Electronic Supplementary Information

Double oxidation of α-(alkylideneamino)nitriles to imides by molecular oxygen under mild basic conditions

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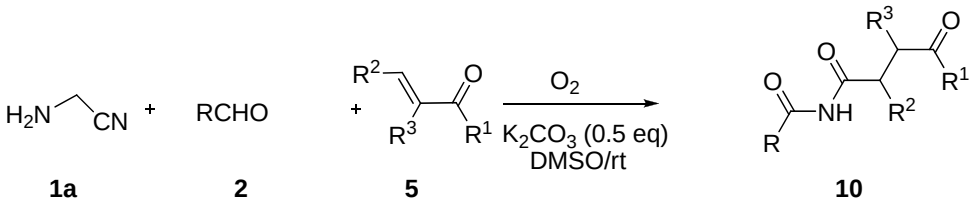
Contents

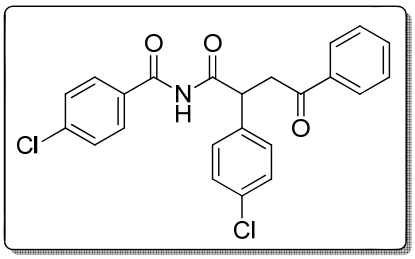
I. General Information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by column chromatography on flash silica gel (300−400 mesh). Melting points were uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were determined on a Varian 500 MHz and 125 MHz, respectively, with TMS as the internal standard. All shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

II. Typical Procedures and Analytical Data



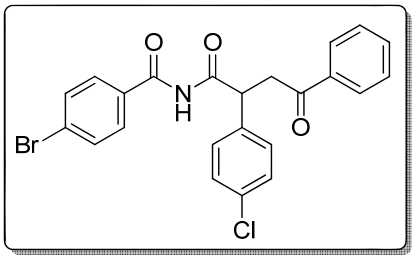
1a **2** **5** **10**



10aa, 4-chloro-*N*-(2-(4-chlorophenyl)-4-oxo-4-phenylbutanoyl)benzamide.

To a solution of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol) in DMSO (5.0 mL) was added triethylamine (0.08 mL, 0.6 mmol) and stirred at room temperature for 1.0 h. Then, 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) was added and further stirred at room temperature for about 4.0 h. After **2a** was consumed as indicated by TLC, K_2CO_3 (34.5 mg, 0.25 mmol) was added in one portion under oxygen atmosphere following with the dropwise addition of DMSO solution (2.0 mL) of enone **5a** (121 mg, 0.5 mmol). The reaction mixture was stirred at room temperature and was monitored by TLC. After enone **5a** was consumed, the resulting mixture was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL × 2). The aqueous layer was treated with 10% NaClO solution (5 mL) and collected. The combined organic layers were dried over anhydrous Na_2SO_4, evaporated *in vacuo*, and the residue was purified by column chromatography (EtOAc/PE (petroleum ether) = 1/10, V/V) to give **10aa** (191 mg, 90% calculated from **5a**). Reaction time 12.0 h.

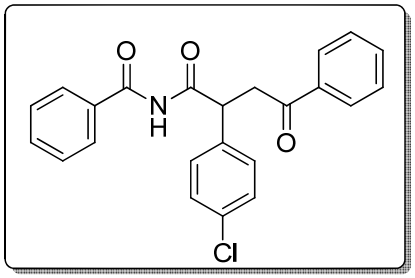
Colorless crystals, m.p. 215–217 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.29 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.08 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.41 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.41 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 8.68 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 43.9, 46.2, 128.1, 128.2, 128.7, 129.1, 129.2, 130.0, 133.5, 133.7, 135.8, 136.0, 139.7, 164.0, 174.7, 197.6. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{18}Cl_2NO_3^+$ ($[M+H]^+$) 426.0658. Found 426.0657.



10ba, 4-bromo-*N*-(2-(4-chlorophenyl)-4-oxo-4-phenylbutanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-bromobenzaldehyde **2b** (111 mg, 0.6 mmol) and enone **5a** (121 mg, 0.5 mmol) gave **10ba** (183 mg, 78%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 9.0 h.

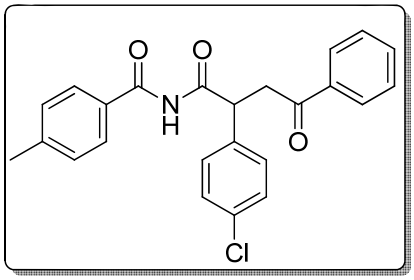
Colorless crystals, m.p. 210–212 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.29 (dd, *J* = 18.0, 3.5 Hz, 1H), , 4.07 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.41 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.54–7.60 (m, 3H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.76 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 43.8, 46.2, 128.1, 128.2, 128.7, 129.1, 129.3, 130.0, 131.6, 132.1, 133.6, 133.7, 135.8, 136.0, 164.3, 175.0, 197.6. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{18}BrClNO_3^+$ ($[M+H]^+$) 470.0153. Found 470.0158.



10ca, *N*-(2-(4-chlorophenyl)-4-oxo-4-phenylbutanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), benzaldehyde **2c** (61 μL, 0.6 mmol) and enone **5a** (121 mg, 0.5 mmol) gave **10ca** (164 mg, 84%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 26.0 h.

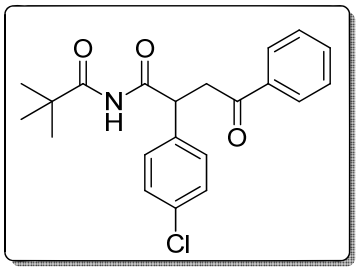
Colorless crystals, m.p. 190–192 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.29 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.09 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.46 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.43–7.47 (m, 6H), 7.55–7.59 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.65 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 43.8, 46.2, 127.7, 128.1, 128.6, 128.9, 129.0, 130.0, 132.8, 133.1, 133.4, 133.6, 136.0, 136.1, 165.0, 174.9, 197.6. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{19}ClNO_3^+$ ($[M+H]^+$) 392.1048. Found 392.1051.



10da, *N*-(2-(4-chlorophenyl)-4-oxo-4-phenylbutanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-methylbenzaldehyde **2d** (71 μL, 0.6 mmol) and enone **5a** (121 mg, 0.5 mmol) gave **10da** (168 mg, 83%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 27.0 h.

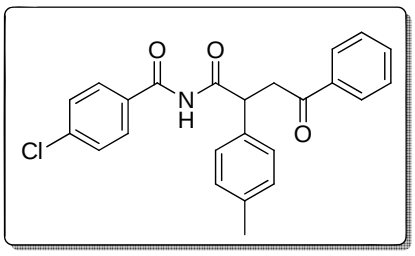
Colorless crystals, m.p. 223–225 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.29 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.09 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.48 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.43–7.47 (m, 4H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.57 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.6, 43.8, 46.1, 127.7, 128.1, 128.6, 129.0, 129.6, 129.9, 130.0, 133.4, 133.5, 136.1, 144.1, 164.8, 174.9, 197.6. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{21}ClNO_3^+$ ($[M+H]^+$) 406.1204. Found 406.1214.



10ea, 2-(4-chlorophenyl)-4-oxo-4-phenyl-*N*-pivaloylbutanamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), pivalaldehyde **2e** (66 μL, 0.6 mmol) and enone **5a** (121 mg, 0.5 mmol) gave **10ea** (139 mg, 75%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 12 V/V). Reaction time 12.0 h.

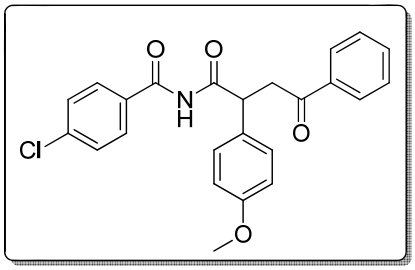
Colorless crystals, m.p. 132–134 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.20 (s, 9H), 3.23 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.03 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.32 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.06 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 27.0, 40.2, 43.7, 45.8, 128.0, 128.6, 128.9, 129.9, 133.4(2C), 136.0, 136.1, 175.0, 176.4, 197.5. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{23}ClNO_3^+$ ($[M+H]^+$) 372.1361. Found 372.1363.



