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# Supporting Information

## *N*-Heterocyclic Carbene-Catalyzed Double Acylation of Enones with Benzils

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**General remarks.**

NMR spectra were taken on a Varian 400-MR ($^1$H, 399.82 MHz; $^{13}$C, 100.54 MHz) spectrometer or Varian 500-MR ($^1$H, 499.82 MHz; $^{13}$C, 125.68 MHz) spectrometer using residual chloroform ($^1$H, $\delta$ = 7.26) or $CDCl_3$ ($^{13}$C, $\delta$ = 77.0) as an internal standard. Mass spectra were obtained at 70 eV on a Simadzu GC-MS QP5050 spectrometer. High-resolution mass spectra were recorded with Thermo Fisher Scientific LTQ Orbitrap XL (ESI or APCI/FTMS mode). Melting points were measured on a Shimadzu melting point apparatus and are uncorrected. TLC monitoring was performed with Merck silica gel (60 $F_{254}$). All reactions were conducted with a standard Schlenk technique under nitrogen atmosphere. DCE and DMF solvents were distilled from CaH. EtOH was dried over Mg powder. $Et_3N$ and DIPEA bases were distilled from molecular sieves 4Å. The Lewis acids, other than Ti(O*i*Pr)$_4$, were dried by heat gun under vacuum.

**Materials.**

Symmetrical 1,2-diketones **1** were conventionally prepared by benzoin condensation of the corresponding aldehydes with KCN, followed by $CrO_3$ or $NH_4NO_3$ oxidation. Unsymmetrical diketones **1f** was prepared by the reaction of *p*-tolylmagnesium bromide with phenylglyoxal, generated from 2,2-dihydroxyacetophenone by the azeotropic dehydration with toluene, and subsequent oxidation with dioxygen in the presence of $ZnCl_2$ and DABCO.[1] Enones **2** were obtained by the oxidation of allylic alcohols prepared from aldehydes and vinylmagnesium bromide. The NHC salts, 3-(2,4,6-Trimethyl-phenyl)-5,6,7,8-tetrahydro-4*H*-cycloheptathiazol-3-ium perchlorate (**A**),[2] 2-Phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium chloride (**D**)[3] and 1,3-dimesityl-1*H*-imidazol-3-ium chloride (**E**),[4] were prepared according to the literature procedures. 3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium chloride (**B**) and 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium bromide (**C**) were purchased from Aldrich.

**General procedure for the double acylation of enone with benzil.**

A Schlenk tube was charged with benzil (**1a)** (105 mg, 0.5 mmol), thiazolium salt **A** (37 mg, 0.1 mmol), phenyl vinyl ketone (**2a**) (65 mg, 0.5 mmol), DMF (1 mL), and DIPEA (13 mg, 0.1 mmol) under $N_2$. The mixture was stirred at 50 °C for 12 h. After

quenching with water, accurately weighted diphenylmethane was added to the mixture as an internal standard. The organic layer was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated in vacuum. The residue was measured by $^1H$ NMR to determine NMR yield of **3aa** (94% yield). Then, the crude product was purified by column chromatography on silica gel with hexane-EtOAc eluent to give analytically pure sample (157 mg, 92% yield).

**2-Benzoyl-1,4-diphenylbutane-1,4-dione (3aa).**[5]

Isolated in 92% yield as yellow solid: mp 156-157 °C; $R_f$ = 0.39 (Hexane / EtOAc = 5 / 1); $^1H$ NMR ($CDCl_3$, 399.82 MHz) δ 3.78 (2H, d, *J* = 6.4 Hz, $CH_2$), 6.13 (1H, t, *J* = 6.4 Hz, CH), 7.46 (6H, t, *J* = 6.4 Hz), 7.58 (3H, t, *J* = 7.4 Hz), 8.00-8.03 (6H, m); $^{13}C$ NMR ($CDCl_3$, 100.54 MHz) δ 38.0, 51.3, 128.3, 128.6, 128.9, 133.6, 133.7, 135.5, 136.0, 195.7, 196.6 (one carbon was obscured); MS *m/z* 324 (100), 323 (32), 247 (29), 105 (68), 77 (72); HRMS *m/z* ($[M+Na]^+$) calcd for $C_{23}H_{18}O_3Na$, 365.1148, found 365.1151.

**2-Benzoyl-4-phenyl-1-(*o*-tolyl)butane-1,4-dione (3ab).**

Isolated in 58% yield as a yellow oil: $R_f$ = 0.39 (Hexane / EtOAc = 5 / 1); $^1H$ NMR ($CDCl_3$, 399.82 MHz) δ 2.41 (3H, s, $CH_3$), 3.67 (1H, dd, *J* = 18.4, 5.6 Hz, C*H*H), 3.91 (1H, dd, *J* = 18.2, 7.0 Hz, CH*H*), 6.06 (1H, br t, *J* = 6.4 Hz, CH), 7.20-7.28 (2H, m), 7.33-7.46 (1H, m) , 7.40-7.48 (4H, m), 7.52-7.59 (2H, m), 7.87 (1H, d, *J* = 7.6 Hz), 7.96 (2H, d, *J* = 7.2 Hz) 8.01 (2H, d, *J* = 7.2 Hz); $^{13}C$ NMR ($CDCl_3$, 100.54 MHz) δ 20.9, 38.1, 54.1, 125.8, 128.2, 128.3, 128.6, 128.8, 131.6, 132.0, 133.5, 133.6, 135.7, 136.1, 137.0, 139.0, 196.0, 196.9, 198.6 (one carbon was obscured): MS *m/z* 338 (78), 207 (41), 119 (100), 105 (69), 91 (37); HRMS *m/z* ($[M+Na]^+$) calcd for $C_{24}H_{20}O_3Na$, 379.1305, found 379.1307.

**2-Benzoyl-4-phenyl-1-(*m*-tolyl)butane-1,4-dione (3ac).**

Isolated in 80% yield as a white solid; mp 100-102 °C; $R_f$ = 0.41 (Hexane / EtOAc = 5 / 1); $^1H$ NMR ($CDCl_3$, 399.82 MHz) δ 2.38 (3H, s, $CH_3$), 3.73 (1H, dd, *J* = 18.0, 6.4 Hz, C*H*H), 3.82 (1H, dd, *J* = 17.8, 6.6 Hz, CH*H*), 6.12 (1H, t, *J* = 6.6 Hz, CH), 7.33-7.40 (2H, m), 7.44-7.48 (4H, m), 7.55-7.59 (2H, m), 7.82 (2H, d, *J* = 8.4 Hz), 8.00-8.03 (4H, m); $^{13}C$ NMR ($CDCl_3$, 100.54 MHz) δ 21.3, 38.0, 51.4, 125.9, 128.3, 128.6, 128.8,

128.9, 129.1, 133.5, 133.6, 134.5, 135.5, 135.6, 136.1, 138.8, 195.7, 196.0, 196.6 (one carbon was obscured); MS *m/z* 338 (100), 119 (62), 105 (68), 91 (27), 77 (37); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{24}H_{20}O_3Na$, 379.1305, found 379.1306.

**2-Benzoyl-4-phenyl-1-(*p*-tolyl)butane-1,4-dione (3ad).**[6]

Isolated in 89% yield as a yellow oil: $R_f$ = 0.42 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 2.40 (3H, s, $CH_3$), 3.73 (1H, dd, *J* = 18.0, 6.2 Hz, C*H*H), 3.81 (1H, dd, *J*= 18.0, 6.2 Hz, CH*H*), 6.10 (1H, t, *J* = 6.4 Hz, CH), 7.23 (2H, d, *J* = 7.2 Hz), 7.43-7.48 (4H, m) , 7.55-7.59 (2H, m), 7.93 (2H, d, *J* = 7.6 Hz), 8.01 (4H, t, *J* = 8.0 Hz); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 21.7, 38.0, 51.3, 128.3, 128.6, 128.8, 128.9, 129.6, 132.9, 133.5, 133.6, 135.6, 136.1, 144.7, 195.4, 195.7, 196.7 (one carbon was obscured); MS *m/z* 338 (100), 220 (31), 119 (78), 105 (60), 77 (31); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{24}H_{20}O_3Na$, 379.1305, found 379.1297.

**2-Benzoyl-1-mesityl-4-phenylbutane-1,4-dione (3ae).**[7]

Isolated in 13% yield as a yellow solid: mp 124-126 °C; $R_f$ = 0.45 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 2.16 (6H, s, $2CH_3$), 2.13 (3H, s, $CH_3$), 3.78 (1H, dd, *J*= 18.4, 4.4 Hz, C*H*H), 4.05 (1H, dd, *J*= 18.4, 8.8 Hz, CH*H*), 5.76 (1H, dd, *J*= 8.8, 4.4 Hz, CH), 6.68 (2H, s), 7.32 (2H, t, *J* = 7.8 Hz), 7.48 (3H, t, *J* = 7.8 Hz), 7.57-7.61 (1H, m), 7.81 (2H, d, *J* = 7.6 Hz), 7.03 (2H, d, *J* = 7.2 Hz); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 19.5, 21.0, 37.7, 57.9, 128.26, 128.32, 128.5, 128.60, 128.64, 133.08, 133.11, 133.5, 136.2, 137.0, 137.9, 139.2, 195.5, 197.6, 202.7; MS *m/z* 366 (17), 281 (13), 207 (100); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{26}H_{24}O_3Na$, 407.1618, found 407.1629.

**2-Benzoyl-1-(*p*-anisyl)-4-phenylbutane-1,4-dione (3af).**[7]

Isolated in 75% yield as a white solid; mp 109-111 °C; $R_f$ = 0.23 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.69 (1H, dd, *J* = 18.0, 6.0 Hz, C*H*H), 3.85 (3H, s, $OCH_3$), 3.85 (1H, dd, *J* = 18.0, 7.0 Hz, CH*H*), 6.08 (1H, br t, *J* = 6.4 Hz, CH), 6.92-6.95 (2H, m), 7.26-7.48 (4H, m) , 7.54-7.59 (2H, m) , 8.00-8.03 (6H, m); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.0, 51.1, 55.5, 114.1, 128.2, 128.3, 128.59, 128.61, 128.8, 131.1, 133.48, 133.53, 135.6, 136.1, 164.0, 194.3, 195.7, 196.8; MS *m/z* 354 (97), 207 (100), 135 (53), 105 (32), 77 (46); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{24}H_{20}O_4Na$, 395.1254, found 395.1259.

**2-Benzoyl-1-(2-chlorophenyl)-4-phenylbutane-1,4-dione (3ag).**

Isolated in 53% yield as a yellow oil: $R_f$ = 0.33 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.77 (1H, dd, *J* = 18.0, 6.8 Hz, C*H*H), 3.91 (1H, dd, *J* = 18.2, 6.6 Hz, CH*H*), 6.14 (1H, t, *J* = 6.6 Hz, CH), 7.26-7.61 (10H, m), 7.95 (2H, d, *J* = 8.6 Hz), 8.01 (2H, d, *J* = 8.2 Hz); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.0, 55.5, 127.0, 128.3, 128.66, 128.70, 128.74, 129.7, 130.5, 131.0, 132.1, 133.6, 135.95, 135.99, 138.0, 195.4, 196.8, 197.2 (one carbon was obscured); MS *m/z* 360 (45), 358 (100), 139 (52), 105 (67), 77 (58); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{23}H_{17}ClO_3Na$, 399.0758; found 399.0758.

**2-Benzoyl-1-(4-chlorophenyl)-4-phenylbutane-1,4-dione (3ah).**

Isolated in 87% yield as a white solid: mp 109-111°C; $R_f$ = 0.40 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.71 (1H, dd, *J* = 18.0, 6.0 Hz, C*H*H), 3.85 (1H, dd, *J* = 18.0, 6.8 Hz, CH*H*), 6.01 (1H, dd, *J* = 6.8, 6.0 Hz, CH), 7.41-7.50 (6H, m), 7.57-7.62 (2H, m), 7.93-7.97 (2H, m), 7.99-8.02 (4H, m); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.0, 51.3, 128.3, 128.66, 128.69, 129.0, 129.2, 130.0, 133.6, 133.9, 134.0, 135.3, 135.9, 140.1, 194.4, 195.6, 196.5; MS *m/z* 360 (37), 358 (91), 139 (57), 105 (100), 77 (60); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{23}H_{17}ClO_3Na$, 399.0758, found 399.0767.

**2-Benzoyl-1-(4-cyanophenyl)-4-phenylbutane-1,4-dione (3ai).**

Isolated in 37% yield as a white solid: mp 144-146 °C; $R_f$ = 0.25 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.60 (1H, dd, *J* = 18.0, 4.4 Hz, C*H*H), 4.01 (1H, dd, *J* = 18.2, 7.8 Hz, CH*H*), 6.07 (1H, dd, *J* = 7.8, 4.4 Hz, CH), 7.46-7.53 (4H, m), 7.59-7.66 (2H, m), 7.75 (2H, d, *J* = 8.8 Hz), 7.99-8.03 (4H, m), 8.07 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.1, 51.7, 116.6, 117.8, 128.3, 128.7, 128.8, 128.9, 129.2, 132.7, 133.8, 134.2, 134.9, 135.7, 139.0, 194.3, 195.7, 196.3; MS *m/z* 349 (100), 272 (22), 105(25), 77 (26); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{24}H_{17}NO_3Na$, 390.1101, found 390.1107.

**2-Benzoyl-1-(1-naphthyl)-4-phenylbutane-1,4-dione (3aj).**

Isolated in 67% yield as a yellow solid: mp 44-46 °C; $R_f$ = 0.39 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.75 (1H, dd, *J* = 18.0, 6.0 Hz, C*H*H), 4.00 (1H,

dd, *J* = 18.2, 7.2 Hz, CH*H*), 6.23 (1H, dd, *J*= 7.2, 6.0 Hz, CH), 7.36 (2H, t, *J* = 7.8 Hz), 7.44-7.52 (5H, m) , 7.54-7.59 (2H, m), 7.82 (1H, d, *J*=8.2 Hz), 7.94-7.97 (3H, m), 8.01-8.04 (2H, m), 8.11 (1H, d, *J* = 7.2 Hz), 8.52 (1H, d, *J* = 8.8 Hz); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.2, 54.6, 124.3, 125.7, 126.6, 127.6, 128.1, 128.2, 128.3, 128.63, 128.65, 128.8, 130.4, 133.1, 133.6, 133.9, 135.2, 135.7 136.1, 196.0, 197.0 198.6 (one carbon was obscured); MS *m/z* 374 (100), 269 (36), 127 (65), 105 (65), 77 (39); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{27}H_{20}O_3Na$, 415.1305, found 415.1304.

**2-Benzoyl-1-(2-naphthyl)-4-phenylbutane-1,4-dione (3ak).**

Isolated in 87% yield as a yellow solid: mp 107-109 °C; $R_f$ = 0.40 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.79 (1H, dd, *J* = 18.0, 6.0 Hz, C*H*H), 3.91 (1H, dd, *J* = 18.0, 7.2 Hz, CH*H*), 6.29 (1H, br t, *J* = 6.2 Hz, CH), 7.44-7.49 (4H, m), 7.55-7.63 (4H, m) , 7.86-7.94 (3H, m), 8.05 (5H, t, *J* = 8.0 Hz), 8.56 (1H, s); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.2, 51.5, 124.1, 127.0, 127.8, 128.3, 128.7, 128.90, 128.94 129.7, 130.6, 132.5, 132.8, 133.6, 133.7, 135.7, 135.8, 136.1, 195.6, 195.8, 196.8 (two carbons were obscured); MS *m/z* 374 (100), 207 (53), 127 (68), 105 (33), 77 (33); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{27}H_{20}O_3Na$, 415.1305, found 415.1300.

**2-Benzoyl-4-phenyl-1-(thiophen-2-yl)butane-1,4-dione (3al).**

Isolated in 87% yield as a yellow solid: mp 139-141 °C; $R_f$ = 0.35 (Hexane / EtOAc = 5 /1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.74 (1H, dd, *J* = 18.0, 6.0 Hz, C*H*H), 3.89 (1H, dd, *J* = 18.0, 6.8 Hz, CH*H*), 5.95 (1H, br t, *J* = 6.4 Hz, CH), 7.11 (1H, dd, *J* = 5.2, 4.0 Hz), 7.43-7.48 (4H, m) , 7.55-7.60 (2H, m), 7.65 (1H, dd, *J* = 5.0, 1.2 Hz), 7.85 (1H, dd, *J* = 4.0, 1.2 Hz), 7.98-8.10 (4H, m); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.3, 52.8, 128.2, 128.4, 128.6, 128.7, 128.9, 133.0, 133.5, 133.7, 135.0, 135.6, 135.9, 142.8, 188.1, 194.9, 196.5; MS *m/z* 330 (100), 111 (55), 105 (55), 77 (56); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{21}H_{16}O_3SNa$, 371.0712, found 371.0714.

**2-Benzoyl-4-phenyl-1-(thiophen-3-yl)butane-1,4-dione (3am).**

Isolated in 89% yield as a yellow solid: mp 146-148 °C; $R_f$ = 0.35 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.74 (1H, dd, *J* = 18.0, 6.4 Hz, C*H*H), 3.85 (1H, dd, *J* = 18.0, 6.8 Hz, CH*H*), 5.92 (1H, br t, *J*= 6.4 Hz, CH), 7.32 (1H, dd, *J*= 5.0, 3.0 Hz), 7.45-7.49 (4H, m) , 7.56-7.61 (3H, m), 8.00-8.05 (4H, m), 8.19 (1H, dd, *J*= 2.8, 1.2

Hz); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 38.1, 53.3, 126.9, 127.3, 128.3, 128.65, 128.69, 128.9, 133.4, 133.6, 133.7, 135.7, 136.0, 140.8, 189.5, 195.4, 196.6; MS *m/z* 330 (100), 207 (51), 111 (57), 105 (33), 77 (36); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{21}H_{16}O_3SNa$, 371.0712, found 371.0716.

**3-Benzoyl-1-phenylpentane-1,4-dione (3an).**[8]

Isolated in 68% yield as a yellow solid: mp 83-84 °C; $R_f$ = 0.35 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 2.25 (3H, s, $CH_3$), 3.61 (1H, dd, *J* = 18.4, 6.4 Hz, C*H*H), 3.80 (1H, dd, *J* = 18.2, 7.0 Hz, CH*H*), 5.30 (1H, br t, *J* = 6.6 Hz, CH), 7.44-7.48 (2H, m), 7.51-7.65 (4H, m) , 7.98 (2H, dd, *J* = 8.4, 1.2 Hz), 8.07-8.09 (2H, m); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 29.6, 38.0, 56.7, 128.2, 128.6, 128.9, 129.0, 133.5, 133.9, 135.9, 136.0, 196.2, 196.9, 202.3; MS *m/z* 262 (100), 247 (60), 105 (48), 77 (25); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{18}H_{16}O_3Na$, 303.0992, found 303.0993.

**2-Benzoyl-1,4-di-*p*-tolylbutane-1,4-dione (3ba).**

Isolated in 48% yield as a yellow oil: $R_f$ = 0.3 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 499.82 MHz) δ 2.40 (3H, s, $CH_3$), 2.41 (3H, s, $CH_3$), 3.69 (1H, dd, *J*= 18.0, 6.0 Hz, C*H*H), 3.81 (1H, dd, *J* = 18.0, 6.0 Hz, CH*H*), 6.10 (1H, t, *J* = 6.0 Hz, CH), 7.25-7.27 (4H, m), 7.45 (2H, t, *J* = 7.5 Hz), 7.57 (1H, t, *J* = 7.5 Hz), 7.92 (4H, t, *J* = 7.5 Hz), 8.01 (2H, d, *J* = 7.5 Hz); $^{13}$C NMR ($CDCl_3$, 125.68 MHz) δ 21.7, 37.9, 51.3, 128.4, 128.6, 128.8, 128.9, 129.3, 129.6, 133.0, 133.5, 133.7, 135.7, 144.4, 144.7, 195.5, 195.8, 196.3; MS *m/z* 370 (1), 352 (100), 275 (7), 234 (21), 119 (78); HRMS: *m/z* ([M+Na]$^+$) calcd for $C_{25}H_{22}O_3Na$, 393.1461, found 393.1466.

**2-Benzoyl-1,4-bis(*p*-anisyl)butane-1,4-dione (3ca).**

Isolated in 16% yield as a yellow oil: $R_f$ = 0.09 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.64 (1H, dd, *J* = 18.0, 6.2 Hz, C*H*H), 3.80 (1H, dd, *J* = 18.0, 6.8 Hz, CH*H*), 3.86 (3H, s, $OCH_3$), 3.87 (3H, s, $OCH_3$), 6.07 (1H, br t, *J* = 6.4 Hz, CH), 6.91-6.96 (4H, m), 7.43-7.47 (2H, m) 7.54-7.59 (1H, m) 7.98-8.04 (6H, m); $^{13}$C NMR ($CDCl_3$, 125.68 MHz) δ 37.7, 51.2, 55.47, 55.51, 113.8, 114.1, 128.4, 128.6, 128.8, 129.2, 130.6, 131.1, 133.5, 135.7, 163.8, 163.9, 194.4, 195.2, 195.8; MS *m/z* 384 (100), 369 (25), 207 (15), 105 (13); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{25}H_{22}O_5Na$, 425.1359, found 425.1364.

**2-Benzoyl-1,4-bis(4-chlorophenyl)butane-1,4-dione (3da).**

Isolated as a yellow solid in 70% yield: mp 151-153ºC; $R_f$ = 0.25 (Hexane / AcOEt = 10 1 ) ; $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.66 (1H, dd, *J* = 18.0, 5.6 Hz, C*H*H), 3.80 (1H, dd, *J* = 18.0, 6.8 Hz, CH*H*), 6.04 (1H, br t, *J* = 6.4 Hz, CH), 7.42 (2H, d, *J* = 8.4 Hz), 7.44, (2H, d, *J* = 8.4 Hz), 7.45 (2H, t, *J* = 7.2 Hz), 7.60 (1H, t, *J* = 7.2 Hz), 7.93-7.95 (4H, m), 8.00 (2H, d, *J* = 7.2 Hz); $^{13}$C NMR ($CDCl_3$, 100.53 MHz) δ 37.9, 51.4, 128.6, 129.01,129.04, 129.2, 129.7, 130.0, 133.9, 134.0, 134.3, 135.2, 140.1, 140.2, 194.3, 195.4, 195.5; MS *m/z* 392 (100), 207 (43), 179 (25), 139 (38), 105 (93); HRMS *m/z* ([M + Na]$^+$) calcd for $C_{23}H_{16}Cl_2O_3Na$ 433.0369, found 433.0370.

