Supporting Information

Iron-catalyzed tandem cyclization of olefinic dicarbonyl compounds with benzylic Csp^3-H bonds for the synthesis of dihydrofurans

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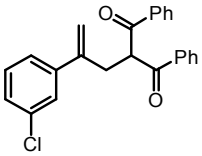
General Information

All Reactions were carried out under an atmosphere of nitrogen with the strict exclusion of air. Column chromatography was carried out on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III-400 in solvents as indicated. Chemical shift are reported in ppm from $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm^{-1}. HRMS were obtained on a Q-TOF micro spectrometer.

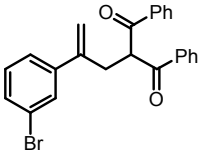
Starting Materials

All of olefinic dicarbonyl compounds **2** were synthesized according to the literature, and the NMR spectroscopy were in full accordance with the data in the literature.[1]

Characterization of New Starting Materials



2e: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.6 Hz, 4H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 4H), 7.30-7.20(m, 4H), 5.33 (t, *J* = 6.8 Hz, 1H), 5.25 (s, 1H), 5.15 (s, 1H), 3.31 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 143.8, 142.0, 135.9, 134.5, 133.6, 129.8, 128.8, 128.6, 127.9, 126.7, 124.6, 116.6, 54.9, 34.9 ppm; IR (KBr): υ_{max} 1698, 1595, 1447, 1268 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}ClNaO_2$ $[M+Na]^+$ 397.0966, found 397.0951.



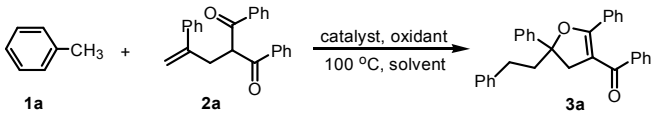
2f: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.6 Hz, 4H), 7.80-7.53 (m, 2H), 7.45-7.39 (m, 6H), 7.25-7.20 (m, 2H), 5.32 (t, *J* = 6.8 Hz, 1H), 5.24 (s, 1H), 5.15 (s, 1H), 3.31 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 143.8, 142.3, 135.9, 133.6, 130.9, 130.1, 129.7, 129.6, 128.8, 128.6, 125.1, 122.7, 116.7, 54.9, 35.0 ppm; IR (KBr): υ_{max} 1698, 1595, 1448, 1268 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}BrNaO_2$ $[M+Na]^+$ 441.0461, found 441.0452.

Optimization of Reaction Conditions

General Procedure

A 10 mL oven-dried Schlenk-tube was charged with catalyst (See Table S1). The tube was evacuated and backfilled with nitrogen (three times). **2a** (0.2 mmol, 1.0 equiv), toluene **2a** and oxidants (See Table S1) in 1 mL solvent were added by syringe. The tube was then sealed and the mixture was stirred for 24 h at 100 ^{o}C. Upon completion of the reaction, the mixture was diluted with EtOAc, filtered through a pad of Celite, and the filtrate was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/25 to 1/10) to yield the product **3a** as a colorless oil.

Table S1 Optimization of the reaction conditions[a]

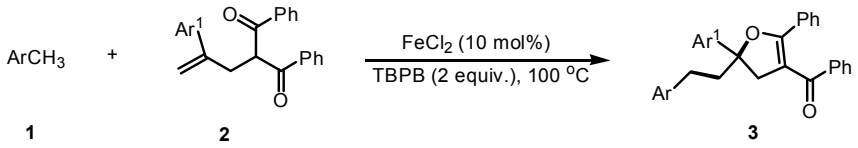


1a 2a 3a

Entry	Catalyst (mol%)	Oxidant (equiv.)	Solvent	Yield[b] (%)
1	Cu_2O (10)	TBPB (2.0)	CH_3CN	n.r.[c]
2	Cu_2O (10)	TBPB (2.0)	EtOAc	6
3	Cu_2O (10)	TBPB (2.0)	DMF	n.r.[c]
4	Cu_2O (10)	TBPB (2.0)	DMSO	13
5	Cu_2O (10)	TBPB (2.0)	PhCl	16
6	Cu_2O (10)	TBPB (2.0)	dioxane	n.r.[c]
7[d]	Cu_2O (10)	TBPB (2.0)	-	50
8[d]	Cu_2O (10)	TBHP (2.0)	-	29
9[d]	Cu_2O (10)	DTBP (2.0)	-	trace
10[d]	Cu_2O (10)	DCP (2.0)	-	trace
11[d]	CuCl (10)	TBPB (2.0)	-	66
12[d]	CuBr (10)	TBPB (2.0)	-	67
13[d]	$Cu(OAc)_2$ (10)	TBPB (2.0)	-	63
14[d]	$CuBr_2$ (10)	TBPB (2.0)	-	55
15[d]	CuO (10)	TBPB (2.0)	-	63
16[d]	$FeCl_3$ (10)	TBPB (2.0)	-	67
17[d]	$Fe(OAc)_2$ (10)	TBPB (2.0)	-	51
18[d]	**$FeCl_2$ (10)**	**TBPB (2.0)**	**-**	**74 (70)[e]**
19[d]	$FeCl_2$ (5)	TBPB (2.0)	-	56
20[d]	$FeCl_2$ (20)	TBPB (2.0)	-	50
21[d]	$FeCl_2$ (10)	TBPB (2.0)	-	63[f]
22[d]	$FeCl_2$ (10)	TBPB (2.0)	-	23[g]
23[d]	$FeCl_2$ (10)	TBPB (2.0)	-	66[h]
24[d]	$FeCl_2$ (10)	TBPB (1.0)	-	45
25[d]	$FeCl_2$ (10)	TBPB (3.0)	-	55
26[d]		TBPB (2.0)	-	49
27[d]	$FeCl_2$ (10)			n.r.[c]

[a] Reaction conditions: 10 mol% of catalyst, **2a** (0.2 mmol, 1.0 equiv.), oxidant (2.0 equiv.), toluene (**1a**, 1.0 mmol, 5.0 equiv.), solvent (1.0 mL), 100 °C, 24 h, under N_2. [b] Yield of isolated product. [c] n.r. = no reaction. [d] **1a** (1 mL). [e] Yield on a 1 mmol scale is given in parentheses. [f] under air. [g] 80 °C. [h] 120 °C.

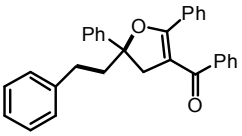
General Procedure for the Oxidative Cyclization of Olefinic Dicarbonyl Compounds with Benzylic Hydrocarbons



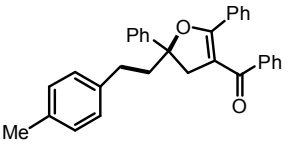
1 2 3

A 10 mL oven-dried Schlenk-tube was charged with $FeCl_2$ (2.5 mg, 10 mol%), dicarbonyl compounds (**2**, 0.2 mmol, 1.0 equiv.). The tube was evacuated and backfilled with nitrogen (three times). TBPB (0.4 mmol, 2.0 equiv.) in 1 mL of benzylic hydrocarbons were added by syringe. The tube was then sealed and the mixture was stirred for 24 h at 100 ^{o}C. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/25 to 1/10) to give the corresponding products **3** or **4** in yields listed in Table 2 and Table 3.

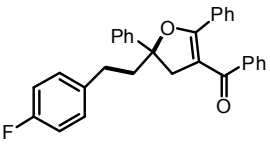
Characterization of Products 3



3a: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.2 Hz, 2H), 7.48-7.42 (m, 4H), 7.37-7.21 (m, 7H), 7.19-7.06 (m, 7H), 3.64 (d, *J* = 15.2 Hz, 1H), 3.63 (d, *J* = 15.2 Hz, 1H), 2.85 (td, *J* = 12.4, 4.0 Hz, 1H), 2.60 (td, *J* = 12.4, 4.0 Hz, 1H), 2.51 (td, *J* = 12.4, 4.0 Hz, 1H), 2.42 (td, *J* = 12.4, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.7, 144.8, 141.5, 139.0, 131.0, 130.1, 130.0, 129.4, 128.8, 128.5, 128.4, 128.3, 127.6, 127.3, 125.9, 124.7, 111.7, 90.5, 45.7, 44.5, 30.3 ppm; IR (KBr): υ_{max} 1614, 1493, 1448, 1365, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{26}KO_2$ $[M+K]^+$ 469.1564, found 469.1564.

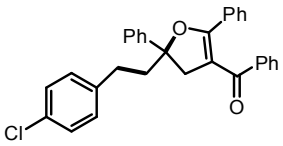


3b: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.34-7.28 (m, 3H), 7.23-7.19 (m, 2H), 7.11-7.03 (m, 8H), 3.61 (d, *J* = 15.6 Hz, 1H), 3.57 (d, *J* = 15.6 Hz, 1H), 2.78 (td, *J* = 13.2, 4.0 Hz, 1H), 2.57-2.36 (m, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.8, 144.8, 139.0, 138.4, 135.3, 131.0, 130.2, 130.0, 129.4, 129.1, 128.8, 128.5, 128.1, 127.6, 127.3, 124.7, 111.7, 90.6, 45.7, 44.7, 29.9, 20.9 ppm; IR (KBr): υ_{max} 1614, 1514, 1492, 1447, 1365, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{28}NaO_2$ $[M+Na]^+$ 467.1981, found 467.1962.

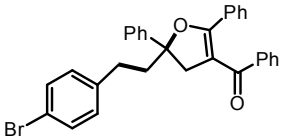


3c: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.2 Hz, 2H), 7.46-7.40 (m, 4H) 7.35 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.24-7.20 (m, 2H), 7.14-7.05 (m, 6H), 6.94 (t, *J* = 8.4 Hz, 2H), 3.63 (d, *J* = 14.8 Hz, 1H), 3.58 (d, *J* = 15.2 Hz, 1H), 2.81 (td, *J* = 13.2, 4.4 Hz,

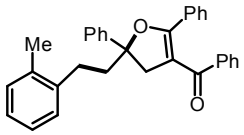
1H), 2.59-2.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.6, 161.3 (d, *J* = 242.1 Hz), 144.7, 139.0, 137.1 (d, *J* = 3.0 Hz), 131.1, 130.1, 129.6 (d, *J* = 7.7 Hz), 129.4, 128.8, 128.6, 127.7, 127.6, 127.4, 124.7, 115.1 (d, *J* = 21.1 Hz), 111.7, 90.4, 45.8, 44.6, 29.6 ppm; IR (KBr): υ_{max} 1721, 1596, 1510, 1448, 1366, 1223 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}FNaO_2$ $[M+Na]^+$ 471.1731, found 471.1718.



3d: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.46-7.32 (m, 6H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.25-7.20 (m, 4H), 7.13-7.04 (m, 6H), 3.60 (d, *J* = 14.8 Hz, 1H), 3.58 (d, *J* = 15.2 Hz, 1H), 2.77 (td, *J* = 13.2, 4.0 Hz, 1H), 2.53-2.39 (m, 2H), 2.36 (td, *J* = 13.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.6, 144.7, 140.0, 138.9, 131.6, 131.1, 130.1, 129.7, 129.4, 128.8, 128.6, 128.5, 127.7, 127.6, 127.4, 124.7, 111.7, 90.4, 45.8, 44.4, 29.8 ppm; IR (KBr): υ_{max} 1721, 1595, 1492, 1448, 1366, 1250 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}ClNaO_2$ $[M+Na]^+$ 487.1435, found 487.1417.

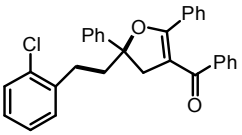


3e: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.51 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40-7.32 (m, 5H), 7.28-7.20 (m, 4H), 7.13-7.01 (m, 6H), 3.61 (d, *J* = 14.8 Hz, 1H), 3.57 (d, *J* = 15.2 Hz, 1H), 2.80-2.73 (m, 1H), 2.55-2.42 (m, 2H), 2.38-2.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.5, 144.6, 140.5, 139.0, 131.4, 131.1, 130.1, 129.4, 128.8, 128.6, 127.7, 127.6, 127.4, 124.7, 119.6, 111.6, 90.4, 45.9, 44.3, 29.9 ppm; IR (KBr): υ_{max} 1614, 1490, 1447, 1365, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}BrNaO_2$ $[M+Na]^+$ 531.0930, found 531.0925.

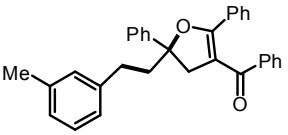


3f: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz,

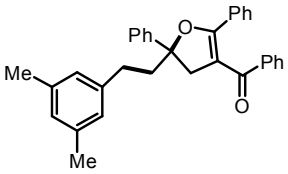
$CDCl_3$): δ = 7.57-7.55 (m, 2H), 7.47-7.40 (m, 4H), 7.37-7.33 (m, 3H), 7.24-7.21 (m, 2H), 7.15-7.05 (m, 8H), 3.62 (s, 2H), 2.82 (td, *J* = 12.8, 4.4 Hz, 1H), 2.55 (td, *J* = 13.2, 4.4 Hz, 1H), 2.44 (td, *J* = 12.0, 4.4 Hz, 1H), 2.37-2.32 (m, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 164.7, 144.7, 139.7, 139.0, 135.8, 131.1, 130.2, 130.0, 129.4, 128.8, 128.7, 128.5, 127.7, 127.6, 127.4, 126.1, 124.7, 111.8, 90.6, 45.7, 43.3, 27.7, 19.1 ppm; IR (KBr): υ_{max} 1721, 1595, 1492, 1448, 1366, 1248 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{28}NaO_2$ $[M+Na]^+$ 467.1982, found 467.1974.



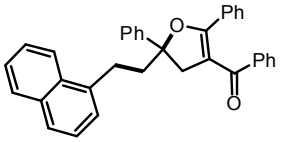
3g: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.45-7.40 (m, 4H), 7.35-7.32 (m, 4H), 7.24-7.20 (m, 2H), 7.17-7.05 (m, 7H), 3.61 (s, 2H), 2.98 (td, *J* = 13.2, 4.4 Hz, 1H), 2.67 (td, *J* = 13.2, 4.4 Hz, 1H), 2.50 (td, *J* = 13.6, 4.4 Hz, 1H), 2.35 (td, *J* = 13.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 164.8, 144.6, 139.1, 139.0, 133.9, 131.1, 130.4, 130.2, 130.0, 129.5, 128.9, 128.5, 127.7, 127.6, 127.5, 127.4, 126.9, 124.7, 111.8, 90.5, 45.8, 42.4, 28.5 ppm; IR (KBr): υ_{max} 1614, 1492, 1446, 1364, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}ClNaO_2$ $[M+Na]^+$ 487.1435, found 487.1430.



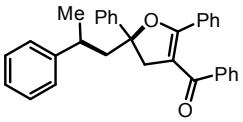
3h: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.53 (m, 2H), 7.46-7.38 (m, 4H), 7.35-7.30 (m, 3H), 7.24-7.20 (m, 2H), 7.18-7.05 (m, 5H), 7.01-6.96 (m, 3H), 3.63 (d, *J* = 15.2 Hz, 1H), 3.59 (d, *J* = 15.2 Hz, 1H), 2.79 (td, *J* = 12.8, 4.4 Hz, 1H), 2.58-2.45 (m, 2H), 2.39 (td, *J* = 13.2, 4.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.8, 144.9, 141.5, 139.0, 138.0, 131.1, 130.2, 130.0, 129.4, 129.1, 128.8, 128.5, 128.3, 127.7, 127.6, 127.3, 126.6, 125.3, 124.7, 111.7, 90.6, 45.7, 44.6, 30.3, 21.3 ppm; IR (KBr): υ_{max} 1721, 1611, 1492, 1448, 1364, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{28}NaO_2$ $[M+Na]^+$ 467.1982, found 467.1969.



3i: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.54 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.46-7.40 (m, 4H) 7.36-7.31 (m, 3H), 7.25-7.21 (m, 2H), 7.14-7.05 (m, 4H), 6.83-6.79 (m, 3H), 3.63 (d, *J* = 15.2 Hz, 1H), 3.59 (d, *J* = 15.2 Hz, 1H), 2.80-2.71 (m, 1H), 2.56-2.35 (m, 3H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.8, 144.9, 141.4, 139.1, 137.9, 131.1, 130.2, 130.0, 129.4, 128.8, 128.5, 128.4, 127.7, 127.6, 127.5, 127.3, 126.1, 124.7, 111.7, 90.6, 45.7, 44.6, 30.1, 21.2 ppm; IR (KBr): υ_{max} 1722, 1608, 1492, 1448, 1365, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{30}NaO_2$ $[M+Na]^+$ 481.2138, found 481.2114.



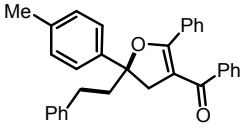
3j: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 9.2, 1.2 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.51-7.46 (m, 3H), 7.44-7.35 (m, 8H), 7.30-7.20 (m, 3H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 2H), 3.64 (s, 2H), 3.30 (td, *J* = 12.8, 4.4 Hz, 1H), 2.99 (td, *J* = 12.8, 4.4 Hz, 1H), 2.67-2.59 (m, 1H), 2.53-2.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 164.6, 144.7, 139.0, 137.7, 133.9 131.6, 131.1, 130.2, 130.1, 129.5, 128.9, 128.8, 128.6, 127.7, 127.6, 127.5, 126.8, 125.9, 125.8, 125.6, 125.5, 124.8, 123.5, 111.9, 90.8, 45.9, 43.8, 27.6 ppm; IR (KBr): υ_{max} 1595, 1492, 1447, 1364, 1247 cm^{-1}; HRMS (ESI) calcd for $C_{35}H_{28}KO_2$ $[M+K]^+$ 519.1721, found 519.1721.



