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Electronic Supplementary Information

for

Catalyst- and Additive-Free Baeyer−Villiger-type Oxidation of α-Iodocyclopentenones to α-Pyrones: Using Air as the Oxidant

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1. General Experimental Information

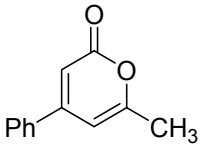
Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. α-Iodocyclopentenones **1** were prepared following literature procedures.[S1] Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (Petroleum ether:EtOAc as eluent). ^{1}H and ^{13}C NMR spectra were recorded with Bruker AVQ-400 or 600 spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), brs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets), dt (doublet of triplet) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT95XP LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

2. General Experimental Procedures for Baeyer−Villiger-type Oxidation of α-Iodocyclopentenones to α-Pyrones

The solution of α-iodocyclopentenones **1** (0.3 mmol) in DMA (3 mL) was stirred at 120 °C for 1-3 h under an air atmosphere. Upon completion, the reaction mixture was cooled to room temperature, then saturated sodium thiosulfate solution was added and the resulting mixture was extracted with ethyl acetate (10 mLx3), the combined organic layers were washed with brine, dried over $MgSO_4$, concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1 to 1:1) to give the desired α-pyrone products **2.**

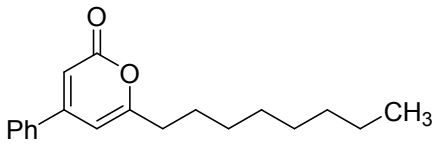
3. Analytical Data:

6-Methyl-4-phenyl-2H-pyran-2-one (2a)[S2]



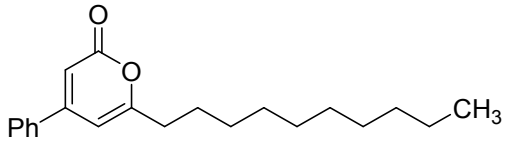
Product **2a** was obtained as a colorless solid in 72% yield (41 mg) following the general procedure, mp 90-91 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56-7.55 (m, 2H), 7.47-7.45 (m, 3H), 6.34 (s, 1H), 6.30 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 162.2, 155.5, 135.8, 130.6, 129.2, 126.7, 108.1, 103.5, 20.2.

6-Octyl-4-phenyl-2H-pyran-2-one (2b)[S3]



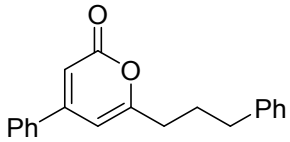
Product **2b** was obtained as yellow oil in 62% yield (53 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57-7.56 (m, 2H), 7.47-7.45 (m, 3H), 6.34 (s, 1H), 6.29 (d, J =1.3 Hz, 1H), 2.54 (t, J = 7.6 Hz, 2H), 1.73-1.68 (m, 2H), 1.30-1.24 (m, 10H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 163.6, 155.5, 136.0, 130.6, 129.1, 126.7, 108.3, 102.8, 34.1, 31.8, 29.3, 29.1, 29.1, 27.0, 22.6, 14.1.

6-Decyl-4-phenyl-2H-pyran-2-one (2c)



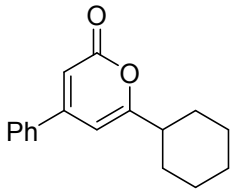
Product **2c** was obtained as a pale-red solid in 61% yield (57 mg) following the general procedure, mp 59-61 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57-7.56 (m, 2H), 7.47-7.45 (m, 3H), 6.34 (d, J = 1.3 Hz, 1H), 6.29 (s, 1H), 2.54 (t, J = 7.6 Hz, 2H), 1.73-1.68 (m, 2H), 1.37-1.26 (m, 14H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 163.6, 155.5, 136.0, 130.6, 129.1, 126.7, 108.3, 102.8, 34.1, 31.9, 29.6, 29.5, 29.3, 29.3, 29.0, 27.0, 22.7, 14.1; HRMS (ESI) calcd. for $C_{21}H_{28}O_2Na$ $[M+Na]^+$: 335.1982, found: 335.1984.

4-Phenyl-6-(3-phenylpropyl)-2H-pyran-2-one (2d)



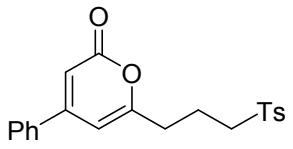
Product **2d** was obtained as a yellow solid in 65% yield (57 mg) following the general procedure, mp 65-66 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.48-7.47 (m, 3H), 7.31-7.28 (m, 2H), 7.22-7.19 (m,3H), 6.36 (s, 1H), 6.28 (s, 1H), 2.72 (t, J = 7.4 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H), 2.07 (t, J = 7.5 Hz, 2H);^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 163.5, 155.4, 141.1, 135.9, 130.6, 129.2, 128.5, 126.7, 126.1, 108.4, 103.0, 35.1, 33.5, 28.5; HRMS (ESI) calcd. for $C_{20}H_{18}O_2Na$ $[M+Na]^+$: 313.1199, found: 313.1202.

6-Cyclohexyl-4-phenyl-2H-pyran-2-one (2e)[S3]



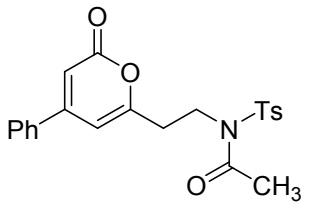
Product **2e** was obtained as a pale-yellow solid in 68% yield (52 mg) following the general procedure, mp 96-97 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.48-7.46 (m, 3H), 6.34 (d, J = 1.3 Hz, 1H), 6.26 (d, J = 0.8 Hz, 1H), 2.48 (tt, J = 11.8, 3.3 Hz, 1H), 2.04-2.01 (m, 2H), 1.87-1.84 (m, 2H), 1.47 (qd, J = 12.5, 3.0 Hz, 2H), 1.39-1.32 (m, 2H), 1.28-1.23 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 163.6, 155.6, 136.2, 130.5, 129.1, 126.7, 108.4, 100.9, 42.5, 30.6, 25.9, 25.8.

4-Phenyl-6-(3-tosylpropyl)-2H-pyran-2-one (2f)



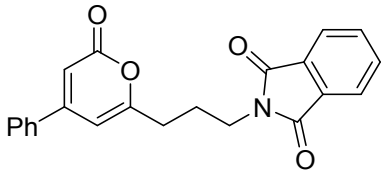
Product **2f** was obtained as a yellow solid in 61% yield (68 mg) following the general procedure, mp 134-136 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.48-7.45 (m, 3H), 7.35 (d, J = 7.9 Hz, 2H), 6.34 (d, J = 11.9 Hz, 2H), 3.14 (t, J = 7.6 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.43 (s, 3H), 2.16-2.10 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.0, 163.0, 155.2, 145.1, 135.8, 135.5, 130.8, 130.1, 129.2, 128.1, 126.7, 108.9, 103.8, 55.0, 32.3, 21.6, 20.5; HRMS (ESI) calcd. for $C_{21}H_{20}O_4SNa$ $[M+Na]^+$: 391.0975, found: 391.0978.

***N*-(2-(2-oxo-4-phenyl-2H-pyran-6-yl)ethyl)-N-tosylacetamide (2g)**



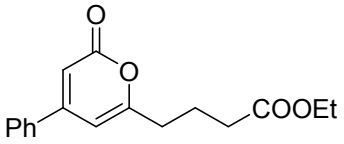
Product **2g** was obtained as a colorless solid in 62% yield (77 mg) following the general procedure, mp 153-155 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.58-7.56 (m, 2H), 7.48-7.46 (m, 3H), 7.35 (d, J = 8.2 Hz, 2H), 6.38 (d, J = 4.4 Hz, 2H), 4.12 (t, J = 7.0 Hz, 2H), 2.95 (t, J = 7.1 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 163.0, 161.4, 155.2, 145.3, 136.3, 135.6, 130.7, 130.1, 129.2, 127.4, 126.7, 109.2, 104.6, 44.6, 34.4, 25.0, 21.7; HRMS (ESI) calcd. for $C_{22}H_{21}NO_5SNa$ $[M+Na]^+$: 434.1033, found: 434.1035.

2-(3-(2-Oxo-4-phenyl-2H-pyran-6-yl)propyl)isoindoline-1,3-dione (2h)



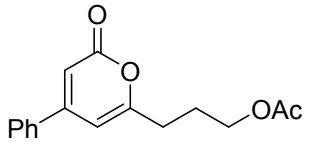
Product **2h** was obtained as a pale-yellow solid in 72% yield (78 mg) following the general procedure, mp 113-114 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.71-7.69 (m, 2H), 7.57-7.56 (m, 2H), 7.47-7.45 (m,3H), 6.39 (d, J = 0.5 Hz, 1H), 6.31 (d, J = 1.4 Hz, 1H), 3.80 (t, J = 6.8 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.16-2.11 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 164.0, 163.2, 155.3, 135.7, 134.1, 132.0, 130.7, 129.2, 126.7, 123.3, 108.5, 103.3, 37.0, 31.4, 25.8; HRMS (ESI) calcd. for $C_{22}H_{17}NO_4Na$ $[M+Na]^+$: 382.1050, found: 382.1053.

Ethyl 4-(2-oxo-4-phenyl-2H-pyran-6-yl)butanoate (2i)



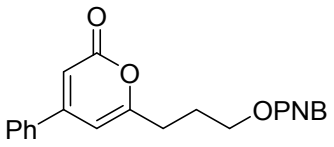
Product **2i** was obtained as a yellow solid in 68% yield (58 mg) following the general procedure, mp 86-88 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58-7.57 (m, 2H), 7.50-7.47 (m, 3H), 6.37 (d, J = 1.5 Hz, 1H), 6.33 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.41 (t, J = 7.3 Hz, 2H), 2.08-2.05 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 164.5, 163.3, 155.3, 135.7, 130.7, 129.2, 126.7, 108.6, 103.3, 60.5, 33.2, 33.2, 22.2, 14.2; HRMS (ESI) calcd. for $C_{17}H_{18}O_4Na$ $[M+Na]^+$: 309.1097, found: 309.1100.

3-(2-Oxo-4-phenyl-2H-pyran-6-yl)propyl acetate (2j)



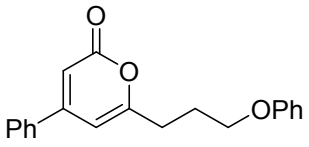
Product **2j** was obtained as yellow oil in 68% yield (56 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56-7.55 (m, 2H), 7.47-7.45 (m, 3H), 6.35 (s, 1H), 6.33 (s, 1H), 4.13 (t, J = 6.2 Hz, 2H), 2.64 (t, J = 7.7 Hz, 2H), 2.08-2.03 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 164.3, 163.3, 155.4, 135.7, 130.7, 129.2, 126.7, 108.6, 103.2, 63.16, 30.78, 26.04, 20.88; HRMS (ESI) calcd. for $C_{16}H_{16}O_4Na$ $[M+Na]^+$: 295.0941, found: 295.0943.

3-(2-Oxo-4-phenyl-2H-pyran-6-yl)propyl 4-nitrobenzoate (2k)



Product **2k** was obtained as a yellow solid in 72% yield (82 mg) following the general procedure, mp 124-125 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27-8.25 (m, 2H), 8.13-8.16 (m, 2H),7.54-7.52 (m, 2H), 7.48-7.45 (m, 3H), 6.35 (s, 2H), 4.48 (t, J = 6.2 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 2.28-2.24 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.6, 164.0, 163.1, 155.3, 150.6, 135.5, 135.3, 130.8, 130.7, 129.2, 126.6, 123.6, 108.7, 103.3, 64.8, 31.0, 26.0; HRMS (ESI) calcd. for $C_{21}H_{17}NO_6Na$ $[M+Na]^+$: 402.0948, found: 402.0951.

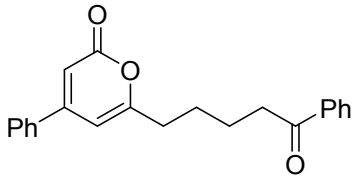
6-(3-Phenoxypropyl)-4-phenyl-2H-pyran-2-one (2l)



Product **2l** was obtained as a yellow solid in 60% yield (55 mg) following the general procedure, mp 67-69 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.46-7.44 (m, 3H), 7.29-7.26 (m, 2H), 6.95 (t, J = 7.3 Hz, 1H), 6.90 (dd, J = 8.7, 0.9 Hz, 2H), 6.37 (d, J = 1.5 Hz, 1H), 6.33 (d, J = 1.3 Hz, 1H), 4.04 (t, J = 5.9 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H), 2.23-2.20 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 163.5, 158.7,

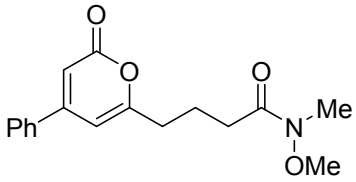
155.5, 135.8, 130.6, 129.5, 129.2, 126.7, 120.9, 114.5, 108.6, 103.4, 66.3, 30.8, 26.7; HRMS (ESI) calcd. for $C_{20}H_{18}O_3Na$ $[M+Na]^+$: 329.1148, found: 329.1150.

6-(5-Oxo-5-phenylpentyl)-4-phenyl-2H-pyran-2-one (2m)



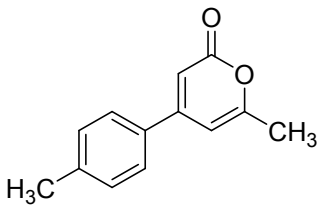
Product **2m** was obtained as yellow oil in 54% yield (54 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.95 (m, 2H), 7.59-7.55 (m, 3H), 7.48-7.45 (m, 5H), 6.36 (d, J = 1.4 Hz, 1H), 6.34 (s,1H), 3.04 (t, J = 6.7 Hz, 2H), 2.63 (t, J = 6.8 Hz, 2H), 1.85-1.82 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.7, 165.2, 163.5, 155.5, 136.9, 135.9, 133.1, 130.6, 129.2, 128.7, 128.0, 126.7, 108.4, 103.0, 38.0, 34.0, 26.6, 23.5; HRMS (ESI) calcd. for $C_{22}H_{20}O_3Na$ $[M+Na]^+$: 355.1305, found: 355.1308.

***N*-methoxy-N-methyl-4-(2-oxo-4-phenyl-2H-pyran-6-yl)butanamide (2n)**



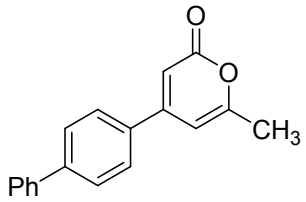
Product **2n** was obtained as yellow oil in 46% yield (41 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57-7.56 (m, 2H), 7.47-7.45 (m, 3H), 6.35 (d, J = 5.6 Hz, 2H), 3.67 (s, 3H), 3.18 (s, 3H), 2.64 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 6.7 Hz, 2H), 2.09-2.03 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 163.4, 155.4, 135.8, 130.6, 129.2, 126.7, 108.5, 103.1, 61.3, 33.3, 32.2, 30.7, 29.7, 21.9; HRMS (ESI) calcd. for $C_{17}H_{19}NO_4Na[M+Na]^+$: 324.1206, found: 324.1209.

6-Methyl-4-(p-tolyl)-2H-pyran-2-one (2o) [S2]



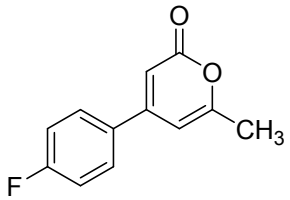
Product **2o** was obtained as a pale-yellow solid in 65% yield (39 mg) following the general procedure, mp 101-102 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.32 (s, 1H), 6.29 (s, 1H), 2.40 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6, 162.0, 155.3, 141.1, 132.8, 129.9, 126.6, 107.4, 103.4, 21.4, 20.2.

4-([1,1'-Biphenyl]-4-yl)-6-methyl-2H-pyran-2-one (2p)



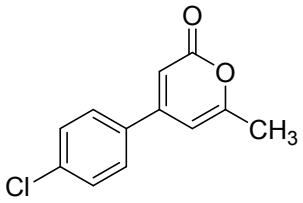
Product **2p** was obtained as a colorless solid in 72% yield (57 mg) following the general procedure, mp 173-175 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70-7.61 (m, 6H), 7.47 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 6.41 (s, 1H), 6.35 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 162.2, 155.0, 143.5, 139.8, 134.5, 129.0, 128.1, 127.8, 127.1, 127.1, 107.8, 103.3, 20.2; HRMS (ESI) calcd. for $C_{18}H_{14}O_2Na$ $[M+Na]^+$: 285.0886, found: 285.0891.

4-(4-Fluorophenyl)-6-methyl-2H-pyran-2-one (2q) [S6]



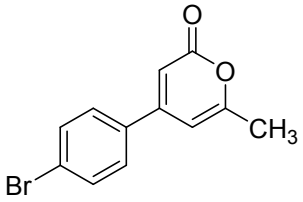
Product **2q** was obtained as a pale-yellow solid in 64% yield (44 mg) following the general procedure, mp 113-114 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.13 (t, J = 8.5 Hz, 2H), 6.27 (s, 1H), 6.25 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7 (d, J = 251.9 Hz), 163.4, 163.2, 154.3, 131.9 (d, J = 3.3 Hz), 128.7 (d, J = 8.7 Hz), 116.3 (d, J = 21.8 Hz), 107.9, 103.2, 20.2.

4-(4-Chlorophenyl)-6-methyl-2H-pyran-2-one (2r) [S2]



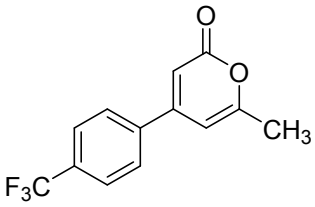
Product **2r** was obtained as a colorless solid in 70% yield (46 mg) following the general procedure, mp 126-127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.30 (s, 1H), 6.25 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.2, 162.5, 154.2, 136.9, 134.2, 129.4, 128.0, 108.2, 103.1, 20.2.

4-(4-Bromophenyl)-6-methyl-2H-pyran-2-one (2s) [S2]



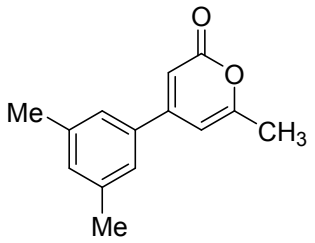
Product **2s** was obtained as a yellow solid in 67% yield (53 mg) following the general procedure, mp 116-118 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 6.31 (s, 1H), 6.24 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 162.5, 154.3, 134.7, 132.4, 128.2, 125.2, 108.3, 103.0, 20.2.

6-Methyl-4-(4-(trifluoromethyl)phenyl)-2H-pyran-2-one (2t) [S5]



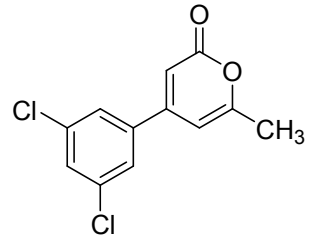
Product **2t** was obtained as a colorless solid in 54% yield (41 mg) following the general procedure, mp 141-142 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 6.34 (s, 1H), 6.27 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 154.1, 139.4, 132.3 (q, J = 32.8 Hz), 127.1, 126.1 (q, J = 3.8 Hz), 123.7 (q, J = 272.4 Hz), 109.3, 103.2, 20.2.

4-(3,5-Dimethylphenyl)-6-methyl-2H-pyran-2-one (2u) [S6]



Product **2u** was obtained as a yellow solid in 56% yield (36 mg) following the general procedure, mp 87-89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.10 (s, 1H), 6.31 (s, 1H), 6.28 (s, 1H), 2.36 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6, 161.9, 155.8, 138.8, 135.8, 132.3, 124.5, 107.9, 103.7, 21.3, 20.1.

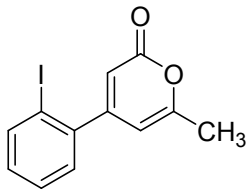
4-(3,5-Dichlorophenyl)-6-methyl-2H-pyran-2-one (2v)



Product **2v** was obtained as a yellow solid in 67% yield (51 mg) following the general procedure, mp 197-199 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 1.6 Hz, 1H), 7.41 (d, J = 1.7 Hz, 2H), 6.29 (s, 1H), 6.20 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz,

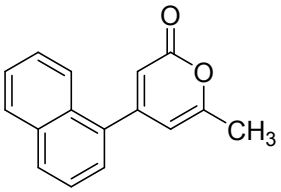
$CDCl_3$) δ 163.0, 162.6, 152.8, 138.9, 136.0, 130.3, 125.2, 109.3, 102.8, 20.2; HRMS (ESI) calcd. for $C_{12}H_8{}^{35}Cl_2O_2Na$ $[M+Na]^+$: 276.9794, found: 276.9796.

4-(2-Iiodophenyl)-6-methyl-2H-pyran-2-one (2w)



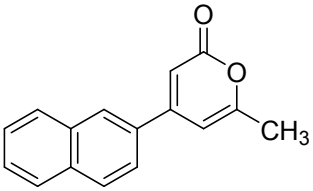
Product **2w** was obtained as a pale-red solid in 62% yield (58mg) following the general procedure, mp 66-67 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.9 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.21 (dd, J = 7.6, 1.3 Hz, 1H), 7.09 (td, J = 8.0,1.4 Hz, 1H), 6.09 (s, 1H), 6.03 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 161.6, 159.1, 142.1, 140.0, 130.6, 128.8, 128.5, 112.0, 106.1, 95.0, 20.1; HRMS (ESI) calcd. for $C_{12}H_9IO_2Na$ $[M+Na]^+$: 334.9539, found: 334.9543.

6-Methyl-4-(naphthalen-1-yl)-2H-pyran-2-one (2x)



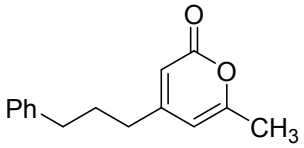
Product **2x** was obtained as a pale-yellow solid in 65% yield (46 mg) following the general procedure, mp 113-115 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.91 (m, 3H), 7.56-7.50 (m, 3H), 7.42 (dd, J = 7.1, 1.0 Hz, 1H), 6.31 (s, 1H), 6.21 (d, J = 0.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 161.5, 156.9, 135.3, 133.7, 123.0, 129.9, 128.7, 127.0, 126.5, 125.9, 125.3, 124.9, 112.1, 106.8, 20.1; HRMS (ESI) calcd. for $C_{16}H_{12}O_2Na$ $[M+Na]^+$: 259.0730, found: 259.0732.

6-Methyl-4-(naphthalen-2-yl)-2H-pyran-2-one (2y)



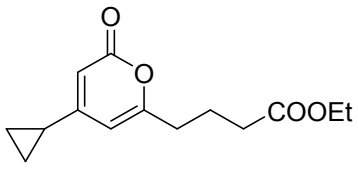
Product **2y** was obtained as a pale-yellow solid in 67% yield (48 mg) following the general procedure, mp 150-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.93-7.87 (m, 3H), 7.64 (dd, J = 8.5, 1.3 Hz, 1H), 7.58-7.54 (m, 2H), 6.48 (s, 1H), 6.44 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 162.6, 155.3, 134.2, 133.1, 133.0, 129.1, 128.7, 127.8, 127.6, 127.0, 126.8, 123.5, 108.4, 103.5, 20.2; HRMS (ESI) calcd. for $C_{16}H_{12}O_2Na$ $[M+Na]^+$: 259.0730, found: 259.0734.

6-Methyl-4-(3-phenylpropyl)-2H-pyran-2-one (2z) [S4]



Product **2z** was obtained as yellow oil in 64% yield (44 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, J = 7.4 Hz, 2H), 7.21-7.15 (m, 3H), 5.94 (s, 1H), 5.83 (s, 1H), 2.65 (t, J = 7.6 Hz, 2H), 2.37 (t, J = 7.6 Hz, 2H), 2.20 (s, 3H), 1.91-1.86 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 161.5, 160.0, 141.2, 128.5, 128.4, 126.1, 109.8, 105.5, 35.1, 34.6, 29.6, 19.9.

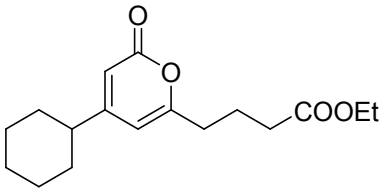
Ethyl 4-(4-cyclopropyl-2-oxo-2H-pyran-6-yl)butanoate (2aa)



Product **2aa** was obtained as yellow oil in 50% yield (38 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (s, 1H), 5.61 (s, 1H), 4.13-4.09 (m, 2H), 2.48 (t, J = 7.3 Hz, 2H), 2.33 (td, J = 7.3, 2.3 Hz, 2H), 1.97-1.94 (m, 2H), 1.66-

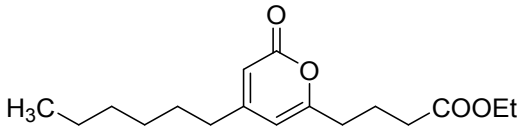
1.63 (m, 1H), 1.26-1.22 (m, 3H), 1.07-1.05 (m, 2H), 0.80-0.79 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 163.9, 163.0, 162.8, 106.7, 102.1, 60.5, 33.2, 33.0, 22.1, 15.4, 14.2, 10.0; HRMS (ESI) calcd. for $C_{14}H_{18}O_4Na$ $[M+Na]^+$: 273.1097, found: 273.1101.

Ethyl 4-(4-cyclohexyl-2-oxo-2H-pyran-6-yl)butanoate (2ab)



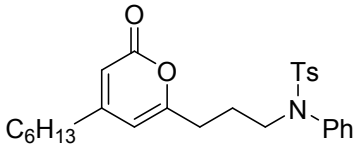
Product **2ab** was obtained as yellow oil in 54% yield (47 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (s, 1H), 5.87 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 2.48 (t, J = 7.5 Hz, 2H), 2.32 (t, J = 7.3 Hz, 2H), 2.23-2.18 (m, 1H), 1.97-1.92 (m, 2H), 1.82-1.77 (m, 4H), 1.70 (d, J = 13.1 Hz, 1H), 1.33-1.17 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 164.7, 163.7, 163.6, 108.4, 104.3, 60.5, 43.7, 33.2, 32.9, 31.7, 26.1, 25.7, 22.1, 14.2; HRMS (ESI) calcd. for $C_{17}H_{24}O_4Na$ $[M+Na]^+$: 315.1567, found: 315.1569.

Ethyl 4-(4-hexyl-2-oxo-2H-pyran-6-yl)butanoate (2ac)



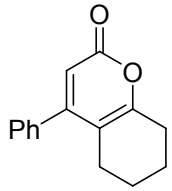
Product **2ac** was obtained as yellow oil in 60% yield (53 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.93 (s, 1H), 5.85 (s, 1H), 4.13 (q, J = 14.2, 7.1 Hz, 2H), 2.51 (t, J = 7.6 Hz, 2H), 2.34 (t, J = 7.4 Hz, 4H), 2.01-1.96 (m, 2H), 1.55-1.51 (m, 2H), 1.32-1.23 (m, 9H), 0.88 (t, J = 5.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 163.7, 163.3, 160.3, 110.1, 105.3, 60.5, 35.3, 33.2, 32.9, 31.5, 28.7, 28.1, 22.5, 22.1, 14.2, 14.0; HRMS (ESI) calcd. for $C_{17}H_{26}O_4Na$ $[M+Na]^+$: 317.1723, found: 317,1728.