**2-Benzoyl-1,4-bis(4-bromophenyl)butane-1,4-dione (3ea).**

Isolated in 73% yield as a yellow solid: mp 158-159ºC; $R_f$=0.25 (Hexane / AcOEt = 10 / 1); $^1$H NMR ($CDCl_3$, 499.82 MHz) δ 3.65 (1H, dd, *J* = 18.0, 6.0 Hz, C*H*H), 3.79 (1H, dd, *J* = 18.0, 7.0 Hz, CH*H*), 6.03 (1H, br t, *J* = 6.5 Hz, CH), 7.48 (2H, t, *J* = 8.0 Hz), 7.58-7.62 (5H, m), 7.856 (2H, d, *J* = 9.0 Hz), 7.861 (2H, d, *J* = 8.5 Hz), 8.00 (2H, d, *J* = 8.5 Hz); $^{13}$C NMR ($CDCl_3$, 125.68 MHz) δ 37.9, 51.3, 128.7, 128.9, 129.0, 129.1, 129.8, 130.1, 132.0, 132.2, 134.0, 134.3, 134.6, 135.1, 194.5, 195.5, 195.6 ; MS *m/z* 482 (100), 207 (29), 202 (13), 183(23), 155 (12); HRMS *m/z* ([M + Na]$^+$) calcd for $C_{23}H_{16}Br_2O_3Na$ 520.9358, found 520.9366.

**2-benzoyl-1-phenyl-4-(p-tolyl)butane-1,4-dione (3fa).**[6]

This product was obtained as a mixture of **3fa** and **3ad** in 80% yield in a ratio of 40 / 60, because they could not be separated by column chromatography. Assignment of the spectra to **3fa** was done by omitting the signals of **3ad** from those of the mixture. **3fa**: yellow oil; $R_f$ = 0.42 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 2.40 (3H, s, $CH_3$), 3.76 (2H, d, *J* = 6.4 Hz, $CH_2$), 6.13 (1H, t, *J* = 6.4 Hz, CH), 7.25-7.28 (2H, m), 7.44-7.48 (4H, m), 7.55-7.60 (2H, m), 7.92 (2H, t, *J* = 8.8 Hz), 8.00-8.03 (4H, m); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 21.7, 37.9, 51.3, 128.4, 128.82, 128.88, 128.91, 129.3, 133.6, 135.5, 144.5, 195.8, 196.2; MS *m/z* 338 (100), 119 (75), 105 (71), 91 (33), 77 (46); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{24}H_{20}O_3Na$, 379.1305; found 379.1310.

**2-Benzoyl-4-(4-chlorophenyl)-1-phenylbutane-1,4-dione (3ga).**[9]

Isolated in 85 % yield as a mixture of **3ga** and **3ah** in a ratio of 55 / 45. Assignment of the spectra to **3ga** was done as described above. **3ga**: yellow oil; $R_f$ = 0.40 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 3.73 (2H, d, *J* = 6.4 Hz, $CH_2$), 6.12 (1H, t, *J* = 6.4 Hz, CH), 7.36-7.45 (6H, m), 7.52-7.55 (2H, m), 7.89-8.02 (6H, m); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 37.8, 51.2, 128.5, 128.8, 129.5, 133.6, 134.2, 135.3, 139.7, 195.4, 195.5 (one carbon was obscured); MS *m/z* 254 (31), 220 (25), 139 (36), 105 (100), 77 (47); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{23}H_{17}ClO_3Na$, 399.0758, found 399.0766.

**2-Benzoyl-1-phenylpentane-1,4-dione (3ha).**[8]

The reaction of **1h** with **2a** gave a mixture of **3ha** and **3an** in a ratio of 83 /17, which could be separated by column chromatography to provide the two products in 35% and 7% yields, respectively. **3ha**: yellow oil; $R_f$ = 0.20 (Hexane / EtOAc = 5 /1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 2.28 (3H, s, $CH_3$), 3.20 (2H, d, *J* = 6.4 Hz, $CH_2$), 5.88 (1H, t, *J* = 6.4 Hz, CH), 7.46 (4H, t, *J* = 7.6 Hz), 7.56-7.60 (2H, m), 7.95-7.97 (4H, m); $^{13}$C NMR ($CDCl_3$, 100.54 MHz) δ 30.0, 42.0, 51.5, 128.6, 128.9, 133.7, 135.4, 195.7, 205.2; MS *m/z* 262 (27), 158 (31), 158 (23), 105 (100), 77 (53); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{18}H_{16}O_3Na$, 303.0992; found 303.0991.

**3-Benzoylhexane-2,5-dione (3ia).**[10]

Isolated in 16% yield as a yellow oil: $R_f$ = 0.13 (Hexane : AcOEt = 5 / 1); $^1$H NMR ($CDCl_3$, 399.82 MHz) δ 2.18 (3H, s, $CH_3$), 2.23 (3H, s, $CH_3$), 3.02 (1H, dd, *J* = 18.0, 6.5 Hz, C*H*H), 3.20 (1H, dd, *J* = 18.0, 6.5 Hz, CH*H*), 5.08 (1H, t, *J* = 6.5 Hz, CH), 7.51 (2H, t, *J* = 7.5 Hz,), 7.63 (1H, t, *J* = 7.5 Hz,), 8.00 (2H, d, *J* = 7.5 Hz,); $^{13}$C NMR ($CDCl_3$, 100.53 MHz) δ 29.4, 29.8, 42.0, 56.7, 128.8, 129.0, 133.9, 135.8, 196.1, 202.4, 205.4 ; MS *m/z* 218 ($M^+$, 1), 133 (64), 105 (100), 96 (52), 77 (80); HRMS *m/z* ([M + Na]$^+$) calcd for $C_{13}H_{14}O_3Na$ 241.0835, found 241.0836.

**2-Benzoylcyclooctane-1,4-dione (3ja).**

Isolated in 27% yield as a yellow oil: $R_f$ = 0.38 (Hexane : AcOEt = 3 : 1) ; $^1$H NMR ($CDCl_3$, 499.82 MHz) δ 1.80-1.87 (2H, m),1.98-2.06 (2H, m), 2.37-2.41 (1H, m), 2.56-2.65 (3H, m), 2.68 (1H, dd, *J* = 12.0, 4.5 Hz, CHC*H*H), 3.45 (1H, t, *J* = 12.0, CHCH*H*), 4.86 (1H, dd, *J* = 12.0, 4.5 Hz, C*H*$CH_2$), 7.46 (2H, t, *J* =7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz),

7.85 (2H, d, $J$ = 7.5 Hz); $^{13}$C NMR ($CDCl_3$, 100.53 MHz) δ 24.5, 25.4, 40.9, 42.3, 42.5, 59.9, 128.3, 128.9, 133.7, 135.7, 193.4, 209.4, 213.5; MS *m/z* 244 ($M^+$, 27), 133 (26), 105 (100), 77 (72); HRMS *m/z* ([M + Na]$^+$) calcd for $C_{15}H_{16}O_3Na$ 267.0992, found 267.0994.

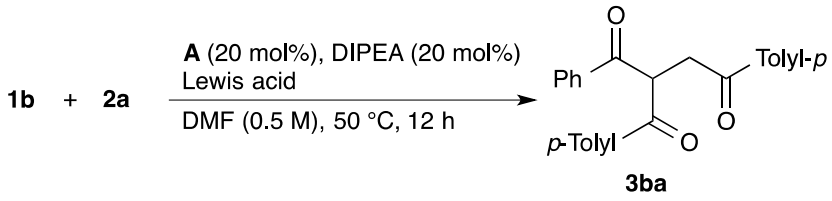
**1,4-Diphenylbutane-1,4-dione (4).**[5]

Isolated as a white solid: mp 147-149 °C; Rf = 0.45 (Hexane / EtOAc = 5 / 1); $^1$H NMR ($CDCl_3$, 499.82 MHz) δ 3.47 (4H, s, $CH_2$), 7.48 (4H, t, $J$ = 7.5 Hz), 7.58 (2H, t, $J$ = 7.5 Hz), 8.04 (4H, d, $J$ = 7.5 Hz); $^{13}$C NMR ($CDCl_3$, 125.68 MHz) δ 32.5, 128.1, 128.6, 133.1, 136.7, 198.7; MS *m/z* 238 ($M^+$, 12), 133 (15), 105 (100), 77 (82); HRMS *m/z* ([M+Na]$^+$) calcd for $C_{16}H_{14}O_2Na$, 261.0886; found 261.0889.

**Attempt to improve the product yields of 3 by use of Lewis acid co-catalysts.**

The reaction of **1b** with **2a** gave **3ba** in 55% yield under the standard conditions as described in the text. In order to improve the yield, effect of Lewis acid co-catalysts was investigated (Table S1). Consequently, 20 mol% of anhydrous LiCl and $MgCl_2$ gave **3ba** in 88% and 90% yields, respectively.

**Table S1** Effect of Lewis acids




**3ba**

| Entry | Lewis Acid | Mol % | Yield (%)[a] |
|---|---|---|---|
| 1 | none | – | 55 |
| 2 | LiCl | 20 | 88 |
| 3 | LiCl | 40 | 74 |
| 5 | $MgCl_2$ | 20 | 90 |
| 6 | $MgCl_2$ | 40 | 79 |
| 7 | $Mg(OtBu)_2$ | 20 | 73 |
| 8 | $Sc(OTf)_3$ | 20 | 0 |
| 9 | $Ti(OiPr)_4$ | 20 | 46 |

[a] NMR yield.

Representative results using $MgCl_2$ in other reactions are summarized in Table S2.

The product yields of **3** were improved in most of the reaction tested. However, the effect was not always positive, for example, yields of **3ag** and **3ea** were nearly unchanged.

**Table S2** Improvement of the product yields

| Entry | Product | Yield (%)[a] without $MgCl_2$ | Yield (%)[a] with $MgCl_2$[b] |
|---|---|---|---|
| 1 | **3ab** | 70 | 83 |
| 2 | **3ae** | 14 | 23 |
| 3 | **3ag** | 53 | 58 |
| 4 | **3an** | 72 | 79 |
| 5 | **3ca** | 20 | 49 |
| 6 | **3ea** | 76 | 81 |
| 7 | **3ha**+**3an** | 40 + 8 | 39 + 23 |

[a] NMR yield. [b] $MgCl_2$ (20 mol%).

**References.**


1 P. Muthupandi and G. Sekar, *Tetrahedron Lett*., 2011, **52**, 692-695.

2 R. Lebeuf, K. Hirano and F. Glorius, *Org. Lett*., 2008, **10**, 4243-4246.

3 M. S. Kerr, J. Read de Alaniz and T. Rovis, *J. Org. Chem.,* 2005, **70**, 5725-5728.

4 A. J. Arduengo III, H. V. Rasika, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.,* 1992, **114**, 5530-5534.

5 X. Zheng, S. Lu and Z. Li, *Org. Lett*., 2013, **15**, 5432-5435.

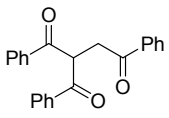
6 T. Ibata, M. Hamaguchi and H. Nishigaki, *Chem. Lett*., 1976, **5**, 1267-1270.

7 C.-K. Dien and R. E. Lutz, *J. Org. Chem*., 1956, **21**, 1492-1509.

8 H. Stetter and F. Jonas, *Tetrahedron Lett*., 1981, **22**, 4945-4948.

9 S. Mataka, H. Suzuki and K. Uehara, *Bull. Chem. Soc. Jpn*., 1992, **65**, 2611-2615.

10 T. S. Cantrell, A. C. Allen and H. Ziffer, *J. Org. Chem.,* 1989, **54**, 140-145.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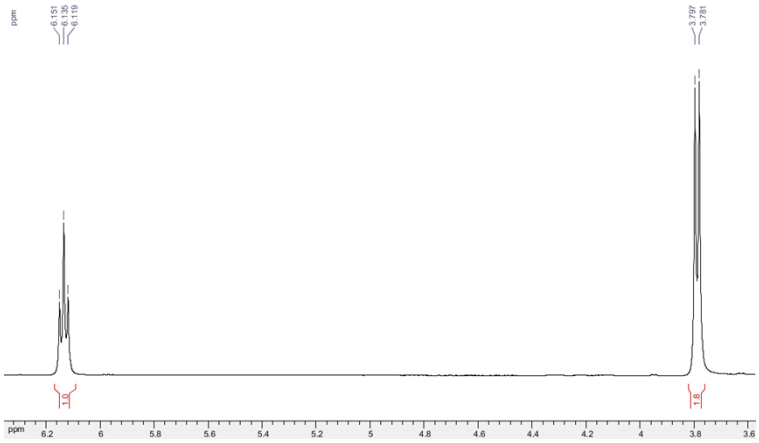
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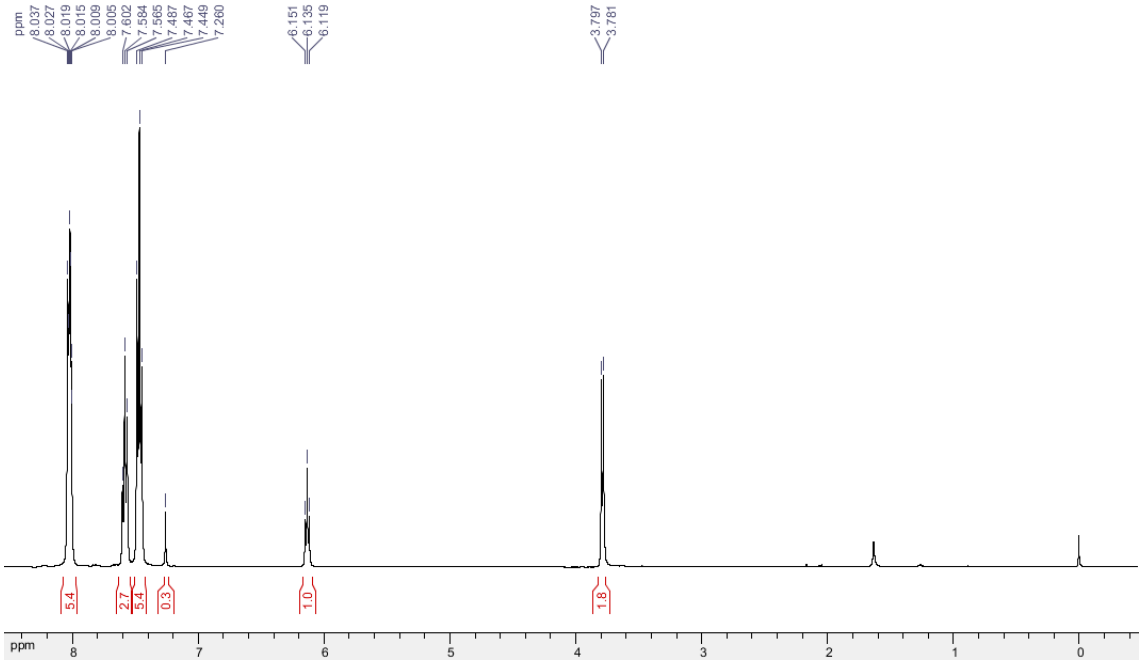
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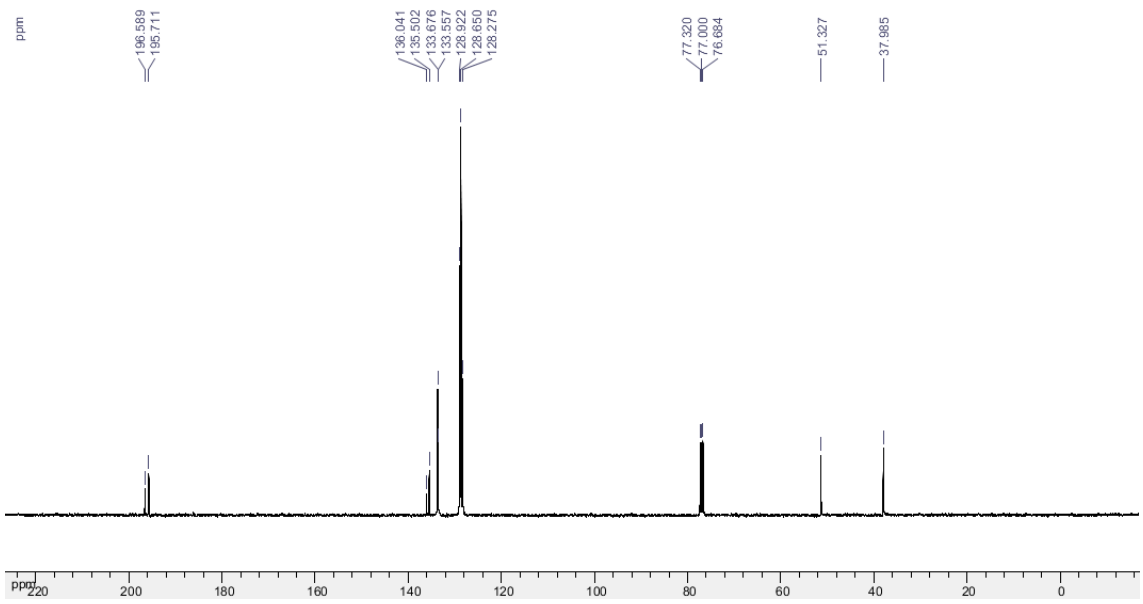
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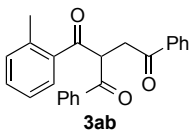
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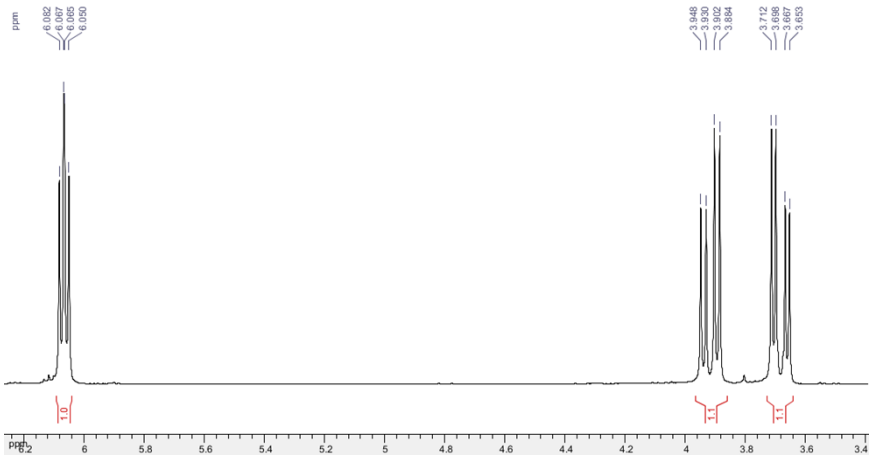
**3ab**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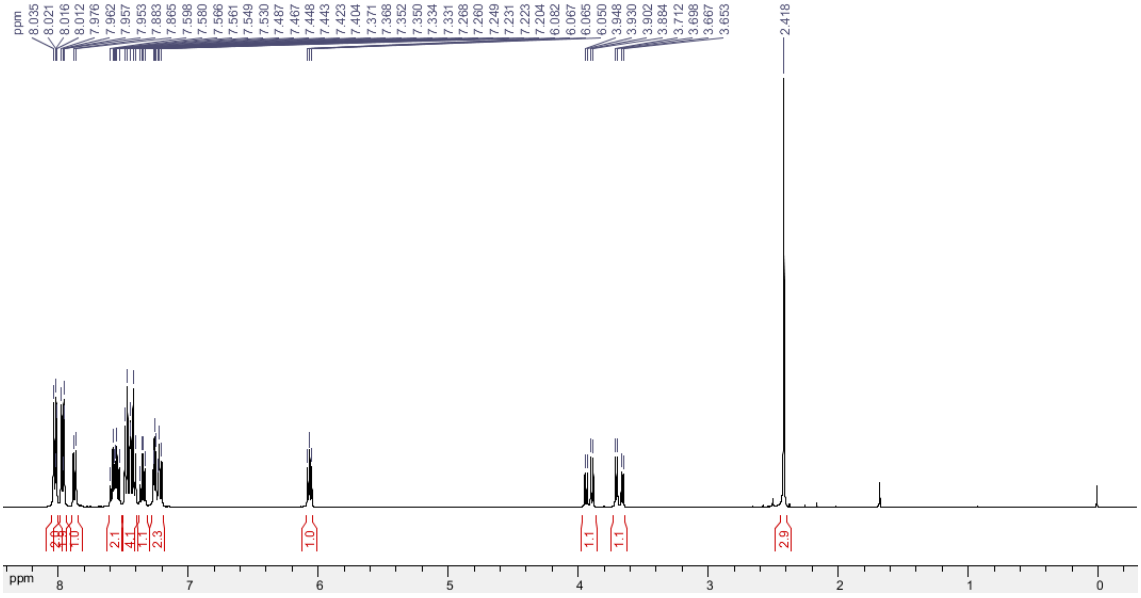
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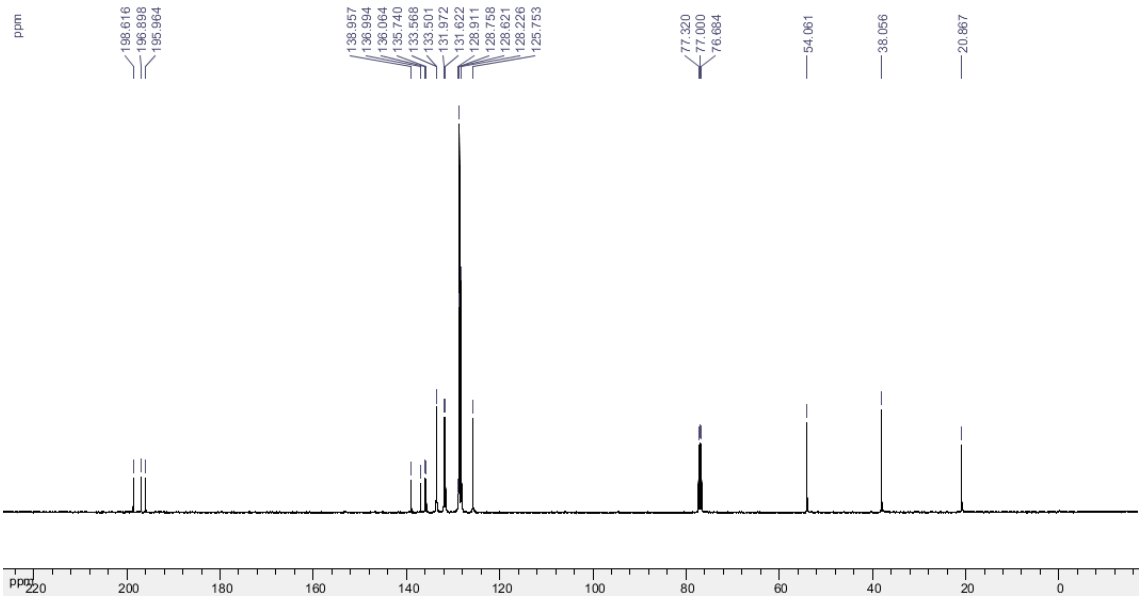
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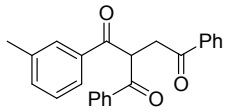