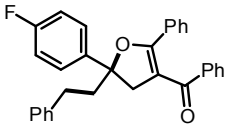
3k: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.3-7.36 (m, 4H), 7.31-7.27 (m, 1H), 7.23-7.19 (m, 6H), 7.14-7.04 (m, 7H), 3.50 (d, *J* = 13.6 Hz, 1H), 3.46 (d, *J* = 13.2 Hz, 1H), 2.79-2.77 (m, 1H), 2.53-2.48 (m, 2H), 1.32 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 164.5, 147.8, 144.8, 139.1, 131.1, 130.1, 130.0, 129.4, 128.9,

128.4, 127.6, 127.2, 127.1, 126.7, 125.9, 124.8, 111.5, 91.2, 50.5, 46.9, 36.3, 23.5 ppm; IR (KBr): υ_{max} 1615, 1493, 1448, 1363, 1260 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{28}NaO_2$ $[M+Na]^+$ 467.1982, found 467.1977.

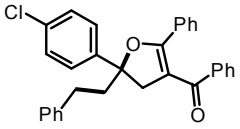
Characterization of Products 4



4a: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.38 (m, 4H), 7.32-7.19 (m, 8H) 7.17-7.04 (m, 7H), 3.61 (d, *J* = 15.2 Hz, 1H), 3.56 (d, *J* = 15.2 Hz, 1H), 2.81 (td, *J* = 13.2, 4.4 Hz, 1H), 2.58 (td, *J* = 13.2, 4.4 Hz, 1H), 2.51-2.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 164.9, 141.8, 141.6, 139.1, 137.0, 131.0, 130.2, 130.0, 129.4, 129.2, 128.8, 128.4, 128.3, 127.7, 127.6, 125.9, 124.7, 111.8, 90.7, 45.7, 44.5, 30.4, 21.1 ppm; IR (KBr): υ_{max} 1596, 1493, 1449, 1366, 1248 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{28}NaO_2$ $[M+Na]^+$ 467.1982, found 467.1961.

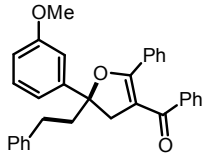


4b: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.48 (m, 2H), 7.41-7.39 (m, 2H) 7.29-7.26 (m, 4H), 7.23-7.05 (m, 11H), 3.61 (d, *J* = 15.2 Hz, 1H), 3.56 (d, *J* = 14.8 Hz, 1H), 2.81 (td, *J* = 12.8, 4.4 Hz, 1H), 2.61-2.45 (m, 2H), 2.36 (td, *J* = 13.2, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.5, 162.0 (d, *J* = 244.6 Hz), 141.3, 140.6 (d, *J* = 3.1 Hz), 138.9, 131.2, 130.1, 130.0, 129.4, 128.8, 128.5, 128.3, 127.7, 126.5 (d, *J* = 8.0 Hz), 126.0, 115.4 (d, *J* = 21.3 Hz), 111.7, 90.2, 45.7, 44.5, 30.3 ppm; IR (KBr): υ_{max} 1721, 1601, 1510, 1449, 1366, 1237 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}FNaO_2$ $[M+Na]^+$ 471.1731, found 471.1730.

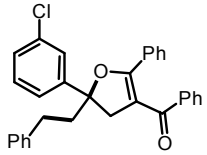


4c: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.44 (m, 2H), 7.41-7.38 (m, 4H) 7.29-7.07 (m, 13H), 3.59 (d, *J* = 14.8 Hz, 1H), 3.53 (d, *J* = 15.2 Hz, 1H), 2.81 (td, *J* = 13.2, 4.4 Hz, 1H), 2.59-2.44 (m, 2H), 2.34 (td, *J* = 13.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.4, 143.4, 141.2, 138.8, 133.2, 131.2, 130.2, 129.9, 129.4, 128.8, 128.7, 128.5, 128.3,

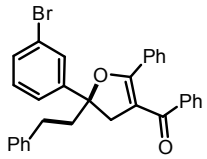
127.7, 126.2, 126.0, 111.6, 90.1, 45.7, 44.4, 30.3; IR (KBr): υ_{max} 1721, 1596, 1492, 1449, 1366, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}ClNaO_2$ $[M+Na]^+$ 487.1435, found 487.1423.



4d: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.30-7.15 (m, 9H), 7.12-7.04 (m, 6H), 6.86 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.85 (s, 3 H), 3.58 (s, 2H), 2.79 (td, *J* = 13.2, 4.4 Hz, 1H), 2.57 (td, *J* = 13.6, 4.4 Hz, 1H), 2.47 (td, *J* = 13.6, 4.4 Hz, 1H), 2.37 (td, *J* = 12.8, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 164.7, 159.8, 146.6, 141.6, 139.0, 131.1, 130.2, 130.0, 129.7, 129.4, 128.9, 128.4, 128.3, 127.7, 127.6, 125.9, 117.1, 112.2, 111.8, 111.1, 90.5, 55.3, 45.8, 44.5, 30.4; IR (KBr): υ_{max} 1721, 1610, 1492, 1449, 1365, 1250 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{28}NaO_3$ $[M+Na]^+$ 483.1931, found 483.1922.

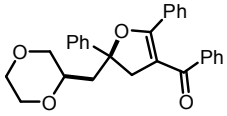


4e: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 1.6 Hz, 1H), 7.42-7.37 (m, 4H), 7.34-7.28 (m, 5H), 7.25-7.21 (m, 2H), 7.19-7.06 (m, 7H), 3.60 (d, *J* = 14.8 Hz, 1H), 3.56 (d, *J* = 15.2 Hz, 1H), 2.83 (td, *J* = 13.2, 4.4 Hz, 1H), 2.58 (td, *J* = 12.4, 4.4 Hz, 1H), 2.48 (td, *J* = 13.2, 4.4 Hz, 1H), 2.36 (td, *J* = 12.8, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 164.3, 147.0, 141.2, 138.8, 134.6, 131.2, 130.2, 129.9, 129.4, 128.8, 128.5, 128.3, 127.7, 127.6, 126.0, 125.1, 123.0, 111.6, 89.9, 45.7, 44.4, 30.3; IR (KBr): υ_{max} 1595, 1573, 1493, 1448, 1365, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}ClNaO_2$ $[M+Na]^+$ 487.1435, found 487.1425.

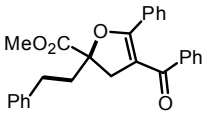


4f: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:10); ^1H NMR (400 MHz,

$CDCl_3$): δ = 7.69 (t, *J* = 1.6 Hz, 1H), 7.48-7.39 (m, 5H), 7.32-7.27 (m, 4H), 7.25-7.21 (m, 2H), 7.19-7.05 (m, 7H), 3.60 (d, *J* = 15.2 Hz, 1H), 3.55 (d, *J* = 15.2 Hz, 1H), 2.83 (td, *J* = 12.8, 4.4 Hz, 1H), 2.58 (td, *J* = 12.0, 4.8 Hz, 1H), 2.48 (td, *J* = 13.2, 4.8 Hz, 1H), 2.36 (td, *J* = 12.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =193.3, 164.3, 147.3, 141.2, 138.8, 131.2, 130.5, 130.2, 129.9, 129.4, 128.8, 128.5, 128.0, 127.7, 126.0, 123.4, 122.8, 111.6, 89.8, 45.7, 44.4, 30.3; IR (KBr): υ_{max} 1615, 1493, 1448, 1364, 1249, 1140, 1073 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}BrNaO_2$ $[M+Na]^+$ 531.0930, found 531.0916.

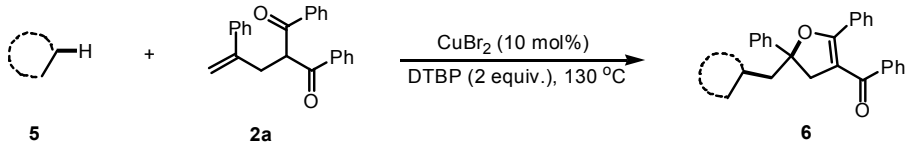


4g:Two diastereomers isolated as unseparable mixture (ratio 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.47 (m, 3H), 7.44-7.38 (m, 4H), 7.34-7.27 (m, 2H), 7.22-7.19 (m, 2H), 7.13-7.06 (m, 4H), 3.82-3.67 (m, 2H), 3.64-3.52 (m, 5H), 3.49-3.31 (m, 2H), 2.40-2.31 (m, 1H), 2.18-2.15 (m, 0.5H), 2.02-1.97 (m, 0.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 164.3, 164.0, 145.5, 143.8, 138.9, 131.2, 130.1, 130.0, 129.4, 129.3, 128.9, 128.6, 128.5, 127.7, 127.8, 127.6, 127.5, 124.8, 124.5, 124.3, 112.0, 111.7, 89.4, 88.9, 72.4, 72.2, 71.4, 71.3, 66.7, 66.6, 66.3, 66.2, 46.5, 45.5, 44.4 ppm; IR (KBr): υ_{max} 1723, 1614, 1493, 1447, 1363, 1249, 1120 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}NaO_4$ $[M+Na]^+$ 449.1723, found 449.1715.



4h: A colorless oil, R_f 0.15 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.32-7.19 (m, 9H) 7.11-7.05 (m, 4H), 3.83 (s, 3H), 3.56 (d, *J* = 15.6 Hz, 1H), 3.42 (d, *J* = 15.6 Hz, 1H), 2.92 (td, *J* = 13.6, 4.8 Hz, 1H), 2.72 (td, *J* = 13.6, 4.8 Hz, 1H), 2.50 (td, *J* = 13.6, 4.8 Hz, 1H), 2.36 (td, *J* = 13.6, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 172.7, 165.0, 140.6, 138.5, 131.4, 130.2, 129.5, 128.9, 128.5, 128.4, 127.7, 126.2, 111.1, 88.2, 52.8, 42.5, 39.3, 30.2 ppm; IR (KBr): υ_{max} 1744, 1596, 1617, 1447, 1365, 1246 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}NaO_4$ $[M+Na]^+$ 435.1567, found 435.1559.

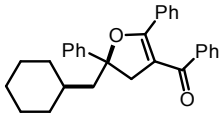
General Procedure for the Oxidative Cyclization of 2a with Alkanes and Cyclohexene



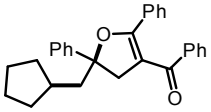
5 **2a** **6**

A 10 mL oven-dried Schlenk-tube was charged with $CuBr_2$ (4.4 mg, 10 mol%), **2a** (0.2 mmol, 1.0 equiv.). The tube was evacuated and backfilled with nitrogen (three times). DTBP (0.4 mmol, 2.0 equiv.) in 1 mL of alkanes or cyclohexene were added by syringe. The tube was then sealed and the mixture was stirred for 24 h at 130 °C. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/25 to 1/10) to give the corresponding products **6** in yields listed in Table 4.

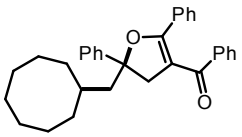
Characterization of Products 6



6a: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.48 (m, 2H), 7.47-7.36 (m, 4H), 7.32-7.28 (m, 3H), 7.22-7.18 (m, 2H), 7.11-7.03 (m, 4H), 3.52 (s, 2H), 2.11 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.01 (dd, *J* = 14.8, 5.2 Hz, 1H), 1.84-1.81 (m, 1H), 1.57-1.34 (m, 4H), 1.17-0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 164.8, 145.4, 139.1, 131.0, 130.3, 129.9, 129.4, 128.8, 128.4, 127.6, 127.1, 124.7, 111.7, 91.5, 50.0, 46.9, 34.5, 34.4, 33.9, 26.2 ppm; IR (KBr): υ_{max} 1615, 1492, 1447, 1363, 1246, 1146 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{30}NaO_2$ $[M+Na]^+$ 445.2138, found 445.2134.



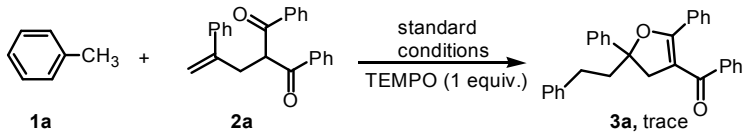
6b: A colorless oil l, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.48 (m, 2H), 7.41-7.37 (m, 4H), 7.32-7.30 (m, 3H), 7.23-7.19 (m, 2H), 7.12-7.03 (m, 4H), 3.57 (d, *J* = 15.2 Hz, 1H), 3.53(d, *J* = 14.8 Hz, 1H), 2.24 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.17 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.87-1.77 (m, 2H), 1.61-1.38 (m, 5H), 1.20-1.15 (m, 1H), 1.06-0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 164.8, 145.6, 139.2, 131.0, 130.3, 129.9, 129.4, 128.8, 128.4, 127.6, 127.1, 124.7, 111.7, 91.4, 48.7, 46.5, 36.3, 34.1, 33.8, 25.0, 24.8 ppm; IR (KBr): υ_{max} 1614, 1574, 1492, 1447, 1363, 1246 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{28}NaO_2$ $[M+Na]^+$ 431.1982, found 431.1980.



6c: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.0 Hz, 2H), 7.42-7.34 (m, 4H), 7.31-7.29 (m, 3H), 7.22-7.19 (m, 2H), 7.11-7.03 (m, 4H), 3.53 (s, 2H), 2.15 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.15 (dd, *J* = 14.4, 4.4 Hz, 1H), 1.71-1.26 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 164.8, 145.4, 139.2, 131.0, 130.3, 129.9, 129.4, 128.8, 128.3, 127.6, 127.1, 124.8, 111.7,

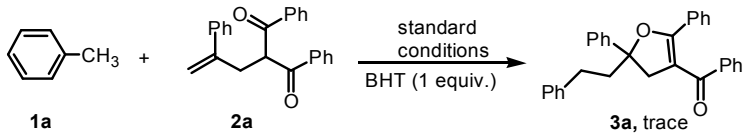
91.6, 50.1, 46.7, 33.4, 33.1, 32.9, 27.3, 26.2, 25.0 ppm; IR (KBr): υ_{max} 1617, 1492, 1446, 1362, 1246, 1149 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{34}NaO_2$ $[M+Na]^+$ 473.2451, found 473.2432.

Investigation of the Reaction Mechanism



1a **2a** **3a,** trace

When the TEMPO was added to the reaction of **1a** with **2a** under the standard conditions, only trace amount of the desired product **3a** was detected. The result indicates that the radical intermediate should be involved in the catalytic cycle of the reaction.



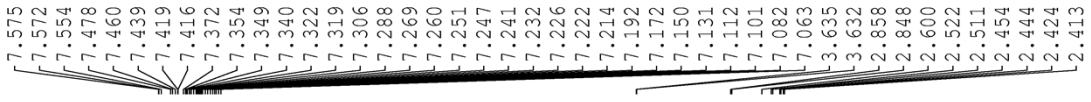
1a **2a** **3a,** trace

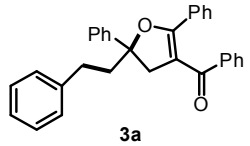
When the BHT was added to the reaction of **1a** with **2a** under the standard conditions, only trace amount of the desired product **3a** was detected. The result indicates that the radical intermediate should be involved in the catalytic cycle of the reaction.

References

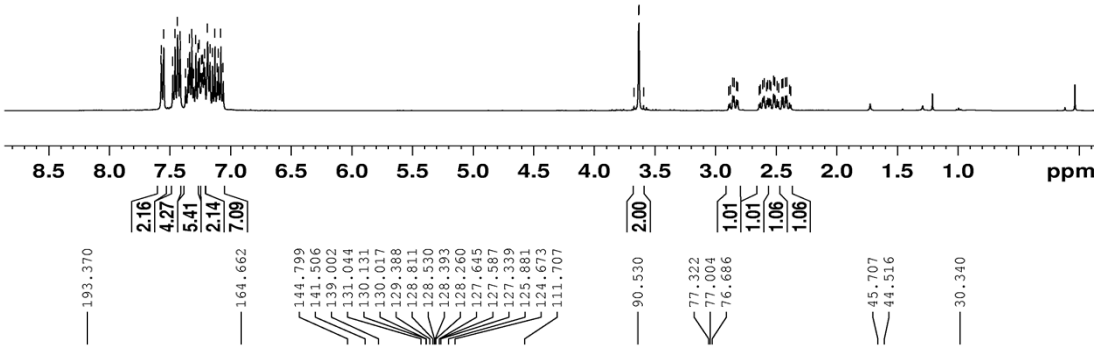
1 Y. Zhao, X. Jiang and Y.-Y. Yeung. *Angew. Chem.*, *Int. Ed.*, 2013, **52**, 8597.

