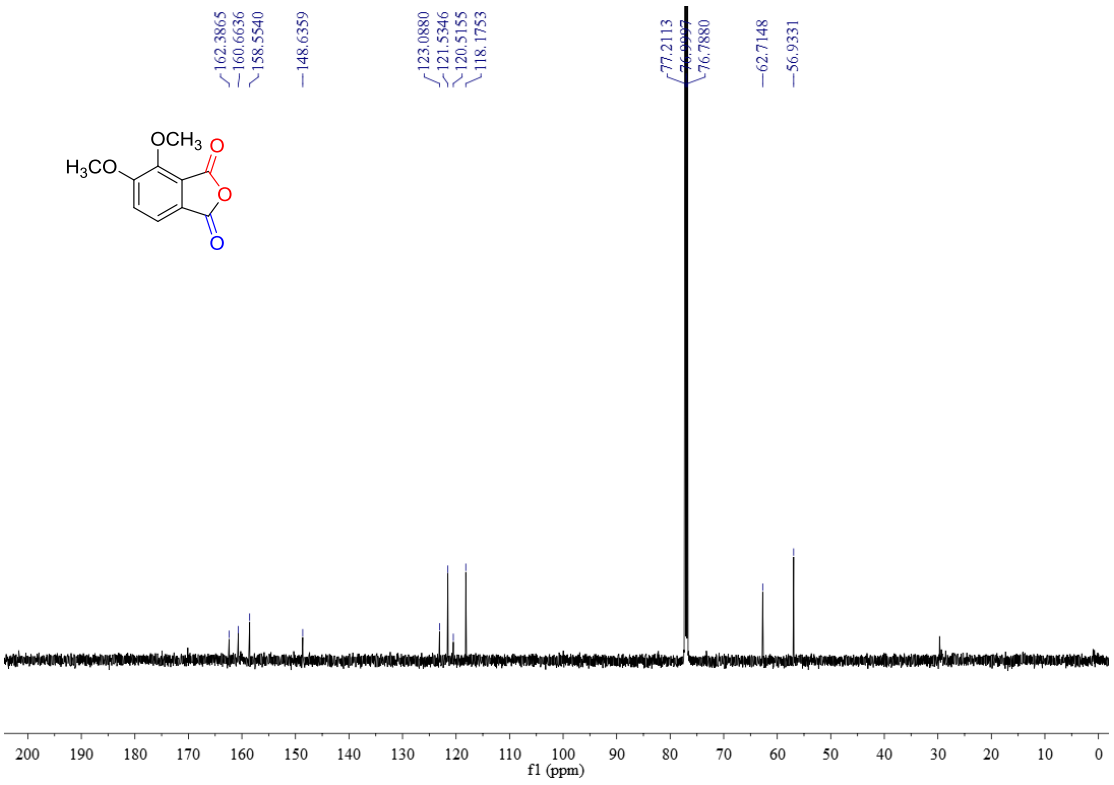
^{13}C NMR spectra of compound 2s



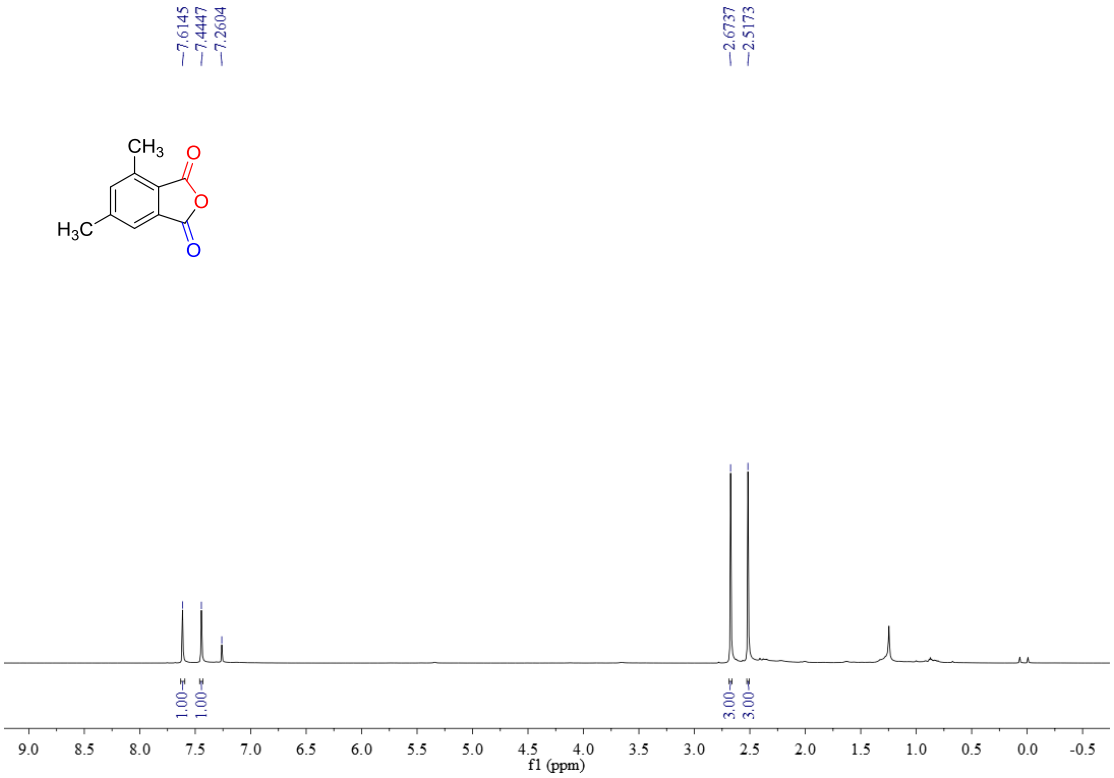