***N*-(3-(4-hexyl-2-oxo-2H-pyran-6-yl)propyl)-4-methyl-N-phenylbenzenesulfonamide (2ad)**



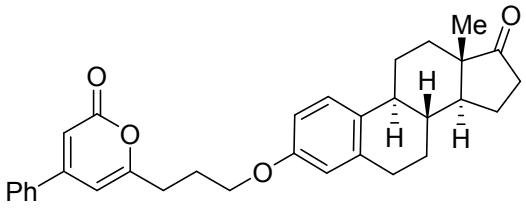
Product **2ad** was obtained as yellow oil in 60% yield (84 mg) following the general procedure; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.2 Hz, 2H), 7.30-7.28 (m, 3H), 7.21 (d, J = 8.2 Hz, 2H), 7.02-7.01 (m, 2H), 5.91 (s, 1H), 5.88 (s, 1H), 3.55 (t, J = 6.4 Hz, 2H), 2.54 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 2.33 (t, J = 7.7 Hz, 2H), 1.78-1.74 (m, 2H), 1.54-1.50 (m, 2H), 1.32-1.27 (m, 6H), 0.87 (t, J = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4, 163.2, 160.6, 143.6, 138.9, 134.9, 129.4, 129.2, 128.6, 128.1, 127.7, 110.0, 105.9, 49.3, 35.3, 31.5, 30.4, 28.7, 28.0, 25.3, 22.5, 21.5, 14.0; HRMS (ESI) calcd. for $C_{27}H_{33}NO_4SNa$ $[M+Na]^+$: 490.2023, found: 490.2025.

4-Phenyl-5,6,7,8-tetrahydro-2H-chromen-2-one (2ae)



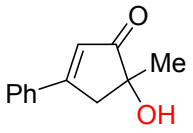
Product **2ae** was obtained as a colorless solid in 53% yield (36 mg) following the general procedure, mp 89-90 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.38 (m, 3H), 7.25-7.23 (m, 2H), 6.04 (s, 1H), 2.57 (td, J = 6.5, 0.6 Hz, 2H), 2.20 (tt, J = 6.1, 1.6 Hz, 2H), 1.82-1.78 (m, 2H), 1.64-1.60 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6, 159.9, 159.4, 136.7, 129.0, 128.5, 127.6, 112.1, 112.1, 27.9, 25.0, 22.4, 21.7; HRMS (ESI) calcd. for $C_{15}H_{14}O_2Na$ $[M+Na]^+$: 249.0886, found: 249.0890.

6-(3-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)propyl)-4-phenyl-2H-pyran-2-one (2af)



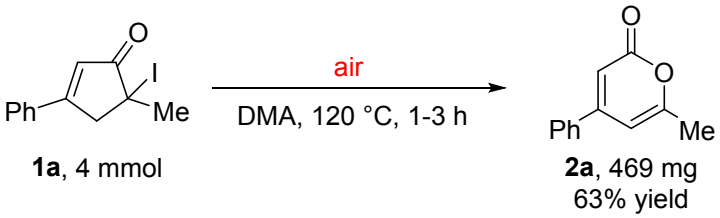
Product **2af** was obtained as a colorless solid in 63% yield (91 mg) following the general procedure, mp 137-139 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53-7.44 (m, 5H), 7.19 (d, J = 8.5 Hz, 1H), 6.71-6.70 (m, 1H), 6.63 (s, 1H), 6.37 (s, 1H), 6.33 (s, 1H), 4.01 (t, J = 5.6 Hz, 2H), 2.89-2.86 (m, 2H), 2.78 (t, J = 7.4 Hz, 2H), 2.52-2.48 (m, 1H), 2.41-2.35 (m, 1H), 2.26-1.94 (m, 8H), 1.66-1.41 (m, 5H), 0.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.9, 164.8, 163.4, 156.8, 155.4, 137.9, 135.8, 132.3, 130.6, 129.2, 126.7, 126.4, 114.5, 112.2, 108.6, 103.4, 66.3, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 30.8, 29.7, 26.7, 26.6, 25.9, 21.6, 13.9; HRMS (ESI) calcd. for $C_{32}H_{34}O_4Na$ $[M+Na]^+$: 505.2349, found: 505.2353.

5-Hydroxy-5-methyl-3-phenylcyclopent-2-en-1-one (3a)[S1]



Product **3a** was obtained as a pale-yellow solid, mp 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.52-7.44 (m, 3H), 6.55 (t, J = 1.6 Hz, 1H), 3.20 (dd, J= 17.7, 1.7 Hz, 1H), 3.09 (dd, J = 17.7, 1.6 Hz, 1H), 2.71 (s, 1H), 1.44 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 171.1,133.6, 131.8, 129.0, 127.1, 123.0, 75.7, 44.2, 25.7; HRMS (ESI) calcd. for $C_{12}H_{13}O_2$ $[M+H]^+$: 189.0910, found 189.0921.

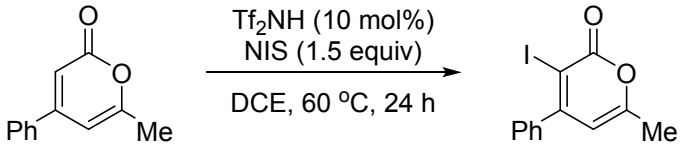
4. Scale-up Experiments and Synthetic Applications



1a, 4 mmol

2a, 469 mg
63% yield

The solution of α-Iodocyclopentenones **1a** (4 mmol) in DMA (40 mL) was stirred at 120 °C for 3 h under an air atmosphere. Upon completion, the reaction mixture was cooled to room temperature, then saturated sodium thiosulfate aqueous solution was added and the resulting mixture was extracted with ethyl acetate (20 mLx3), the combined organic layers were washed with brine, dried over $MgSO_4$, concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1) to give the desired α-pyrone product **2a** in 63% yield (469 mg).

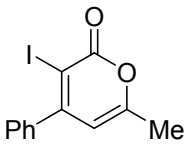


2a

4, 76% yield

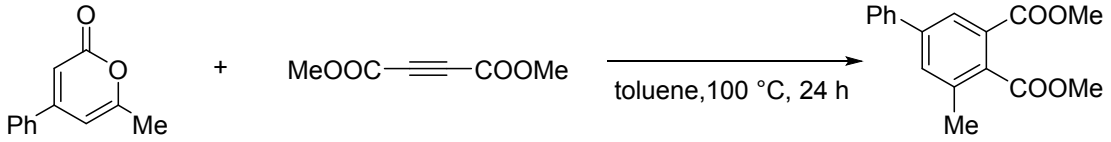
To a solution of **2a** (112 mg, 0.6 mmol) and *N*-iodosuccinimide (202 mg, 0.9 mmol) in DCE (6 mL) was added Tf_2NH (17 mg, 0.06 mmol), the reaction mixture was stirred at 60 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1) to give the product **4** (142 mg, 76% yield).

3-Iodo-6-methyl-4-phenyl-2H-pyran-2-one (4)



Colorless solid, mp 156-158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.44 (m, 3H), 7.36-7.35 (m, 2H), 6.02 (d, J = 0.8 Hz, 1H), 2.26 (d, J = 0.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 161.0, 160.6, 140.6, 129.5, 128.6, 127.5, 106.6, 84.8, 19.4; HRMS (ESI) calcd. for $C_{12}H_9IO_2Na$ $[M+Na]^+$: 334.9539, found: 334.9542.

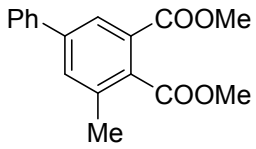
Synthetic applications of 2a and 4:



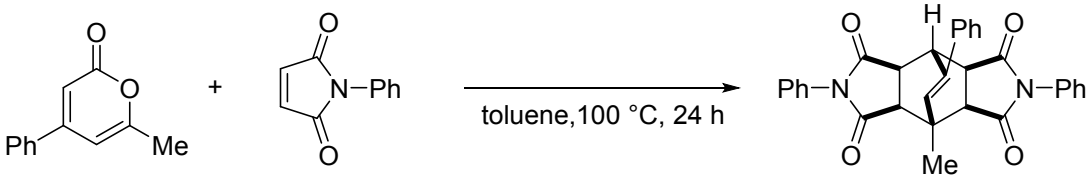
2a **5**, 80% yield

Diels-Alder reaction: To a solution of **2a** (112 mg, 0.6 mmol) in toluene (6 mL) was added dimethyl acetylenedicarboxylate (171 mg, 1.2 mmol), the reaction mixture was stirred at 100 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 5:1) to give the product **5** (136 mg, 80% yield).

Dimethyl 5-methyl-[1,1'-biphenyl]-3,4-dicarboxylate (5) [S7]



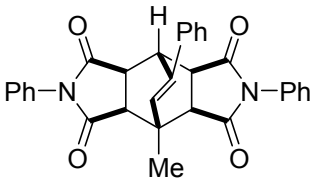
Colorless solid, mp 102-103 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 1.4 Hz, 1H), 7.62-7.59 (m, 3H), 7.47-7.44 (m, 2H) , 7.40-7.37 (m, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 166.4, 142.2, 139.4, 136.2, 133.9, 133.0, 129.0, 128.5, 128.1, 127.2, 126.2, 52.6, 19.3.



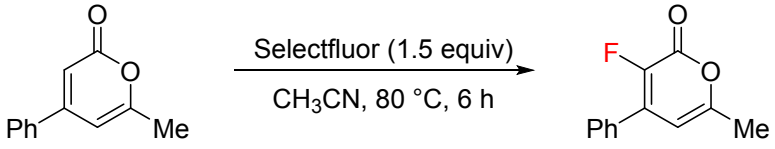
2a **6**, 92% yield

Diels-Alder reaction: To a solution of **2a** (112 mg, 0.6 mmol) in toluene (6 mL) was added *N*-Phenylmaleimide (260 mg, 1.5 mmol), the reaction mixture was stirred at 100 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure, the resulting residuewas purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 5:1 to 1:1) to give the product **6** (270 mg, 92% yield).

4-methyl-2,6,9-triphenyl-3a,4,4a,7a,8,8a-hexahydro-4,8-ethenopyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone (6) [S8,S9]



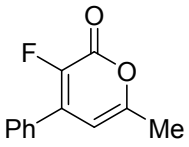
Colorless solid, mp 248-249 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43-7.26 (m, 11H), 7.02-7.01 (m, 4H), 6.25 (d, J = 0.8 Hz, 1H), 4.44 (t, J = 2.9 Hz, 1H), 3.30 (dd, J = 8.2, 3.1 Hz, 2H), 2.93 (d, J = 8.2 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.3, 174.7, 142.1, 136.2, 131.4, 129.2, 129.0, 128.9, 128.8, 128.3, 126.3, 125.6, 48.6, 44.5, 41.7, 37.1, 19.9; HRMS (ESI) calcd. for $C_{31}H_{24}N_2O_4Na$ $[M+Na]^+$: 511.1628, found: 511.1633.



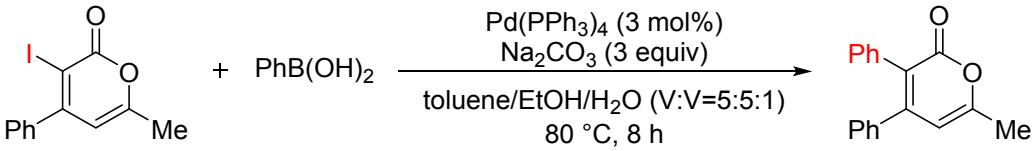
2a **7**, 37% yield

To a solution of **2a** (112 mg, 0.6 mmol) in CH_3CN (6 mL) was added selectfluor (319 mg, 0.9 mmol), the reaction mixture was stirred at 80 °C for 6 h. Upon completion, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1) to give the product **7** (45 mg, 37% yield).

3-fluoro-6-methyl-4-phenyl-2H-pyran-2-one (7)

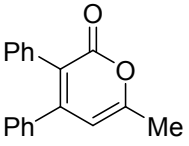


Colorless solid, mp 137-138 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.50-7.45 (m, 3H), 6.11 (dd, J = 4.7, 0.8 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7 (d, J = 28.9 Hz), 156.3 (d, J = 7.3 Hz), 142.1 (d, J = 254.3 Hz), 134.8 (d, J = 8.8 Hz), 131.1 (d, J = 2.6 Hz), 130.3, 128.9, 128.5 (d, J = 4.4 Hz), 103.9, 19.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -143.54 (d, J = 4.0 Hz); HRMS (ESI) calcd. for $C_{12}H_9FO_2Na$ $[M+Na]^+$: 227.0479, found: 227.0481.

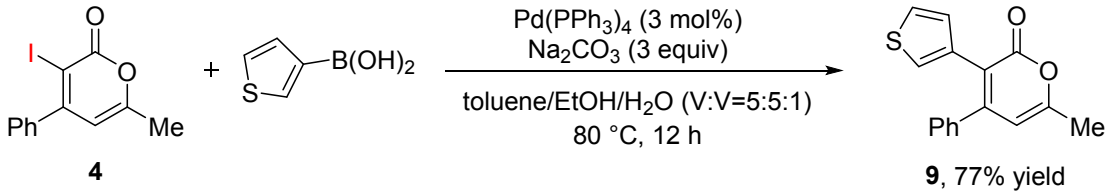


Suzuki-Miyaura-coupling: The 3-iodo-6-methyl-4-phenyl-2H-pyran-2-one **4** (94 mg, 0.3 mmol), $PhB(OH)_2$ (55 mg, 0.45 mmol), $Pd(PPh_3)_4$ (11 mg, 0.009 mmol) and Na_2CO_3 (95 mg, 0.9 mmol) were dissolved in mixed solution (5.5 ml, toluene: EtOH: H_2O = 2.5: 2.5: 0.5), the reaction mixture was stirred at 80 °C for 8 h. Upon completion, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1) to give the product **8** (45 mg, 80% yield).

6-Methyl-3,4-diphenyl-2H-pyran-2-one (8) [S5]



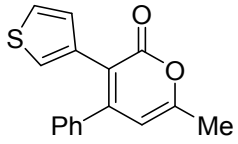
Colorless solid, mp 111-113 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.21 (m, 6H), 7.17-7.15 (m, 2H), 7.12-7.10 (m, 2H), 6.20 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 160.1, 152.7, 137.6, 133.9, 130.9, 128.7, 128.3, 128.0, 127.6, 122.0, 107.1, 19.9.



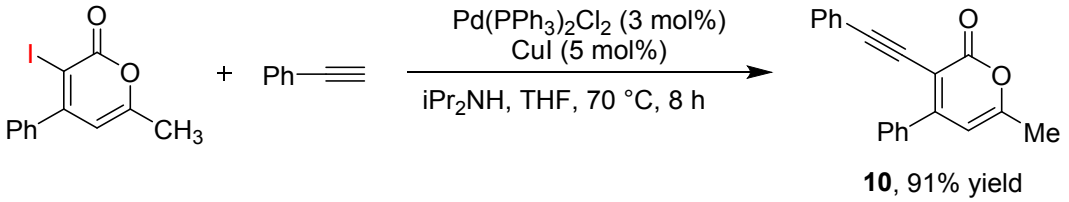
4 **9**, 77% yield

Suzuki-Miyaura-coupling: The 3-iodo-6-methyl-4-phenyl-2H-pyran-2-one **4** (94 mg, 0.3 mmol), 3-thiopheneboronic acid (58 mg, 0.45 mmol), $Pd(PPh_3)_4$ (11 mg, 0.009 mmol) and Na_2CO_3 (95 mg, 0.9 mmol) were dissolved in mixed solution (5.5 ml, toluene: EtOH: H_2O = 2.5: 2.5: 0.5), the reaction mixture was stirred at 80 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1) to give the product **9** (62 mg, 77% yield).

6-Methyl-4-phenyl-3-(thiophen-3-yl)-2H-pyran-2-one (9):

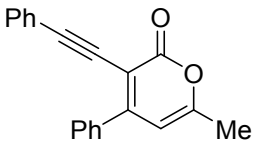


Red solid, mp 147-149 °C; ^{1}H NMR (600 MHz, CDCl3) δ 7.32-7.26 (m, 3H), 7.23-7.22 (m, 1H), 7.23-7.22 (m, 1H), 7.15-7.14 (m, 2H), 7.11-7.09 (m, 1H), 6.76 (dd, J = 5.0, 1.1 Hz, 1H), 6.13 (d, J = 0.7 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, CDCl3) δ 163.1, 159.6, 152.4, 138.0, 133.3, 129.5, 128.9, 128.5, 128.3, 126.7, 124.0, 117.1, 107.2, 19.9; HRMS (ESI) calcd. for $C_{16}H_{12}O_2SNa$ $[M+Na]^+$: 291.0450, found: 291.0454.



Sonogashira-coupling: The 3-iodo-6-methyl-4-phenyl-2H-pyran-2-one **4** (94 mg, 0.3 mmol), phenylacetylene (58 mg, 0.45 mmol), $PdCl_2(PPh_3)_2$ (3 mol%),CuI (5 mol%) and diisopropylamine (0.5 ml) were dissolved in THF (5 ml) under N_2, the reaction mixture was stirred at 70 °C for 8 h. Upon completion, the reaction mixture was cooled to room temperature and quenched by NH_4Cl (saturated aq.). The mixture was diluted with 10 mL water and extracted with EtOAc (10 mLx3). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1) to give the product **10** (78 mg, 91% yield).

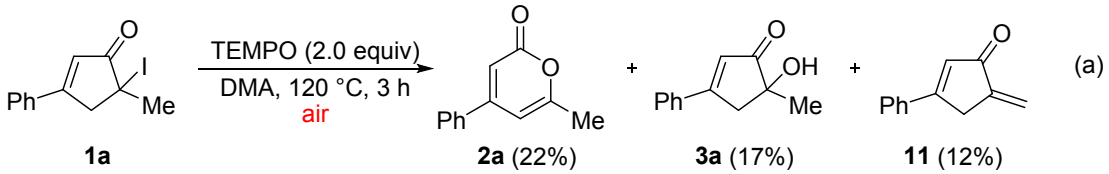
6-Methyl-4-phenyl-3-(phenylethynyl)-2H-pyran-2-one (10)



Yellow solid, mp 168-170 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.75 (m, 2H), 7.52-7.50 (m, 3H), 7.41-7.39 (m, 2H), 7.31-7.28 (m, 3H), 6.24 (d, J = 0.8 Hz, 1H), 2.36 (d, J = 0.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 160.6, 156.6, 136.5, 131.6, 130.2, 128.6, 128.4, 128.4, 128.3, 122.9, 106.2, 105.7, 97.3, 83.8, 20.2; HRMS (ESI) calcd. for $C_{20}H_{14}O_2Na$ $[M+Na]^+$: 309.0886, found: 309.0891.

5. Control Experiments:

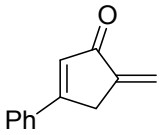
*Scheme S1a: Control Experiment of **1a** with **TEMPO** under the atmosphere of air:*



1a **2a** (22%) **3a** (17%) **11** (12%) (a)

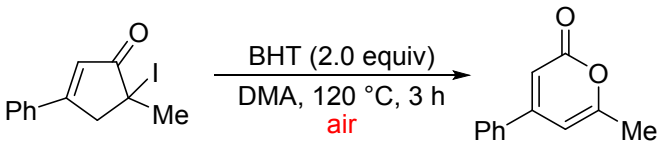
The solution of α-iodocyclopentenones **1a** (0.3 mmol) and **TEMPO** (0.6 mmol) in DMA (3 mL) was stirred at 120 °C for 3 h under an air atmosphere. Upon completion, the reaction mixture was cooled to room temperature, then sodium thiosulfate aqueous solution was added and the resulting mixture was extracted with ethyl acetate (10 mLx3), the combined organic layers were washed with brine, dried over $MgSO_4$, concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1 to 5:1) to give the desired α-pyrone products **2a** in 22% yield, along with **3a** and compound **11** in 17% and 12% yields, respectively.

5-methylene-3-phenylcyclopent-2-en-1-one (11)



Product **11** was obtained as a white solid, mp 125-127 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.67 (m, 2H), 7.48-7.45 (m, 3H), 6.79 (s, 1H), 6.16 (s, 1H), 5.51 (s, 1H), 3.65 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 168.0, 142.3, 133.5, 131.5, 129.1, 129.0, 126.9, 116.6, 34.1; HRMS (ESI) calcd. for $C_{12}H_{11}O$ $[M+H]^+$: 171.0804, found 171.0813.

*Scheme S1b: Control Experiment of **1a** with **BHT** under the atmosphere of air:*

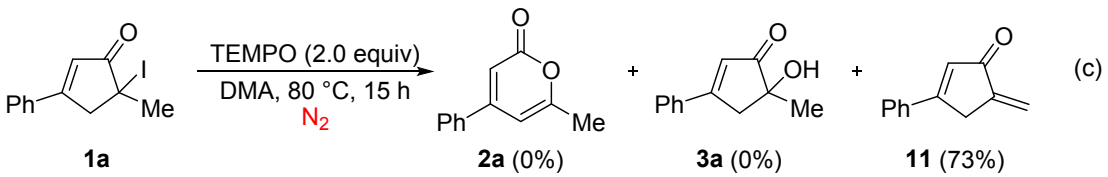


1a **2a** (67%) (b)

The solution of α-iodocyclopentenones **1a** (0.3 mmol) and **BHT** (0.6 mmol) in DMA (3 mL) was stirred at 120 °C for 3 h under an air atmosphere. Upon completion, the

reaction mixture was cooled to room temperature, then sodium thiosulfate aqueous solution was added and the resulting mixture was extracted with ethyl acetate (10 mLx3), the combined organic layers were washed with brine, dried over $MgSO_4$,concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1 to 5:1) to give the desired α-pyrone products **2a** in 67% yield.

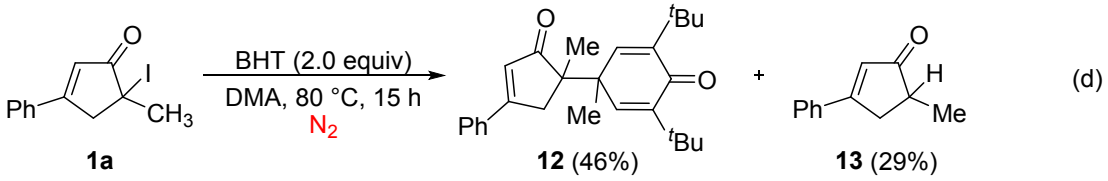
*Scheme S1c: Control Experiment of **1a** with **TEMPO** under the atmosphere of N_2:*



1a **2a** (0%) **3a** (0%) **11** (73%) (c)

The solution of α-iodocyclopentenones **1a** (0.3 mmol) and **TEMPO** (0.6 mmol) in DMA (3 mL) was stirred at 80 °C for 15 h under a N_2 atmosphere. Upon completion, the reaction mixture was cooled to room temperature, then sodium thiosulfate aqueous solution was added and the resulting mixture was extracted with ethyl acetate (10 mLx3), the combined organic layers were washed with brine, dried over $MgSO_4$,concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1 to 5:1) to only give **11** in 73%.

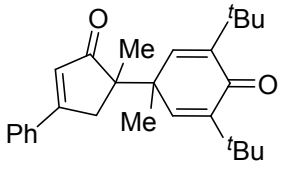
*Scheme S1d: Control Experiment of **1a** with **BHT** under the atmosphere of N_2:*



1a **12** (46%) **13** (29%) (d)

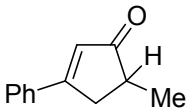
The solution of α-iodocyclopentenones **1a** (0.3 mmol) and **BHT** (0.6 mmol) in DMA (3 mL) was stirred at 80 °C for 15 h under a N_2 atmosphere. Upon completion, the reaction mixture was cooled to room temperature, then sodium thiosulfate aqueous solution was added and the resulting mixture was extracted with ethyl acetate (10 mLx3), the combined organic layers were washed with brine, dried over $MgSO_4$,concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 10:1 to 5:1) to give **12** in 46% yield, and **13** in 29% yield.

2,6-Di-tert-butyl-4-methyl-4-(1-methyl-2-oxo-4-phenylcyclopent-3-en-1-yl)cyclohexa-2,5-dien-1-one (12)



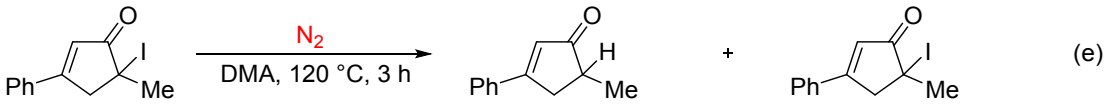
Product **12** was obtained as colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57-7.56 (m, 2H), 7.46-7.41 (m, 3H), 6.89 (s, 1H), 6.48 (s, 1H), 6.39 (d, J =2.9 Hz, 1H), 2.89 (d, J =17.7 Hz, 1H), 2.54 (d, J = 18.1 Hz, 1H), 1.29 (s, 3H), 1.28 (s, 9H), 1.21 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.2, 186.0, 171.4, 148.0, 147.2, 143.9, 143.4, 133.5, 131.5, 129.0, 126.7, 125.7, 52.4, 43.8, 41.0, 35.0, 34.8, 29.6, 29.4, 20.8, 19.9; HRMS (ESI) calcd. for $C_{27}H_{35}O_2$ $[M+H]^+$: 391.2632, found 391.2652.

5-methyl-3-phenylcyclopent-2-en-1-one (13)[S1,S10]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7-7.59 (m, 2H), 7.51-7.43 (m, 3H), 6.54 (t, J = 1.6 Hz, 1H), 3.33-3.26 (ddd, J = 18.4, 7.2, 1.6 Hz,1H), 2.68-2.55 (m, 2H), 1.28 (d, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 172.0, 134.0, 131.2, 128.9, 126.8, 126.2, 40.7, 37.5, 16.6.

*Scheme S1e: Control Experiment of **1a** under the atmosphere of N_2:*



1a **13** (41%) **1a** recovered (45%)

The solution of α-iodocyclopentenones **1a** (0.3 mmol) in DMA (3 mL) was stirred at 120 °C under a N_2 atmosphere. After stirred for 3 h, the reaction mixture was cooled to room temperature, then sodium thiosulfate aqueous solution was added and the resulting mixture was extracted with ethyl acetate (10 mLx3), the combined organic layers were washed with brine, dried over $MgSO_4$, concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel

(eluent: petroleum ether: EtOAc = 10:1 to 5:1) to give **13** in 41% yield, and the recovery of **1a** in 45% yield.