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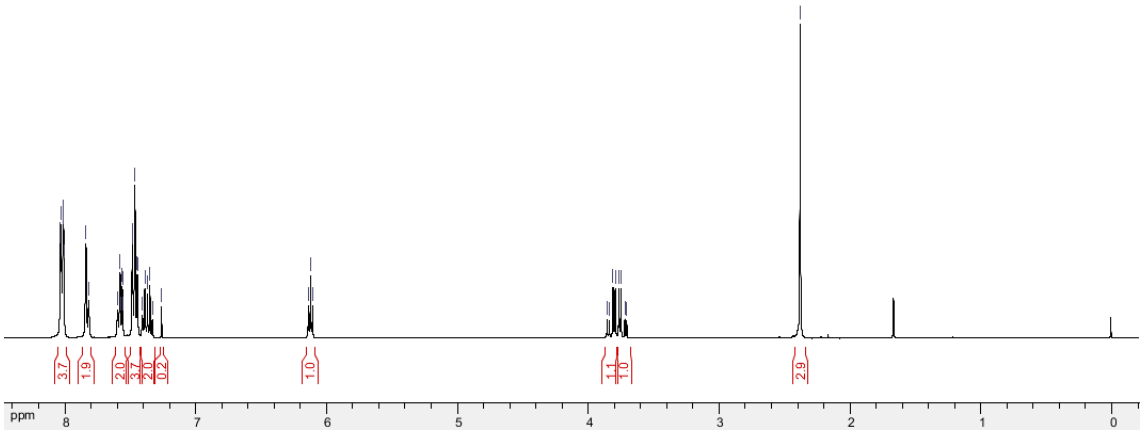

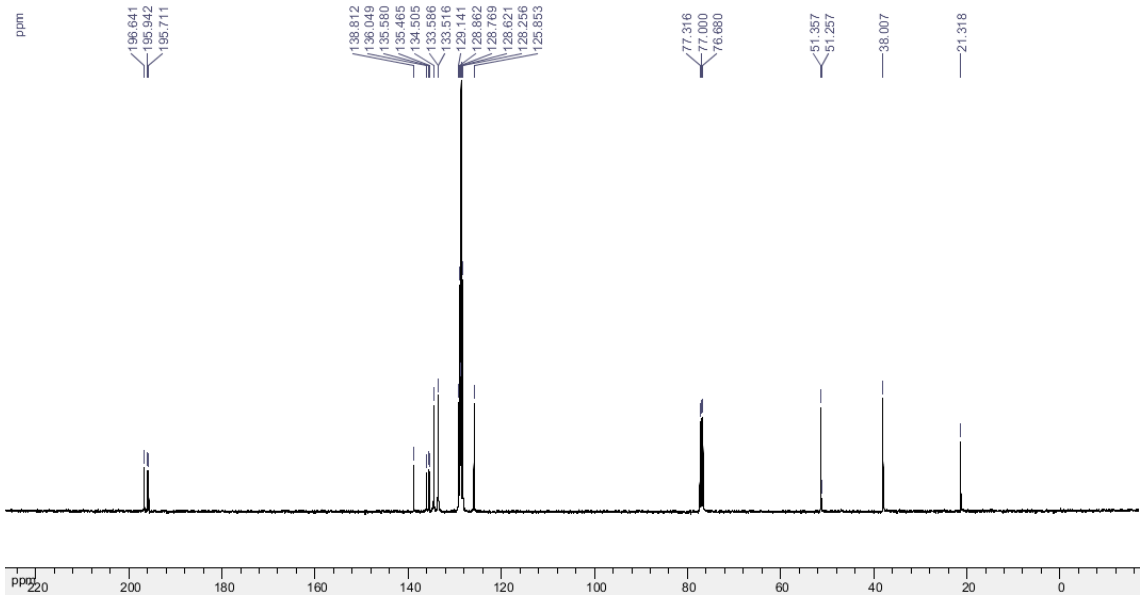

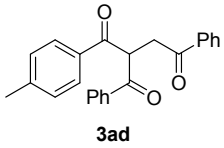
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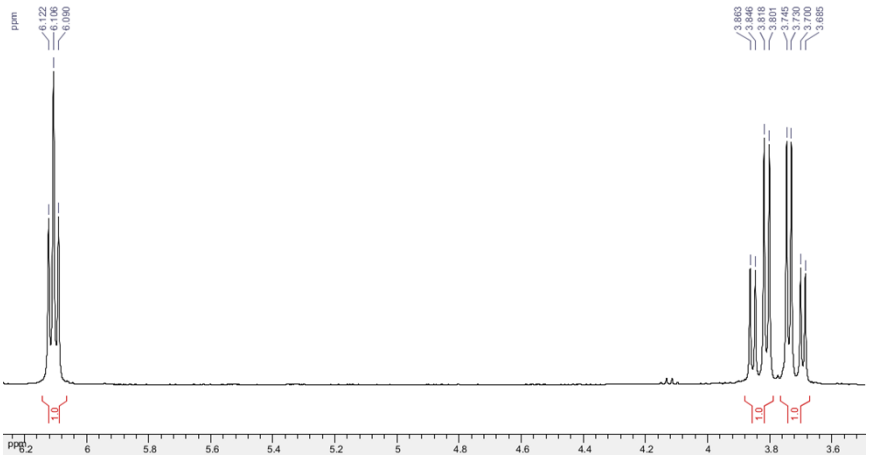
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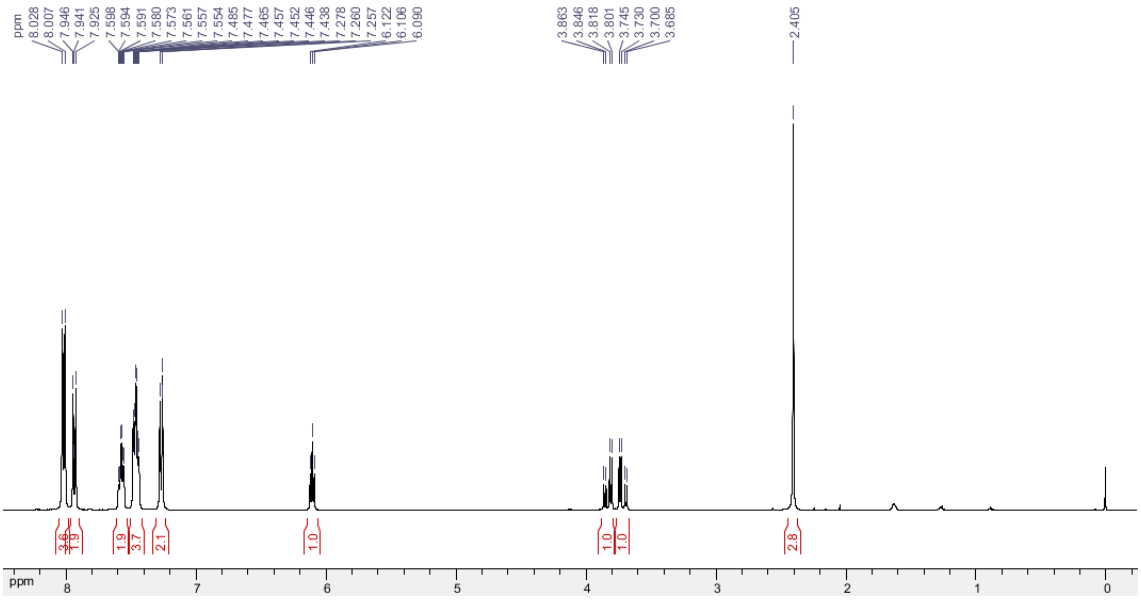
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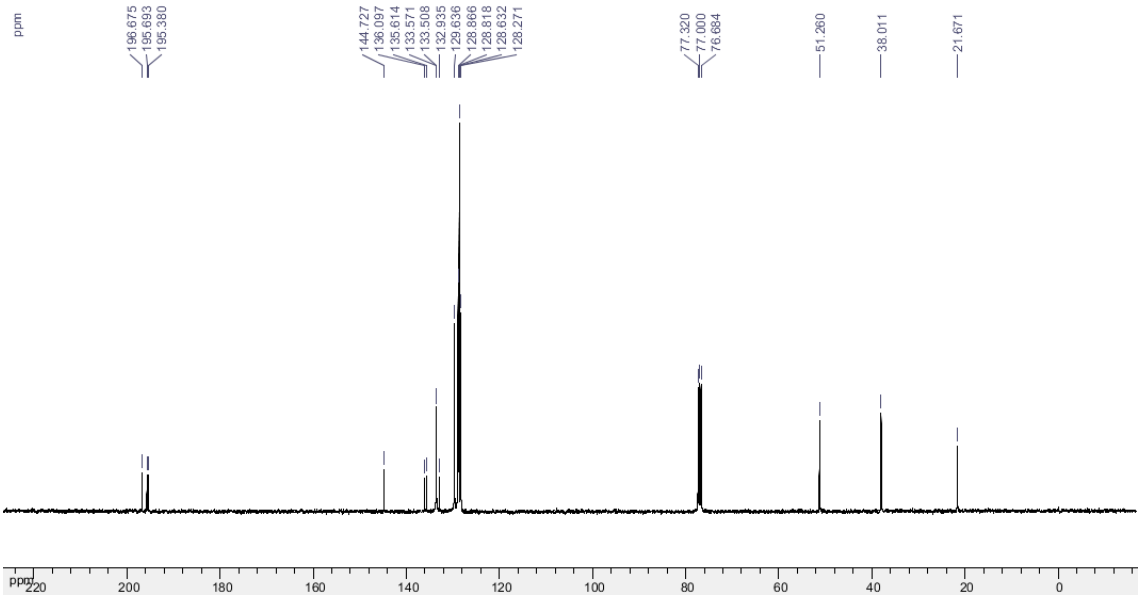
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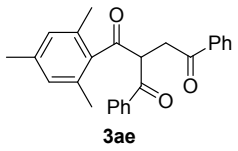
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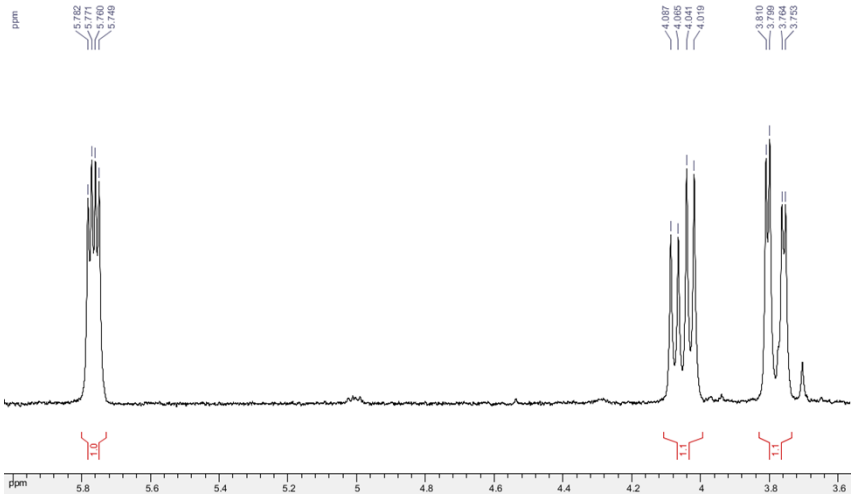
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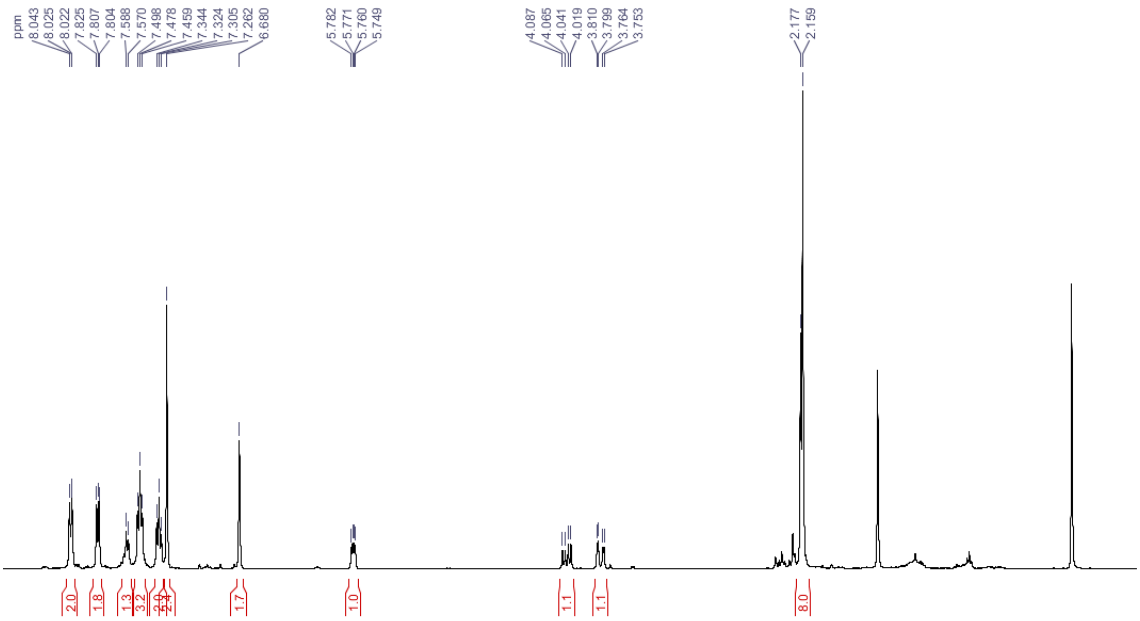
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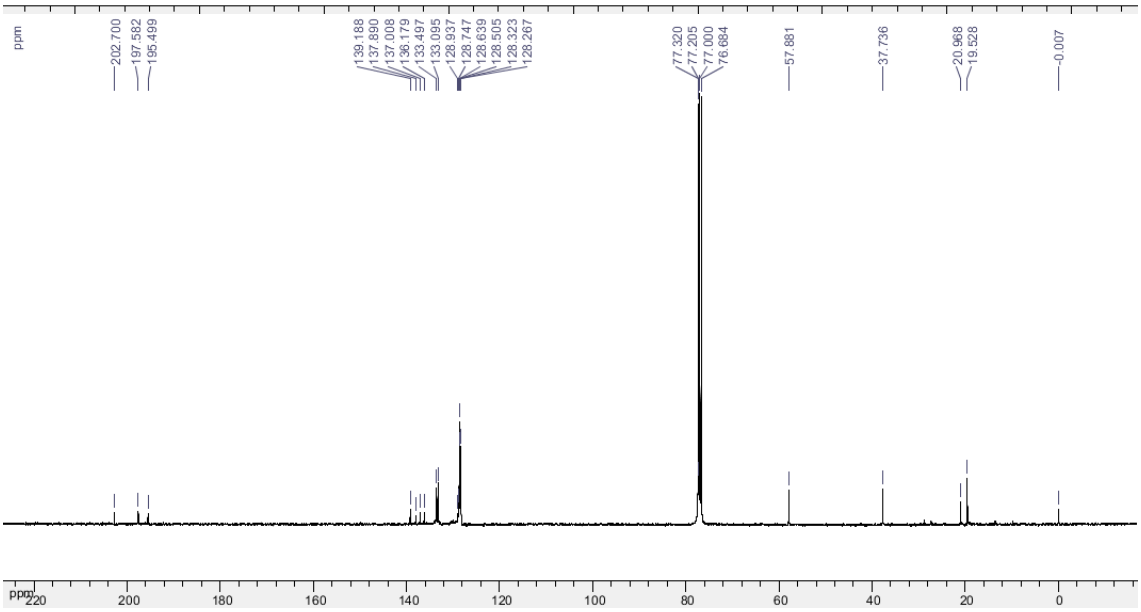
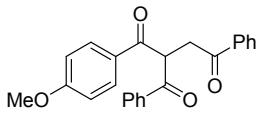
7.262
6.680
5.782
5.771
5.760
5.749
4.087
4.065
4.041
4.019
3.810
3.799
3.764
3.753
2.177
2.159
2.0
1.8
1.3
3.2
2.4
1.7
1.0
1.1
1.1
8.0


ppm
202.700
197.582
195.499
139.188
137.890
137.008
136.179
133.497
133.095
128.937
128.747
128.639
128.505
128.323
128.267
77.320
77.205
77.000
76.684
57.881
37.736
20.968
19.528
0.007
ppm
220
200
180
160
140
120
100
80
60
40
20
0

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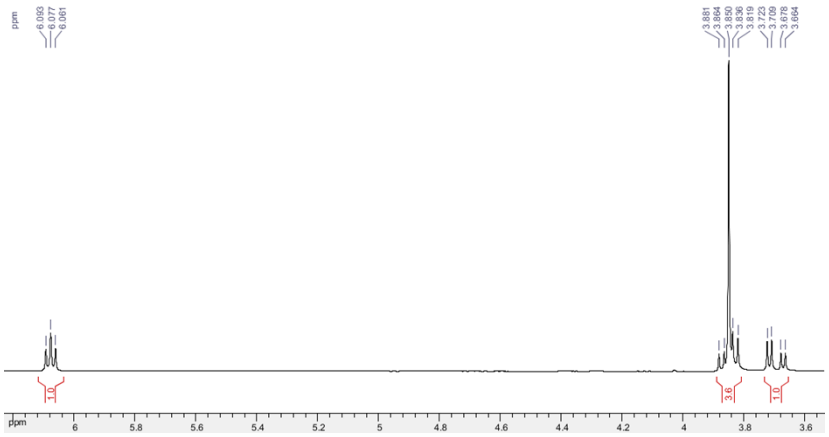
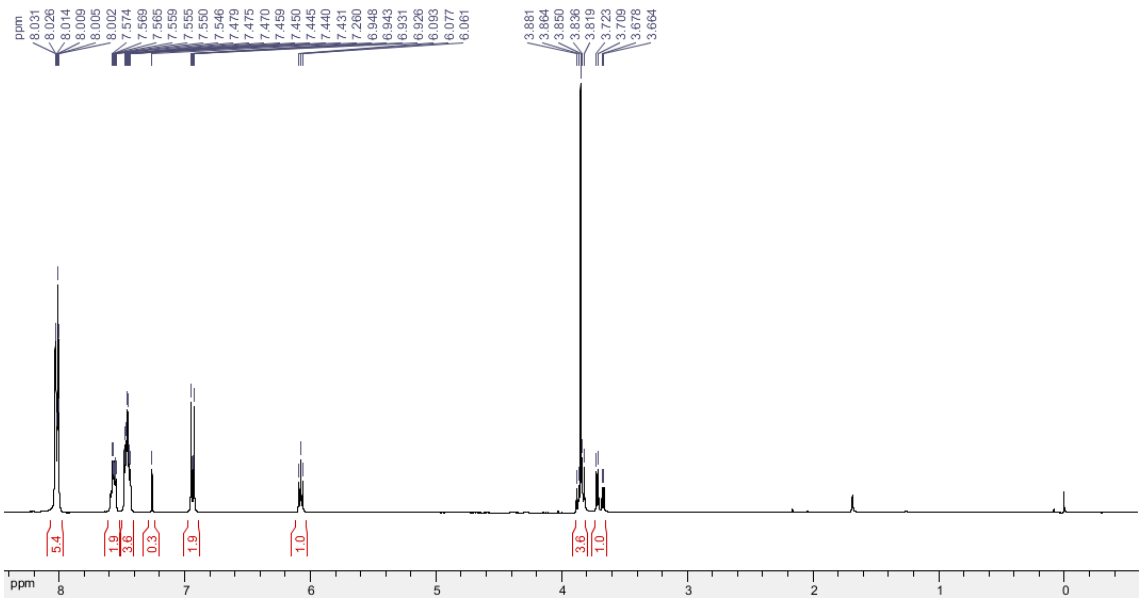
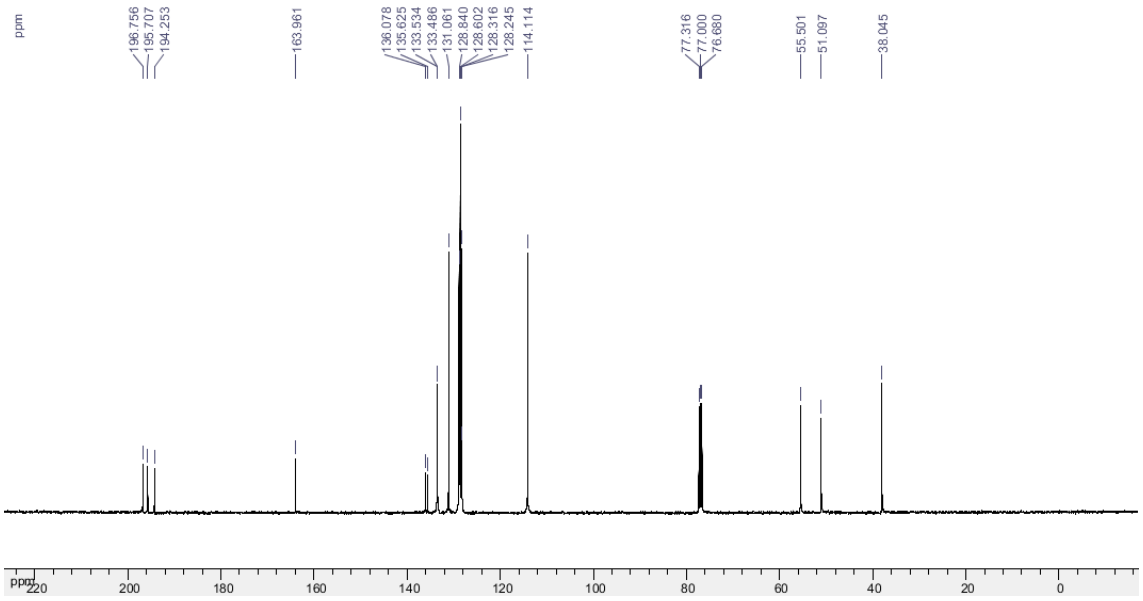
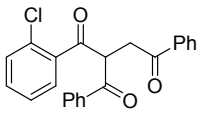
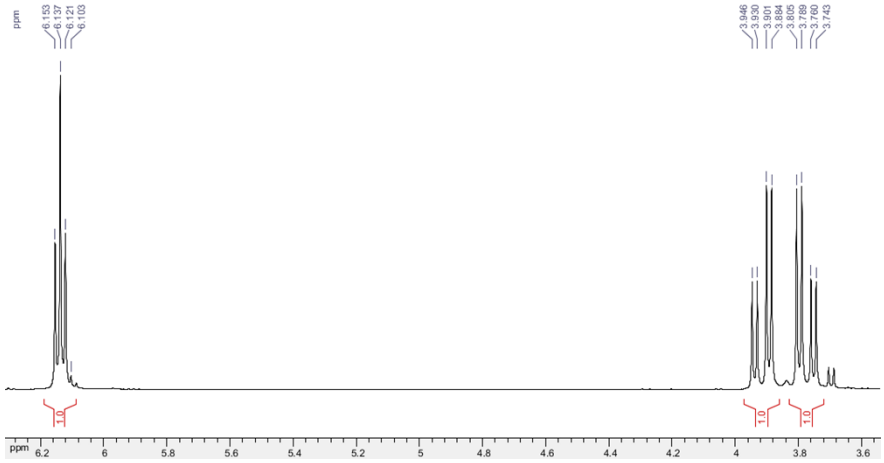