^{1}H NMR spectra of compound 2t



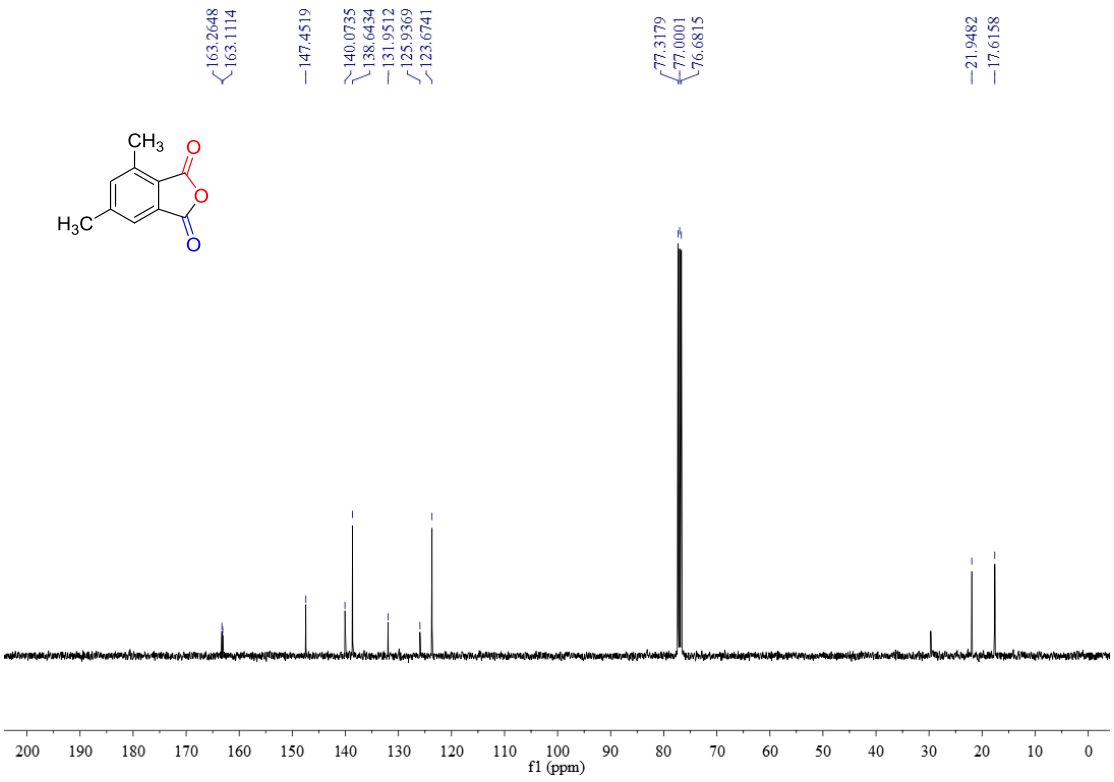
^{13}C NMR spectra of compound 2t