10ab, 4-chloro-*N*-(4-oxo-4-phenyl-2-(*p*-tolyl)butanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 1-phenyl-3-(*p*-tolyl)prop-2-en-1-one **5b** (111 mg, 0.5 mmol) gave **10ab** (170 mg, 84%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 24.0 h.

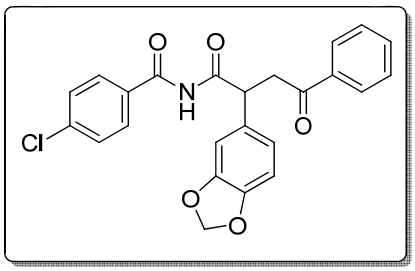
Colorless crystals, m.p. 249– 251 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.33 (s, 3H), 3.29 (d, *J* = 18.5 Hz, 1H), 4.08 (dd, *J* = 18.5, 11.0 Hz, 1H), 5.31 (d, *J* =11.0 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.81 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.1, 43.9, 46.6, 128.1, 128.4, 128.6, 129.0, 129.2, 129.7, 131.4, 133.4, 134.4, 136.2, 137.5, 139.4, 164.2, 175.0, 198.0. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{21}ClNO_3^+$ ($[M+H]^+$) 406.1204. Found 406.1214.



10ac, 4-chloro-*N*-(2-(4-methoxyphenyl)-4-oxo-4-phenylbutanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one **5c** (119 mg, 0.5 mmol) gave **10ac** (172 mg, 82%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 25.0 h.

Colorless crystals, m.p. 161–163 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.26 (d, *J* = 18.0 Hz, 1H), 3.77 (s, 3H), 4.06 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.32 (d, *J* = 11.0 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 7.0 Hz, 2H), 9.38 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 43.9, 46.0, 55.2, 114.3, 128.0, 128.6, 128.8, 129.2, 129.4, 129.6, 131.3, 133.4, 136.0, 139.2, 159.0, 164.5, 175.9, 198.0. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{21}ClNO_4^+$ ($[M+H]^+$) 422.1154. Found 422.1160.

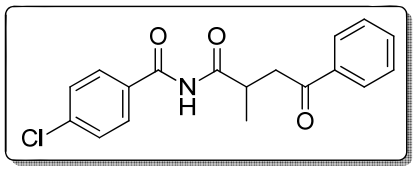


10ad, *N*-(2-(benzo[*d*][1,3]dioxol-5-yl)-4-oxo-4-phenylbutanoyl)-4-chlorobenzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 3-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylprop-2-en-1-one **5d** (126 mg, 0.5 mmol) gave **10ad** (191 mg,

88%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 10.0 h.

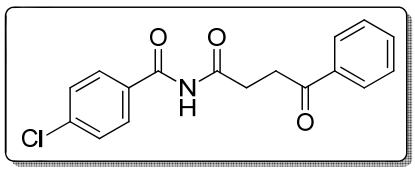
Colorless crystals, m.p. 169–171 °C. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 3.29 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.06 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.29 (dd, *J* = 11.0, 3.5 Hz, 1H), 5.95 (s, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.97 (d, *J* = 1.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 8.62 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 43.9, 46.4, 101.1, 108.6, 108.8, 121.9, 128.0, 128.6, 129.1(2C), 130.8, 131.3, 133.4, 136.1, 139.5, 147.1, 148.0, 164.1, 174.8, 197.9. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{19}ClNO_5^+$ ($[M+H]^+$) 436.0946. Found 436.0949.



10ae, 4-chloro-*N*-(2-methyl-4-oxo-4-phenylbutanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 1-phenylbut-2-en-1-one **5e** (73 mg, 0.5 mmol) gave **10ae** (99 mg, 60%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 12 V/V). Reaction time 24.0 h.

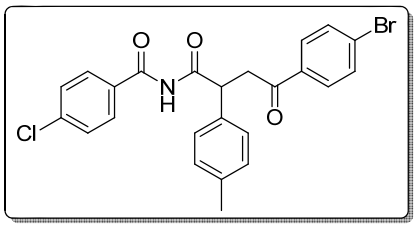
Colorless crystals, m.p. 175–177 °C. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 1.37 (d, *J* = 6.5 Hz, 3H), 3.13 (dd, *J* = 18.0, 3.5 Hz, 1H), 3.67 (dd, *J* = 18.0, 11.0 Hz, 1H), 3.95–3.99 (m, 1H), 7.44–7.48 (m, 4H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 8.98 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 17.0, 36.0, 42.6, 128.0, 128.6, 129.1, 129.2, 131.4, 133.4, 136.2, 139.4, 164.2, 177.7, 198.6. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{17}ClNO_3^+$ ($[M+H]^+$) 330.0891. Found 330.0881.



10af, 4-chloro-*N*-(4-oxo-4-phenylbutanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 1-phenylprop-2-en-1-one **5f** (66 mg, 0.5 mmol) gave **10af** (110 mg, 70%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 12 V/V). Reaction time 24.0 h.

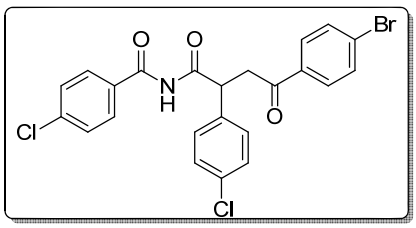
Colorless crystals, m.p. 112–114 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.48–2.51 (m, 2H), 2.96–3.01 (m, 1H), 3.13–3.18 (m, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 8.53 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 33.4, 34.4, 128.0, 128.6, 129.1, 130.1, 132.9, 133.3, 136.4, 138.1, 159.9, 177.8, 197.9. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{15}ClNO_3^+$ ($[M+H]^+$) 316.0735. Found 316.0741.



10ag, *N*-(4-(4-bromophenyl)-4-oxo-2-(*p*-tolyl)butanoyl)-4-chlorobenzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 1-(4-bromophenyl)-3-(*p*-tolyl)prop-2-en-1-one **5g** (150 mg, 0.5 mmol) gave **10ag** (205 mg, 85%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 14.0 h.

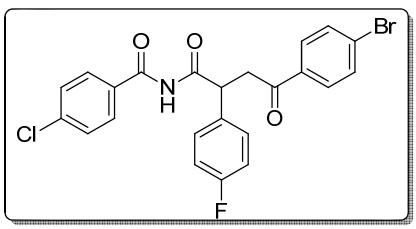
Colorless crystals, m.p. 116–118 ^{o}C. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 2.38 (s, 3H), 3.23 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.05 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.31 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 8.55 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 21.2, 43.8, 46.6, 128.4, 128.6, 129.1, 129.6, 129.7, 131.3, 131.9, 134.1, 134.9, 137.7, 139.5, 164.1, 174.7, 197.0. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{20}BrClNO_3$+ ($[M+H]^+$) 484.0310. Found 484.0309.



10ah, *N*-(4-(4-bromophenyl)-2-(4-chlorophenyl)-4-oxobutanoyl)-4-chlorobenzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 1-(4-bromophenyl)-3-(4-chlorophenyl)prop-2-en-1-one **5h** (160 mg, 0.5 mmol) gave **10ah** (224 mg, 89%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 8.0 h.

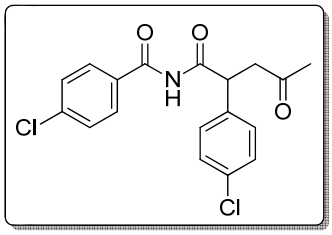
Colorless crystals, m.p. 195–197 ^{o}C. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 3.23 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.02 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.42 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 6.5 Hz, 2H), 7.44 (d, *J* = 6.5 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 8.75 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 43.7, 46.1, 128.8, 129.1, 129.2(2C), 129.6, 129.9, 131.0, 132.0, 133.8, 134.7, 135.6, 139.7, 164.1, 175.0, 196.6. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{17}BrCl_2NO_3^+$ ($[M+H]^+$) 503.9763. Found 503.9759.