6. ^{1}H and ^{13}C NMR Spectra

Figure S1. ^{1}H and ^{13}C NMR Spectra of 2a

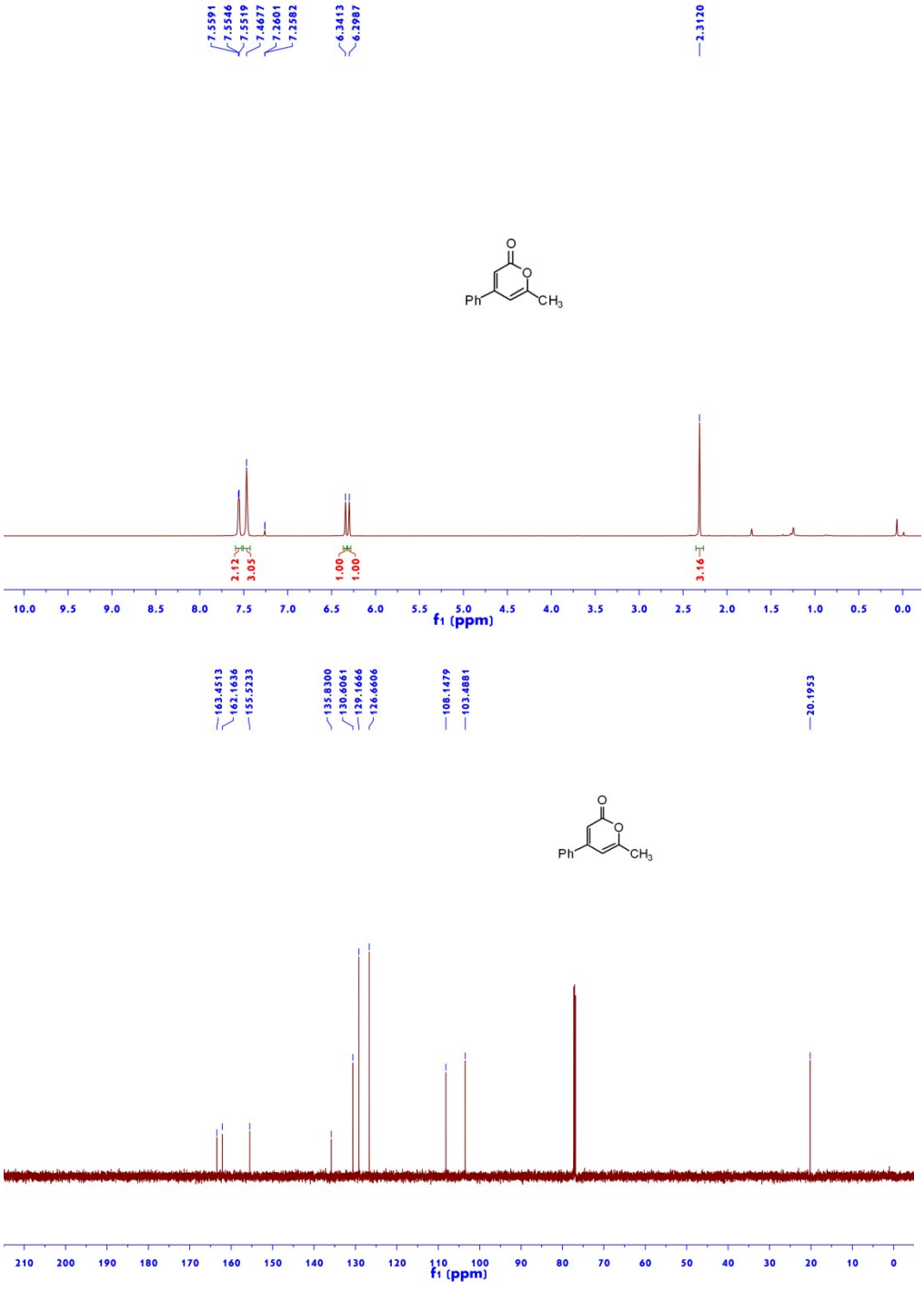


Figure S2. ^{1}H and ^{13}C NMR Spectra of 2b

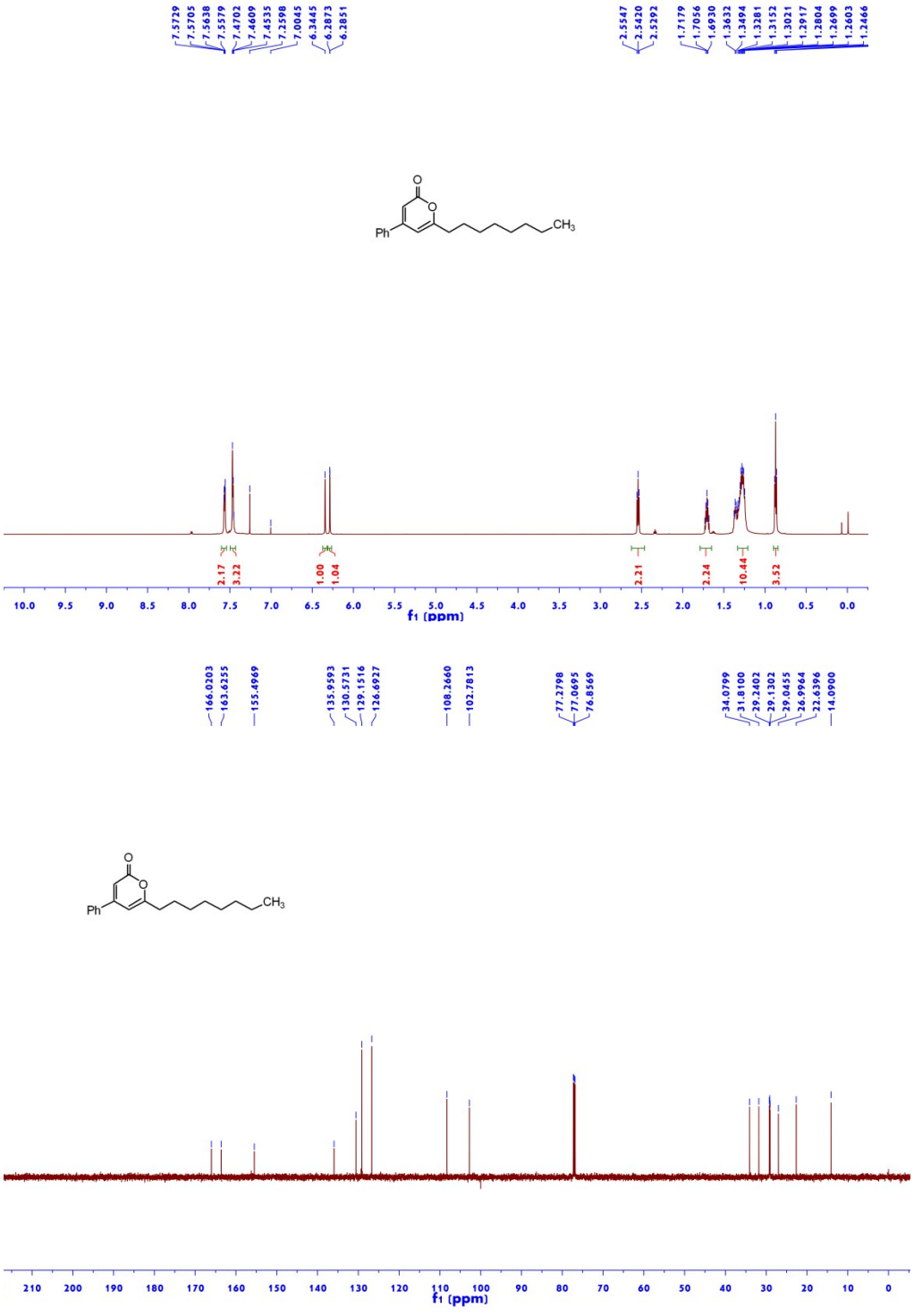


Figure S3. ^{1}H and ^{13}C NMR Spectra of 2c

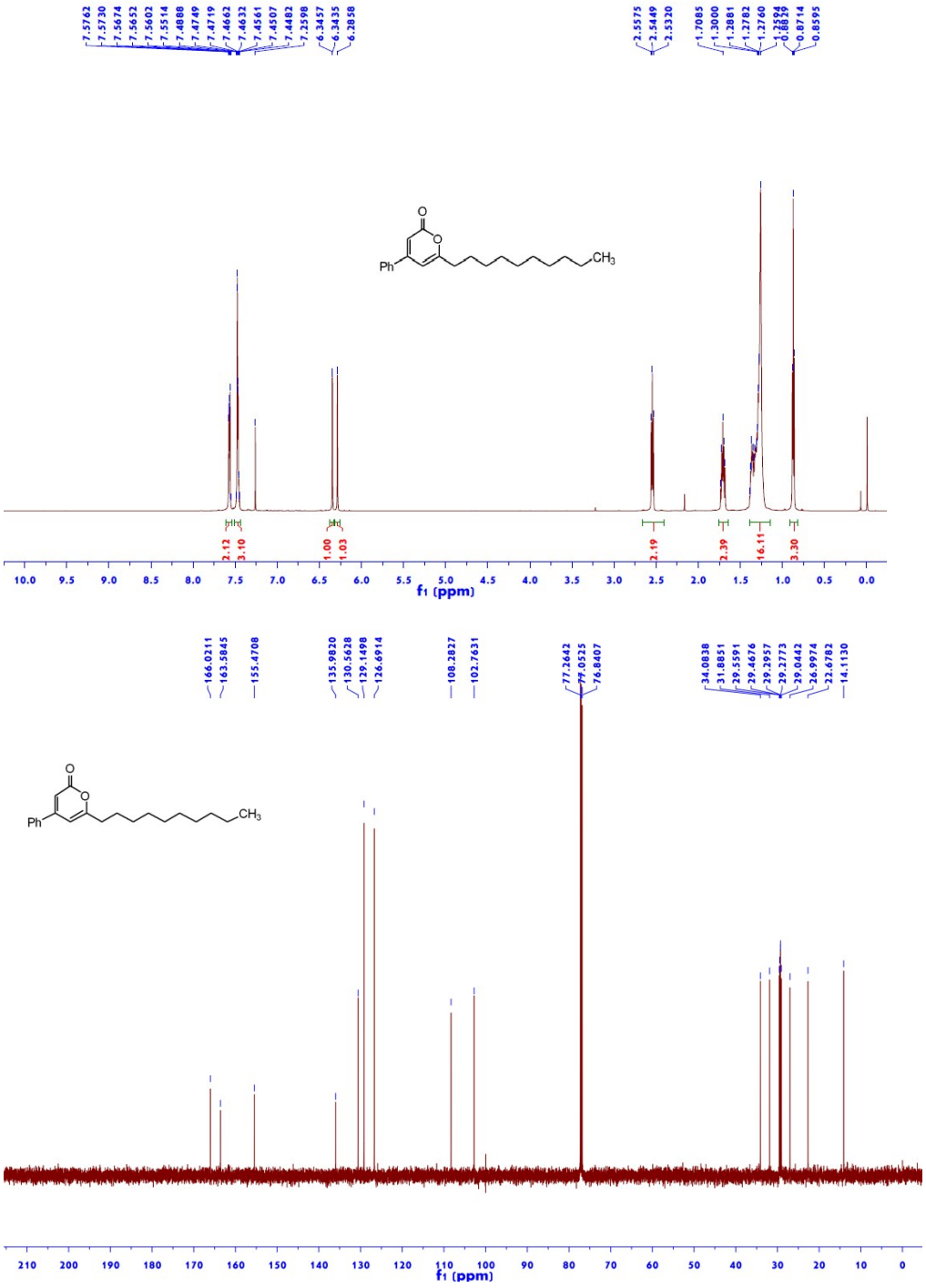


Figure S4. ^{1}H and ^{13}C NMR Spectra of 2d

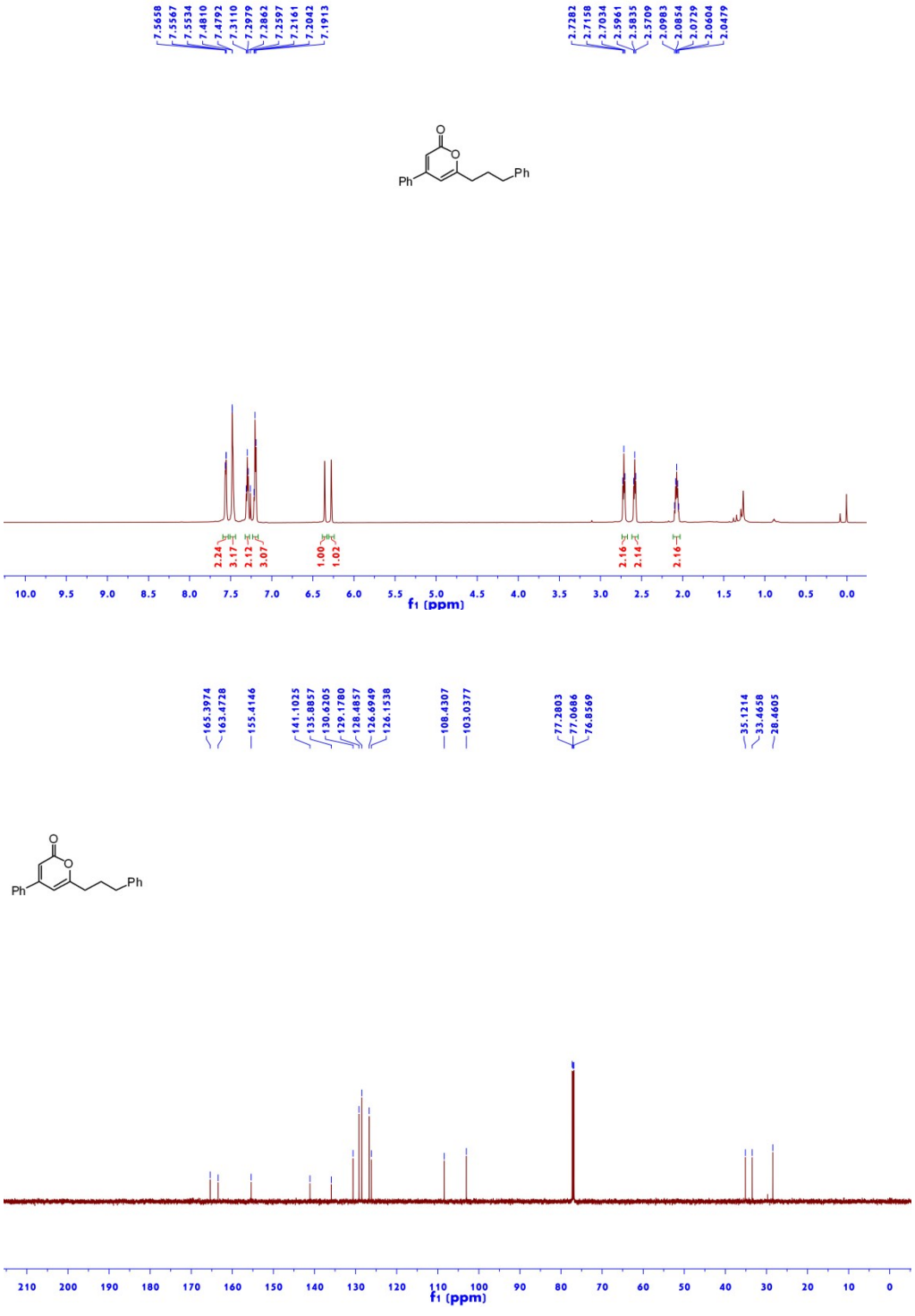


Figure S5. ^{1}H and ^{13}C NMR Spectra of 2e

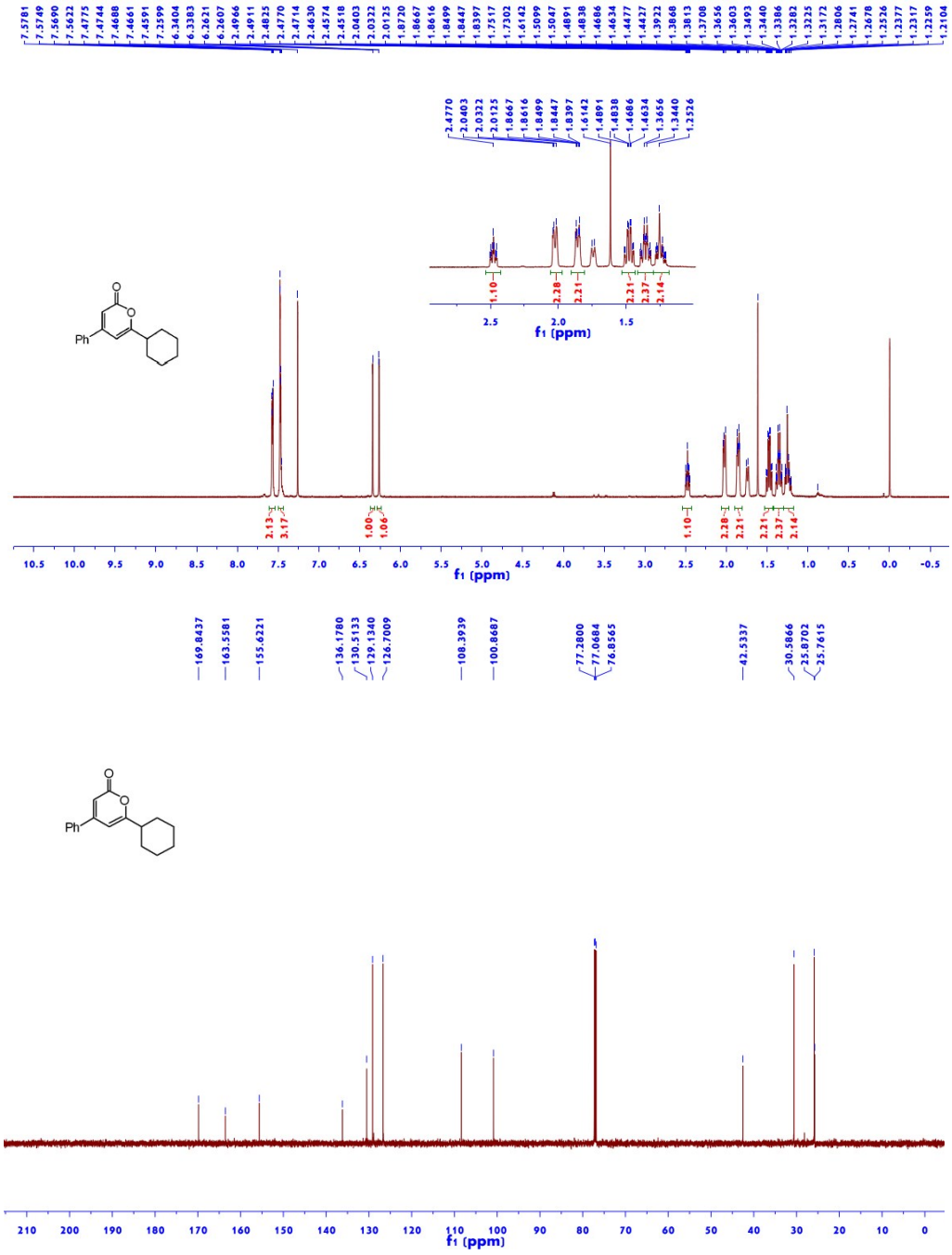


Figure S6. ^{1}H and ^{13}C NMR Spectra of 2f

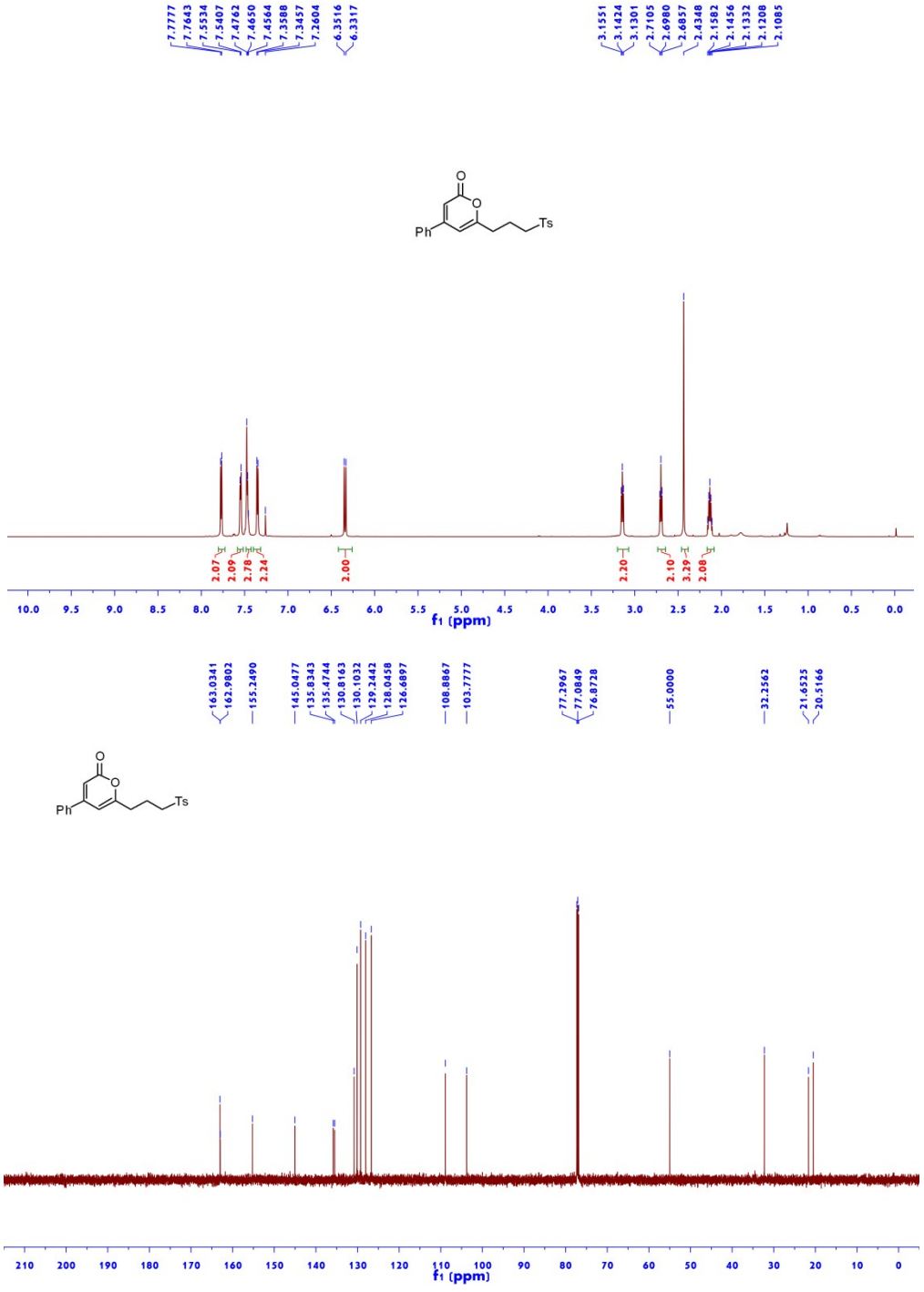


Figure S7. ^{1}H and ^{13}C NMR Spectra of 2g

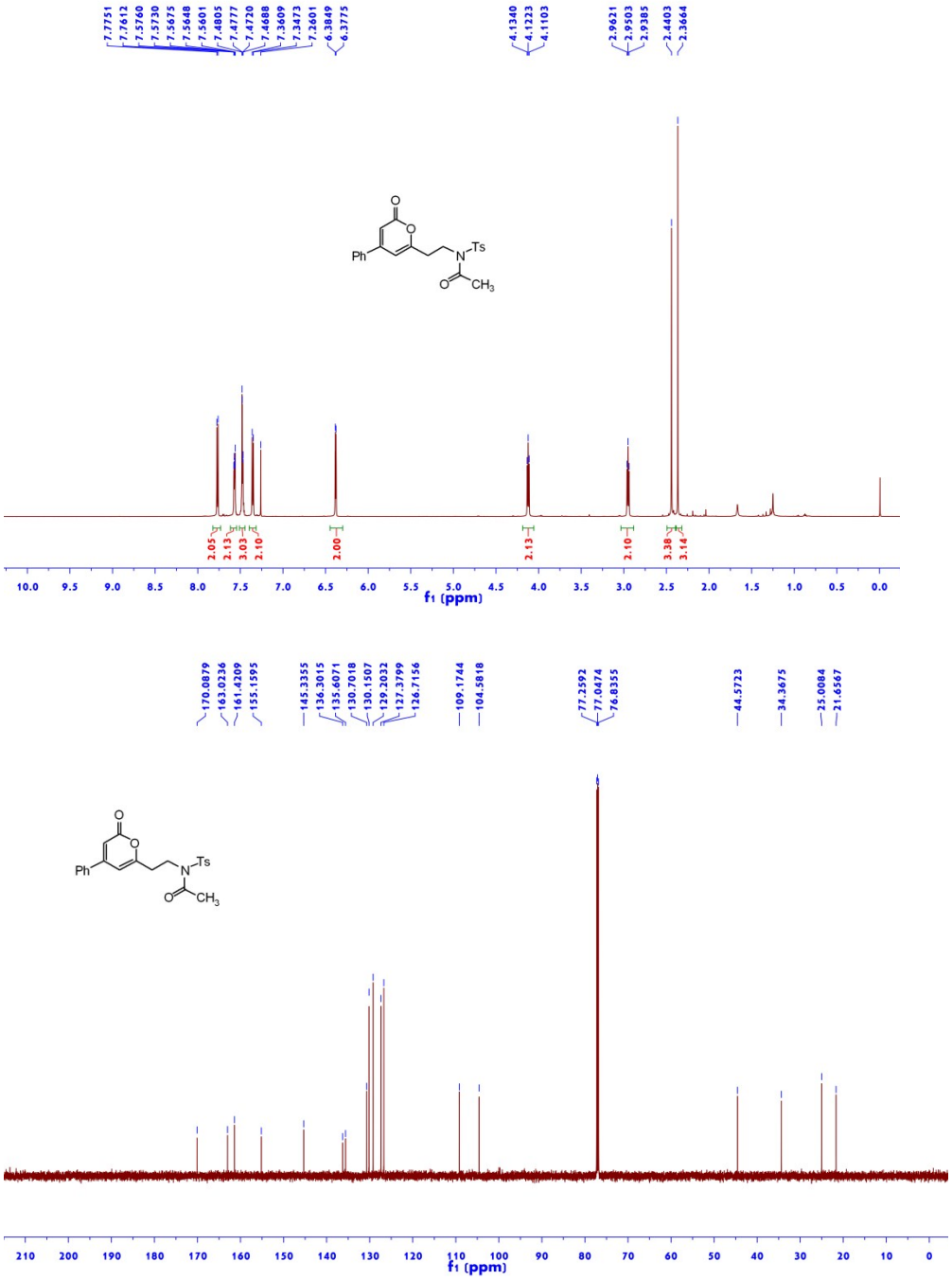