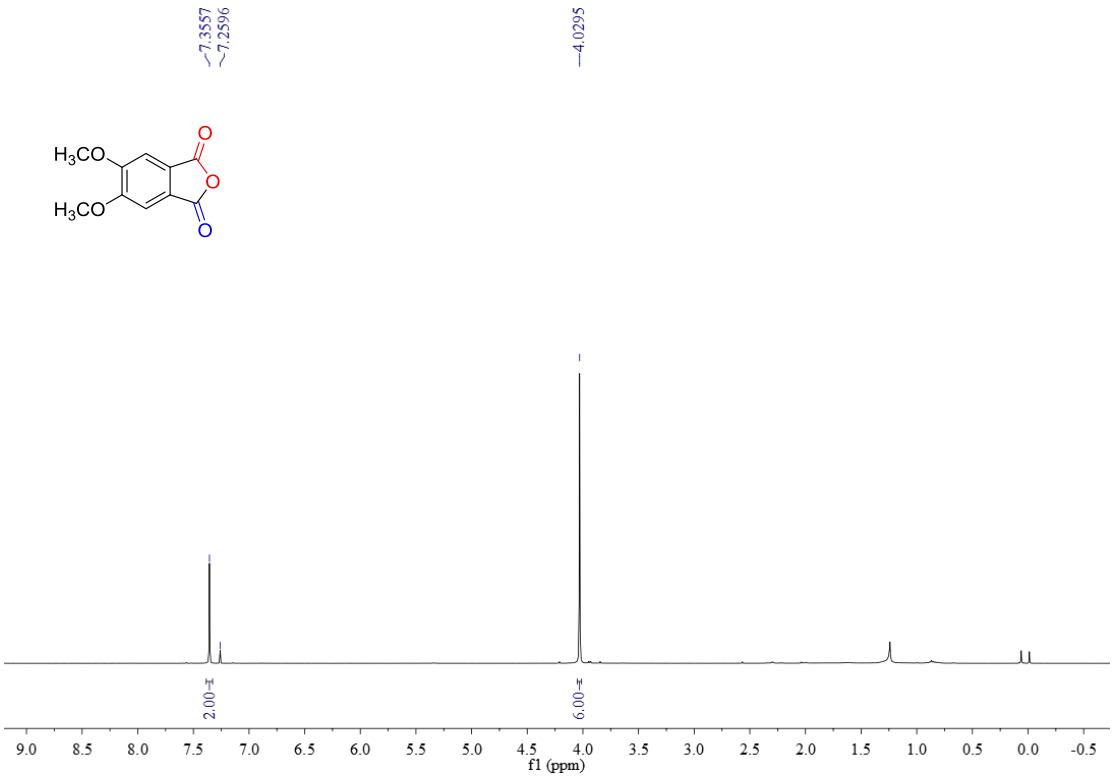
^{1}H NMR spectra of compound 2u



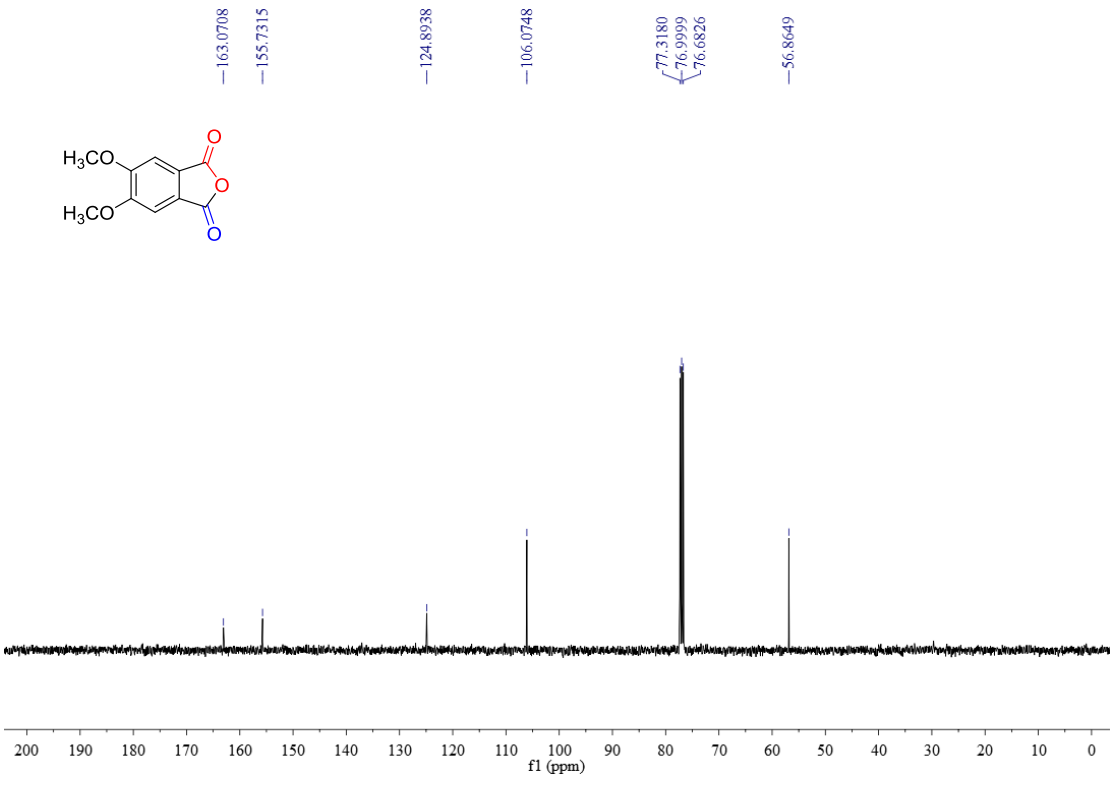
^{13}C NMR spectra of compound 2u



