Electronic Supplementary Information

Facile Synthesis of 2-Methylenecyclobutanones via $Ca(OH)_2$-Catalyzed Direct Condensation of Cyclobutanone with Aldehydes and $(PhSe)_2$-Catalyzed Baeyer-Villiger Oxidation to 4-Methylenebutanolides

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CONTENTS

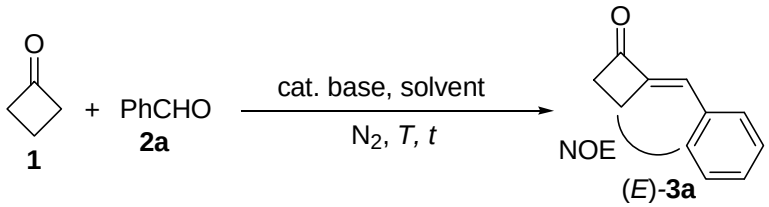
Experimental Section

General Methods. The chemicals, cyclobutanone, aldehydes, bases, solvents, and organoselenium catalysts were all purchased. Liquid aldehydes were redistilled under vacuum before use. Solid aldehydes were recrystallized in EtOH/H_2O under N_2 before use. All reactions were monitored by TLC and/or GC analysis. GC yields were calculated according to the internal standard curve. (*E*)-2-Methylenecyclobutanones **3** and (*E*)-4-methylenebutanolides **4** were all purified by column chromatogram. ^1H and ^{13}C NMR and NOESY spectra were recorded on a Bruker Avance 600 instrument (600 MHz for ^1H and 150 MHz for ^{13}C NMR spectroscopy) by using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Chemical shifts for ^1H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) and *J*-values were shown in Hz. ^{77}Se NMR were recorded on an Agilent DD2 600 instrument (114 MHz) by using D_2O as the solvent. Melting points were measured using a WRS-2A digital instrument. Mass spectra were measured on a Thermo Trace DSQ II or a Shimadzu GCMS-QP2010 Ultra spectrometer (EI). Elemental analysis was performed on an Elementar Vario EL cube instrument. HRMS (ESI) analysis was measured on a Bruker microTOF-Q II instrument.

General Procedure for Preparation of (*E*)-2-MCBones 3. To a 10 mL round-bottomed flask was added 0.1 mmol of $Ca(OH)_2$. A solution of aldehyde **2** (1.0 mmol) and cyclobutanone **1** (3.0 mmol) in 3 mL of anhydrous ethanol were then injected via a syringe under N_2. The mixture was then stirred at 80 ^oC for 24 hours under N_2. The solvent was evaporated under vacuum and the residue was purified through flash column chromatogram (eluent: petroleum ether: EtOAc 9:1) to give (*E*)-**3**.

General Procedure for $(PhSe)_2$-Catalyzed Baeyer-Villiger Oxidation of (*E*)-2-MCBones 3 to (*E*)-4-Methylenebutanolides with H_2O_2. (*E*)-2-MCBones **3** (0.3 mmol) and $(PhSe)_2$ (0.015 mmol) were added to a reaction tube. A solution of H_2O_2 (1.5 mmol) in 1 mL of CH_3CN was then injected via a syringe. The mixture was then stirred at room temperature (ca. 30 ^oC) for 24 h. After the reaction completed as monitored by TLC, 2 mL of water was added and the mixture was extracted with EtOAc (2 mL×3). The combined organic layer was dried over Na_2SO_4 and the solvent evaporated under vacuum. The residue was purified by flash column chromatogram (eluent: petroleum ether: EtOAc 8:1) to give (*E*)-**4**.

Table S1. Detailed Optimization of the Reaction Conditions for Preparation of (*E*)-2-MCBones **3**.[a]

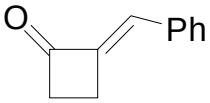


run	**1** (equiv.)	base (mol%)	solvent (mL)	*T* (°C)	*t* (h)	**3a**%[b]
1	1.2	NaOH (10)	EtOH (2)	80	24	2
2	1.5	NaOH (10)	EtOH (2)	80	24	7
3	3	NaOH (10)	EtOH (2)	80	24	38
4	4	NaOH (10)	EtOH (2)	80	24	41
5	**5**	**NaOH (10)**	**EtOH (2)**	**80**	**24**	**47**
6	5	NaOH (5)	EtOH (2)	80	24	33
7	5	NaOH (20)	EtOH (2)	80	24	3
8	5	NaOH (40)	EtOH (2)	80	24	0
9	6	NaOH (10)	EtOH (2)	80	24	46
10	5	KOH (10)	EtOH (2)	80	24	21
11	5	CsOH (10)	EtOH (2)	80	24	10
12	5	LiOH (10)	EtOH (2)	80	24	18
13	5	$Mg(OH)_2$ (10)	EtOH (2)	80	24	7
14	**5**	**$Ca(OH)_2$ (10)**	**EtOH (2)**	**80**	**24**	**68**
15	5	$Sr(OH)_2 \cdot 8H_2O$ (10)	EtOH (2)	80	24	17
16	5	$Ba(OH)_2 \cdot 8H_2O$ (10)	EtOH (2)	80	24	27
17	5	$Fe(OH)_3$ (10)	EtOH (2)	80	24	3
18	5	Na_2CO_3 (10)	EtOH (2)	80	24	37
19	5	$NaHCO_3$ (10)	EtOH (2)	80	24	25
20	5	K_2CO_3 (10)	EtOH (2)	80	24	34
21	5	$CaCO_3$ (10)	EtOH (2)	80	24	8
22	5	BeO (10)	EtOH (2)	80	24	2
23	5	MgO (10)	EtOH (2)	80	24	17
24	5	CaO (10)	EtOH (2)	80	24	23

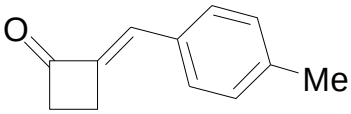
25	5	Et_3N (10)	EtOH (2)	80	24	2
26	5	DBU (10)	EtOH (2)	80	24	33
27	5	$Ca(OH)_2$ (10)	MeOH (2)	reflux	24	35
28	5	$Ca(OH)_2$ (10)	*i*-PrOH (2)	80	24	42
29	5	$Ca(OH)_2$ (10)	*t*-BuOH (2)	80	24	50
30	5	$Ca(OH)_2$ (10)	MeCN (2)	80	24	57
31	5	$Ca(OH)_2$ (10)	THF (2)	reflux	24	32
32	5	$Ca(OH)_2$ (10)	Cyclohexanol (2)	80	24	61
33	5	$Ca(OH)_2$ (10)	EtOH (2)	60	24	52
34	5	$Ca(OH)_2$ (10)	EtOH (2)	40	24	31
25	5	$Ca(OH)_2$ (10)	Cyclohexanol (2)	100	24	42
36	5	$Ca(OH)_2$ (10)	EtOH (0.5)	80	24	41
37	5	$Ca(OH)_2$ (10)	EtOH (1)	80	24	57
38	**5**	**$Ca(OH)_2$ (10)**	**EtOH (3)**	**80**	**24**	**77 (70)**
39	5	$Ca(OH)_2$ (10)	EtOH (4)	80	24	76
40	5	$Ca(OH)_2$ (10)	EtOH (5)	80	24	72
41	4	$Ca(OH)_2$ (10)	EtOH (3)	80	24	80
42	***3***	***$Ca(OH)_2$ (10)***	***EtOH (3)***	***80***	***24***	***83 (75)***
43	2	$Ca(OH)_2$ (10)	EtOH (3)	80	24	68
44	1.5	$Ca(OH)_2$ (10)	EtOH (3)	80	24	51
45	1	$Ca(OH)_2$ (10)	EtOH (3)	80	24	32
46	3	$Ca(OH)_2$ (10)	EtOH (3)	80	18	64
47	3	$Ca(OH)_2$ (10)	EtOH (3)	80	36	73
48	3	$Ca(OH)_2$ (10)	EtOH (3)	80	48	67
49	3	$Ca(OH)_2$ (20)	EtOH (3)	80	24	75
50	3	$Ca(OH)_2$ (5)	EtOH (3)	80	24	67
51	3	$Ca(OH)_2$ (1)	EtOH (3)	80	24	33

[a] As indicated in the table, the mixture of excess **1**, freshly distilled **2a** (1 mmol), and catalytic amount of a base in a solvent was heated under N_2 and then monitored by GC. [b] GC yields (shown outside the parenthesis, using biphenyl as the internal standard) and isolated yields (shown in parenthesis) are based on **2a**. As determined by NOESY analysis, only the (*E*)-stereomer of **3a** was obtained.

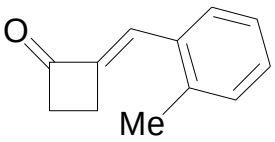
Characterization of the Products



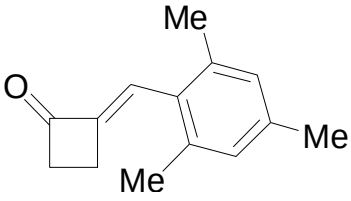
(*E*)-2-Benzylidenecyclobutanone ((*E*)-3a). Soild. m.p. 88.7-90.3 ^{o}C. IR (KBr): 2976, 2932, 2866, 1737, 1645, 1449, 1384, 1228, 1176, 1113, 934, 759, 685 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.52–7.40 (m, 5H), 7.04 (t, *J* = 2.7 Hz, 1H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.99 (dt, *J* = 2.4 Hz, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.7, 146.2, 134.6, 130.1, 130.0, 128.9, 126.5, 45.8, 23.6; *Anal.* Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.67; H, 6.22. Known compound.[1]



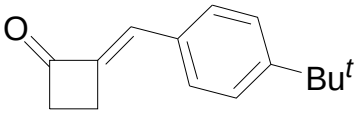
(*E*)-2-(4-Methylphenyl)methylenecyclobutanone ((*E*)-3b). Soild. m.p. 84.3-85.7 ^{o}C. IR (KBr): 2928, 1736, 1646, 1603, 1448, 1103, 919, 810, 523, 498 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 2.7 Hz, 1H), 3.13 (t, *J* = 7.8 Hz, 2H), 2.97 (dt, *J* = 2.4 Hz, *J* = 7.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.7, 145.1, 140.6, 131.8, 130.1, 129.7, 126.6, 45.7, 23.5, 21.6; MS (EI, 70 eV): *m/z* (%) 172 (12, M^+), 157 (58), 129 (100); *Anal.* Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.84; H, 6.90.



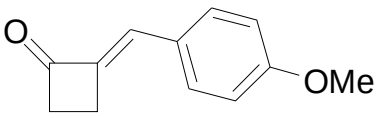
(*E*)-2-(2-Methylphenyl)methylenecyclobutanone ((*E*)-3c). Soild. m.p. 69.0-70.2 ^{o}C. IR (KBr): 2975, 2870, 1732, 1639, 1595, 1481, 1387, 1291, 1260, 1126, 1089, 1033, 889, 799, 763, 711, 491, 463 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.19–7.09 (m, 4H), 3.00 (t, *J* = 7.8 Hz, 2H), 2.84 (dt, *J* = 3.0 Hz, *J* = 7.8 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ198.6, 145.4, 138.4, 131.8, 129.9, 128.9, 126.8, 125.2, 122.5, 44.5, 22.5, 18.7; MS (EI, 70 eV): *m/z* (%) 172 (12, M^+), 158 (12), 157 (100), 143 (10), 129 (90), 128 (46), 127 (15), 116 (31), 115 (65), 105 (14), 89 (9). HRMS calcd for $C_{12}H_{13}O$ ($[M+H]^+$): 173.0961; found: 173.0975.



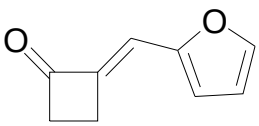
(*E*)-2-(2,4,6-Trimethylphenyl)methylenecyclobutanone ((*E*)-3d). Oil. IR (film): 2937, 1754, 1652, 1611, 1446, 1394, 1225, 1178, 1100, 1033, 852, 736, 668, 591, 564, 561 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.20 (t, *J* = 1.8 Hz, 1H), 6.89 (s, 2H), 3.02 (t, *J* = 7.8 Hz, 2H), 2.55 (dt, *J* = 2.4 Hz, *J* = 7.8Hz, 2H), 2.29 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.8, 149.1, 138.1, 136.6, 129.9, 128.6, 126.8, 44.1, 23.0, 21.1, 20.5; MS (EI, 70 eV): *m/z* (%) 200 (16, M^+), 185 (100), 157 (98); *Anal.* Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.79; H, 8.11.



(*E*)-2-(4-*tert*-Butyl)methylenecyclobutanone ((*E*)-3e). Soild. m.p. 98.3-99.5 °C. IR (KBr): 2961, 2869, 1744, 1644, 1605, 1509, 1464, 1394, 1364, 1127, 1096, 900, 829, 561 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.47–7.42 (m, 4H), 7.02 (s, 1H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.97 (dt, *J* = 2.4 Hz, *J* = 7.5 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ199.7, 153.6, 145.3, 131.8, 130.0, 126.5, 126.0, 45.7, 35.0, 31.2, 23.5; MS (EI, 70 eV): *m/z* (%) 214 (9, M^+), 171 (36), 157 (100), 130 (34), 129 (91), 128 (38), 115 (38), 57 (32). HRMS calcd for $C_{15}H_{19}O$ ($[M+H]^+$): 215.1430; found: 215.1428.

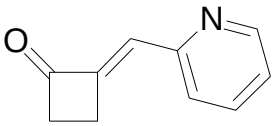


(*E*)-2-(4-Methoxyl)methylenecyclobutanone ((*E*)-3f). Soild. m.p. 79.0-79.6 °C. IR (KBr): 2932, 2840, 1731, 1644, 1600, 1569, 1512, 1462, 1423, 1388, 1305, 1259, 1175, 1122, 1026, 942, 902, 824, 761, 717, 589, 533, 501 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.43 (d, *J* = 8.4 Hz, 2H), 6.95 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.88 (dt, *J* = 2.4 Hz, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ198.8, 160.6, 143.1, 131.3, 126.7, 125.7, 114.0, 54.8, 45.0, 22.7; MS (EI, 70 eV): *m/z* (%) 188 (57, M^+), 187 (24), 160 (87), 159 (69), 157 (71), 145 (100), 129 (51), 117 (78), 115 (40), 89 (40), 77 (20), 63 (22). HRMS calcd for $C_{12}H_{13}O_2$ ($[M+H]^+$): 189.0910; found: 189.0944.

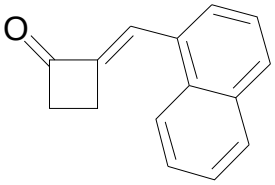


(*E*)-2-(Furan-2-yl)methylenecyclobutanone ((*E*)-3g). Soild. m.p. 59.4-60.5 °C. IR (KBr): 3116, 2937, 2251, 1734, 1639, 1474, 1390, 1328, 1224, 1177, 1108, 1016, 911, 819, 741, 684, 591, 534 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.56 (s, 1H), 6.85 (t, *J* = 3.0 Hz, 1H), 6.66 (d, *J* = 3.0

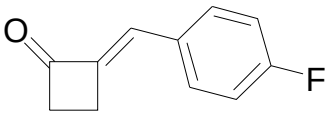
Hz, 1H), 6.51 (t, *J* = 1.8 Hz, 1H), 3.08 (t, *J* = 7.8 Hz, 2H), 2.92 (dt, *J* = 2.4 Hz, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.1, 151.3, 145.3, 143.8, 115.9, 113.4, 112.5, 45.0, 22.9. MS (EI, 70 eV): *m/z* (%) 148 (39, M^+), 120 (85), 91 (100); ***Anal.*** Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.87; H, 5.48.



(*E*)-2-(Pyridine-2-yl)methylenecyclobutanone ((*E*)-3h). Soild. m.p. 81.6-82.9 °C. IR (KBr): 2978, 2934, 2870, 1777, 1750, 1654, 1584, 1467, 1434, 1386, 1294, 1224, 1109, 1084, 1020, 950, 907, 844, 777, 745,612, 510 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 8.68 (d, *J* = 4.2 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.26-7.24 (m, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 3.17-3.11 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.1, 154.0, 150.6, 150.3, 136.4, 125.4, 125.1, 123.5, 46.0, 24.2; MS (EI, 70 eV): *m/z* (%) 159 (3, M^+), 131 (56), 130 (100), 103 (20), 78 (9), 77 (9), 76 (9), 52 (8), 51 (13). HRMS calcd for $C_{10}H_{10}NO$ ($[M+H]^+$): 160.0757; found: 160.0745.

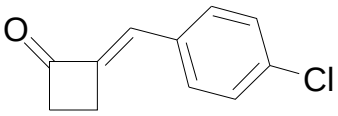


(*E*)-2-(Naphthalen-1-yl)methylenecyclobutanone ((*E*)-3i). Soild. m.p. 98.1-99.2 °C. IR (KBr): 3050, 2932, 1739, 1638, 1508, 1387, 1327, 1227, 1177, 1104, 881, 783, 735, 542, 429 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 8.17 (d, *J* =8.4 Hz, 1H), 7.91-7.88 (m, 3H), 7.80 (d, *J* =4.2 Hz, 1H), 7.59-7.50 (m, 3H), 3.18 (t, *J* =7.8 Hz, 2H), 3.02 (dt, *J* = 2.4 Hz, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.6, 147.6, 133.8, 132.5, 130.6, 129.0, 127.0, 126.6, 126.3, 125.3, 123.2, 122.6, 45.5, 23.7; MS (EI, 70 eV): *m/z* (%) 208 (47, M^+), 179 (100), 165 (88); ***Anal.*** Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.70; H, 5.66.

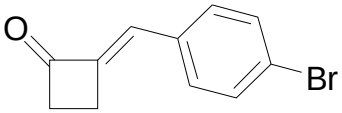


(*E*)-2-(4-Fluorophenyl)methylenecyclobutanone ((*E*)-3j). Soild. m.p. 89.1-90.1 °C. IR (KBr): 2935, 1735, 1644, 1594, 1507, 1392, 1294, 1225, 1159, 1106, 905, 833, 775, 526 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.52-7.50 (m, 2H), 7.12-7.09 (m, 2H), 7.01 (t, *J* = 2.7 Hz, 1H), 3.16

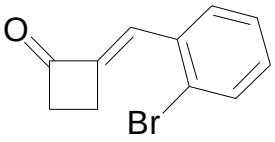
(t, J = 7.8 Hz, 2H), 2.97 (dt, J = 2.4 Hz, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.4, 163.6 (d, J_{CF} = 250.7 Hz), 145.7, 132.0 (d, J_{CF} = 8.4 Hz), 130.8 (d, J_{CF} = 3.3 Hz), 125.2, 116.2 (d, J_{CF} = 21.8 Hz), 45.8, 23.4; MS (EI, 70 eV): *m/z* (%) 176 (27, M^+), 148 (100), 133 (96); ***Anal.*** Calcd for $C_{11}H_9FO$: C, 74.99; H, 5.15. Found: C, 75.08; H, 5.10.



(*E*)-2-(4-Chlorophenyl)methylenecyclobutanone ((*E*)-3k). Soild. m.p. 95.7-97.3 °C. IR (KBr): 2932, 1732, 1645, 1587, 1490, 1403, 1180, 1089, 1011, 892, 817, 703, 518, 491 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.44 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 2.7 Hz, 1H), 3.16 (t, J = 8.1 Hz, 2H), 2.97 (dt, J = 2.4 Hz, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.3, 146.7, 136.0, 133.1, 131.2, 129.2, 125.1, 45.9, 23.5; MS (EI, 70 eV): *m/z* (%) 192 (8, M^+), 157 (39), 129 (100). Known Compound.[1]

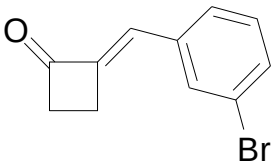


(*E*)-2-(4-Bromophenyl)methylenecyclobutanone ((*E*)-3l). Soild. m.p. 62.1-63.5 °C. IR (KBr): 2927, 1780, 1728, 1640, 1484, 1396, 1176, 1117, 1093, 1069, 1006, 892, 813, 697, 515, 490 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.54 (d, J = 8.4Hz, 2H), 7.37 (d, J = 8.4Hz, 2H), 6.97 (t, J = 1.8 Hz, 1H), 3.16 (t, J = 7.8 Hz, 2H), 2.96 (dt, J = 1.8 Hz, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.3, 146.8, 133.5, 132.2, 131.6, 131.3, 125.2, 45.9, 23.6; MS (EI, 70 eV): *m/z* (%) 236 (4, M^+), 157 (54), 129 (100); ***Anal.*** Calcd for $C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 55.86; H, 3.91.

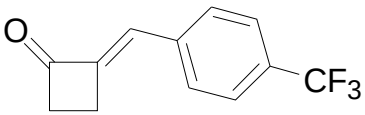


(*E*)-2-(2-Bromophenyl)methylenecyclobutanone ((*E*)-3m). Oil**.** IR (film): 2926, 2177, 1740, 1637, 1461, 1429, 1388, 1277, 1229, 1172, 1126, 1087, 1020, 891, 755, 696, 501, 450 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.63 (t, J = 6.0 Hz, 2H), 7.44 (t, J = 2.7 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 3.16 (t, J = 8.1 Hz, 2H), 2.97 (dt, J = 3.0 Hz, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.1, 148.2, 134.0, 133.7, 131.0, 129.1, 127.5, 127.1, 125.0, 45.8, 23.4; MS (EI, 70 eV): *m/z* (%) 236 (2, M^+), 157 (50), 129 (100); ***Anal.*** Calcd for

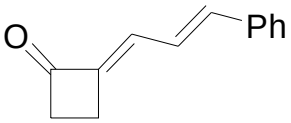
$C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 55.88; H, 3.84.



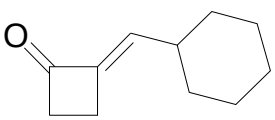
(*E*)-2-(3-Bromophenyl)methylenecyclobutanone ((*E*)-3n). Oil**.** IR (film): 1781, 1737, 1640, 1463, 1126, 1089, 1023, 757, 509, 450 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.63 (t, *J* = 6.0 Hz, 2H), 7.44 (t, *J* = 2.7 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 3.16 (t, *J* = 7.8 Hz, 2H), 2.97 (dt, *J* = 2.4 Hz, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.1, 148.2, 134.0, 133.7, 131.0, 129.1, 127.5, 127.1, 125.0, 45.8, 23.4; MS (EI, 70 eV): *m/z* (%) 236 (1, M^+), 157 (48), 129 (100); *Anal.* Calcd for $C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 55.57; H, 3.68.



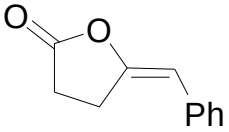
(*E*)-2-(4-Trifluoromethylphenyl)methylenecyclobutanone ((*E*)-3o). Soild. m.p. 92.3-93.7 °C. IR (KBr): 2935, 1734, 1643, 1417, 1321, 1235, 1164, 1113, 1063, 1013, 910, 834, 735, 685, 596, 498 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 2.7 Hz, 1H), 3.21 (t, *J* = 7.8 Hz, 2H), 3.04 (dt, *J* = 2.4 Hz, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.1, 148.7, 138.0, 131.3 (d, J_{CF} = 32.7 Hz), 130.0, 125.8 (m), 124.6, 46.1, 23.7; MS (EI, 70 eV): *m/z* (%) 226 (10, M^+), 198 (15), 170 (50), 157 (100). Known Compound.[1]



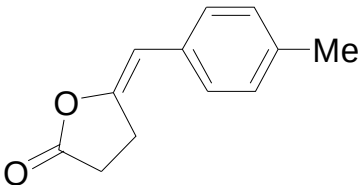
(*E*,*E*)2-(3-Phenyl-allylidene)-cyclobutanone ((*E*,*E*)-3p). Soild. m.p. 72.5-73.5 °C. IR (KBr): 3061, 3027, 2973, 2933, 1724, 1675, 1626, 1449, 1391, 1103, 970, 737, 688, 515 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.40-7.22 (m, 5H), 6.85 (d, *J* = 15.6 Hz, 1H), 6.73 (d, *J* = 11.4 Hz, 1H), 6.66 (dd, *J* = 11.4 Hz, *J* = 15.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.1, 147.6, 142.5, 136.2, 129.2, 128.9, 127.2, 126.6, 123.5, 43.8, 20.8; MS (EI, 70 eV): *m/z* (%) 184 (70, M^+), 156 (83), 155 (66), 141 (100), 128 (95), 127 (40), 115 (67), 102 (27), 91 (40), 78 (27), 77 (28). HRMS calcd for $C_{13}H_{13}O$ ($[M+H]^+$): 185.0961; found: 185.0983.



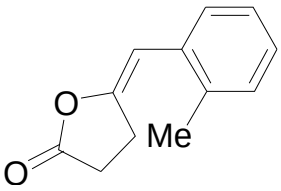
(*E*)-2-Cyclohexylcyclobutanone ((*E*)-3q). Oil. IR (film): 2928, 2853, 1756, 1665, 1448, 1393, 1231, 1110, 1088, 963, 901, 734 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 6.15 (dt, *J* = 2.7 Hz, *J* = 8.4 Hz, 1H), 2.92 (t, J = 7.8 Hz, 2H), 2.63 (td, J = 2.4 Hz, J = 7.8 Hz, 2H), 2.15-2.10 (m, 1H), 1.76-1.71 (m, 4H), 1.33-1.18 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.1, 146.0, 135.7, 43.8, 38.2, 31.7, 25.8, 25.5, 20.6; MS (EI, 70 eV): *m/z* (%) 164 (9, M^+), 163 (14), 136 (17), 135 (100), 107 (26), 93 (22), 81 (32), 80 (14), 79 (54), 67 (22), 55 (21). HRMS calcd for $C_{11}H_{17}O$ ($[M+H]^+$): 165.1274; found: 165.1275.



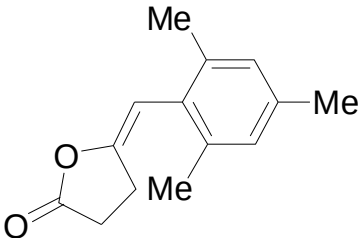
(*E*)-4-Benzylidenebutanolide ((*E*)-4a). Soild. m.p. 94.2-95.7 °C. IR (KBr): 2944, 1801, 1676, 1445, 1371, 1295, 1233, 1173, 1125, 1012, 935, 912, 871, 821, 757, 693, 611, 570, 548, 516, 468, 446, 425 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.36-7.33 (m, 2H), 7.23-7.22 (m, 3H), 6.33 (t, *J* =1.8 Hz, 1H), 3.17 (dt, *J* = 1.8 Hz, *J* = 8.4 Hz, 2H), 2.75 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.2, 151.1, 134.4, 128.7, 127.8, 126.7, 107.1, 27.8, 25.1; MS (EI, 70 eV): *m/z* (%) 174 (100, M^+), 145 (46); *Anal.* Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.93; H, 5.88. Known Compound.[2,3]



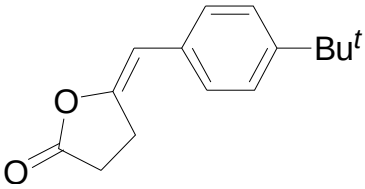
(*E*)-4-(4-Methylphenyl)methylenebutanolide ((*E*)-4b). Soild. m.p. 91.3-92.5 °C. IR (KBr): 2922, 1796, 1671, 1609, 1513, 1443, 1417, 1292, 1210, 1170, 1125, 933, 886, 808, 715, 520, 488 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.15 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.29 (s, 1H), 3.14 (t, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 8.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.3, 150.5, 136.5, 130.2, 129.4, 127.7, 107.0, 27.8, 25.1, 21.2; MS (EI, 70 eV): *m/z* (%) 188 (100, M^+), 145 (52), 132 (78); *Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.75; H, 6.50.



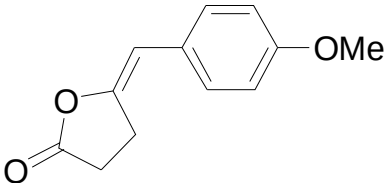
(*E*)-4-(2-Methylphenyl)methylenebutanolide ((*E*)-4c). Oil. IR (film): 2930, 1803, 1730, 1675, 1601, 1485, 1460, 1415, 1381, 1293, 1161, 1121, 1090, 932, 842, 752, 725, 664, 617, 546, 494, 450 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.13-7.08 (m, 4H), 6.30 (s, 1H), 2.96 (dt, J = 1.8 Hz, J = 8.4 Hz, 2H), 2.63 (t, J = 8.4 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ174.4, 151.0, 136.7, 133.0, 130.3, 127.5, 127.1, 125.9, 105.2, 27.9, 24.7, 20.0; MS (EI, 70 eV): *m/z* (%) 188 (100, M^+), 145 (48), 132 (21), 129 (19), 128 (20), 117 (20), 105 (36), 104 (53), 103 (22), 78 (26), 77 (21). HRMS calcd for $C_{12}H_{13}O_2$ ($[M+H]^+$): 189.0910; found: 189.0944.



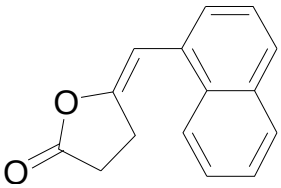
(*E*)-4-(2,4,6-Trimethylphenyl)methylenebutanolide ((*E*)-4d). Soild. m.p. 93.6-94.5 °C**.** IR (KBr): 2922, 1803, 1690, 1612, 1446, 1380, 1340, 1291, 1161, 1106, 1026, 923, 852, 740, 671, 564, 473 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 6.88 (s, 2H), 6.15 (s, 1H), 2.66 (t, *J* = 8.4 Hz, 2H), 2.55 (dt, *J* = 2.4 Hz, *J* = 8.4 Hz, 2H), 2.28 (s, 3H), 2.20 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.8, 150.6, 136.9, 136.7, 129.2, 128.3, 104.0, 27.9, 23.7, 21.0, 20.3; MS (EI, 70 eV): *m/z* (%) 216 (100, M^+), 173 (44), 157 (52); *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.89; H, 7.58.