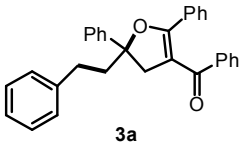
^{1}H NMR and ^{13}C NMR Spectra of the Products 3



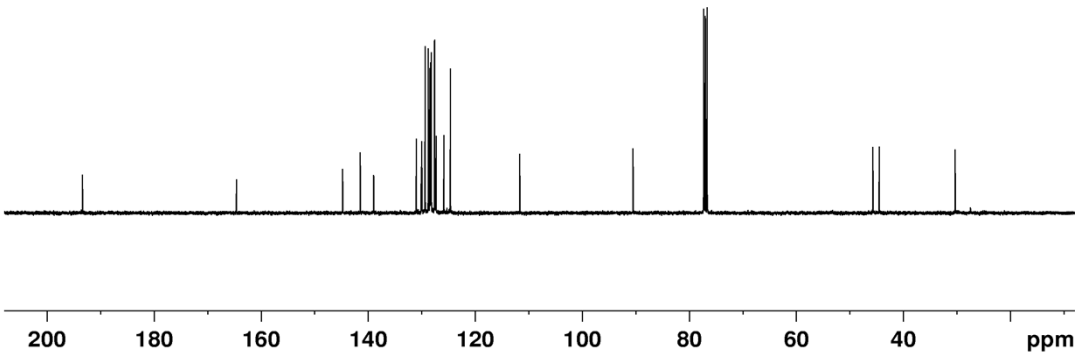


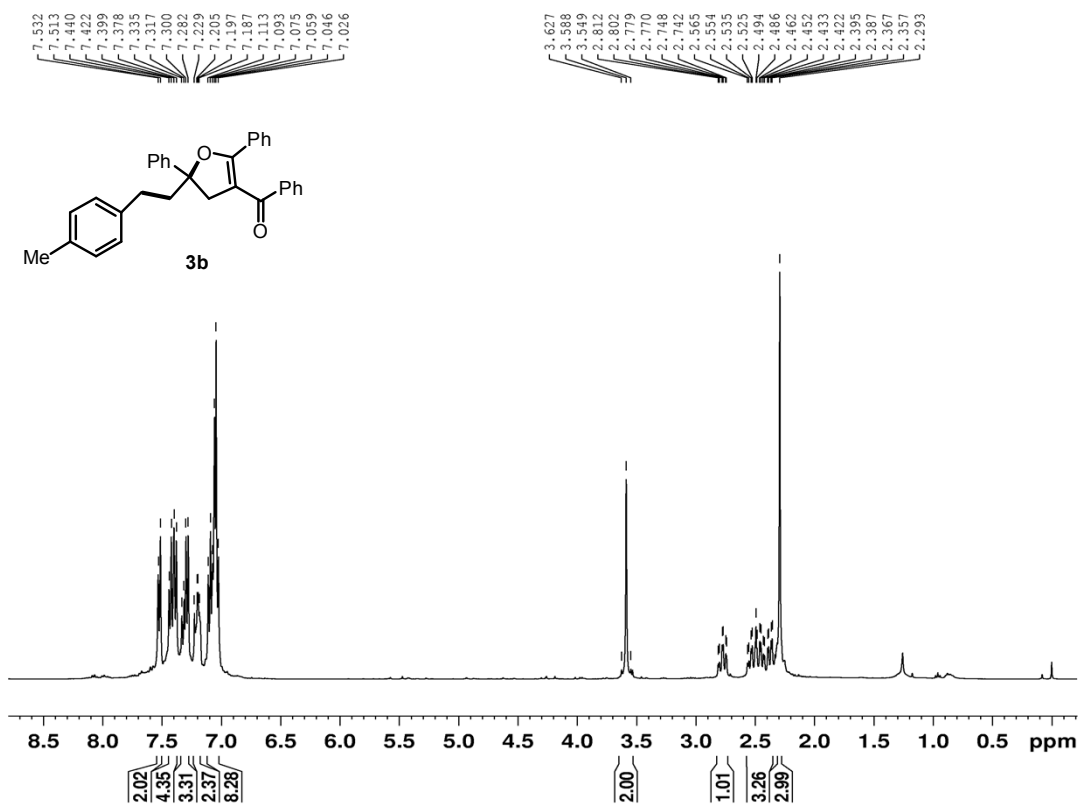
3a





3a

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7.197
7.187
7.113
7.093
7.075
7.059
7.046
7.026
3.627
3.588
3.549
2.812
2.802
2.779
2.770
2.748
2.742
2.565
2.554
2.535
2.525
2.494
2.486
2.462
2.452
2.433
2.422
2.395
2.387
2.367
2.357
2.293
Ph
Ph
O
Ph
O
Me
3b
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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4.35
3.31
2.37
8.28
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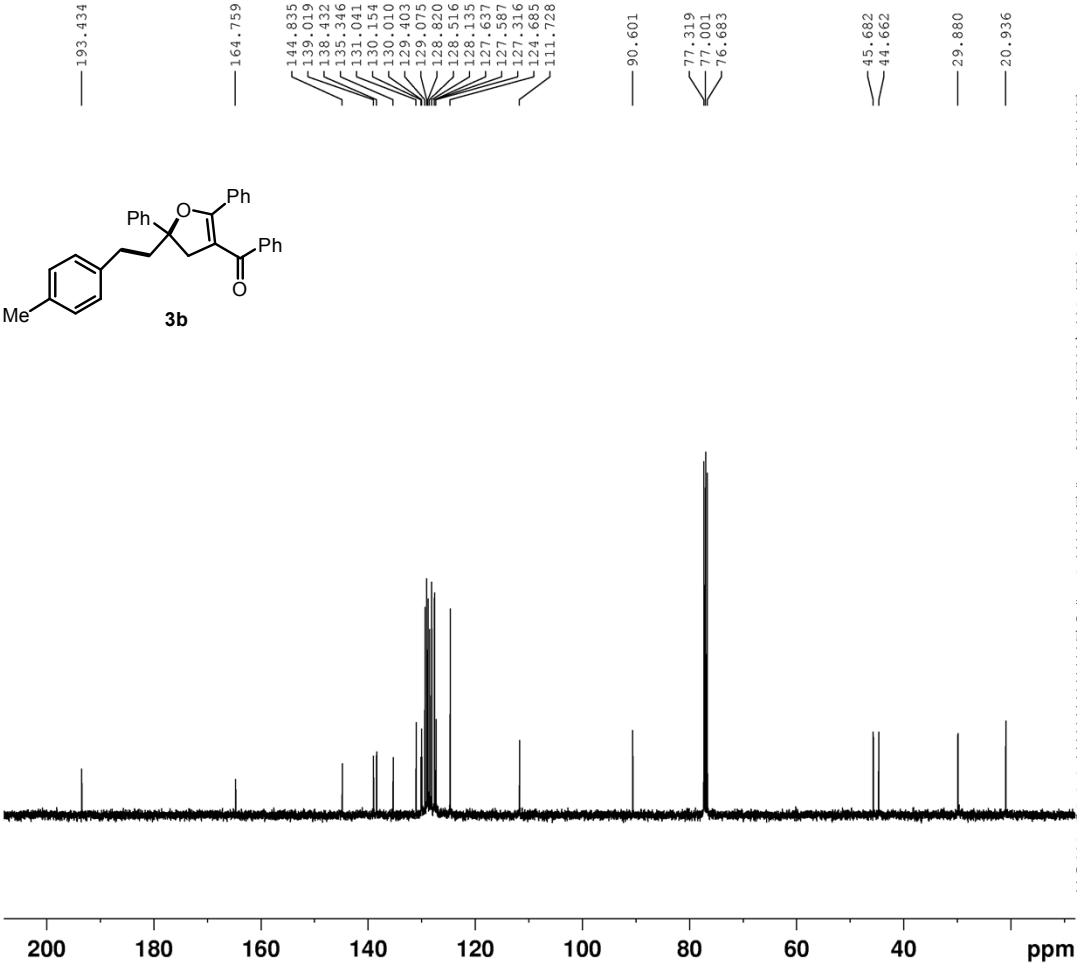
1.01
3.26
2.99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128.135
127.637
127.587
127.316
124.685
111.728
90.601
77.319
77.001
76.683
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44.662
29.880
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Ph
O
Ph
O
Me
3b
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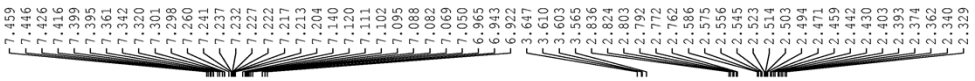
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7.237
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7.227
7.222
7.217
7.213
7.204
7.140
7.120
7.111
7.102
7.095
7.088
7.082
7.069
7.050
6.965
6.943
6.922
3.647
3.610
3.603
3.565
2.836
2.824
2.803
2.792
2.772
2.762
2.586
2.575
2.556
2.545
2.523
2.514
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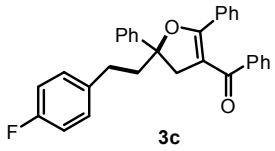
2.362
2.340
2.329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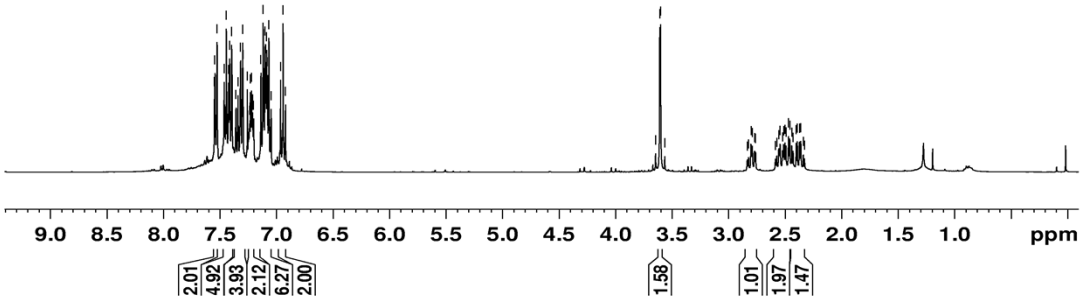
Ph
Ph
O
F

3c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3.0
2.5
2.0
1.5
1.0
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2.00
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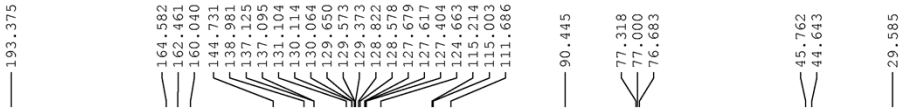
1.01
1.97
1.47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129.573
129.373
128.822
128.578
127.679
127.617
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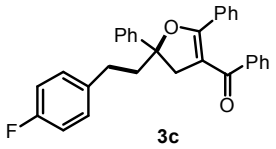
29.585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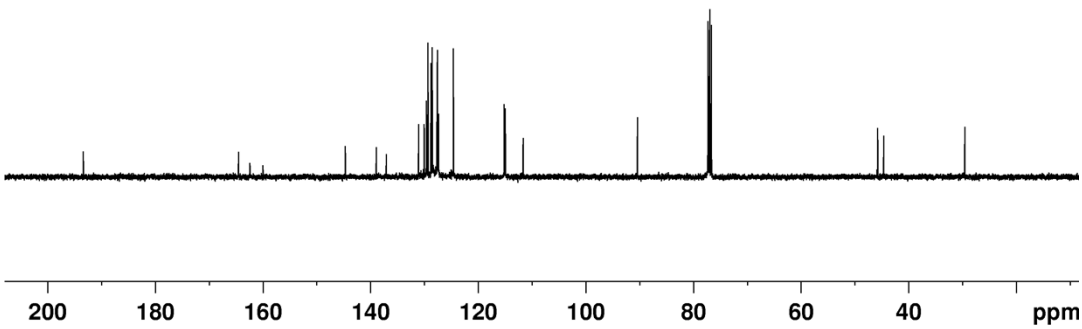
O
Ph
Ph
O
F

3c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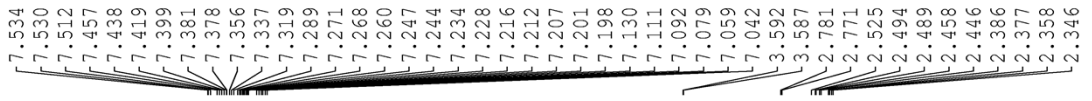
140
120
100
80
60
40
ppm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7.337
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7.289
7.271
7.268
7.260
7.247
7.244
7.234
7.228
7.216
7.212
7.207
7.201
7.198
7.130
7.111
7.092
7.079
7.059
7.042
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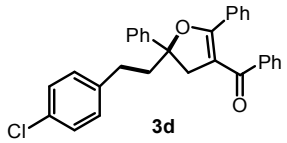
2.358
2.346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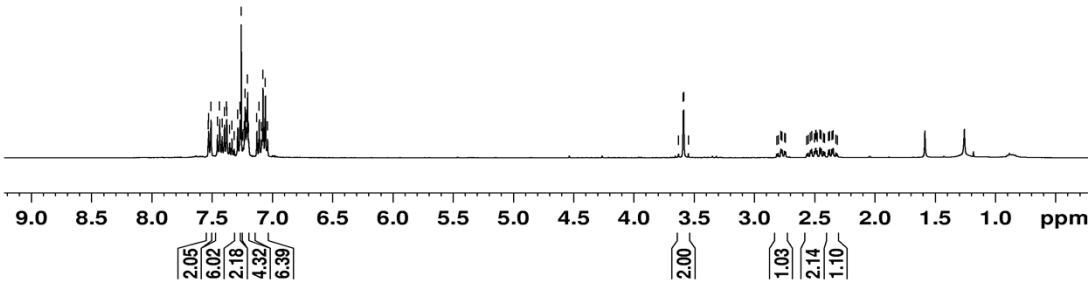
Ph
Ph
O
Cl

3d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6.0
5.5
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4.0
3.5
3.0
2.5
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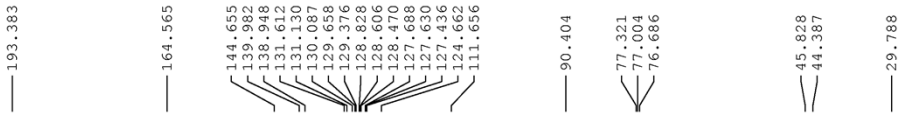
2.14
1.10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130.087
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128.606
128.470
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124.662
111.656
90.404
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76.686
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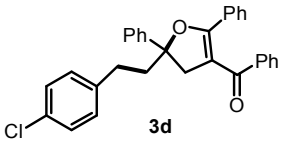
44.387
29.788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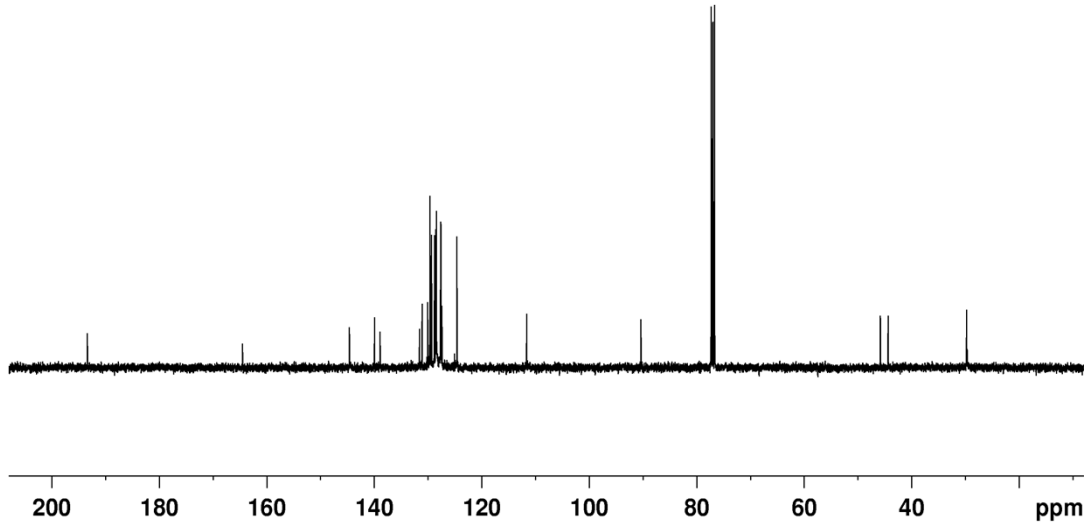
O
Ph
Ph
O
Cl

3d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180
160
140
120
100
80
60
40
ppm


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7.530
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7.510
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7.420
7.399
7.380
7.359
7.343
7.339
7.321
7.284
7.271
7.266
7.260
7.248
7.245
7.242
7.235
7.232
7.226
7.221
7.217
7.212
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7.202
7.199
7.131
7.112
7.102
7.093
7.081
7.061
7.042
7.027
7.006
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3.592
3.587
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2.787
2.764
2.756
2.735
2.731
2.550
2.539
2.521
2.510
2.484
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2.347
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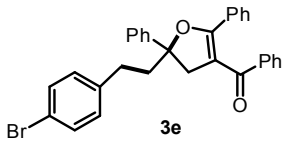
2.268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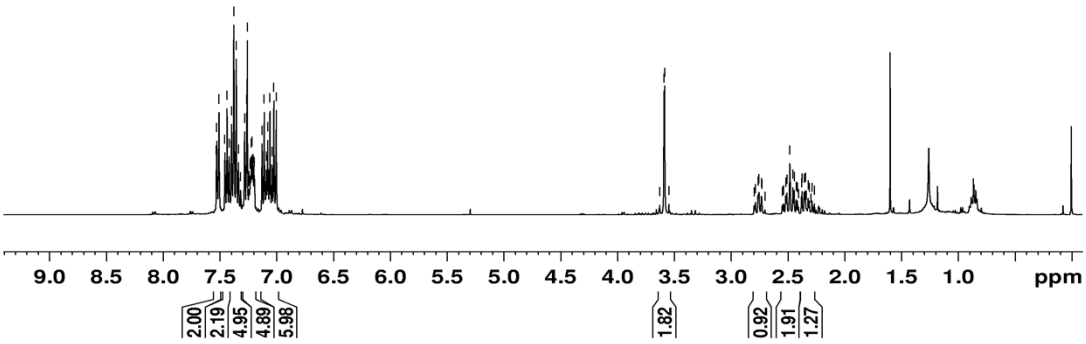
Ph
Ph
O
Br