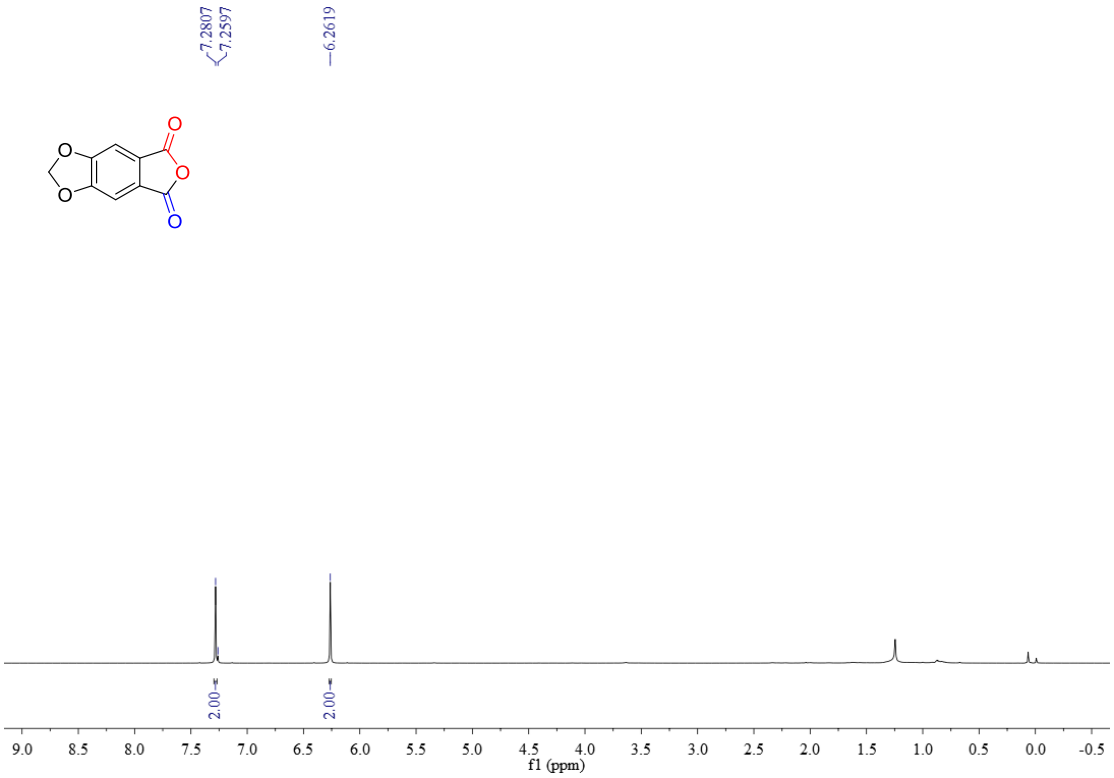
^{1}H NMR spectra of compound 2v



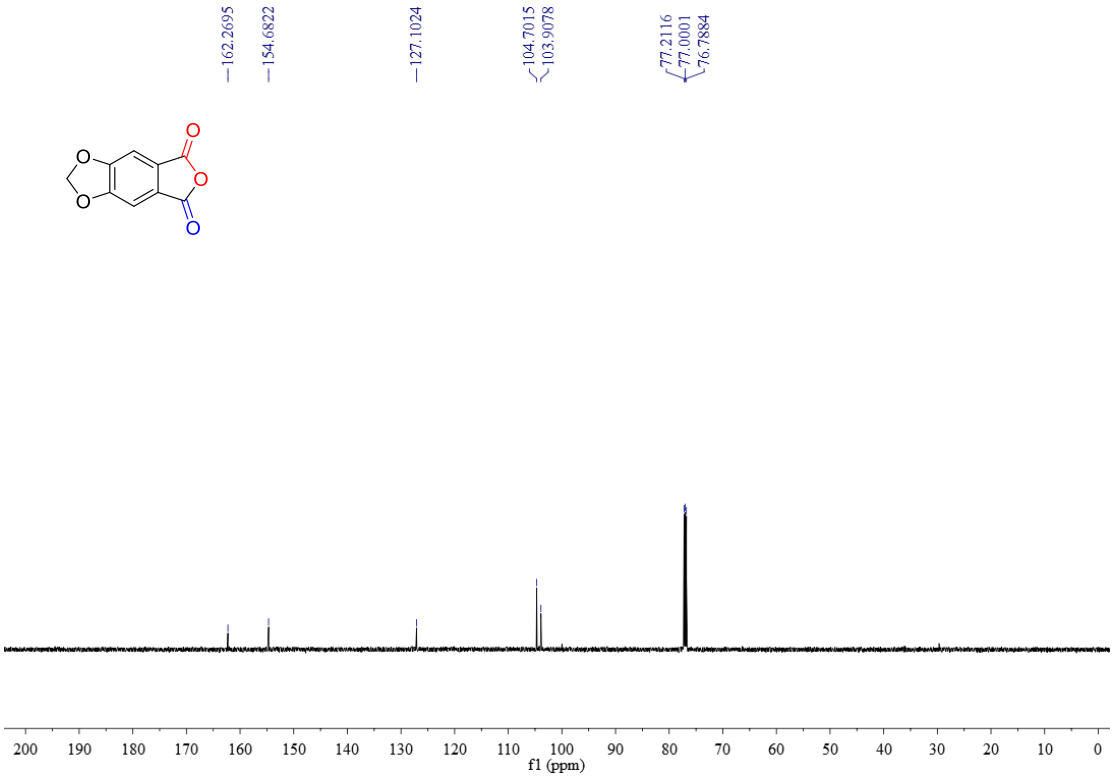