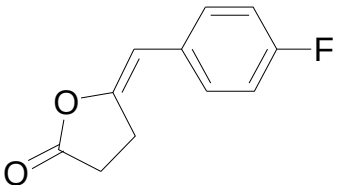
(*E*)-4-(4-*tert*-Butylphenyl)methylenebutanolide ((*E*)-4e). Soild. m.p. 92.6-93.5 °C. IR (KBr): 2963, 2868, 1800, 1737, 1676, 1602, 1512, 1461, 1361, 1292, 1266, 1171, 1104, 1015, 936, 888, 807, 559 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.30 (s, 1H), 3.16 (dt, *J* = 1.8 Hz, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 8.4 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ174.3, 150.6, 149.7, 131.4, 127.5, 125.6, 106.8, 34.6, 31.3, 27.8, 25.1; MS (EI, 70 eV): *m/z* (%) 230 (27, M^+), 216 (16), 215 (100), 159 (13), 145 (9), 131 (13), 115 (10), 91 (9), 55 (8). HRMS calcd for $C_{15}H_{19}O_2$ ($[M+H]^+$): 231.1380; found: 231.1375.



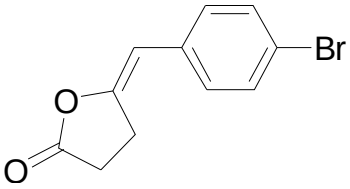
(*E*)-4-(4-Methoxylphenyl)methylenebutanolide ((*E*)-4f). Oil. IR (film): 2938, 2836, 1795, 1679, 1603, 1511, 1443, 1360, 1297, 1233, 1178, 1101, 1033, 939, 828, 733, 523 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.14 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.27 (s, 1H), 3.81 (s, 3H), 3.11 (dt, *J* = 1.8 Hz, *J* = 8.4 Hz, 2H), 2.73 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ174.7, 149.9, 129.0, 116.1, 114.9, 114.2, 106.6, 55.8, 42.0, 25.0; MS (EI, 70 eV): *m/z* (%) 204 (100, M^+), 148 (66), 134 (32), 133 (16), 121 (24), 120 (50), 119 (12), 91 (27), 77 (27), 51 (19). HRMS calcd for $C_{12}H_{13}O_3$ ($[M+H]^+$): 205.0859; found: 205.0872.



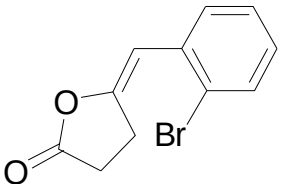
(*E*)-4-(Naphthalen-1-yl)methylenebutanolide ((*E*)-4i). Solid. m.p. 102.3-103.6 ^{o}C. IR (KBr): 2977, 2902, 1803, 1675, 1453, 1400, 1293, 1259, 1166, 1106, 1081, 1048, 927, 880, 780 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.35-7.99 (m, 7H), 6.85 (s, 1H), 3.01-3.04 (t, *J* = 8.4 Hz, 2H), 2.70-2.73 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.5, 152.0, 131.0, 128.6, 127.8, 126.3, 126.1, 125.7, 125.3, 124.3, 104.2, 27.8, 24.6; MS (EI, 70 eV): *m/z* 224 (3, M^+), 207 (38), 57 (100); *Anal.* Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.46; H, 5.18.



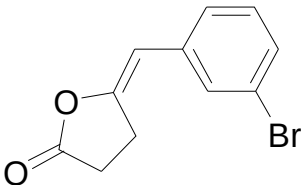
(*E*)-4-(4-Fluorophenyl)methylenebutanolide ((*E*)-4j). Soild. m.p. 93.5-94.6 ^{o}C. IR (KBr): 2929, 2268, 1788, 1672, 1508, 1416, 1292, 1220, 1176, 1105, 929, 878, 837, 741, 655, 524, 483 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.17-7.20 (m, 2H), 7.03-7.06 (m, 2H), 6.30 (s, 1H), 3.13 (dt, *J* = 1.8 Hz, *J* = 8.4 Hz, 2H), 2.75-2.78 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.0, 161.4 (d, J_{CF} = 245.4 Hz), 150.8, 130.4 (d, J_{CF} = 3.3 Hz), 129.3 (d, J_{CF} = 7.8 Hz), 115.6 (d, J_{CF} = 21.3 Hz), 106.0, 27.7, 25.0; MS (EI, 70 eV): *m/z* 192 (88, M^+), 136 (82), 108 (100); *Anal.* Calcd for $C_{11}H_9FO_2$: C, 68.74; H, 4.72. Found: C, 68.58; H, 4.63.



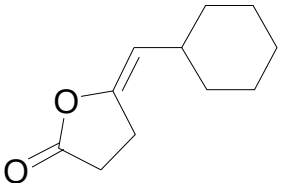
(*E*)-4-(4-Bromophenyl)methylenebutanolide ((*E*)-4l). Soild. m.p. 67.3-68.4 ^{o}C. IR (KBr): 2927, 1803, 1681, 1587, 1489, 1443, 1402, 1293, 1222, 1167, 1098, 1075, 1009, 969, 942, 912, 873, 832, 805, 740, 651, 559, 512 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.26 (s, 1H), 3.13 (t, *J* = 7.8 Hz, 2H), 2.77 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.9, 151.7, 133.3, 131.8, 129.8, 129.3, 106.1, 27.6, 25.1; MS (EI, 70 eV): *m/z* 252 (18, M^+), 89 (100); *Anal.* Calcd for $C_{11}H_9BrO_2$: C, 52.20; H, 3.58. Found: C, 52.08; H, 3.43.



(*E*)-4-(2-Bromophenyl)methylenebutanolide ((*E*)-4m). Oil. IR (film): 2976, 1806, 1676, 1563, 1468, 1437, 1297, 1161, 1123, 1102, 1025, 935, 837, 757, 662, 507 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.61 (d, *J* = 7.2Hz, 1H), 7.24-7.29 (m, 2H), 7.10-7.13 (m, 1H), 6.50 (s, 1H), 3.04-3.08 (m, 2H), 2.72-2.75 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.0, 152.2, 134.3, 133.1, 128.8, 128.4, 127.3, 124.5, 106.6, 27.6, 24.7; MS (EI, 70 eV): *m/z* 252 (32, M^+), 296 (38), 89 (100); *Anal.* Calcd for $C_{11}H_9BrO_2$: C, 52.20; H, 3.58. Found: C, 52.37; H, 3.62.



(*E*)-4-(3-Bromophenyl)methylenebutanolide ((*E*)-4n). Oil. IR (film): 2974, 1806, 1676, 1468, 1437, 1297, 1161, 1123, 1102, 1024, 934, 836, 757, 663, 507, 447 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.61 (d, *J* = 2.4Hz, 1H), 7.25-7.29 (m, 2H), 7.10-7.12 (m, 1H), 6.50 (s, 1H), 3.05 (dt, *J* = 2.4 Hz, *J* = 7.8 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.1, 150.4, 132.4, 131.2, 126.9, 126.5, 125.4, 122.6, 104.7, 25.7, 22.8; MS (EI, 70 eV): *m/z* 252 (31, M^+), 196 (20), 89 (100); *Anal.* Calcd for $C_{11}H_9BrO_2$: C, 52.20; H, 3.58. Found: C, 52.28; H, 3.73.



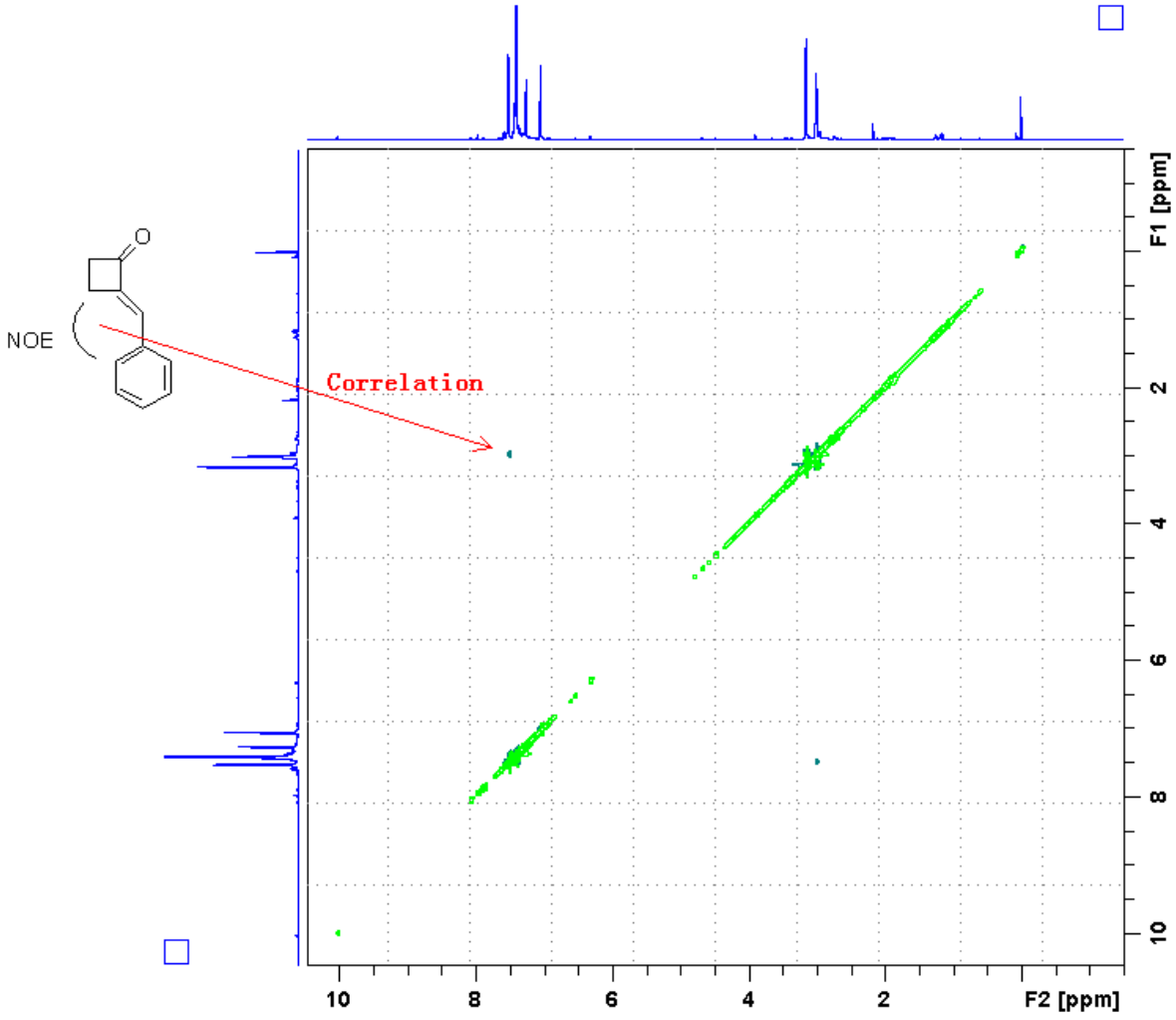
(*E*)-4-Cyclopropylidenebutanolide ((*E*)-4q). Oil. IR (film): 2925, 2851, 1797, 1696, 1447, 1418, 1379, 1345, 1295, 1238, 1175, 1139, 1091, 1012, 975, 911, 839, 664, 581, 536, 454 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 5.09 (d, *J* = 10.2Hz, 1H), 2.84 (t, J = 8.4 Hz, 2H), 2.66 (t, J = 8.4 Hz, 2H), 1.99-1.93 (m, 1H), 1.74-1.64 (m, 4H), 1.31-1.08 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ175.1, 147.9, 110.7, 35.4, 33.3, 27.8, 25.9, 22.6; MS (EI, 70 eV): *m/z* (%) 180 (43, M^+), 137 (100), 109 (56), 99 (56), 95 (65), 82 (66), 81 (92), 80 (51), 67 (50), 55 (67). HRMS calcd for $C_{11}H_{17}O_2$ ($[M+H]^+$): 181.1223; found: 181.1229.

References

1. J. P. Markham, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* 2005, **127**, 9708.
2. WSS: Spectral data were obtained from Wiley Subscription Services, Inc. (US).
3. G. Tsolomiti, A. Tsolomitis, *Hetero. Commun.* 2006, **12**, 93.

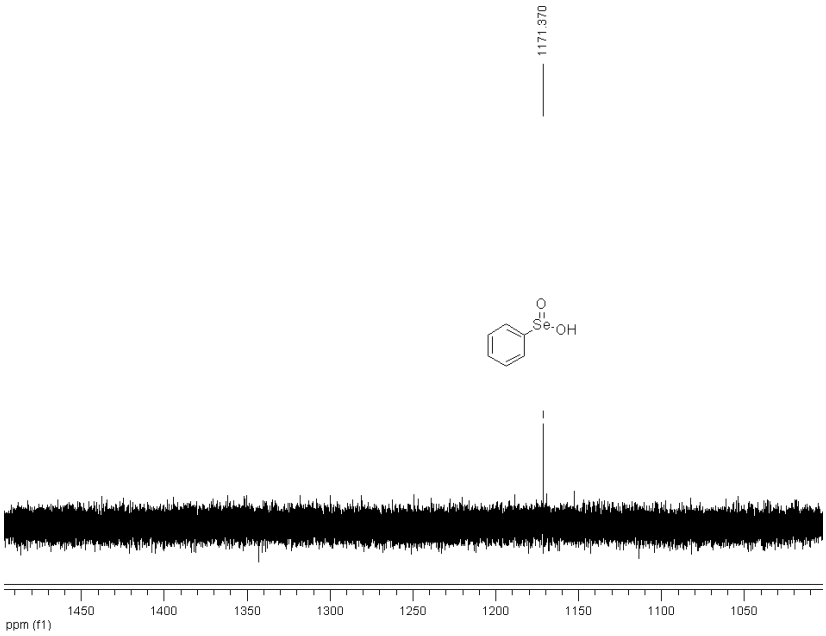
NOESY Spectra of Product (*E*)-3a and Determination of the Products' Stereochemistry

1) As shown in the following NOESY spectra of **3a**, the strong correlation between an aromatic proton (7.40 *ppm*) and the protons of cyclic CH_2 (2.99 *ppm*) confirmed that they are in a *syn*-position, indicating that product **3a** is the (*E*)-stereomer.
2) On the contrary, obviously there is no correlation between the vinylic proton (7.04 *ppm*) and the protons of cyclic CH_2 (2.99 *ppm*), implying that they are in an *anti*-position, which also indicated that product **3a** is the (*E*)-stereomer.
3) The stereochemistry of products (*E*)-**3a**, **3g**, and **3k** were also confirmed by the literature data (*J. Am. Chem. Soc.* **2005**, *127*, 9708).
4) The stereochemistry of other products (*E*)-**3** can be inferred analogously by comparing their NMR spectra and chemical shifts of the corresponding protons with those of **3a**, **3g** and **3k**.

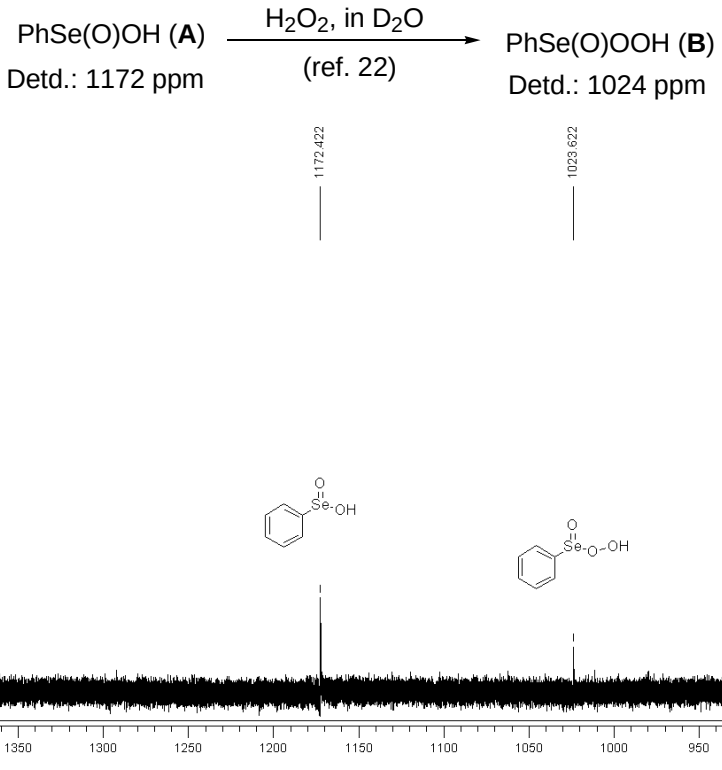


^{77}Se NMR Spectroscopic Analysis of the Involved Organoselenium Species

Step 1. Determined chemical shift of pure benzeneseleninic acid PhSe(O)OH (**A**) in D_2O is 1171 ppm, which is consistent with the literature data (1182 ppm, see: D. Dowd, P. Gettins, *Magn. Reson. Chem.* 1988, **26**, 1).



Step 2. Literature chemical shift of the unstable benzeneseleninoperoxoic acid PhSe(O)OOH (**B**) is not available, but it was reported that **B** could be obtained from **A** by treatment with H_2O_2 (see: L. Syper, J. Mlochowski, *Tetrahedron* 1987, **43**, 207). As shown below, by treating **A** with H_2O_2 in D_2O, a new peak at 1024 ppm was detected, which is most possibly the chemical shift of **B**.

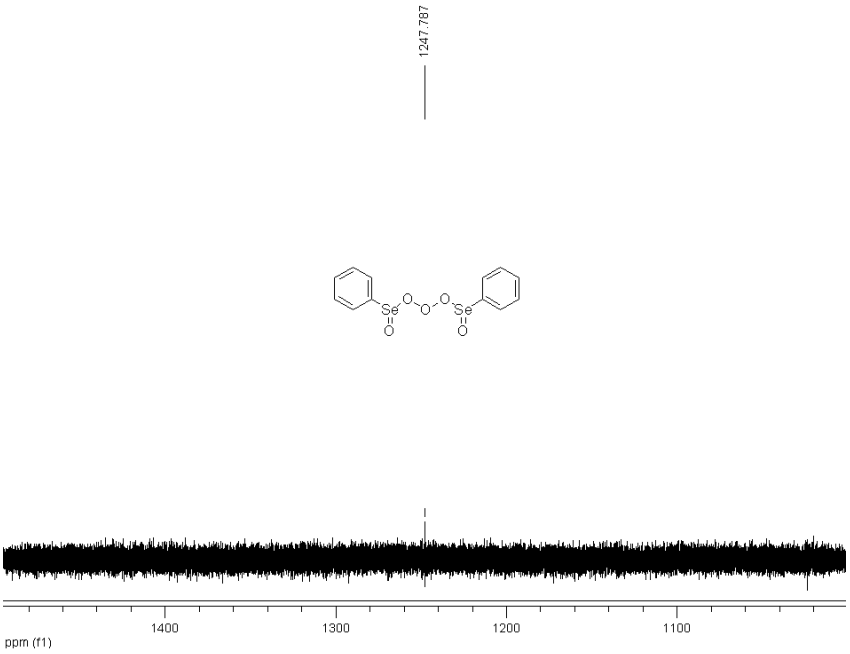


Step 3. By treating $(PhSe)_2$ with H_2O_2 in D_2O, a new peak at 1248 ppm was detected, which, consists with the literature data (1241 ppm, see: http://www.chem.wisc.edu/areas/reich/handouts/nmr/se-data.htm) of benzeneseleninoperoxoic anhydride $[PhSe(O)O]_2O$ (**C**), is thus most possibly the chemical shift of **C**.

$(PhSe)_2 \xrightarrow{H_2O_2,\ in\ D_2O} [PhSe(O)O]_2O$ (**C**)

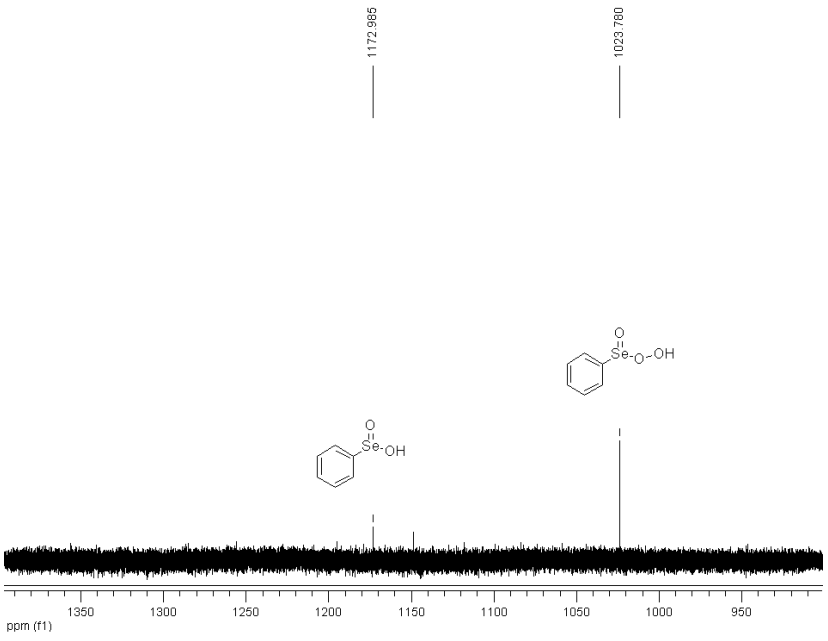
Detd.: 1248 ppm

Lit.:[25] 1241 ppm

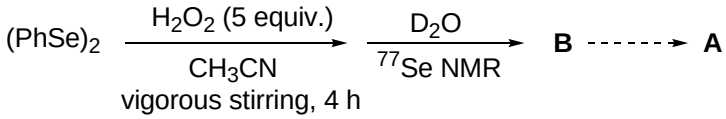


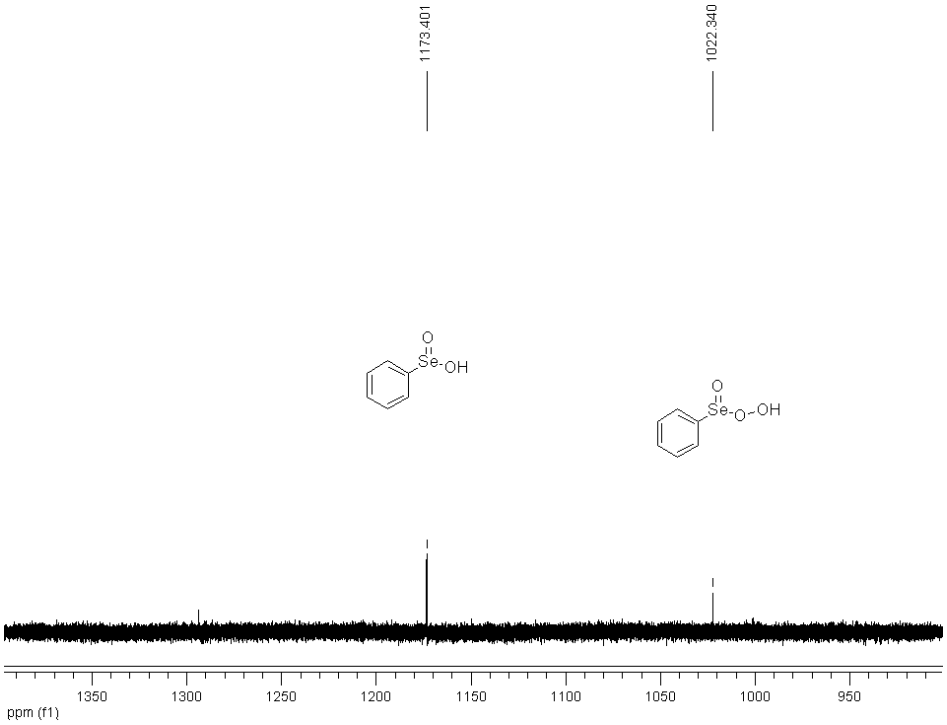
Step 4. After standing for 24 h, the chemical shifts of the above sample (in step 3) changed a lot. As shown below, the peak of $[PhSe(O)O]_2O$ (**C**) disappeared and that of **B** (1024 ppm) appeared as the major one, with generation of small amounts of **A** (1173 ppm).

$[PhSe(O)O]_2O$ (**C**) $\xrightarrow[\text{standing, 24 h}]{H_2O}$ **B** - - - - - - → **A**

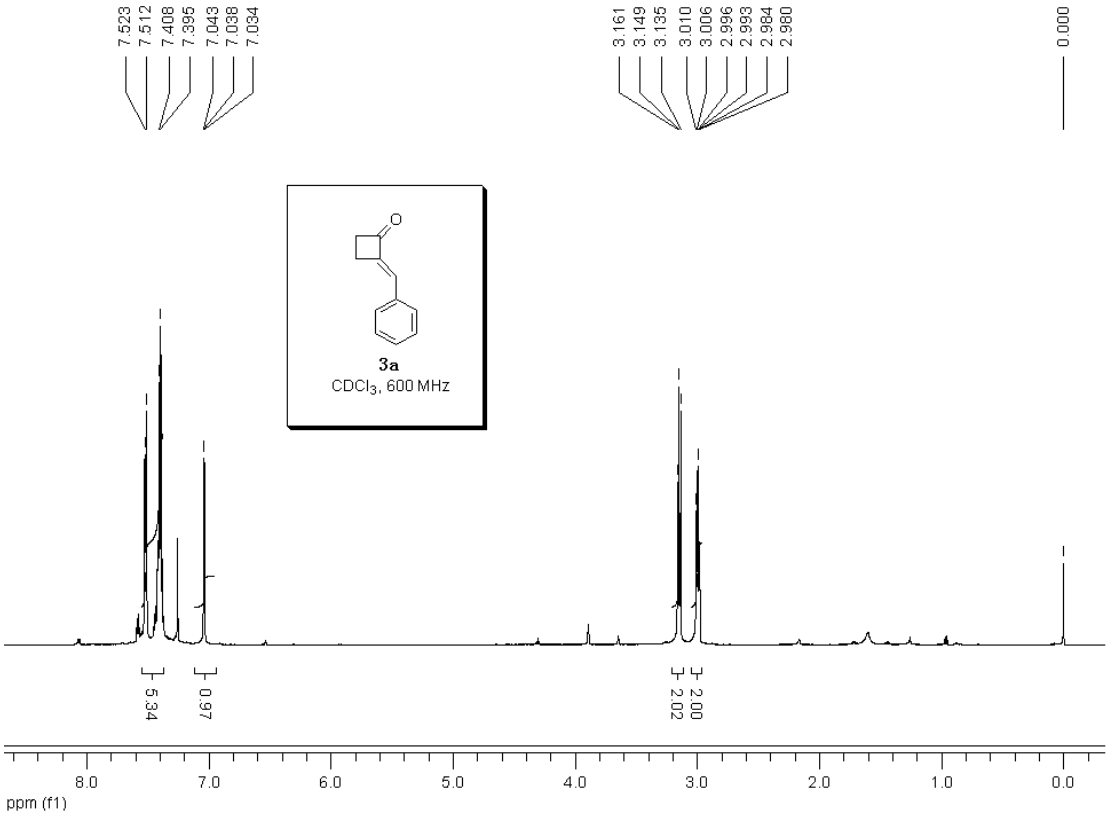


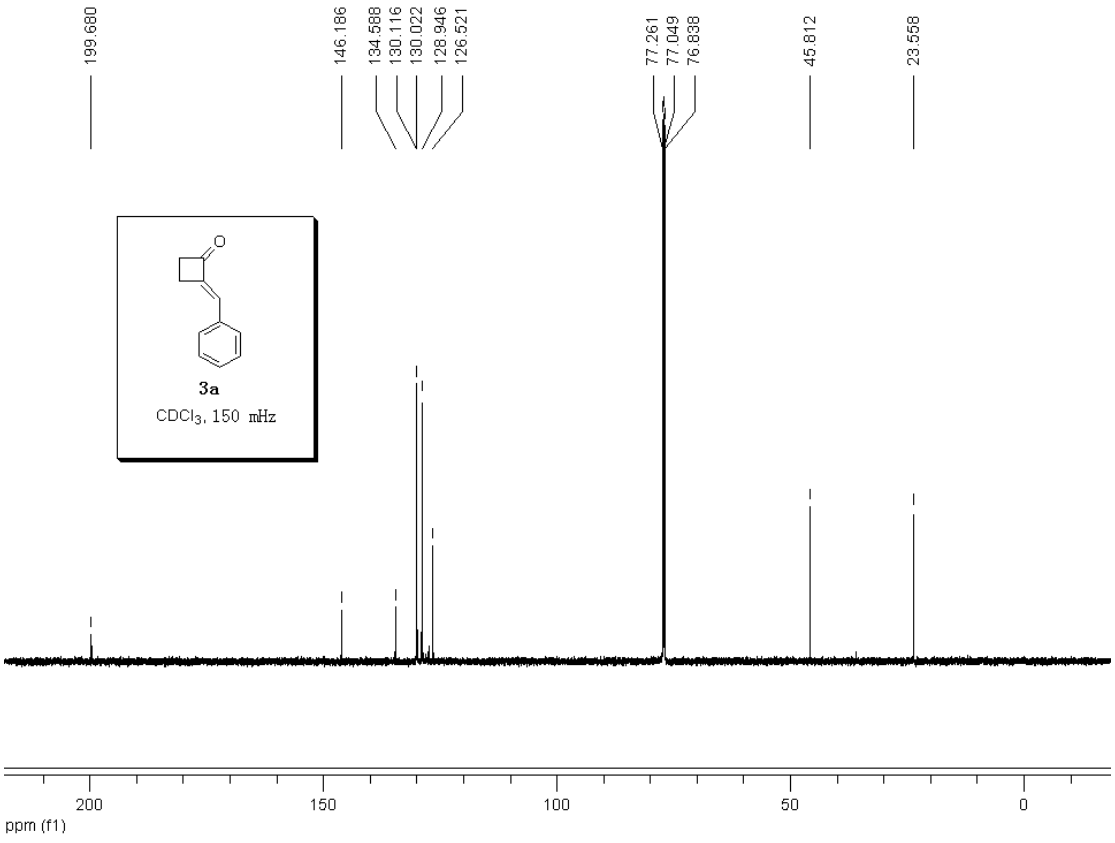
Step 5. On the other hand, as shown below, vigorous stirring of the mixture of $(PhSe)_2$ and H_2O_2 (5 equiv.) in CH_3CN for 4 h could directly afford **A** and **B** without the detection of **C**.