10ai, *N*-(4-(4-bromophenyl)-2-(4-fluorophenyl)-4-oxobutanoyl)-4-chlorobenzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 1-(4-bromophenyl)-3-(4-fluorophenyl)prop-2-en-1-one **5i** (152 mg, 0.5 mmol) gave **10ai** (214 mg, 88%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 7.0 h.

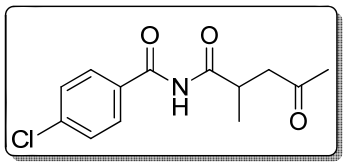
Colorless crystals, m.p. 201–203 °C. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 3.23 (dd, *J* = 18.0, 3.5 Hz, 1H), 4.03 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.43 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.04 (t, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.43 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 8.81 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 43.9, 45.9, 115.8, 115.9, 128.8, 129.1, 129.2, 129.5, 130.2(2C), 131.1, 132.0, 132.8, 134.7, 139.6, 164.2, 175.3, 196.7. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{17}BrClFNO_3^+$ ($[M+H]^+$) 488.0059. Found 488.0051.



10aj, 4-chloro-*N*-(2-(4-chlorophenyl)-4-oxopentanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 4-(4-chlorophenyl)but-3-en-2-one **5j** (90 mg, 0.5 mmol) gave **10aj** (154 mg, 85%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 6.0 h.

Colorless crystals, m.p. 123–125 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.77 (dd, *J* = 18.0, 3.5 Hz, 1H), 3.54 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.19 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 8.67 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 29.7, 46.1, 48.0, 129.0, 129.1, 129.8, 130.9, 131.1, 133.6, 135.6, 139.6, 164.1, 174.6, 206.3. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{16}Cl_2NO_3^+$ ($[M+H]^+$) 364.0502. Found 364.0512.

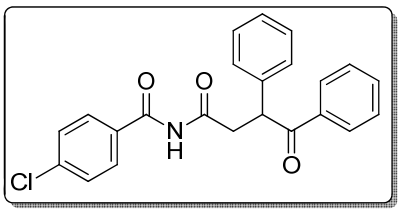


10ak, 4-chloro-*N*-(2-methyl-4-oxopentanoyl)benzamide

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and pent-3-en-2-one **5k** (42 mg, 0.5 mmol) gave **10ak** (96 mg, 72%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 12 V/V). Reaction time 24.0 h.

Yellowish oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.24 (d, *J* = 7.0 Hz, 3H), 2.19 (s, 3H), 2.59 (dd, *J* = 18.5, 3.5 Hz, 1H), 3.11 (dd, *J* = 18.5, 11.0 Hz, 1H), 3.72 (m, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 8.81 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 16.7, 29.8, 35.8, 47.2, 129.1, 129.2,

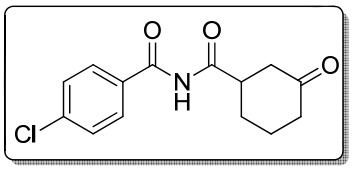
131.2, 139.6, 164.1, 177.3, 207.6. **HRMS** (ESI-TOF) Calcd for $C_{13}H_{15}ClNO_3^+$ ($[M+H]^+$) 268.0735. Found 268.0745.



10al, 4-chloro-*N*-(4-oxo-3,4-diphenylbutanoyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 1,2-diphenylprop-2-en-1-one **5l** (104 mg, 0.5 mmol) gave **10al** (102 mg, 52%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10 V/V). Reaction time 18.0 h.

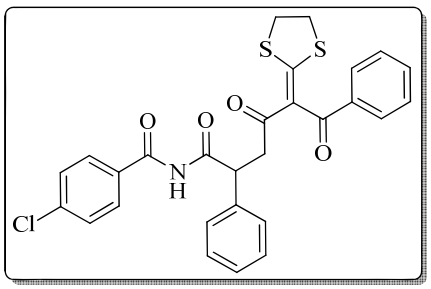
Colorless crystals, m.p. 196–198 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.30 (dd, *J* = 18.5, 3.0 Hz, 1H), 4.12 (dd, *J* = 18.5, 11.0 Hz, 1H), 5.18 (dd, *J* = 11.0, 3.0 Hz, 1H), 7.23 (m, 1H), 7.31 (m, 6H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 9.03 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): 42.5, 49.0, 127.5, 128.2, 128.5, 128.9, 129.1, 129.2 (2C), 130.8, 133.1, 136.1, 137.9, 139.7, 164.6, 174.6, 198.5. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{19}ClNO_3^+$ ($[M+H]^+$) 392.1048. Found 392.1059.



10am, 4-Chloro-*N*-(3-oxocyclohexanecarbonyl)benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and cyclohex-2-enone (49.4 μL, 0.5 mmol) gave **10am** (116 mg, 83%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 10). Reaction time 16.0 h.

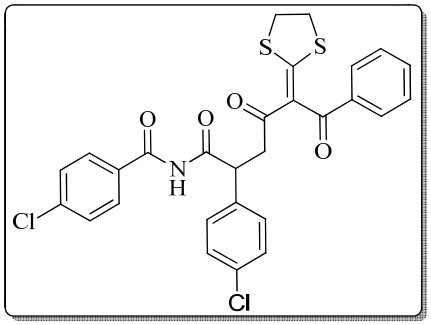
Colorless crystals, m.p. 143–145 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.87–1.91 (m, 2H), 2.07–2.11 (m, 1H), 2.23–2.15 (m, 1H), 2.38–2.45 (m, 2H), 2.55 (dd, *J* = 15.0, 4.5 Hz, 1H), 2.69 (dd, *J* = 15.0, 4.5 Hz, 1H), 3.96–4.01 (m, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 8.50 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 24.0, 27.3, 40.8, 42.5, 44.1, 129.3(2C), 130.7, 139.9, 164.5, 176.9, 209.9. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{14}ClNNaO_3^+$ ($[M+H]^+$) 302.0554. Found 302.0562.



10an, 4-Chloro-*N*-(5-[1,3]dithiolan-2-ylidene-4,6-dioxo-2,6-diphenyl-hexanoyl)-benzamide.

Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 2-(1,3-dithiolan-2-ylidene)-1,5-diphenylpent-4-ene-1,3-dione **5n** (176 mg, 0.5 mmol) gave **10an** (227 mg, 85%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 9 V/V). Reaction time 19.0 h.

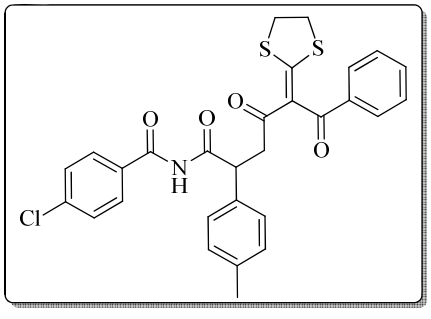
Colorless crystals, m.p. 221–223 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.71 (dd, *J* = 18.0, 3.5 Hz, 1H), 2.27–3.30 (m, 2H), 3.33–3.39 (m, 3H), 5.10 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.20–7.24 (m, 5H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 7.5 Hz, 2H), 8.76 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 36.8, 38.0, 45.7, 47.5, 125.5, 127.5, 128.4, 128.8, 129.0(2C), 129.3, 129.5, 131.4, 133.7, 137.2, 137.3, 139.3, 164.2, 171.2, 174.4, 192.2, 194.6. **HRMS** (ESI-TOF) Calcd for $C_{28}H_{22}ClNNaO_4S_2^+$ ($[M+Na]^+$) 558.0576. Found 558.0579.