Figure S8. ^{1}H and ^{13}C NMR Spectra of 2h

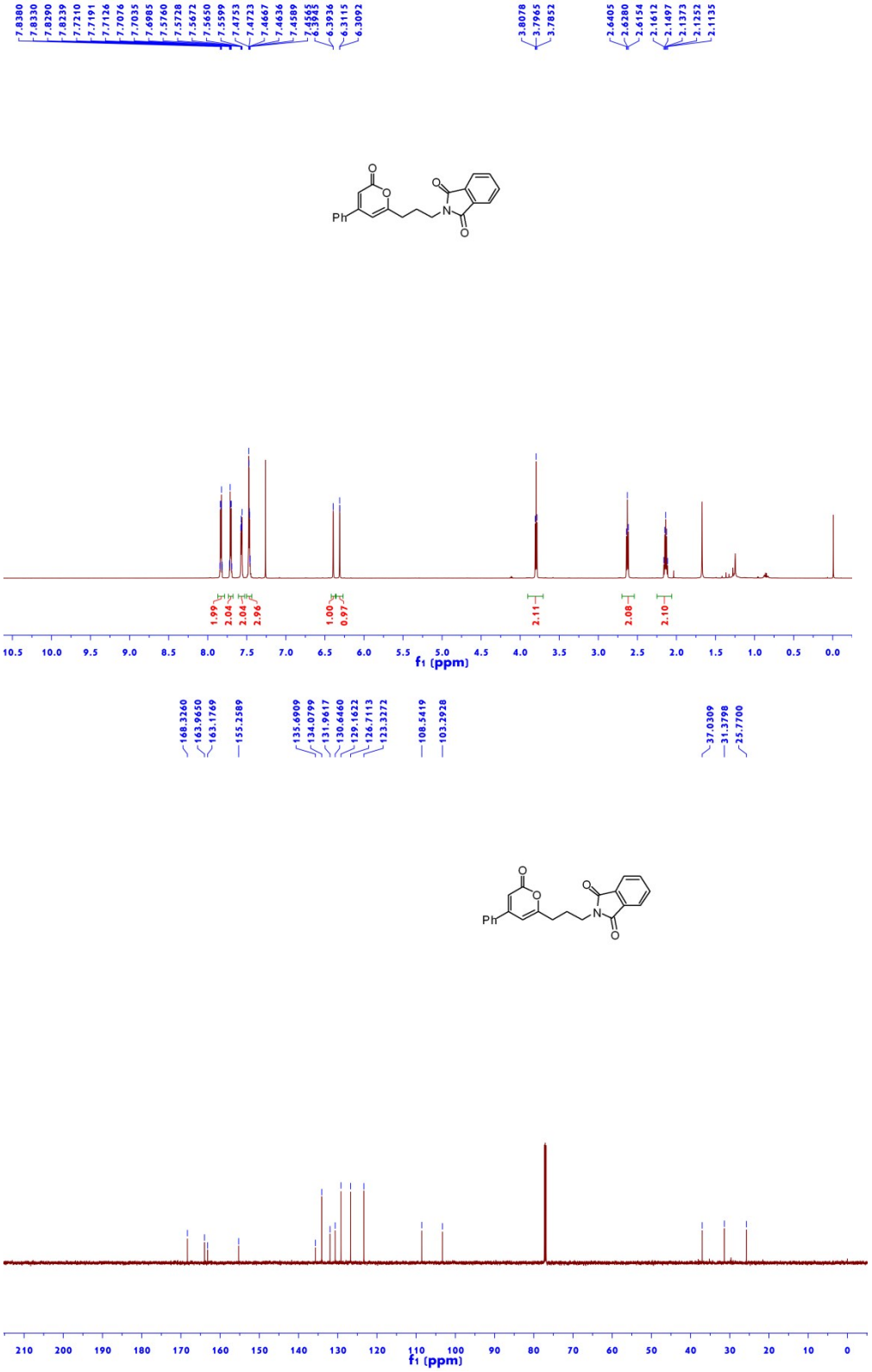


Figure S9. ^{1}H and ^{13}C NMR Spectra of 2i

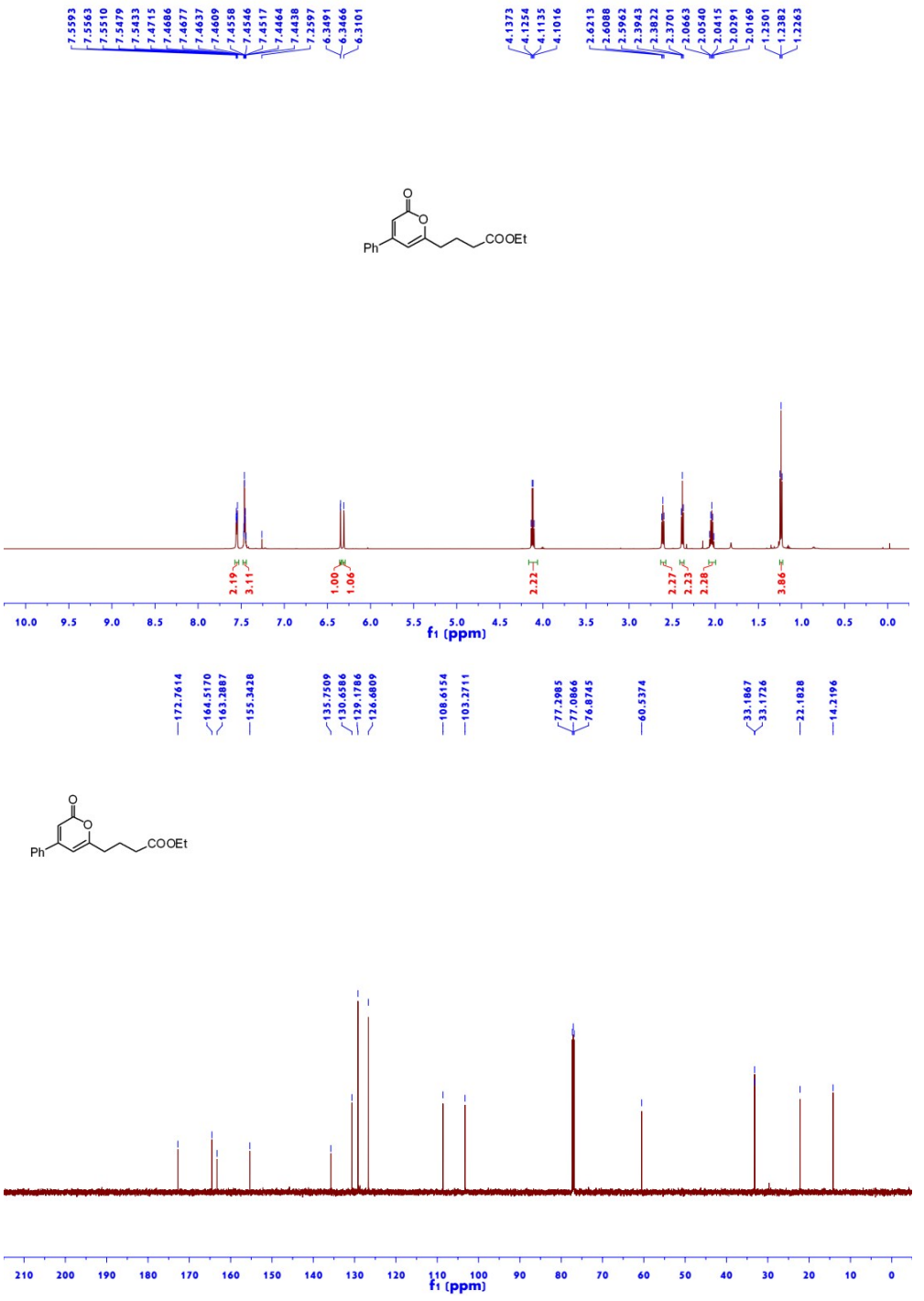


Figure S10. ^{1}H and ^{13}C NMR Spectra of 2j

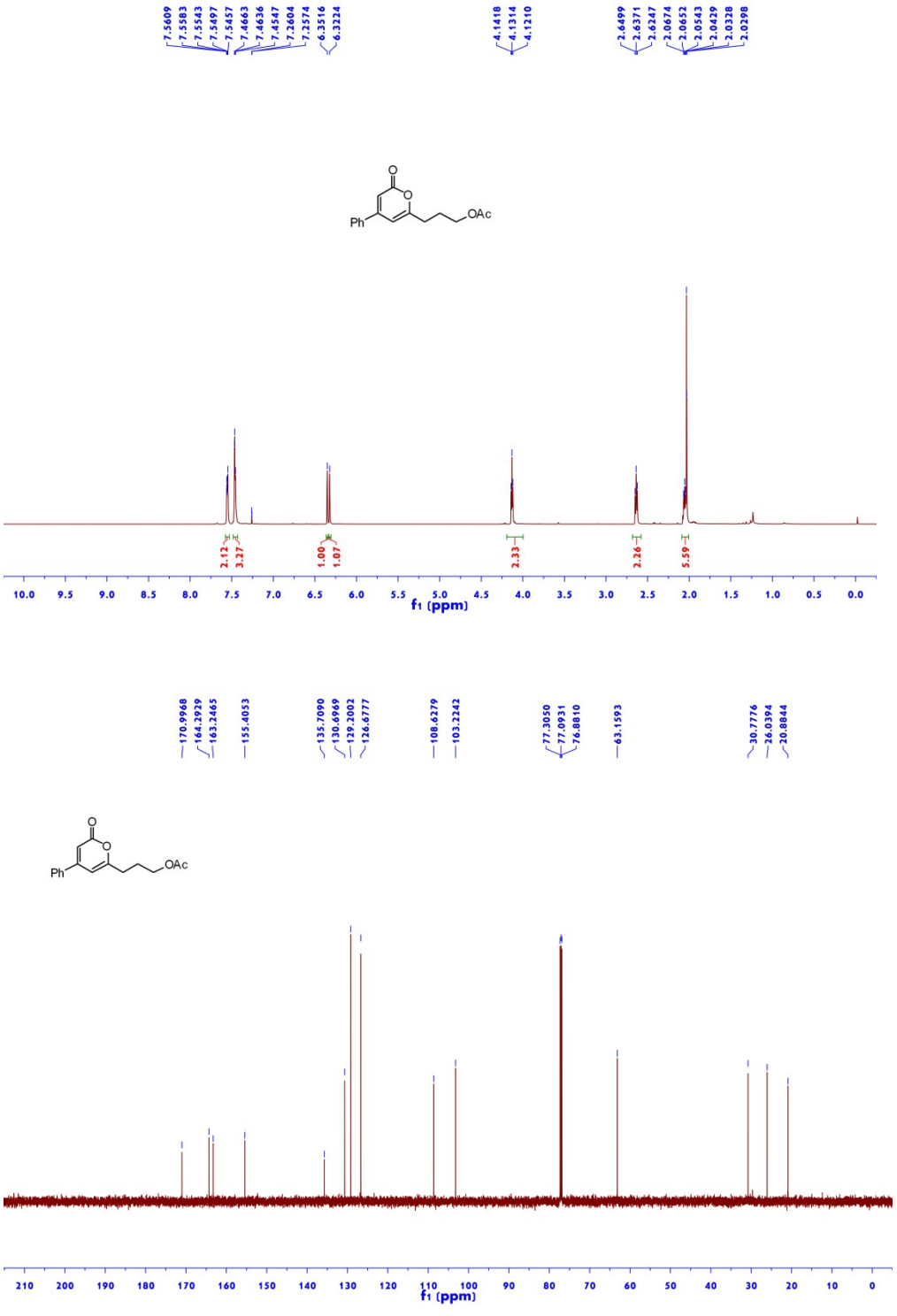


Figure S11. ^{1}H and ^{13}C NMR Spectra of 2k

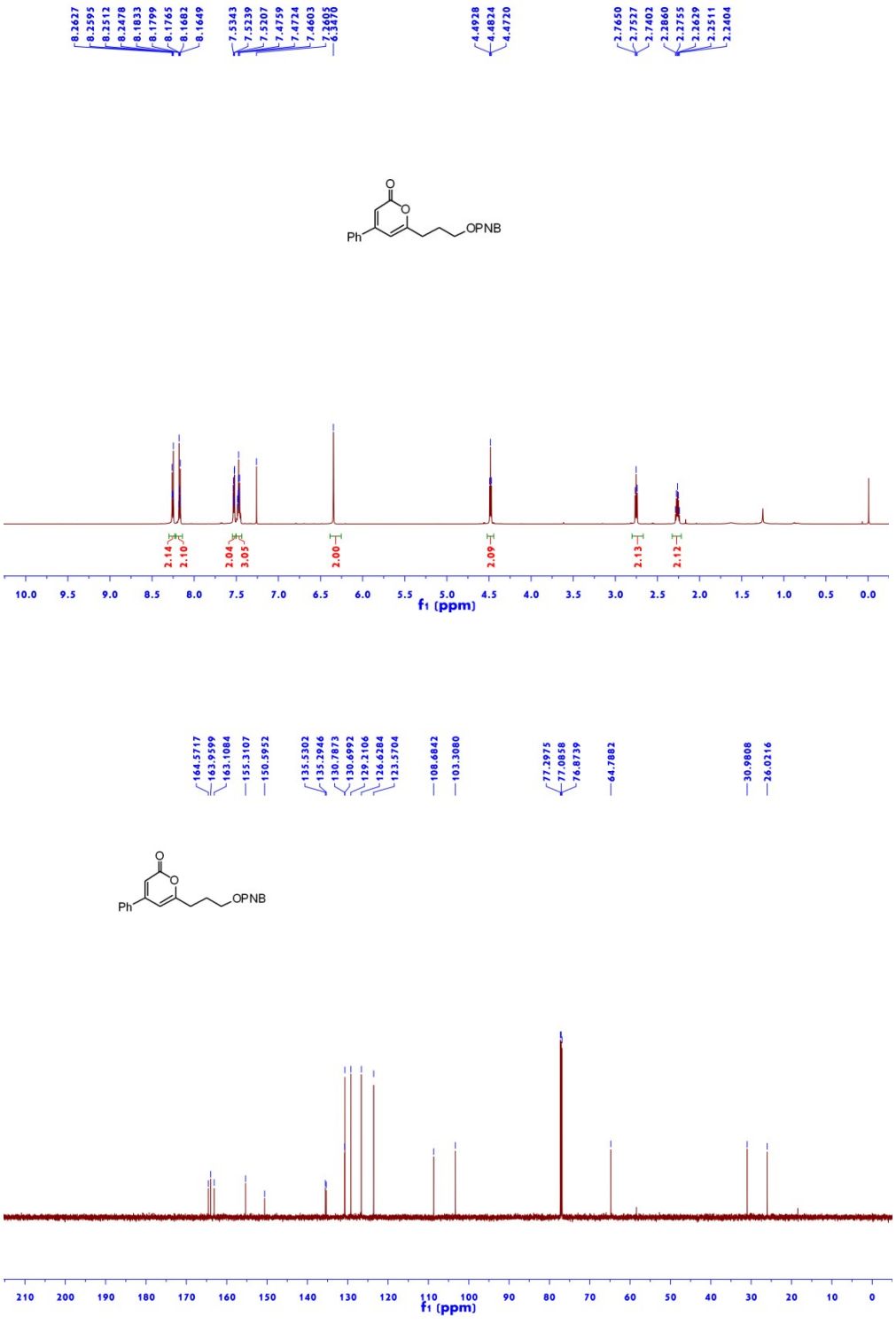


Figure S12. ^{1}H and ^{13}C NMR Spectra of 2l

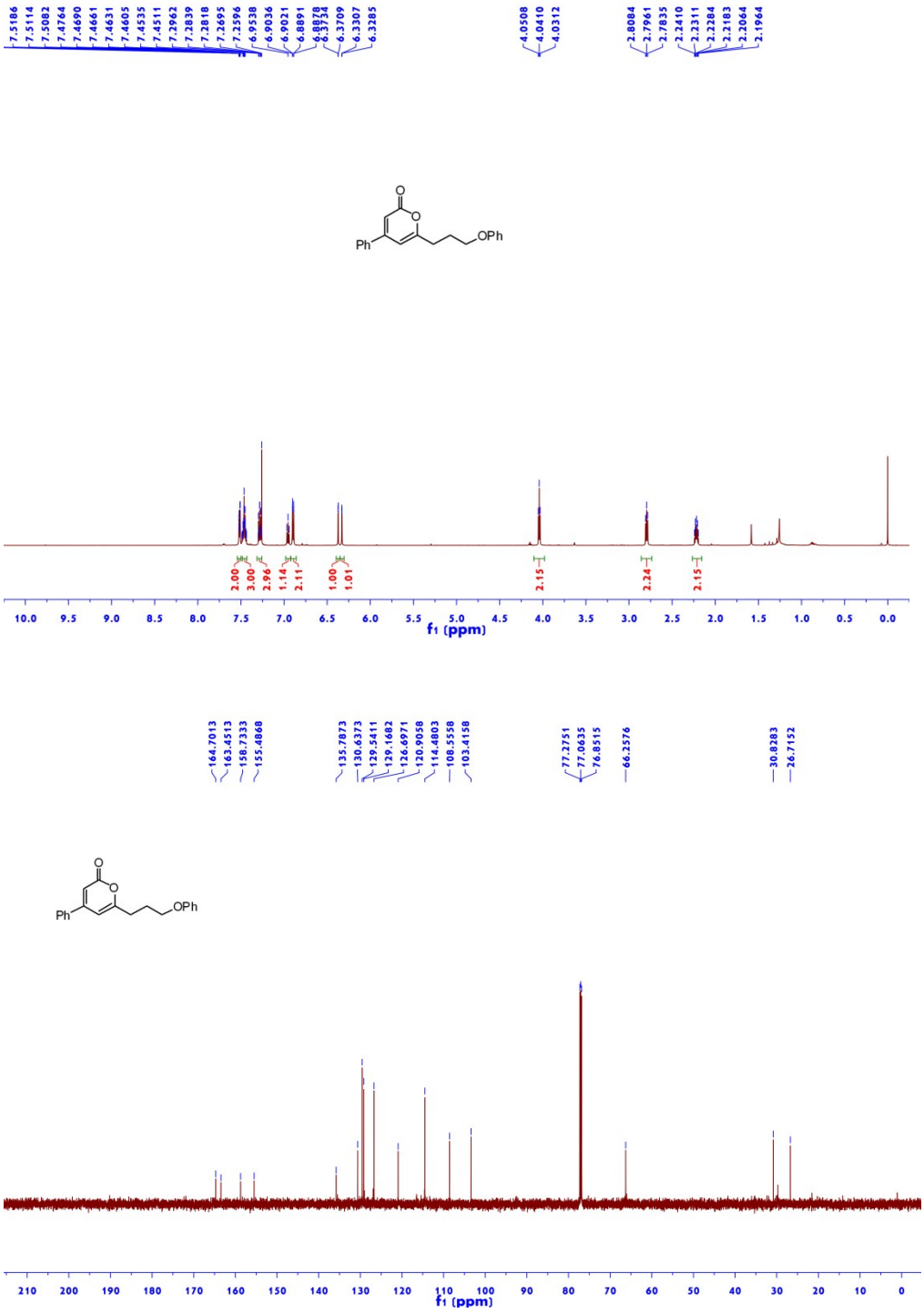


Figure S13. ^{1}H and ^{13}C NMR Spectra of 2m

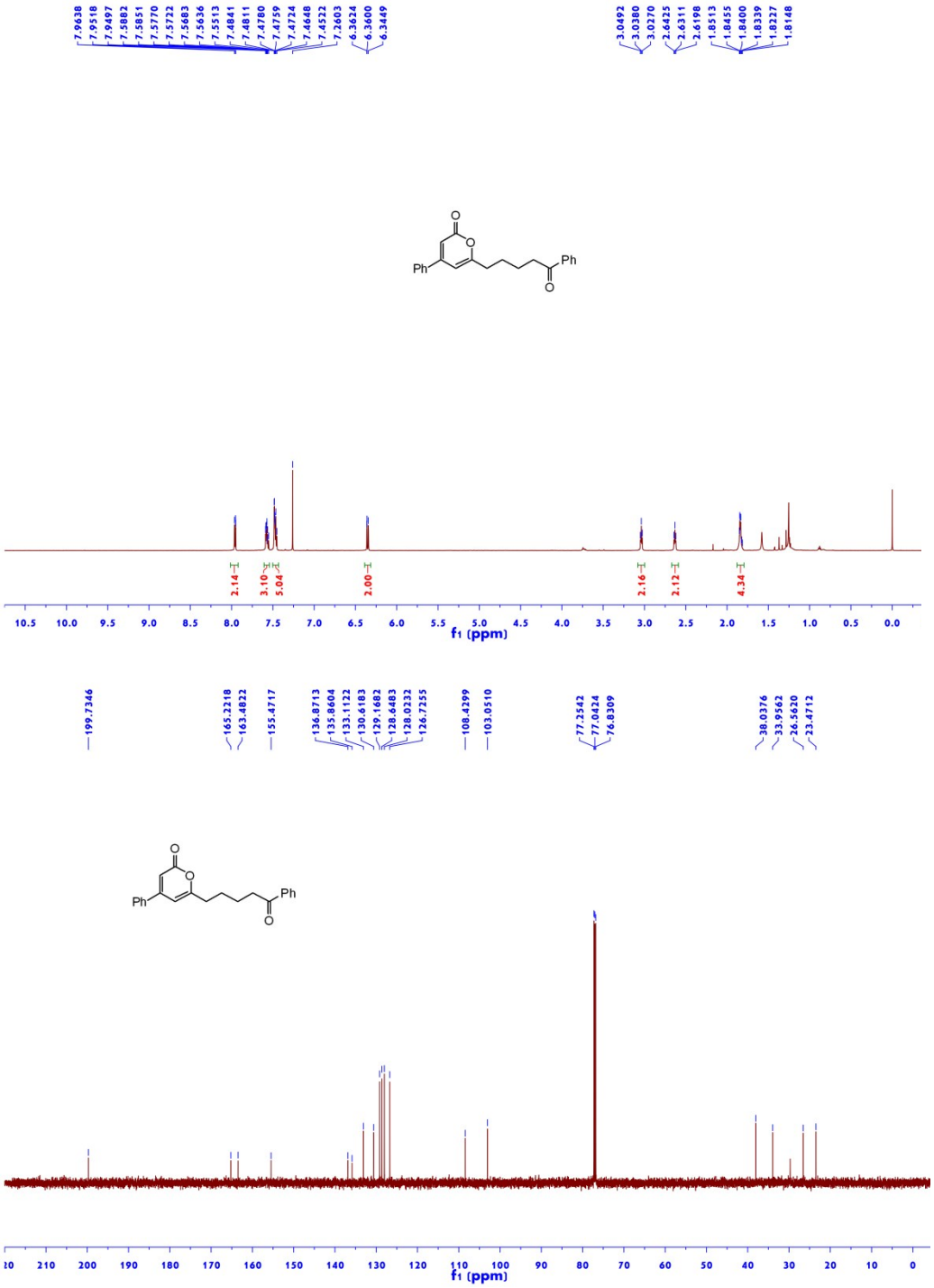


Figure S14. ^{1}H and ^{13}C NMR Spectra of 2n

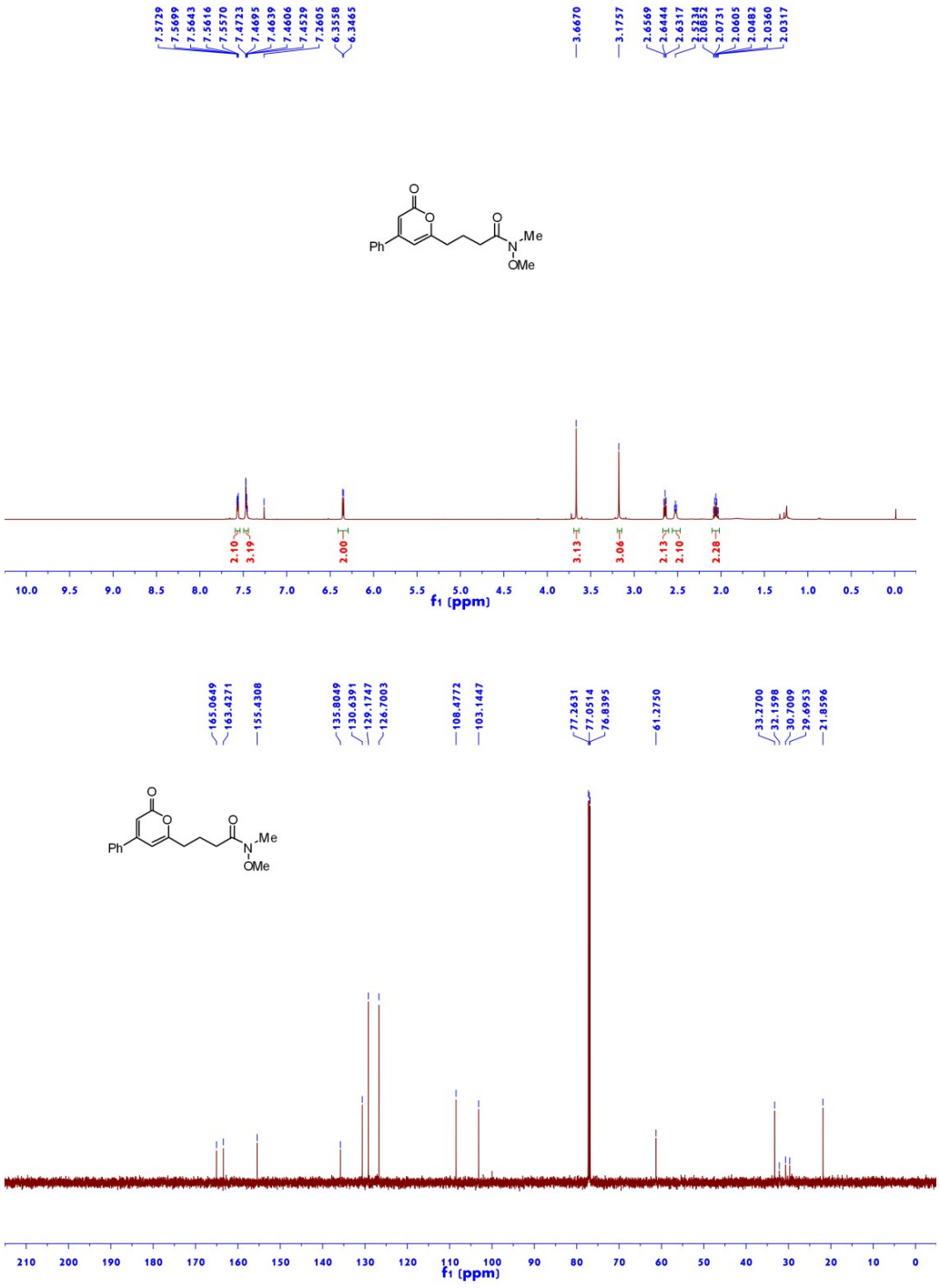


Figure S15. ^{1}H and ^{13}C NMR Spectra of 2o