3e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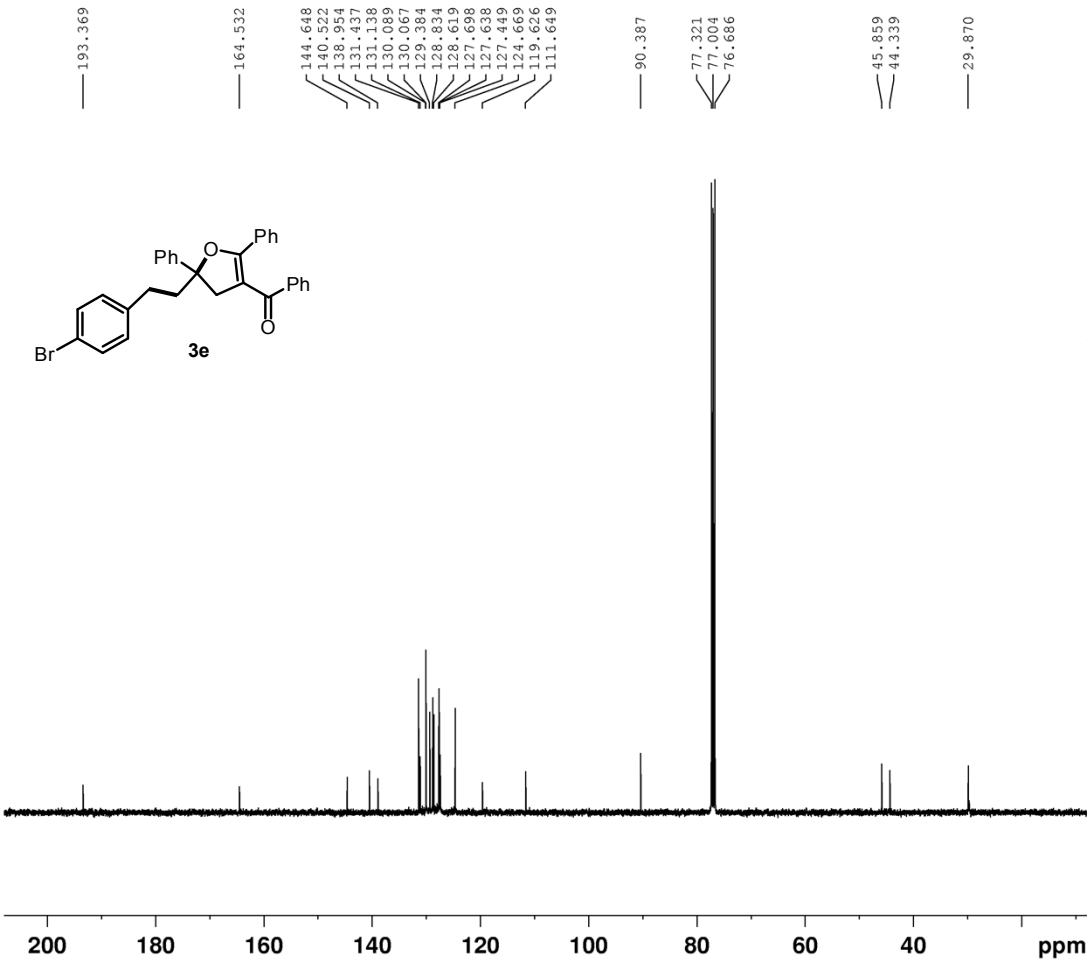
1.27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130.089
130.067
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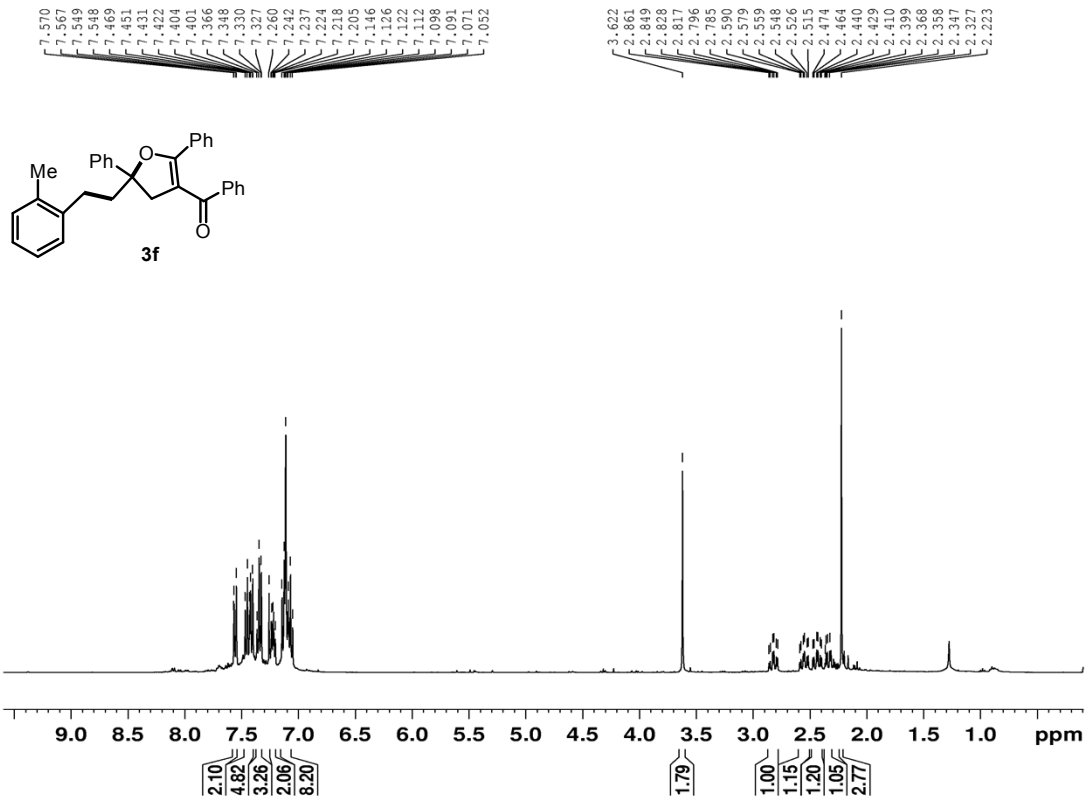
128.619
127.698
127.638
127.449
124.669
119.626
111.649
90.387
77.321
77.004
76.686
45.859
44.339
29.870
200
180
160
140
120
100
80
60
40
ppm

Ph
O
Ph
Ph
O
Br

3e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7.401
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7.330
7.327
7.260
7.242
7.237
7.224
7.218
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7.146
7.126
7.122
7.112
7.098
7.091
7.071
7.052
3.622
2.861
2.849
2.828
2.817
2.796
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2.579
2.559
2.548
2.526
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2.474
2.464
2.440
2.429
2.410
2.399
2.368
2.358
2.347
2.327
2.223
Me
Ph
O
Ph
Ph
O
3f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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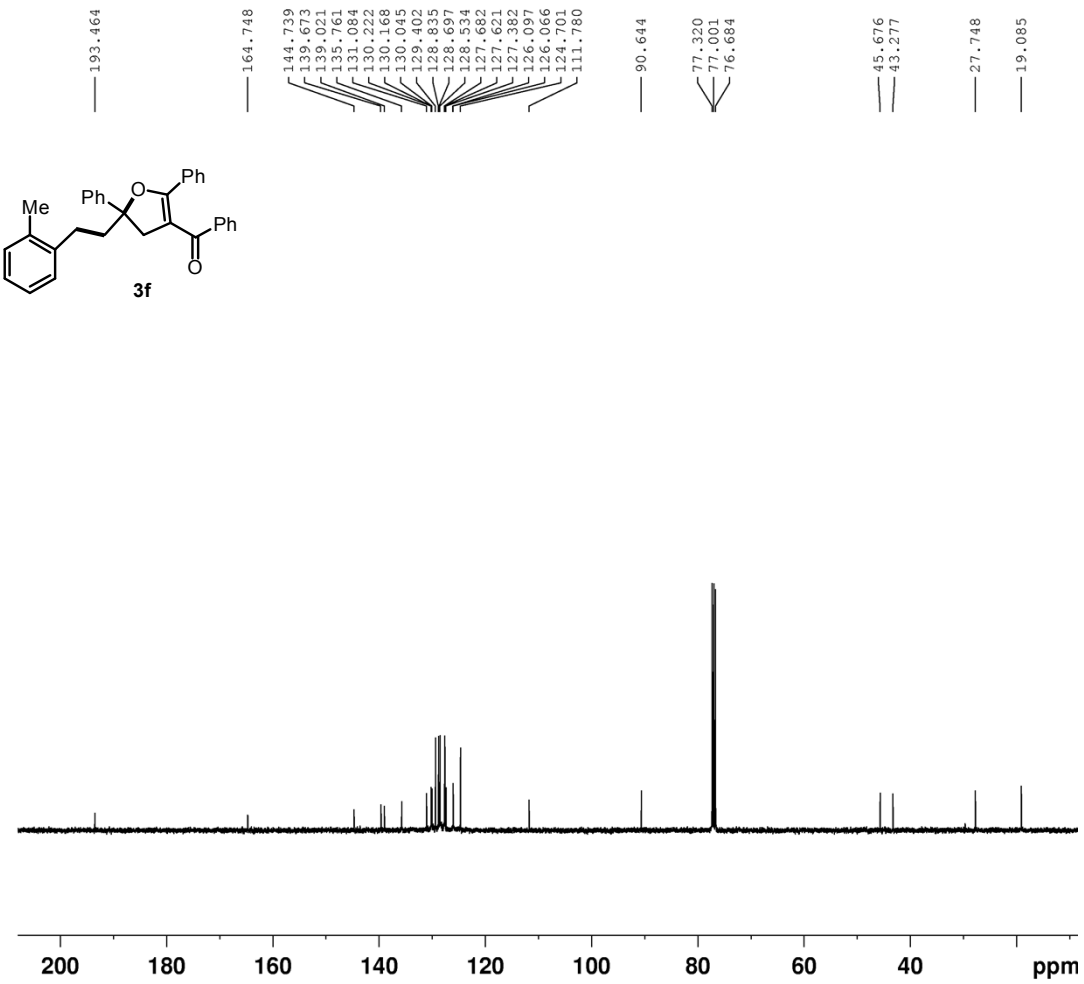
2.77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128.697
128.534
127.682
127.621
127.382
126.097
126.066
124.701
111.780
90.644
77.320
77.001
76.684
45.676
43.277
27.748
19.085
Me
Ph
O
Ph
Ph
O
3f
200 180 160 140 120 100 80 60 40 ppm


7.555
7.552
7.534
7.453
7.449
7.435
7.422
7.415
7.409
7.404
7.401
7.352
7.343
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7.065
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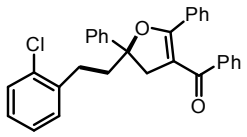
Cl
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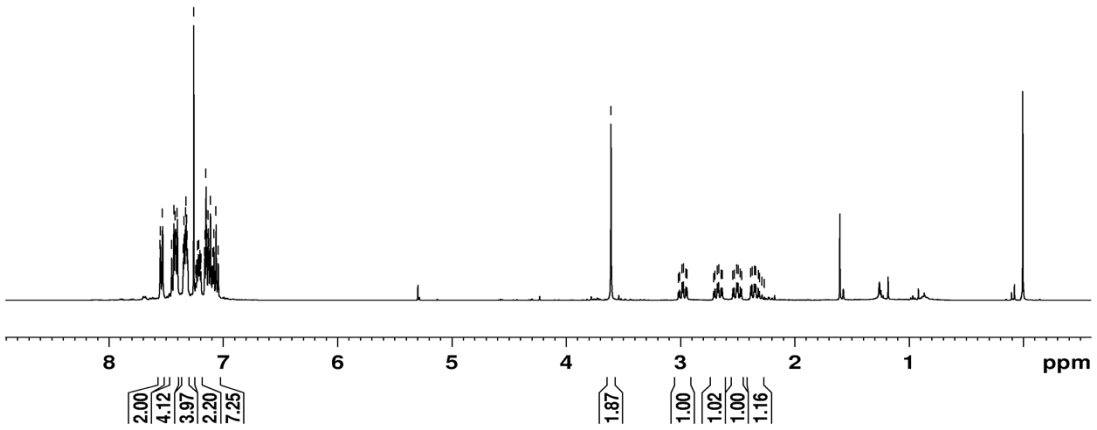
O
Ph
Ph
O

3g


8
7
6
5
4
3
2
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2.20
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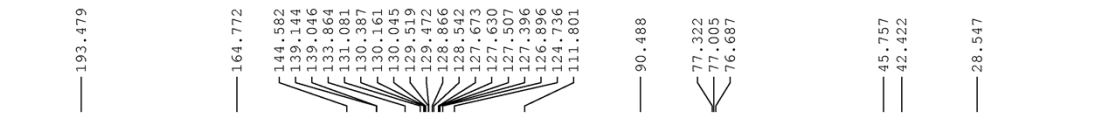
1.02
1.00
1.16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128.866
128.542
127.673
127.630
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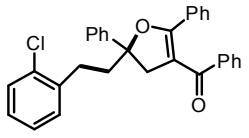
28.547


Cl
Ph
O
Ph
Ph
O

3g

200
180
160
140
120
100
80
60
40
ppm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7.144
7.133
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7.064
7.045
7.006
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3.645
3.607
3.604
3.566
2.829
2.818
2.796
2.787
2.766
2.760
2.584
2.573
2.554
2.544
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2.508
2.497
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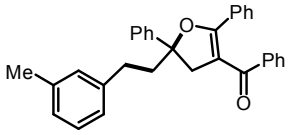
2.445
2.419
2.411
2.310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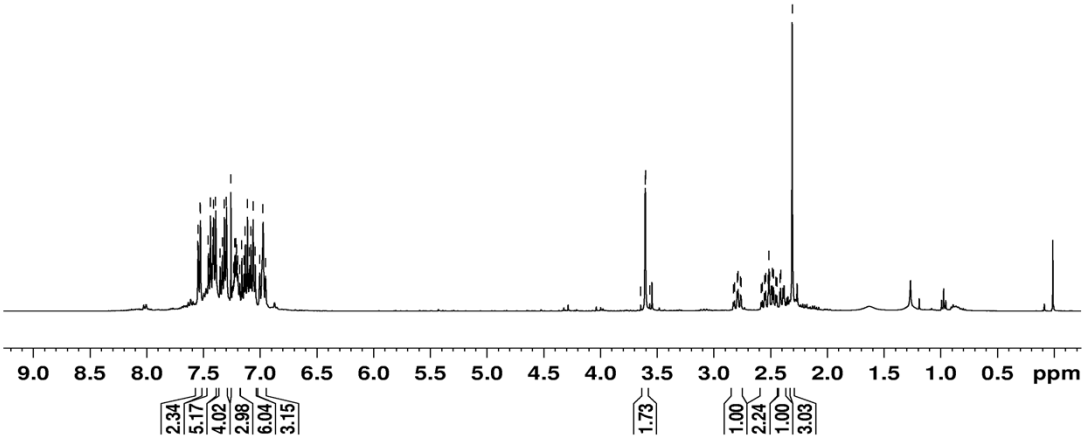
O
Ph
Me
Ph
O

3h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5.5
5.0
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4.0
3.5
3.0
2.5
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1.5
1.0
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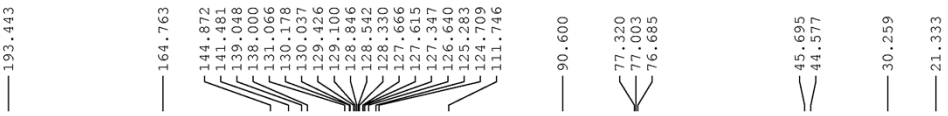
1.00
2.24
1.00
3.03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130.037
129.426
129.100
128.846
128.542
128.330
127.666
127.615
127.347
126.640
125.283
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111.746
90.600
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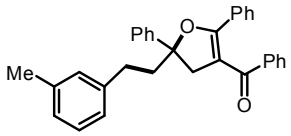
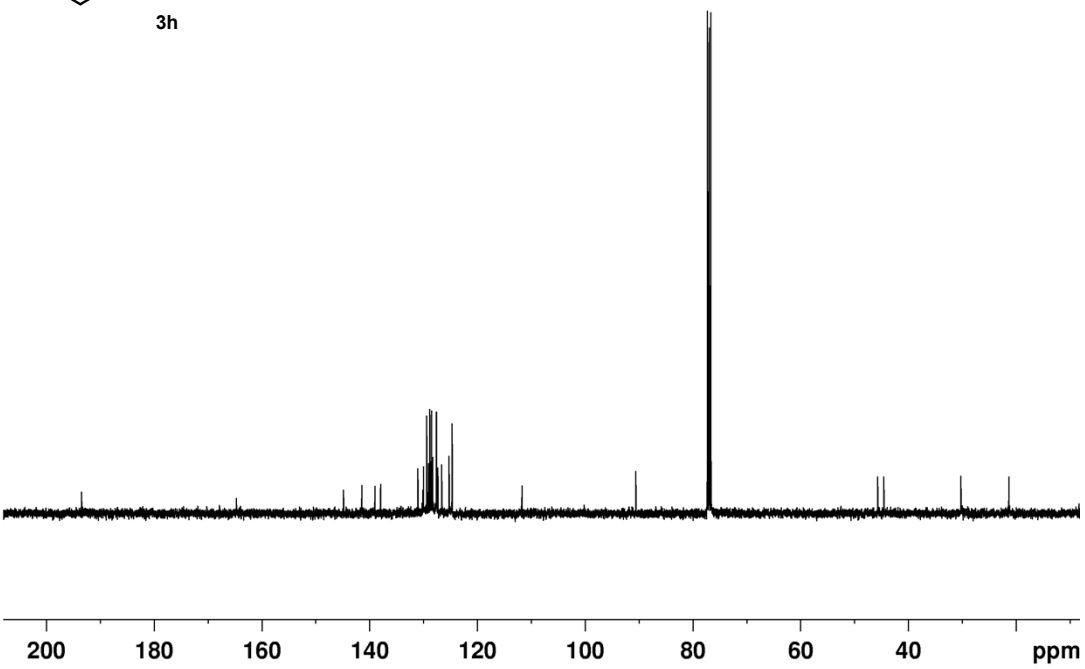
76.685
45.695
44.577
30.259
21.333


Ph
Ph
O
Ph
Me
O

3h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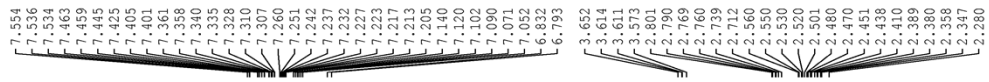
160
140
120
100
80
60
40
ppm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7.425
7.405
7.401
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7.358
7.340
7.335
7.328
7.310
7.307
7.260
7.251
7.242
7.237
7.232
7.227
7.223
7.217
7.213
7.205
7.140
7.120
7.102
7.090
7.071
7.052
6.832
6.793
3.652
3.614
3.611
3.573
2.801
2.790
2.769
2.760
2.739
2.712
2.560
2.550
2.530
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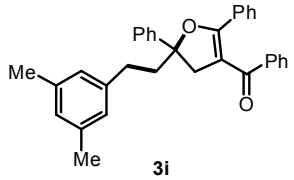
2.358
2.347
2.280