10ao, 4-Chloro-*N*-[2-(4-chloro-phenyl)-5-[1,3]dithiolan-2-ylidene-4,6-dioxo-6-phenyl-hexanoyl]-benzamide.

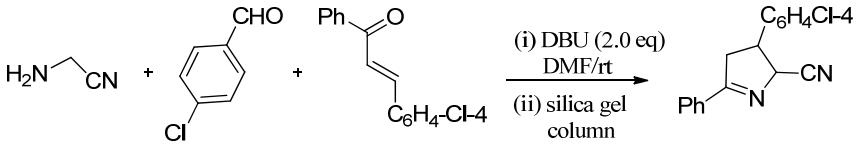
Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 5-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylpent-4-ene-1,3-dione **5o** (193 mg, 0.5 mmol) gave **10ao** (239 mg, 84%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 9 V/V). Reaction time 20.0 h.

Yellowish crystals, m.p. 196–198 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.68 (dd, *J* = 18.0, 4.0 Hz, 1H), 2.27–3.32 (m, 3H), 3.34–3.38 (m, 2H), 5.16 (dd, *J* = 10.5, 4.0 Hz, 1H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 2H), 8.82 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 36.9, 38.0, 45.7, 46.7, 125.4, 128.8, 129.0, 129.1, 129.3, 129.5, 129.8, 131.3, 133.4, 133.7, 135.7, 137.3, 139.5, 164.1, 171.6, 174.5, 192.0, 194.6. **HRMS** (ESI-TOF) Calcd for $C_{28}H_{21}Cl_2NNaO_4S_2^+$ ($[M+Na]^+$) 592.0187. Found 592.0189.

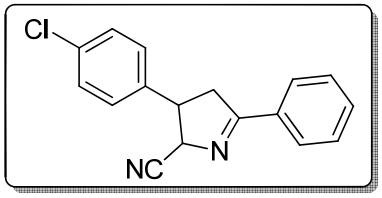


10ap, 4-Chloro-*N*-(5-[1,3]dithiolan-2-ylidene-4,6-dioxo-6-phenyl-2-*p*-tolyl-hexanoyl)-benzamide. Following the procedure for the synthesis of **10aa**, the reaction of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol), 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) and 2-(1,3-dithiolan-2-ylidene)-1-phenyl-5-(*p*-tolyl)pent-4-ene-1,3-dione **5p** (233 mg, 0.5 mmol) gave **10ap** (247 mg, 90%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 9 V/V). Reaction time 24.0 h.

Colorless crystals, m.p. 199–201 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.68 (dd, *J* = 18.0, 3.5 Hz, 1H), 2.27–3.30 (m, 2H), 3.32 (dd, *J* = 18.0, 11.0 Hz, 1H), 3.36–3.39 (m, 1H), 5.03 (dd, *J* = 11.0, 3.5 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H), 8.59 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.0, 36.8, 38.0, 45.8, 47.2, 125.6, 128.2, 129.0(2C), 129.2, 129.5, 129.6, 131.5, 133.7, 134.1, 137.3(2C), 139.2, 164.0, 171.1, 174.2, 192.4, 194.6. **HRMS** (ESI-TOF) Calcd for $C_{29}H_{24}ClNNaO_4S_2^+$ ([M+Na]$^+$) 572.0733. Found 572.0740.



1a **2a** **5a** **7a**



7a, 3-(4-chlorophenyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carbonitrile. *trans*:*cis* = 1.3:1.0[1]

To a solution of 2-aminoacetonitrile hydrochloride (55.1 mg, 0.6 mmol) in DMF (5.0 mL) was added triethylamine (0.08 mL, 0.6 mmol) and stirred at room temperature for 1.0 h. Then, 4-chlorobenzaldehyde **2a** (84 mg, 0.6 mmol) was added and further stirred at room temperature for about 4.0 h. After **2a** was consumed as indicated by TLC, DBU (0.15 mL, 1.0 mmol) was added in one portion following with the enone **5a** (121 mg, 0.5 mmol). The reaction mixture was stirred at room temperature and was monitored by TLC. After enone **5a** was consumed, the resulting mixture was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4, evaporated *in vacuo*, and the residue was purified by column chromatography (EtOAc/PE = 1/9, V/V) to give **7a** (136 mg, 97%).

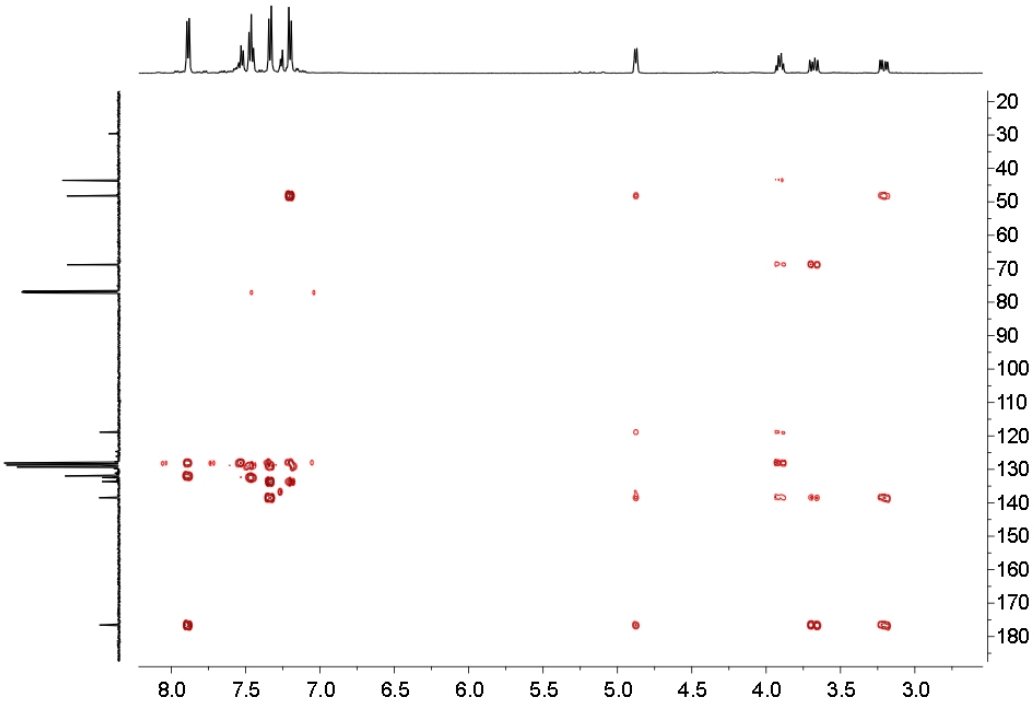
trans-**7a**, yellowish viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.21 (dd, *J* = 17.5, 7.5 Hz, 1H), 3.68 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.91 (m, 1H), 4.88 (d, *J* = 7.0 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 43.6, 48.2, 68.8, 118.9, 128.1(2C), 128.7, 129.3, 132.0, 132.4, 133.6, 138.4, 176.6. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{14}ClN_2$ ([M+H]$^+$) 281.7589. Found 281.7580.

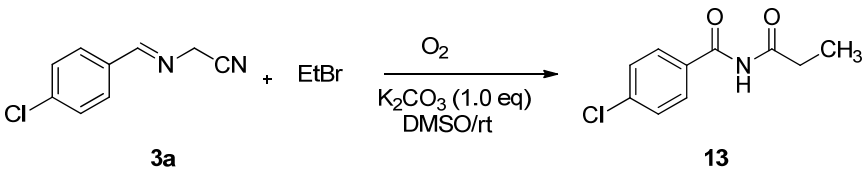
cis-**7a**, yellowish viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.37 (dd, *J* = 17.5, 6.0 Hz, 1H), 3.52 (dd, *J* = 17.5, 9.0 Hz, 1H), 3.93 (m, 1H), 5.31 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5

1 Y. Zhang, L. Pan, X. Xu and Q. Liu, *RSC Adv.*, 2012, **2**, 5138.

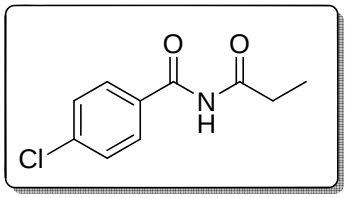
Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.92 (d, J = 7.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 42.5, 45.5, 67.1, 116.9, 128.1, 128.8(2C), 129.1, 132.1, 132.5, 133.8, 137.2, 177.5. **HRMS** (ESI-TOF) Calcd for Calcd for $C_{17}H_{14}ClN_2$ ([M+H]$^+$) 281.7589. Found 281.7580.