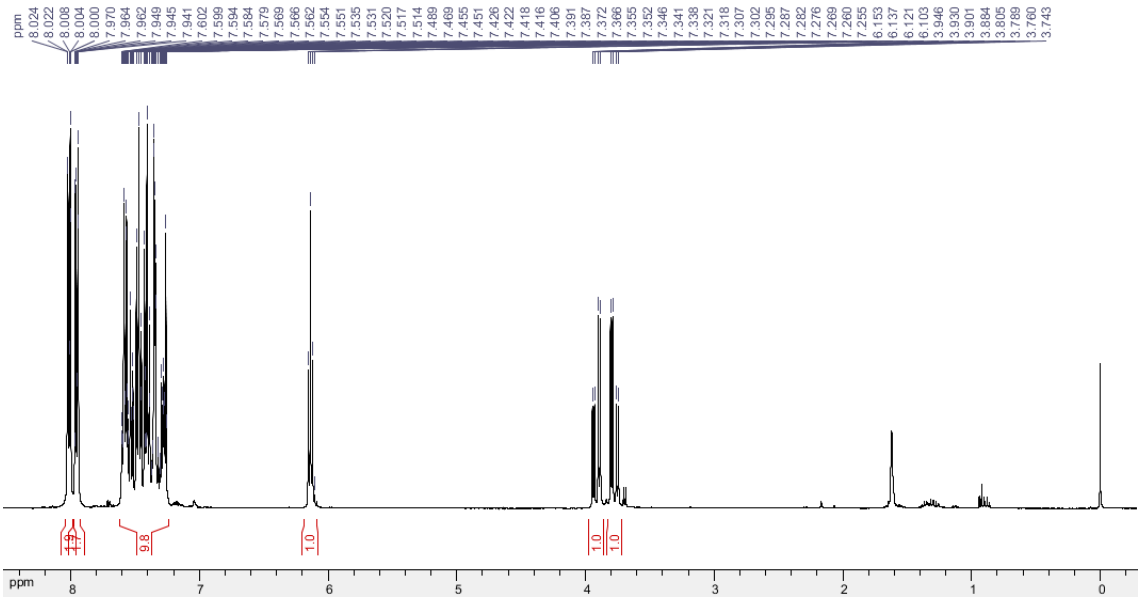


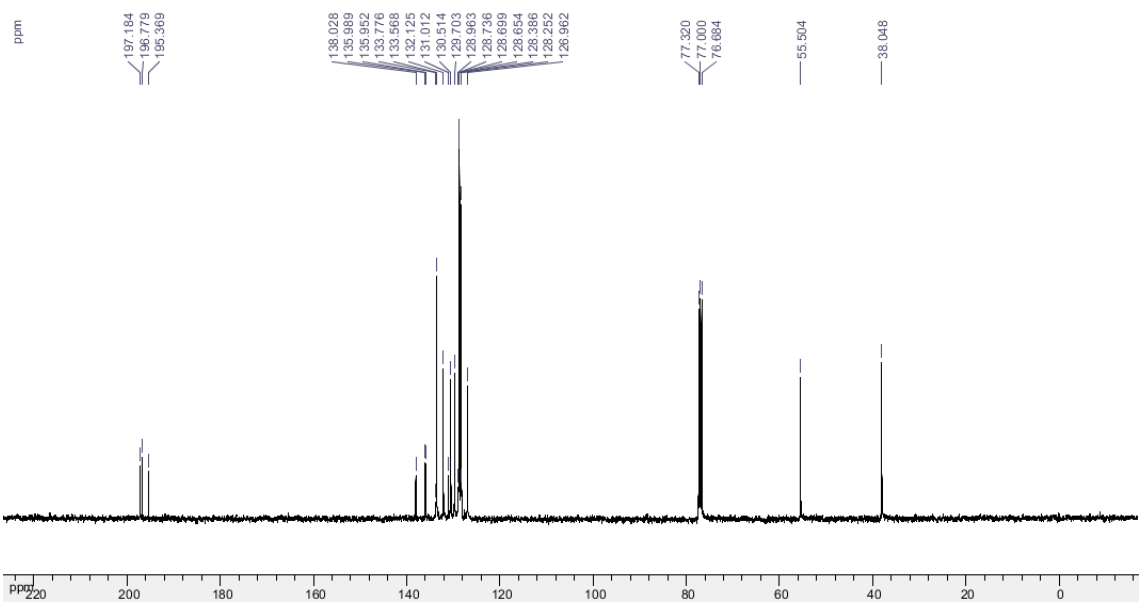



Cl
O
Ph
Ph
O
O

**3ag**


ppm
6.153
6.137
6.121
6.103
3.946
3.930
3.901
3.884
3.805
3.789
3.760
3.743
1.0
1.0
1.0
ppm
6.2
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6


ppm
8.024
8.022
8.008
8.004
8.000
7.970
7.964
7.962
7.949
7.945
7.941
7.602
7.599
7.594
7.584
7.579
7.569
7.566
7.562
7.554
7.551
7.535
7.531
7.520
7.517
7.514
7.489
7.469
7.455
7.451
7.426
7.422
7.418
7.416
7.406
7.391
7.387
7.372
7.366
7.355
7.352
7.346
7.341
7.338
7.321
7.318
7.307
7.302
7.295
7.287
7.282
7.276
7.269
7.260
7.255
6.153
6.137
6.121
6.103
3.946
3.930
3.901
3.884
3.805
3.789
3.760
3.743
4.9
9.8
1.0
1.0
1.0
ppm
8
7
6
5
4
3
2
1
0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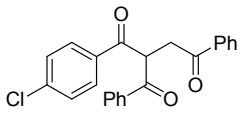
195.369
138.028
135.989
135.952
133.776
133.568
132.125
131.012
130.514
129.703
128.963
128.736
128.699
128.654
128.386
128.252
126.962
77.320
77.000
76.684
55.504
38.048
ppm
220
200
180
160
140
120
100
80
60
40
20
0

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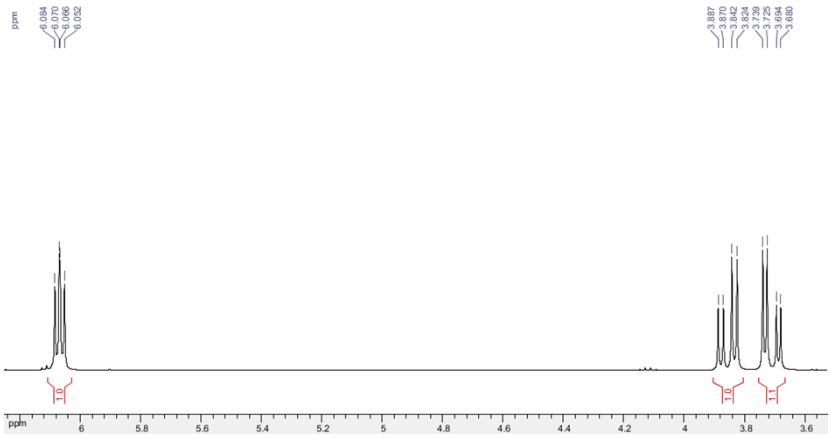
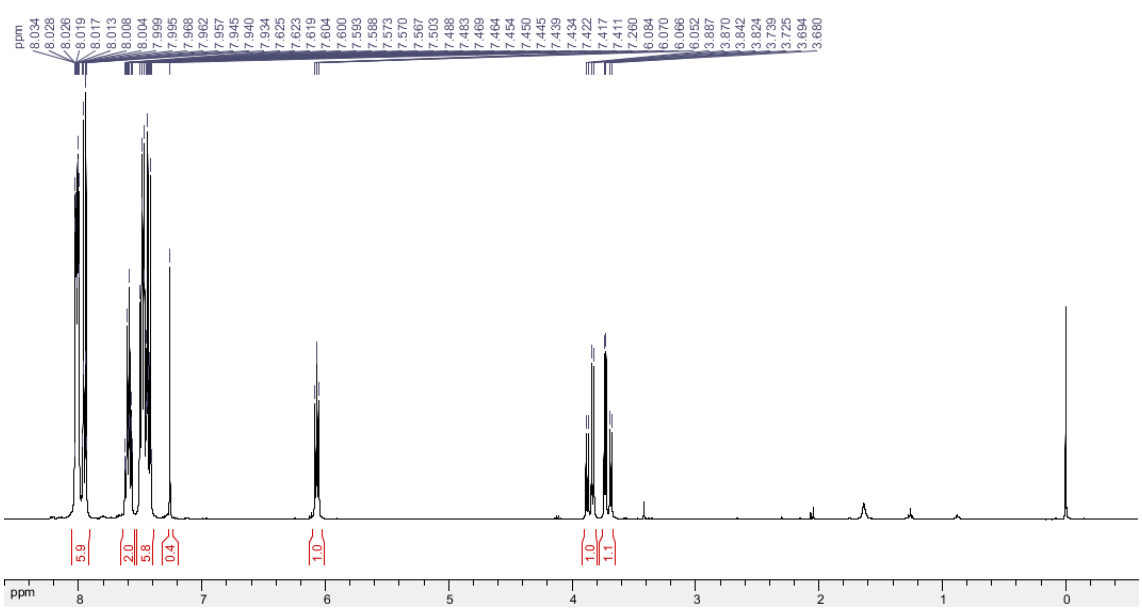
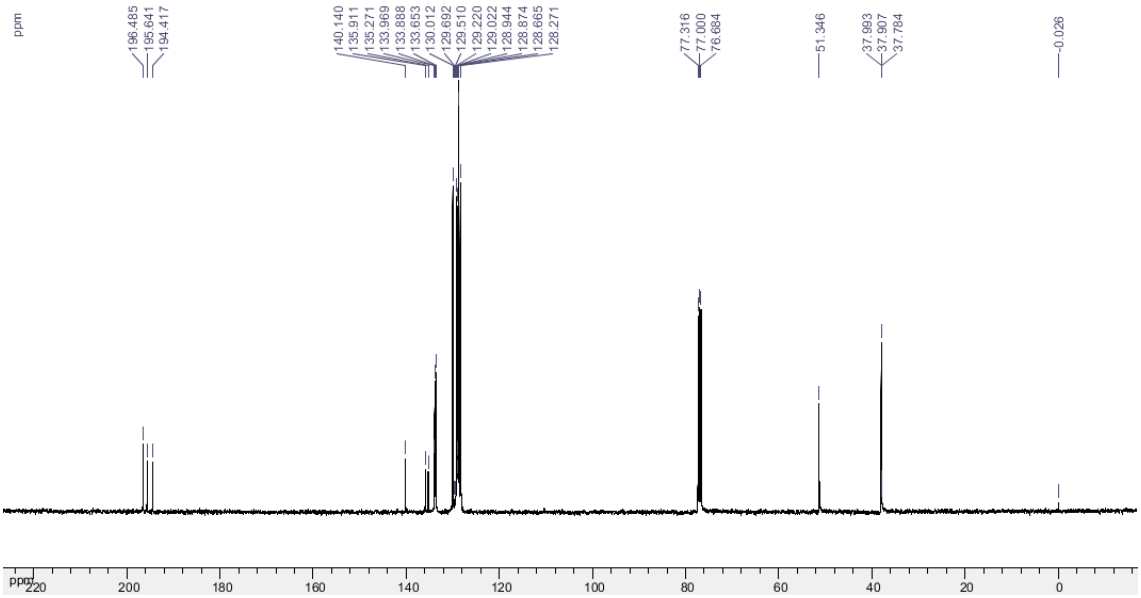
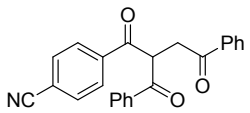
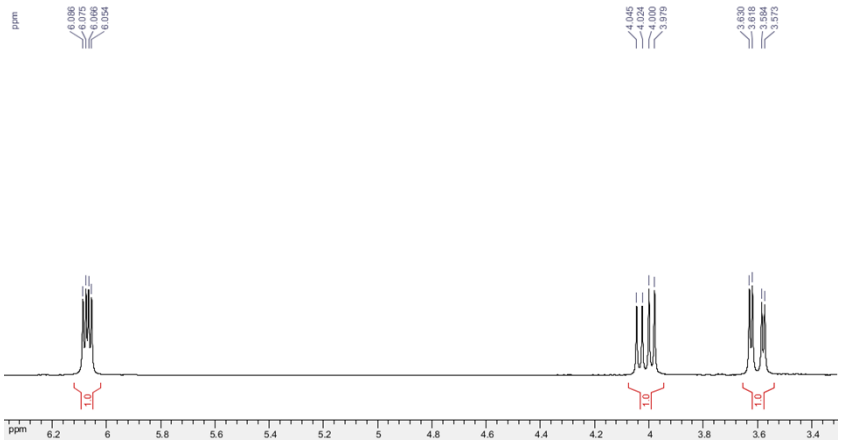


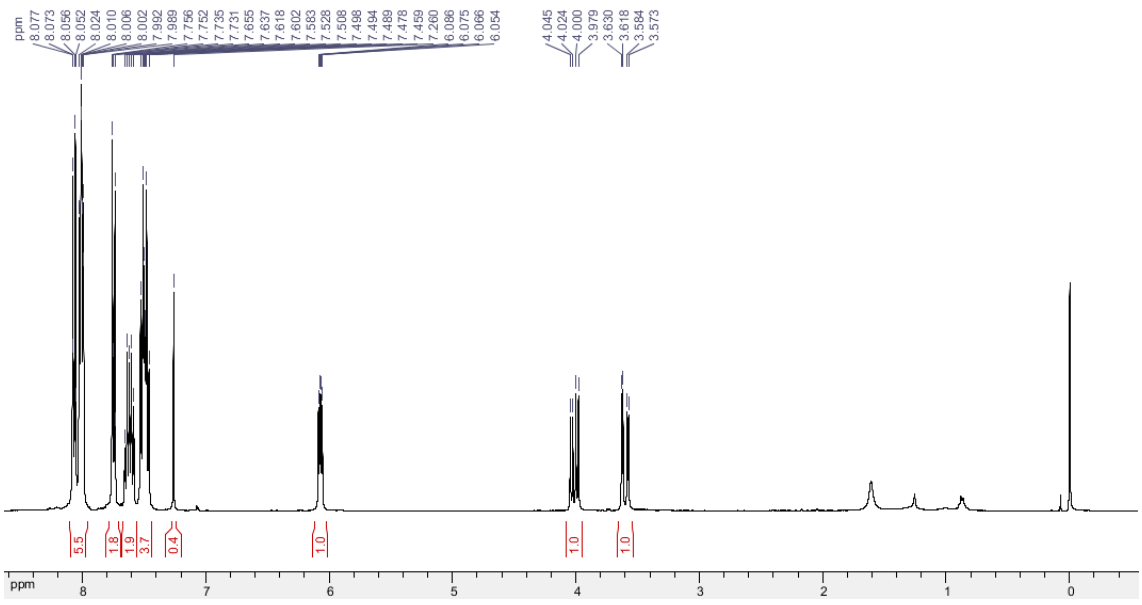


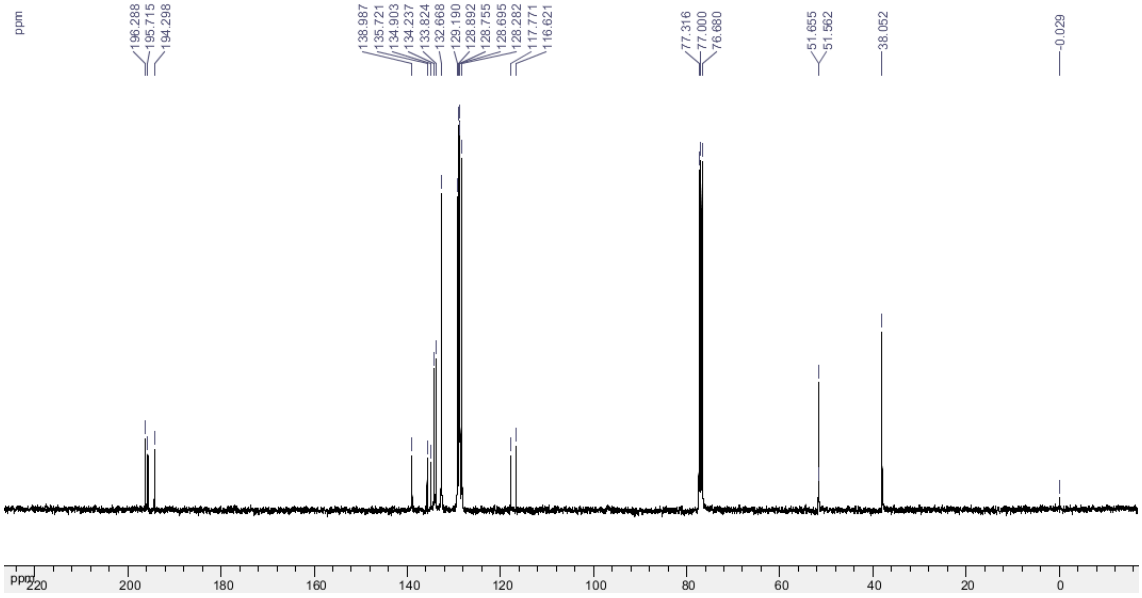


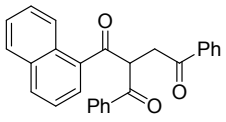



**3ai**

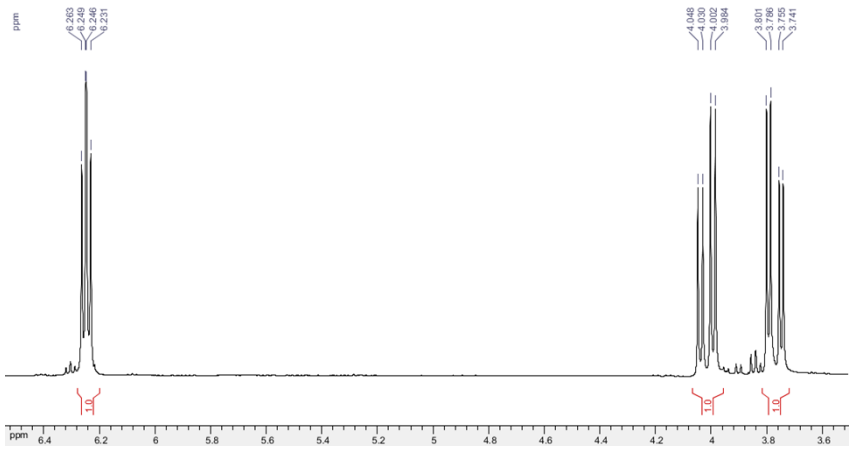


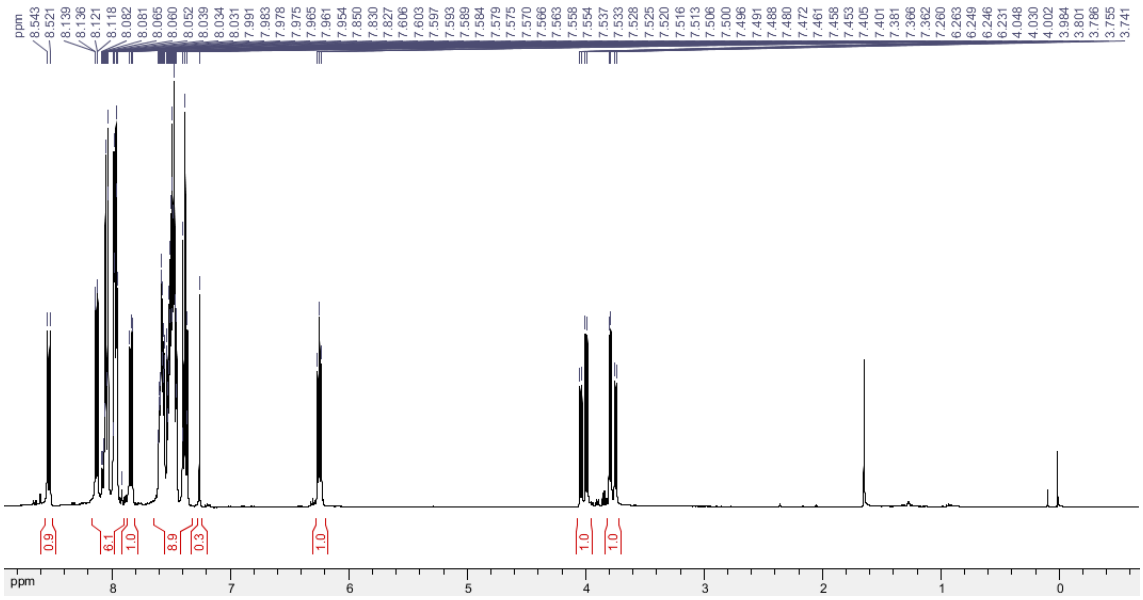


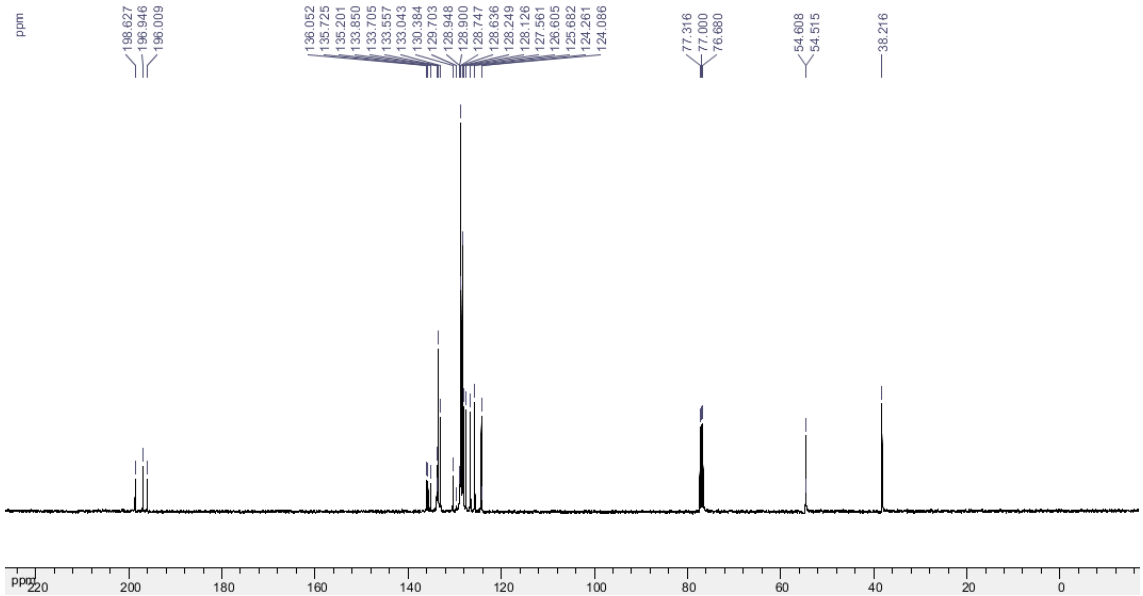


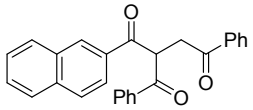

O
Ph
Ph
O
O

**3aj**

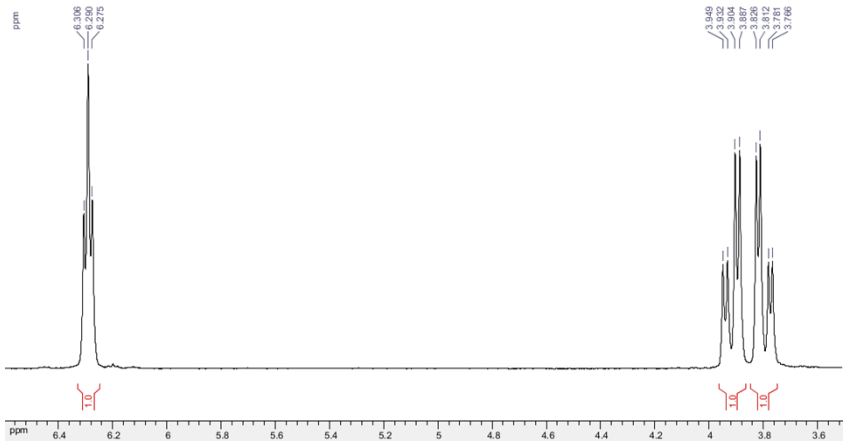

ppm
6.263
6.249
6.246
6.231
4.048
4.030
4.002
3.984
3.801
3.786
3.755
3.741
1.0
1.0
1.0
ppm 6.4 6.2 6 5.8 5.6 5.4 5.2 5 4.8 4.6 4.4 4.2 4 3.8 3.6