Ph
Ph
O
Ph
Me
O
Me

3i

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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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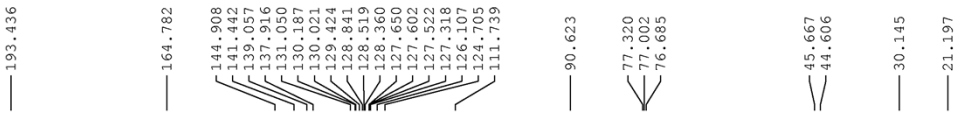
4.20
3.23
2.07
4.06
2.93
1.66
1.00
3.28
5.90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137.916
131.050
130.187
130.021
129.424
128.841
128.519
128.360
127.650
127.602
127.522
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111.739
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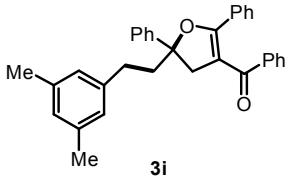
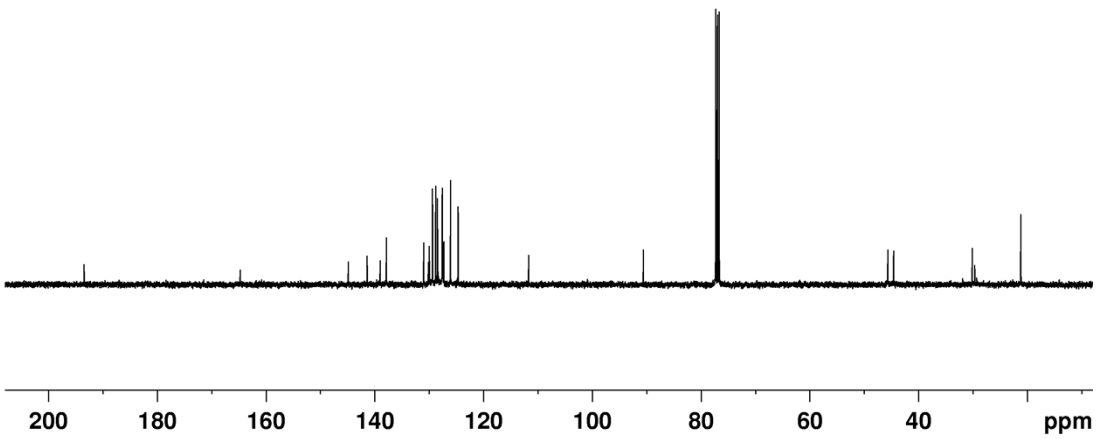
77.002
76.685
45.667
44.606
30.145
21.197


Ph
Ph
O
Ph
Me
O
Me

3i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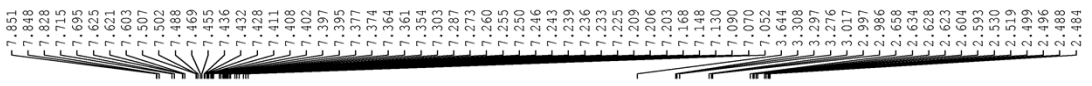
180
160
140
120
100
80
60
40
ppm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7.625
7.621
7.603
7.507
7.502
7.488
7.469
7.455
7.436
7.432
7.428
7.411
7.408
7.402
7.397
7.395
7.377
7.374
7.364
7.361
7.354
7.303
7.287
7.273
7.260
7.255
7.250
7.246
7.243
7.239
7.236
7.233
7.225
7.209
7.206
7.203
7.168
7.148
7.130
7.090
7.070
7.052
3.644
3.308
3.297
3.276
3.017
2.997
2.986
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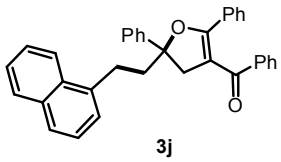
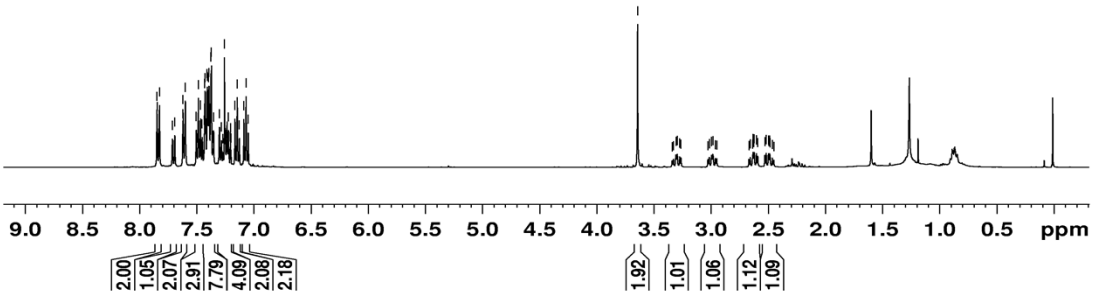
2.593
2.530
2.519
2.499
2.496
2.488
2.484


Ph
O
Ph
Ph
O

3j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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
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7.79
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2.08
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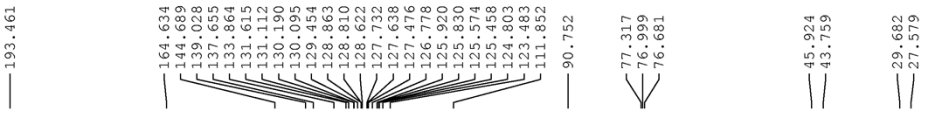
1.92
1.01
1.06
1.12
1.09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131.112
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130.095
129.454
128.863
128.810
128.622
127.732
127.638
127.476
126.778
125.920
125.830
125.574
125.458
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111.852
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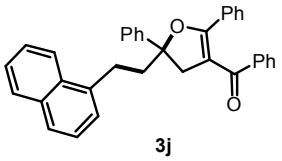
77.317
76.999
76.681
45.924
43.759
29.682
27.579


Ph
O
Ph
Ph
O

3j

200
180
160
140
120
100
80
60
40
ppm


7.457
7.454
7.436
7.394
7.391
7.377
7.374
7.371
7.357
7.308
7.305
7.295
7.290
7.285
7.272
7.260
7.231
7.223
7.219
7.213
7.211
7.205
7.197
7.193
7.186
7.136
7.133
7.118
7.112
7.099
7.077
7.072
7.057
7.042
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3.473
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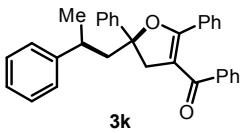
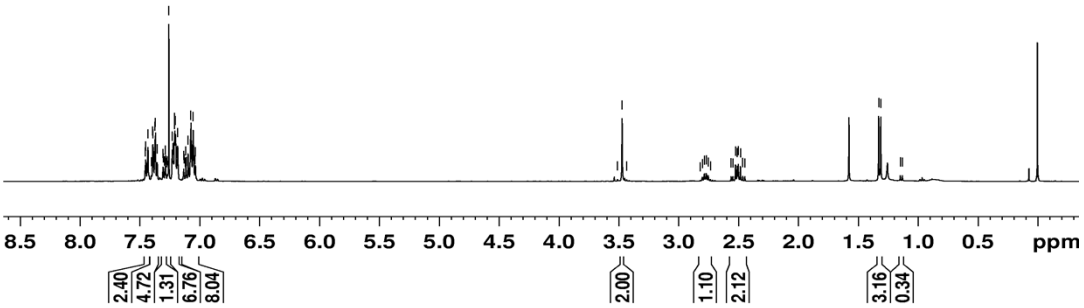
2.526
2.512
2.502
2.484
1.330
1.312


Me
Ph
O
Ph
Ph
O

3k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5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
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2.00
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2.12
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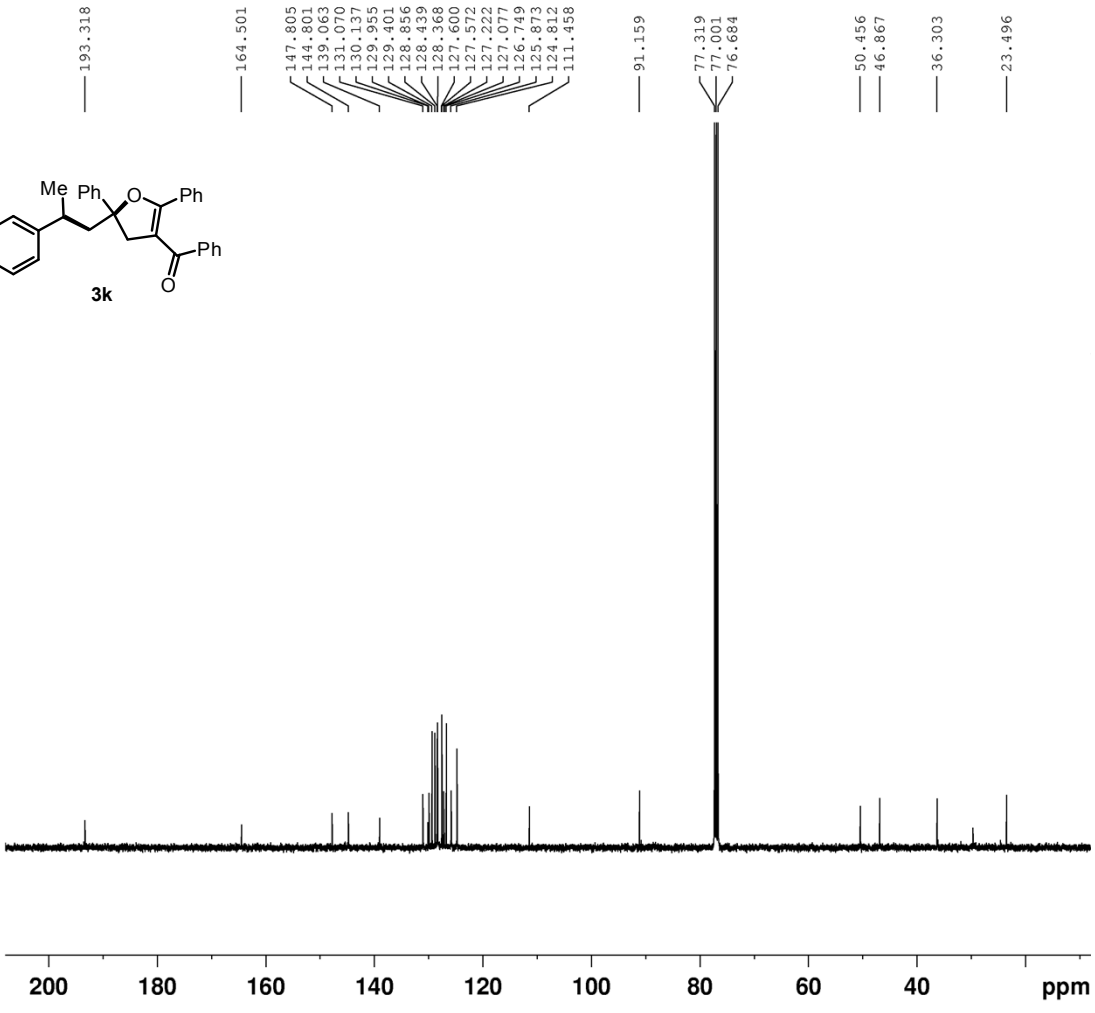
0.34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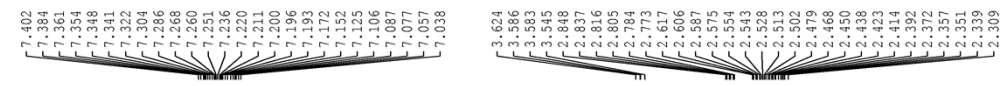
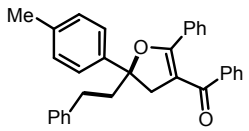
128.439
128.368
127.600
127.572
127.222
127.077
126.749
125.873
124.812
111.458
91.159
77.319
77.001
76.684
50.456
46.867
36.303
23.496
200
180
160
140
120
100
80
60
40
ppm

Me
Ph
O
Ph
Ph
O

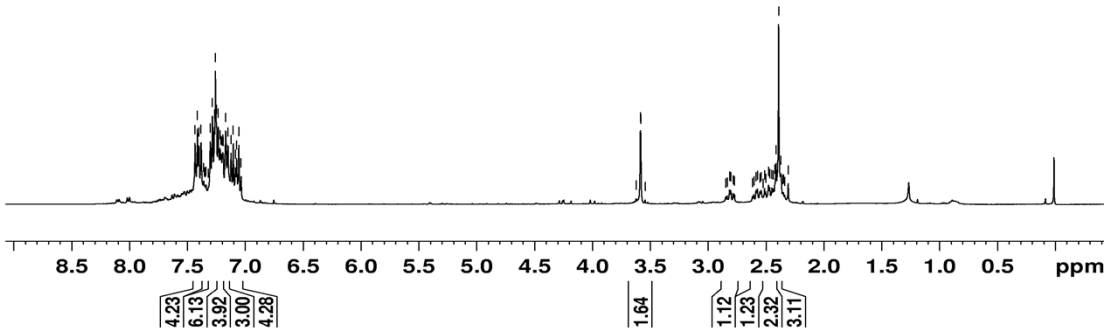
3k

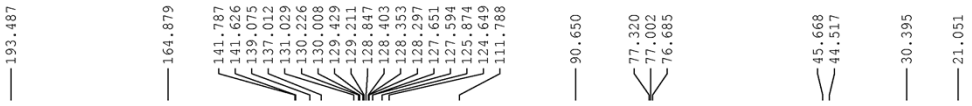
^{1}H NMR and ^{13}C NMR Spectra of the Products 4

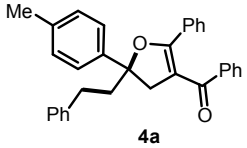




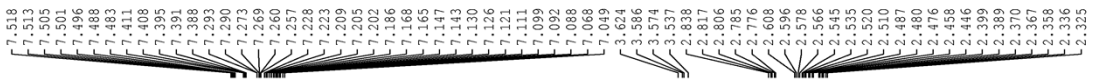
4a







4a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7.290
7.273
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7.257
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7.202
7.186
7.168
7.165
7.147
7.143
7.130
7.126
7.121
7.111
7.099
7.092
7.088
7.068
7.049
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3.586
3.574
3.537
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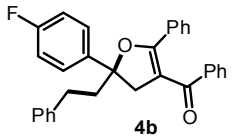
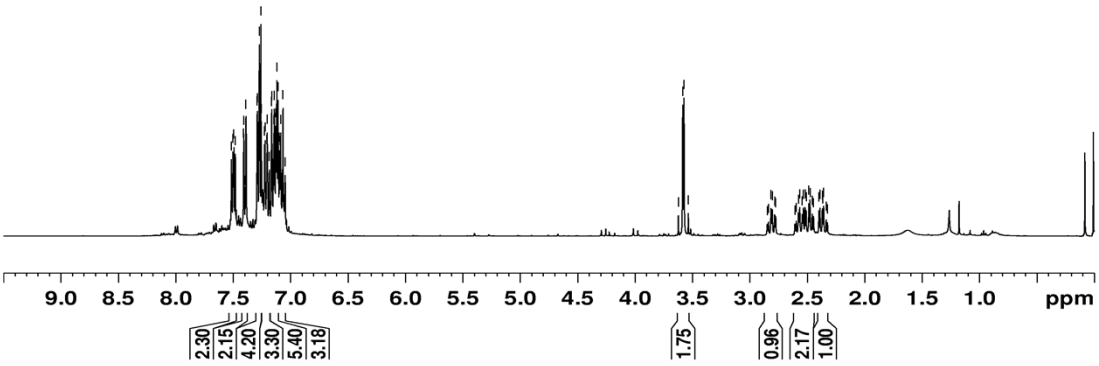
2.336
2.325