^{13}C NMR spectra of compound 2v



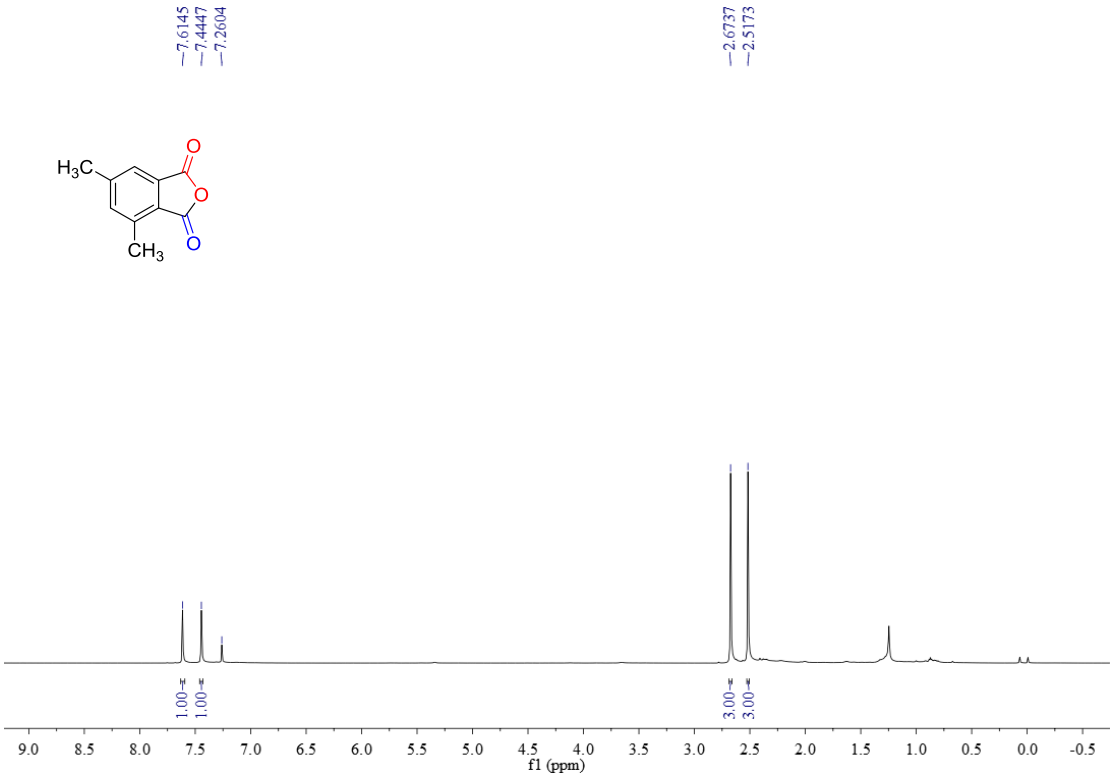
^{1}H NMR spectra of compound 2w