HMBC of **7a**





3a **13**

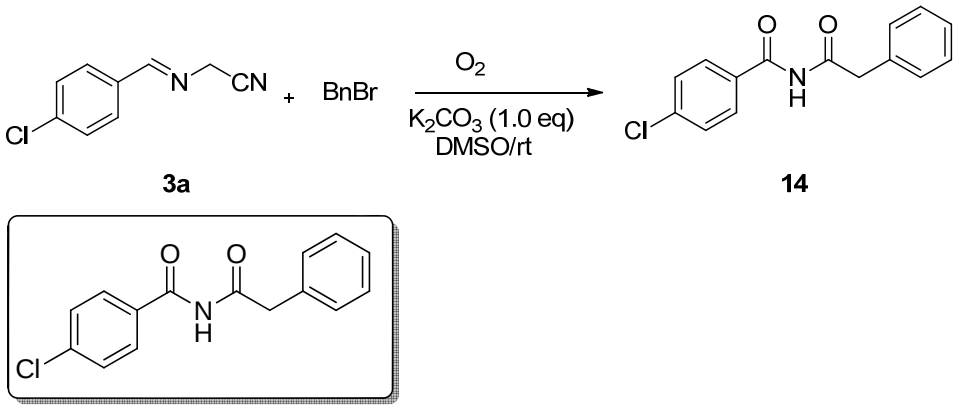


13, 4-chloro-*N*-propionylbenzamide.

To a solution of (*E*)-2-(4-chlorobenzylideneamino)acetonitrile (107 mg, 0.6 mmol) in DMSO (5.0 mL) was added K_2CO_3 (69.0 mg, 0.5 mmol) was added in one portion under oxygen atmosphere following with bromoethane (37 μL, 0.5 mmol). The reaction mixture was stirred at room temperature and was monitored by TLC. After benzyl bromide was consumed, the resulting mixture

was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL × 2). The aqueous layer was treated with 10% NaClO solution (5 mL) and collected. The combined organic layers were dried over anhydrous Na_2SO_4, evaporated *in vacuo*, and the residue was purified by column chromatography (EtOAc/PE = 1/9, V/V) to give **13** (66 mg, 63%). Reaction time 8.0 h.

Yellowish oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.34 (t, *J* = 7.0 Hz, 3H), 4.30 (q, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 8.21 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.2, 62.6, 129.1(2C), 131.3, 139.4, 150.9, 164.1. **HRMS** (ESI-TOF) Calcd for $C_{10}H_{10}ClKNO_2^+$ ($[M+K]^+$) 250.0032. Found 250.0041.

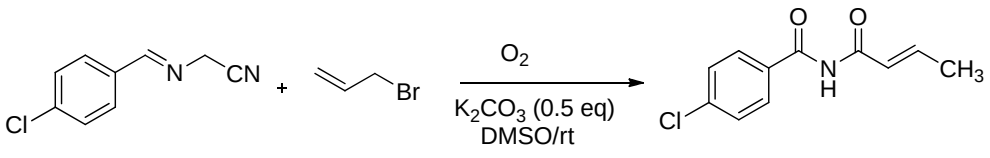


3a **14**

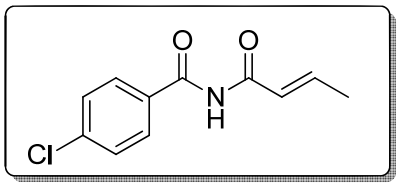
14, 4-chloro-*N*-(2-phenylacetyl)benzamide.

To a solution of (*E*)-2-(4-chlorobenzylideneamino)acetonitrile (107 mg, 0.6 mmol) in DMSO (5.0 mL) was added K_2CO_3 (69.0 mg, 0.5 mmol) was added in one portion under oxygen atmosphere following with benzyl bromide (60 μL, 0.5 mmol). The reaction mixture was stirred at room temperature and was monitored by TLC. After benzyl bromide was consumed, the resulting mixture was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL × 2). The aqueous layer was treated with 10% NaClO solution (5 mL) and collected. The combined organic layers were dried over anhydrous Na_2SO_4, evaporated *in vacuo*, and the residue was purified by column chromatography (EtOAc/PE = 1/10, V/V) to give **14** (102 mg, 75%). Reaction time 6.0 h.

Yellowish crystals, m.p. 117–119 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.25 (s, 2H), 7.36–7.40 (m, 5H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 8.07 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 68.1, 128.7, 128.8, 129.1(2C), 130.5, 131.1, 134.7, 139.5, 150.7, 164.0. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{12}ClKNO_2^+$ ($[M+K]^+$) 312.0188. Found 312.0194.



3a **15**

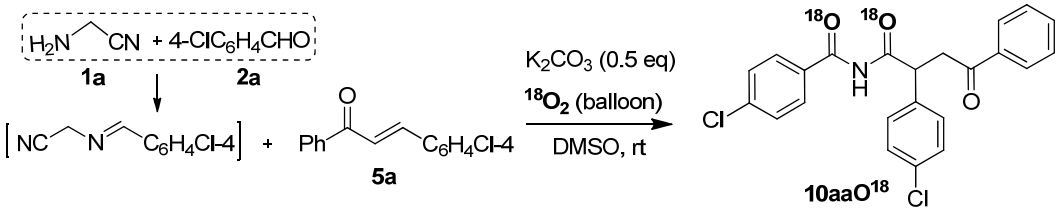


15, (*E*)-*N*-but-2-enoyl-4-chlorobenzamide

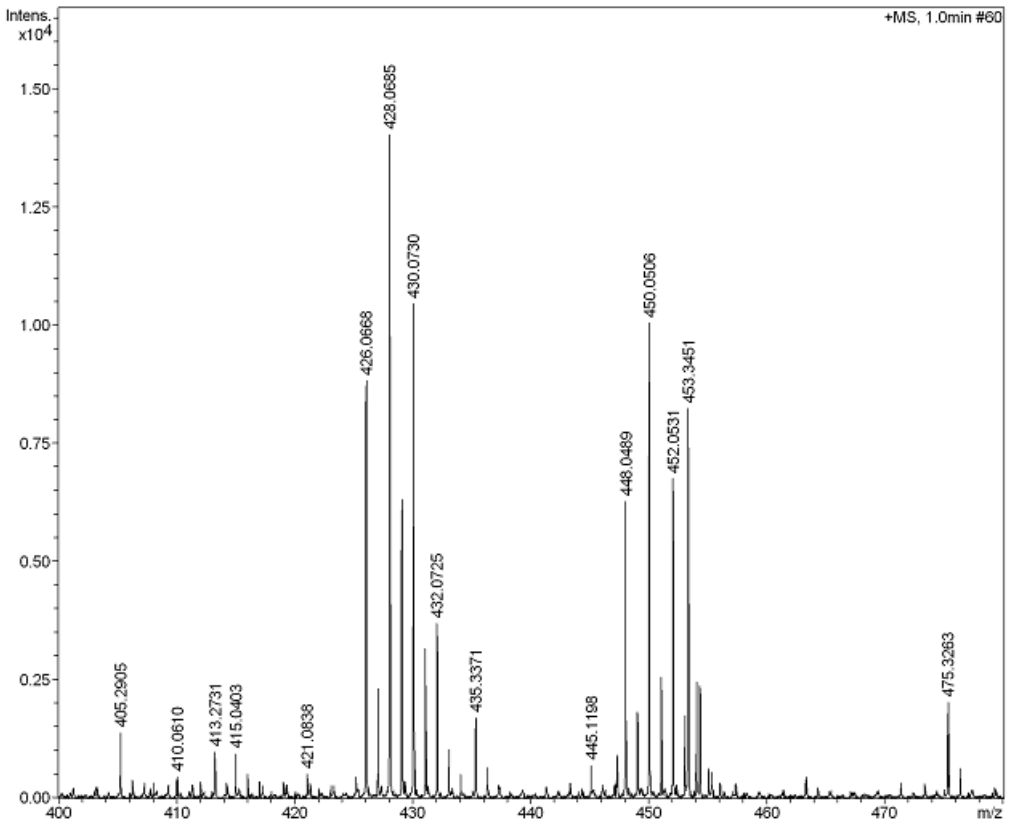
To a solution of (*E*)-2-(4-chlorobenzylideneamino)acetonitrile (107 mg, 0.6 mmol) in DMSO (5.0 mL) was added K_2CO_3 (34.5 mg, 0.25 mmol) was added in one portion under oxygen atmosphere following with allyl bromide (44 μL, 0.5 mmol). The reaction mixture was stirred at room temperature and was monitored by TLC. After benzyl bromide was consumed, the resulting mixture was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL × 2). The aqueous layer was treated with 10% NaClO solution (5 mL) and collected. The combined organic layers were dried over anhydrous Na_2SO_4, evaporated *in vacuo*, and the residue was purified by column chromatography (EtOAc/PE = 1/10, V/V) to give **15** (62.4 mg, 56%). Reaction time 12.0 h.