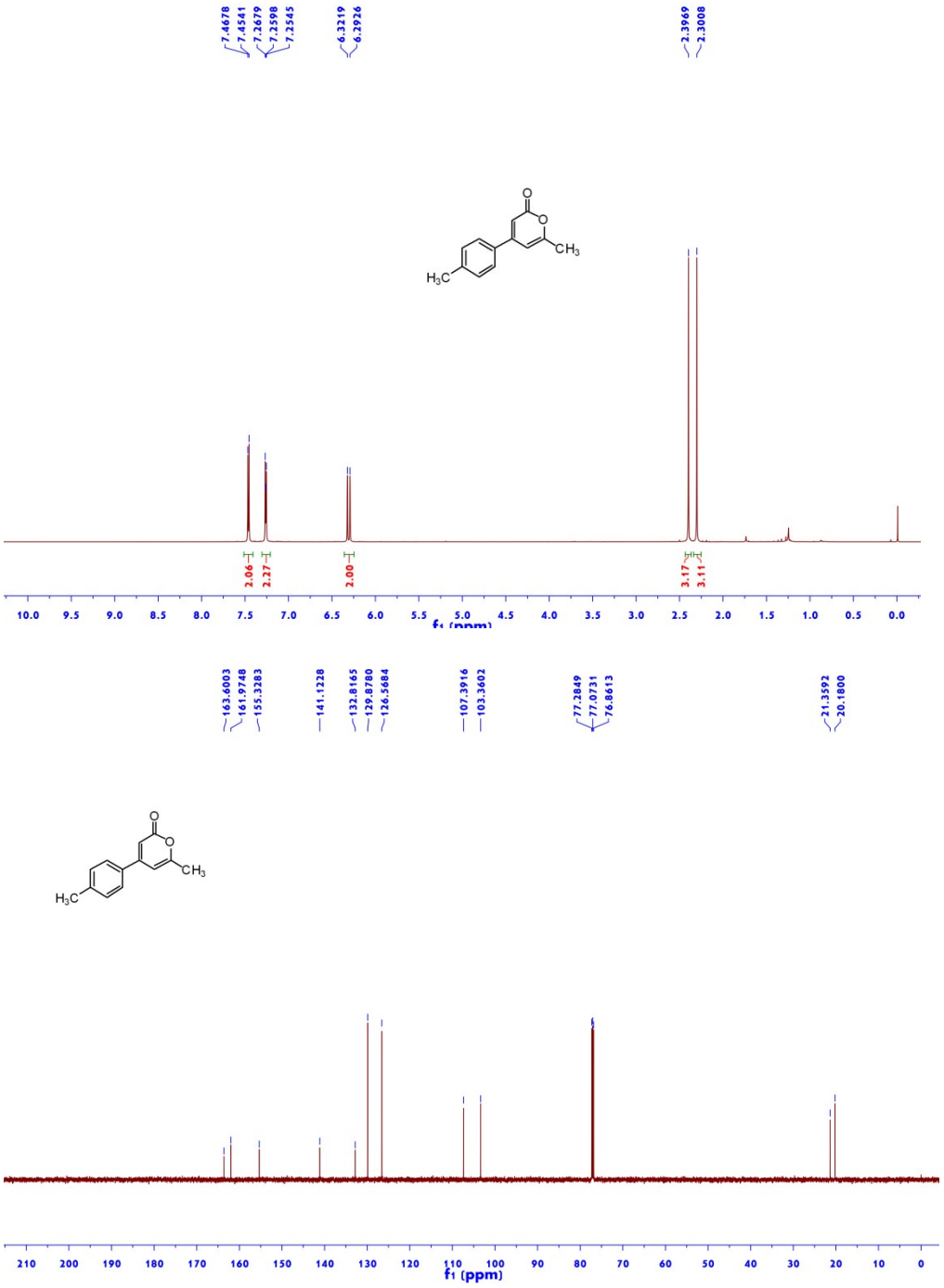


Figure S16. ^{1}H and ^{13}C NMR Spectra of 2p

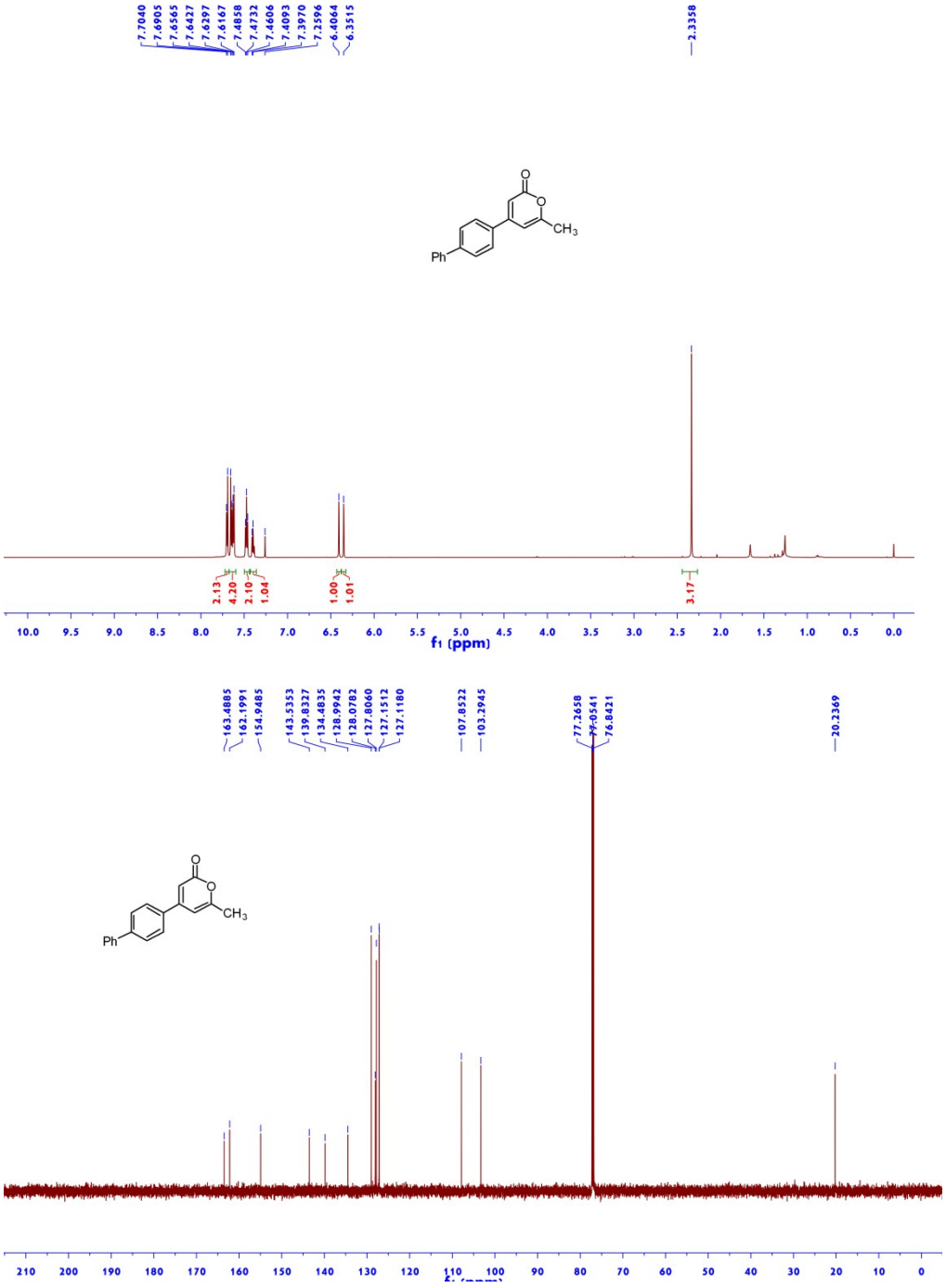


Figure S17. ^{1}H and ^{13}C NMR Spectra of 2q

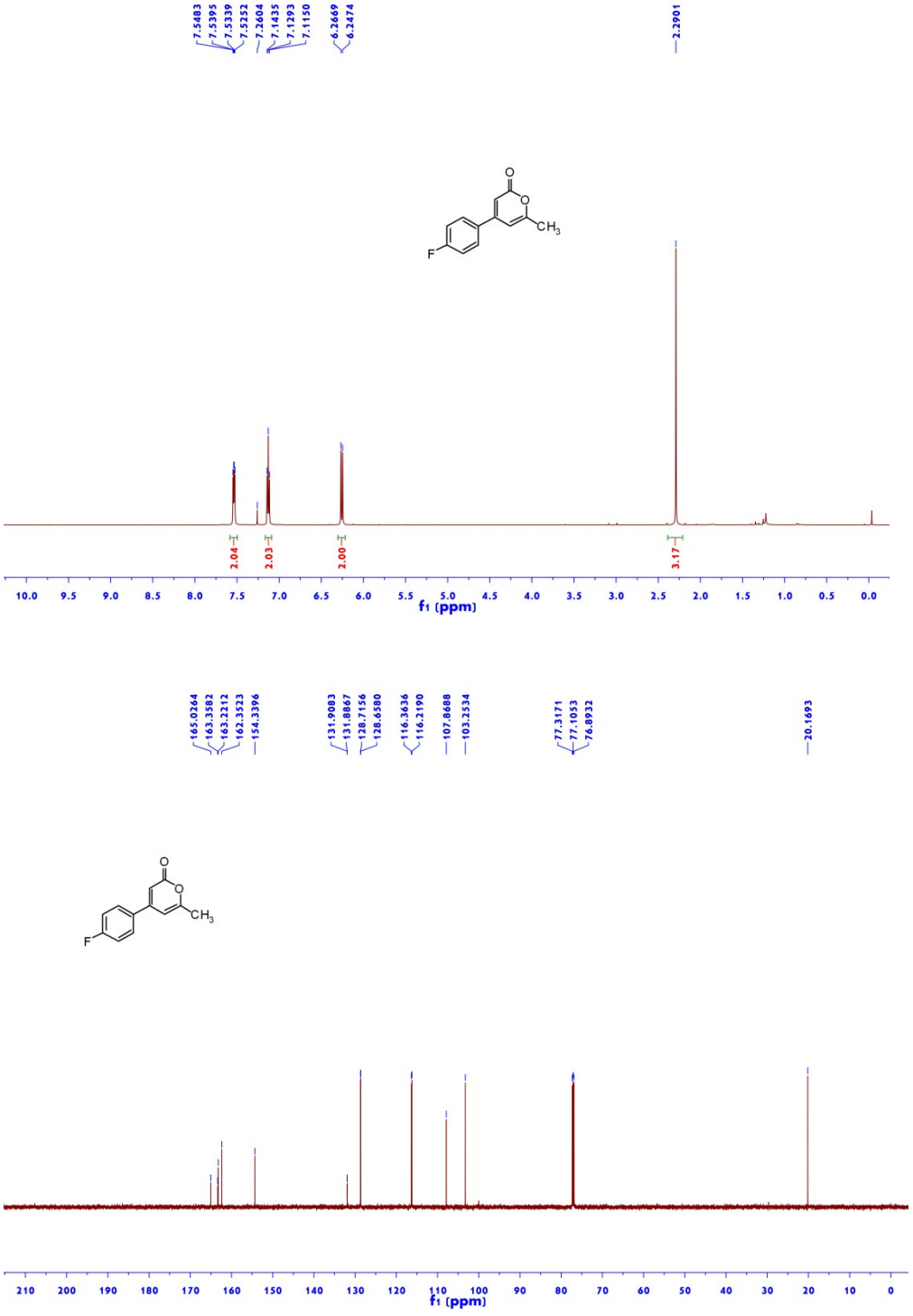


Figure S18. ^{1}H and ^{13}C NMR Spectra of 2r

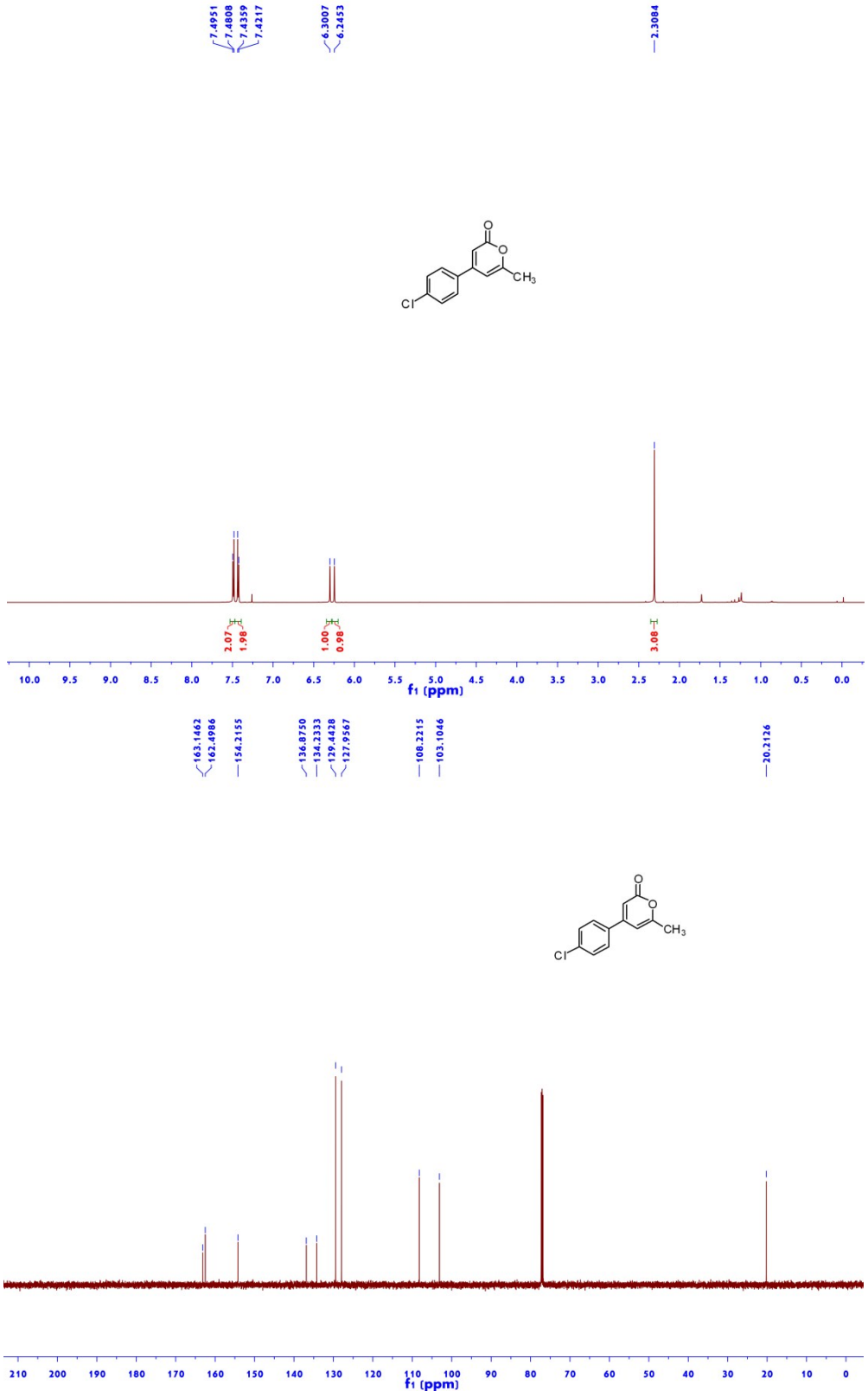


Figure S19. ^{1}H and ^{13}C NMR Spectra of 2s

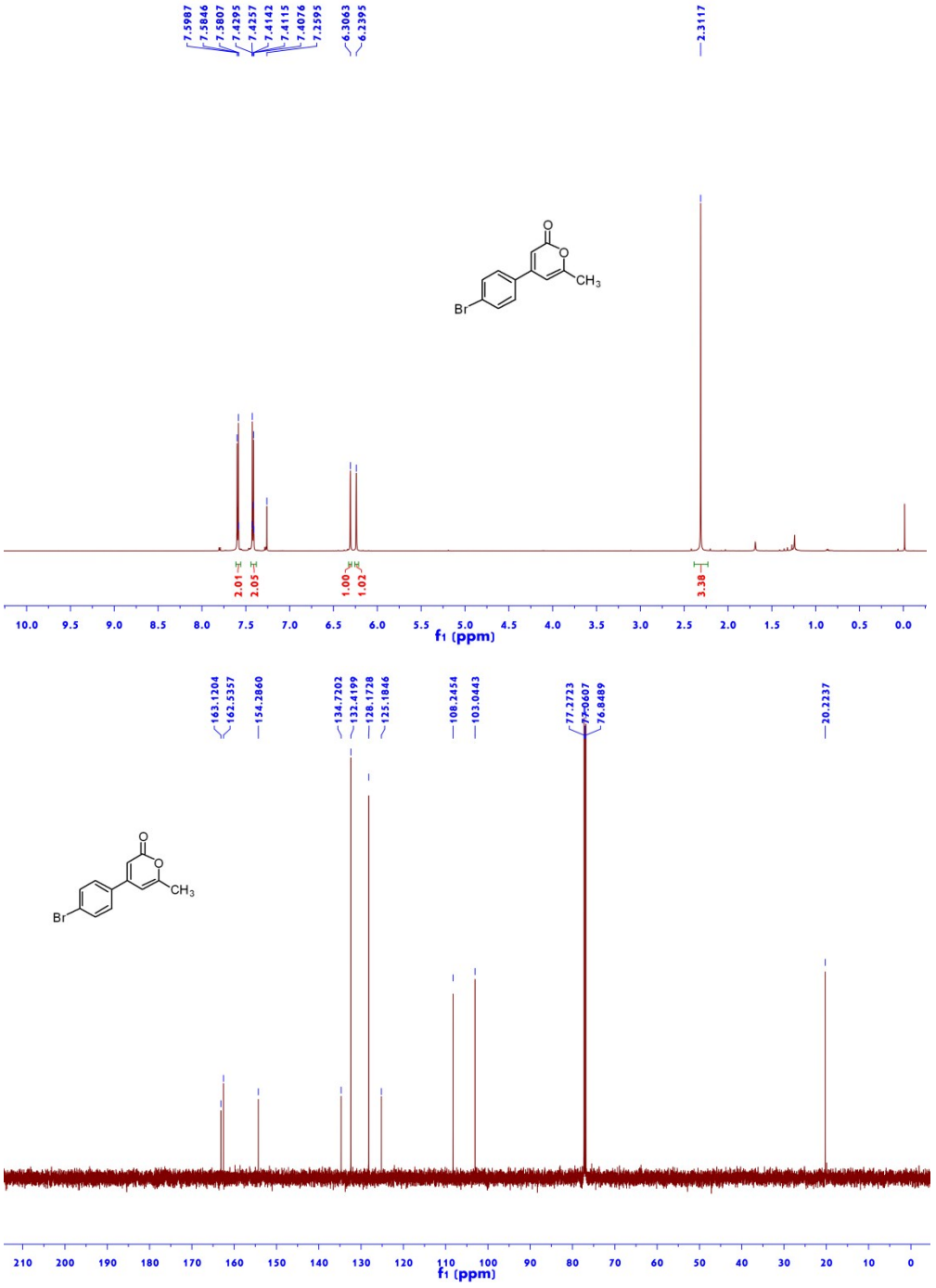


Figure S20. ^{1}H and ^{13}C NMR Spectra of 2t

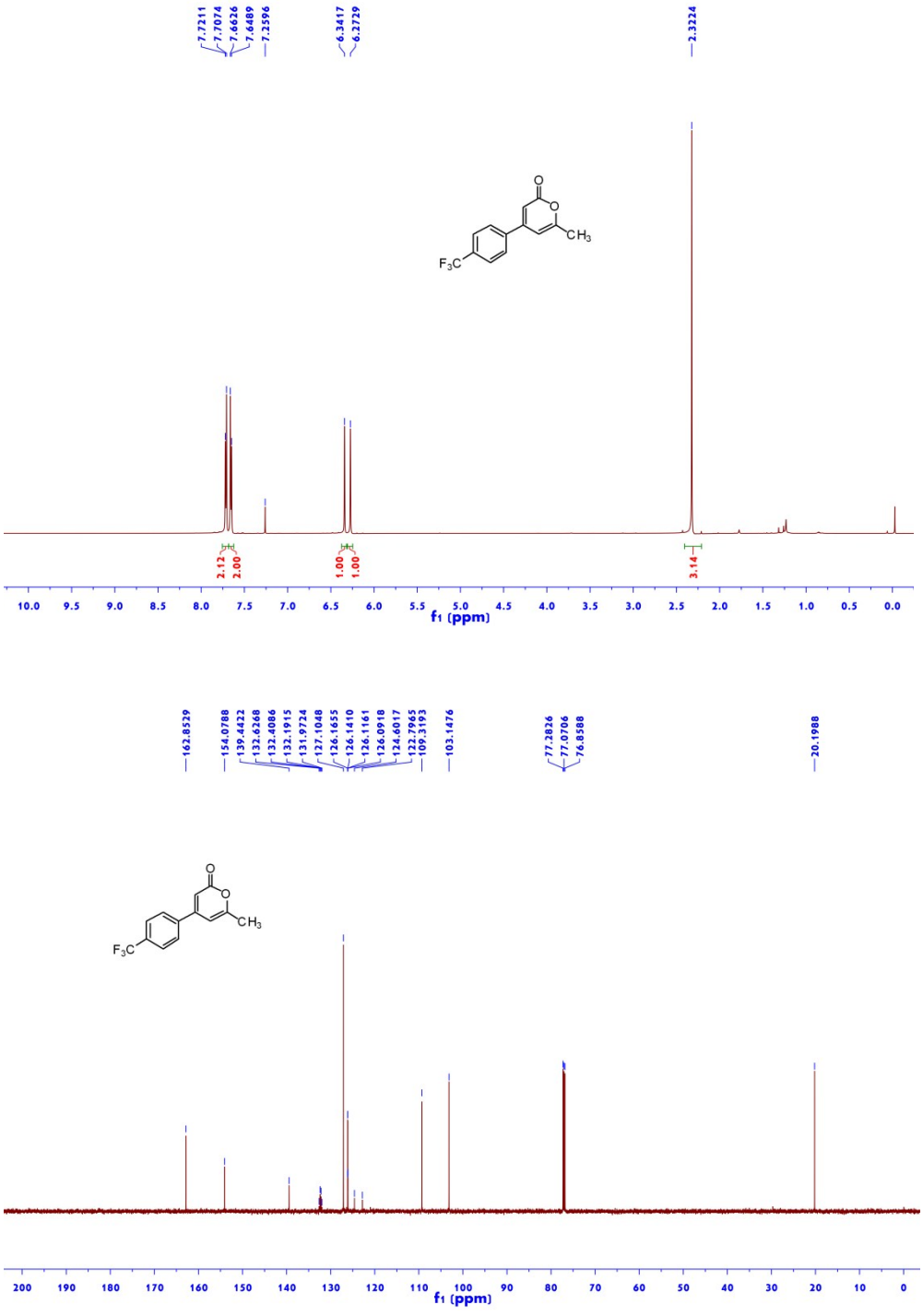


Figure S21. ^{1}H and ^{13}C NMR Spectra of 2u

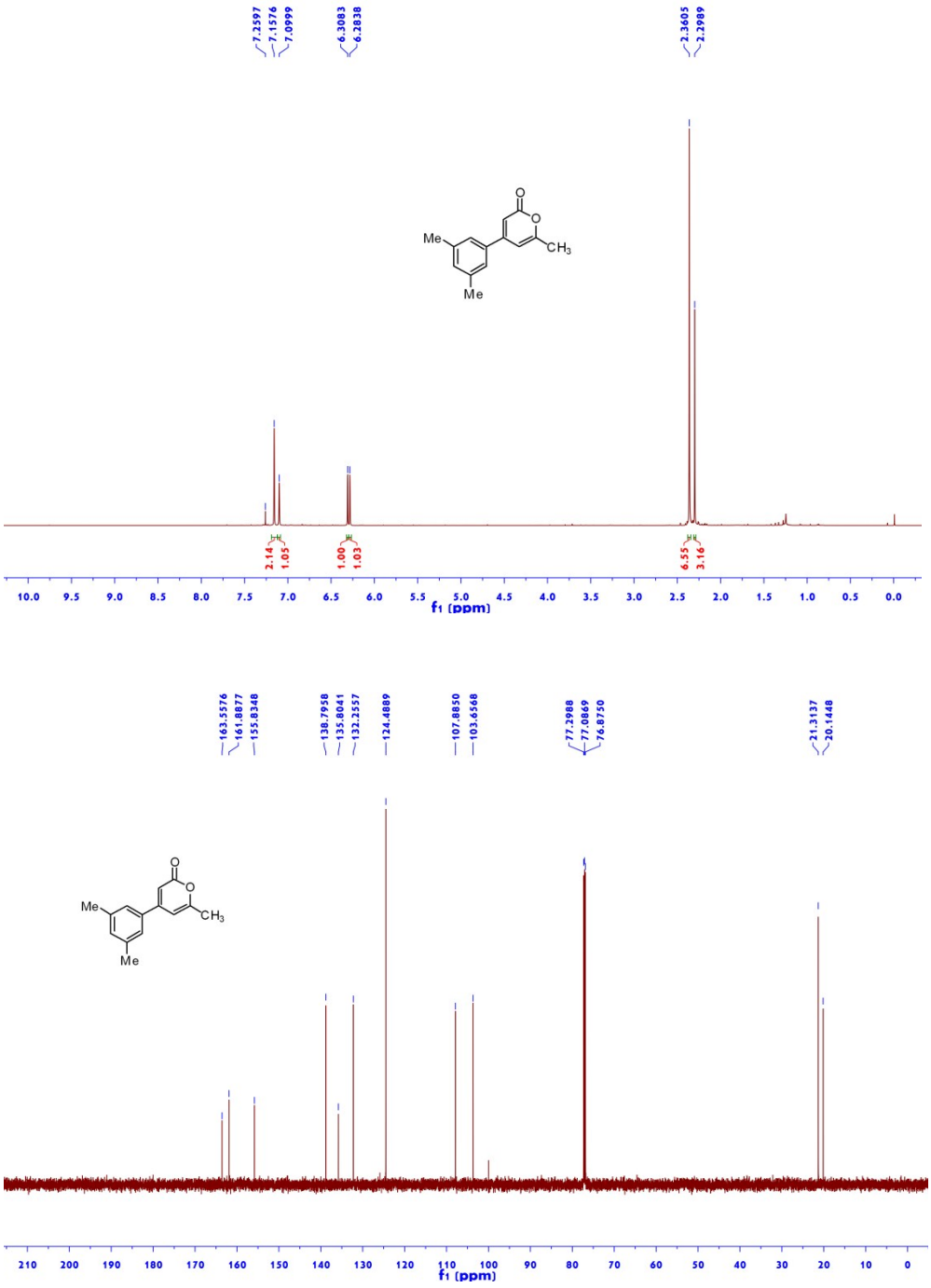


Figure S22. ^{1}H and ^{13}C NMR Spectra of 2v

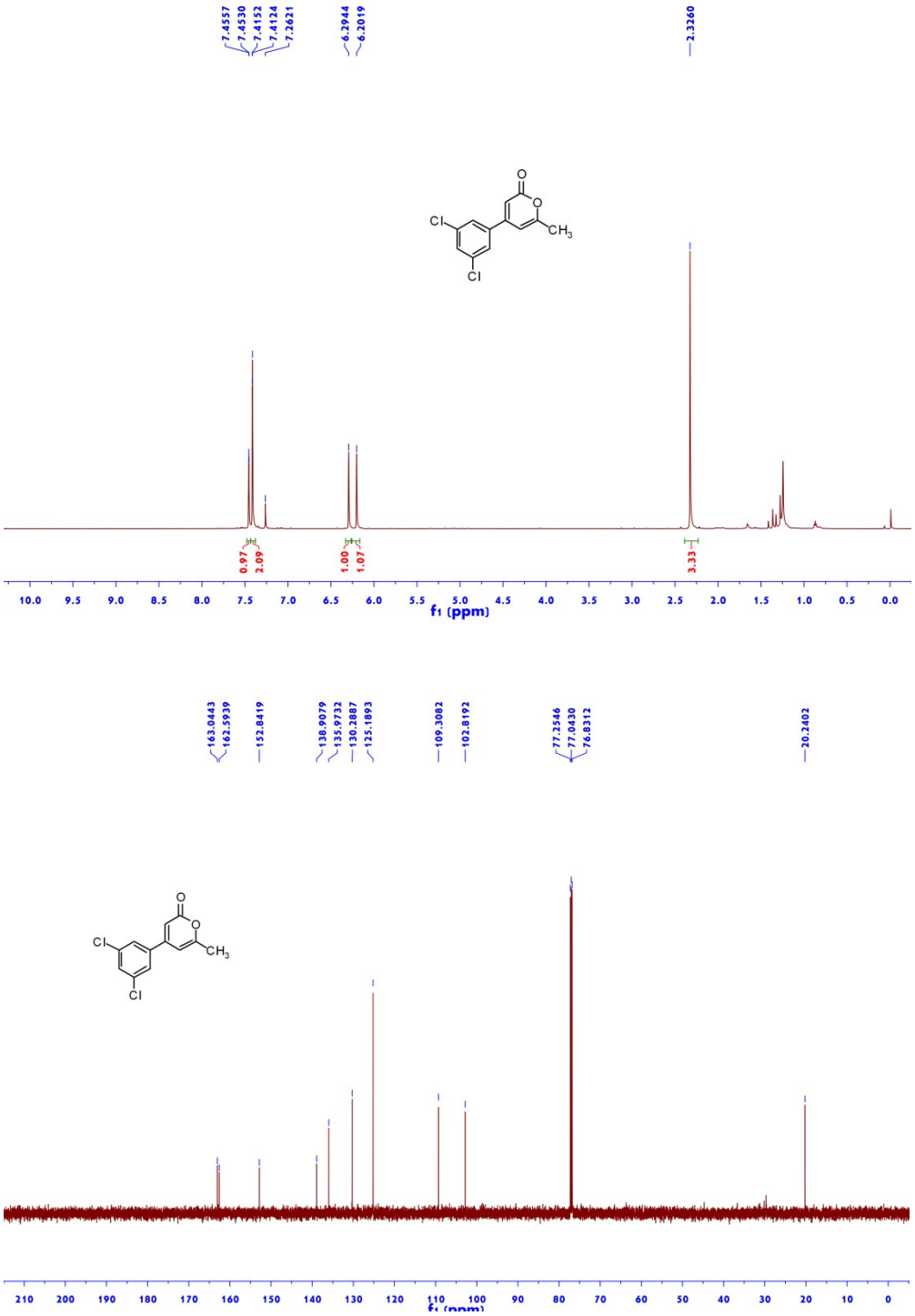