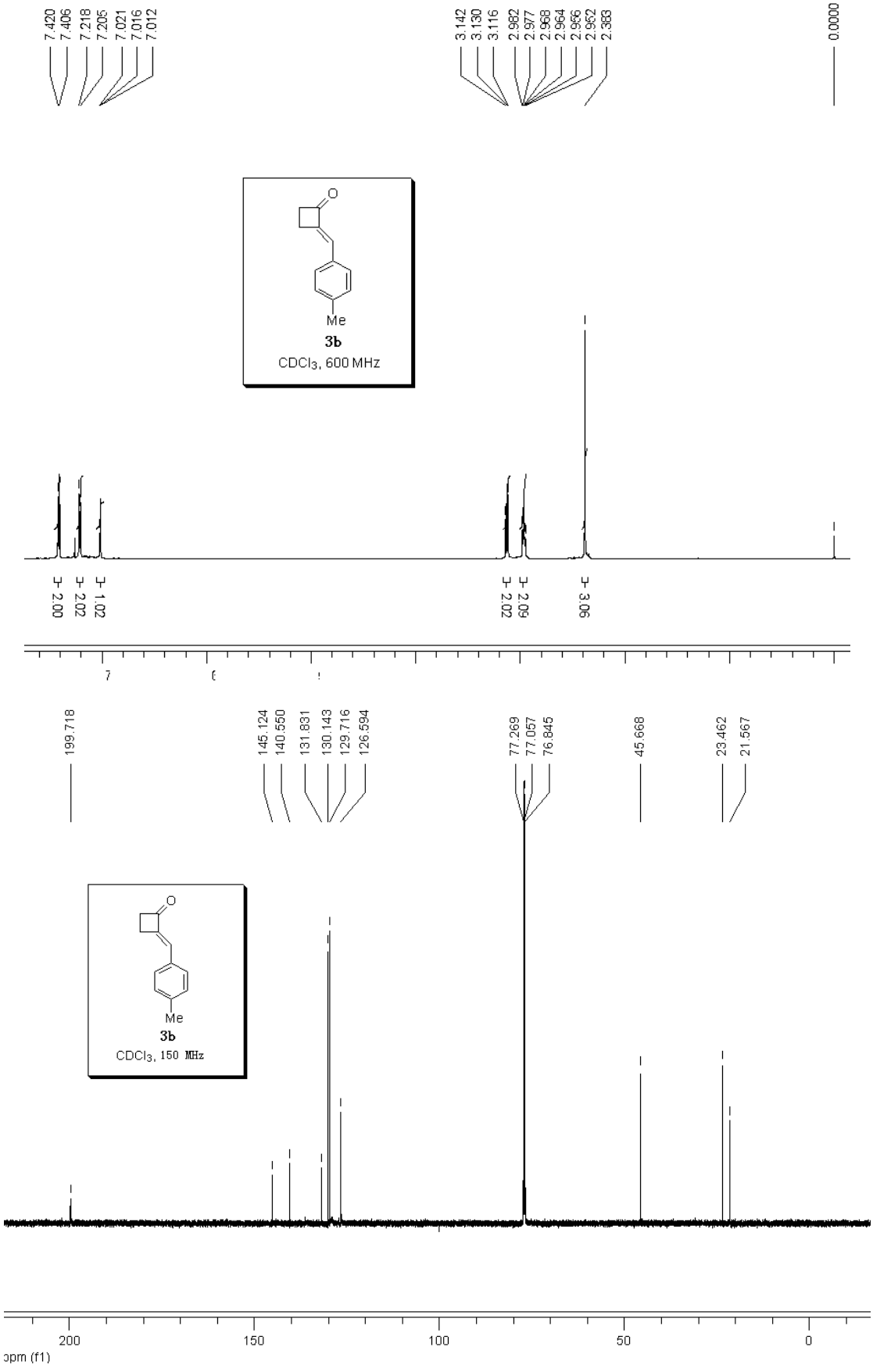




^{1}H and ^{13}C NMR Spectra of Products (*E*)-3 and (*E*)-4



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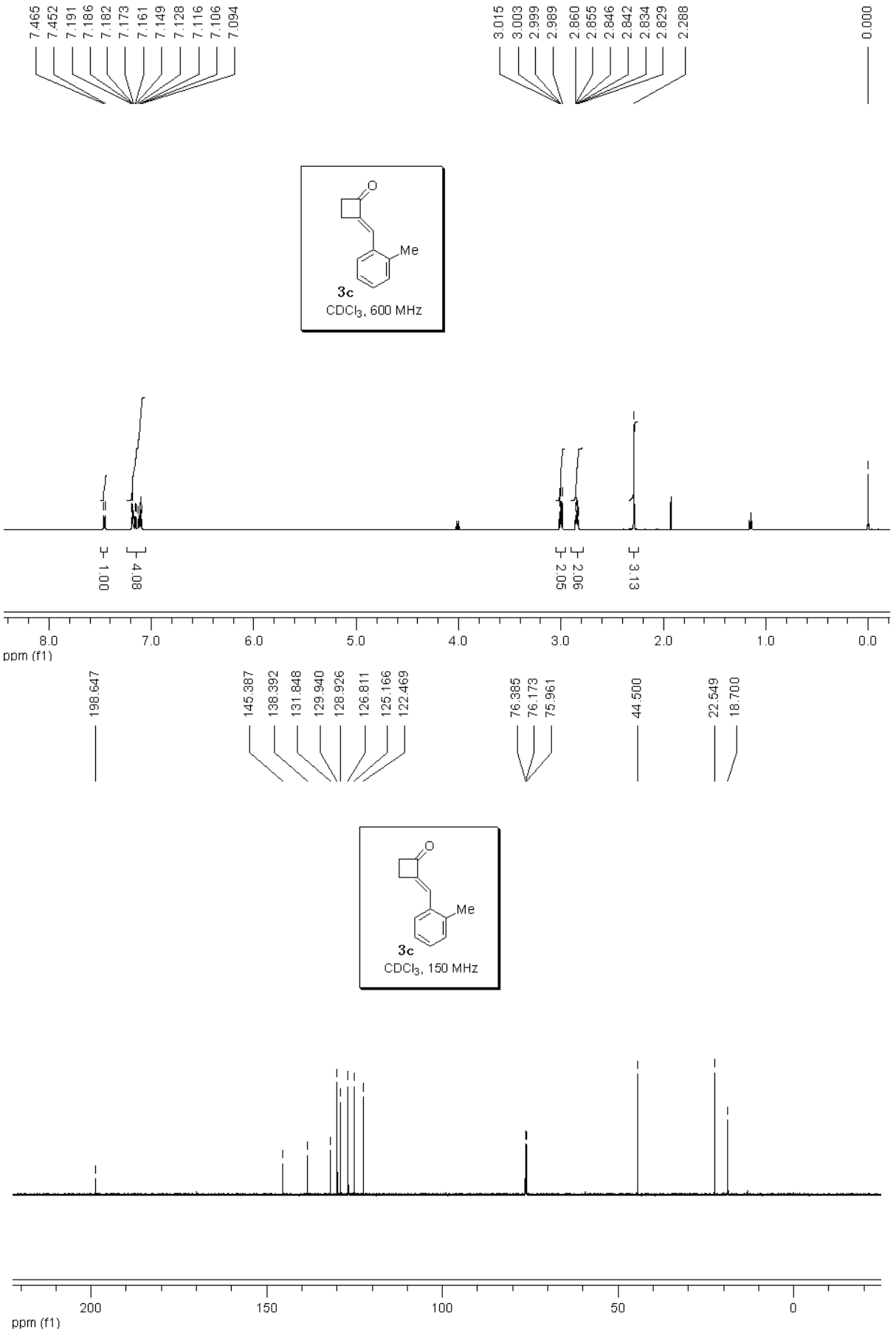
7.218
7.205
7.021
7.016
7.012
3.142
3.130
3.116
2.982
2.977
2.968
2.964
2.956
2.952
2.383
0.0000
Me
3b
CDCl3, 600 MHz
2.00
2.02
1.02
2.02
2.09
3.06
199.718
145.124
140.550
131.831
130.143
129.716
126.594
77.269
77.057
76.845
45.668
23.462
21.567
Me
3b
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)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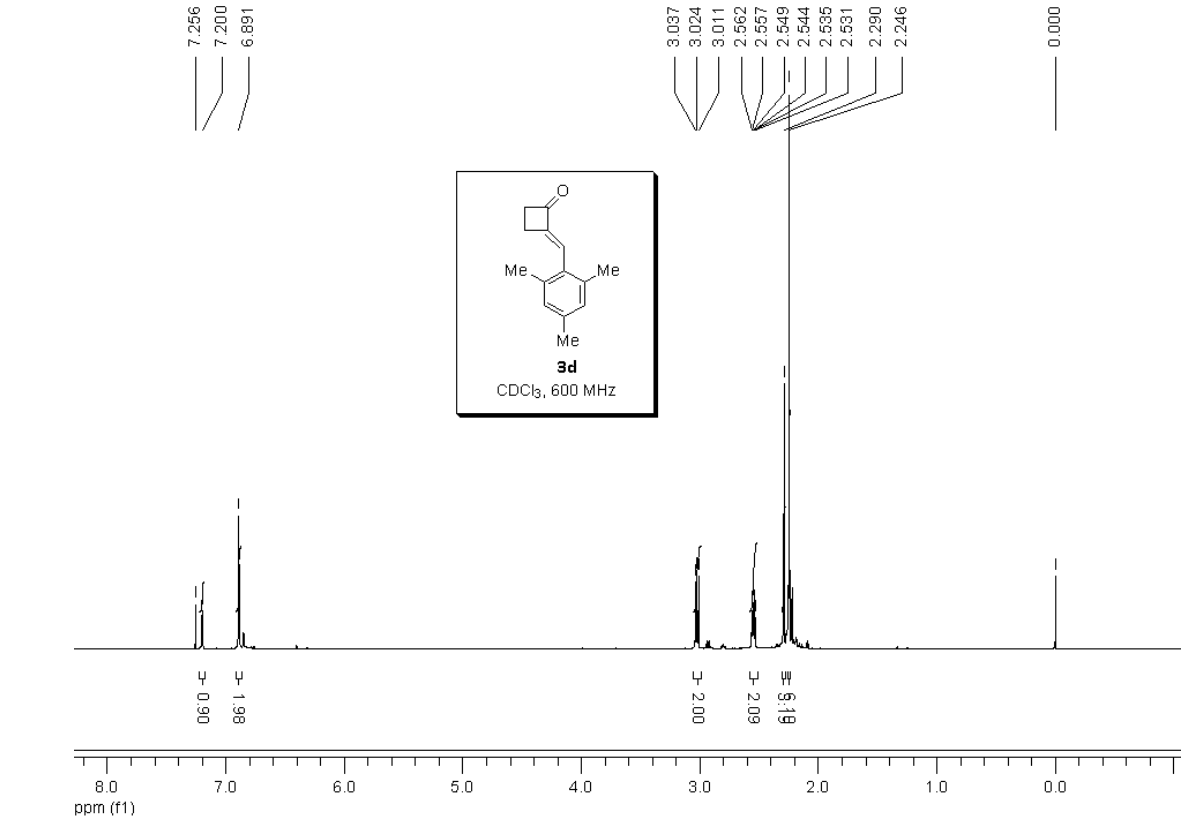
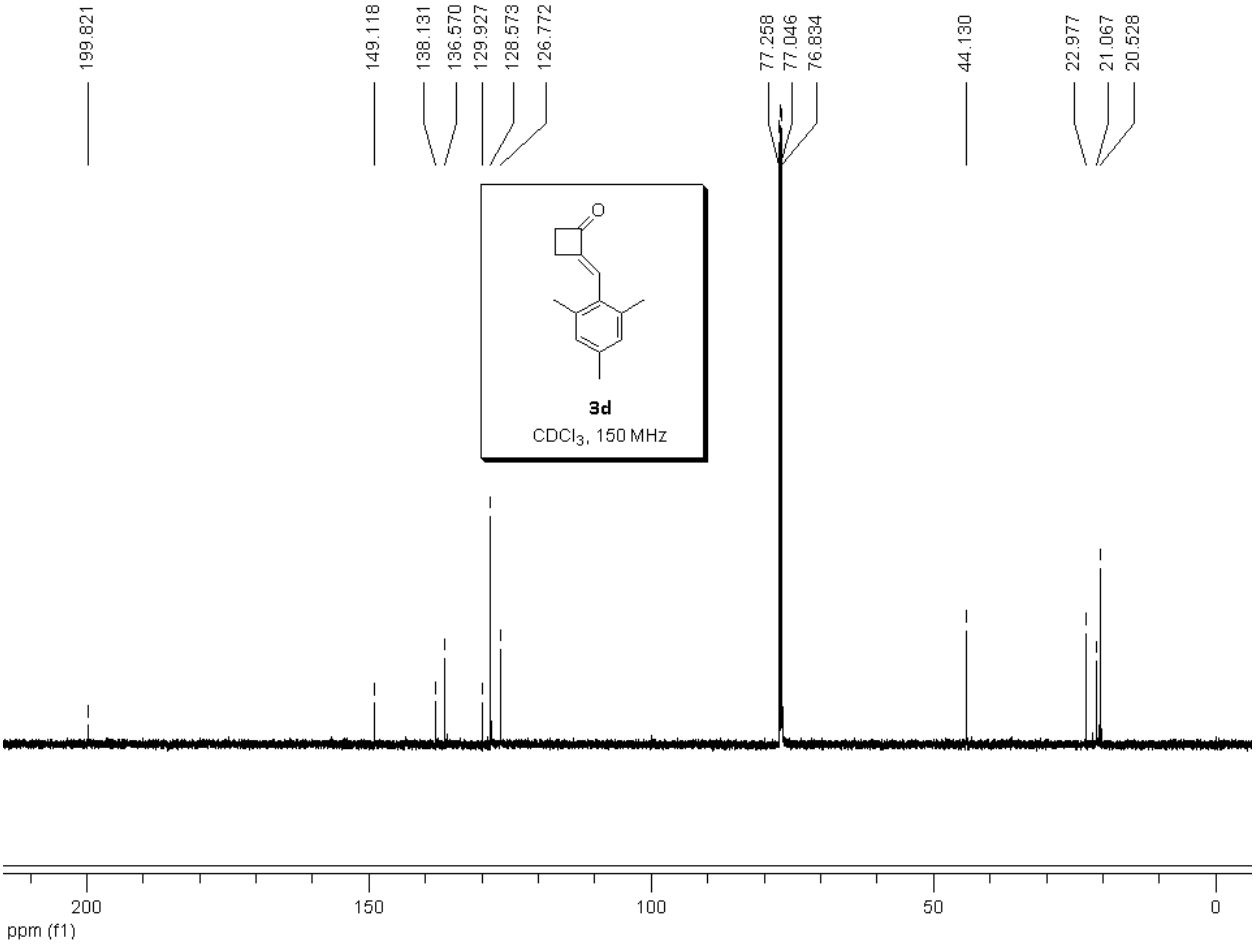
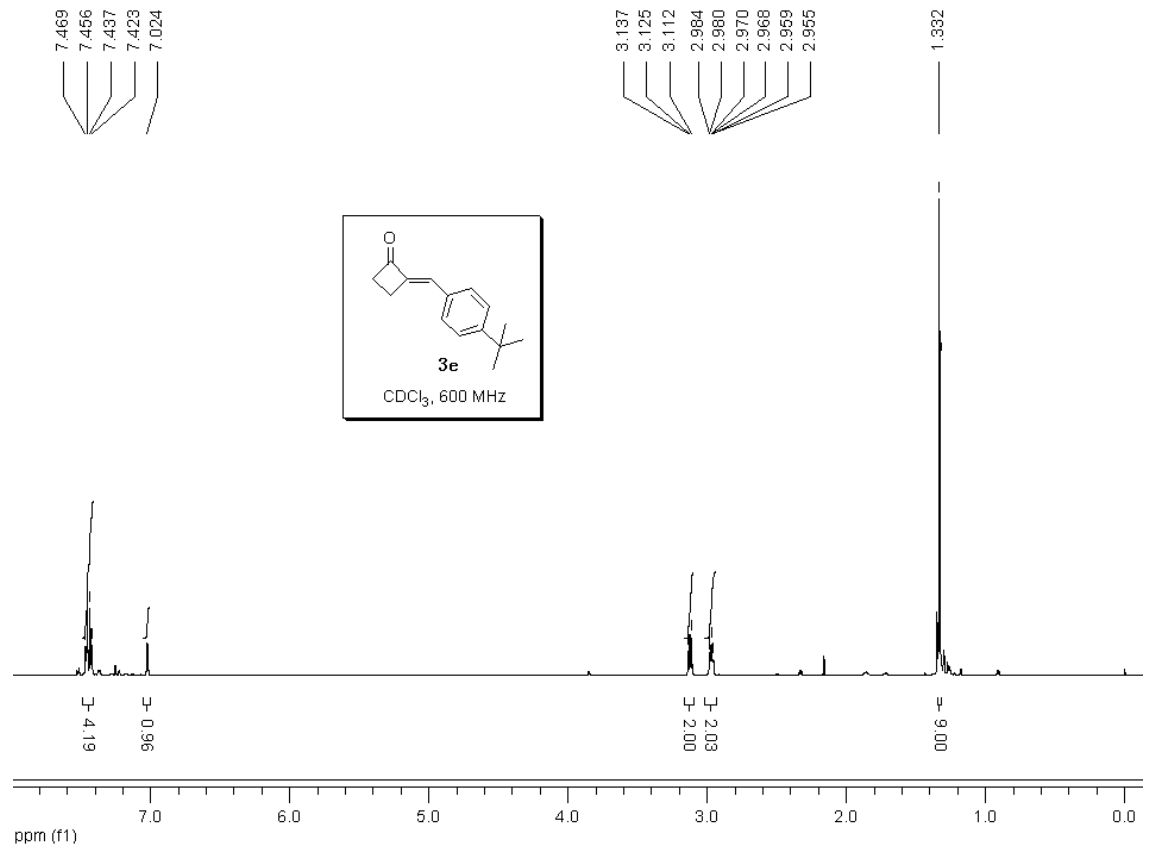
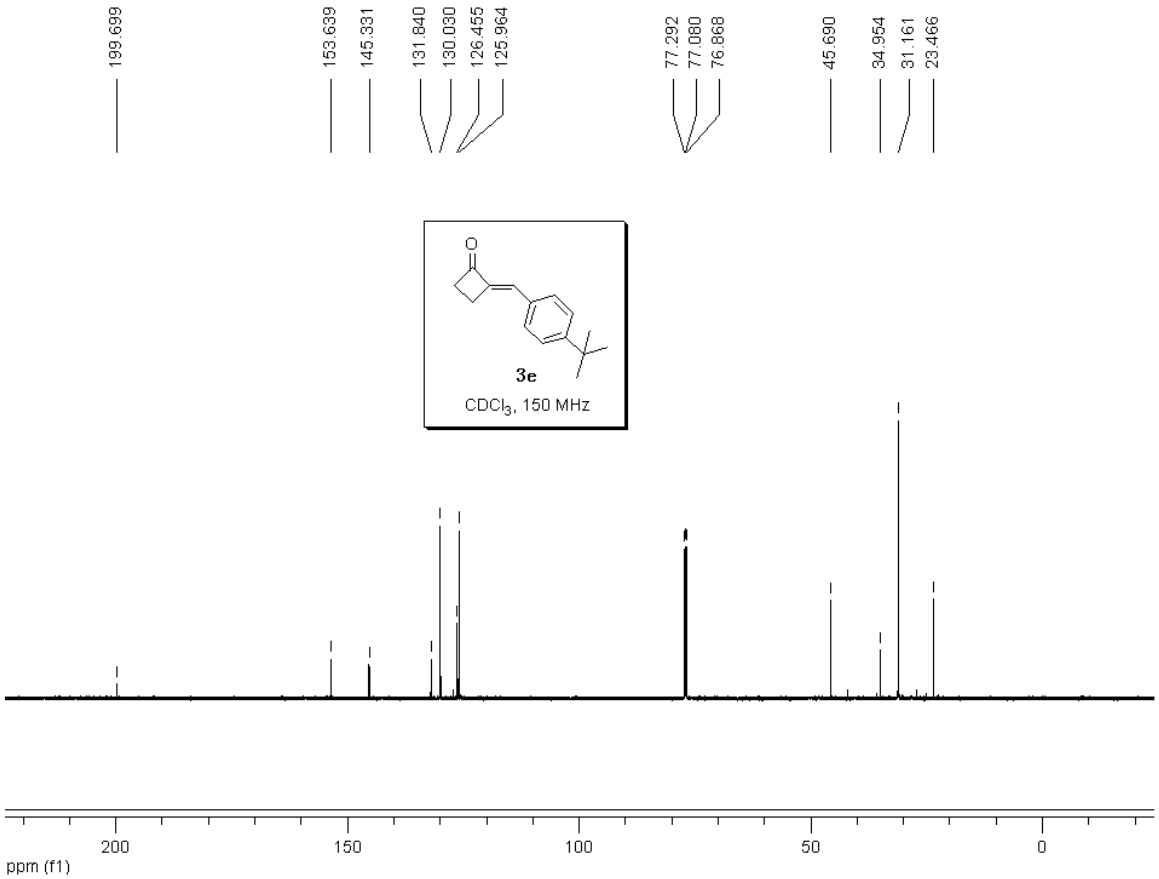
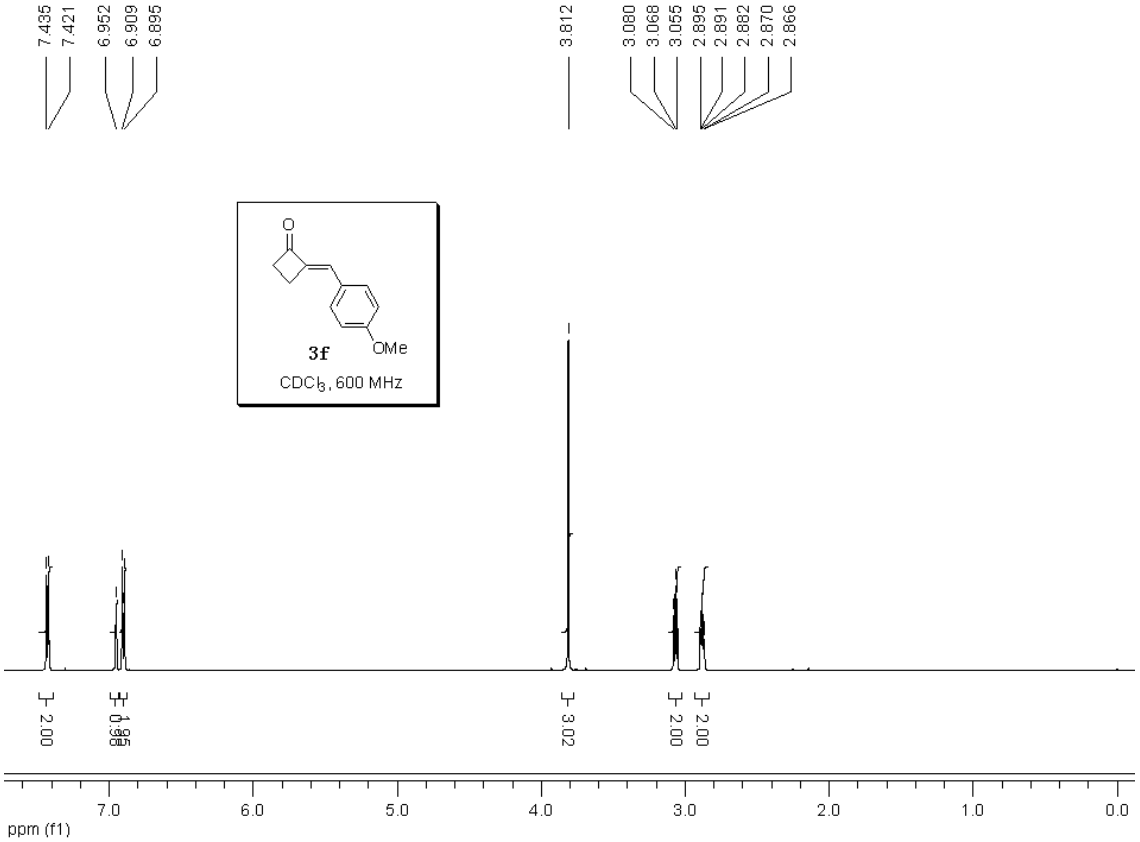
7.452
7.191
7.186
7.182
7.173
7.161
7.149
7.128
7.116
7.106
7.094
3.015
3.003
2.999
2.989
2.860
2.855
2.846
2.842
2.834
2.829
2.288
0.000
Me
3c
CDCl3, 600 MHz
1.00
4.08
2.05
2.06
3.13
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
198.647
145.387
138.392
131.848
129.940
128.926
126.811
125.166
122.469
76.385
76.173
75.961
44.500
22.549
18.700
Me
3c
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)