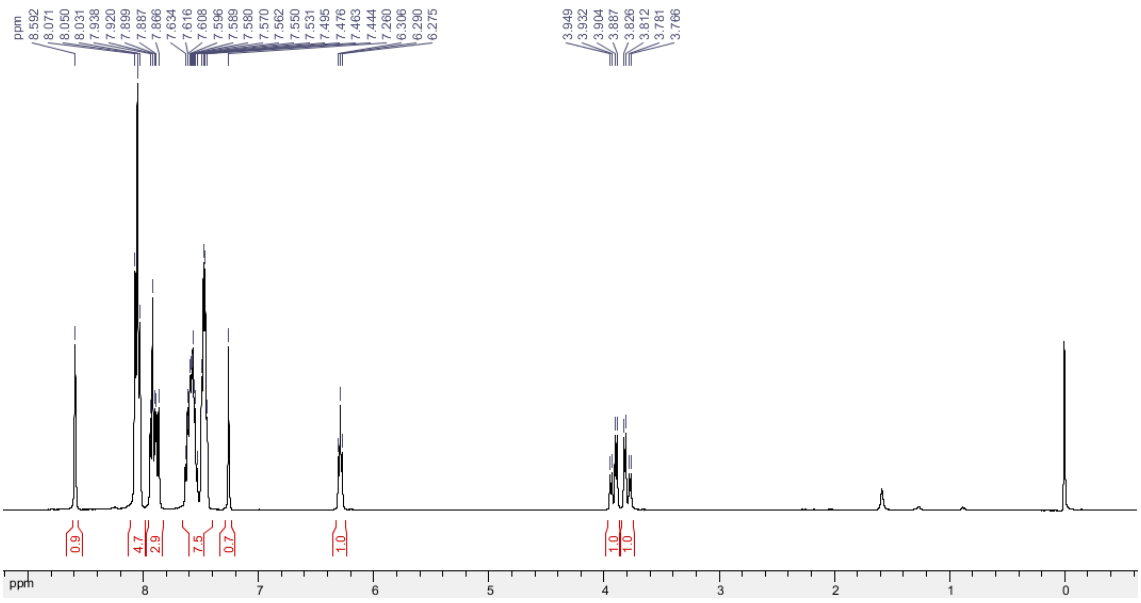

ppm
8.543
8.521
8.139
8.136
8.121
8.118
8.082
8.081
8.065
8.060
8.052
8.039
8.034
8.031
7.991
7.983
7.978
7.975
7.965
7.961
7.954
7.850
7.830
7.827
7.606
7.603
7.597
7.593
7.589
7.584
7.579
7.575
7.570
7.566
7.563
7.558
7.554
7.537
7.533
7.528
7.525
7.520
7.516
7.513
7.506
7.500
7.496
7.491
7.488
7.480
7.472
7.461
7.458
7.453
7.405
7.401
7.381
7.366
7.362
7.260
6.263
6.249
6.246
6.231
4.048
4.030
4.002
3.984
3.801
3.786
3.755
3.741
0.9
6.1
1.0
8.9
0.3
1.0
1.0
1.0
ppm 8 7 6 5 4 3 2 1 0

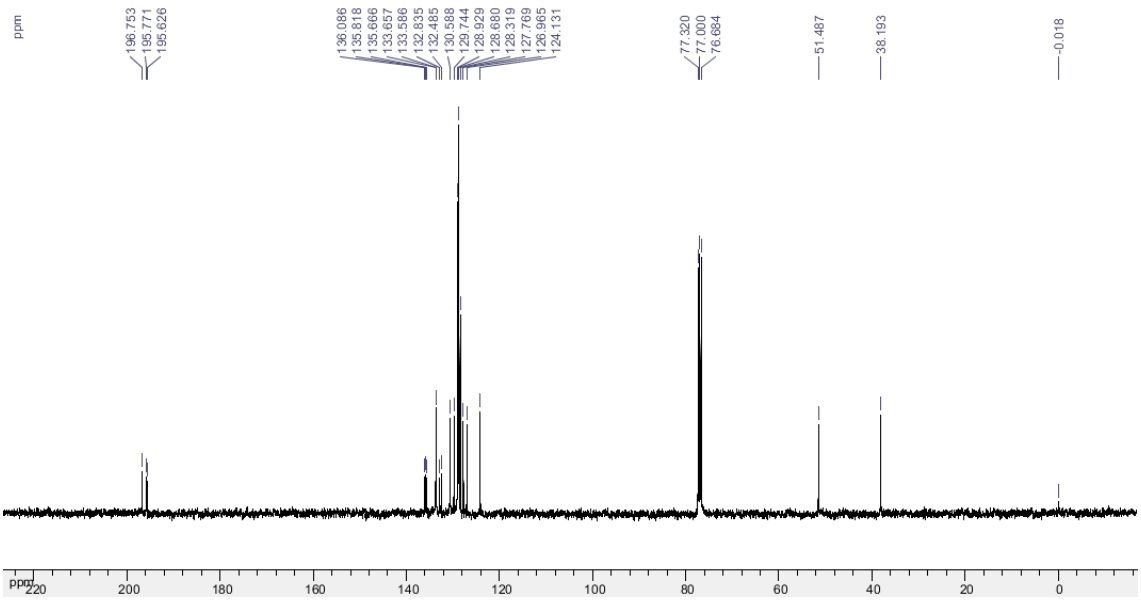

ppm
198.627
196.946
196.009
136.052
135.725
135.201
133.850
133.705
133.557
133.043
130.384
129.703
128.948
128.900
128.747
128.636
128.249
128.126
127.561
126.605
125.682
124.261
124.086
77.316
77.000
76.680
54.608
54.515
38.216
ppm 220 200 180 160 140 120 100 80 60 40 20 0

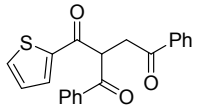

O
Ph
Ph
O
O

**3ak**

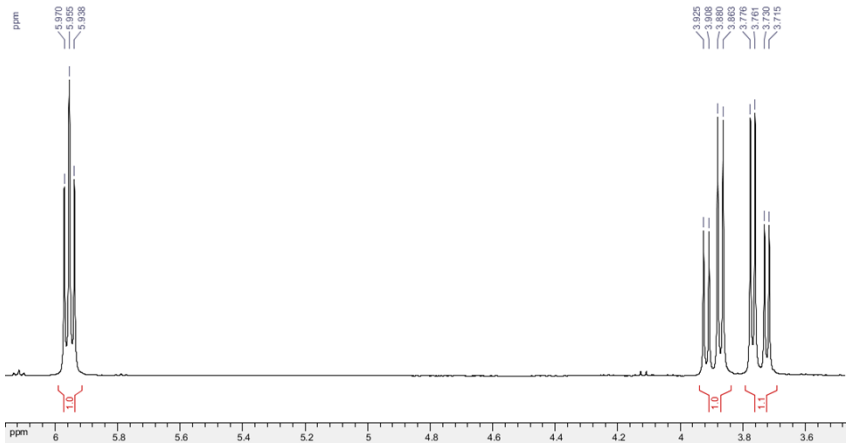

ppm
6.306
6.290
6.275
3.949
3.932
3.904
3.887
3.826
3.812
3.781
3.766
1.0
1.0
1.0
ppm
6.4
6.2
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6

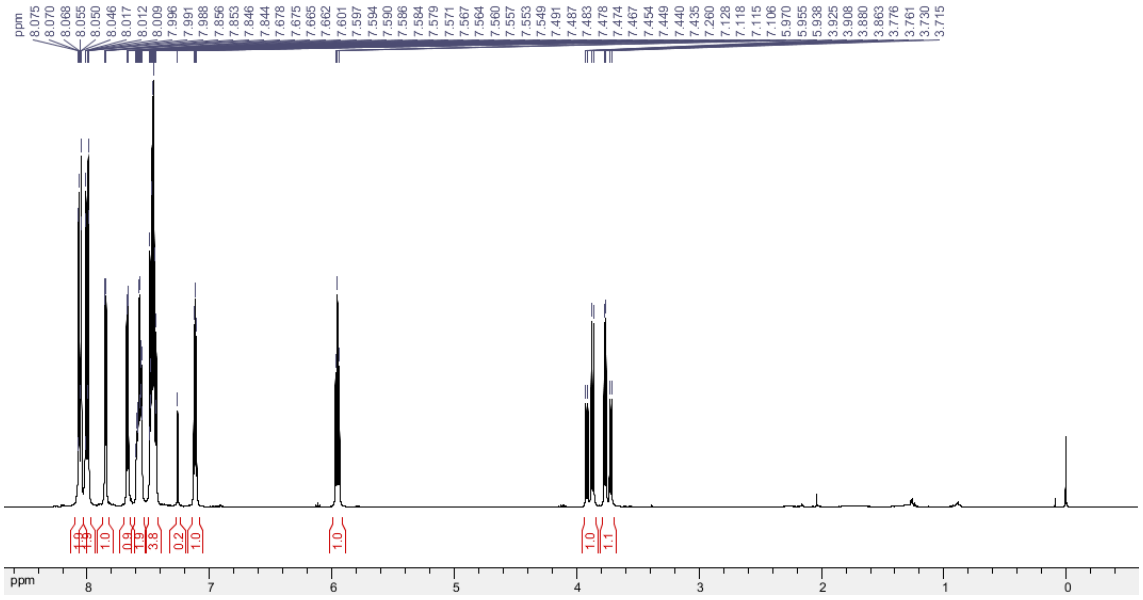

ppm
8.592
8.071
8.050
8.031
7.938
7.920
7.899
7.887
7.866
7.634
7.616
7.608
7.596
7.589
7.580
7.570
7.562
7.550
7.531
7.495
7.476
7.463
7.444
7.260
6.306
6.290
6.275
3.949
3.932
3.904
3.887
3.826
3.812
3.781
3.766
0.9
4.7
2.9
7.5
0.7
1.0
1.0
1.0
ppm
8
7
6
5
4
3
2
1
0

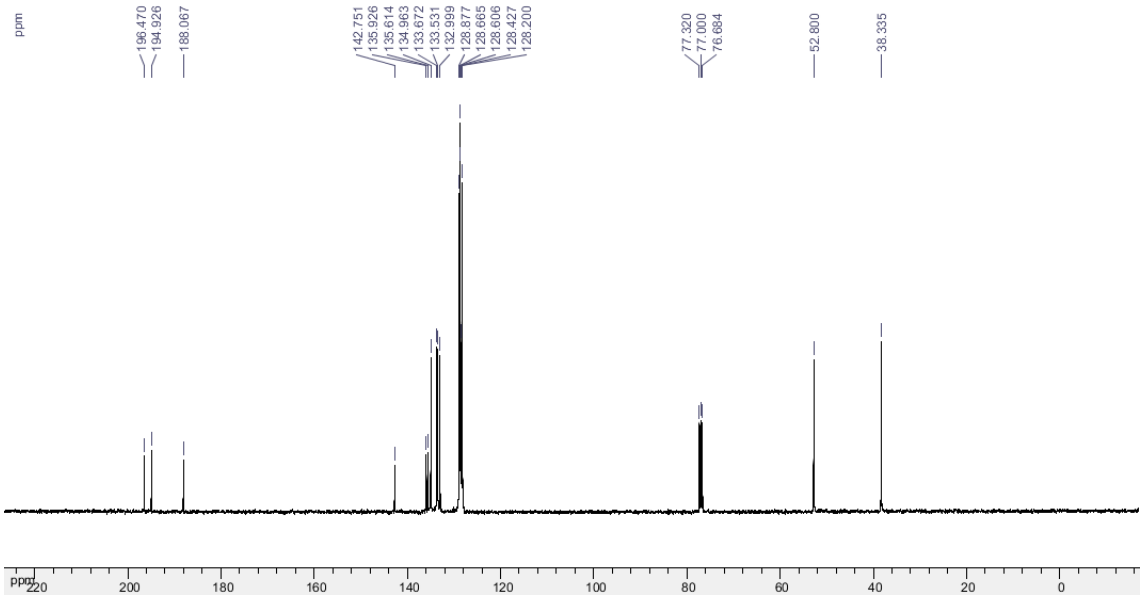

ppm
196.753
195.771
195.626
136.086
135.818
135.666
133.657
133.586
132.835
132.485
130.588
129.744
128.929
128.680
128.319
127.769
126.965
124.131
77.320
77.000
76.684
51.487
38.193
0.018
ppm
220
200
180
160
140
120
100
80
60
40
20
0


O
S
Ph
Ph
O
O

**3al**


ppm
5.970
5.955
5.938
3.925
3.908
3.880
3.863
3.776
3.761
3.730
3.715
1.0
1.0
1.1
ppm
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6


ppm
8.075
8.070
8.068
8.055
8.050
8.046
8.017
8.012
8.009
7.996
7.991
7.988
7.856
7.853
7.846
7.844
7.678
7.675
7.665
7.662
7.601
7.597
7.594
7.590
7.586
7.584
7.579
7.571
7.567
7.564
7.560
7.557
7.553
7.549
7.491
7.487
7.483
7.478
7.474
7.467
7.454
7.449
7.440
7.435
7.260
7.128
7.118
7.115
7.106
5.970
5.955
5.938
3.925
3.908
3.880
3.863
3.776
3.761
3.730
3.715
1.0
1.0
0.9
1.0
3.8
0.2
1.0
1.0
1.1
ppm
8
7
6
5
4
3
2
1
0


ppm
196.470
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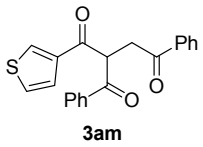
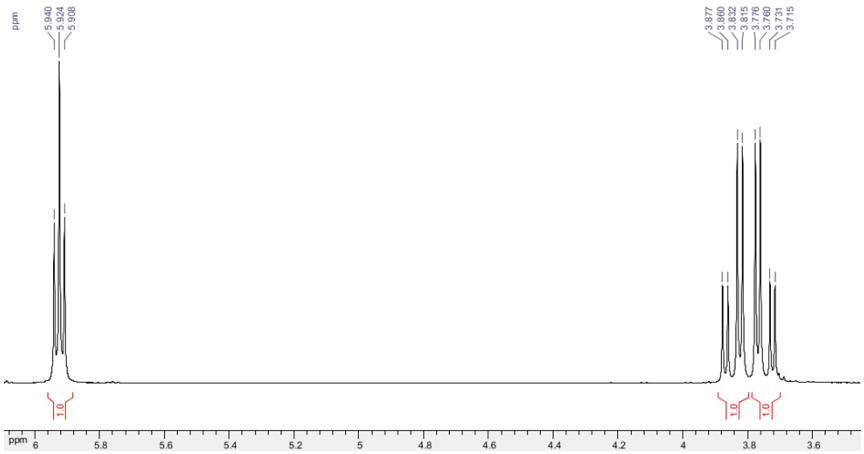
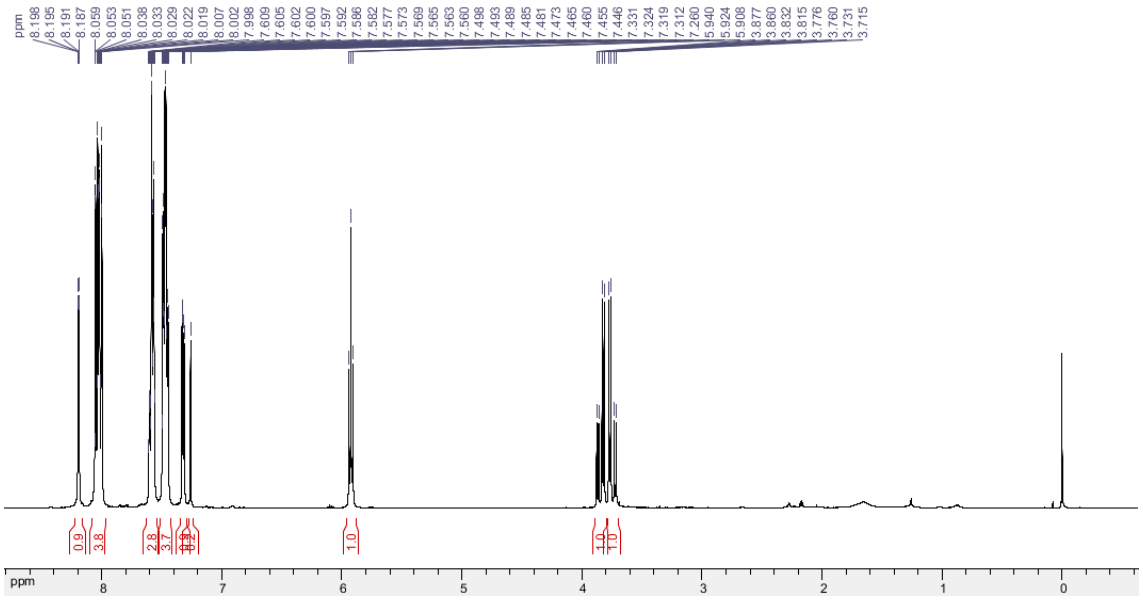
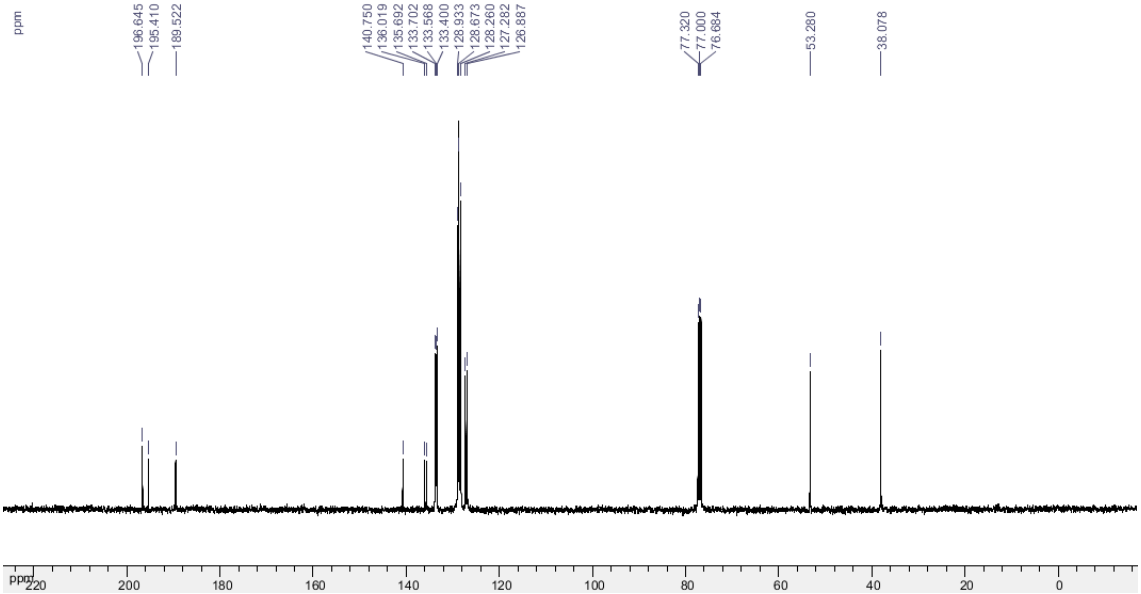
188.067
142.751
135.926
135.614
134.963
133.672
133.531
132.999
128.877
128.665
128.606
128.427
128.200
77.320
77.000
76.684
52.800
38.335
ppm
220
200
180
160
140
120
100
80
60
40
20
0

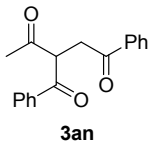

O
Ph
S
Ph
O
O

**3am**

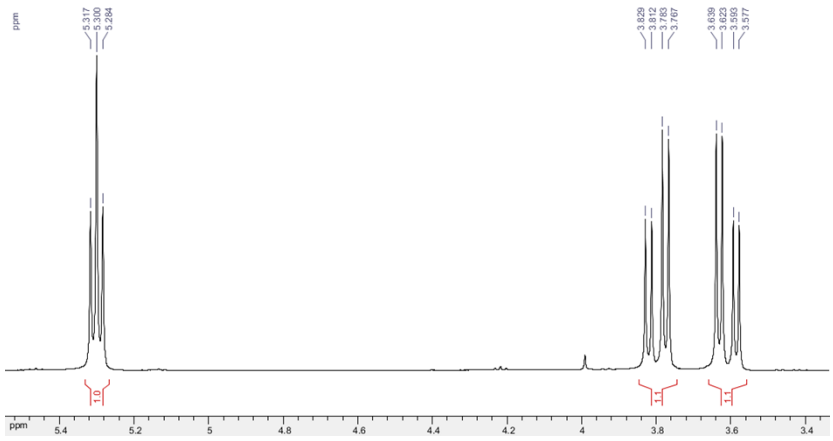

ppm
5.940
5.924
5.908
3.877
3.860
3.832
3.815
3.776
3.760
3.731
3.715
1.0
1.0
1.0
1.0
ppm 6 5.8 5.6 5.4 5.2 5 4.8 4.6 4.4 4.2 4 3.8 3.6