Figure S23. ^{1}H and ^{13}C NMR Spectra of 2w

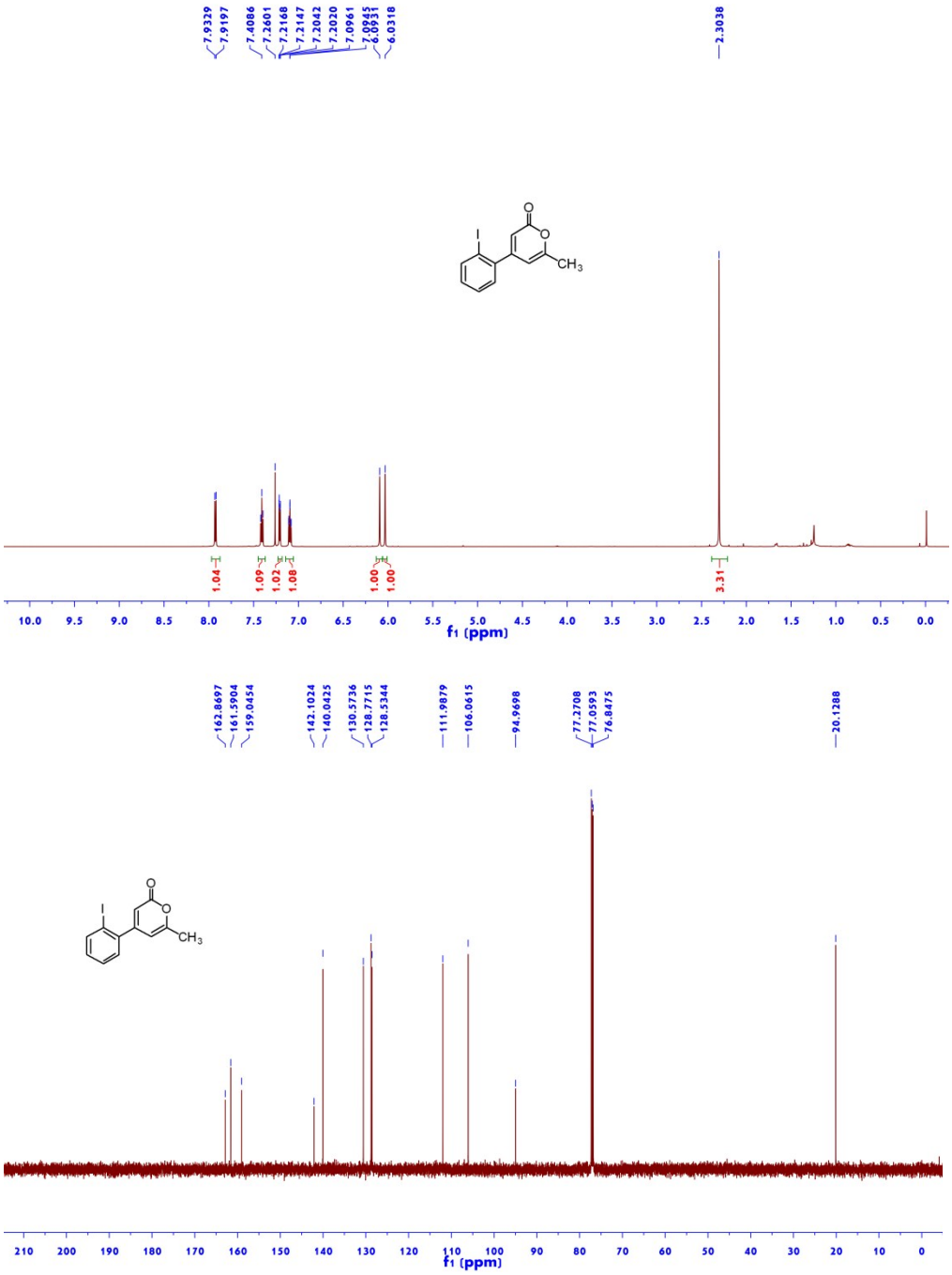


Figure S24. ^{1}H and ^{13}C NMR Spectra of 2x

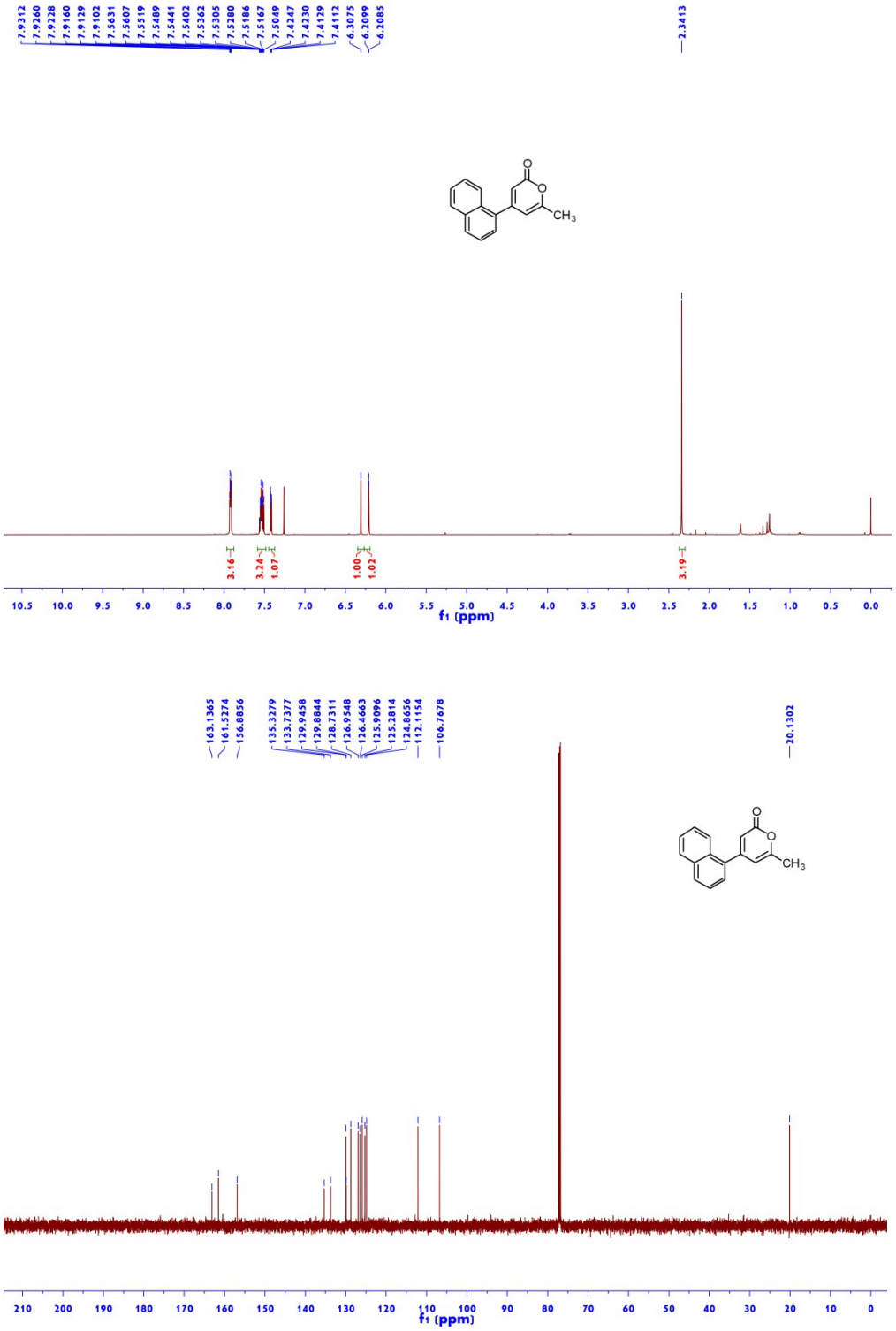


Figure S25. ^{1}H and ^{13}C NMR Spectra of 2y

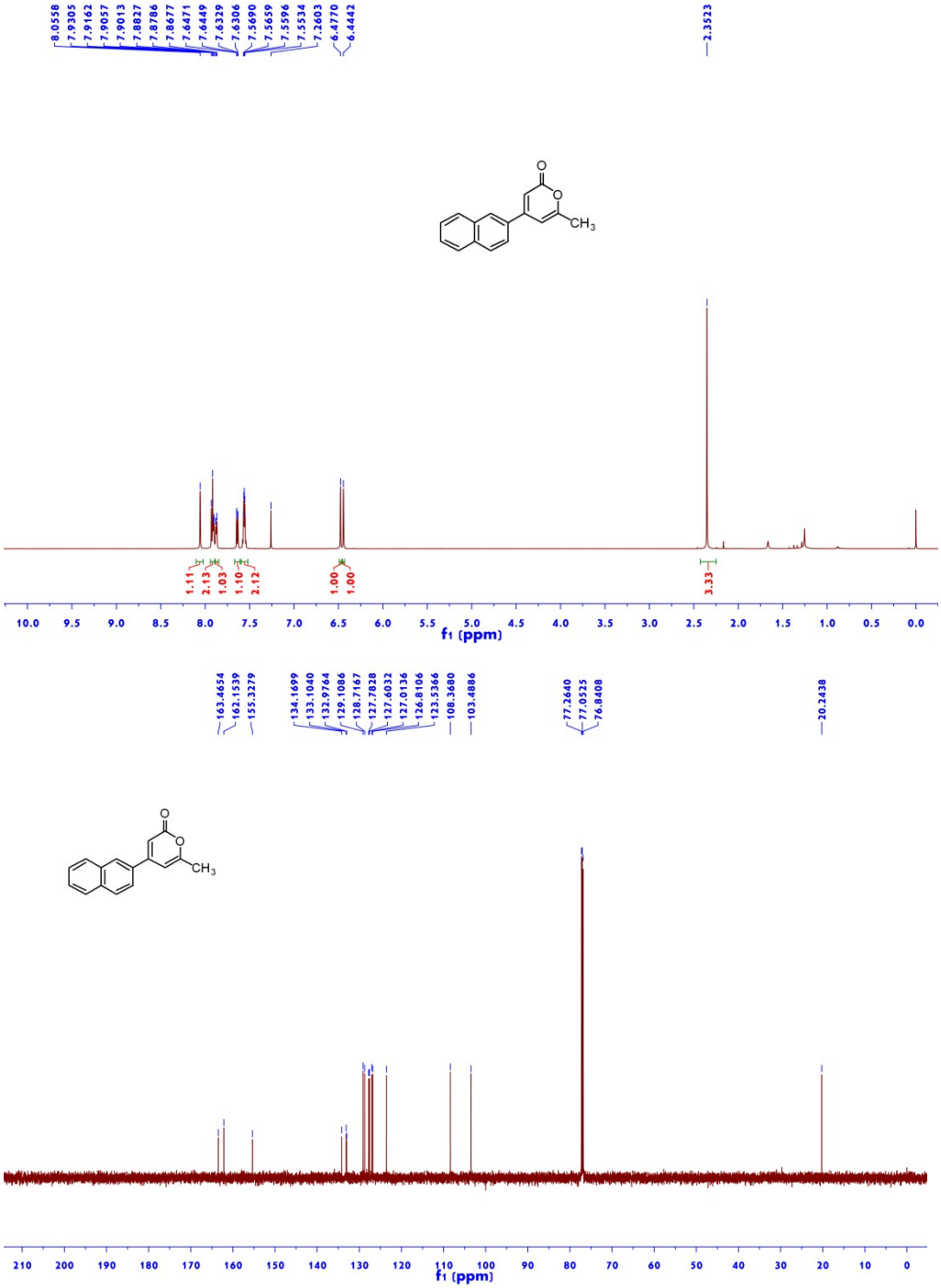


Figure S26. ^{1}H and ^{13}C NMR Spectra of 2z

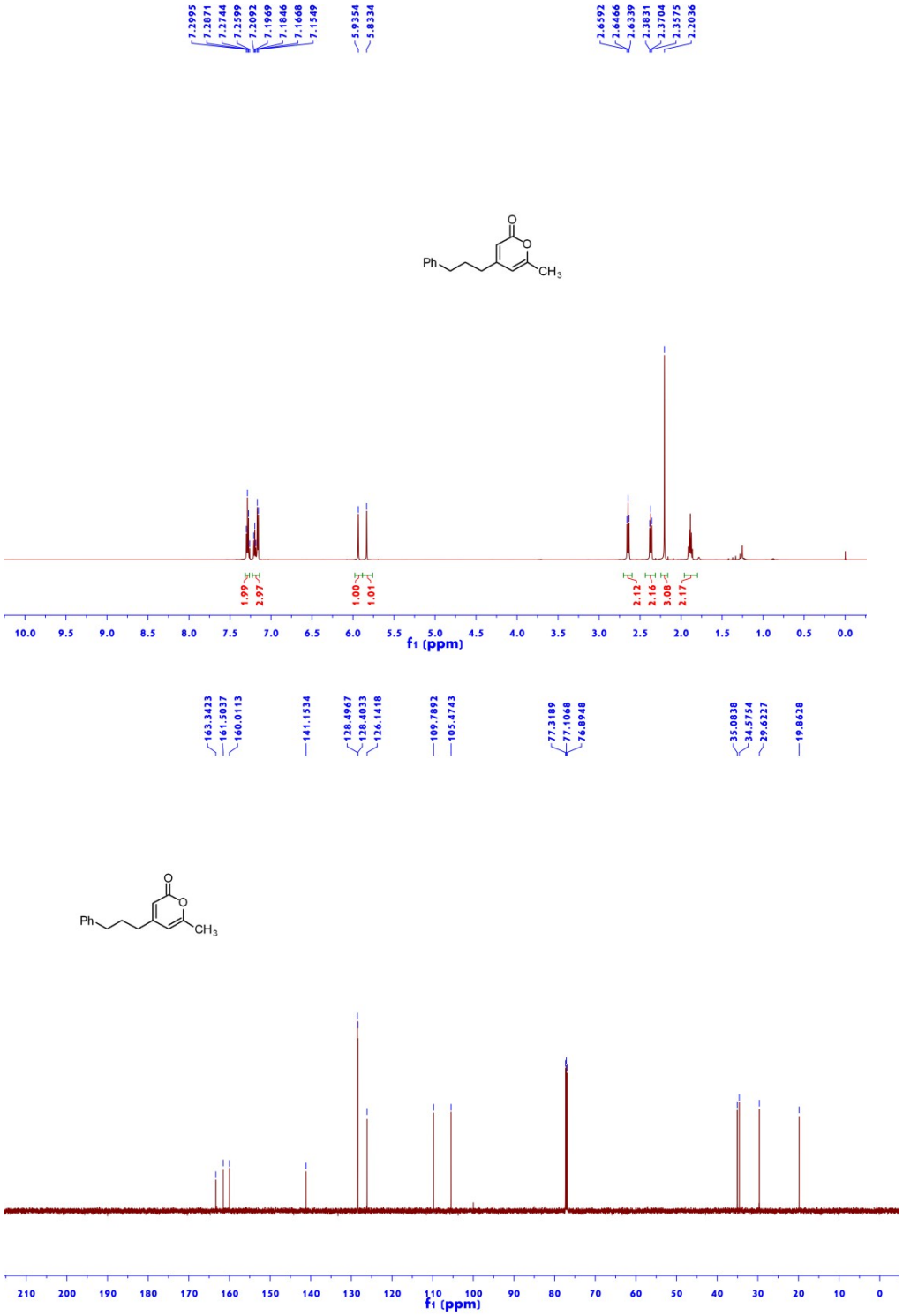


Figure S27. ^{1}H and ^{13}C NMR Spectra of 2aa

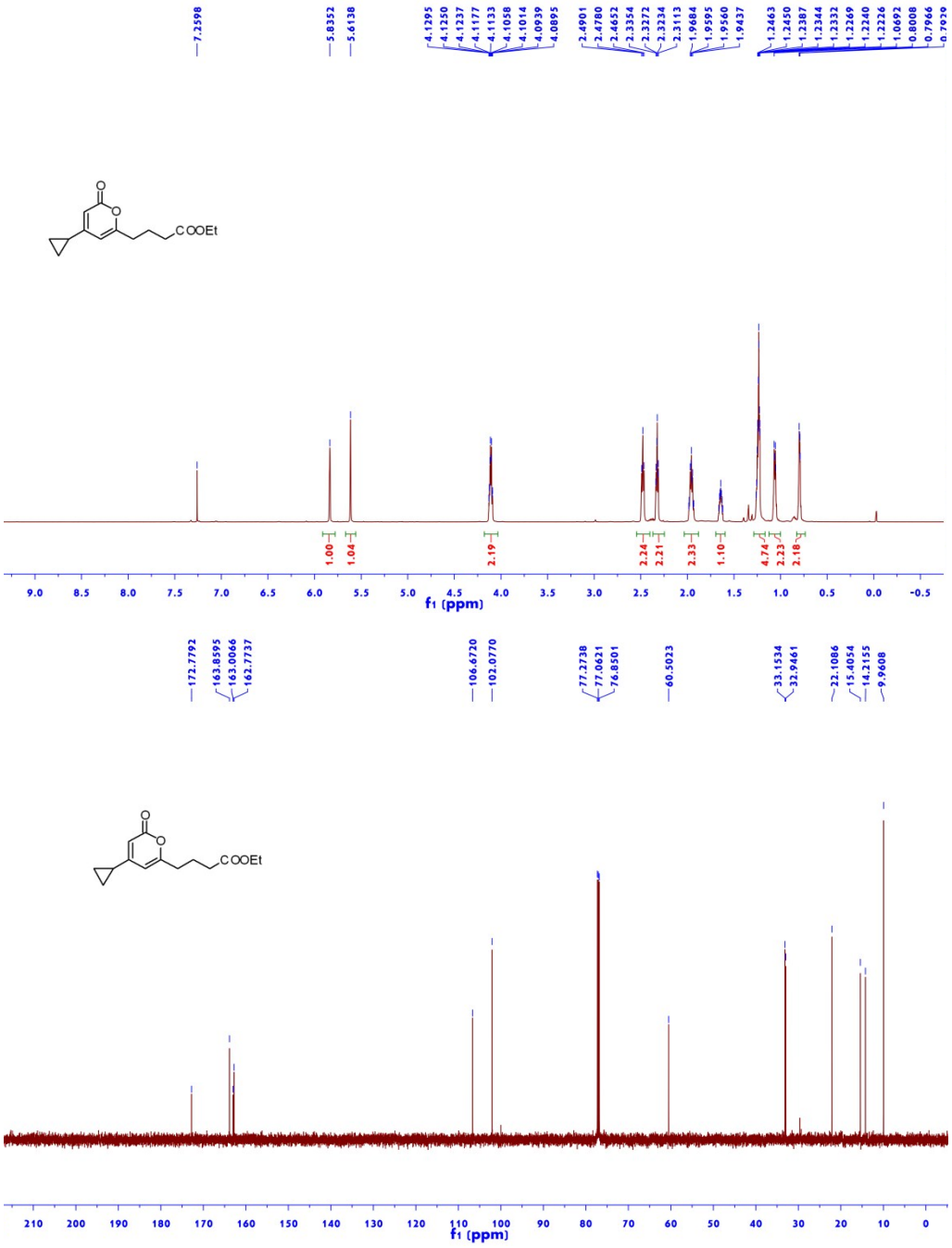


Figure S28. ^{1}H and ^{13}C NMR Spectra of 2ab

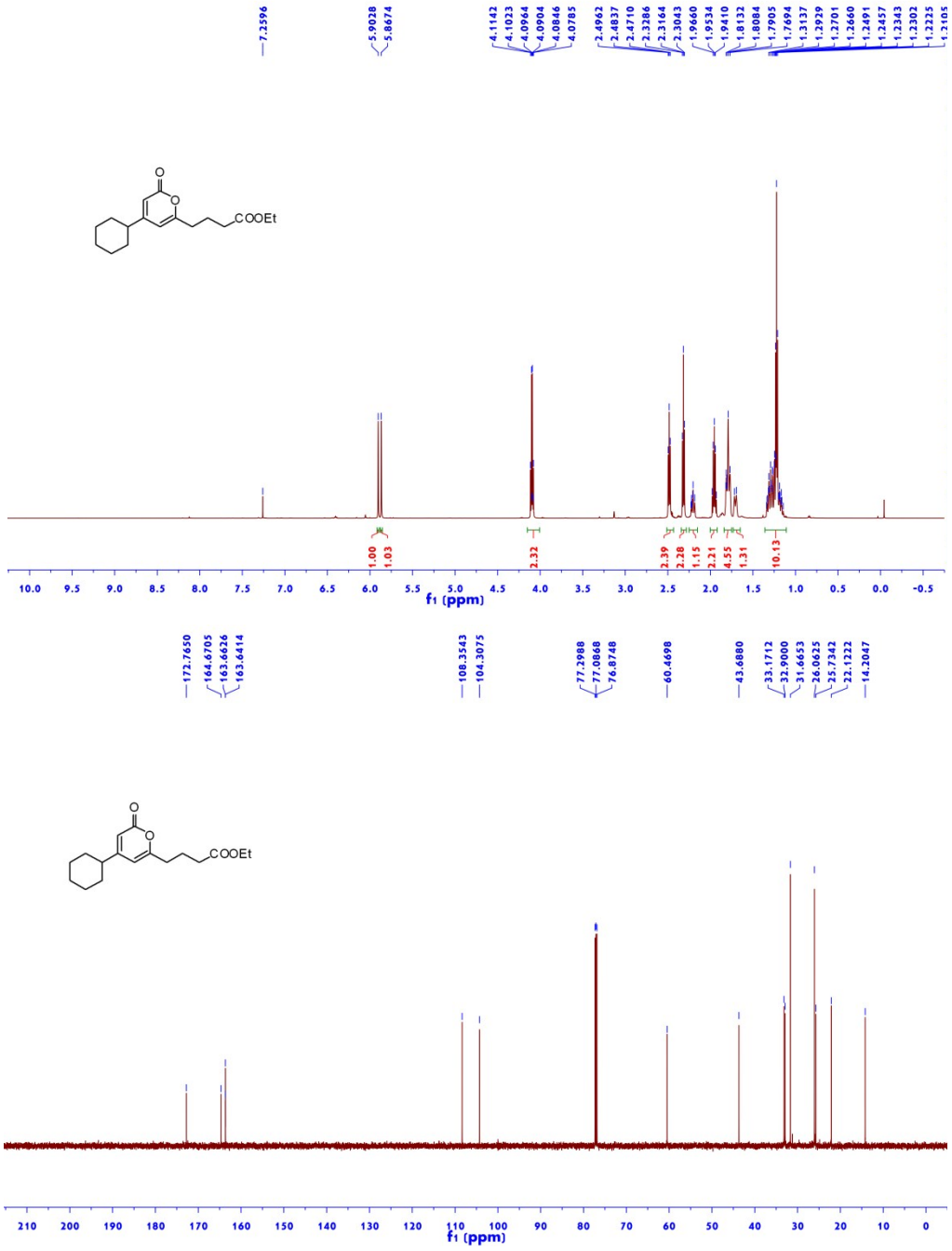


Figure S29. ^{1}H and ^{13}C NMR Spectra of 2ac

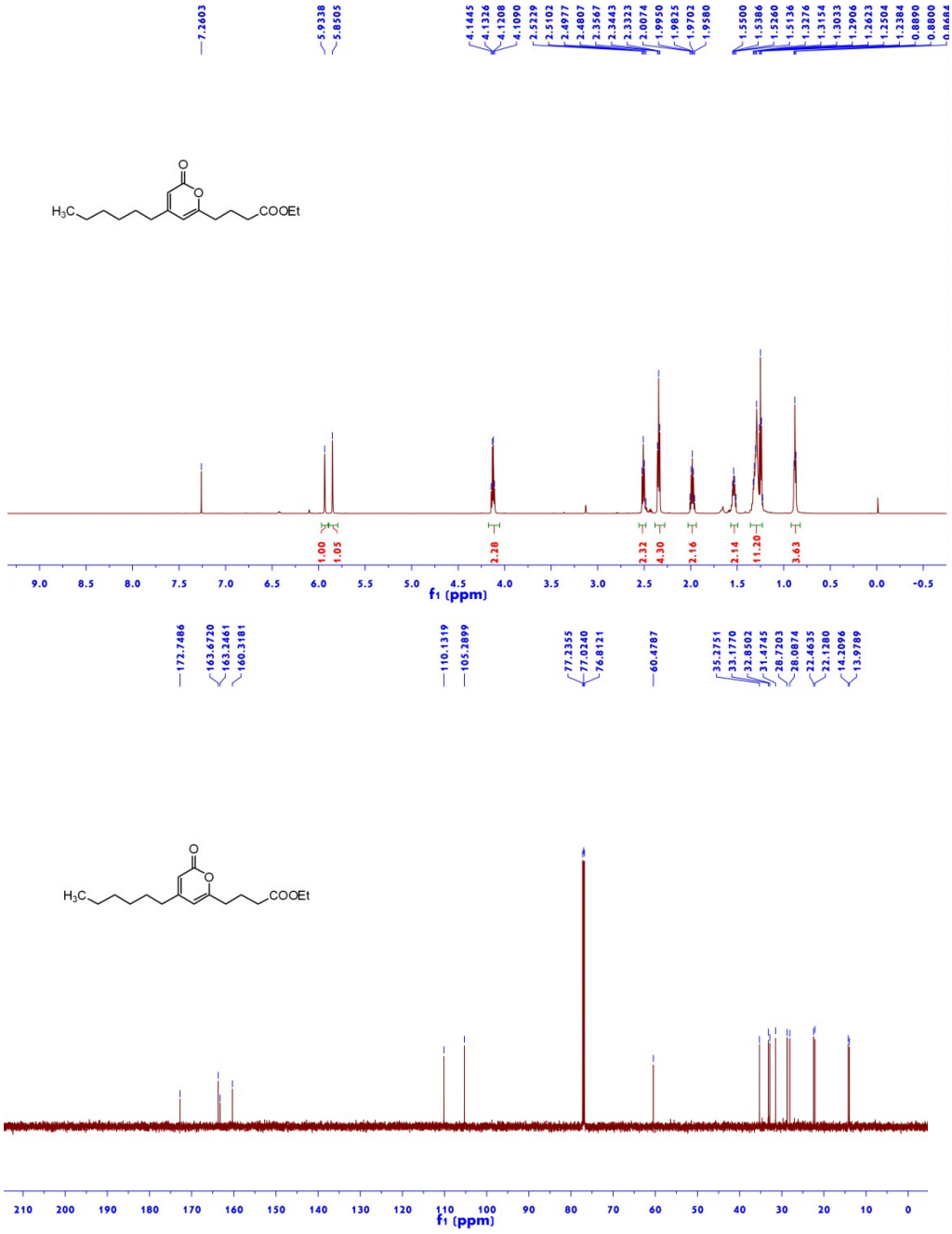