Yellowish crystals, m.p. 85–87 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.00 (d, J = 6.5 Hz, 3H), 7.11 (d, J = 15.5 Hz, 1H), 7.22–7.26 (m, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 8.30 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 18.6, 123.9, 129.1, 129.3, 129.6, 129.9(2C), 147.6, 161.3. **HRMS** (ESI-TOF) Calcd for $C_{11}H_{10}ClKNO_2^+$ ($[M+K]^+$) 262.0032. Found 262.0049.

III. Isotope Labeled O_2 Experiments



HRMS spectrum



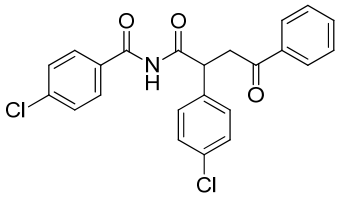
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
426.0668	1	C 23 H 18 Cl 2 N O 3	100.00	426.0658	-2.3	-18.8	354.8	14.5	even	ok

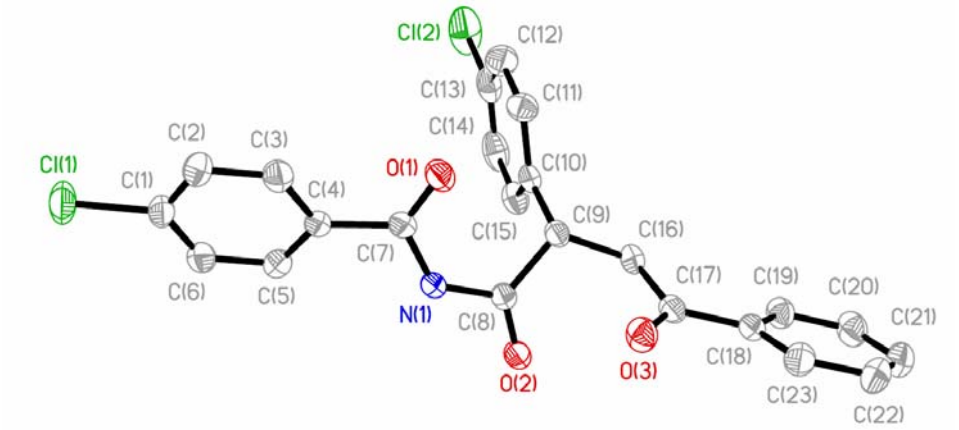
IV. Crystal data and OPTEP drawing of compound **10aa**

Single-crystal X-ray diffraction data was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-Kα (λ = 0.71073 Å) radiation with a ω scan technique. The crystal structures were solved by direct method of SHELXS-97[2] and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined anisotropic.

(1) Crystal data and OPTEP drawing of compound **10aa** (CCDC 938346)

ORTEP drawing:





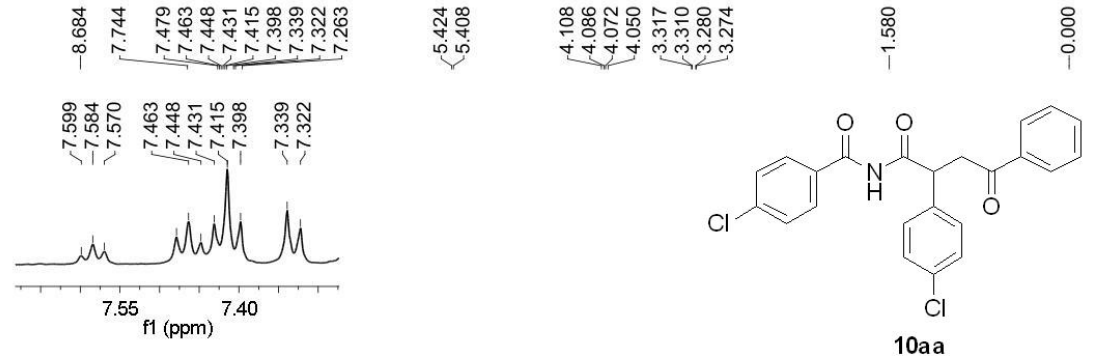
Crystal data:

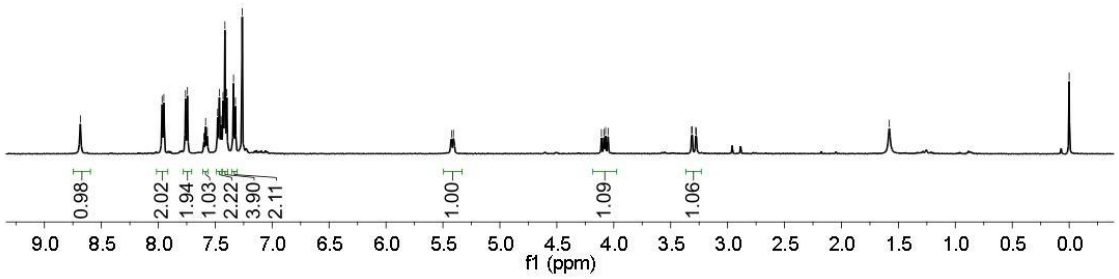
Empirical formula	$C_{23}H_{17}Cl_2NO_3$
Formula weight	426.3
Crystal system	Triclinic
Space group	P -1
a (Å)	9.8294(19)
b (Å)	10.0500(19)
c (Å)	12.1693(23)
α (deg)	114.273(1)
β (deg)	97.114(2)
γ (deg)	105.645(1)
Volume (Å^3)	1016.86(11)
Z	2