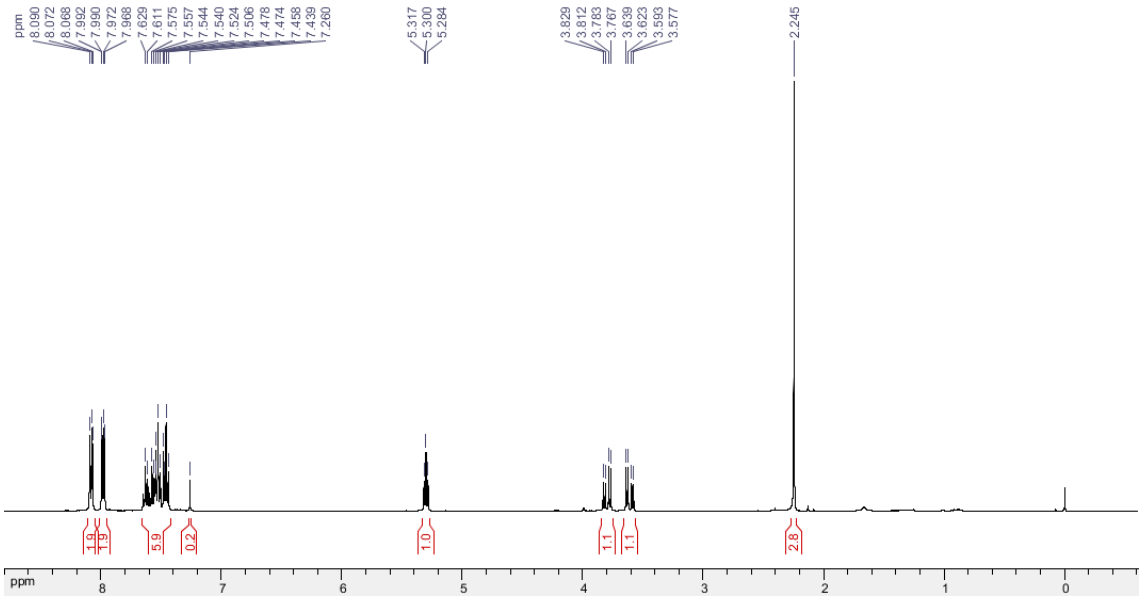

ppm
8.198
8.195
8.191
8.187
8.059
8.053
8.051
8.038
8.033
8.029
8.022
8.019
8.007
8.002
7.998
7.609
7.605
7.602
7.600
7.597
7.592
7.586
7.582
7.577
7.573
7.569
7.565
7.563
7.560
7.498
7.493
7.489
7.485
7.481
7.473
7.465
7.460
7.455
7.446
7.331
7.324
7.319
7.312
7.260
5.940
5.924
5.908
3.877
3.860
3.832
3.815
3.776
3.760
3.731
3.715
0.9
3.8
2.8
3.7
1.0
1.0
1.0
ppm 8 7 6 5 4 3 2 1 0


ppm
196.645
195.410
189.522
140.750
136.019
135.692
133.702
133.568
133.400
128.933
128.673
128.260
127.282
126.887
77.320
77.000
76.684
53.280
38.078
ppm 220 200 180 160 140 120 100 80 60 40 20 0


O
Ph
O
Ph
O

**3an**


ppm
5.317
5.300
5.284
3.829
3.812
3.783
3.767
3.639
3.623
3.593
3.577
1.0
1.1
1.1
ppm
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4


ppm
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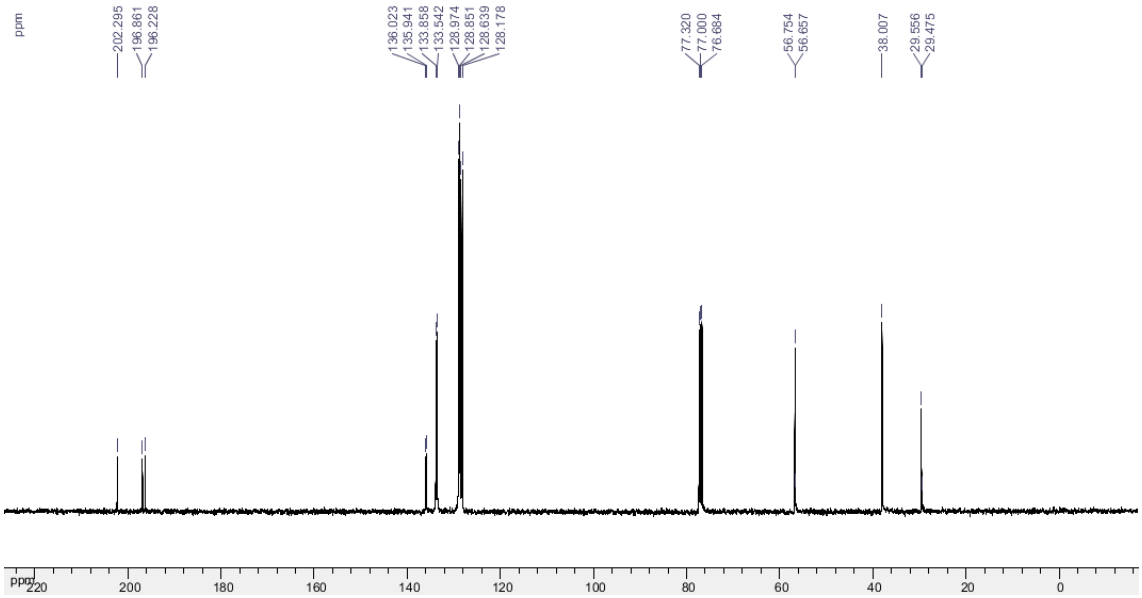
8.072
8.068
7.992
7.990
7.972
7.968
7.629
7.611
7.575
7.557
7.544
7.540
7.524
7.506
7.478
7.474
7.458
7.439
7.260
5.317
5.300
5.284
3.829
3.812
3.783
3.767
3.639
3.623
3.593
3.577
2.245
1.9
1.9
5.9
0.2
1.0
1.1
1.1
2.8
ppm
8
7
6
5
4
3
2
1
0


ppm
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196.228
136.023
135.941
133.858
133.542
128.974
128.851
128.639
128.178
77.320
77.000
76.684
56.754
56.657
38.007
29.556
29.475
ppm
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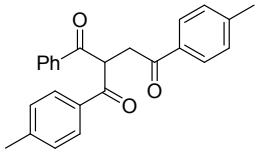
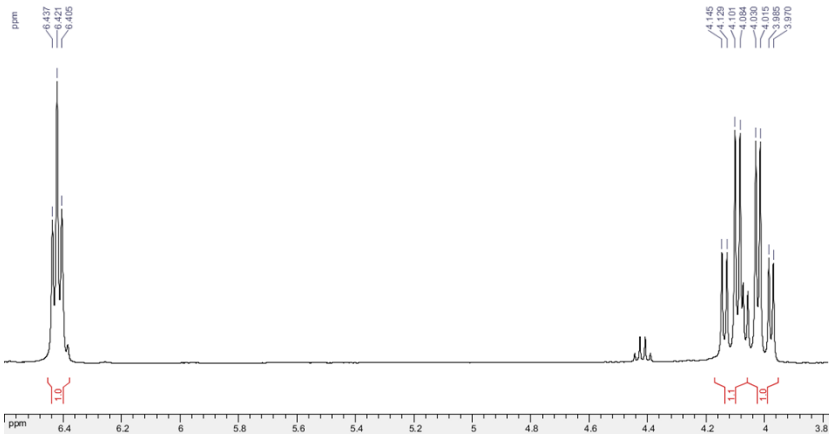
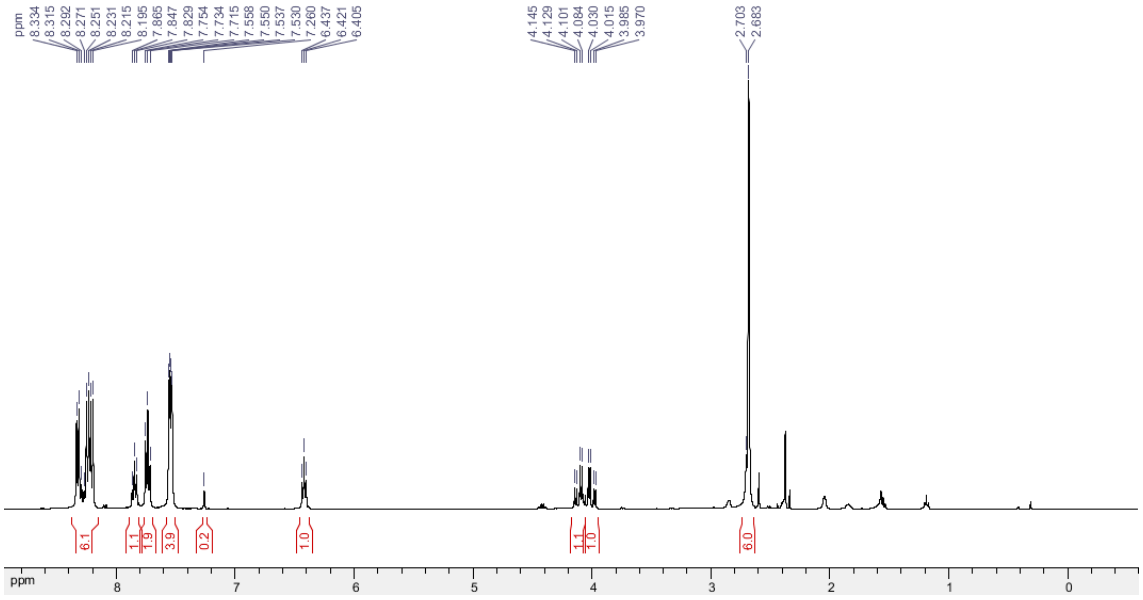
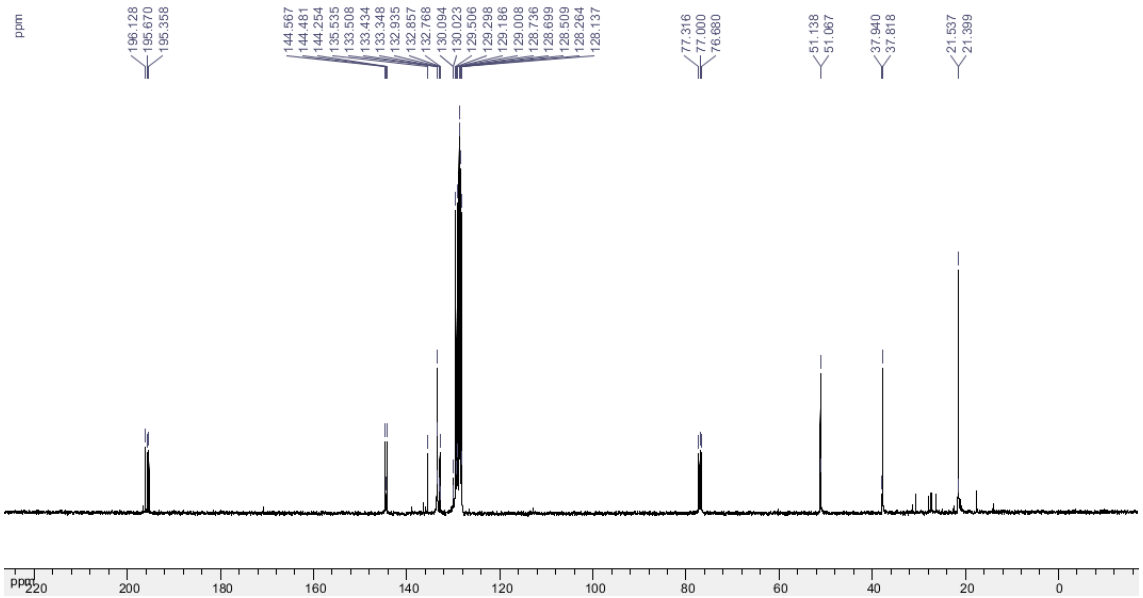
200
180
160
140
120
100
80
60
40
20
0


O
Ph
O
O

**3ba**


ppm
8.437
8.421
8.405
4.145
4.129
4.101
4.084
4.030
4.015
3.985
3.970
1.0
1.1
1.0
6.4
6.2
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8


ppm
8.334
8.315
8.292
8.271
8.251
8.231
8.215
8.195
7.865
7.847
7.829
7.754
7.734
7.715
7.558
7.550
7.537
7.530
7.260
6.437
6.421
6.405
4.145
4.129
4.101
4.084
4.030
4.015
3.985
3.970
2.703
2.683
6.1
1.1
1.9
3.9
0.2
1.0
1.1
1.0
6.0
8
7
6
5
4
3
2
1
0


ppm
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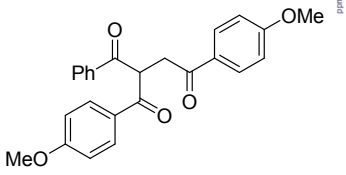
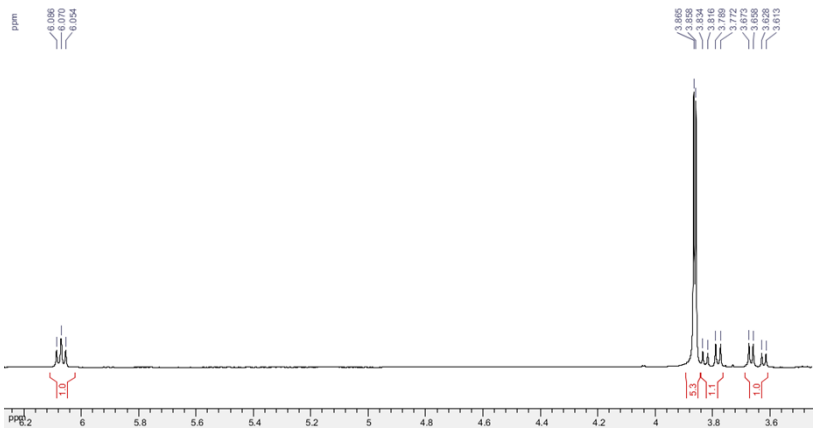
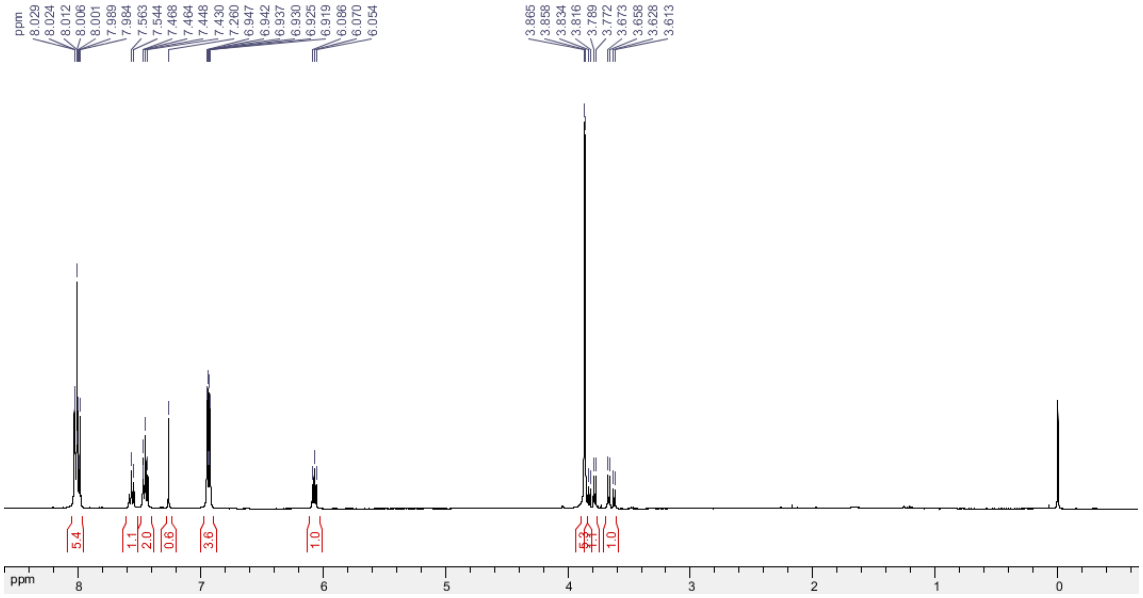
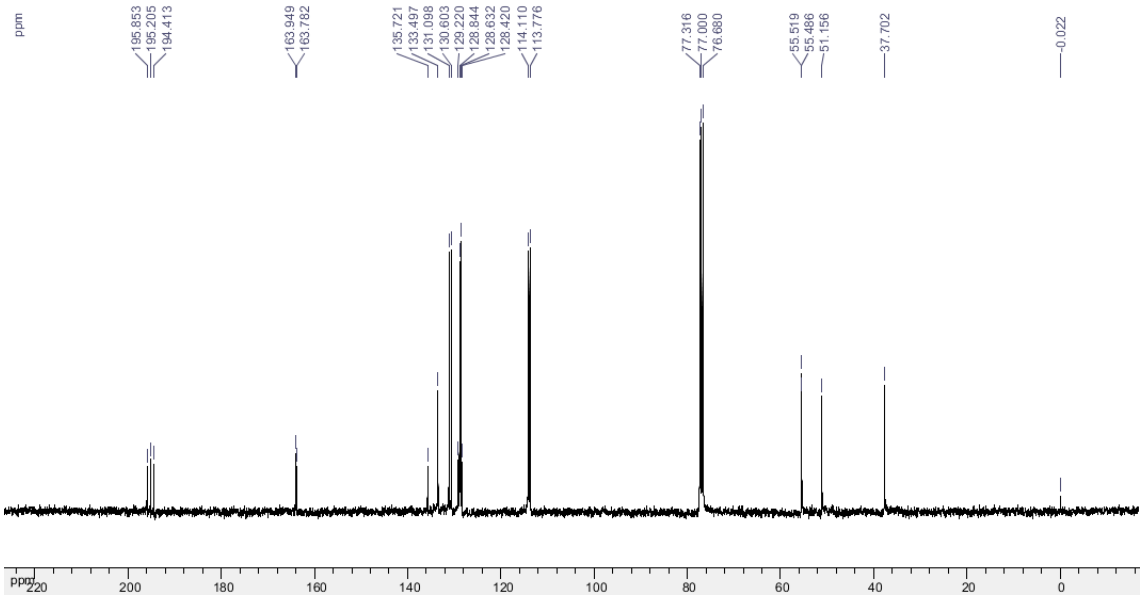
195.358
144.567
144.481
144.254
135.535
133.508
133.434
133.348
132.935
132.857
132.768
130.094
130.023
129.506
129.298
129.186
129.008
128.736
128.699
128.509
128.264
128.137
77.316
77.000
76.680
51.138
51.067
37.940
37.818
21.537
21.399
220
200
180
160
140
120
100
80
60
40
20
0

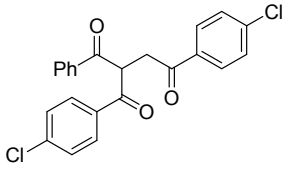



**3ca**

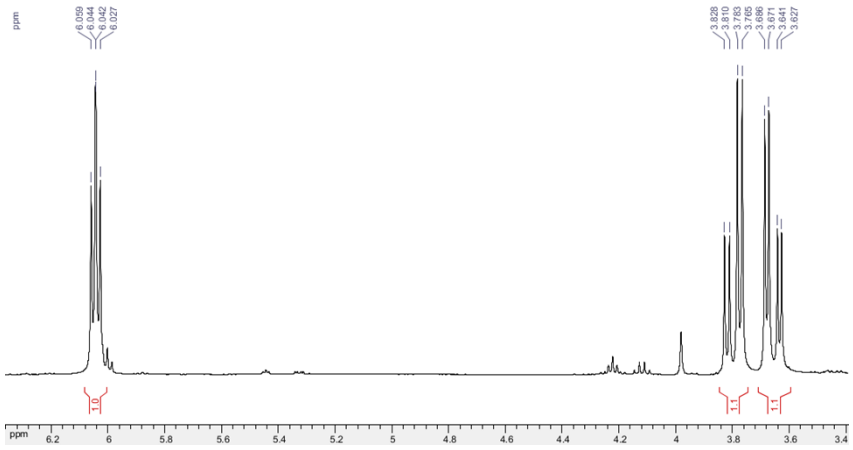


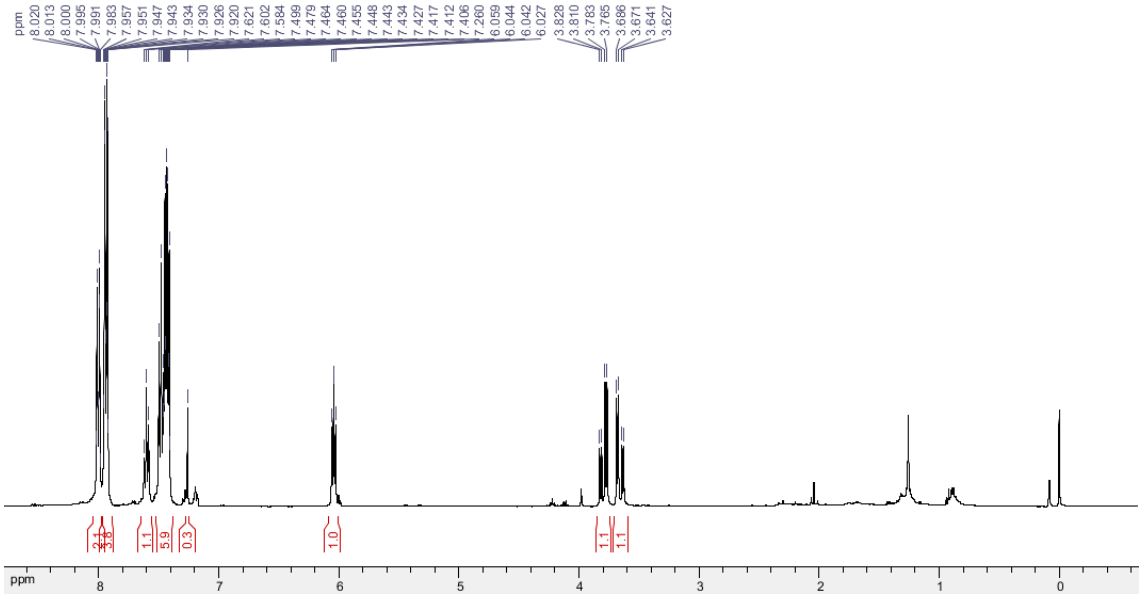


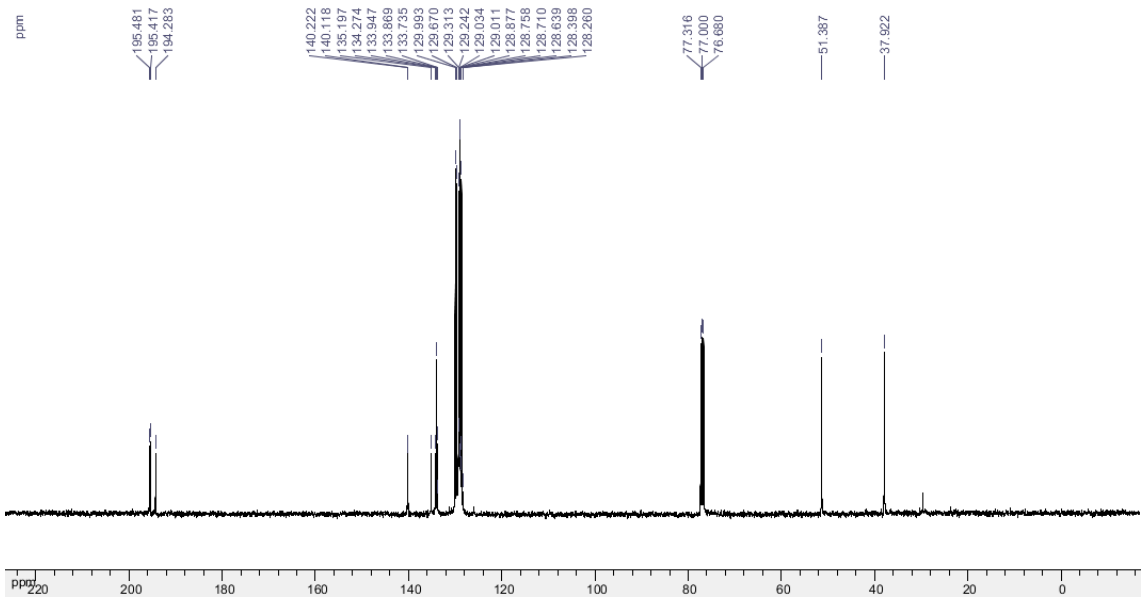


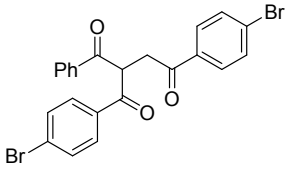

O
Ph
O
O
Cl
Cl

**3da**

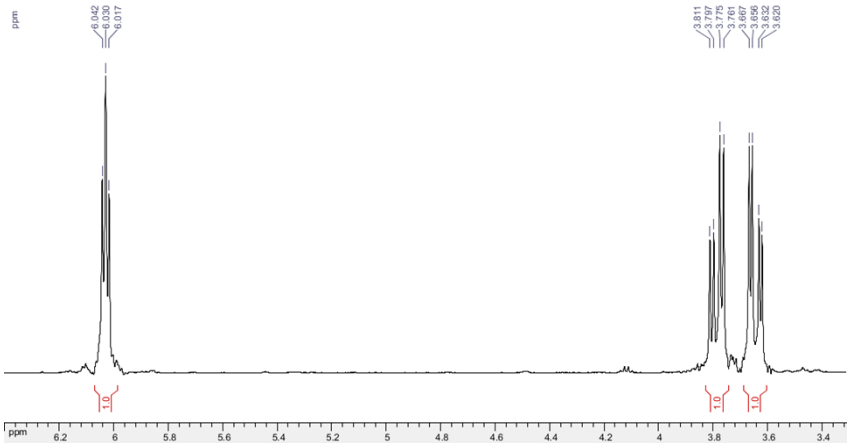

6.059
6.044
6.042
6.027
3.828
3.810
3.783
3.765
3.686
3.671
3.641
3.627
1.0
1.1
1.1
ppm