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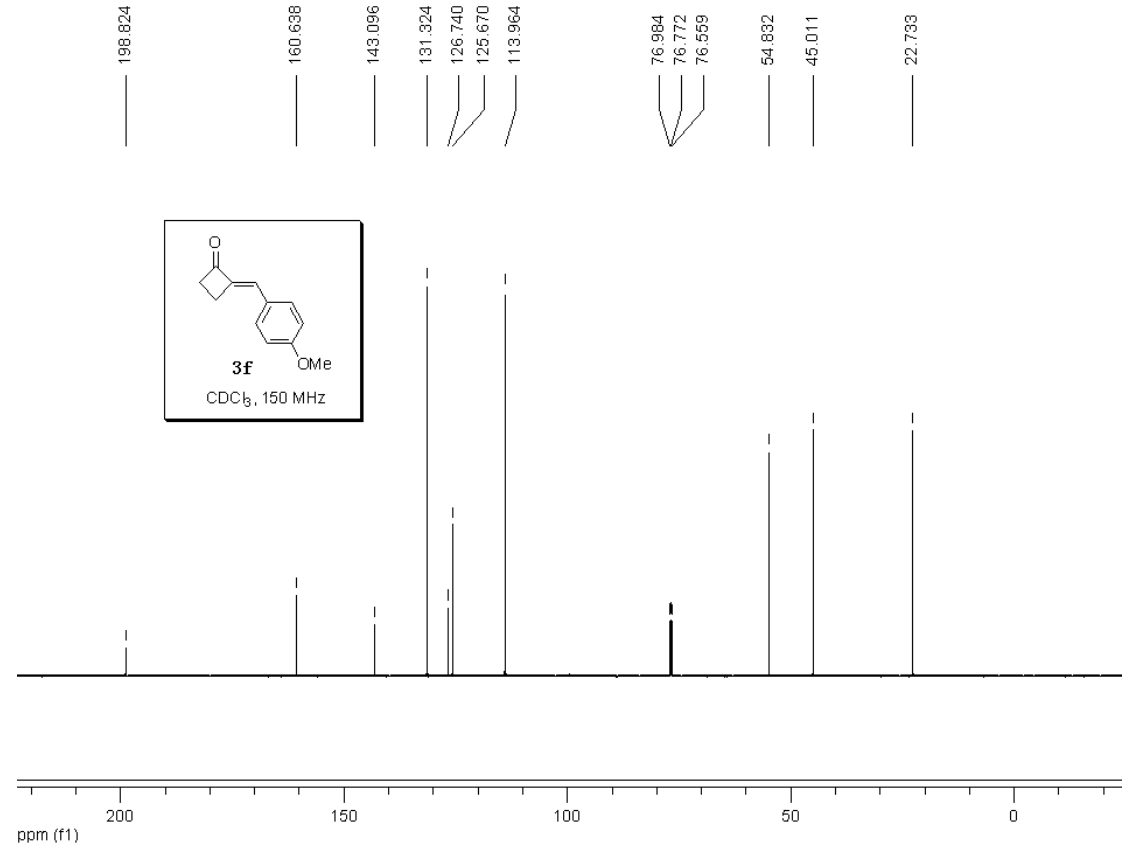
7.421
6.952
6.909
6.895
3.812
3.080
3.068
3.055
2.895
2.891
2.882
2.870
2.866
O
OMe
3f
CDCl3, 600 MHz
2.00
1.98
3.02
2.00
2.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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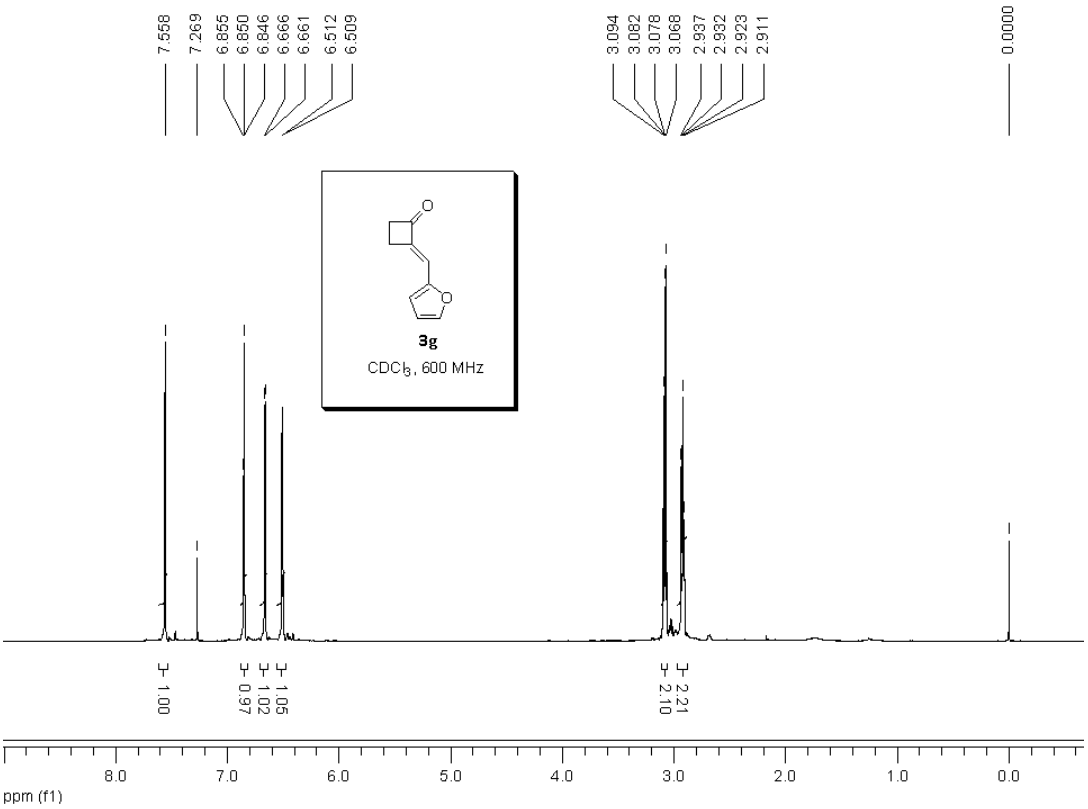
143.096
131.324
126.740
125.670
113.964
76.984
76.772
76.559
54.832
45.011
22.733
O
OMe
3f
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)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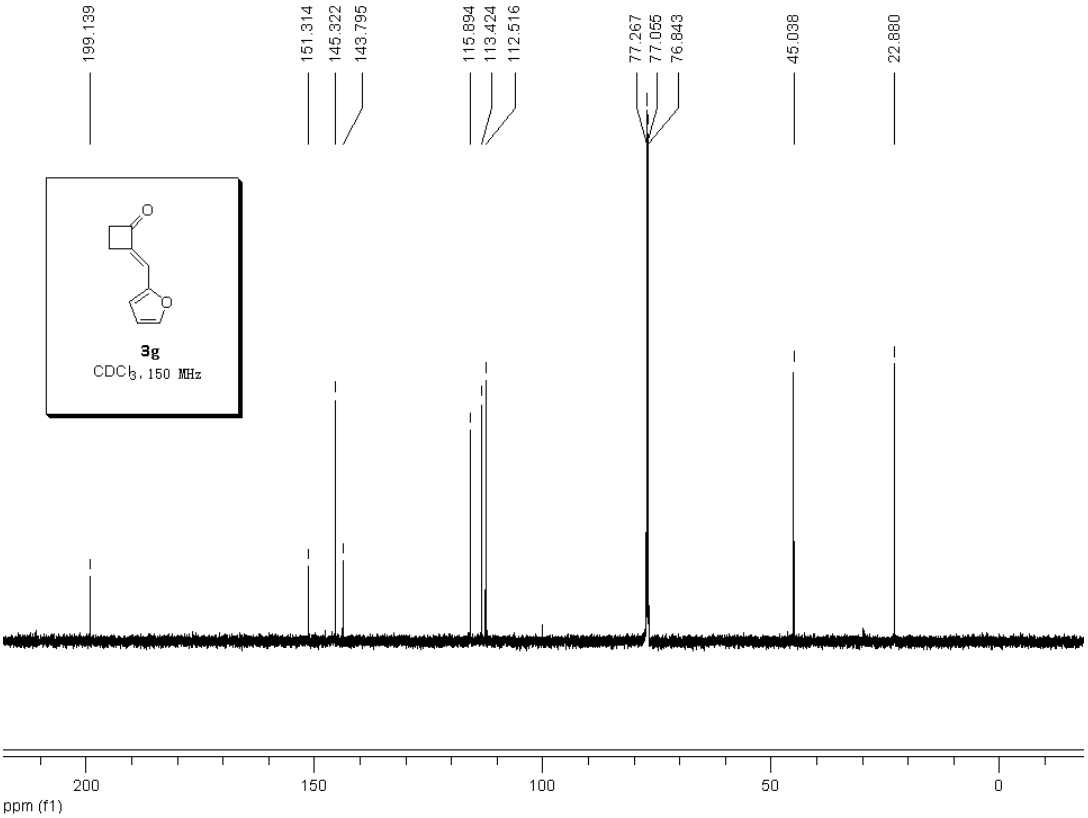
7.269
6.855
6.850
6.846
6.666
6.661
6.512
6.509
3.094
3.082
3.078
3.068
2.937
2.932
2.923
2.911
0.0000
3g
CDCl3, 600 MHz
1.00
0.97
1.02
1.05
2.21
2.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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113.424
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76.843
45.038
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3g
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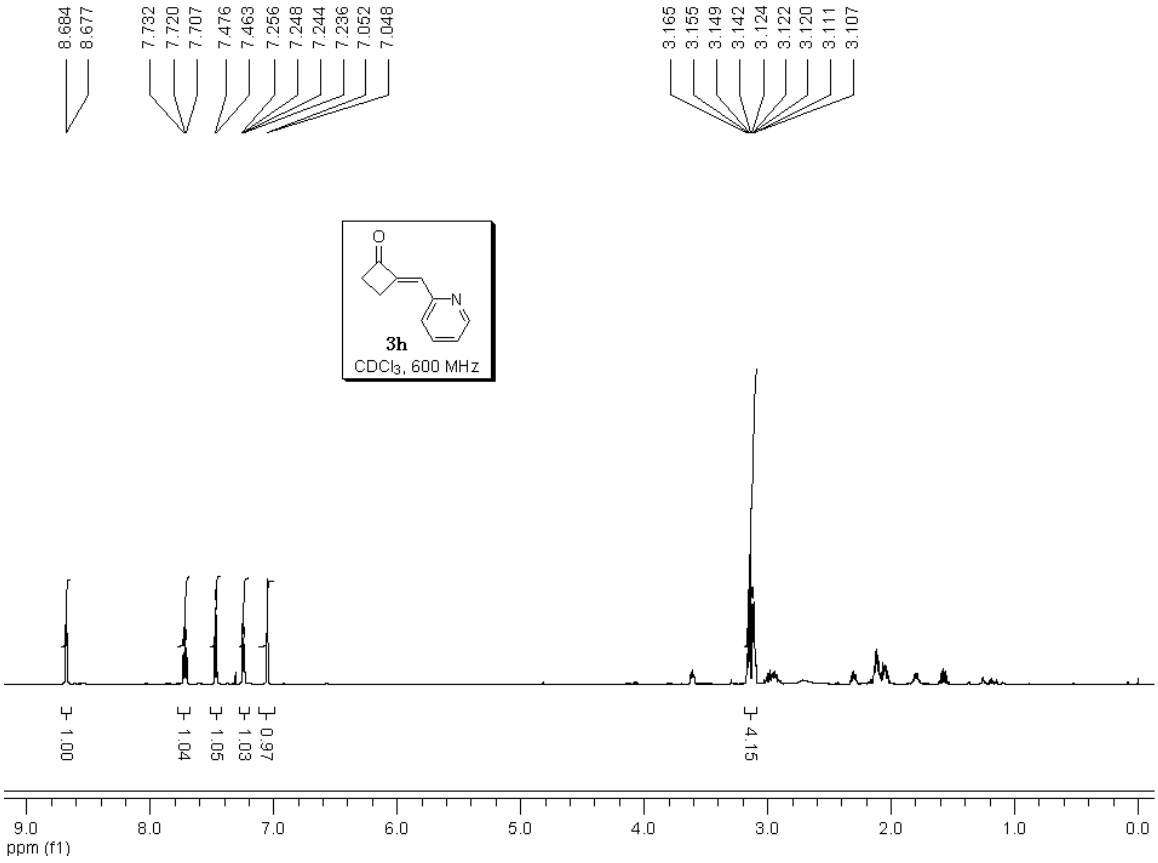
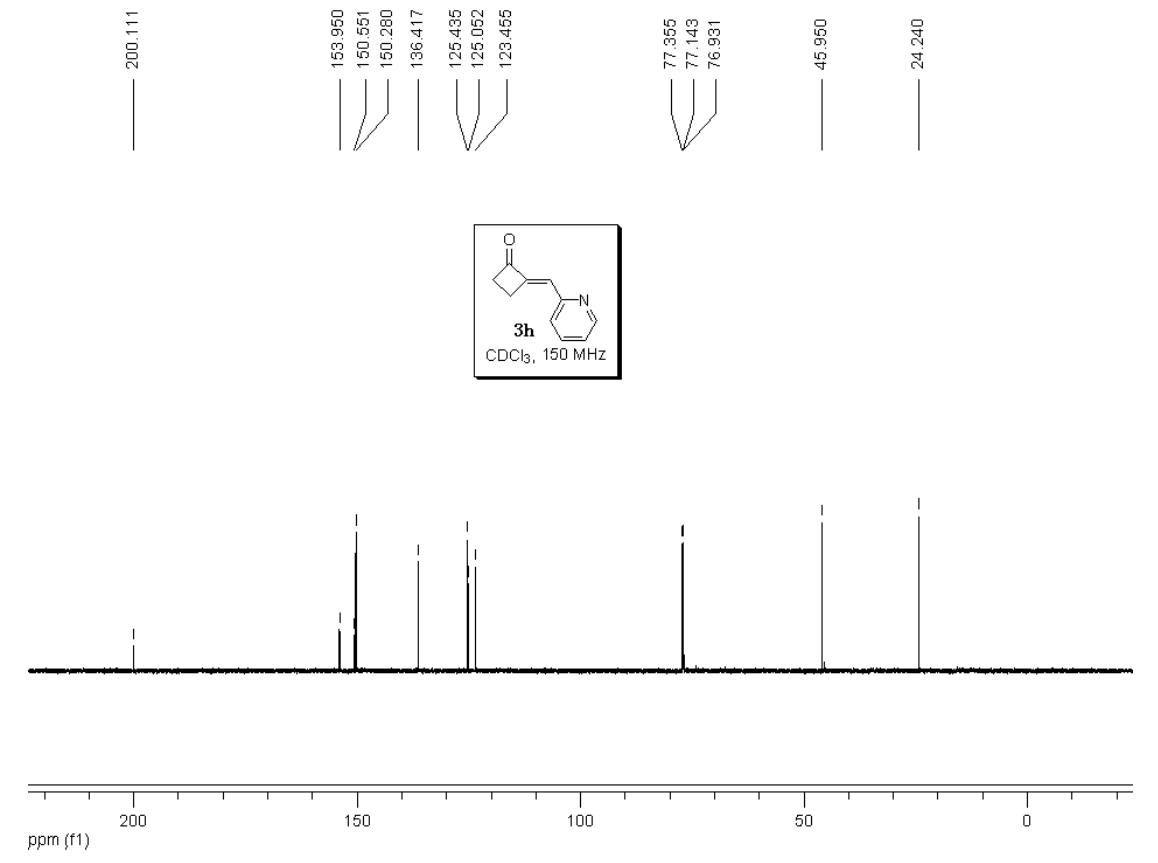
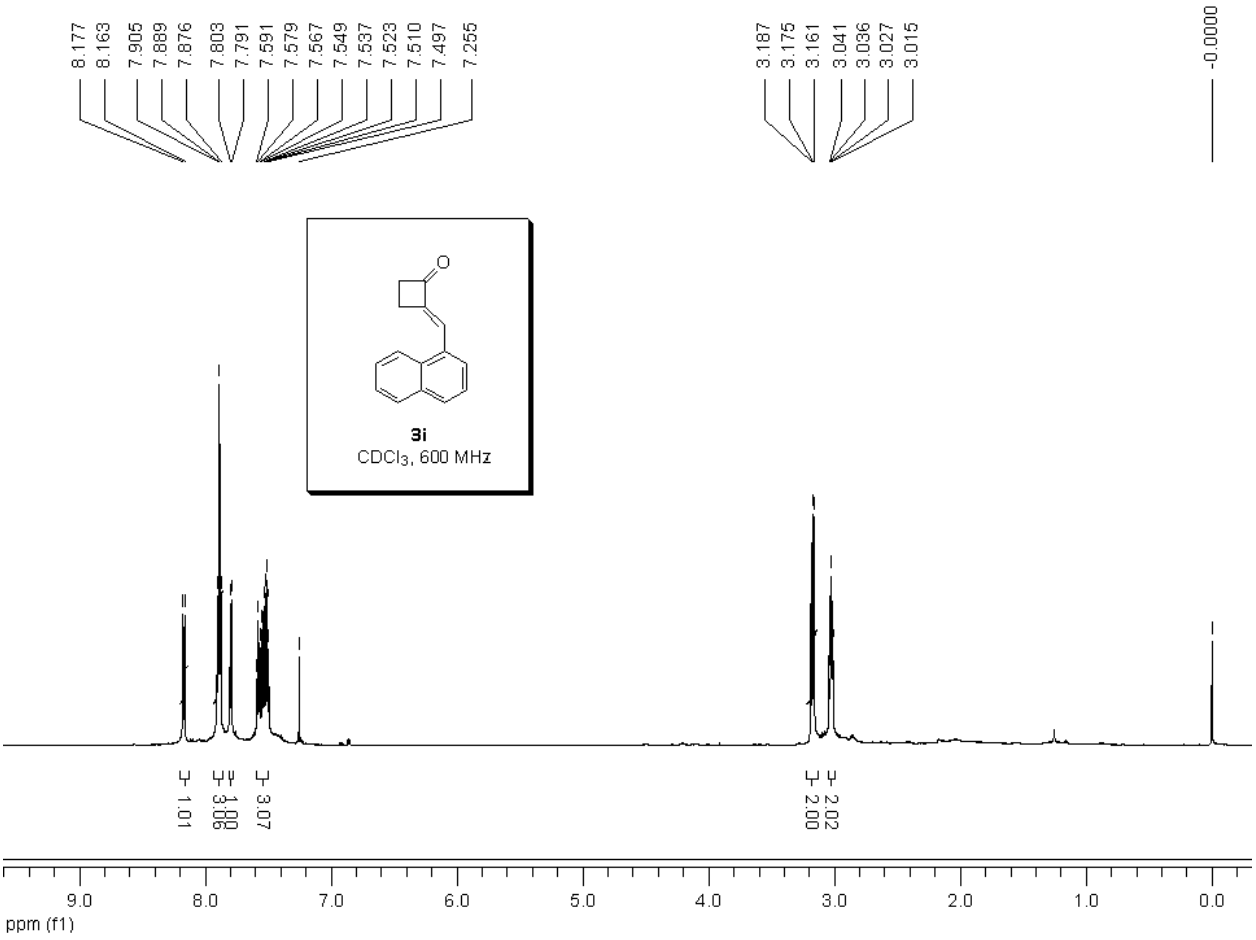
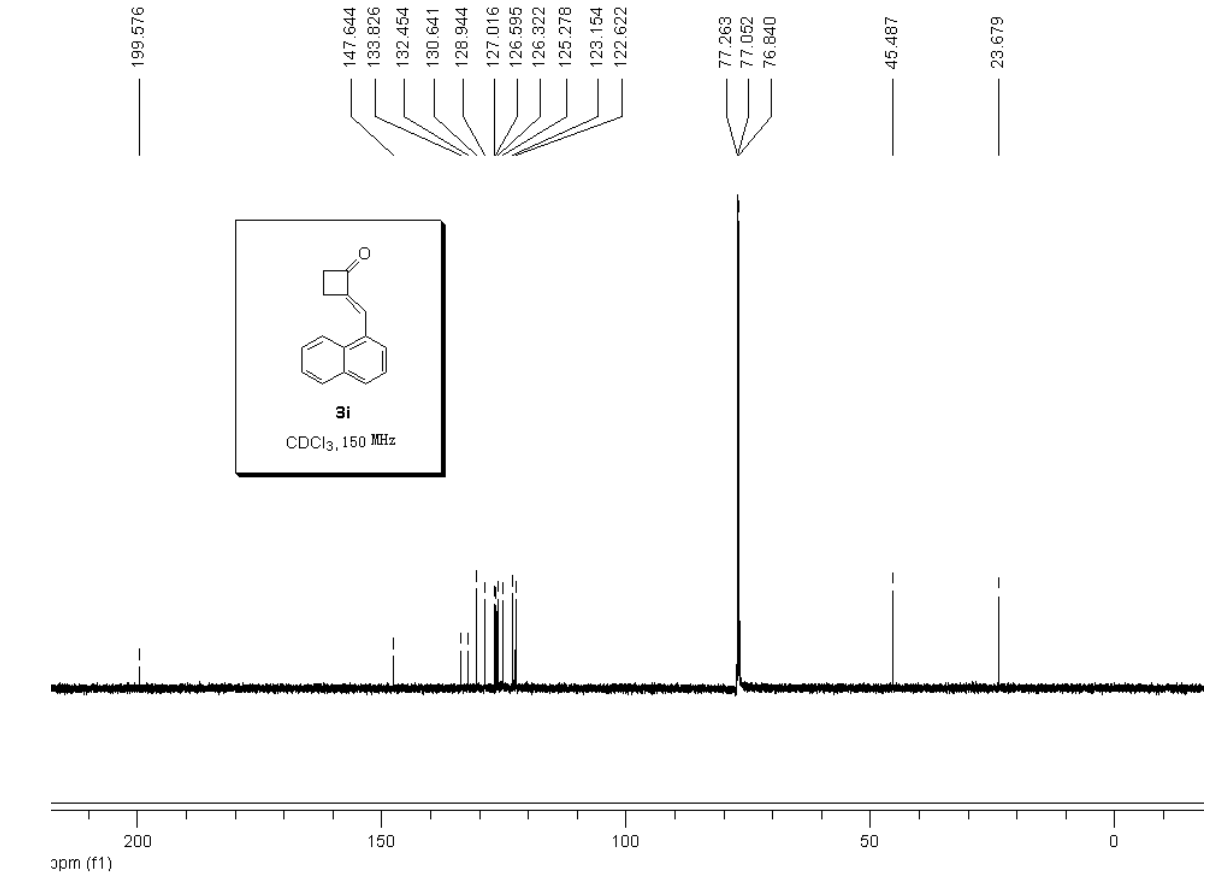
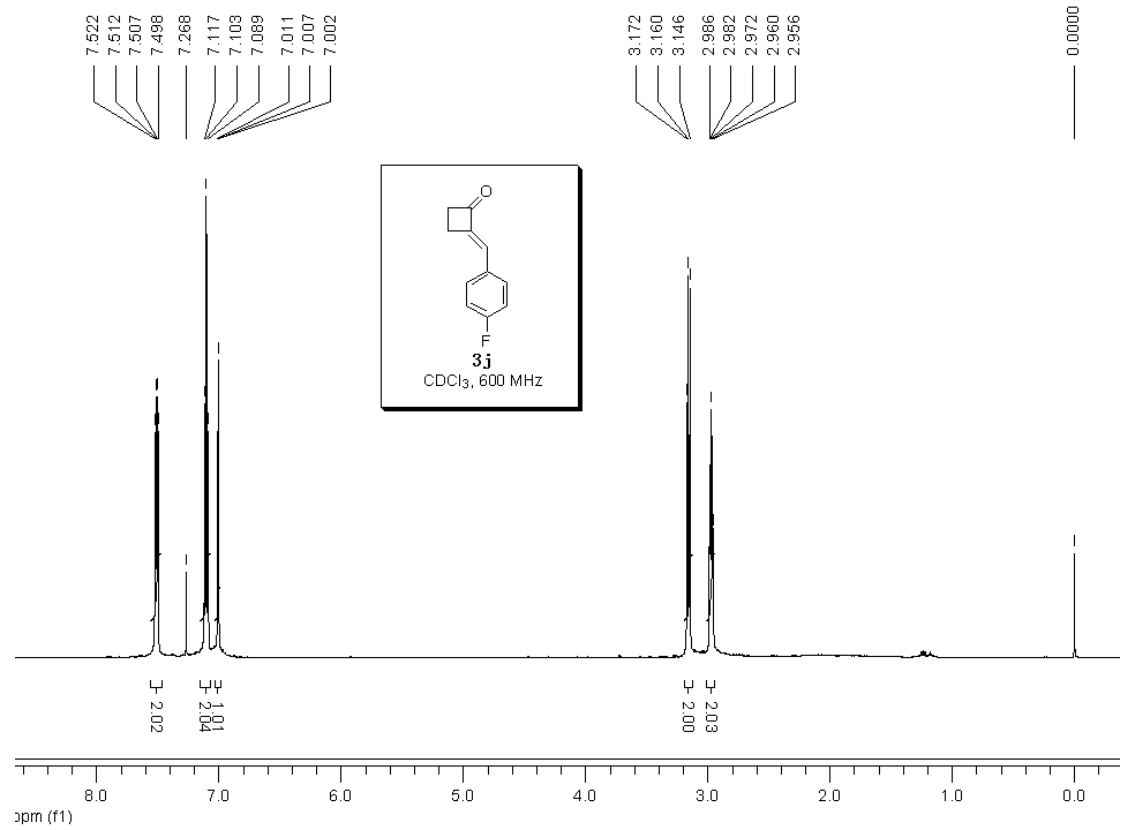
150
100
50
0
ppm (f1)







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7.103
7.089
7.011
7.007
7.002
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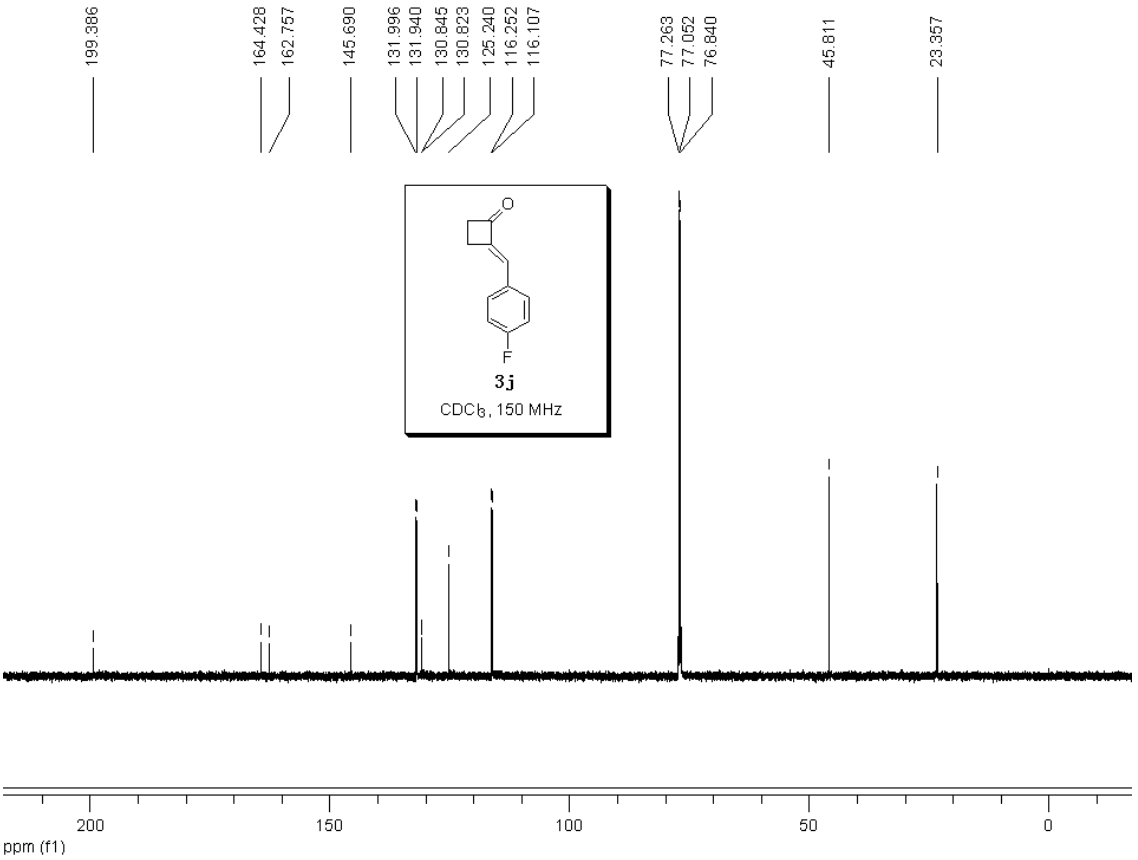
3.160
3.146
2.986
2.982
2.972
2.960
2.956
0.0000
O
F
3j
CDCl3, 600 MHz
2.02
1.04
1.01
2.00
2.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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130.823
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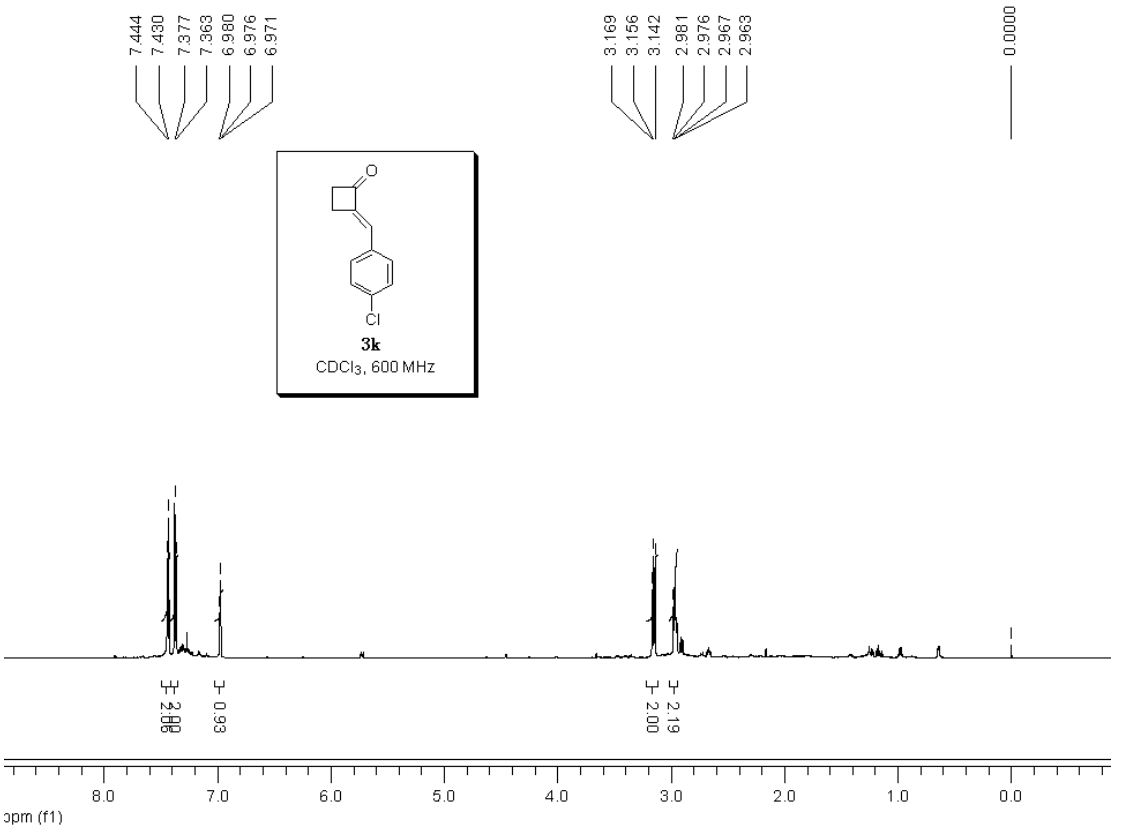
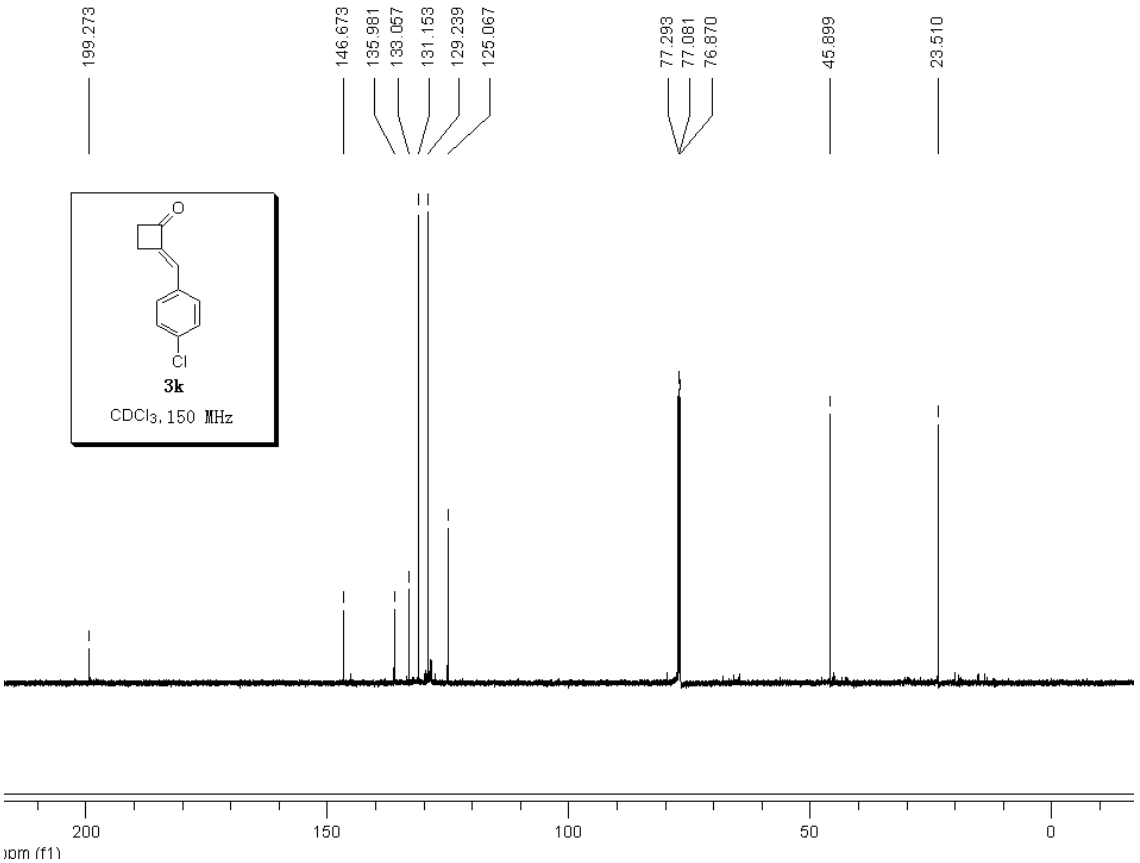
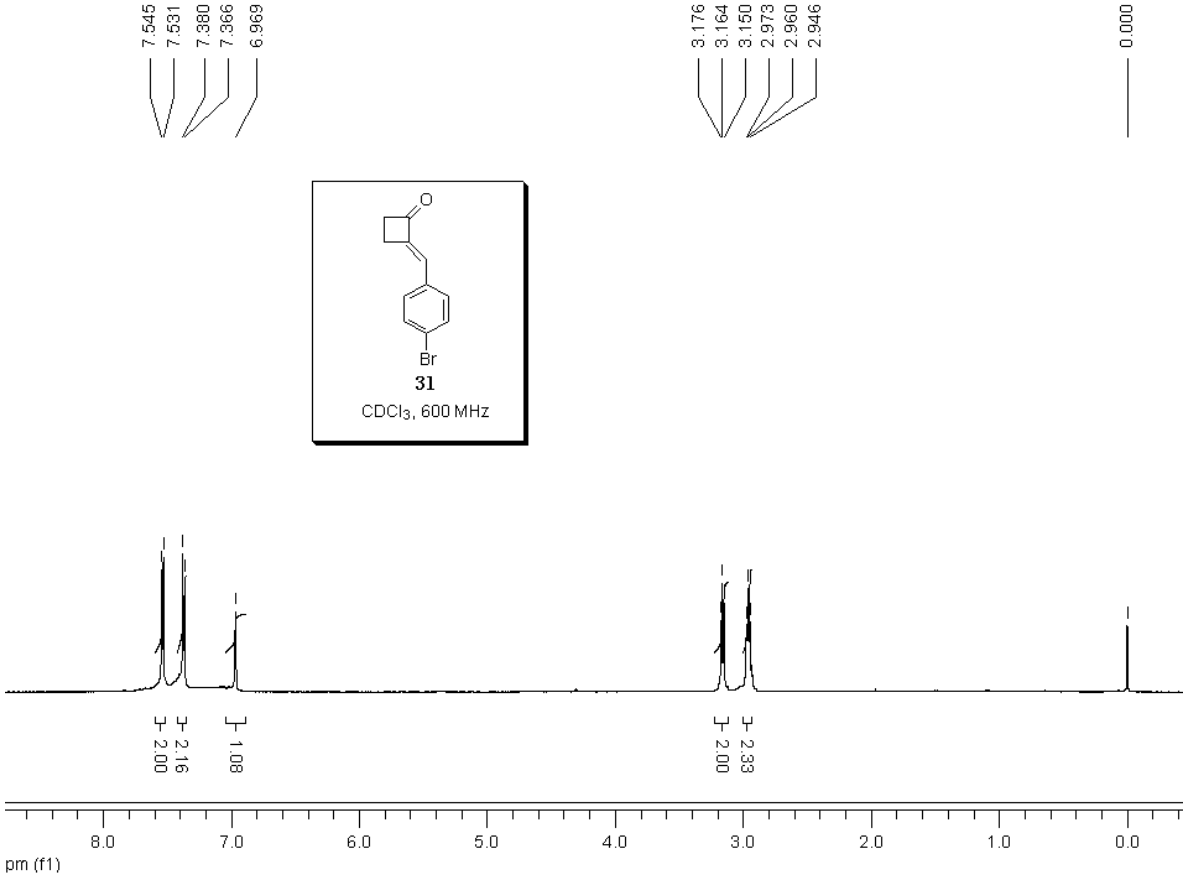
116.107
77.263
77.052
76.840
45.811
23.357
O
F
3j
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)