F
O
Ph
Ph
Ph
O

4b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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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2.15
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3.30
5.40
3.18
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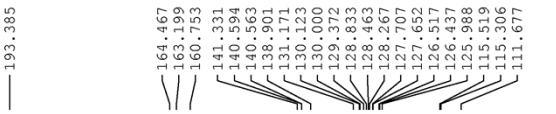
0.96
2.17
1.00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140.563
138.901
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130.123
130.000
129.372
128.833
128.463
128.267
127.707
127.652
126.517
126.437
125.988
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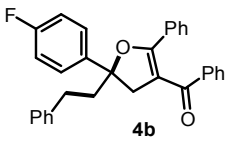
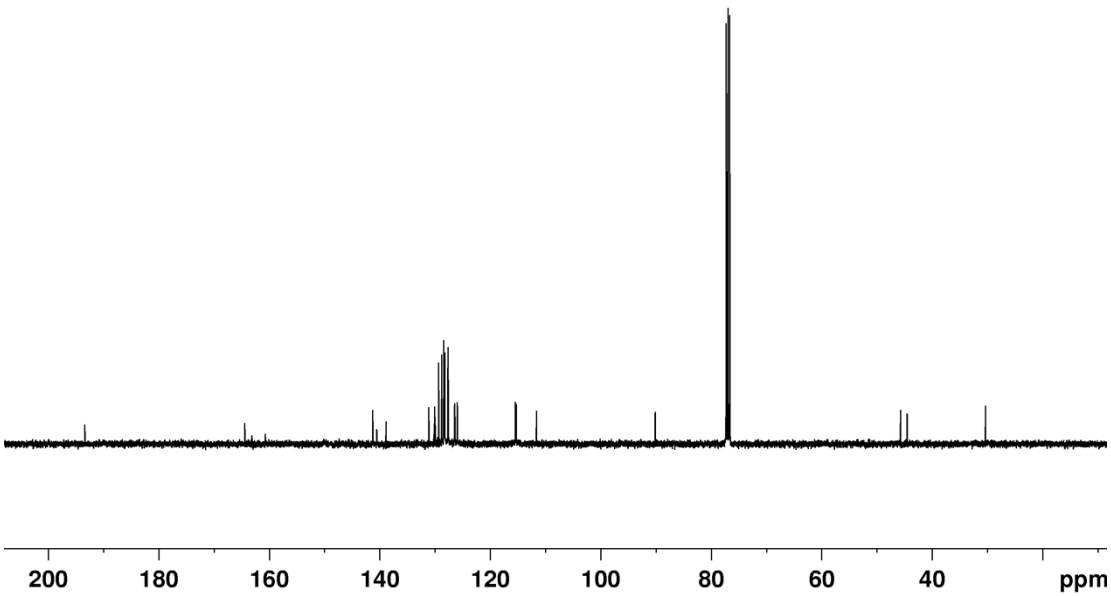
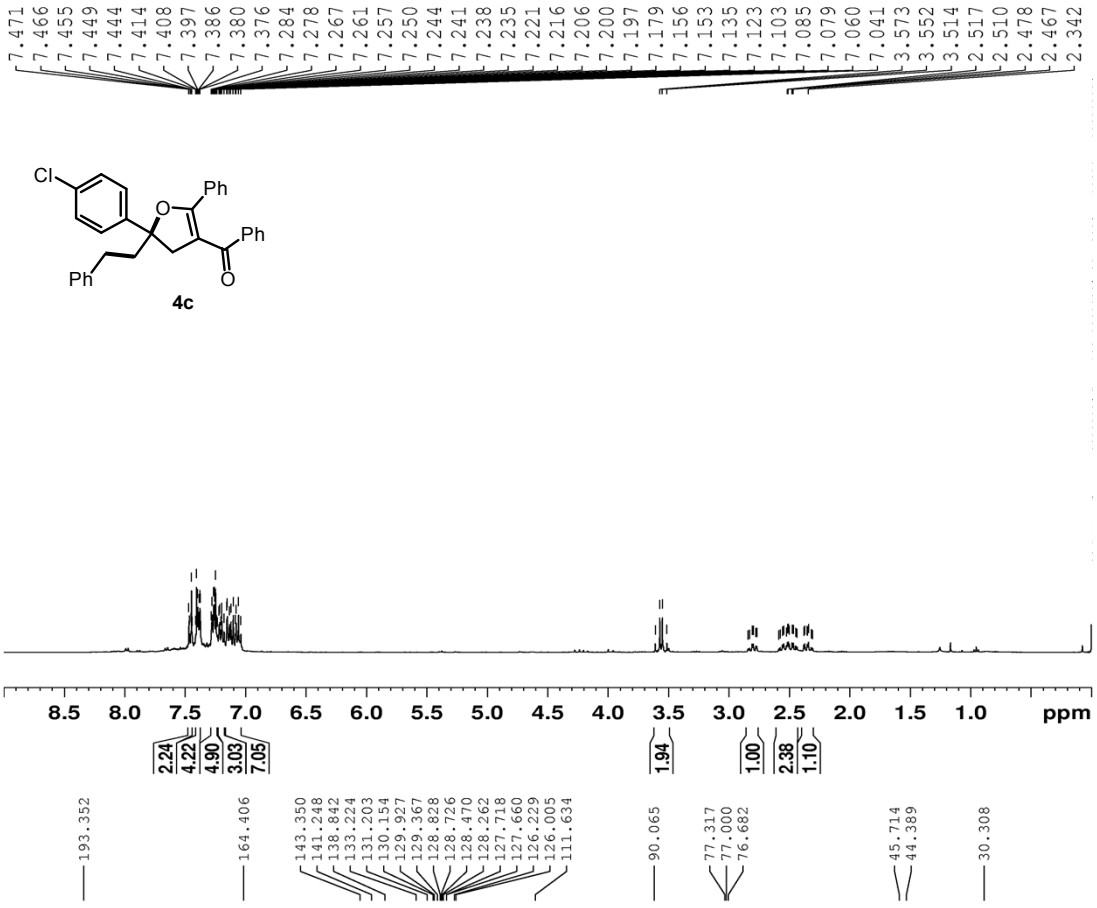
115.306
111.677
90.164
77.316
76.999
76.680
45.742
44.544
30.342


F
O
Ph
Ph
Ph
O

4b


200
180
160
140
120
100
80
60
40
ppm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3.552
3.514
2.517
2.510
2.478
2.467
2.342
Cl
Ph
O
Ph
Ph
O
4c
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.24
4.22
4.90
3.03
7.05
1.94
1.00
2.38
1.10
193.352
164.406
143.350
141.248
138.842
133.224
131.203
130.154
129.927
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128.828
128.726
128.470
128.262
127.718
127.660
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126.005
111.634
90.065
77.317
77.000
76.682
45.714
44.389
30.308
Cl
Ph
O
Ph
Ph
O
4c
200 180 160 140 120 100 80 60 40 ppm


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7.384
7.373
7.352
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2.814
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2.611
2.600
2.581
2.570
2.548
2.537
2.509
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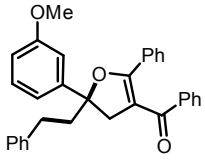
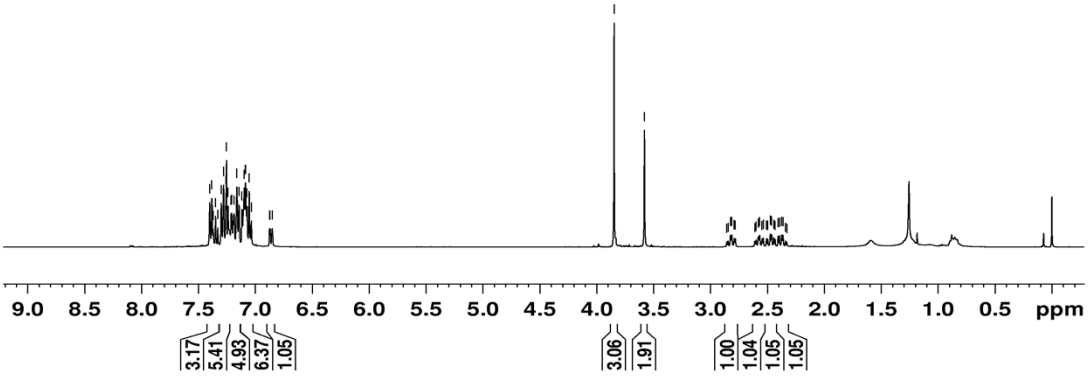
2.446
2.434
2.406
2.395
2.376
2.364
2.342
2.331


OMe
Ph
O
Ph
Ph
O

4d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8.5
8.0
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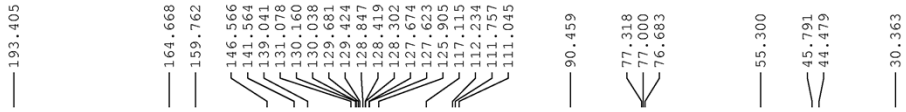
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.17
5.41
4.93
6.37
1.05
3.06
1.91
1.00
1.04
1.05
1.05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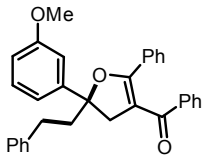
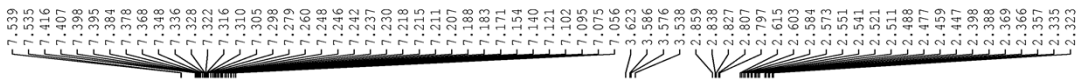
164.668
159.762
146.566
141.564
139.041
131.078
130.160
130.038
129.681
129.424
128.847
128.419
128.302
127.674
127.623
125.905
117.115
112.234
111.757
111.045
90.459
77.318
77.000
76.683
55.300
45.791
44.479
30.363


OMe
Ph
O
Ph
Ph
O

4d

200
180
160
140
120
100
80
60
40
ppm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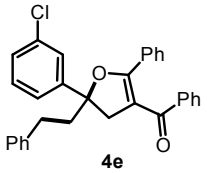
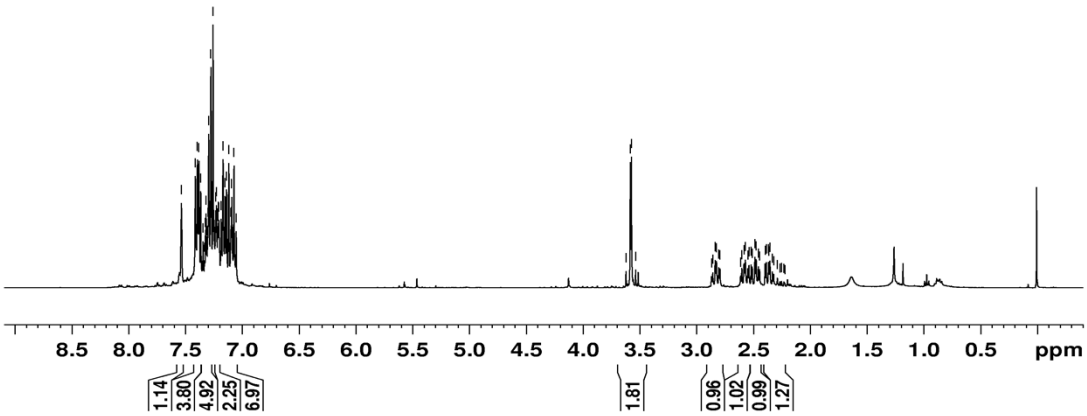
7.535
7.416
7.407
7.398
7.395
7.384
7.378
7.368
7.348
7.336
7.328
7.322
7.316
7.310
7.305
7.298
7.279
7.260
7.248
7.246
7.242
7.237
7.230
7.218
7.215
7.211
7.207
7.188
7.183
7.171
7.154
7.140
7.121
7.102
7.095
7.075
7.056
3.623
3.586
3.576
3.538
2.859
2.838
2.827
2.807
2.797
2.615
2.603
2.584
2.573
2.551
2.541
2.521
2.511
2.488
2.477
2.459
2.447
2.398
2.388
2.369
2.366
2.357
2.335
2.323


Cl
Ph
O
Ph
Ph
O

4e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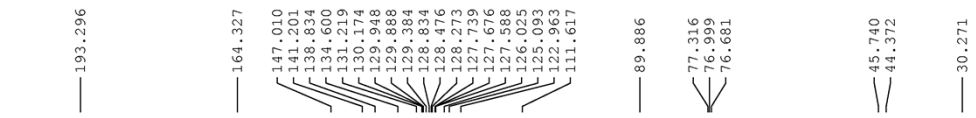
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.14
3.80
4.92
2.25
6.97
1.81
0.96
1.02
0.99
1.27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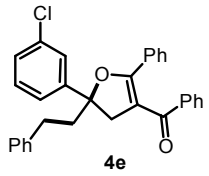
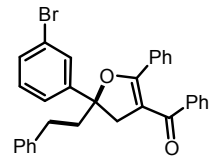
164.327
147.010
141.201
138.834
134.600
131.219
130.174
129.948
129.888
129.384
128.834
128.476
128.273
127.739
127.676
127.588
126.025
125.093
122.963
111.617
89.886
77.316
76.999
76.681
45.740
44.372
30.271


Cl
Ph
O
Ph
Ph
O

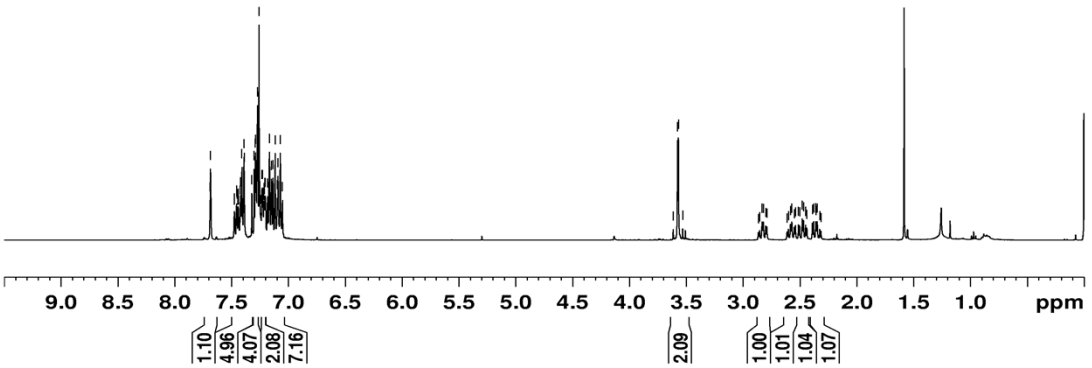
4e

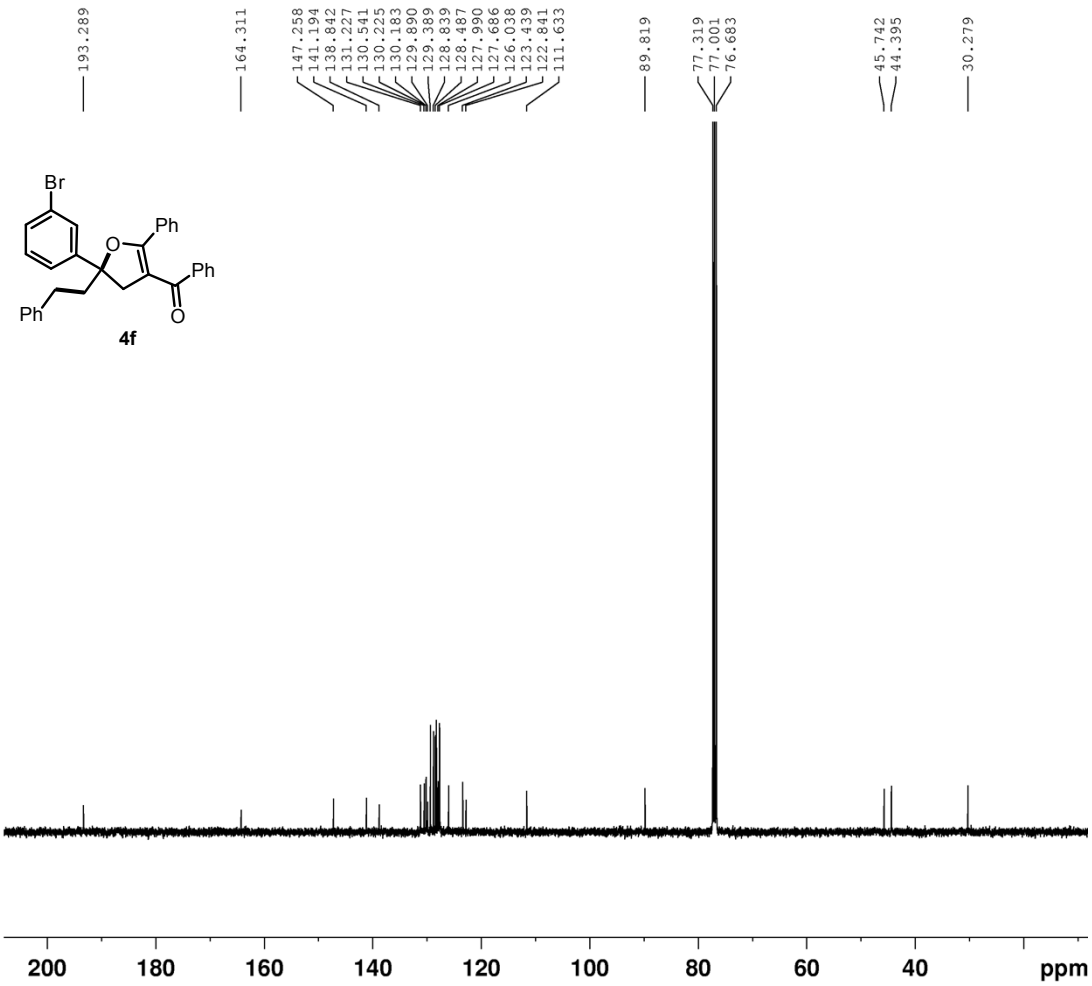
200
180
160
140
120
100
80
60
40
ppm


7.691
7.687
7.682
7.478
7.476
7.458
7.456
7.453
7.446
7.443
7.440
7.426
7.423
7.411
7.393
7.390
7.323
7.304
7.293
7.290
7.284
7.273
7.269
7.260
7.246
7.234
7.227
7.219
7.216
7.212
7.208
7.205
7.186
7.168
7.151
7.137
7.118
7.099
7.093
7.073
7.054
3.615
3.578
3.570
3.532
2.834
2.823
2.802
2.792
2.602
2.584
2.572
2.551
2.540
2.514
2.504
2.481
2.469
2.451
2.439
2.391
2.381
2.361
2.358
2.350
2.327


Br
O
Ph
Ph
Ph
O

4f


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.10
4.96
4.07
2.08
7.16
2.09
1.00
1.01
1.04
1.07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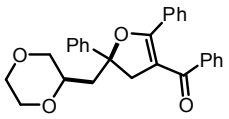
164.311
147.258
141.194
138.842
131.227
130.541
130.225
130.183
129.890
129.389
128.839
128.487
127.990
127.686
126.038
123.439
122.841
111.633
89.819
77.319
77.001
76.683
45.742
44.395
30.279
200
180
160
140
120
100
80
60
40
ppm