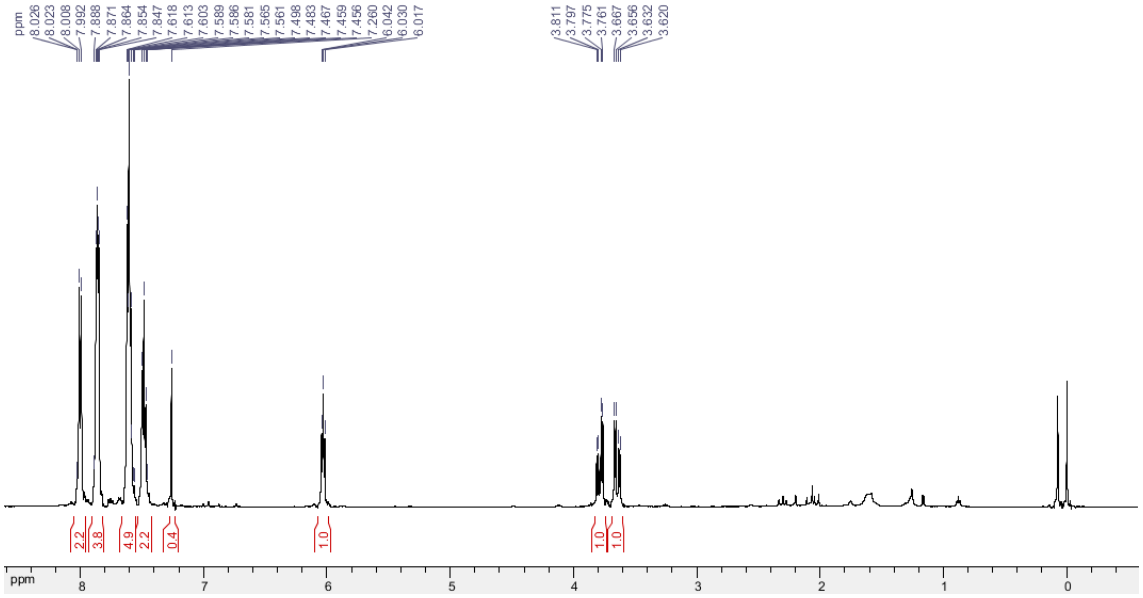

8.020
8.013
8.000
7.995
7.991
7.983
7.957
7.951
7.947
7.943
7.934
7.930
7.926
7.920
7.621
7.602
7.584
7.499
7.479
7.464
7.460
7.455
7.448
7.443
7.434
7.427
7.417
7.412
7.406
7.260
6.059
6.044
6.042
6.027
3.828
3.810
3.783
3.765
3.686
3.671
3.641
3.627
2.1
3.3
1.1
5.9
0.3
1.0
1.1
1.1
ppm


195.481
195.417
194.283
140.222
140.118
135.197
134.274
133.947
133.869
133.735
129.993
129.670
129.313
129.242
129.034
129.011
128.877
128.758
128.710
128.639
128.398
128.260
77.316
77.000
76.680
51.387
37.922
ppm


O
Ph
O
O
Br
Br

**3ea**


ppm
6.042
6.030
6.017
3.811
3.797
3.775
3.761
3.667
3.656
3.632
3.620
1.0
1.0
1.0
1.0
ppm
6.2
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4


ppm
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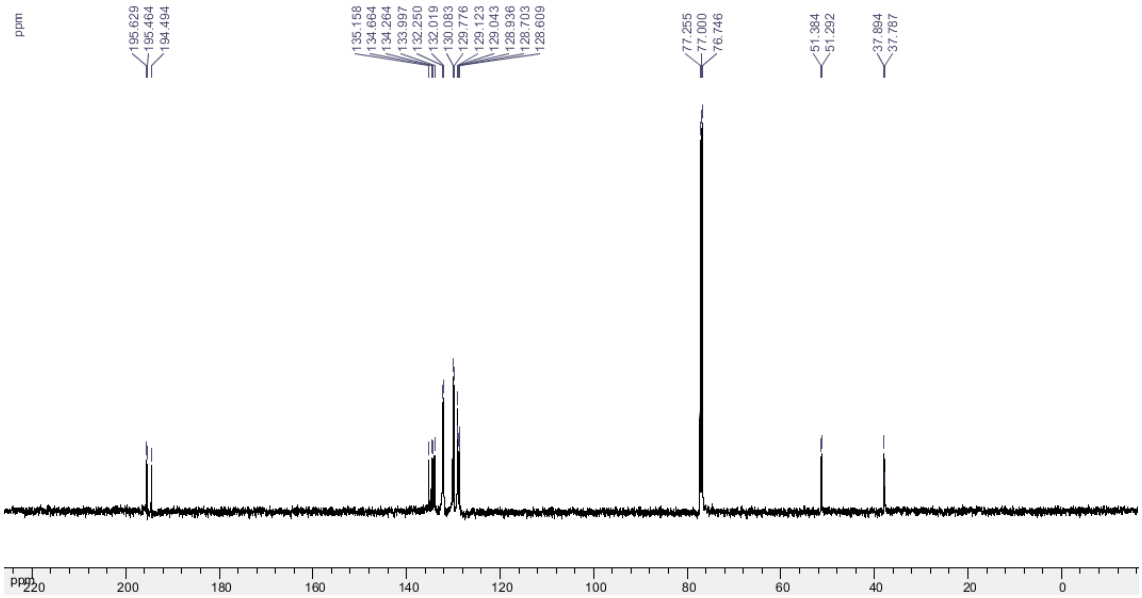
8.023
8.008
7.992
7.888
7.871
7.864
7.854
7.847
7.618
7.613
7.603
7.589
7.586
7.581
7.565
7.561
7.498
7.483
7.467
7.459
7.456
7.260
6.042
6.030
6.017
3.811
3.797
3.775
3.761
3.667
3.656
3.632
3.620
2.2
3.8
4.9
2.2
0.4
1.0
1.0
1.0
ppm
8
7
6
5
4
3
2
1
0


ppm
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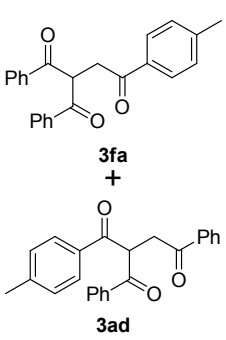
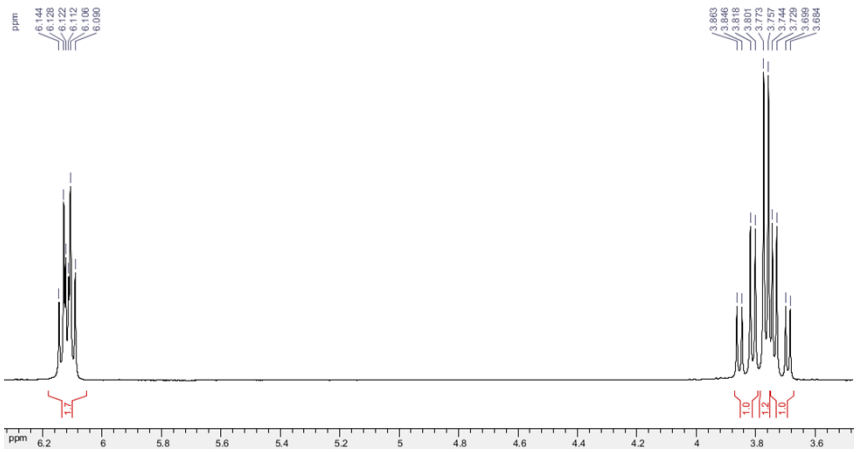
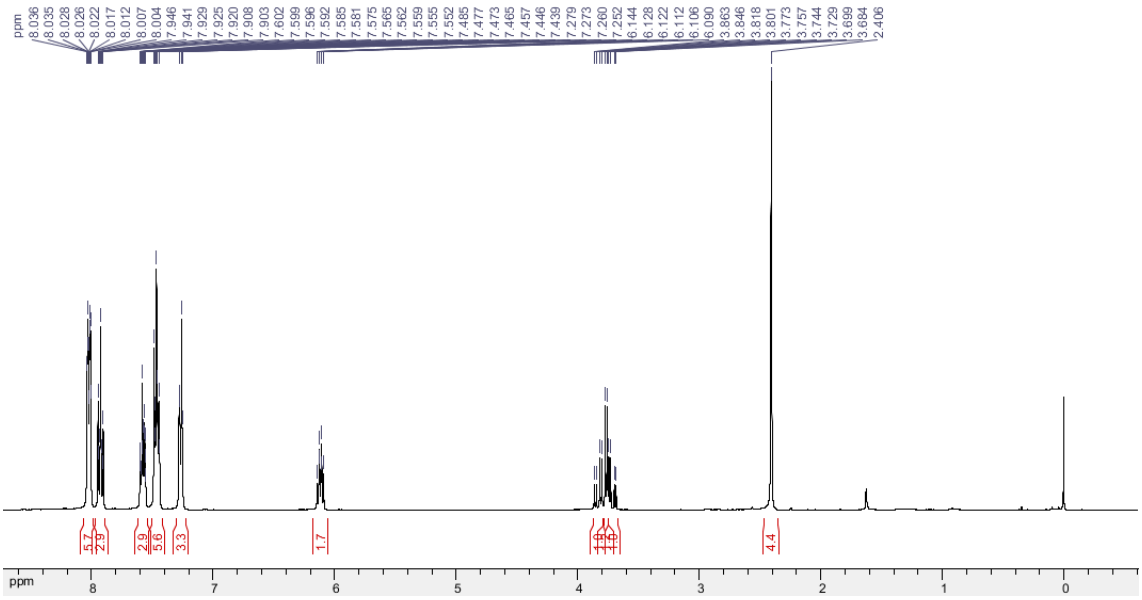
195.464
194.494
135.158
134.664
134.264
133.997
132.250
132.019
130.083
129.776
129.123
129.043
128.936
128.703
128.609
77.255
77.000
76.746
51.384
51.292
37.894
37.787
ppm
220
200
180
160
140
120
100
80
60
40
20
0


Ph
Ph
O
O
O
3fa
+
Ph
Ph
O
O
O
3ad


ppm
6.144
6.128
6.122
6.112
6.106
6.090
3.863
3.846
3.818
3.801
3.773
3.757
3.744
3.729
3.699
3.684
1.7
1.0
1.2
1.0
ppm
6.2
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6


ppm
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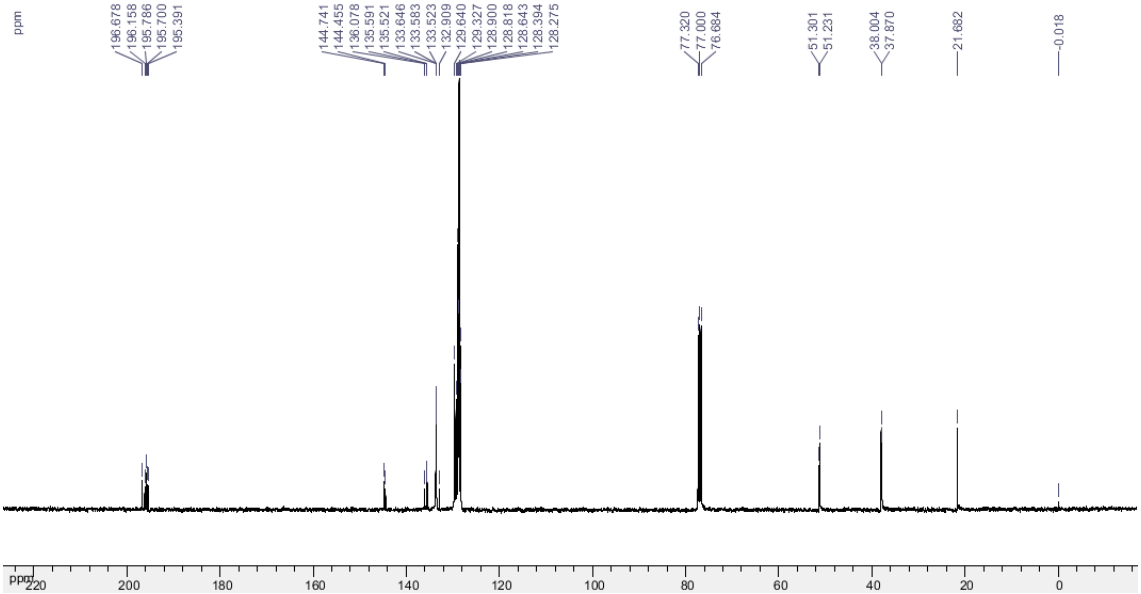
8.026
8.022
8.017
8.012
8.007
8.004
7.946
7.941
7.929
7.925
7.920
7.908
7.903
7.602
7.599
7.596
7.592
7.585
7.581
7.575
7.565
7.562
7.559
7.555
7.552
7.485
7.477
7.473
7.465
7.457
7.446
7.439
7.279
7.273
7.260
7.252
6.144
6.128
6.122
6.112
6.106
6.090
3.863
3.846
3.818
3.801
3.773
3.757
3.744
3.729
3.699
3.684
2.406
5.7
2.9
2.9
5.6
3.3
1.7
4.4
ppm
8
7
6
5
4
3
2
1
0


ppm
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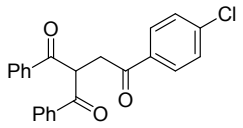
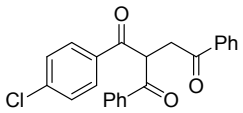
196.158
195.786
195.700
195.391
144.741
144.455
136.078
135.591
135.521
133.646
133.583
133.523
132.909
129.640
129.327
128.900
128.818
128.643
128.394
128.275
77.320
77.000
76.684
51.301
51.231
38.004
37.870
21.682
-0.018
ppm
220
200
180
160
140
120
100
80
60
40
20
0

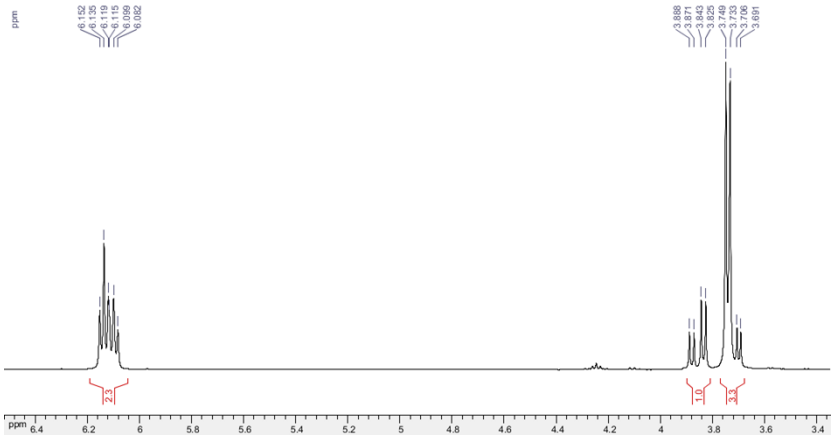

O
Cl
Ph
O
Ph
O

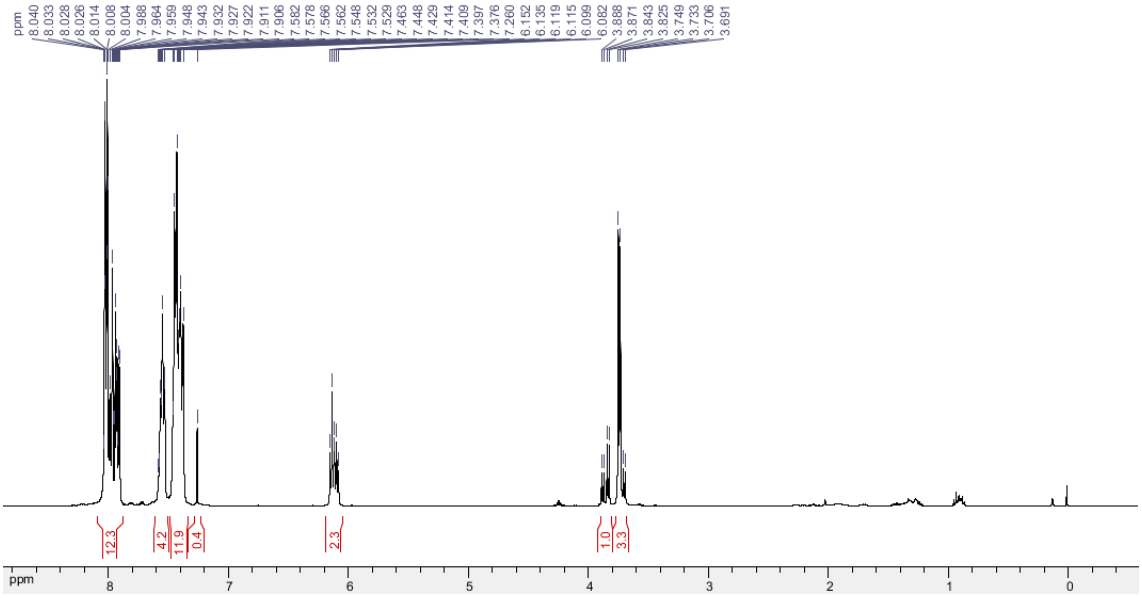
**3ga**

+


O
Ph
Cl
Ph
O
O

**3ah**


ppm
6.152
6.135
6.119
6.115
6.099
6.082
3.898
3.871
3.843
3.825
3.749
3.733
3.706
3.691
2.3
1.0
3.3
ppm
6.4
6.2
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4


ppm
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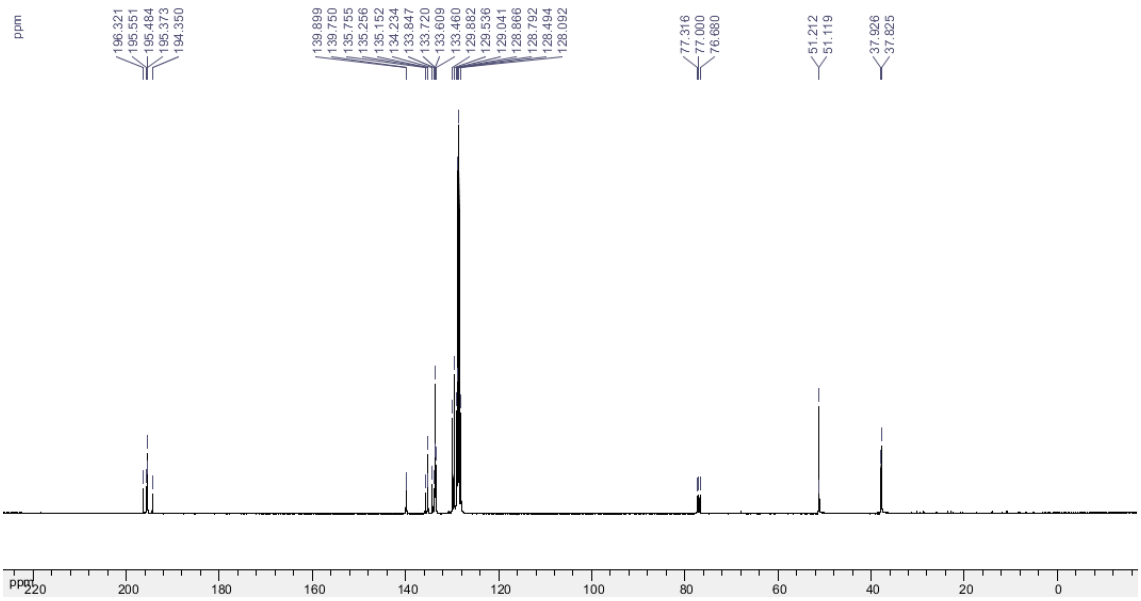
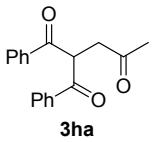
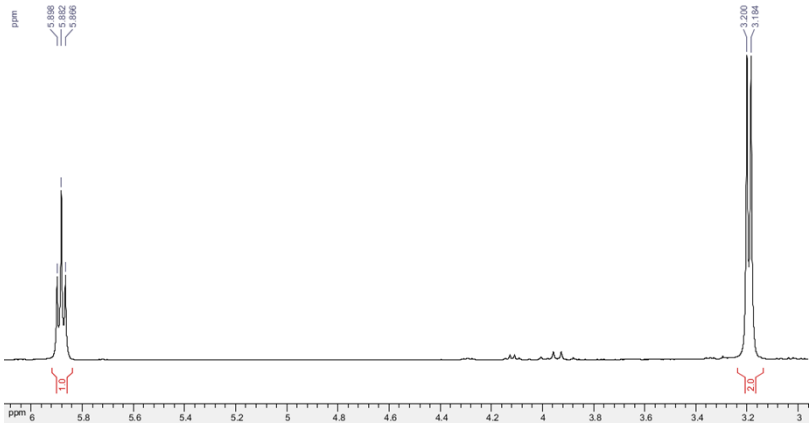
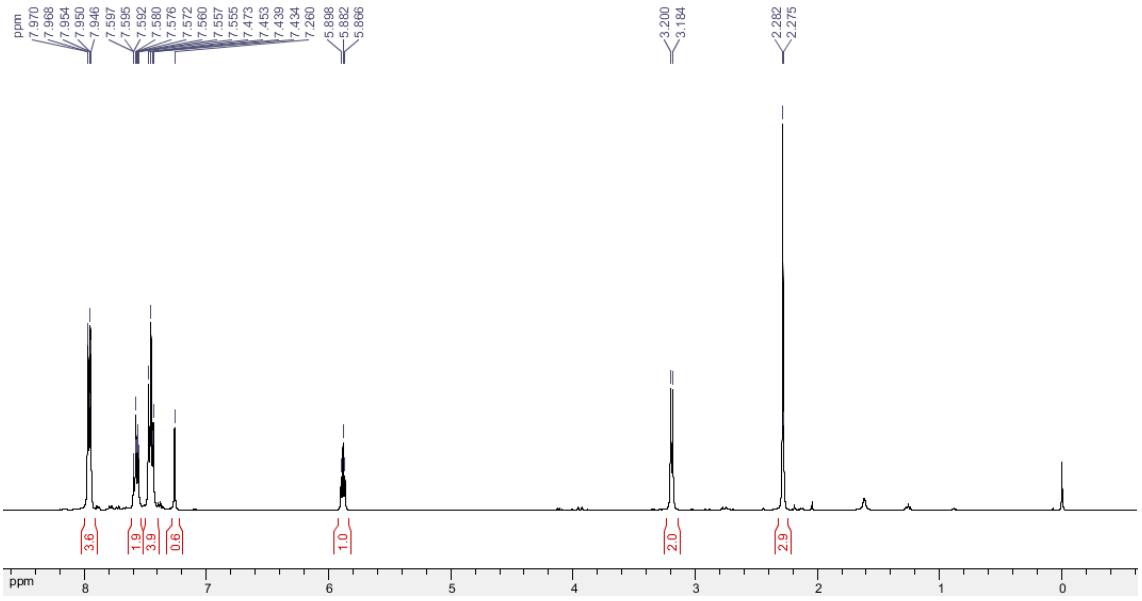
8.033
8.028
8.026
8.014
8.008
8.004
7.988
7.964
7.959
7.948
7.943
7.932
7.927
7.922
7.911
7.906
7.582
7.578
7.566
7.562
7.548
7.532
7.529
7.463
7.448
7.429
7.414
7.409
7.397
7.376
7.260
6.152
6.135
6.119
6.115
6.099
6.082
3.898
3.871
3.843
3.825
3.749
3.733
3.706
3.691
12.3
4.2
11.9
0.4
2.3
1.0
3.3
ppm
8
7
6
5
4
3
2
1
0