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Br
31
CDCl3, 600 MHz
2.00
2.16
1.08
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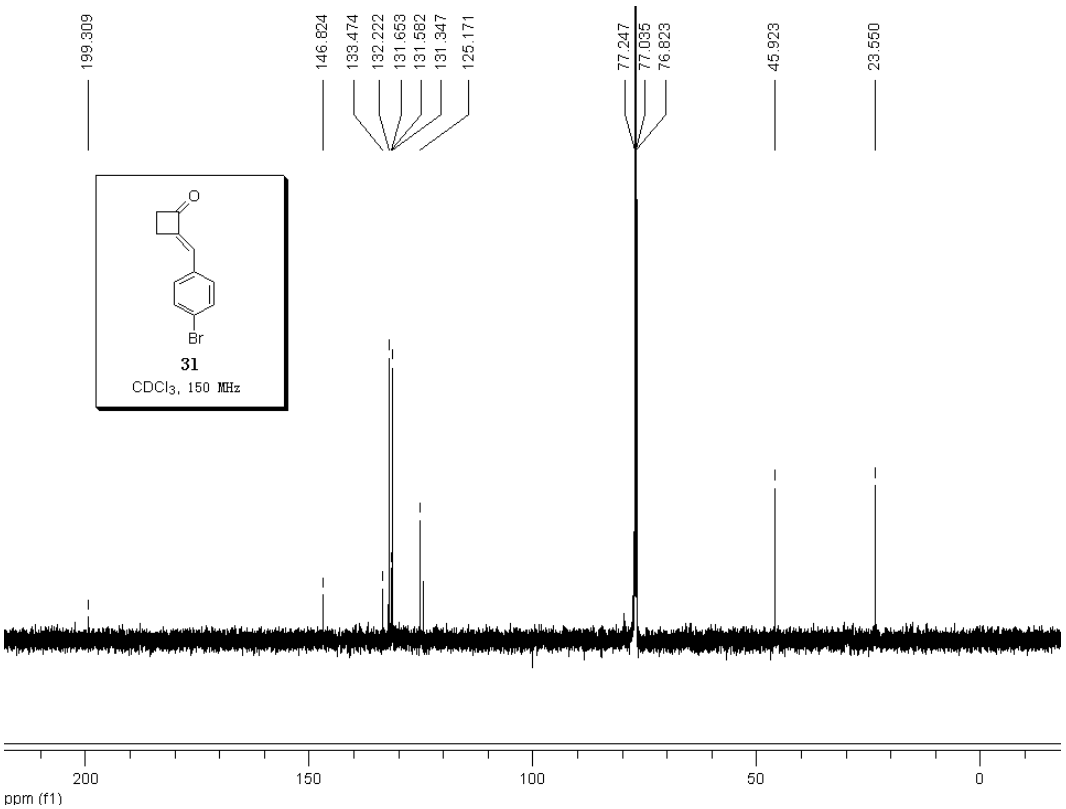
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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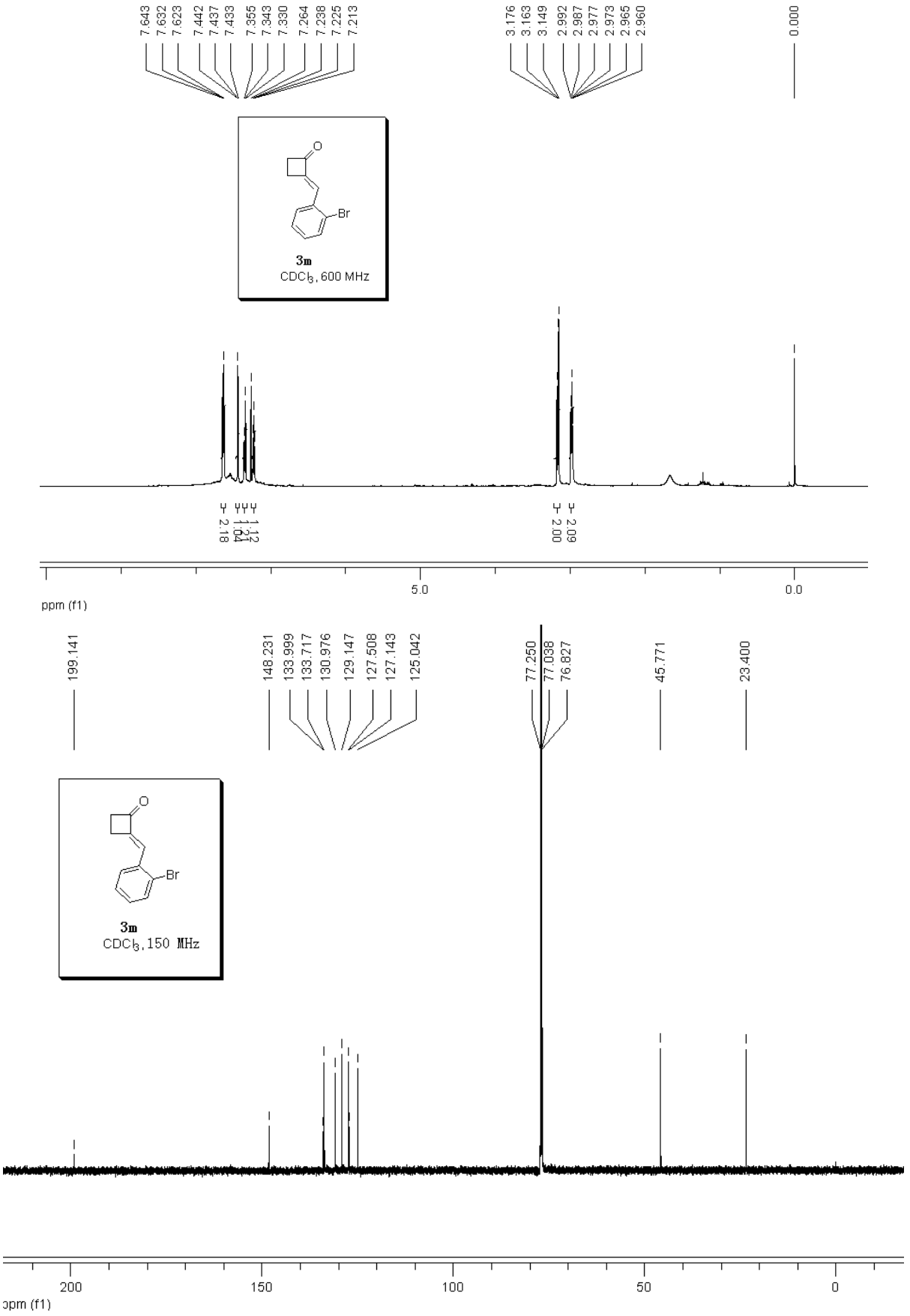
31
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)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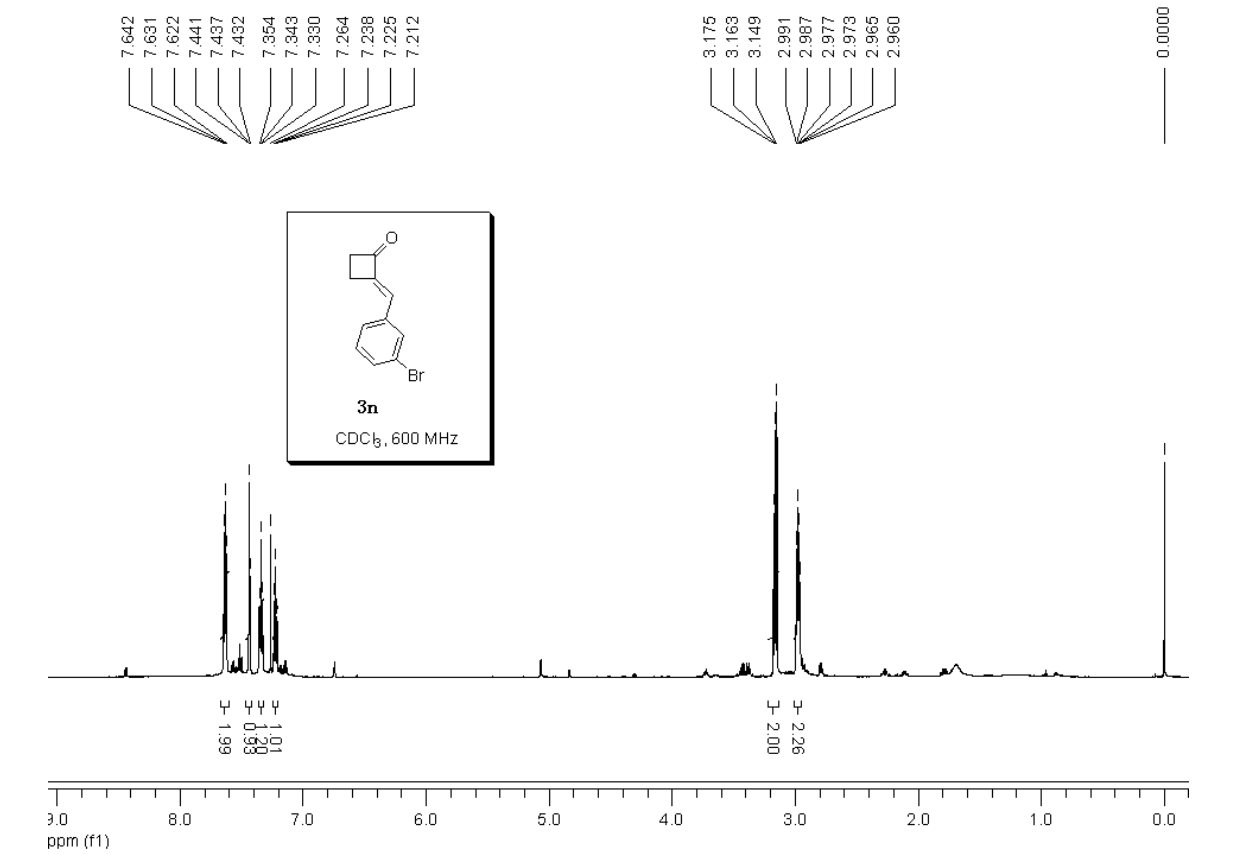
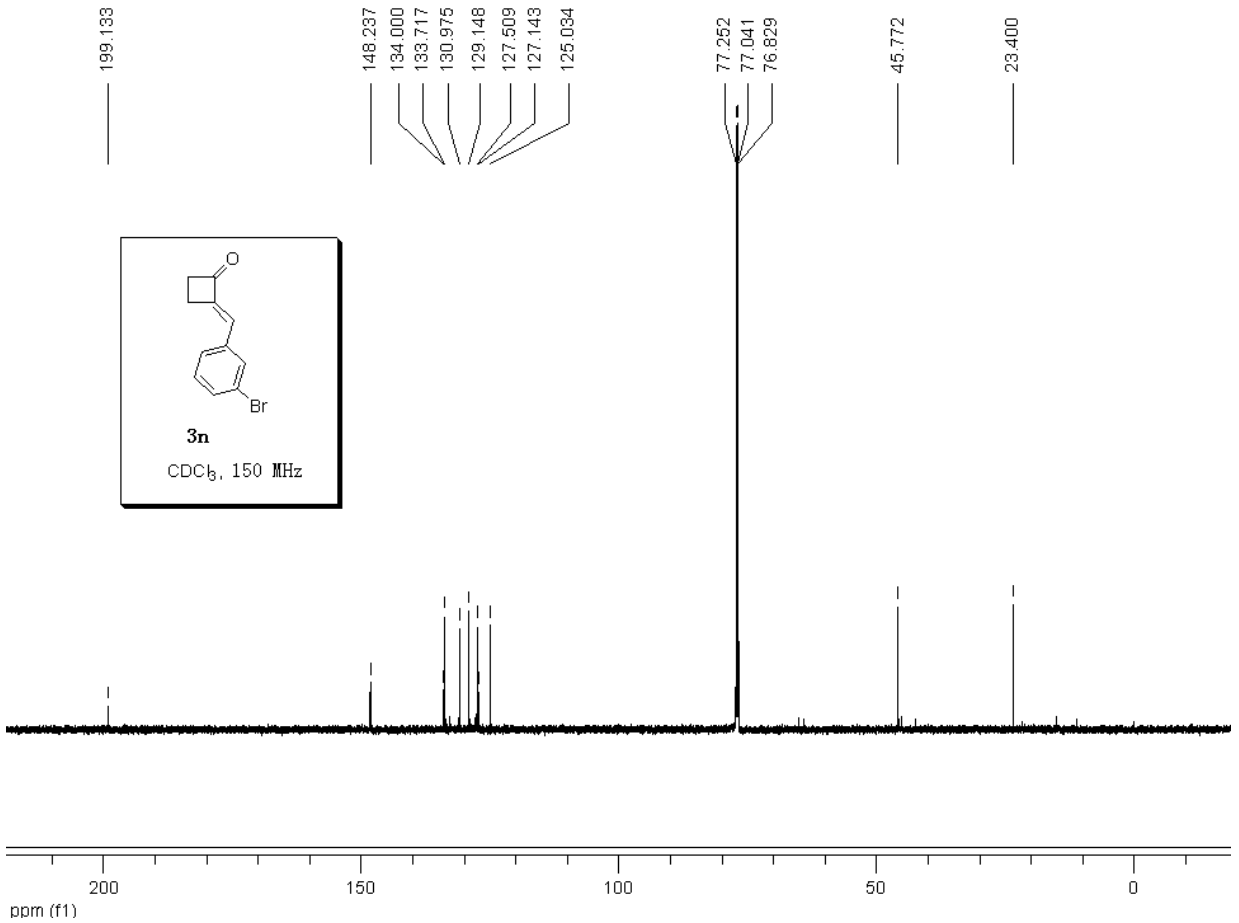
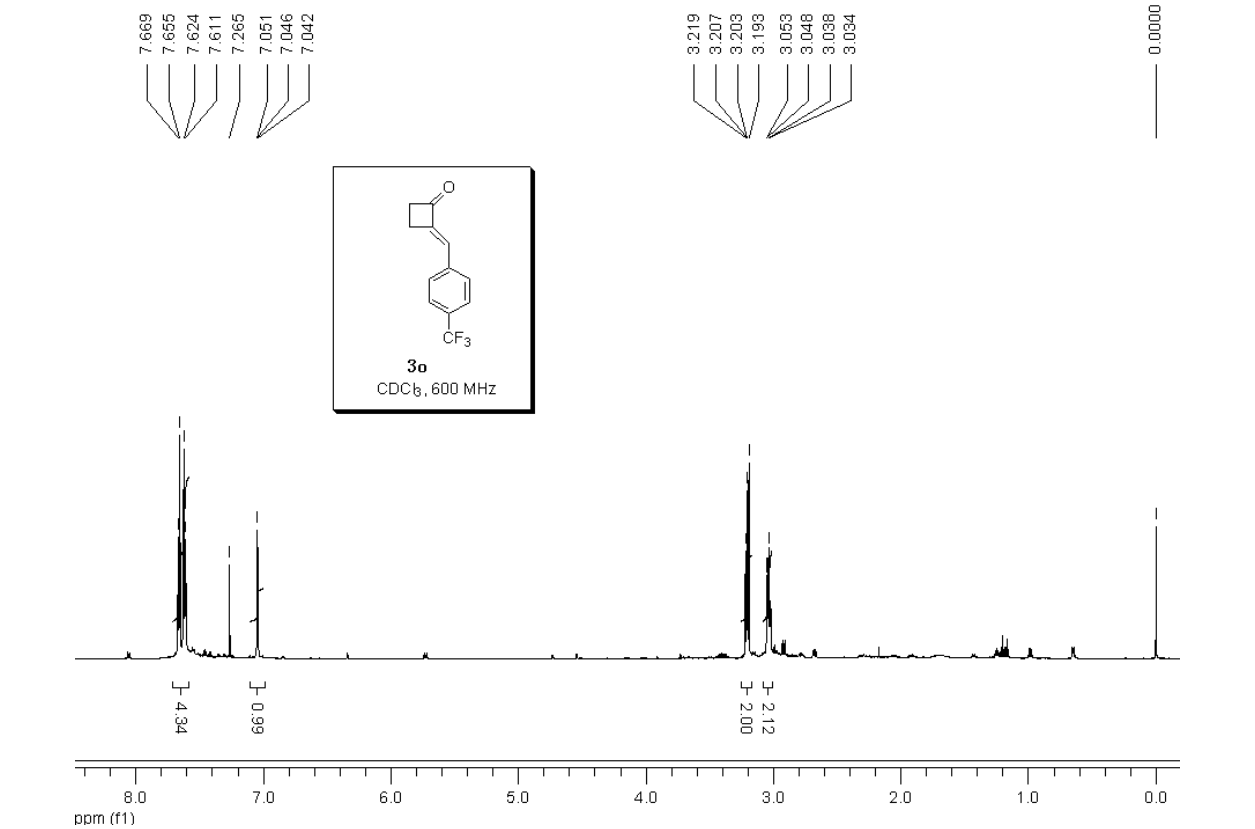
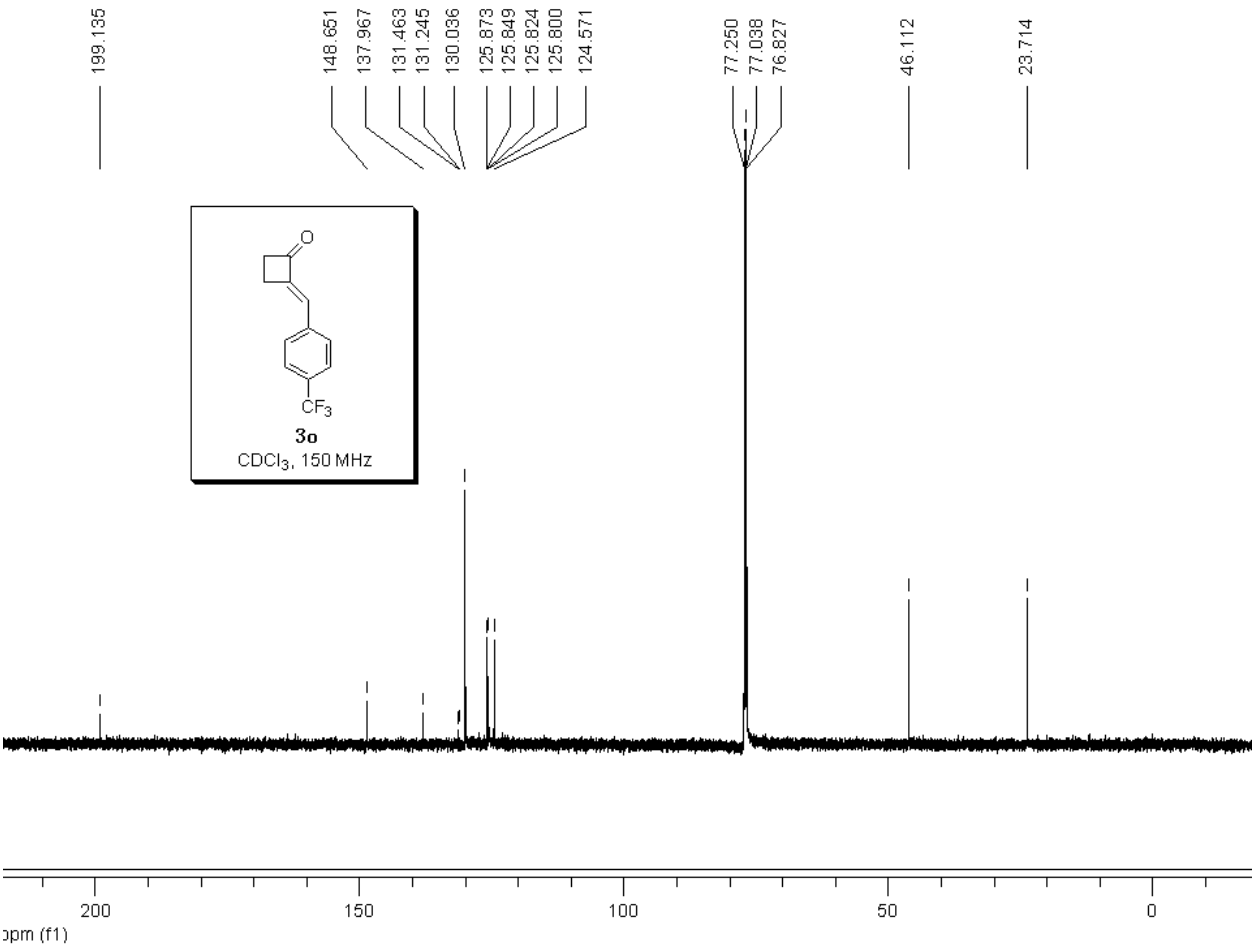
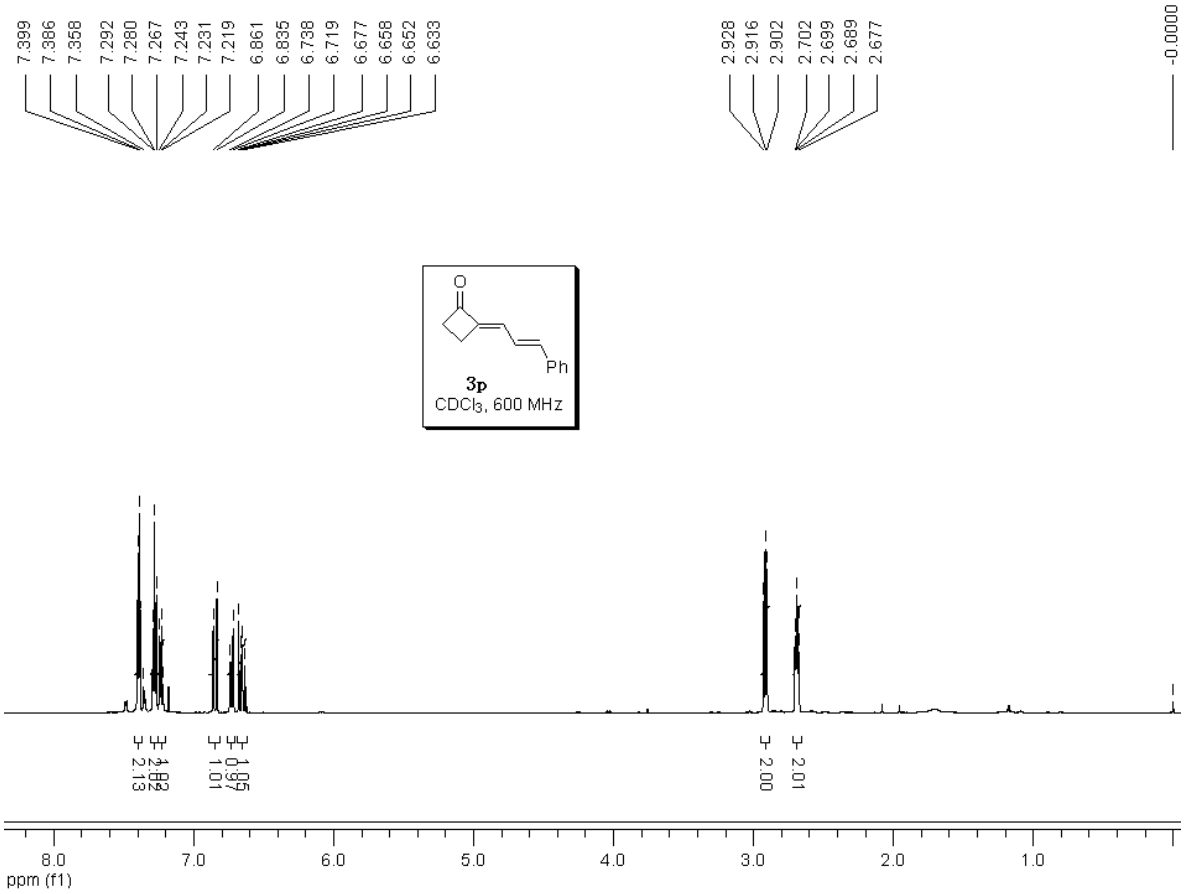
7.213
3.176
3.163
3.149
2.992
2.987
2.977
2.973
2.965
2.960
0.000
O
Br
3m
CDCl3, 600 MHz
2.18
1.04
1.12
2.00
2.09
5.0
0.0
ppm (f1)
199.141
148.231
133.999
133.717
130.976
129.147
127.508
127.143
125.042
77.250
77.038
76.827
45.771
23.400
O
Br
3m
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)