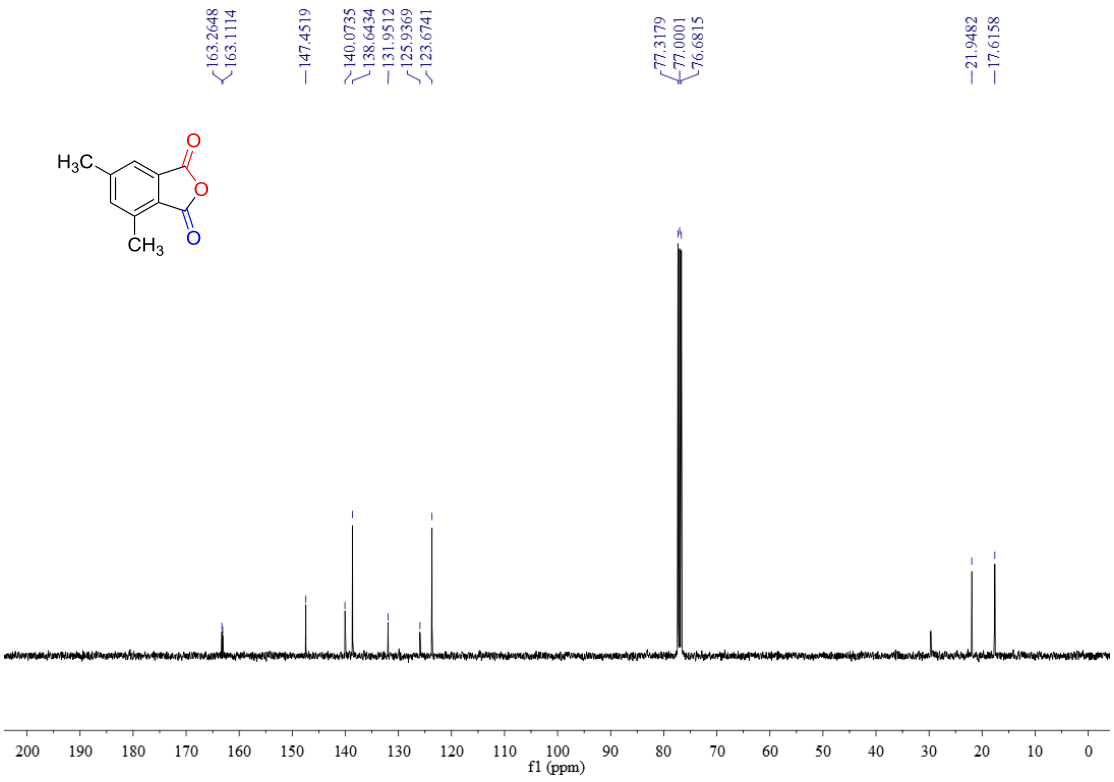
^{13}C NMR spectra of compound 2w



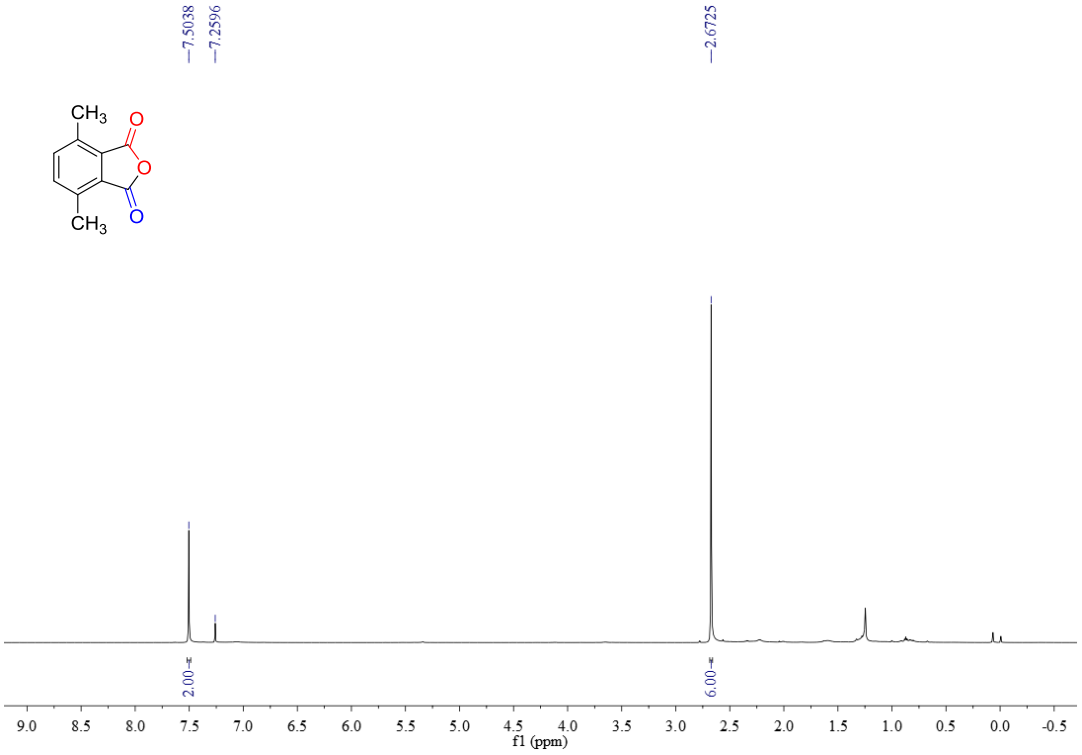
^{1}H NMR spectra of compound 2x



^{13}C NMR spectra of compound 2x



^{1}H NMR spectra of compound 2y



^{13}C NMR spectra of compound 2y