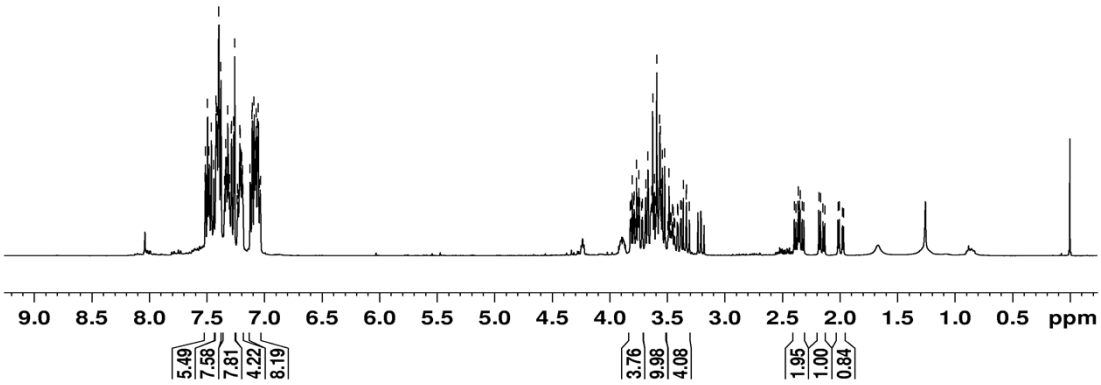
Br
O
Ph
Ph
Ph
O

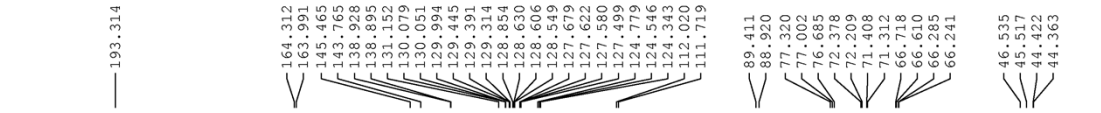
4f


7.518
7.515
7.497
7.486
7.483
7.465
7.442
7.424
7.418
7.414
7.400
7.398
7.381
7.378
7.348
7.338
7.331
7.321
7.317
7.312
7.310
7.305
7.289
7.287
7.269
7.266
7.260
7.234
7.216
7.212
7.207
7.200
7.197
7.193
7.188
7.126
7.110
7.107
7.092
7.083
7.074
7.063
7.056
7.044
7.036
3.806
3.768
3.748
3.689
3.669
3.637
3.628
3.614
3.593
3.588
3.572
3.567
3.562
3.555
3.547
3.544
3.524
3.486
3.362
3.334
2.362


Ph
Ph
O
Ph
O
O
O

4g


9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.49
7.58
7.81
4.22
8.19
3.76
9.98
4.08
1.95
1.00
0.84


193.314
164.312
163.991
145.465
143.765
138.928
138.895
131.152
130.079
130.051
129.994
129.445
129.391
129.314
128.854
128.630
128.606
128.549
127.679
127.622
127.580
127.499
124.779
124.546
124.343
112.020
111.719
89.411
88.920
77.320
77.002
76.685
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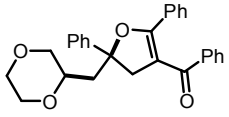
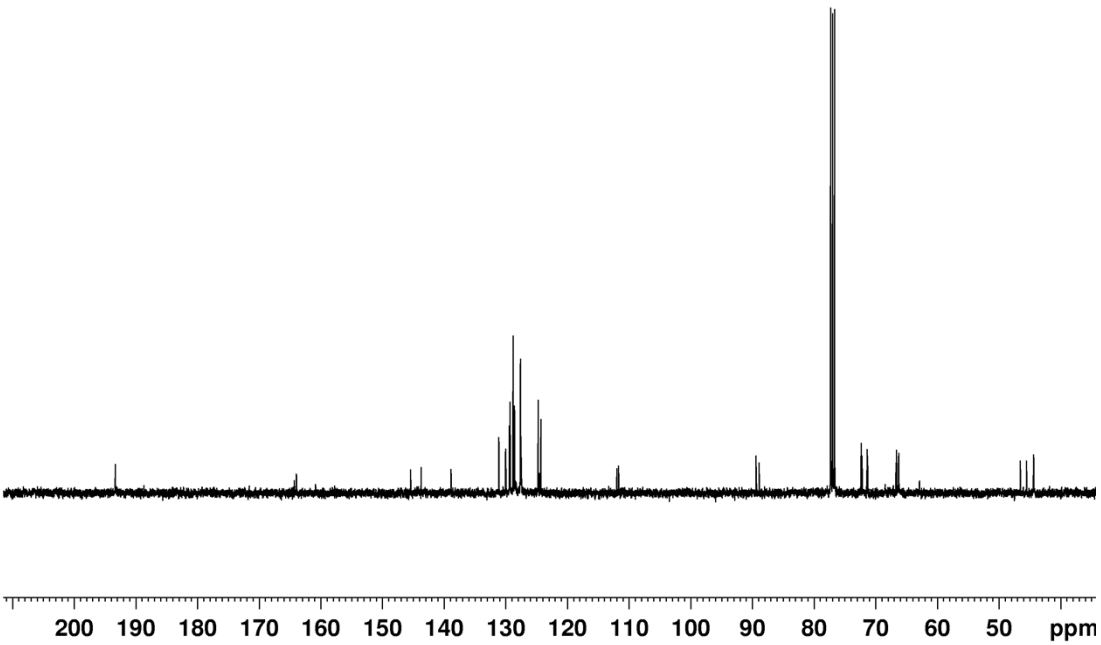
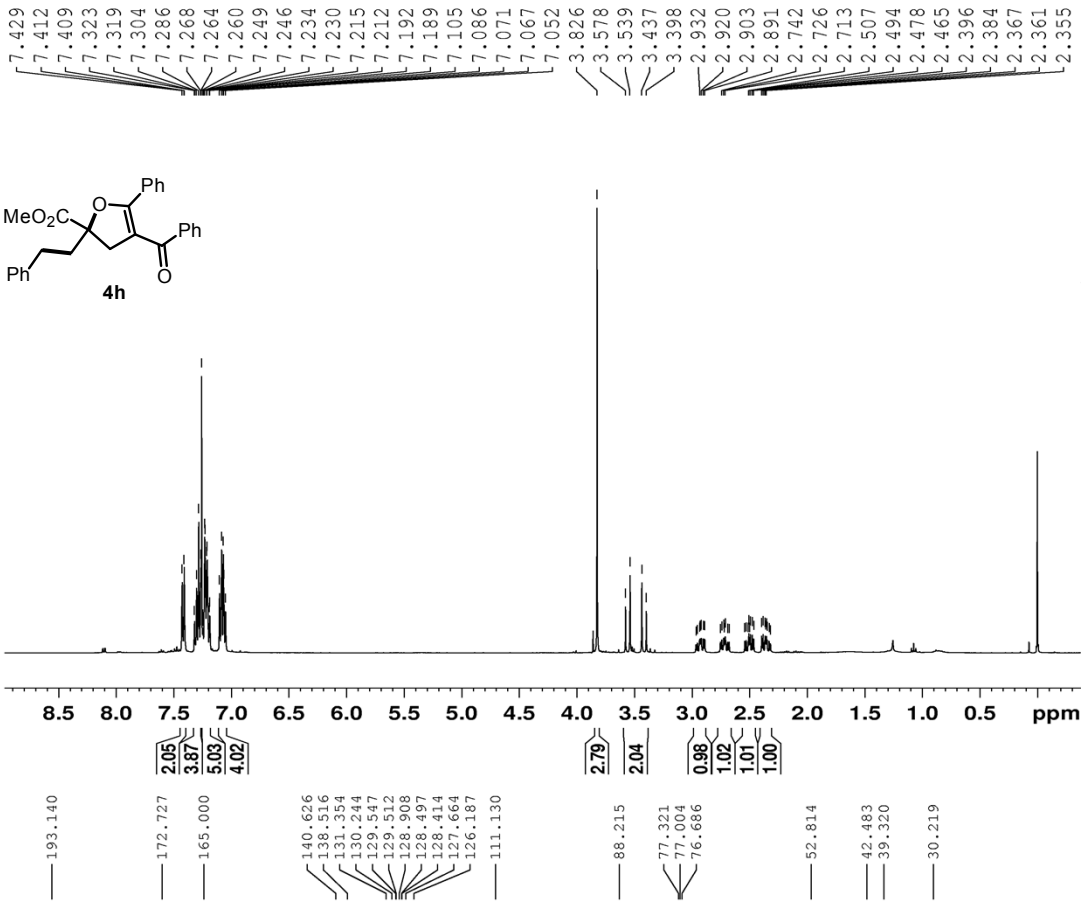
66.285
66.241
46.535
45.517
44.422
44.363


Ph
Ph
O
Ph
O
O
O

4g


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 ppm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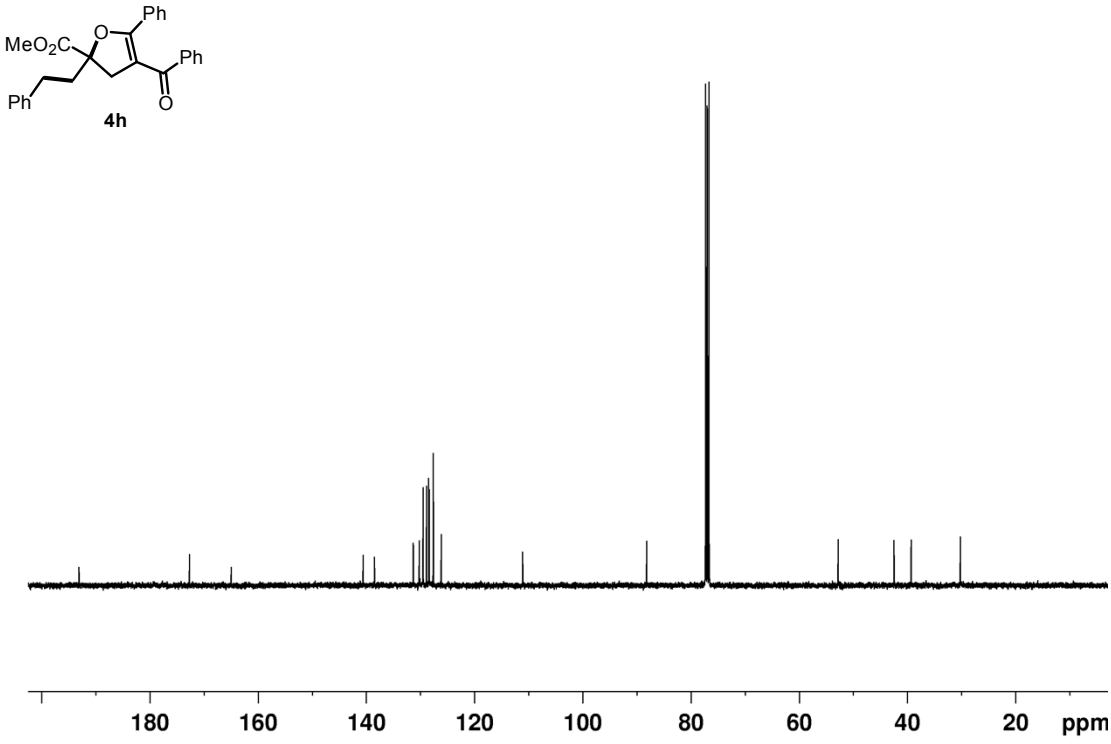
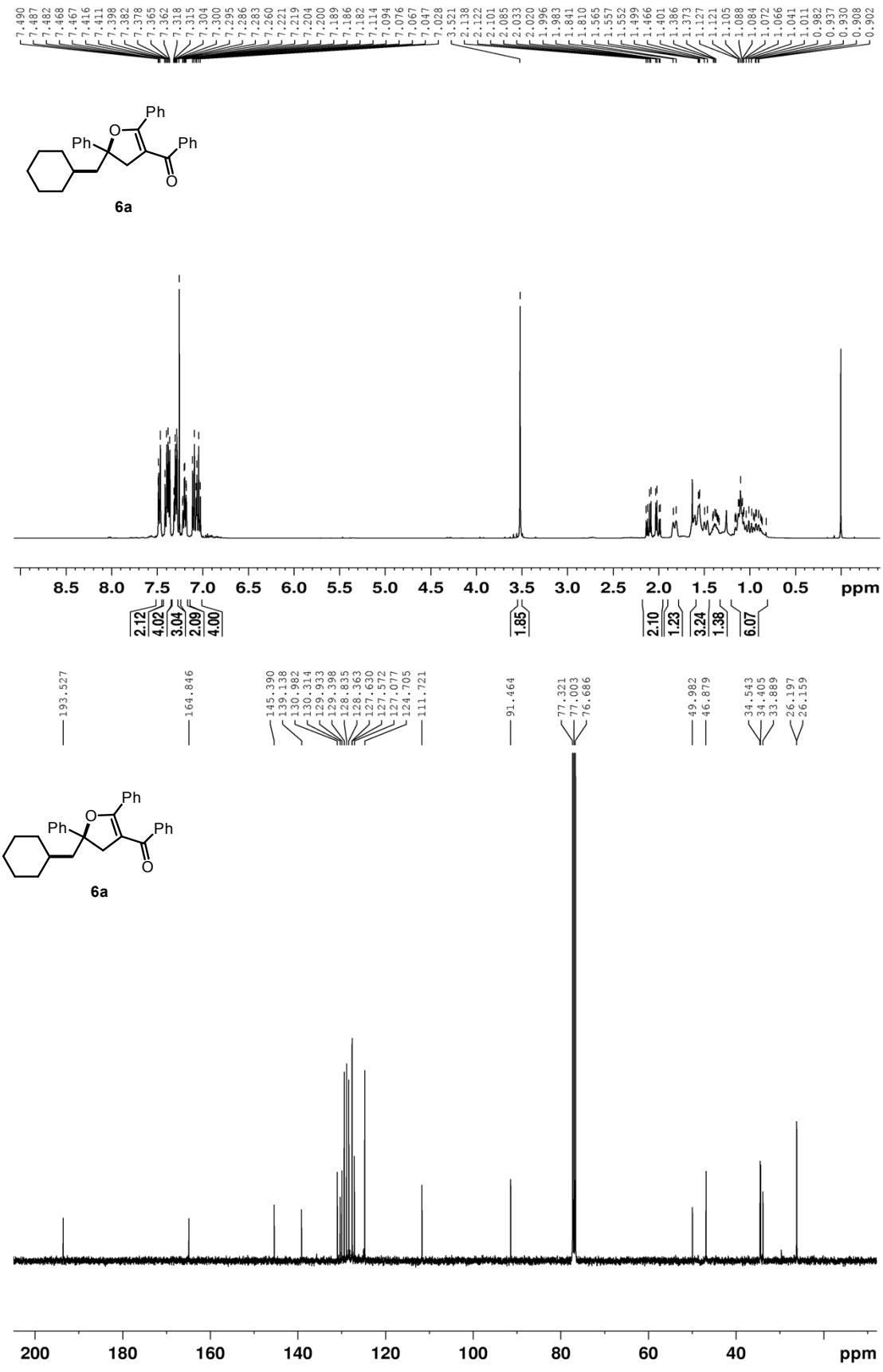
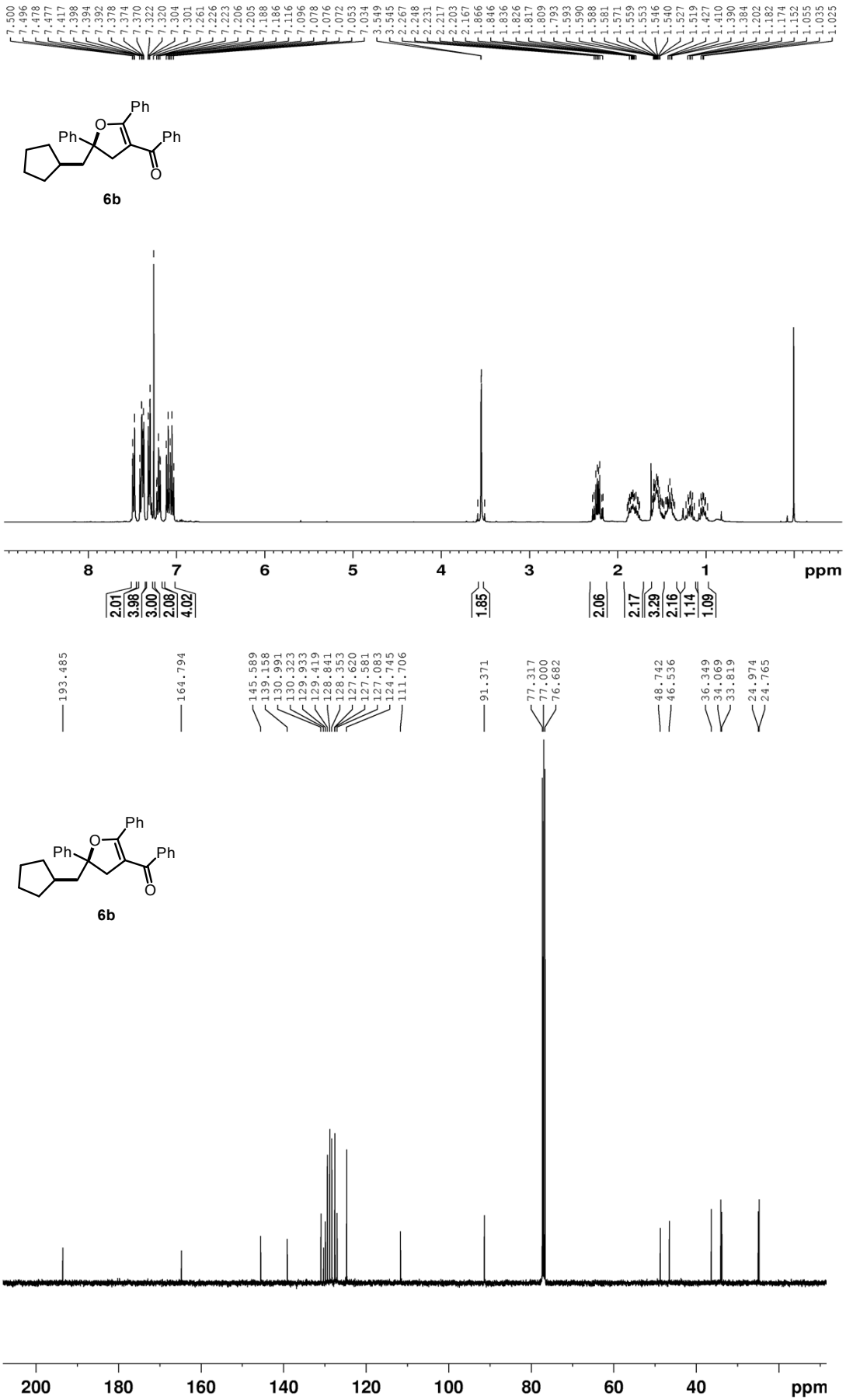
7.319
7.304
7.286
7.268
7.264
7.260
7.249
7.246
7.234
7.230
7.215
7.212
7.192
7.189
7.105
7.086
7.071
7.067
7.052
3.826
3.578
3.539
3.437
3.398
2.932
2.920
2.903
2.891
2.742
2.726
2.713
2.507
2.494
2.478
2.465
2.396
2.384
2.367
2.361
2.355
MeO2C
Ph
O
Ph
Ph
O
4h
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.05
3.87
5.03
4.02
2.79
2.04
0.98
1.02
1.01
1.00
193.140
172.727
165.000
140.626
138.516
131.354
130.244
129.547
129.512
128.908
128.497
128.414
127.664
126.187
111.130
88.215
77.321
77.004
76.686
52.814
42.483
39.320
30.219