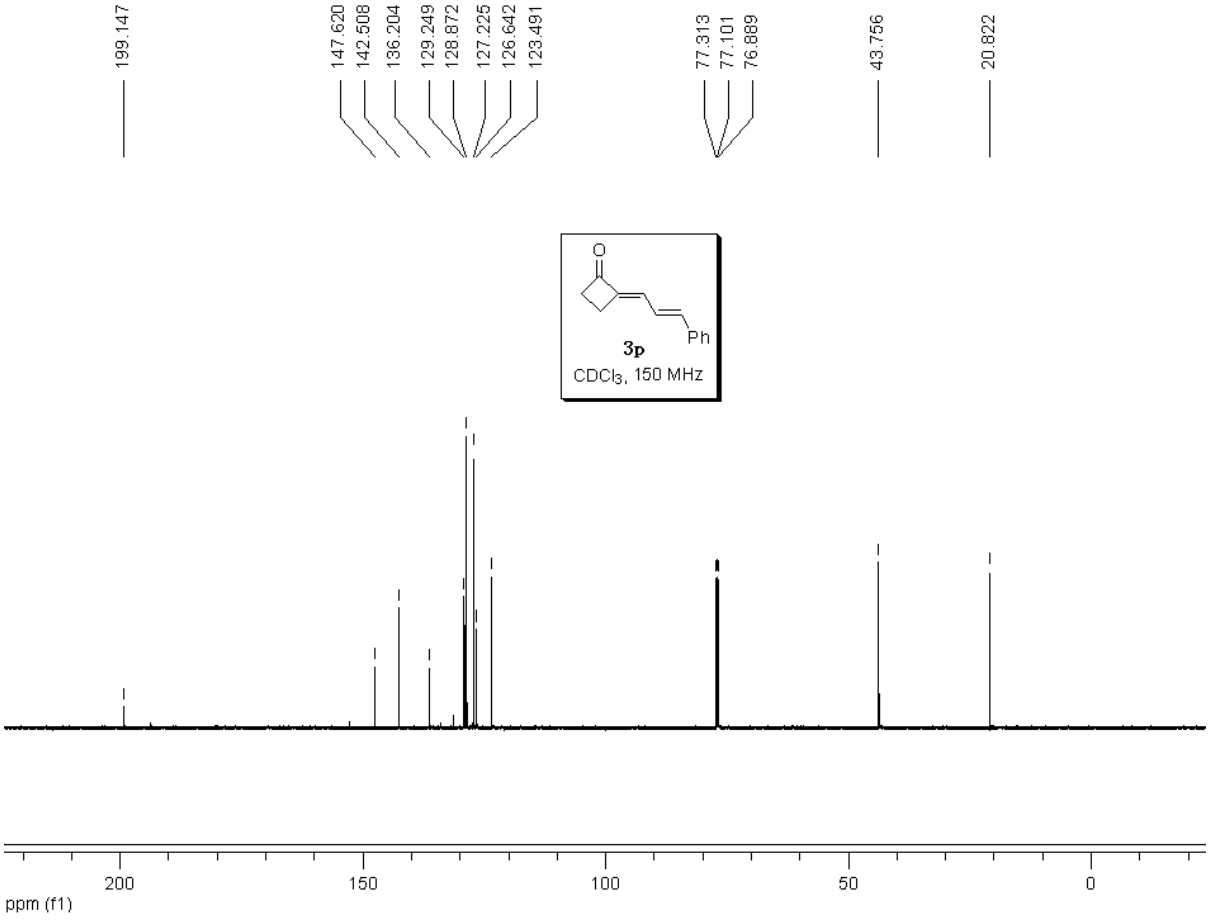


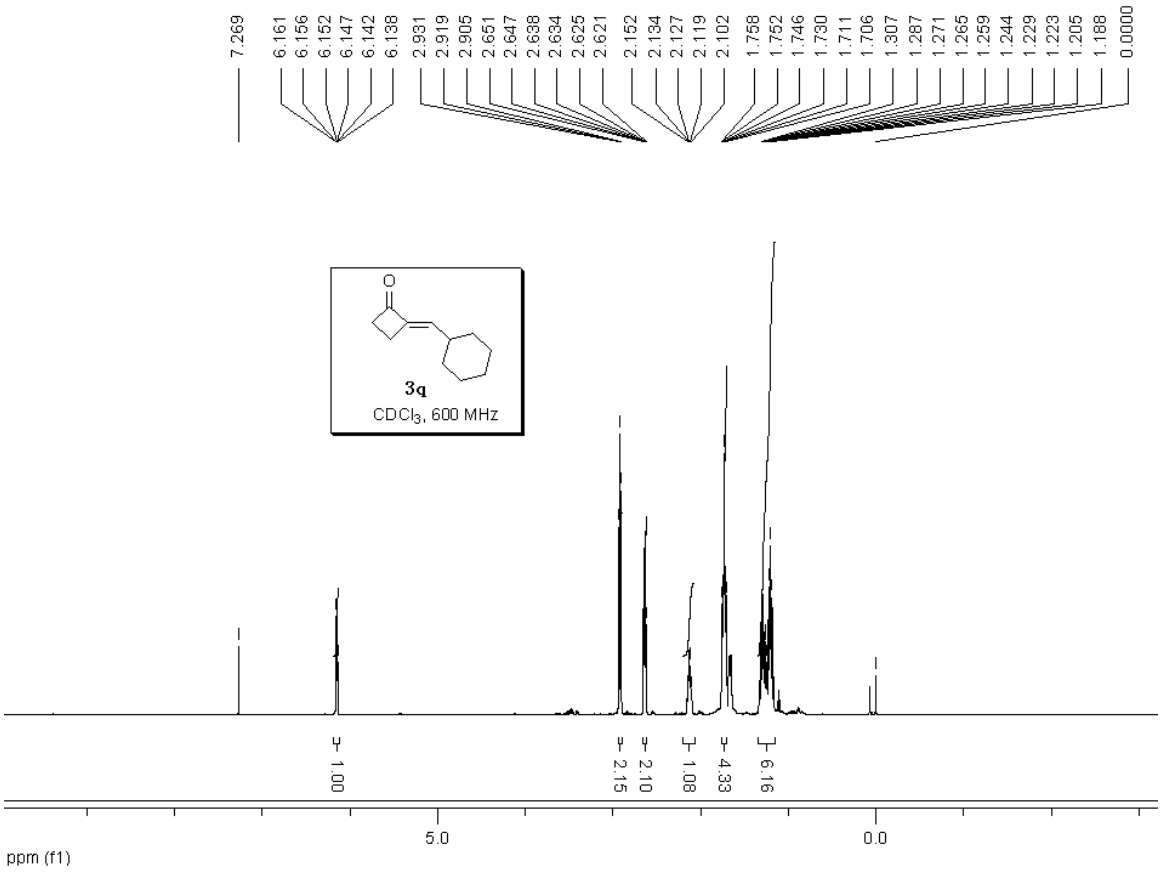


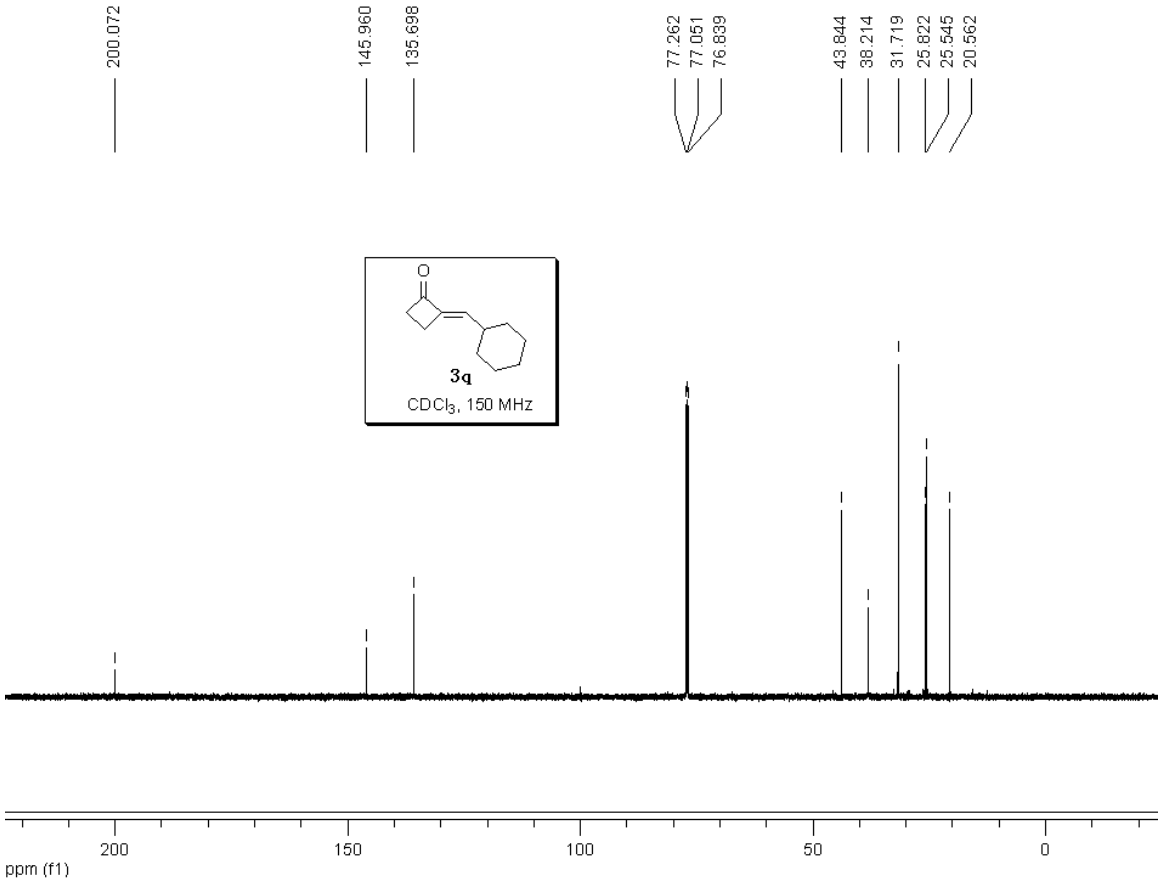


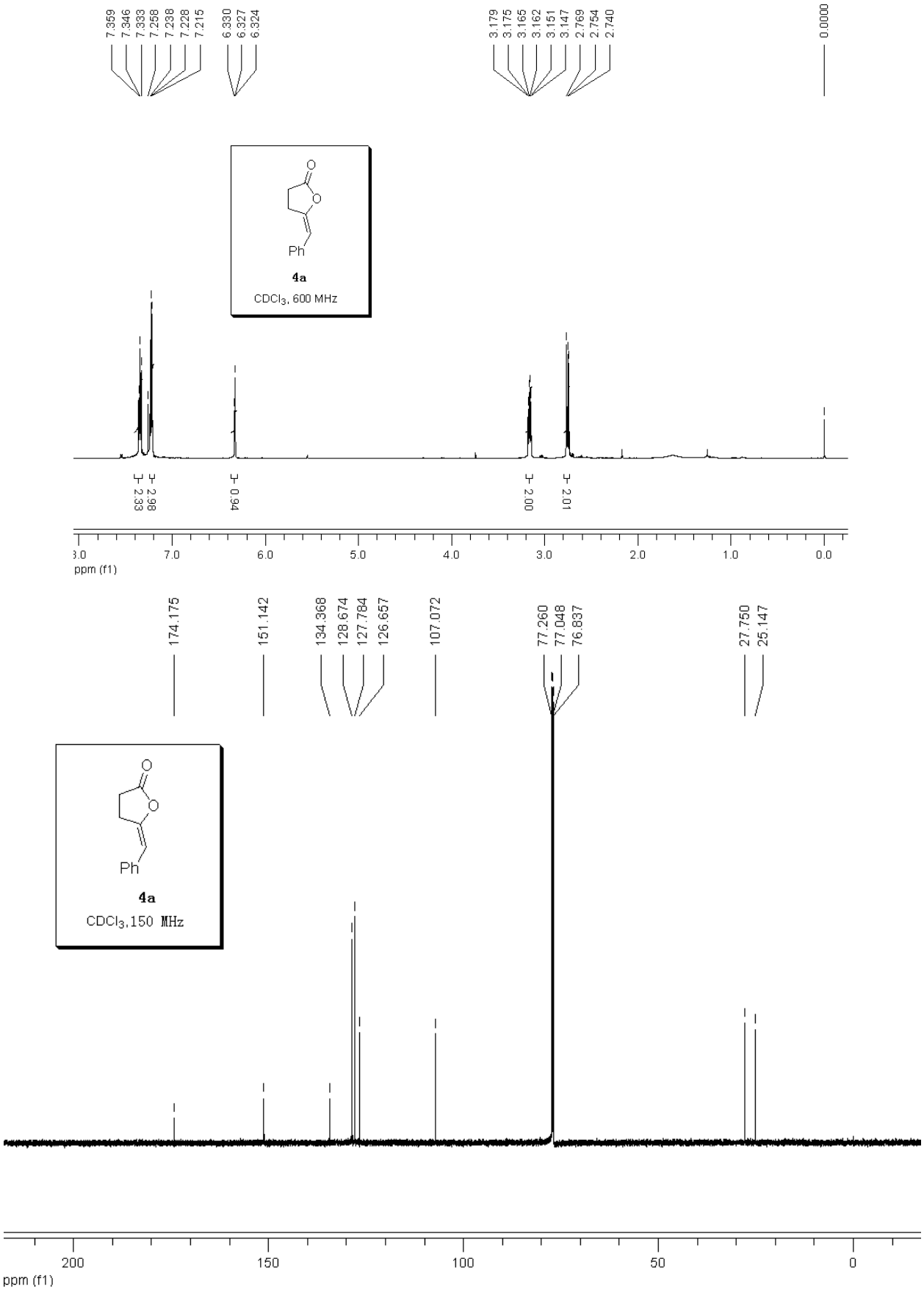


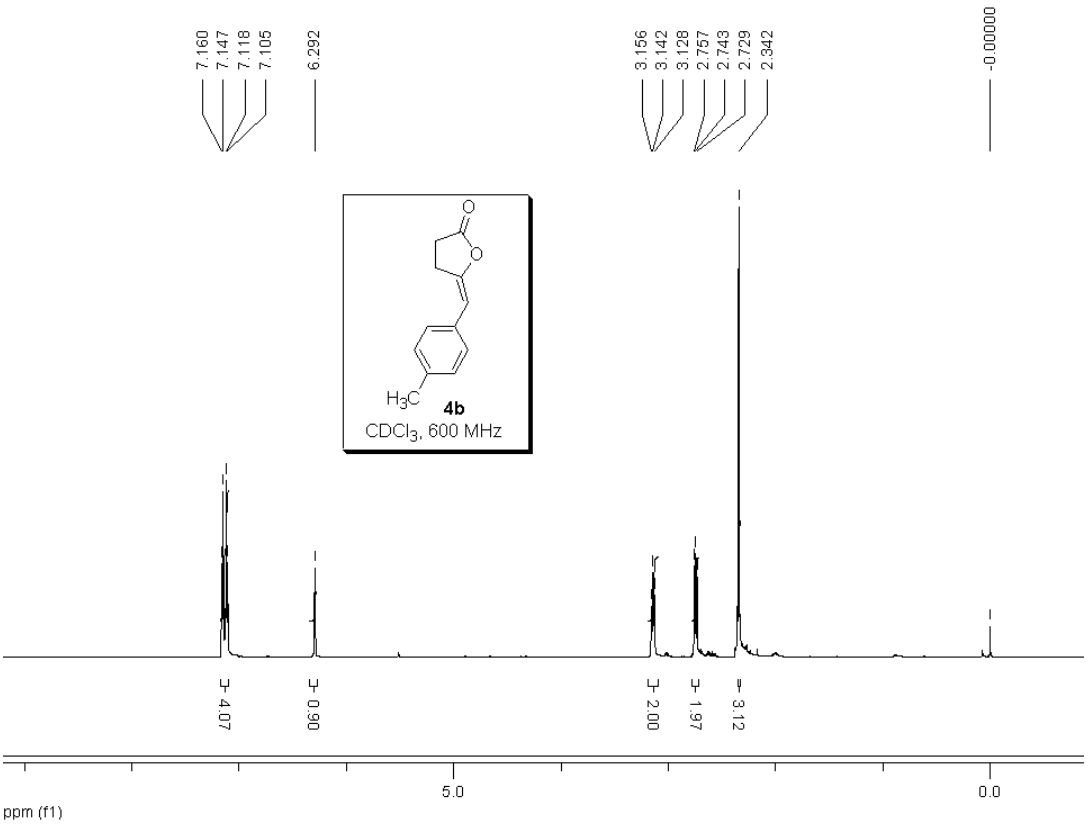


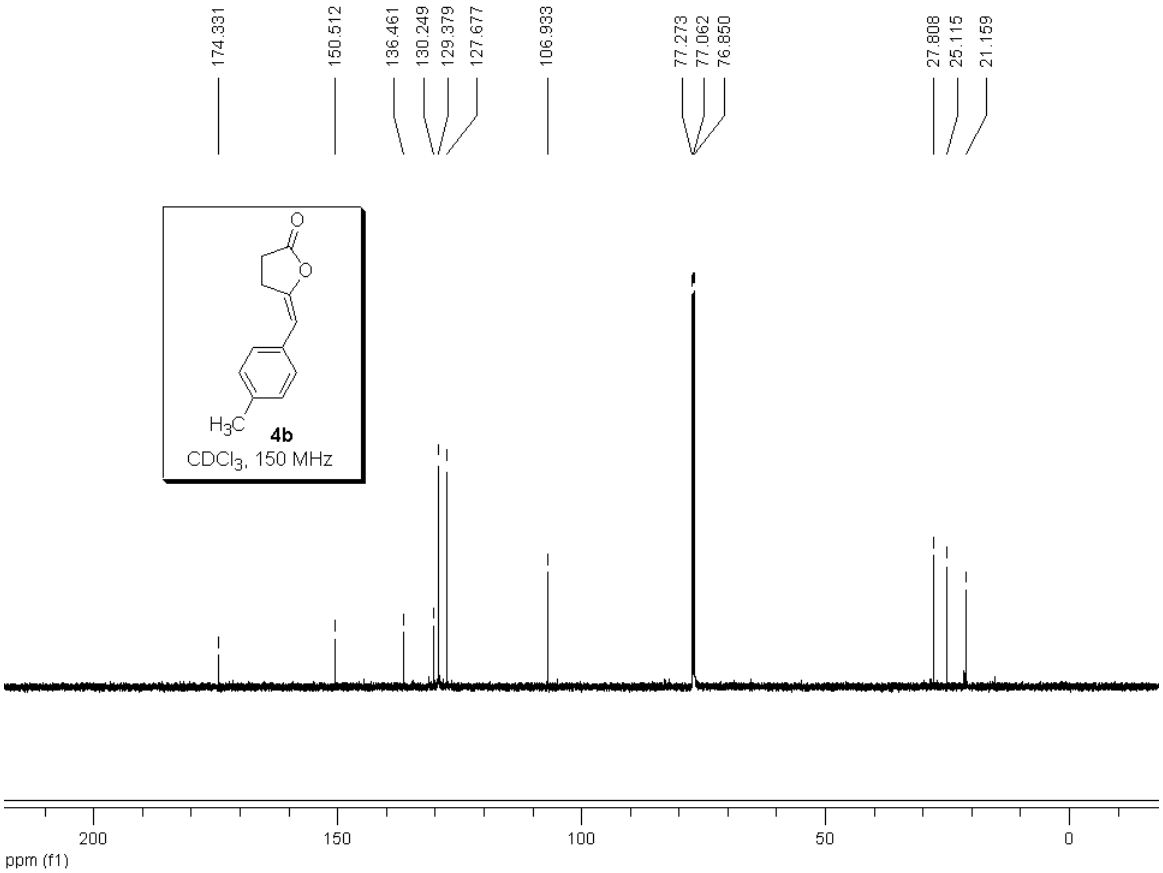


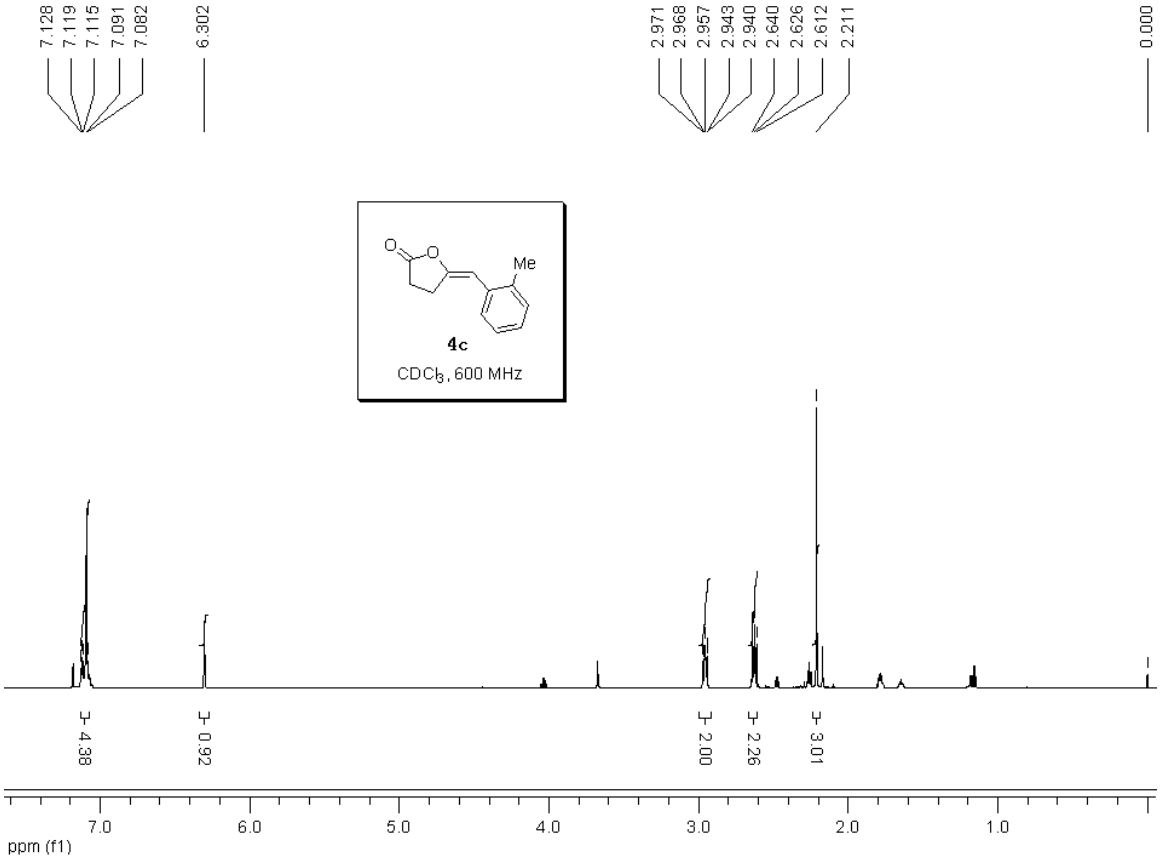


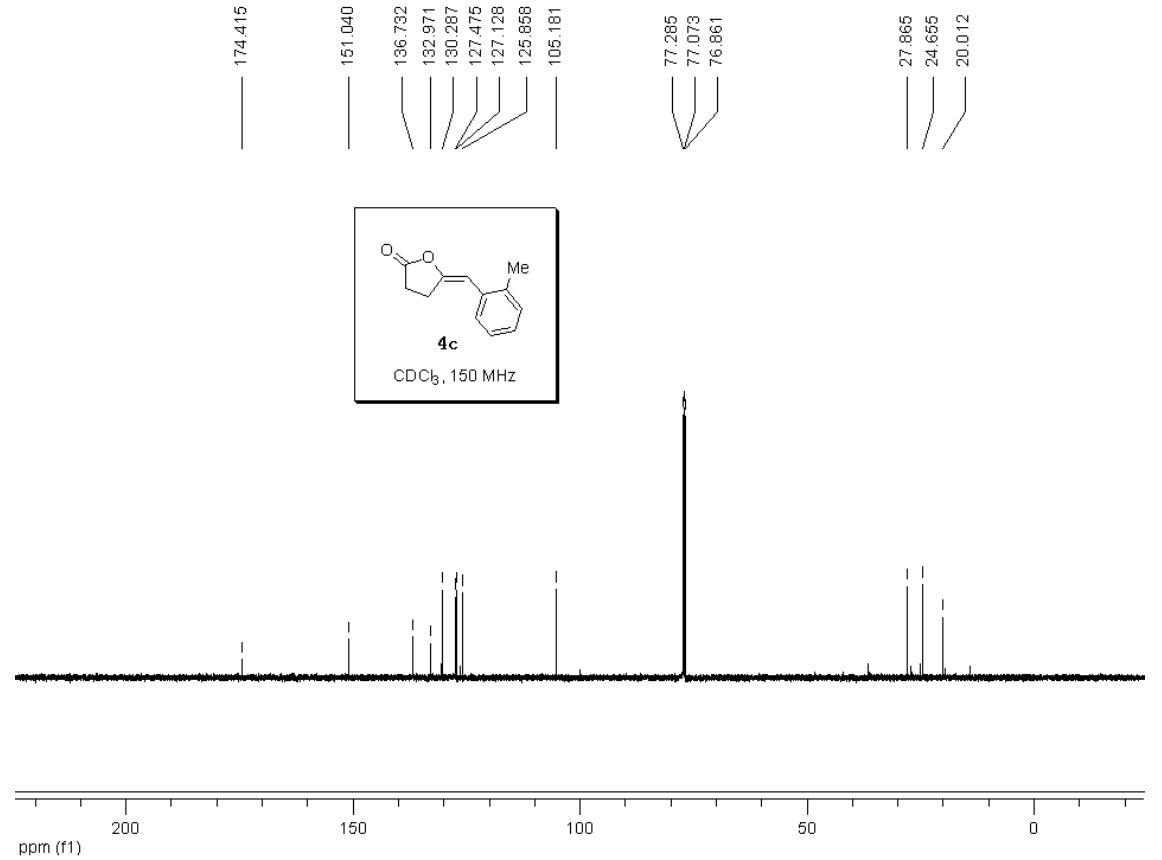


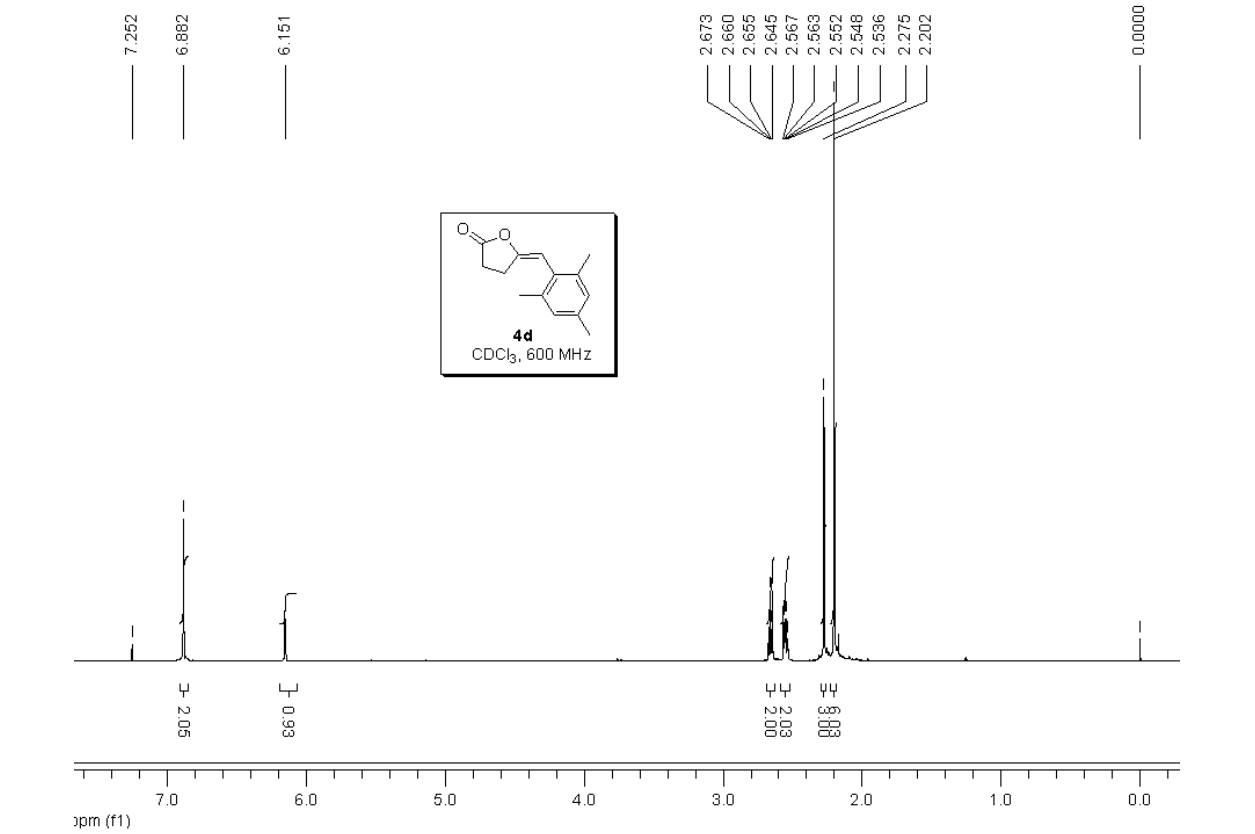

7.359
7.346
7.333
7.258
7.238
7.226
7.215
6.330
6.327
6.324
3.179
3.175
3.165
3.162
3.151
3.147
2.769
2.754
2.740
0.0000
Ph
4a
CDCl3, 600 MHz
2.33
2.98
0.94
2.00
2.01
ppm (f1)
174.175
151.142
134.368
128.674
127.784
126.657
107.072
77.260
77.048
76.837
27.750
25.147
Ph
4a
CDCl3,150 MHz
ppm (f1)