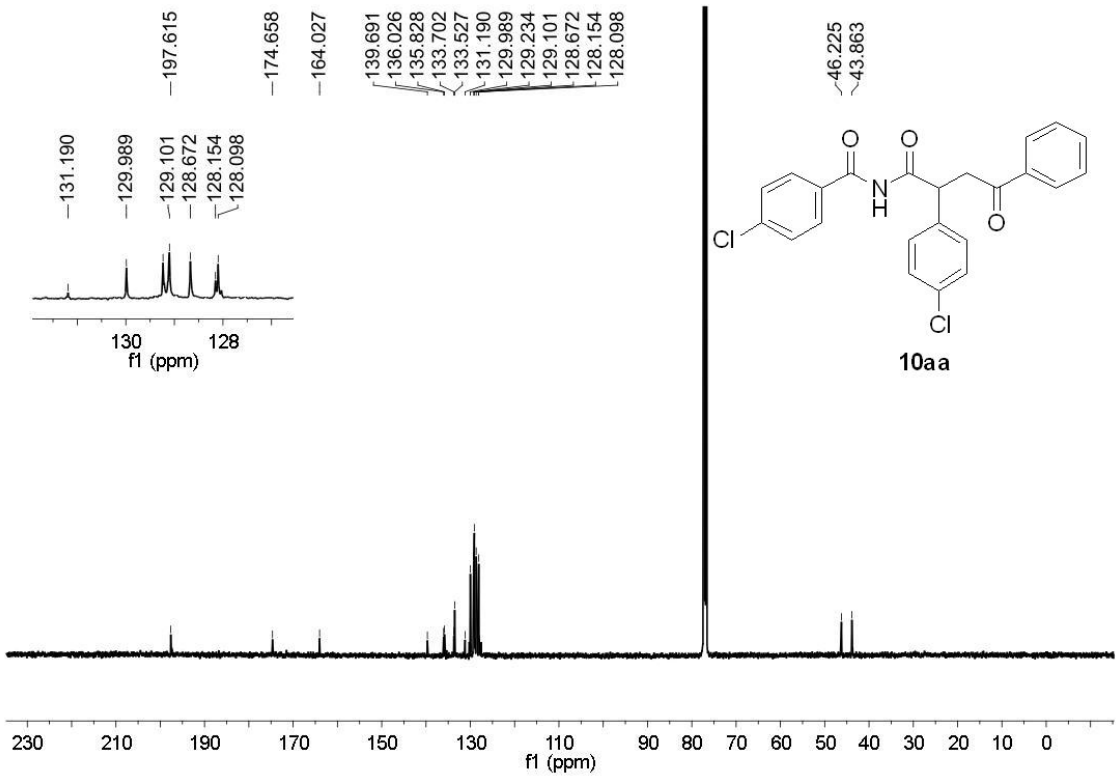
2 G. M. Sheldrick, *SHELXS-97*, *Programs for X-ray Crystal Structure Solution*; University of Göttingen, Göttingen, Germany, 1997.

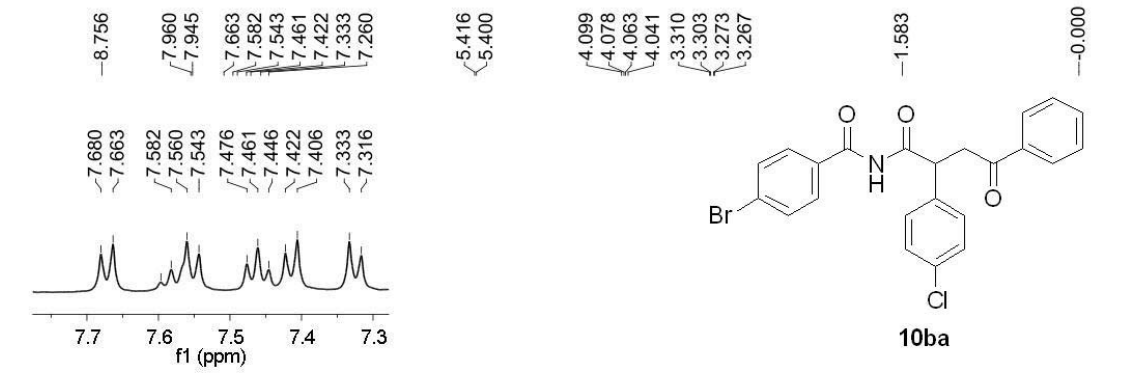
Calculated density (mg/m^3)	1.39
Absorption coefficient (mm^{-1})	0.344
F(000)	439.9
Theta range for data collection (deg)	1.9 to 25.0
Reflections collected/unique	5172/3530
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	R1=0.045, WR2 = 0.106
R indices (all data)	R1=0.060, WR2 =0.115

V. Copies of ^{1}H NMR and ^{13}C NMR spectra





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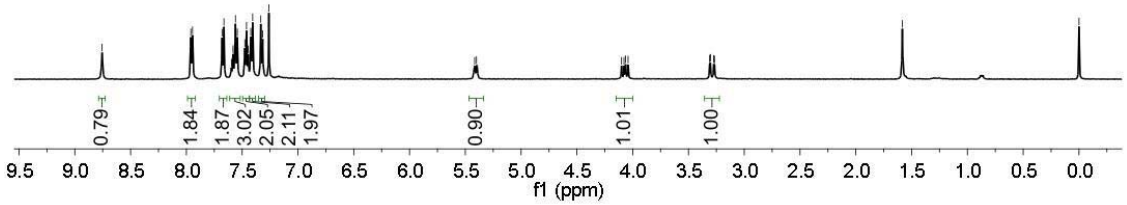
7.960
7.945
7.663
7.582
7.543
7.461
7.422
7.333
7.260
5.416
5.400
4.099
4.078
4.063
4.041
3.310
3.303
3.273
3.267
1.583
0.000
7.680
7.663
7.582
7.560
7.543
7.476
7.461
7.446
7.422
7.406
7.333
7.316
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
Br
O
N
H
O
O
Cl
10ba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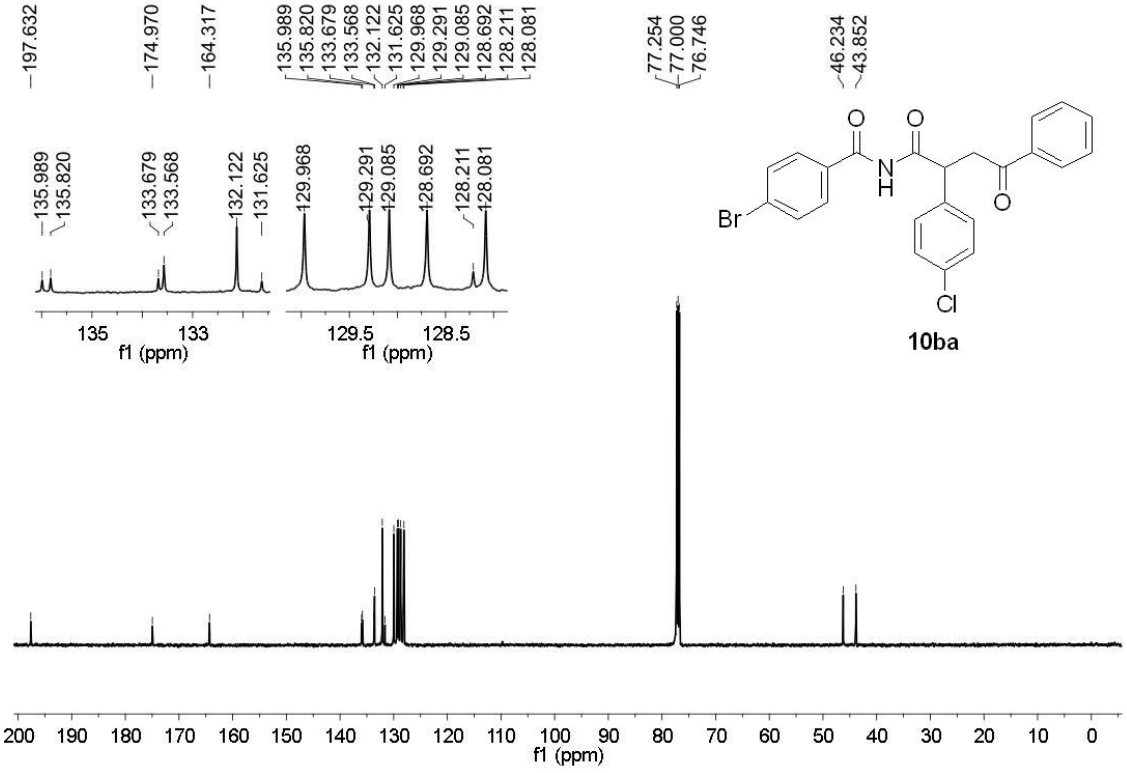
1.87
3.02
2.05
2.11
1.97
0.90
1.01
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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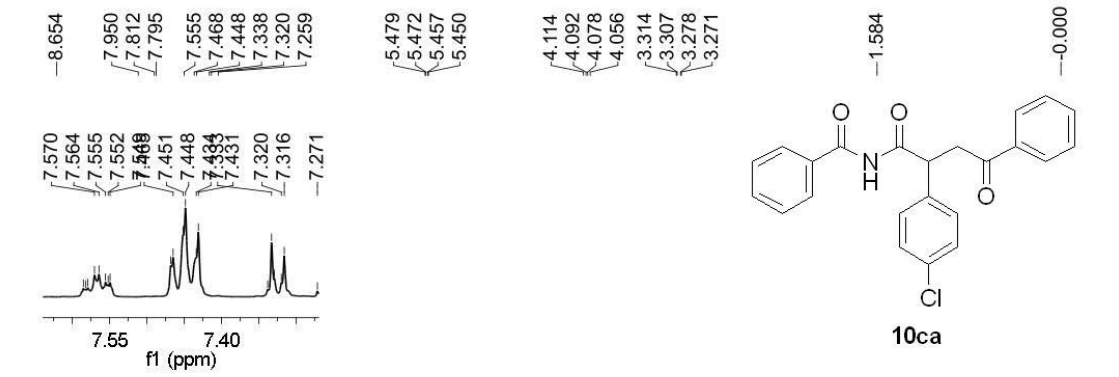
164.317
135.989
135.820
133.679
133.568
132.122
131.625
129.968
129.291
129.085
128.692
128.211
128.081
77.254
77.000
76.746
46.234
43.852
135
133
f1 (ppm)
129.5
128.5
f1 (ppm)
Br
O
N
H
O
O
Cl
10ba
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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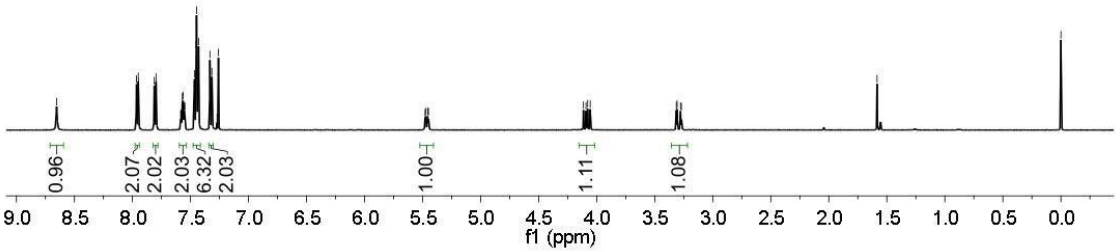
7.795
7.555
7.468
7.448
7.338
7.320
7.259
5.479
5.472
5.457
5.450
4.114
4.092
4.078
4.056
3.314
3.307
3.278
3.271
1.584
0.000
7.570
7.564
7.555
7.552
7.451
7.448
7.320
7.316
7.271
7.55
7.40
f1 (ppm)
O
N
H
O
O
Cl