MeO2C
Ph
O
Ph
Ph
O
4h
180 160 140 120 100 80 60 40 20 ppm

^{1}H NMR and ^{13}C NMR Spectra of the Products 6

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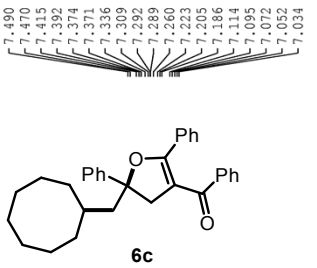
7.478
7.477
7.417
7.398
7.394
7.392
7.378
7.374
7.370
7.322
7.320
7.304
7.301
7.261
7.226
7.223
7.206
7.205
7.188
7.186
7.116
7.096
7.078
7.076
7.072
7.053
7.034
3.549
3.545
2.267
2.248
2.231
2.217
2.203
2.167
1.866
1.846
1.836
1.826
1.817
1.809
1.793
1.593
1.590
1.588
1.581
1.571
1.559
1.553
1.546
1.540
1.527
1.519
1.427
1.410
1.390
1.384
1.202
1.182
1.174
1.152
1.055
1.035
1.025
Ph
O
Ph
Ph
O
6b
8
7
6
5
4
3
2
1
ppm
2.01
3.98
3.00
2.08
4.02
1.85
2.06
2.17
3.29
2.16
1.14
1.09
193.485
164.794
145.589
139.158
130.991
130.323
129.933
129.419
128.841
128.353
127.620
127.581
127.083
124.745
111.706
91.371
77.317
77.000
76.682
48.742
46.536
36.349
34.069
33.819
24.974
24.765
Ph
O
Ph
Ph
O
6b
200
180
160
140
120
100
80
60
40
ppm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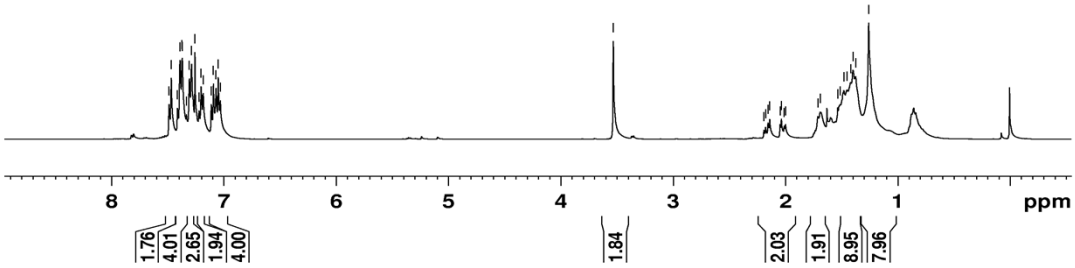
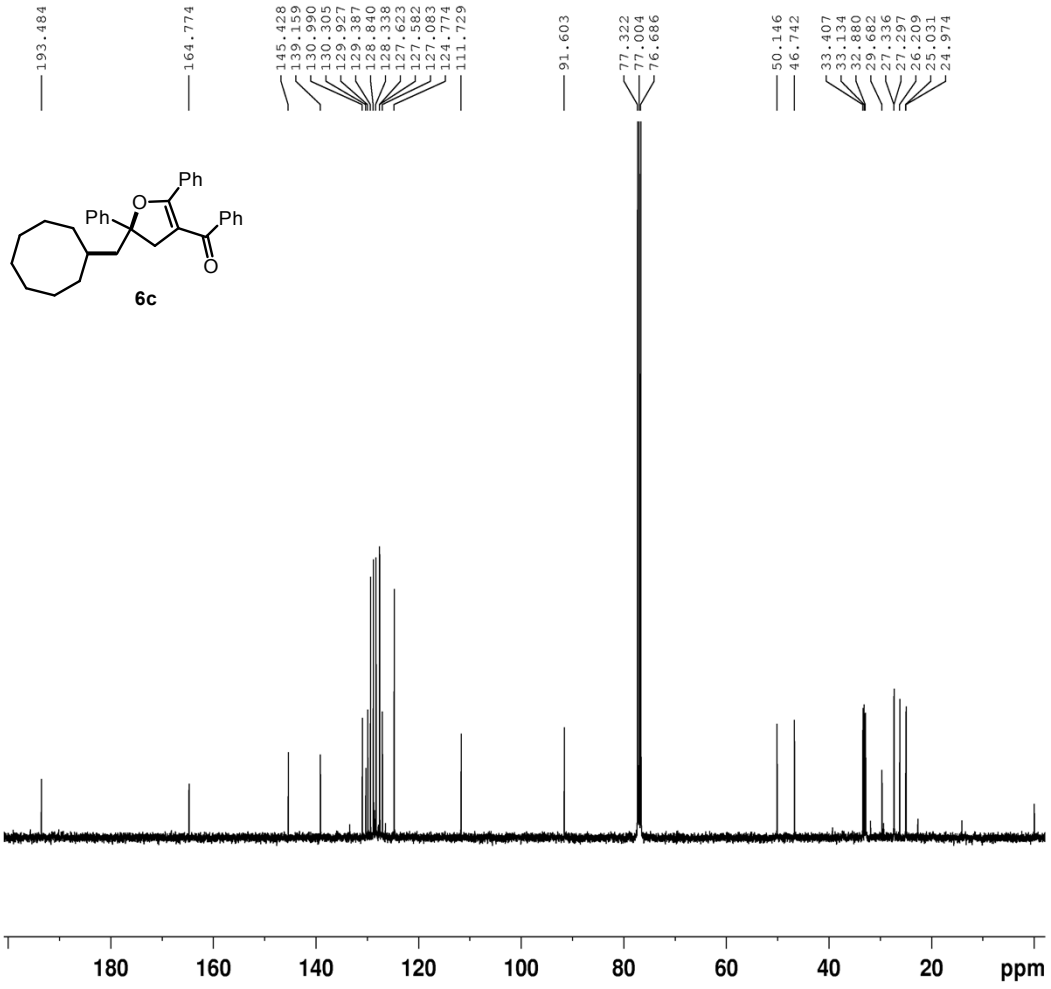
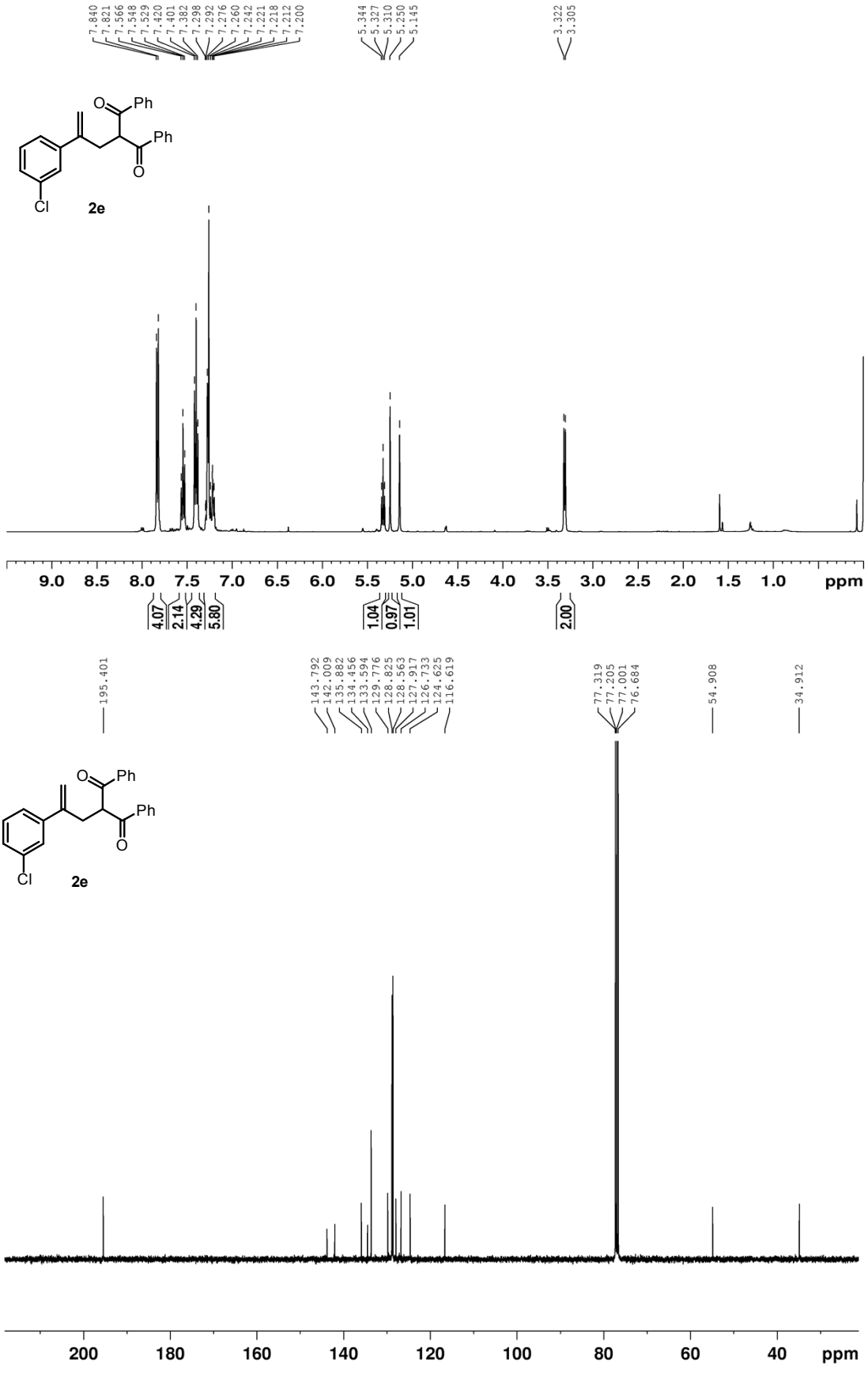
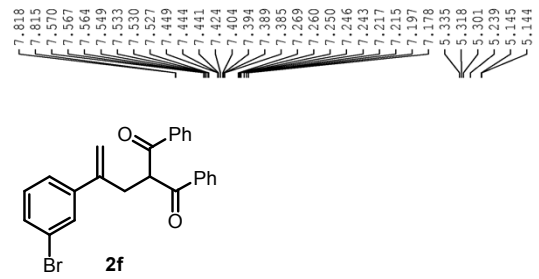
7.392
7.374
7.371
7.336
7.309
7.292
7.289
7.260
7.223
7.205
7.186
7.114
7.095
7.072
7.052
7.034
3.534
2.192
2.177
2.156
2.141
2.048
2.037
2.012
2.000
1.712
1.690
1.536
1.514
1.481
1.453
1.420
1.399
1.377
1.259
Ph
O
Ph
Ph
O
6c


8
7
6
5
4
3
2
1
ppm
1.76
4.01
2.65
1.94
4.00
1.84
2.03
1.91
8.95
7.96


193.484
164.774
145.428
139.159
130.990
130.305
129.927
129.387
128.840
128.338
127.623
127.582
127.083
124.774
111.729
91.603
77.322
77.004
76.686
50.146
46.742
33.407
33.134
32.880
29.682
27.336
27.297
26.209
25.031
24.974
Ph
O
Ph
Ph
O
6c
180
160
140
120
100
80
60
40
20
ppm

^{1}H NMR and ^{13}C NMR Spectra of 2e and 2f

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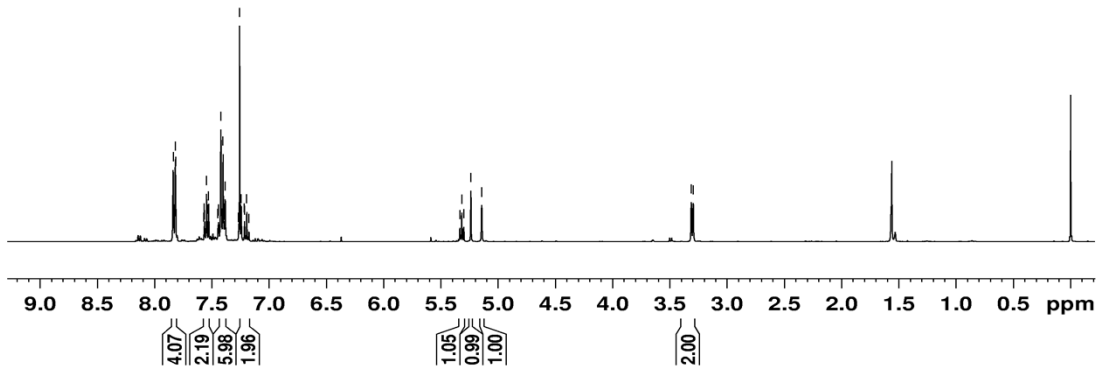
7.564
7.549
7.533
7.530
7.527
7.449
7.444
7.441
7.424
7.404
7.394
7.389
7.385
7.269
7.260
7.250
7.246
7.243
7.217
7.215
7.197
7.178
5.335
5.318
5.301
5.239
5.145
5.144
3.313
3.296
O
Ph
Ph
O
Br
2f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4.5
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3.5
3.0
2.5
2.0
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0.5
ppm
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5.98
1.96
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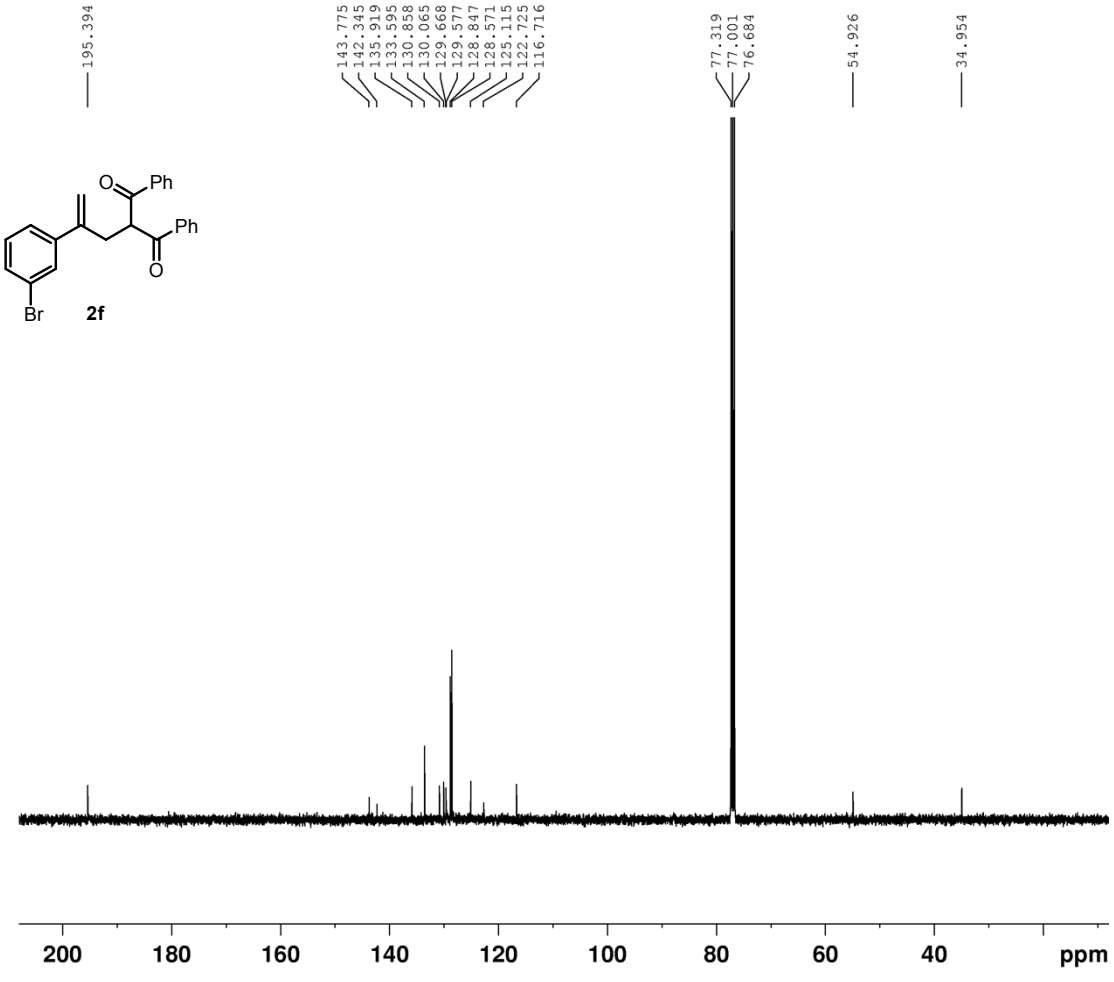
0.99
1.00
2.00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116.716
77.319
77.001
76.684
54.926
34.954
O
Ph
Ph
O
Br
2f
200
180
160
140
120
100
80
60
40
ppm