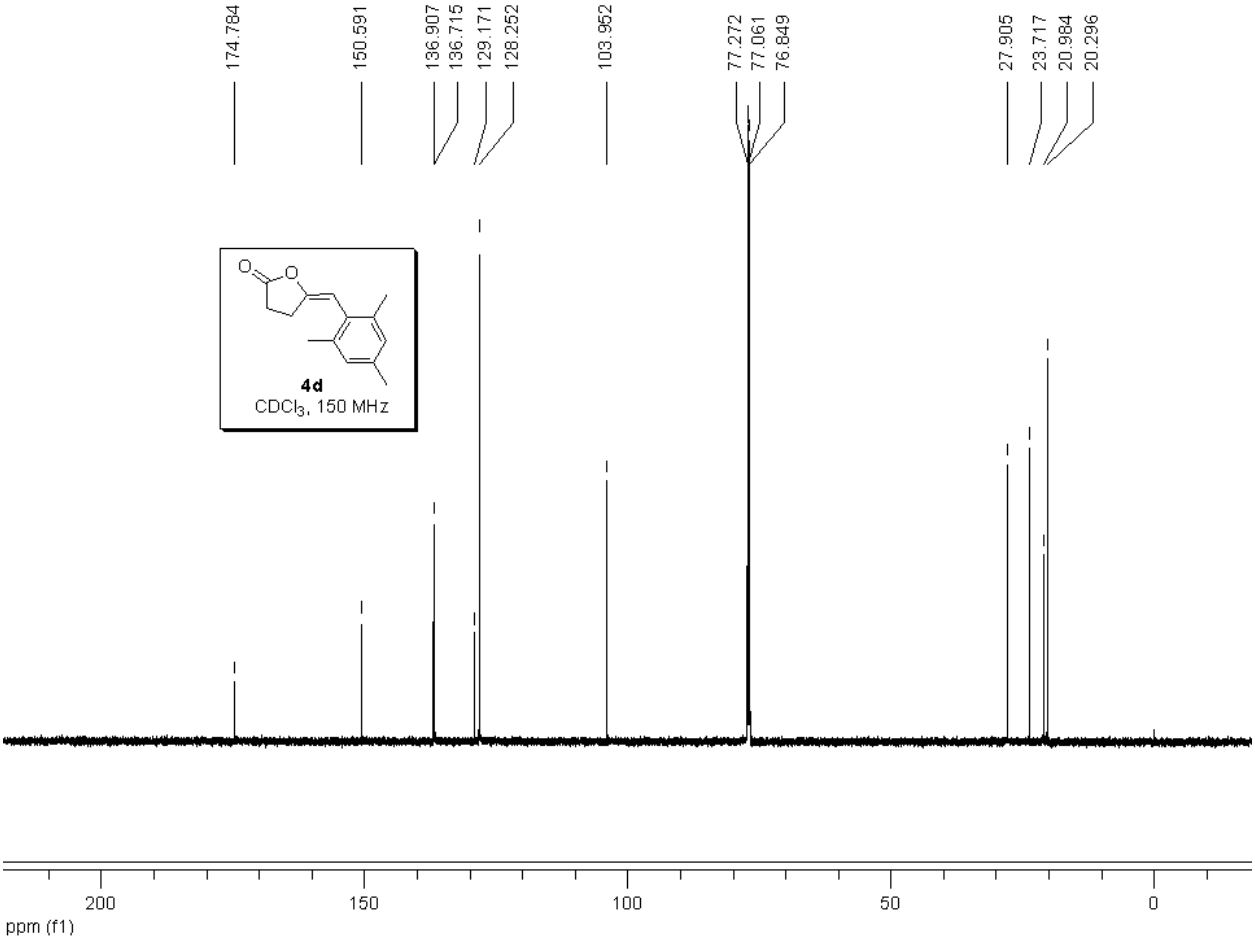


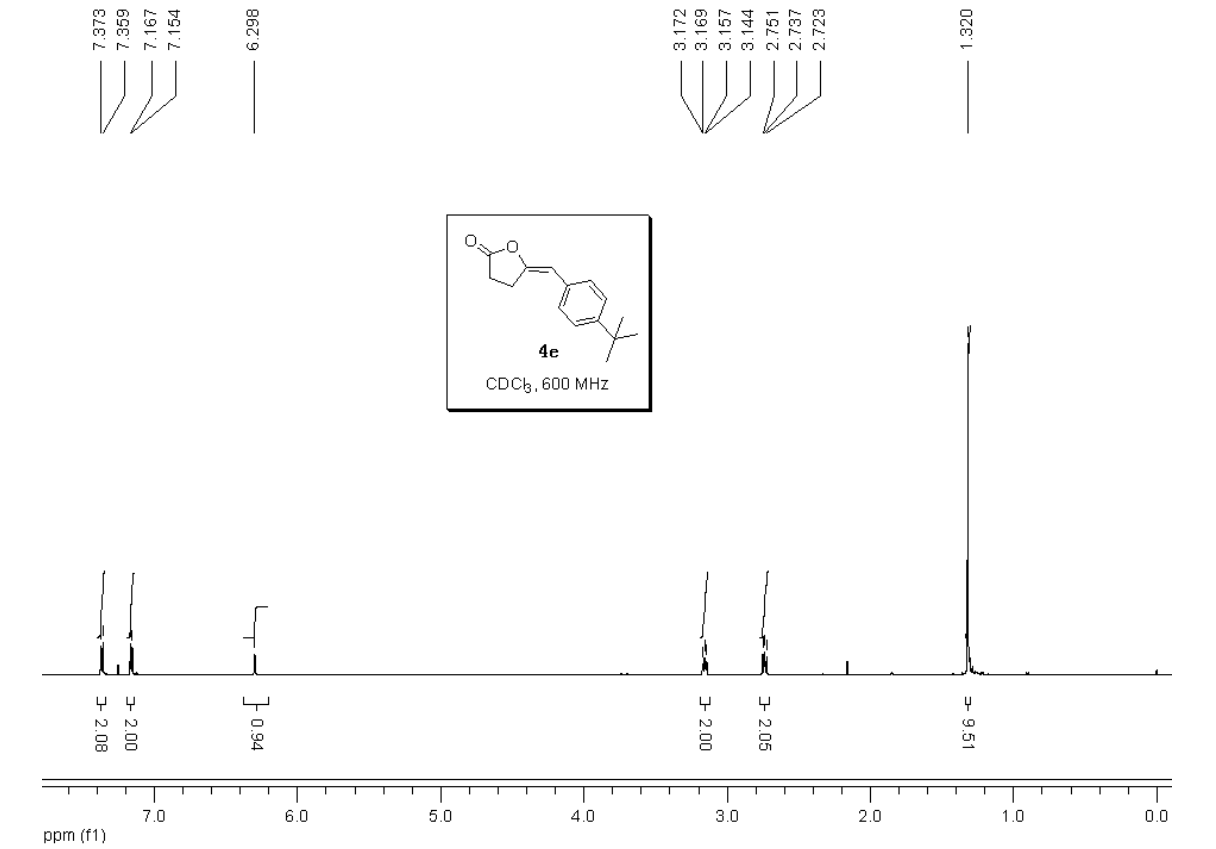


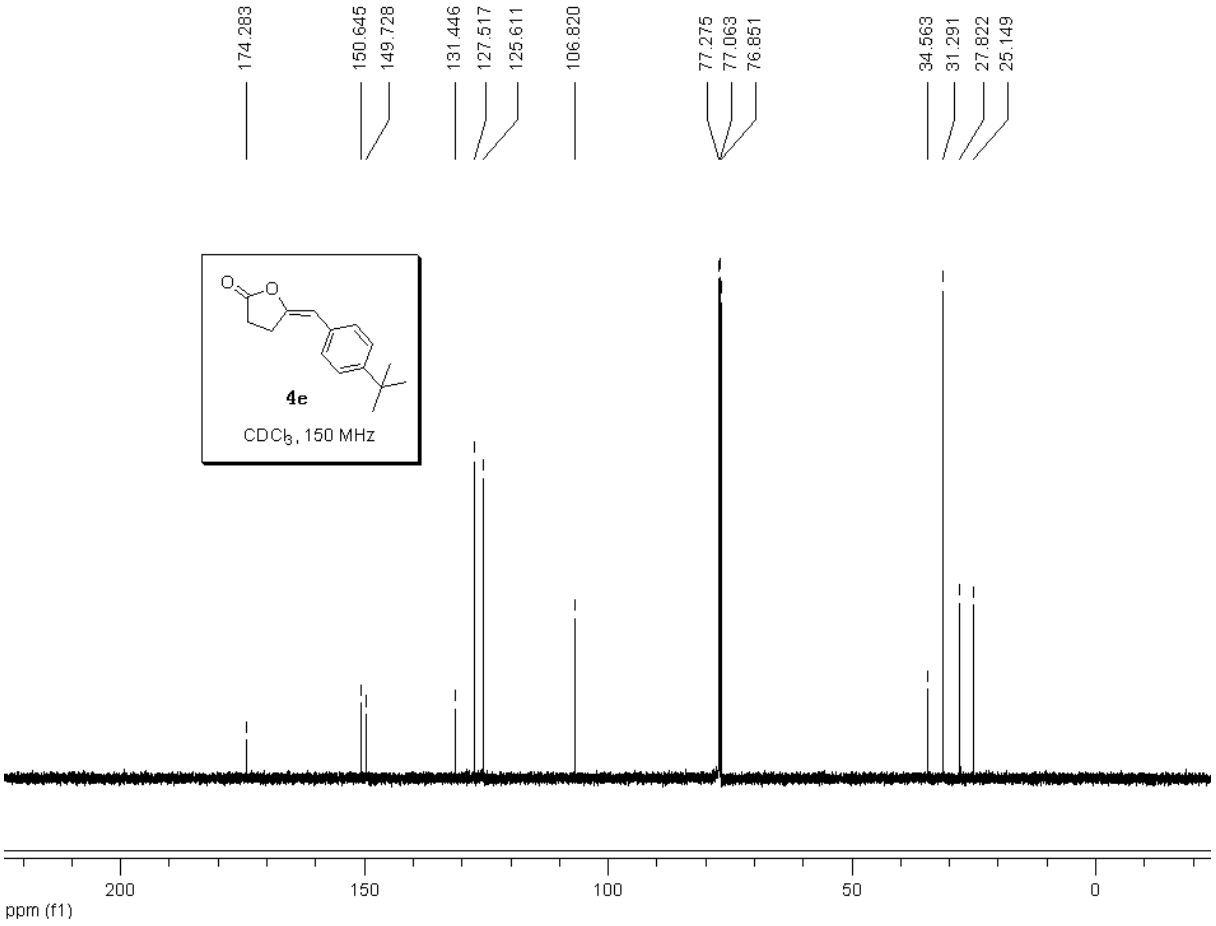

7.128
7.119
7.115
7.091
7.082
6.302
2.971
2.968
2.957
2.943
2.940
2.640
2.626
2.612
2.211
0.000
Me
4c
CDCl3, 600 MHz
4.38
0.92
2.00
2.26
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

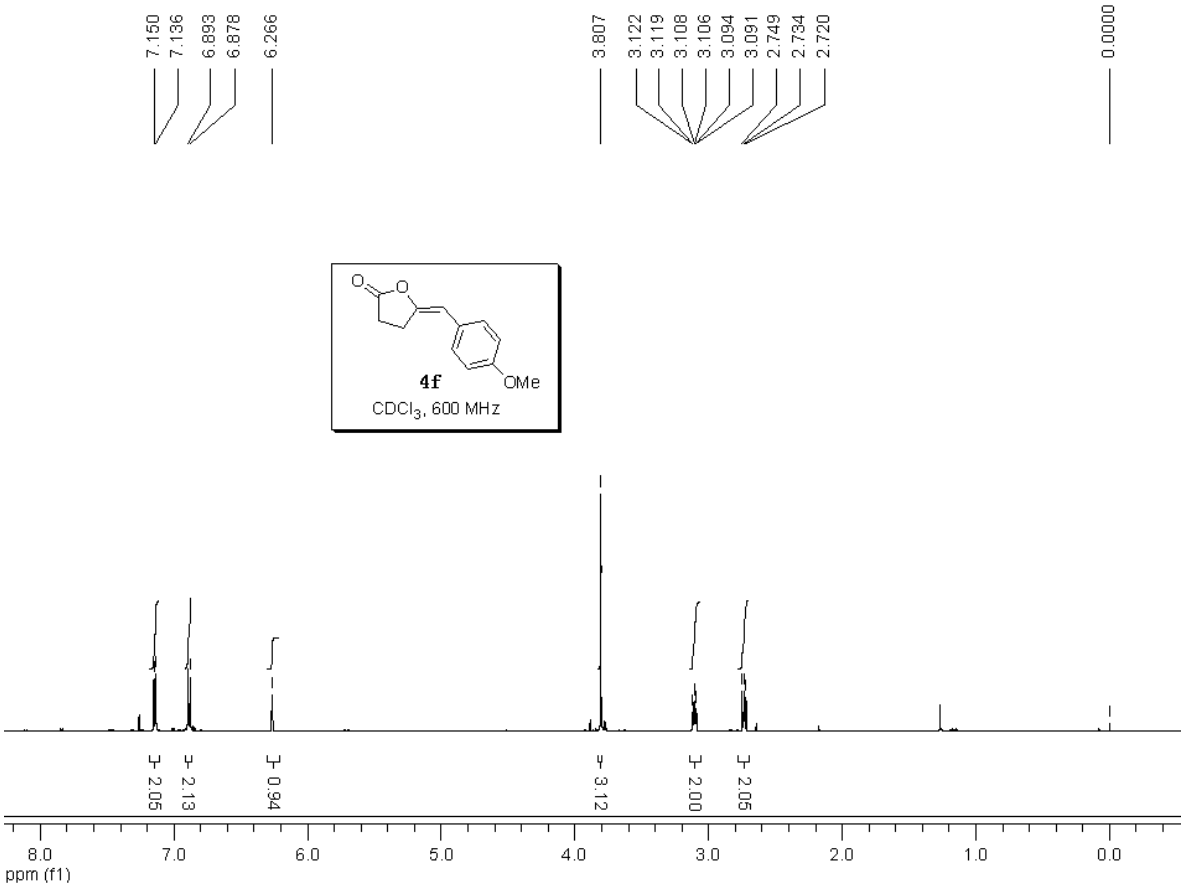

174.415
151.040
136.732
132.971
130.287
127.475
127.128
125.858
105.181
77.285
77.073
76.861
27.865
24.655
20.012
Me
4c
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)

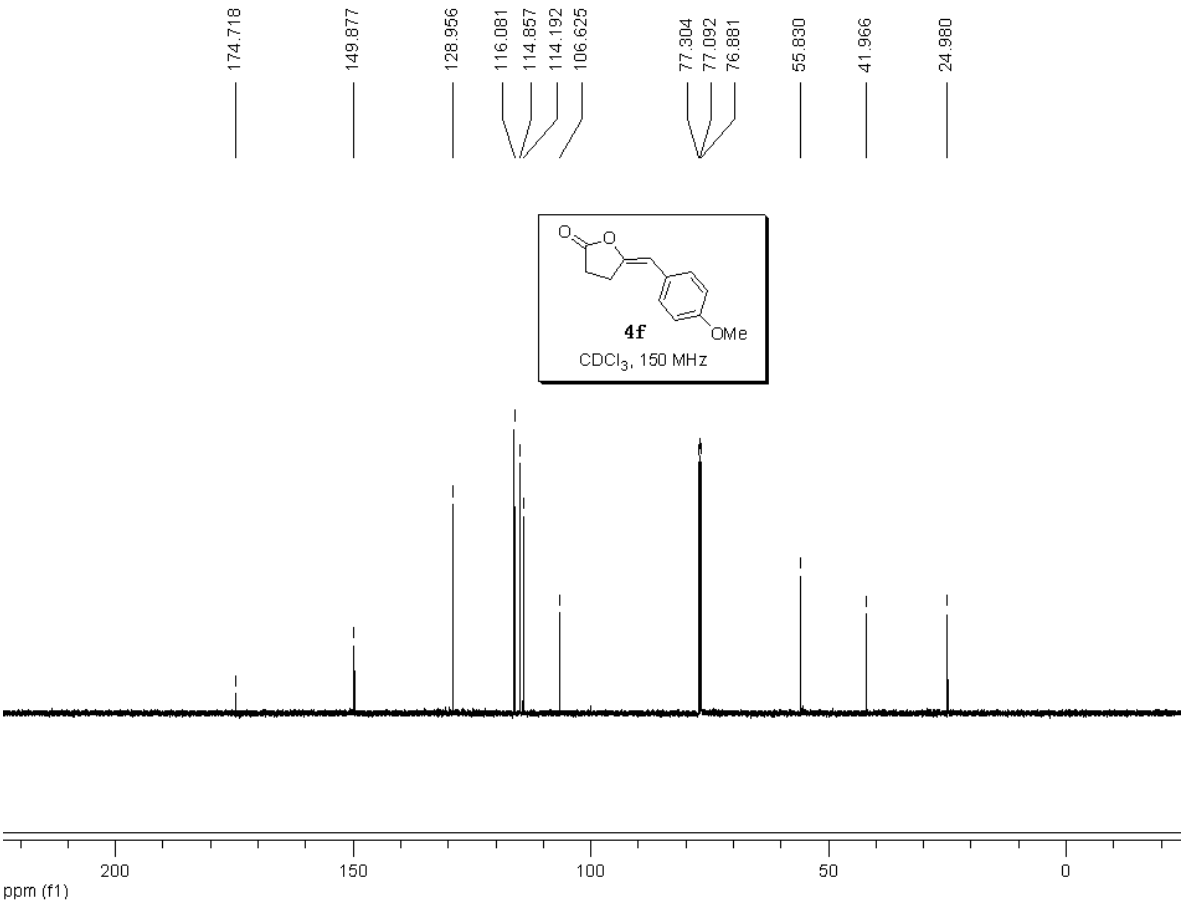


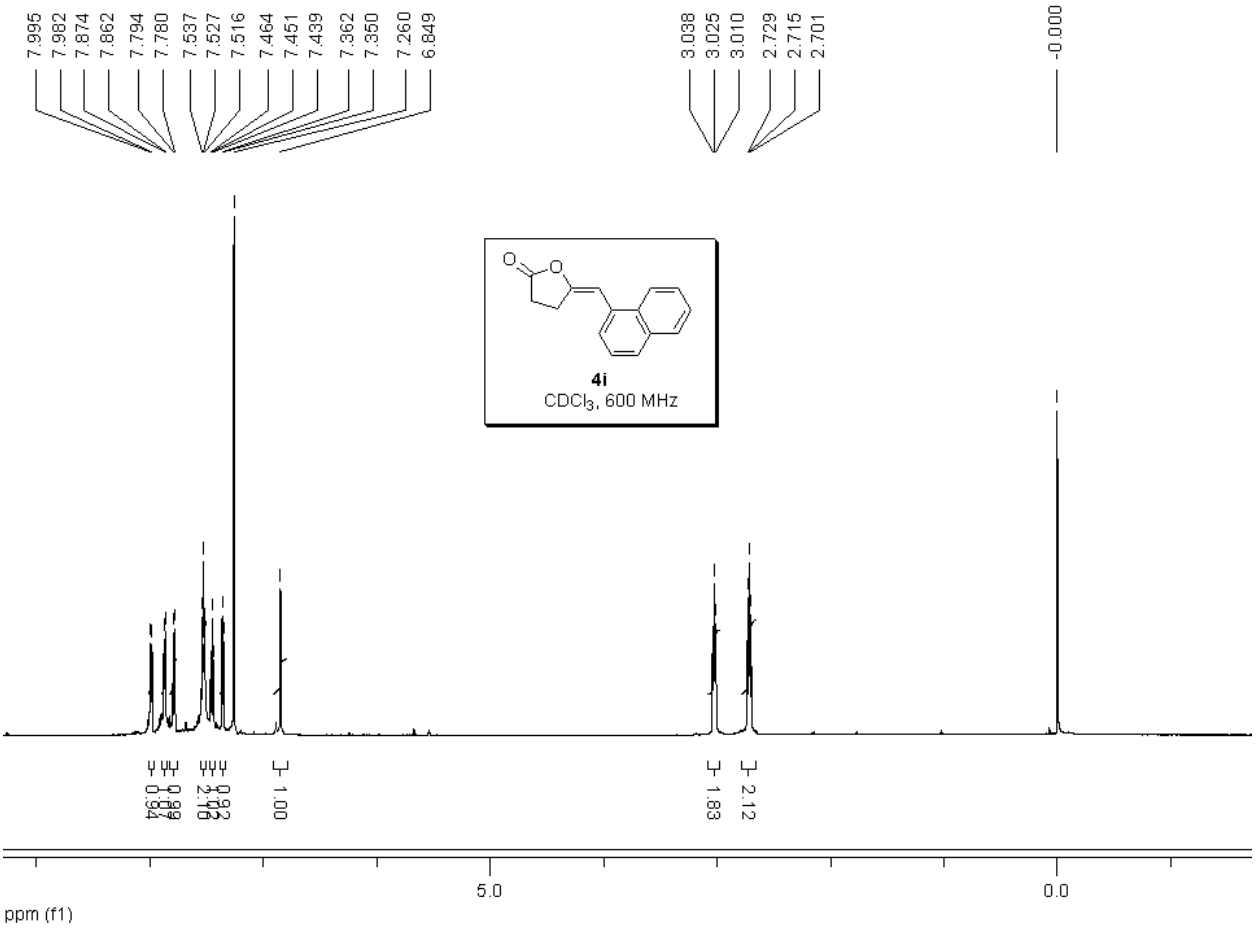


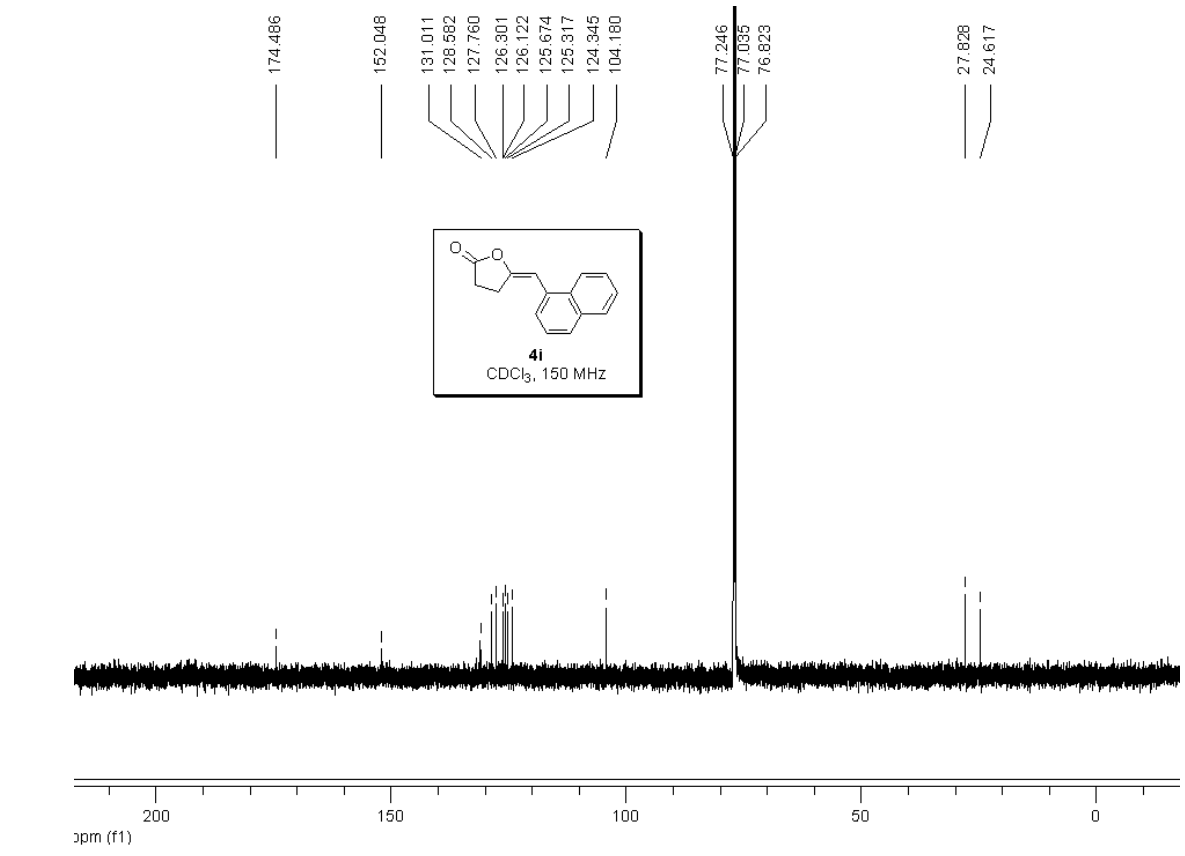


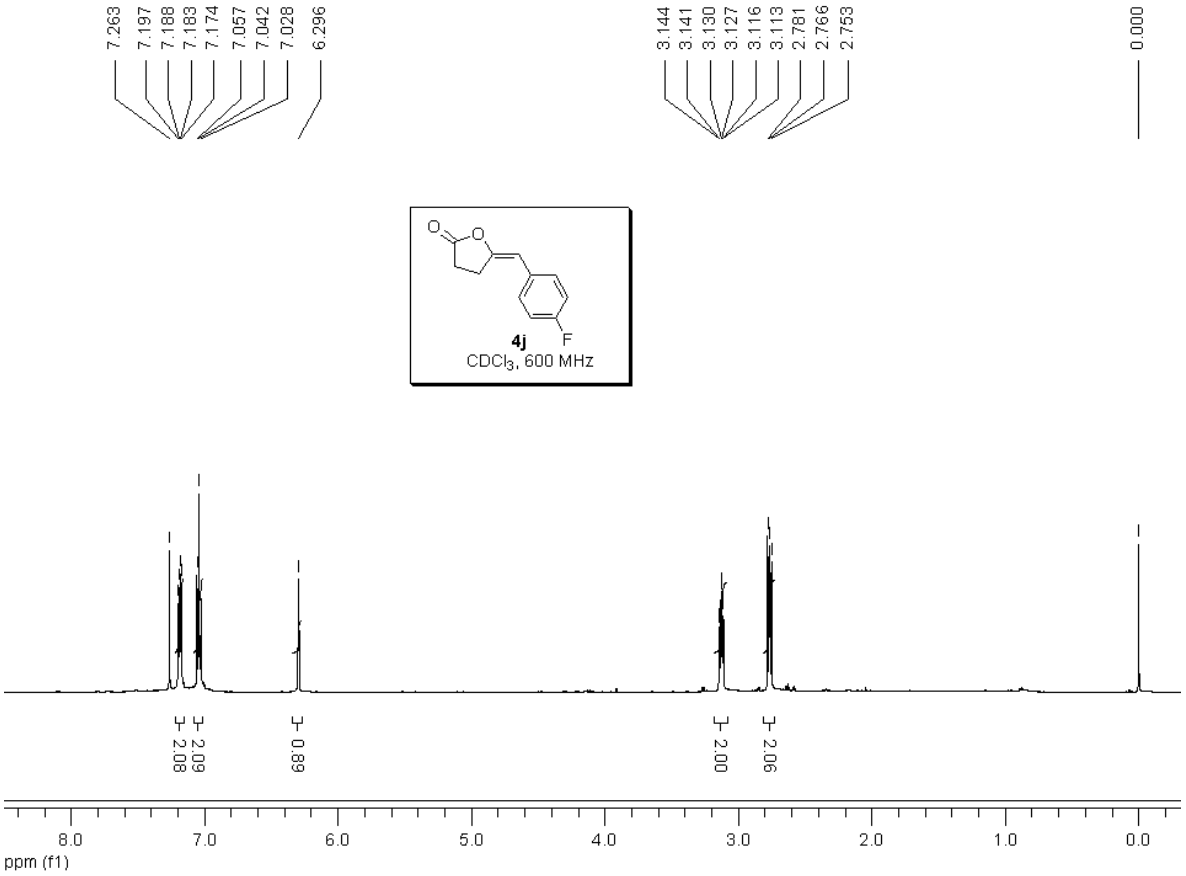


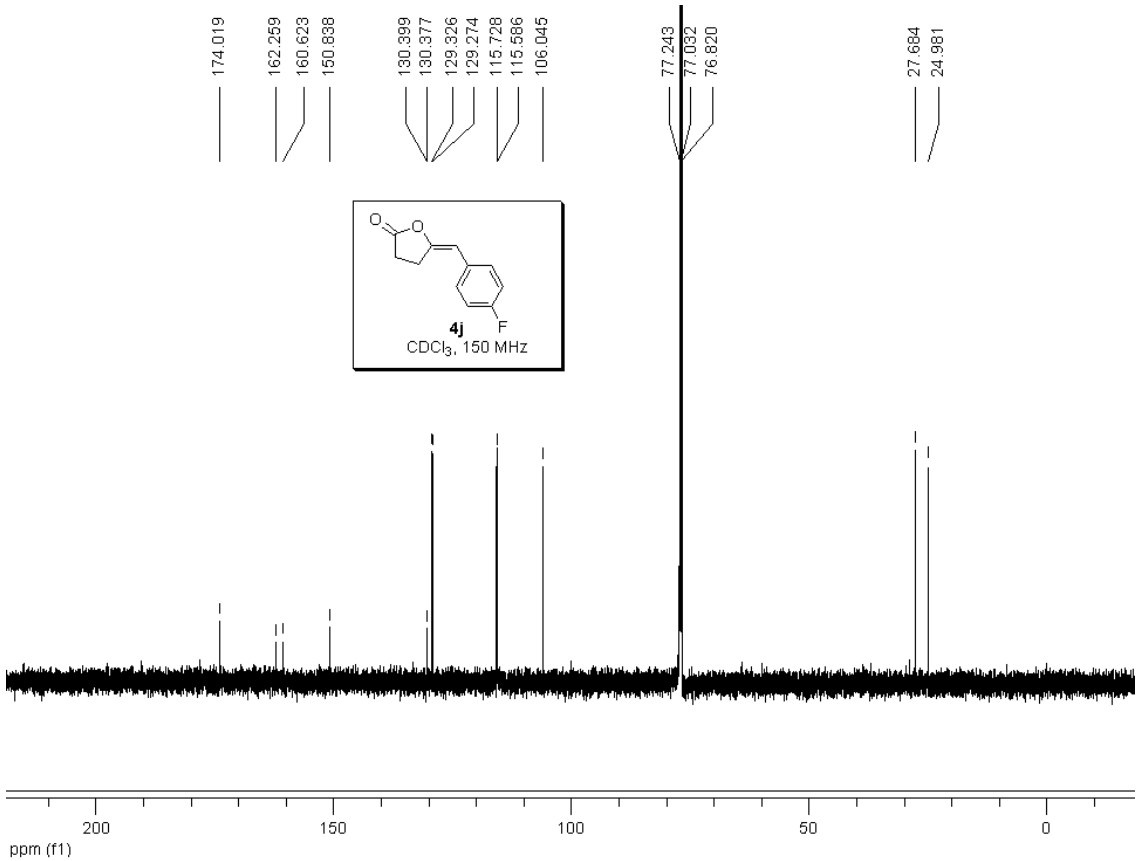

7.150
7.136
6.893
6.878
6.266
3.807
3.122
3.119
3.108
3.106
3.094
3.091
2.749
2.734
2.720
0.0000
4f
OMe
CDCl3, 600 MHz
2.05
2.13
0.94
3.12
2.00
2.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