Figure S30. ^{1}H and ^{13}C NMR Spectra of 2ad

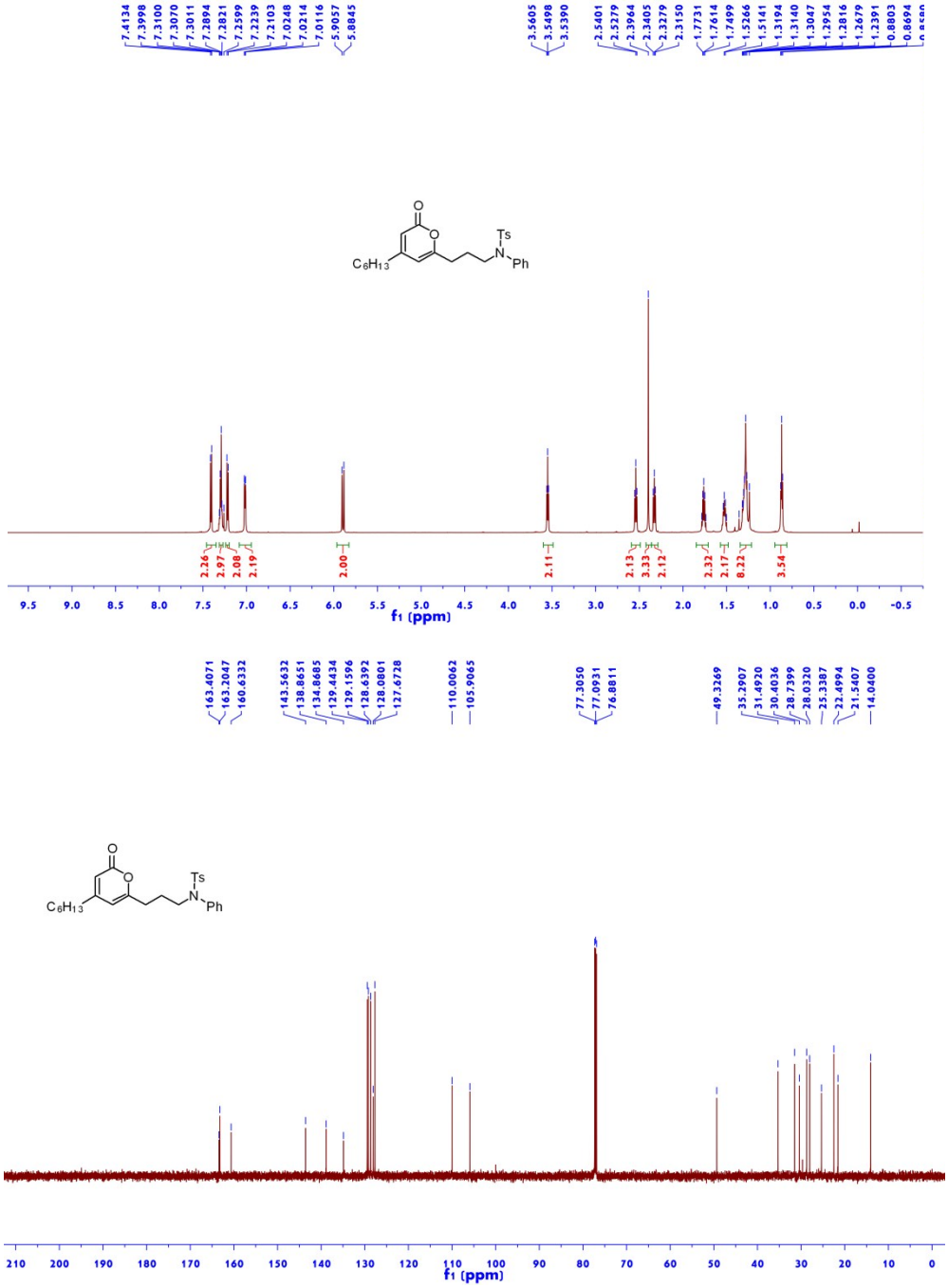


Figure S31. ^{1}H and ^{13}C NMR Spectra of 2ae

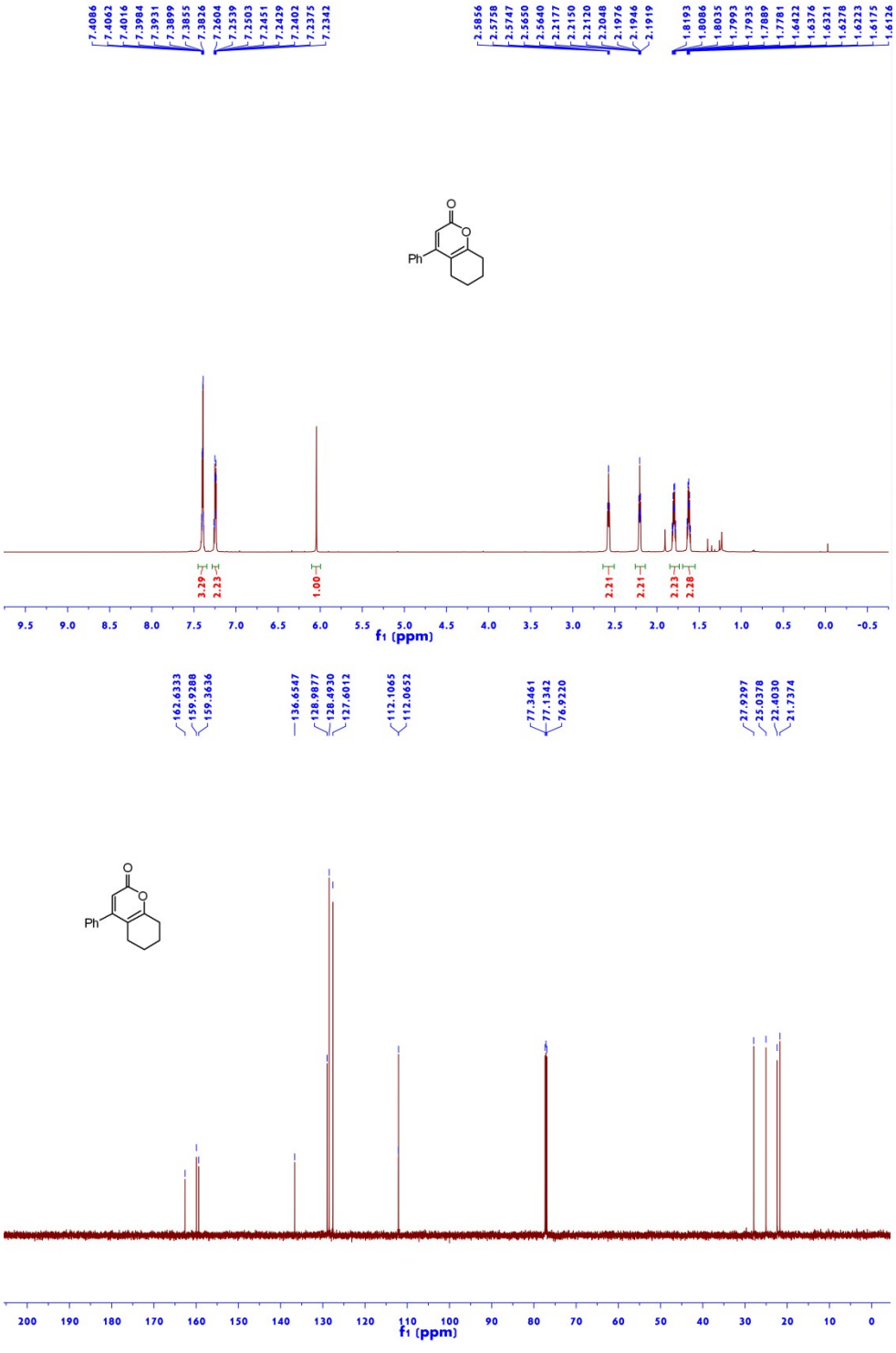


Figure S32. ^{1}H and ^{13}C NMR Spectra of 2af

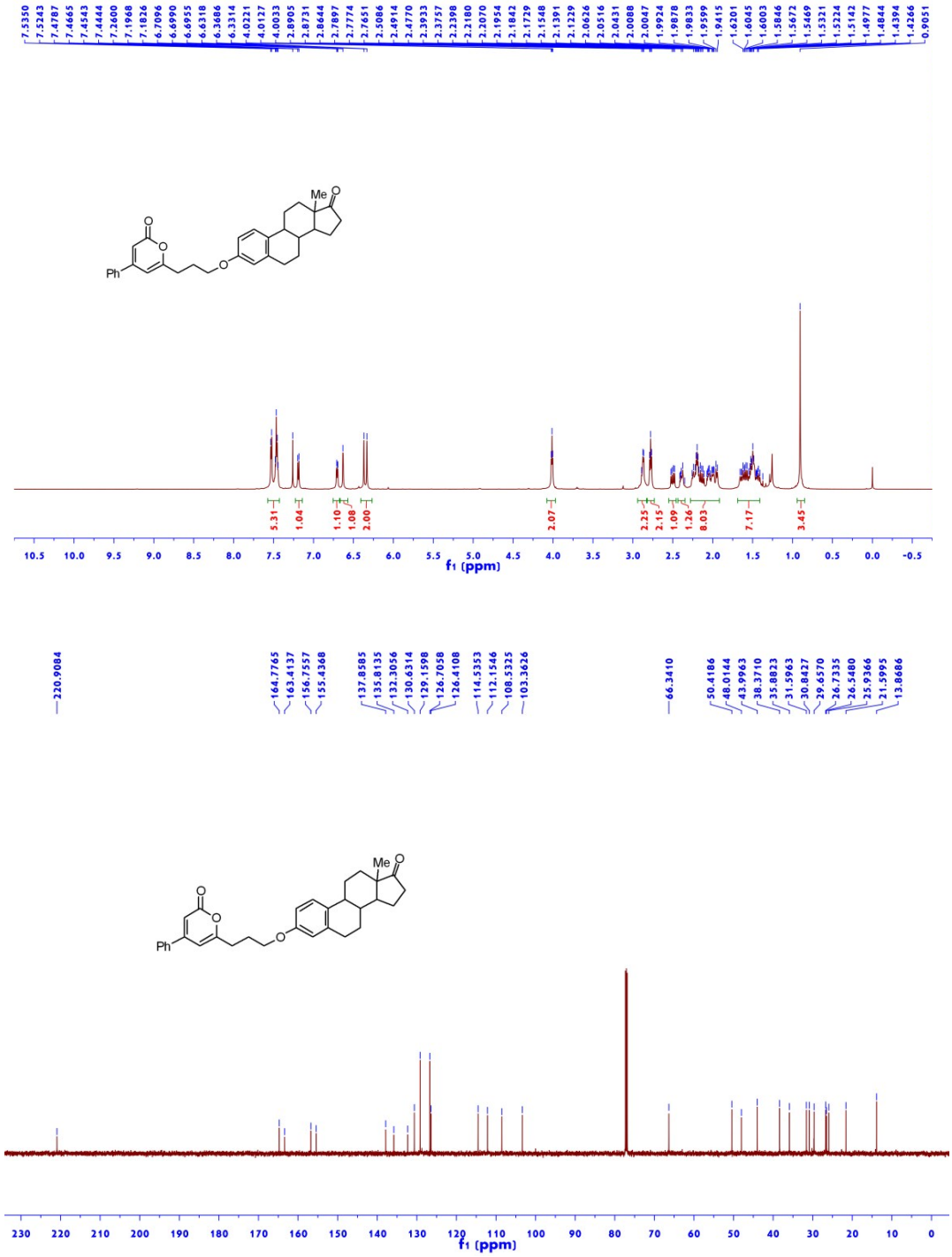


Figure S33. ^{1}H and ^{13}C NMR Spectra of 3a

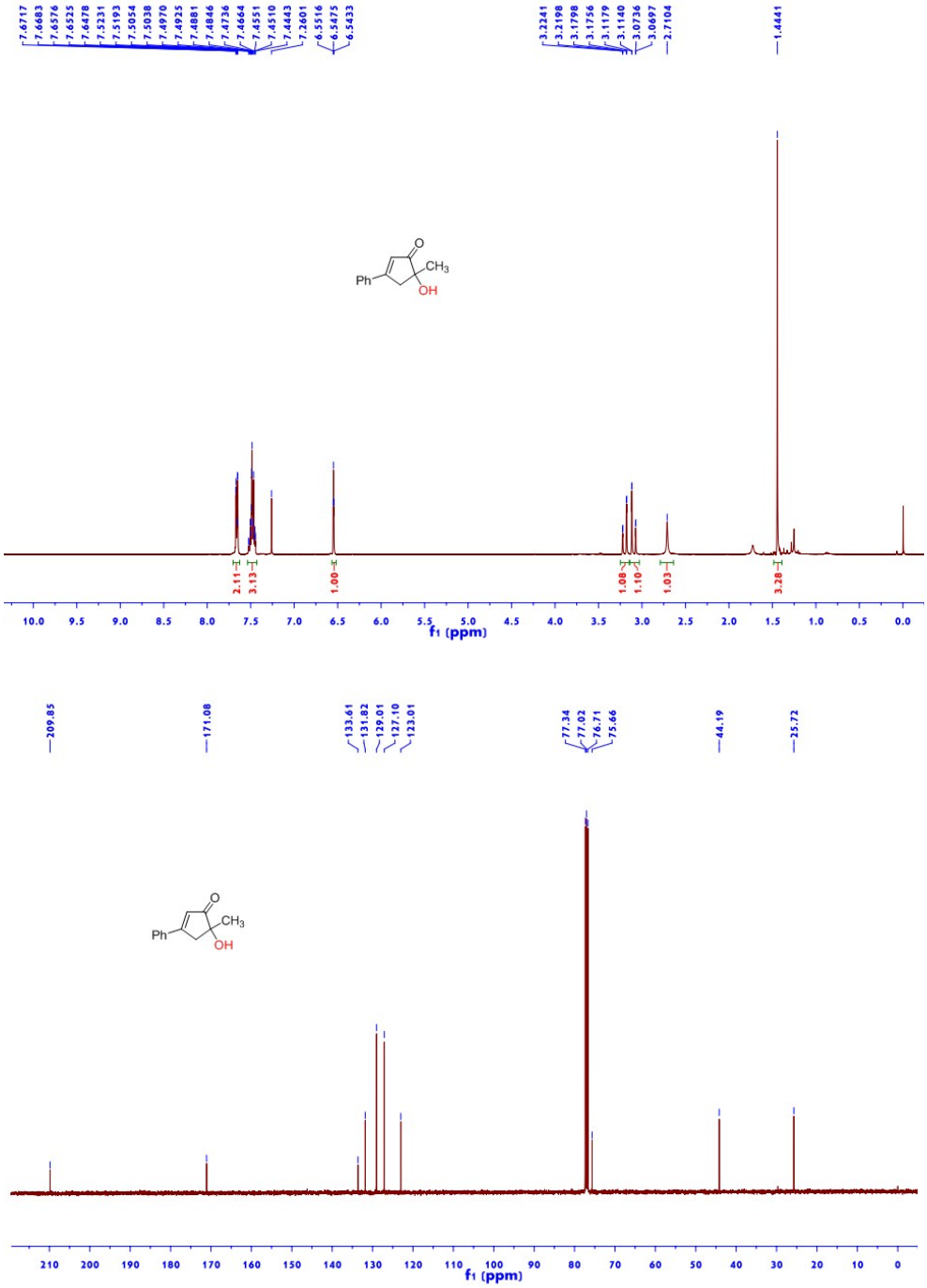


Figure S34. ^{1}H and ^{13}C NMR Spectra of 4

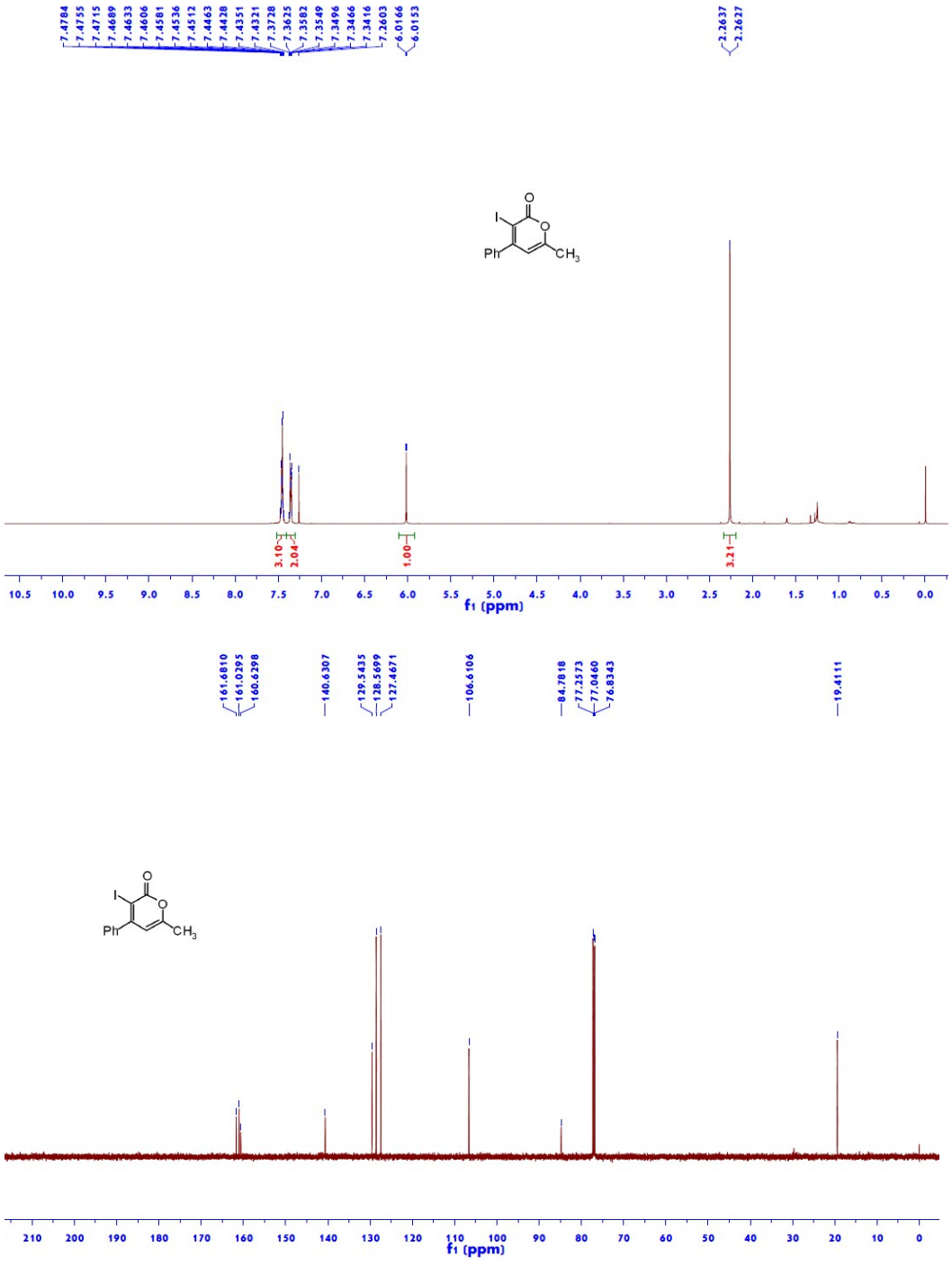


Figure S35. ^{1}H and ^{13}C NMR Spectra of 5

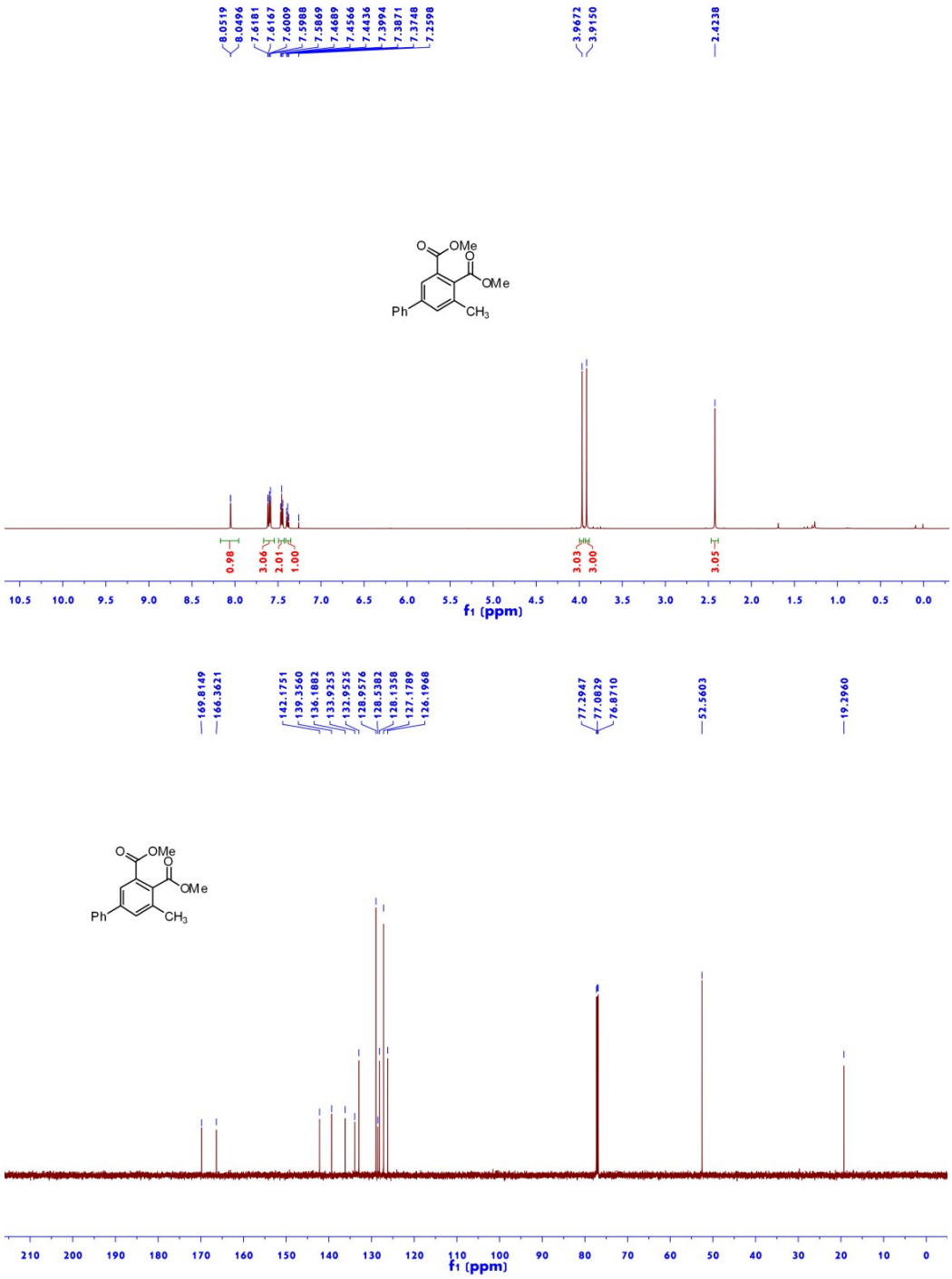


Figure S36. ^{1}H and ^{13}C NMR Spectra of 6

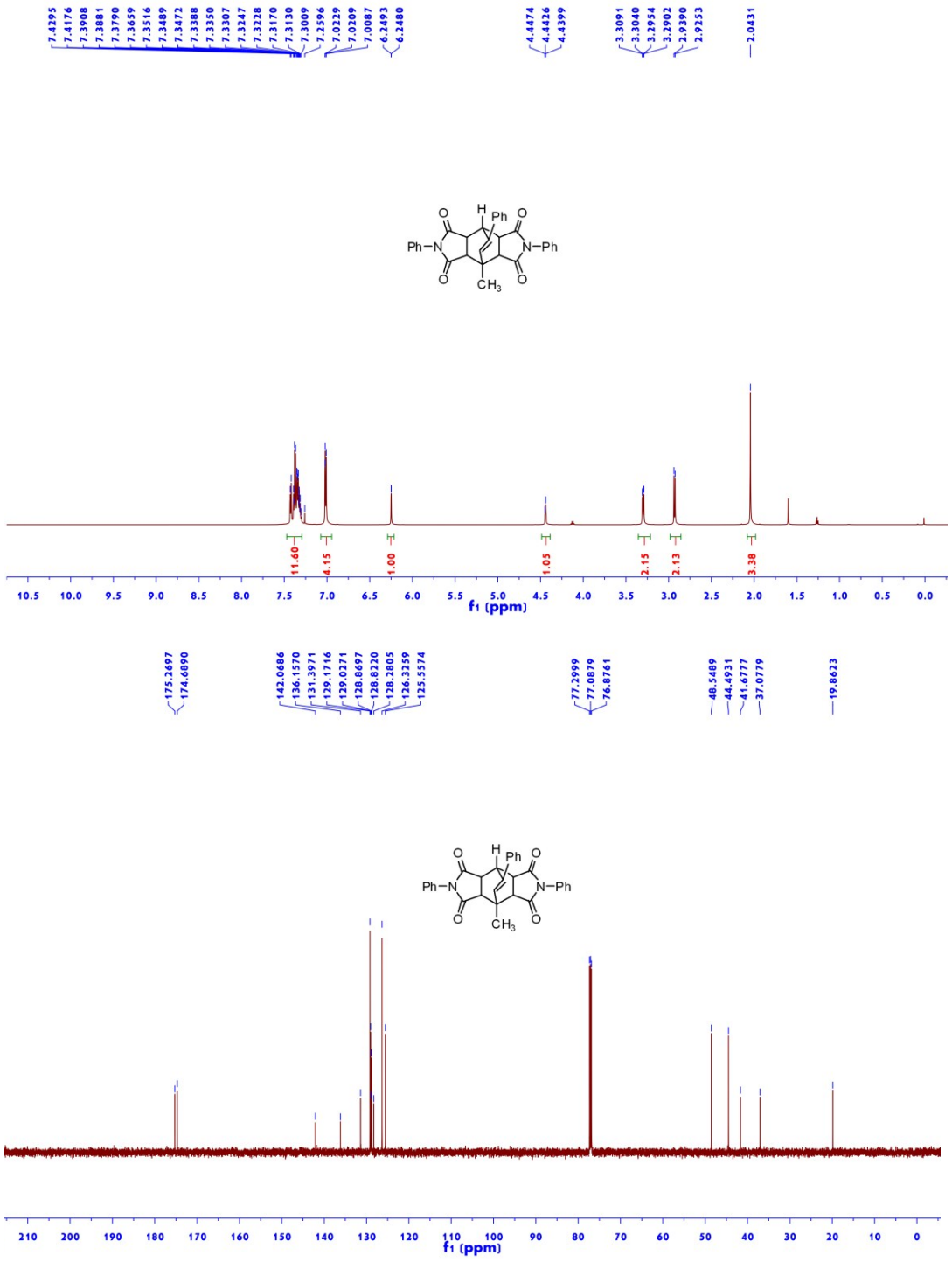
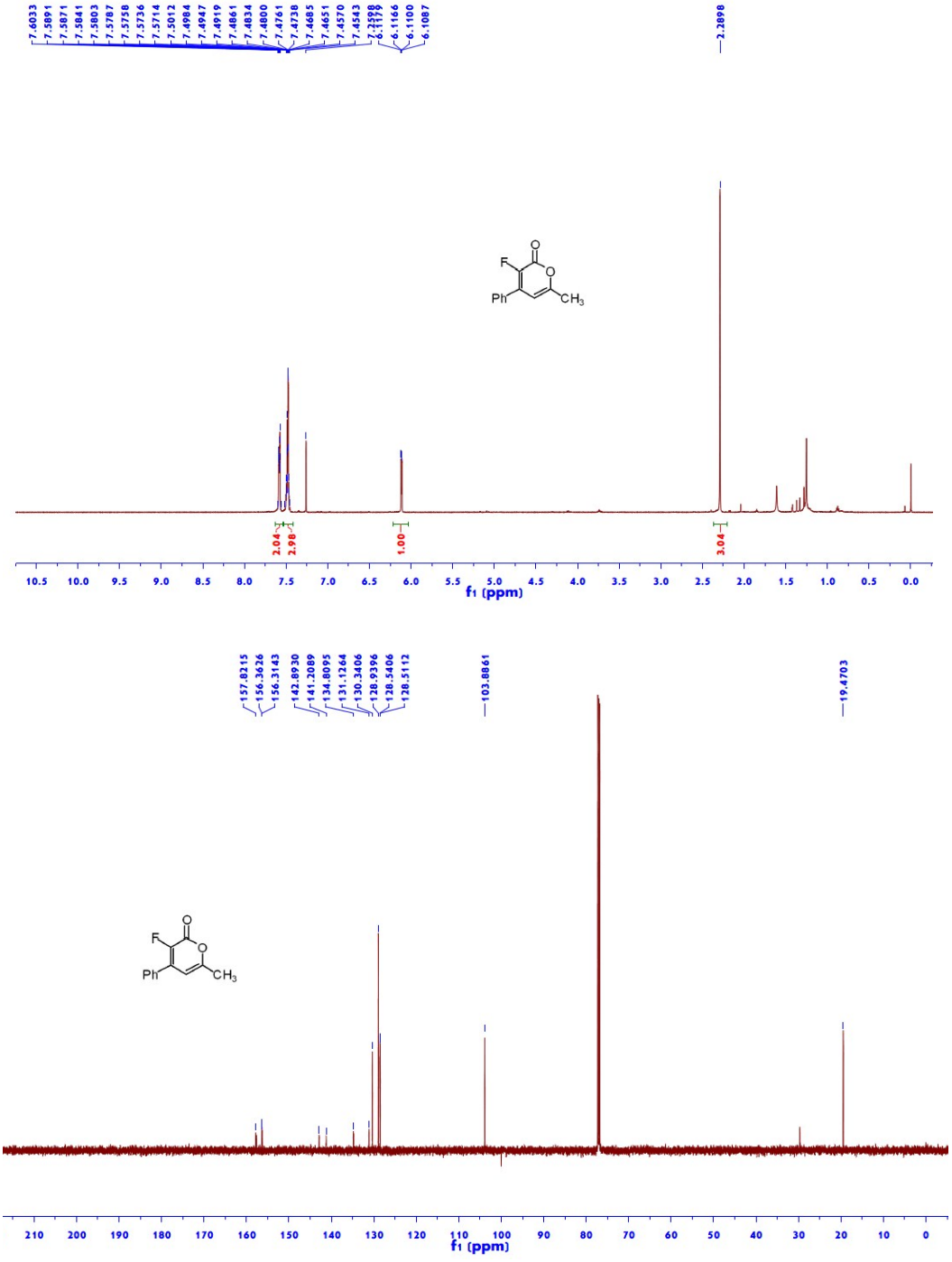