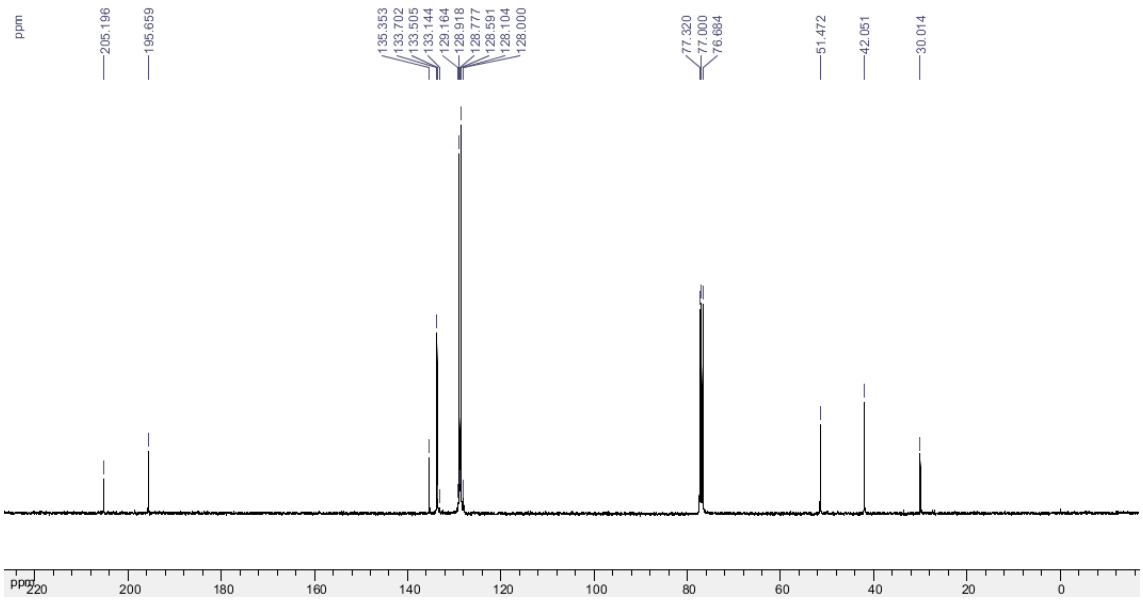

ppm
196.321
195.551
195.484
195.373
194.350
139.899
139.750
135.755
135.256
135.152
134.234
133.847
133.720
133.609
133.460
129.882
129.536
129.041
128.866
128.792
128.494
128.092
77.316
77.000
76.680
51.212
51.119
37.926
37.825
ppm
220
200
180
160
140
120
100
80
60
40
20
0

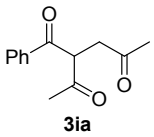

O
Ph
O
Ph
O

**3ha**

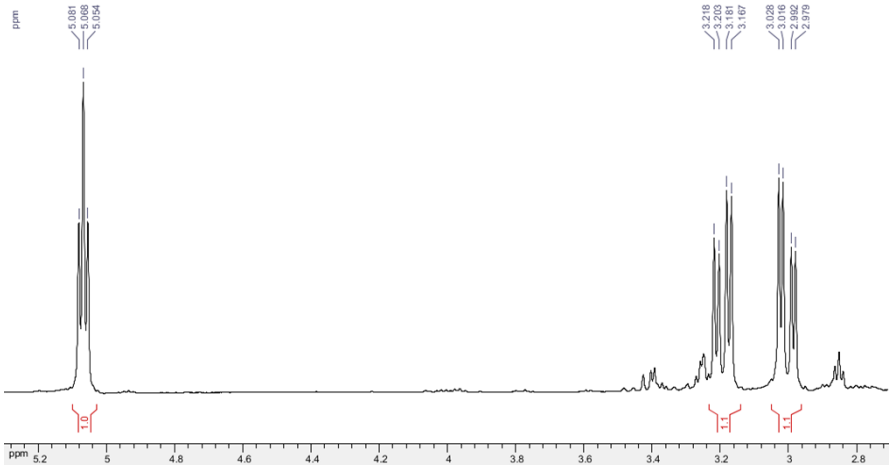

ppm
5.898
5.882
5.866
3.200
3.184
1.0
2.0
ppm 6 5.8 5.6 5.4 5.2 5 4.8 4.6 4.4 4.2 4 3.8 3.6 3.4 3.2 3

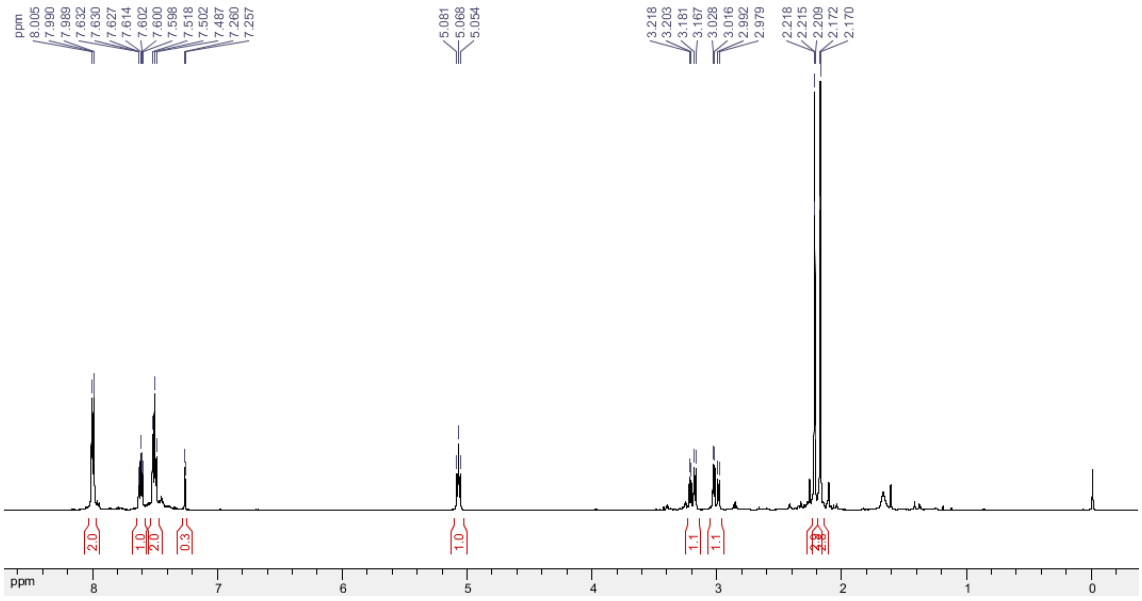

ppm
7.970
7.968
7.954
7.950
7.946
7.597
7.595
7.592
7.580
7.576
7.572
7.560
7.557
7.555
7.473
7.453
7.439
7.434
7.260
5.898
5.882
5.866
3.200
3.184
2.282
2.275
3.6
1.9
3.9
0.6
1.0
2.0
2.9
ppm 8 7 6 5 4 3 2 1 0

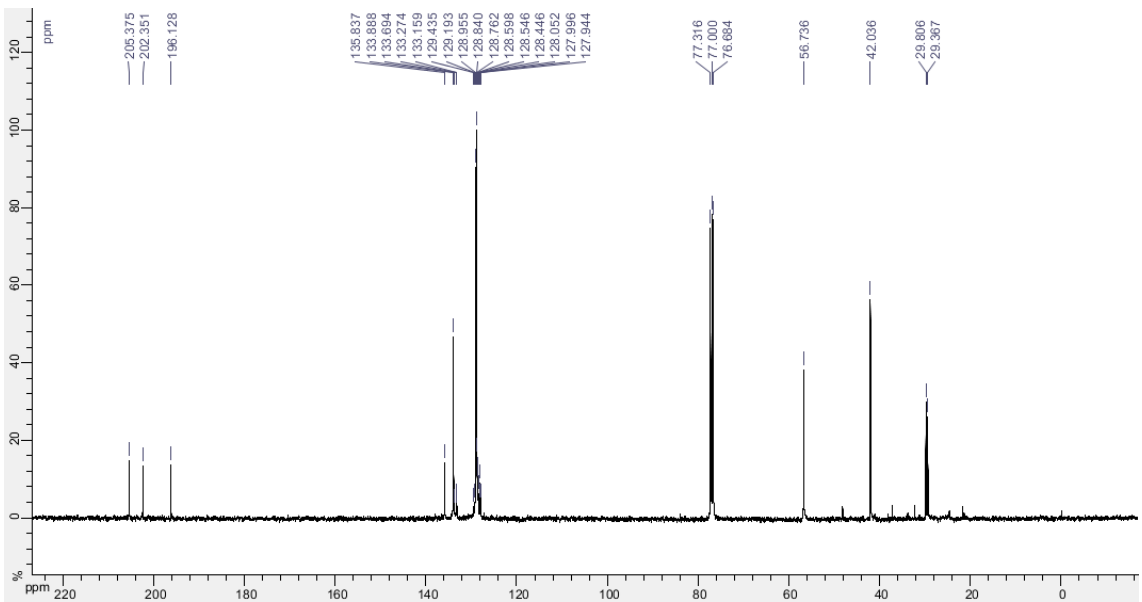

ppm
205.196
195.659
135.353
133.702
133.505
133.144
129.164
128.918
128.777
128.591
128.104
128.000
77.320
77.000
76.684
51.472
42.051
30.014
ppm 220 200 180 160 140 120 100 80 60 40 20 0

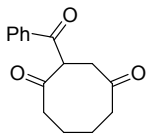

Ph
O
O
O

**3ia**


ppm
5.081
5.068
5.054
3.218
3.203
3.181
3.167
3.028
3.016
2.992
2.979
1.0
1.1
1.1

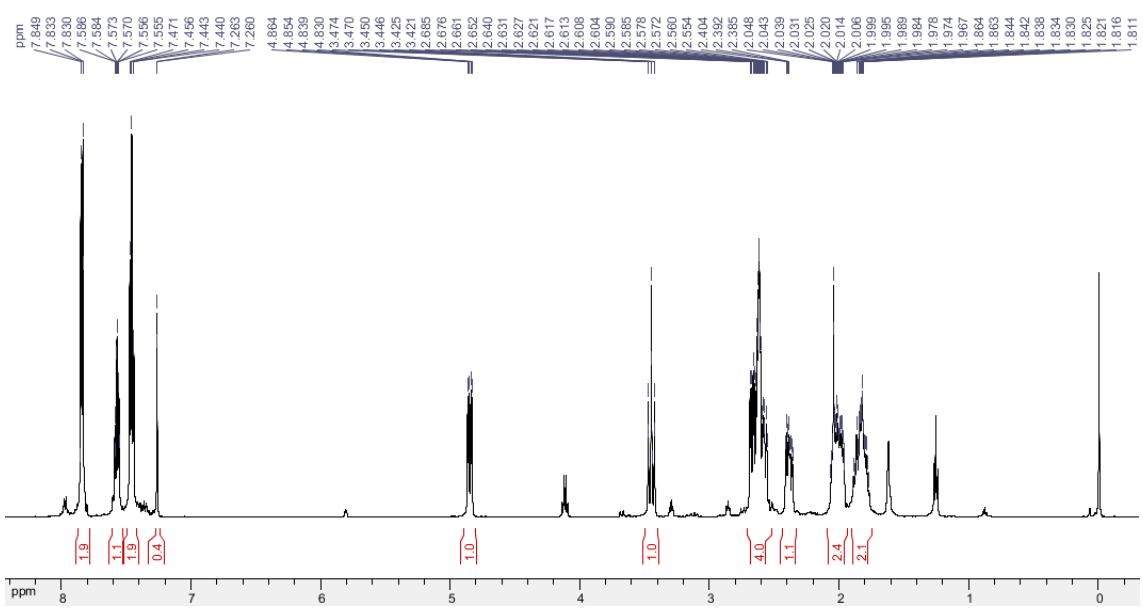

ppm
8.005
7.990
7.989
7.632
7.630
7.627
7.614
7.602
7.600
7.598
7.518
7.502
7.487
7.260
7.257
5.081
5.068
5.054
3.218
3.203
3.181
3.167
3.028
3.016
2.992
2.979
2.218
2.215
2.209
2.172
2.170
2.0
1.0
2.0
0.3
1.0
1.1
1.1
2.3
ppm

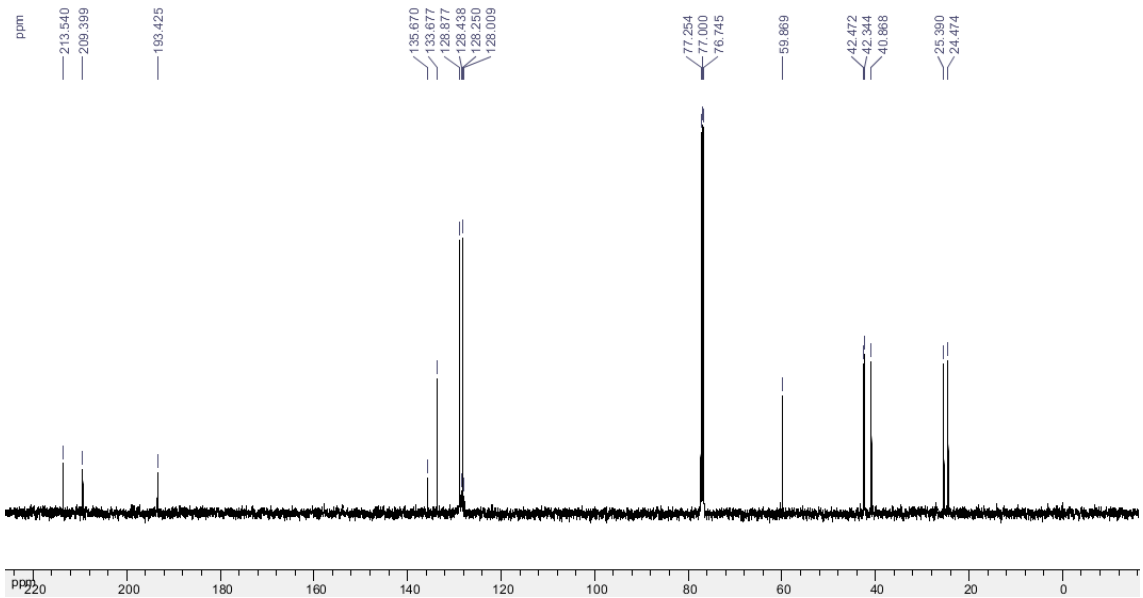

ppm
205.375
202.351
196.128
135.837
133.888
133.694
133.274
133.159
129.435
129.193
128.955
128.840
128.762
128.598
128.546
128.446
128.052
127.996
127.944
77.316
77.000
76.684
56.736
42.036
29.806
29.367
%
ppm

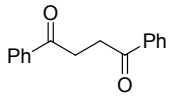

Ph
O
O
O

**3ja**

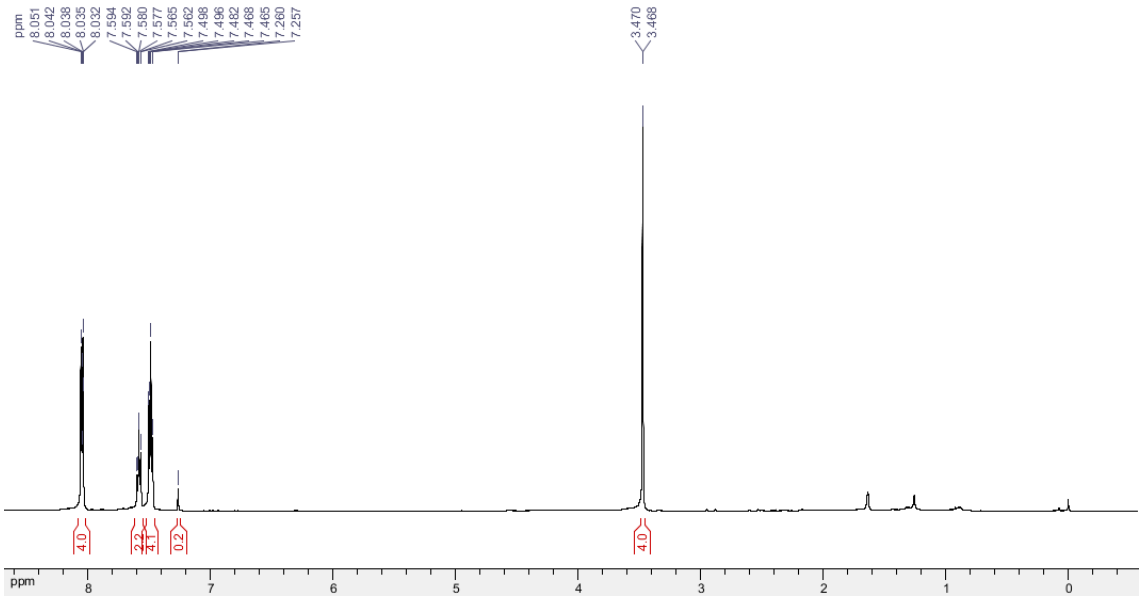

ppm
4.864
4.854
4.839
4.830
3.474
3.470
3.450
3.446
3.442
3.425
3.421
1.0
1.0
ppm
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4

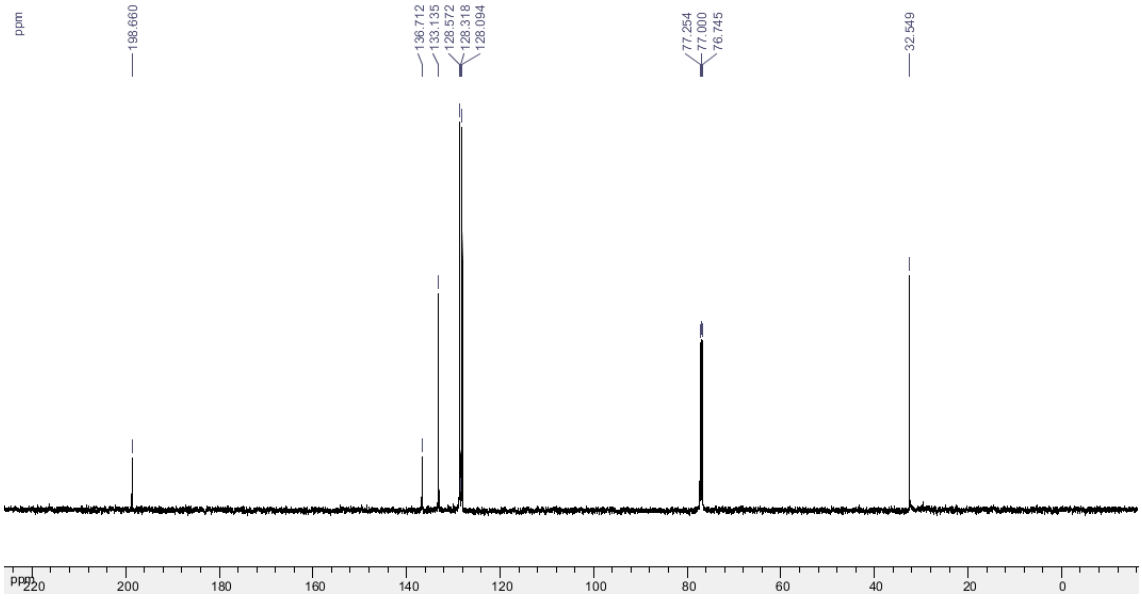

ppm
7.849
7.833
7.830
7.586
7.584
7.573
7.570
7.556
7.555
7.471
7.456
7.443
7.440
7.263
7.260
4.864
4.854
4.839
4.830
3.474
3.470
3.450
3.446
3.425
3.421
2.685
2.676
2.661
2.652
2.640
2.631
2.627
2.621
2.617
2.613
2.608
2.604
2.590
2.585
2.578
2.572
2.560
2.554
2.404
2.392
2.385
2.048
2.043
2.039
2.031
2.025
2.020
2.014
2.006
1.999
1.995
1.989
1.984
1.978
1.974
1.967
1.864
1.863
1.844
1.842
1.838
1.834
1.830
1.825
1.821
1.816
1.811
1.9
1.1
1.9
0.4
1.0
1.0
4.0
1.1
2.4
2.1
ppm
8
7
6
5
4
3
2
1
0


ppm
213.540
209.399
193.425
135.670
133.677
128.877
128.438
128.250
128.009
77.254
77.000
76.745
59.869
42.472
42.344
40.868
25.390
24.474
ppm
220
200
180
160
140
120
100
80
60
40
20
0


O
Ph
Ph
O

**4**


ppm
8.051
8.042
8.038
8.035
8.032
7.594
7.592
7.580
7.577
7.565
7.562
7.498
7.496
7.482
7.468
7.465
7.260
7.257
3.470
3.468
4.0
2.2
4.1
0.2
4.0
ppm
8
7
6
5
4
3
2
1
0


ppm
198.660
136.712
133.135
128.572
128.318
128.094
77.254
77.000
76.745
32.549
ppm
220
200
180
160
140
120
100
80
60
40
20
0