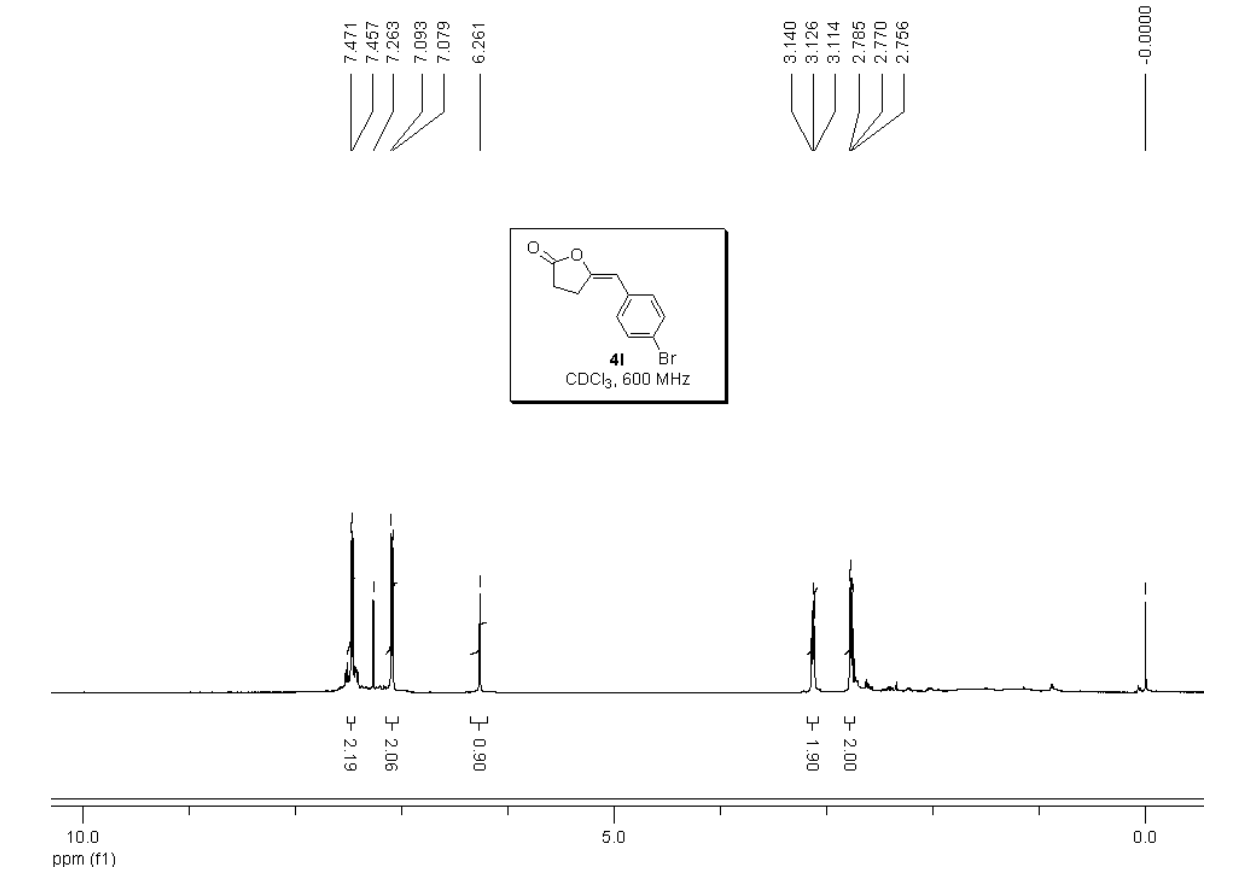

174.718
149.877
128.956
116.081
114.857
114.192
106.625
77.304
77.092
76.881
55.830
41.966
24.980
4f
OMe
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)

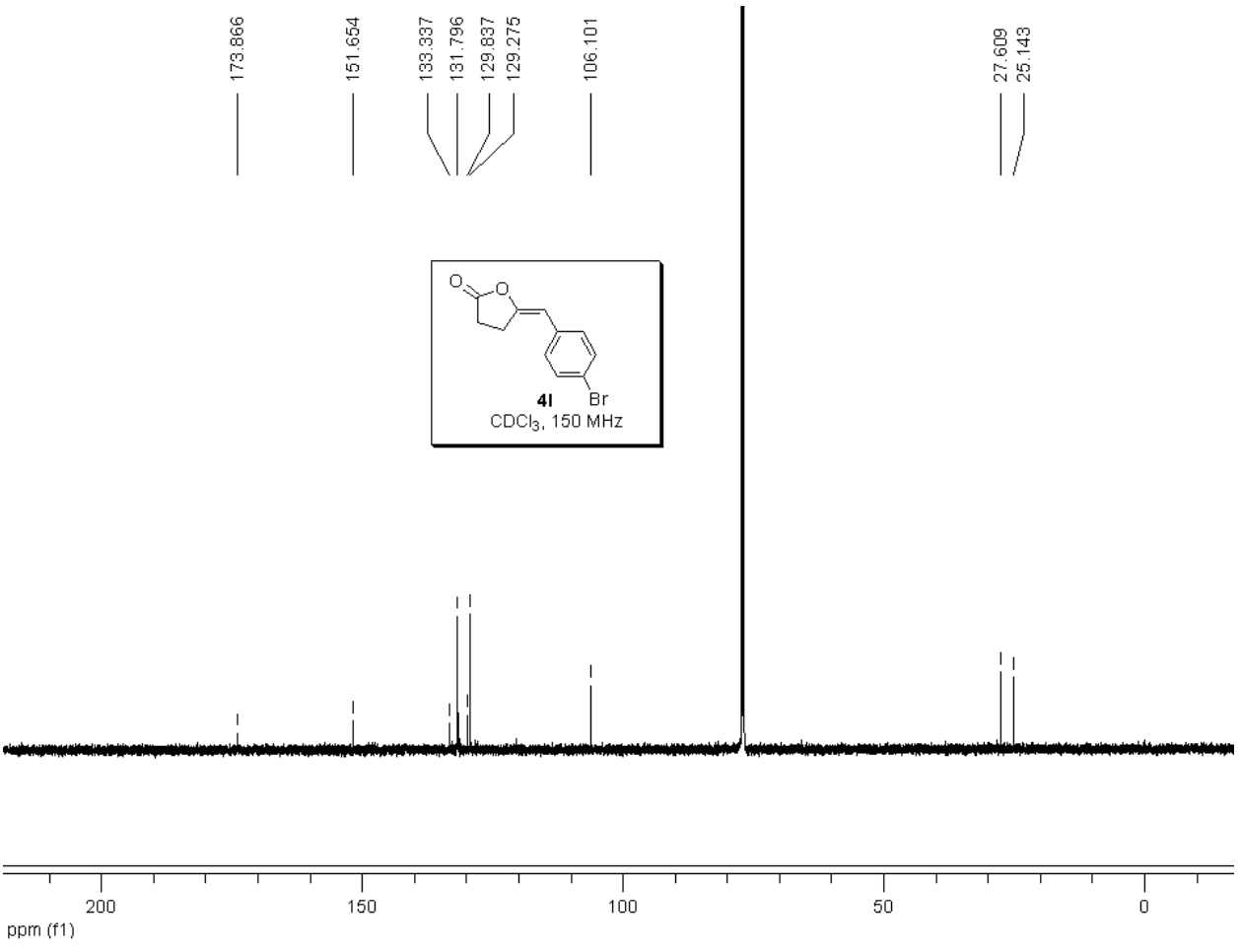


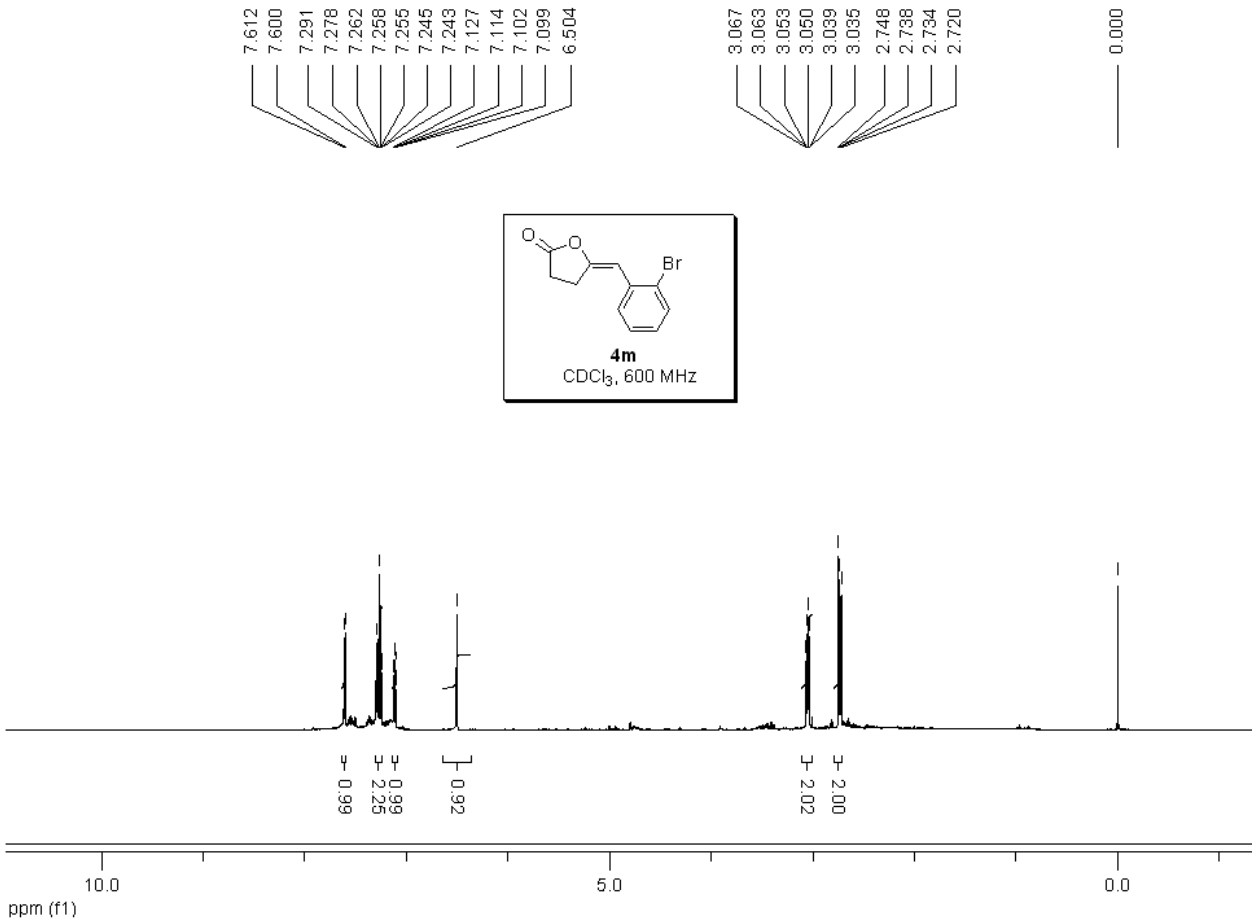


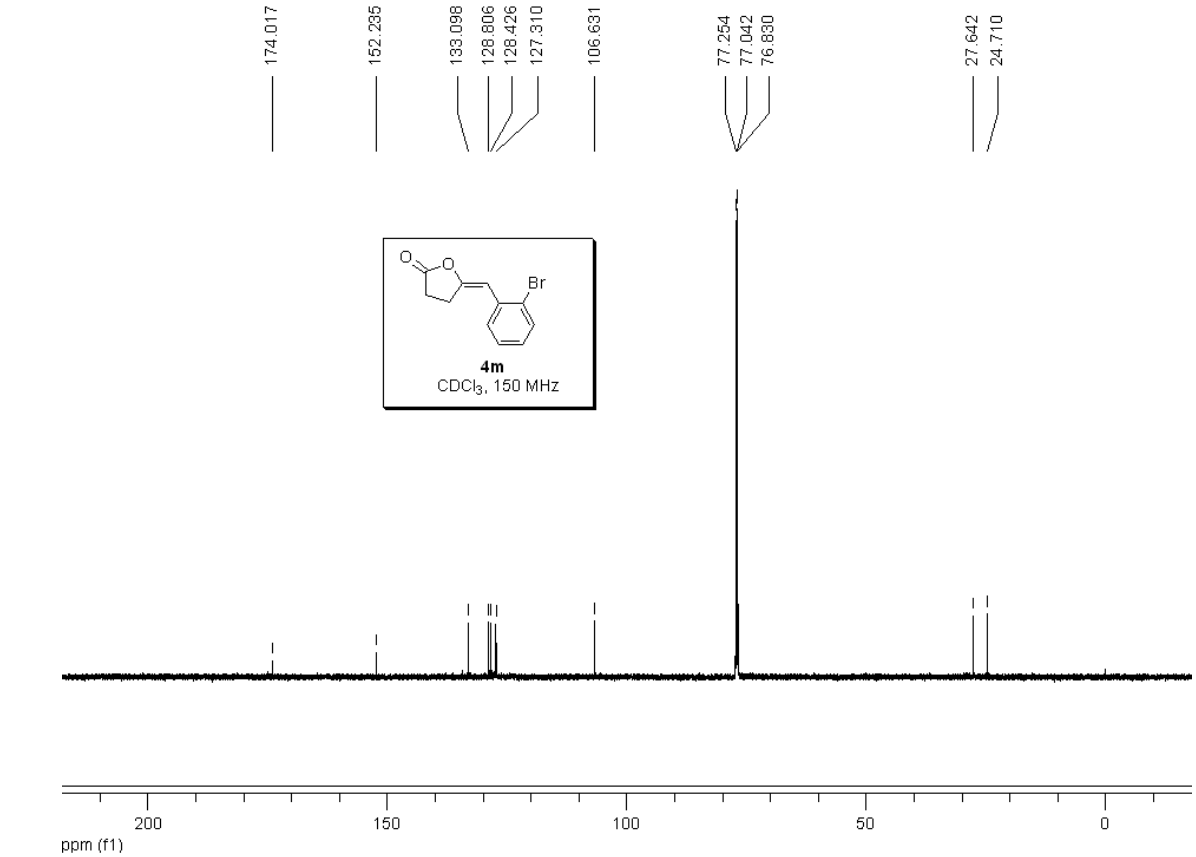

7.263
7.197
7.188
7.183
7.174
7.057
7.042
7.028
6.296
3.144
3.141
3.130
3.127
3.116
3.113
2.781
2.766
2.753
0.000
4j
F
CDCl3, 600 MHz
2.08
2.09
0.89
2.00
2.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

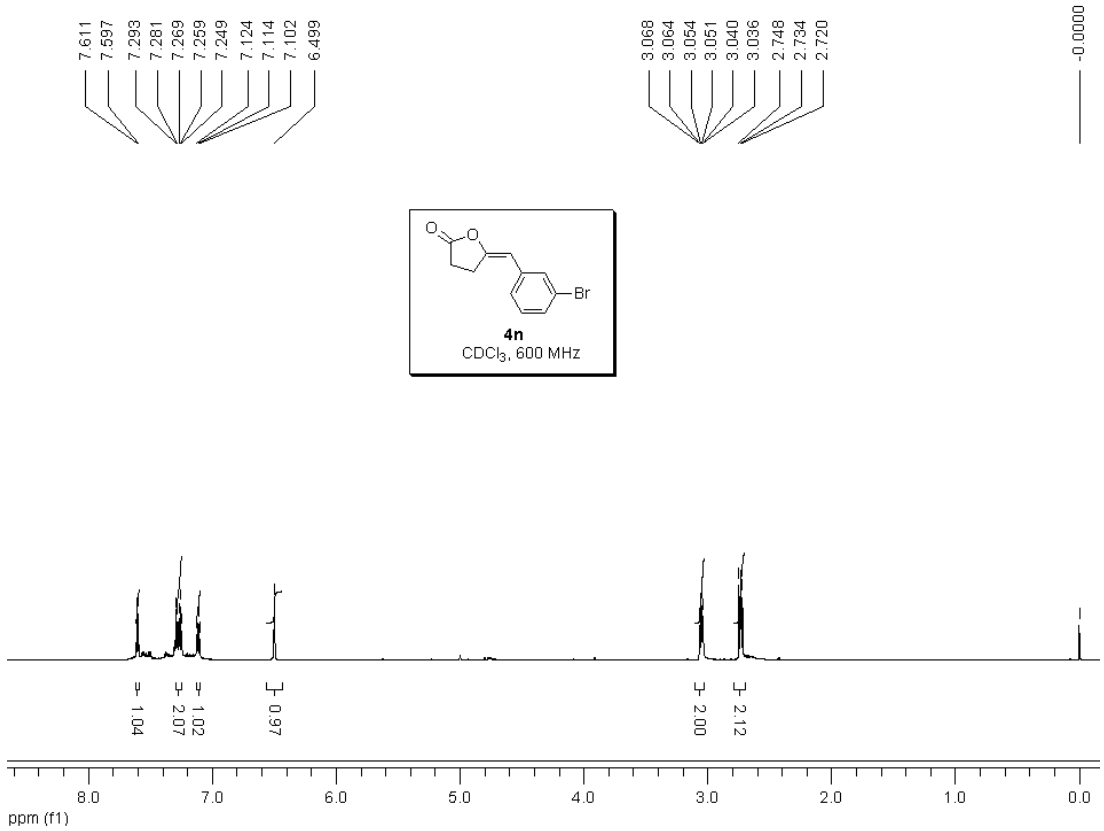

174.019
162.259
160.623
150.838
130.399
130.377
129.326
129.274
115.728
115.586
106.045
77.243
77.032
76.820
27.684
24.981
4j
F
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)

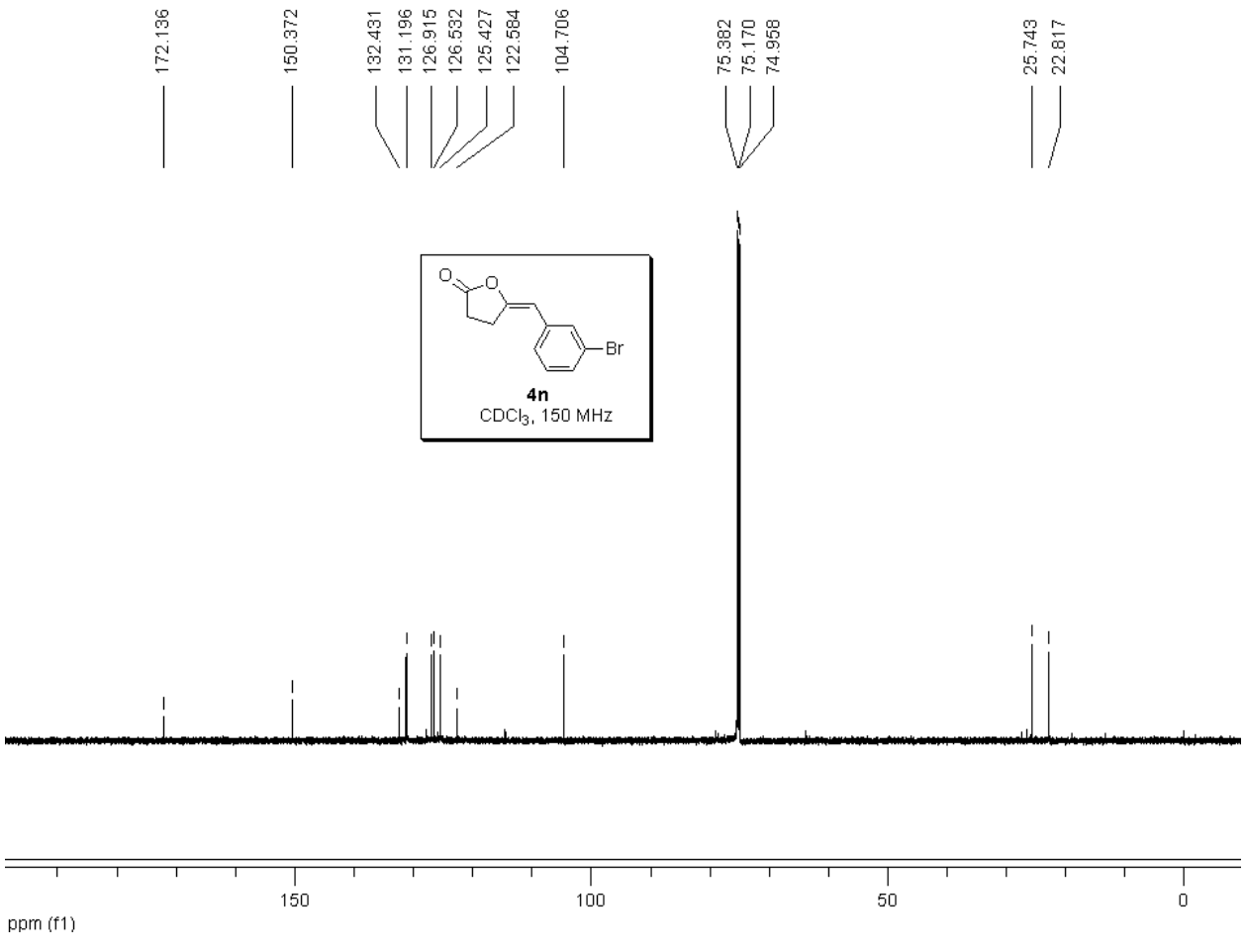

7.471
7.457
7.263
7.093
7.079
6.261
3.140
3.126
3.114
2.785
2.770
2.756
-0.0000
4l
Br
CDCl3, 600 MHz
2.19
2.06
0.90
1.90
2.00
10.0
5.0
0.0
ppm (f1)

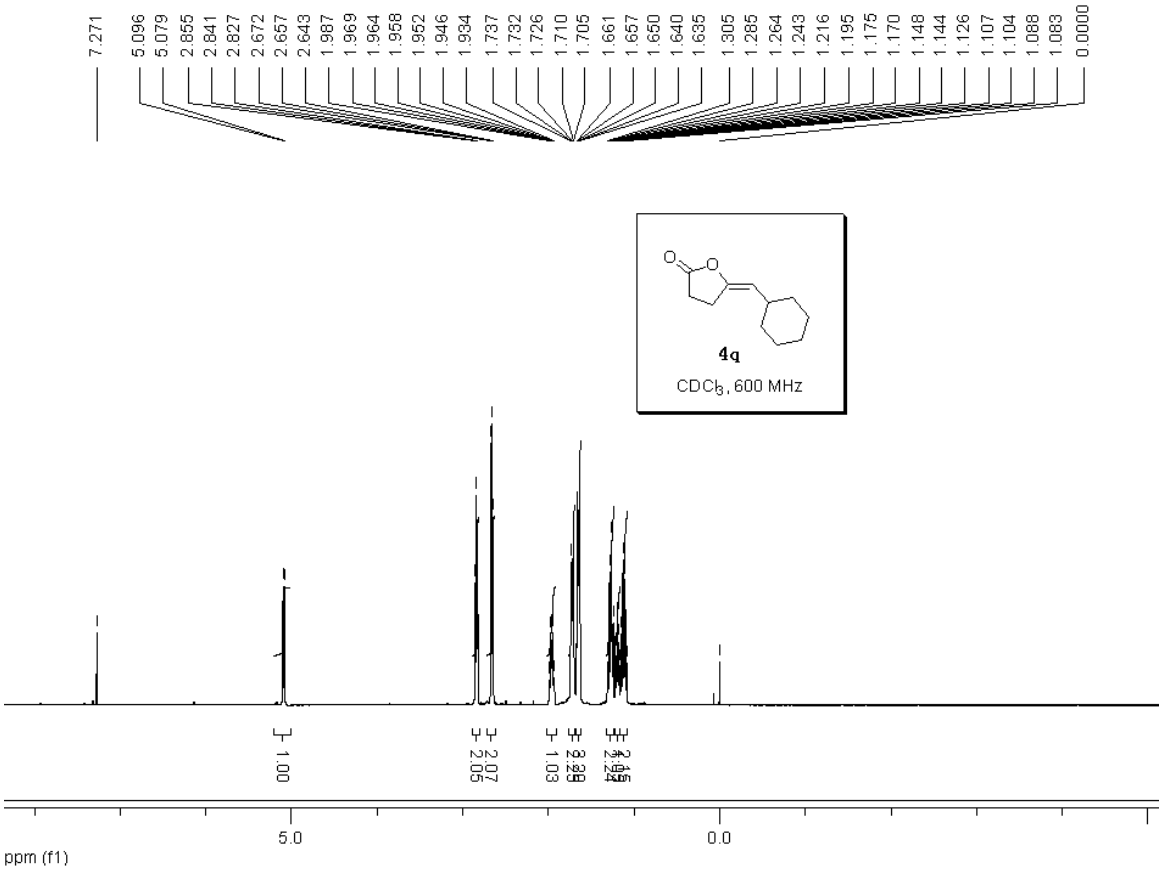

173.866
151.654
133.337
131.796
129.837
129.275
106.101
27.609
25.143
4l
Br
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)

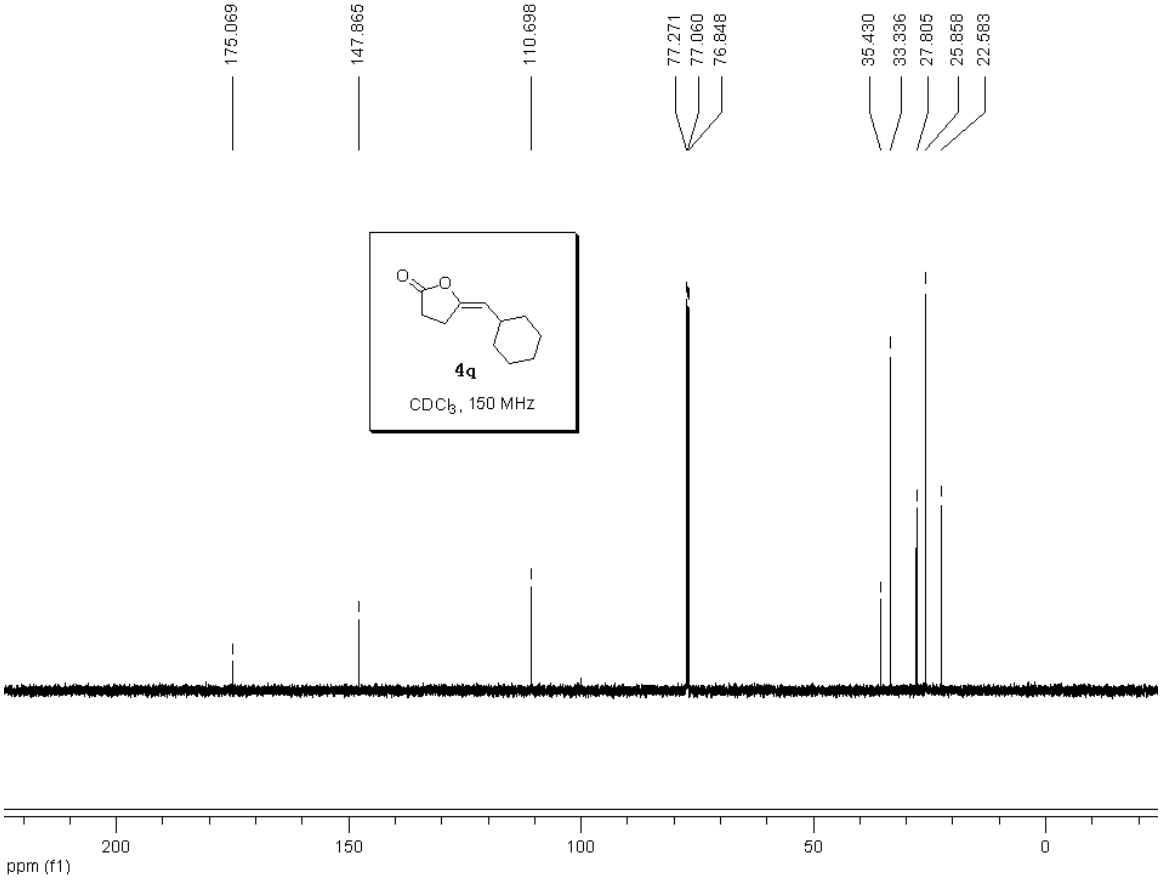

7.612
7.600
7.291
7.278
7.262
7.258
7.255
7.245
7.243
7.127
7.114
7.102
7.099
6.504
3.067
3.063
3.053
3.050
3.039
3.035
2.748
2.738
2.734
2.720
0.000
O
O
Br
4m
CDCl3, 600 MHz
0.99
2.25
0.99
0.92
2.02
2.00
10.0
5.0
0.0
ppm (f1)


174.017
152.235
133.098
128.806
128.426
127.310
106.631
77.254
77.042
76.830
27.642
24.710
O
O
Br
4m
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)


7.611
7.597
7.293
7.281
7.269
7.259
7.249
7.124
7.114
7.102
6.499
3.068
3.064
3.054
3.051
3.040
3.036
2.748
2.734
2.720
-0.0000
4n
CDCl3, 600 MHz
1.04
2.07
1.02
0.97
2.00
2.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


172.136
150.372
132.431
131.196
126.915
126.532
125.427
122.584
104.706
75.382
75.170
74.958
25.743
22.817
4n
CDCl3, 150 MHz
150
100
50
0
ppm (f1)


7.271
5.096
5.079
2.855
2.841
2.827
2.672
2.657
2.643
1.987
1.969
1.964
1.958
1.952
1.946
1.934
1.737
1.732
1.726
1.710
1.705
1.661
1.657
1.650
1.640
1.635
1.305
1.285
1.264
1.243
1.216
1.195
1.175
1.170
1.148
1.144
1.126
1.107
1.104
1.088
1.083
0.0000
4q
CDCl3, 600 MHz
1.00
2.05
2.07
1.03
5.0
0.0
ppm (f1)


175.069
147.865
110.698
77.271
77.060
76.848
35.430
33.336
27.805
25.858
22.583
4q
CDCl3, 150 MHz
200
150
100
50
0
ppm (f1)