Figure S37. ^{1}H, ^{13}C and ^{19}F NMR Spectra of 7



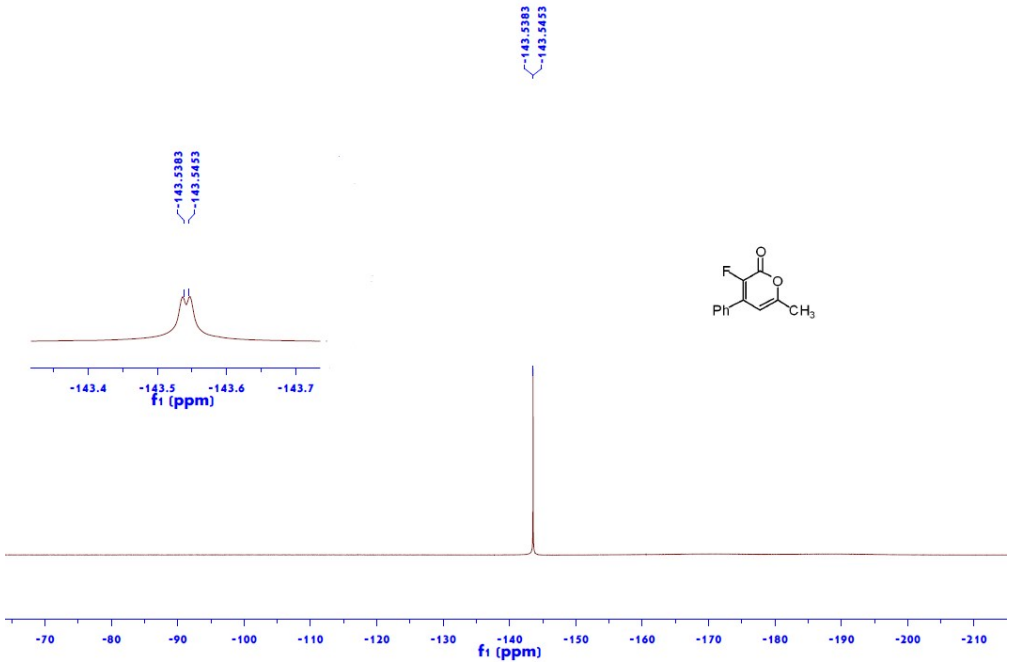

-143.5383
-143.5453
-143.5383
-143.5453
F
O
O
Ph
CH3
-143.4
-143.5
-143.6
-143.7
f1 (ppm)
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Figure S38. ^{1}H and ^{13}C NMR Spectra of 8

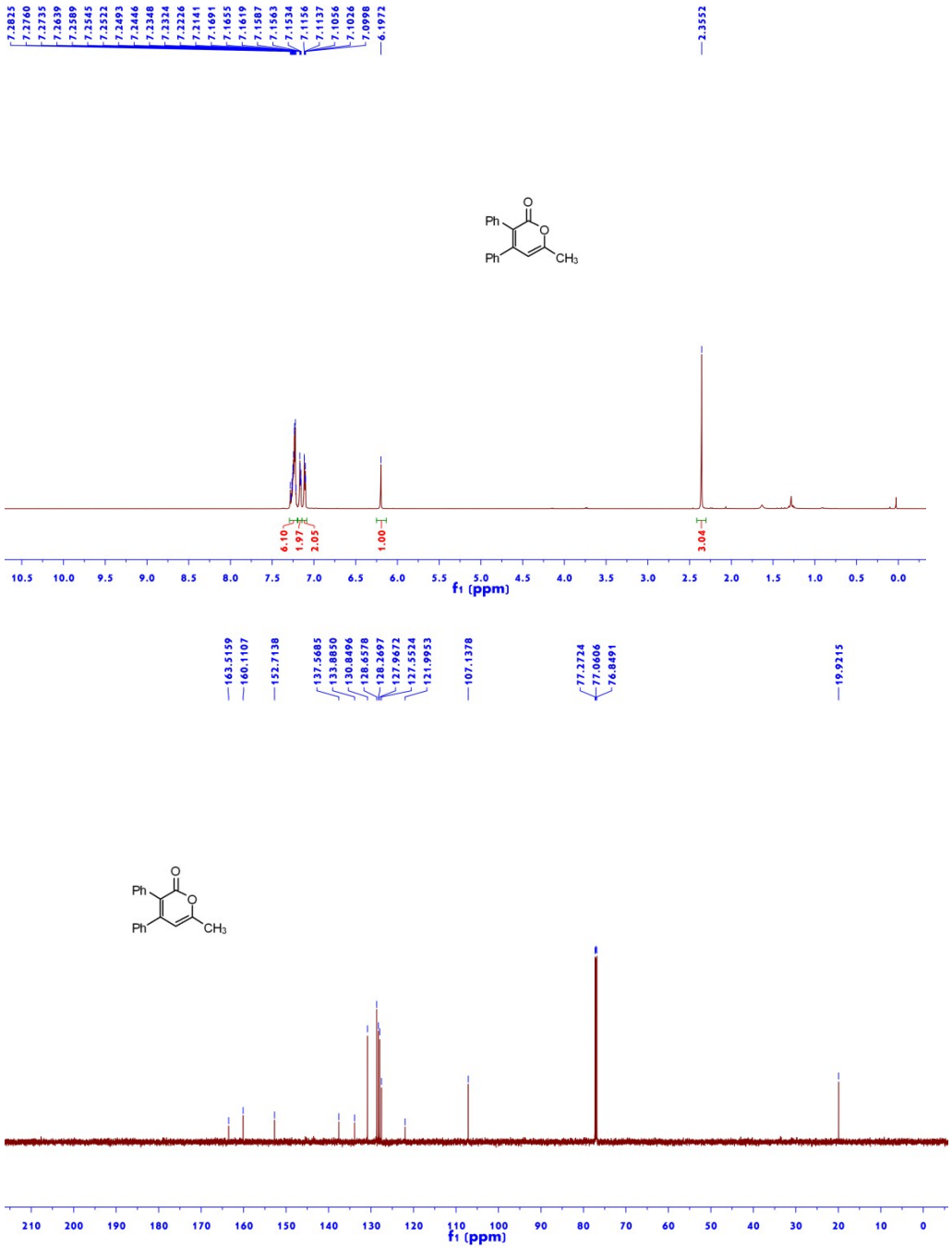


Figure S39. ^{1}H and ^{13}C NMR Spectra of 9

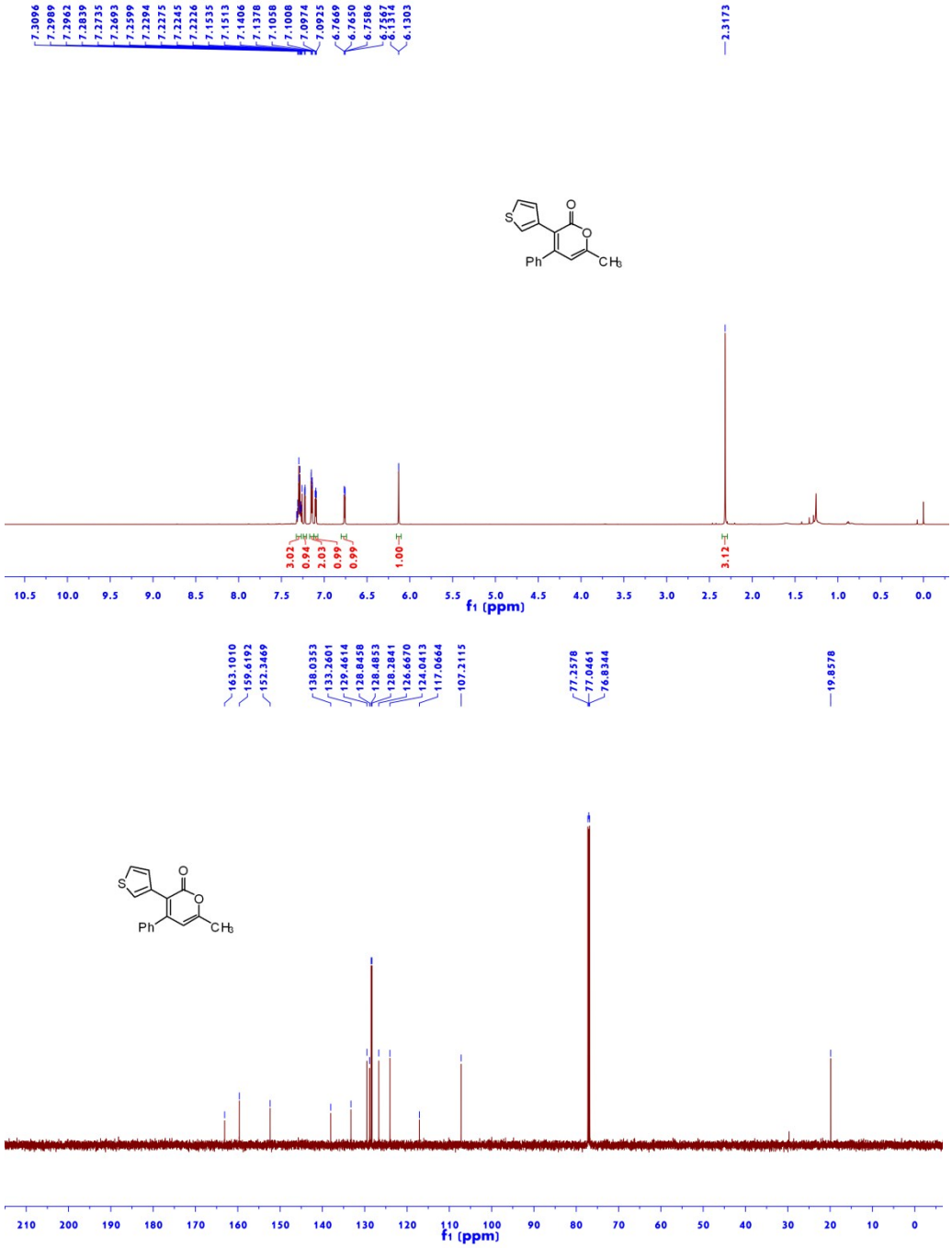


Figure S40. ^{1}H and ^{13}C NMR Spectra of 10

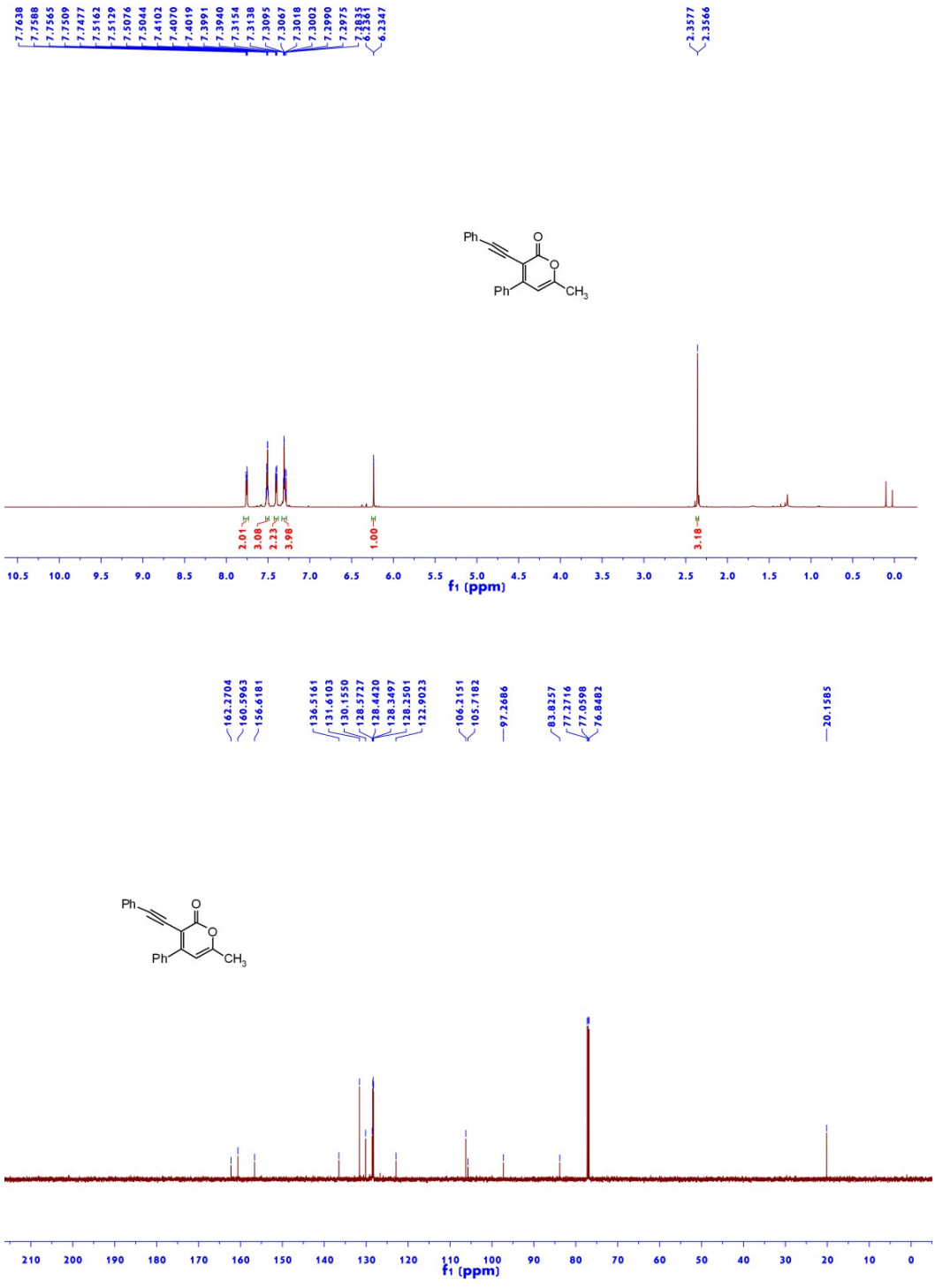


Figure S41. ^{1}H and ^{13}C NMR Spectra of 11

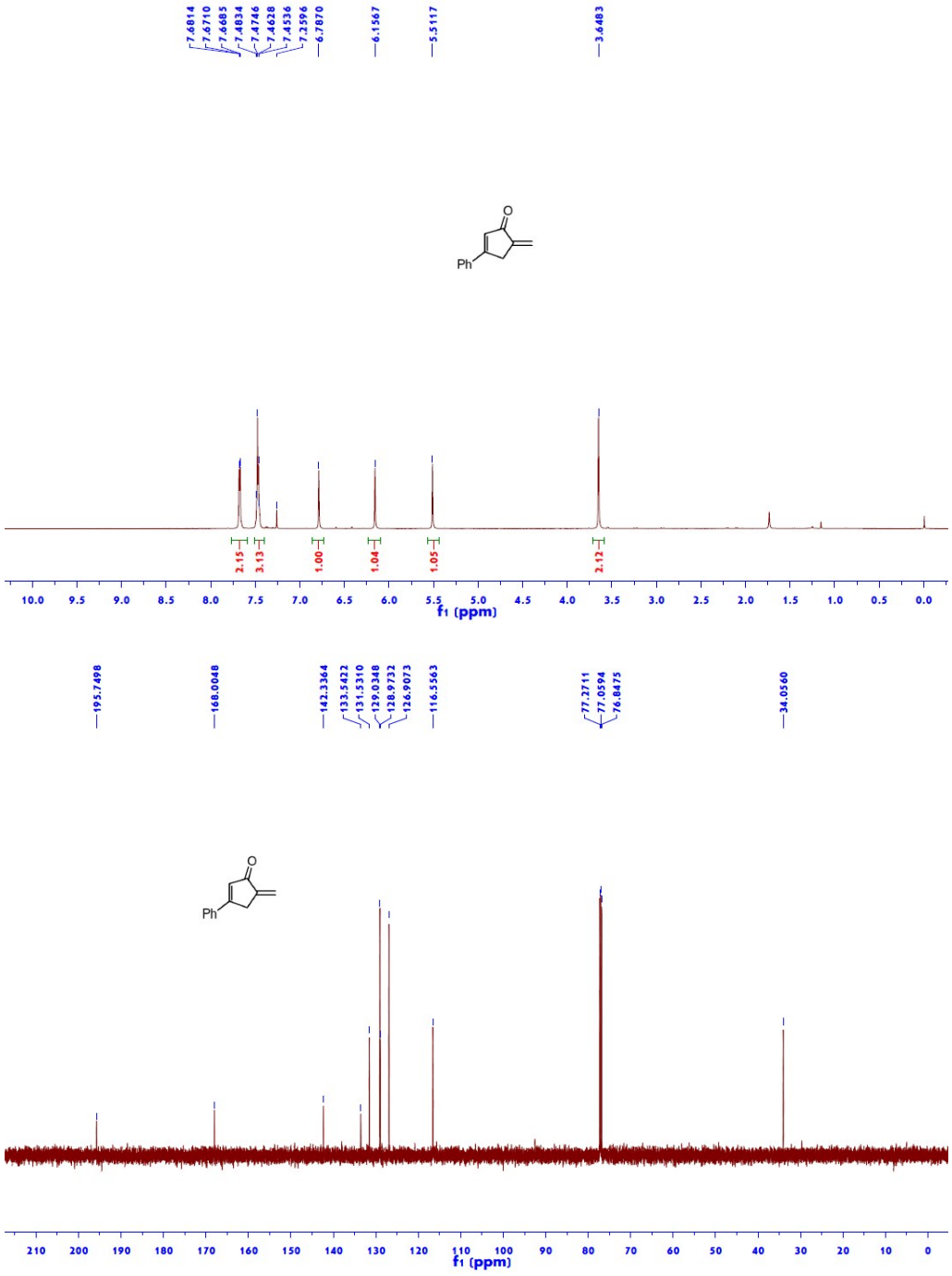


Figure S42. ^{1}H and ^{13}C NMR Spectra of 12

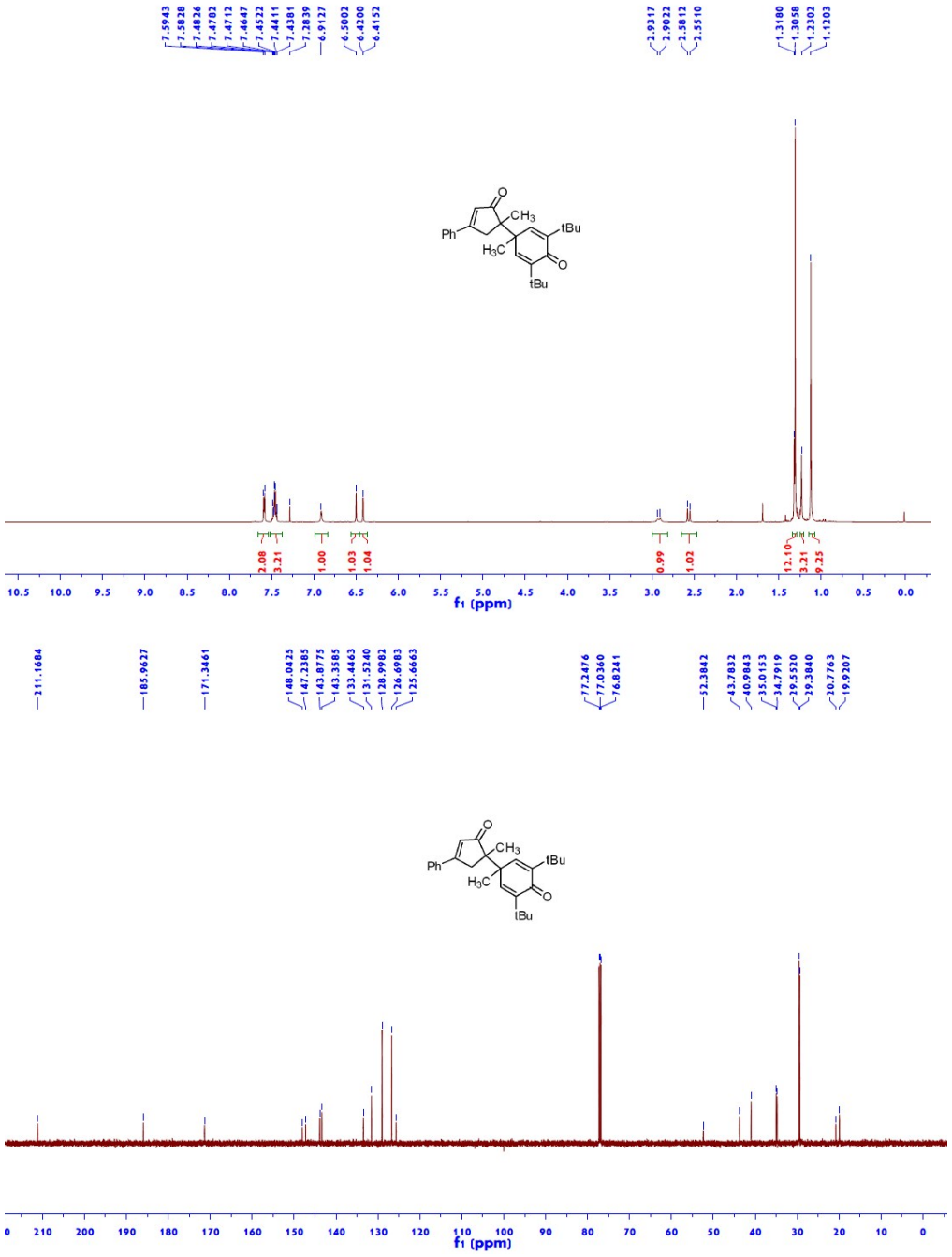
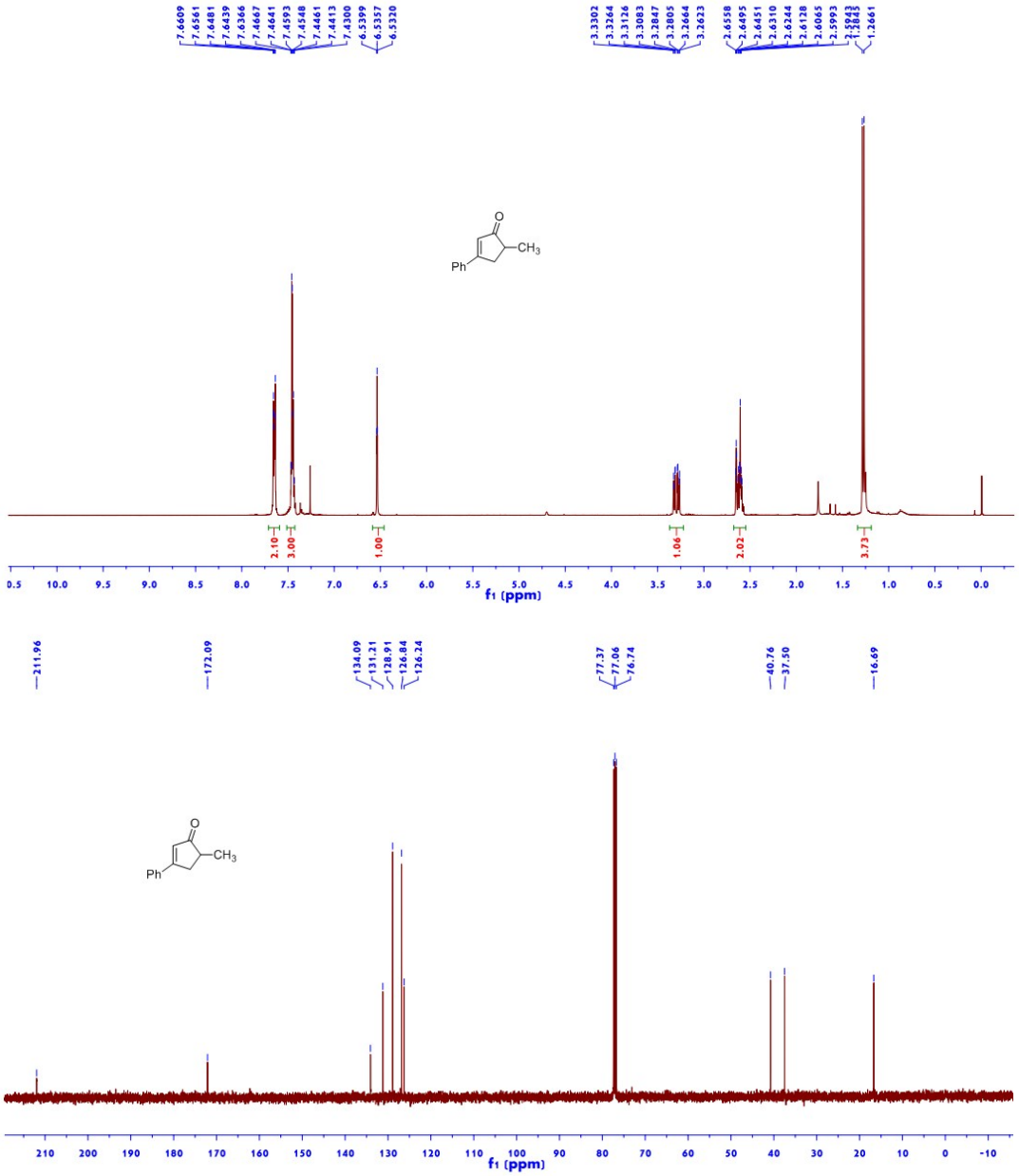
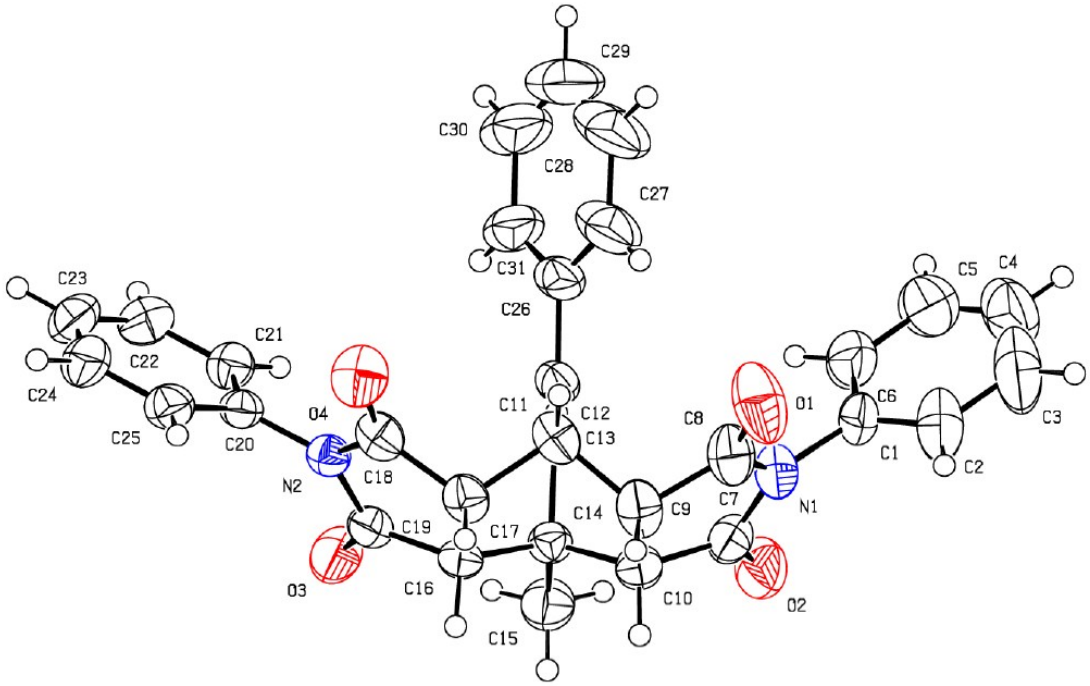


Figure S43. ^{1}H and ^{13}C NMR Spectra of 13



7. ORTEP Drawings

Figure S44. ORTEP Drawing of 6 with Thermal Ellipsoids at 50% Probability Levels[S9]



8. References

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[S9] CCDC 1937263 (**6**), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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