10ca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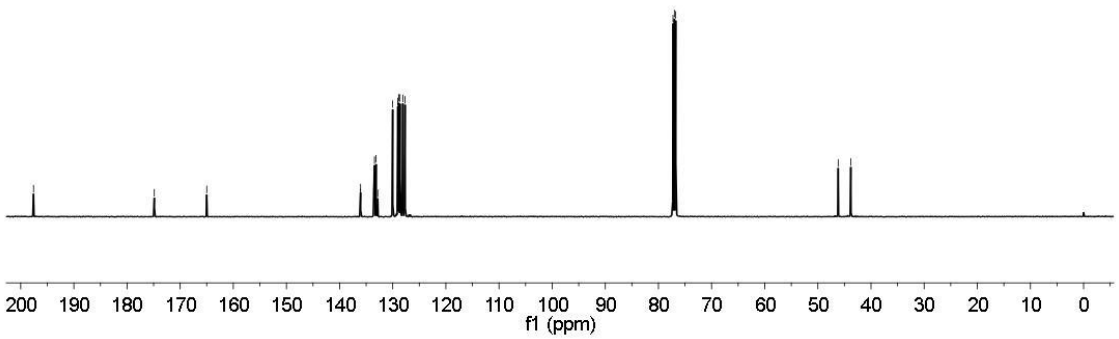
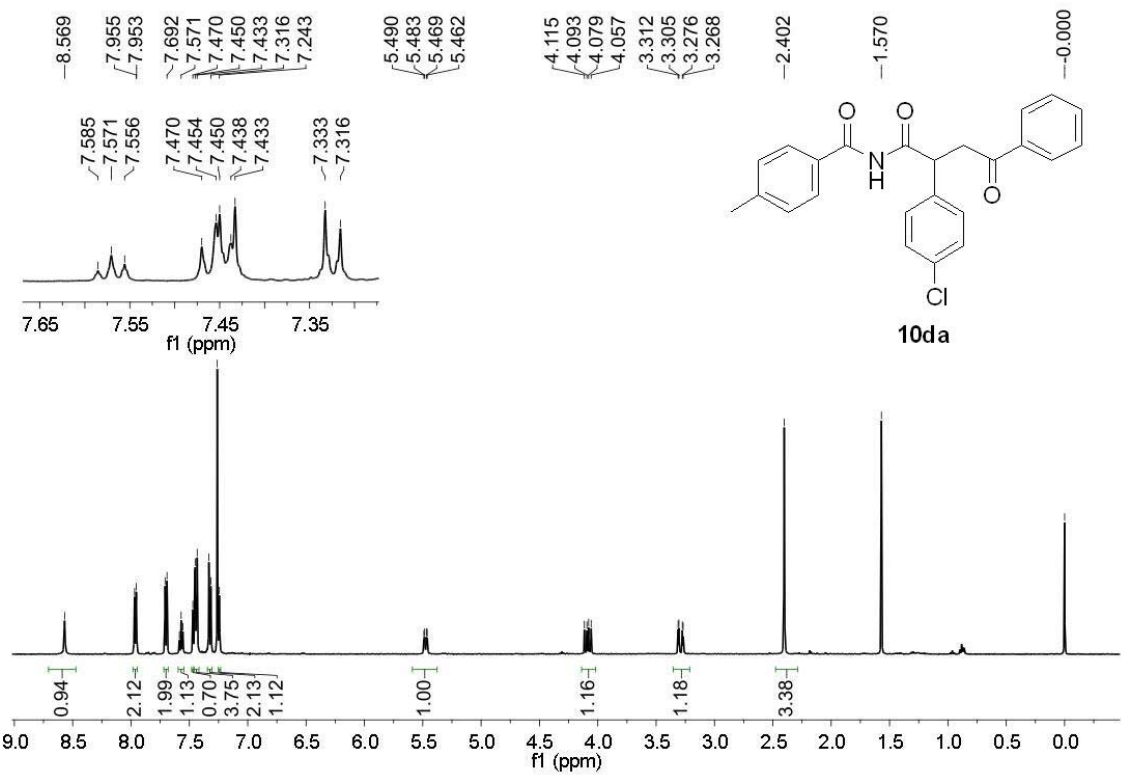
2.07
2.02
2.03
6.32
2.03
1.00
1.11
1.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.588
174.866
164.997
136.102
136.046
133.578
133.432
133.130
132.813
130.008
129.034
128.868
128.629
128.092
127.676
77.254
77.000
76.746
46.176
43.798
130.008
129.034
128.868
128.629
128.092
127.676
129.0
f1 (ppm)
O
N
H
O
O
Cl

10ca


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.692
7.571
7.470
7.450
7.433
7.316
7.243
5.490
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5.469
5.462
4.115
4.093
4.079
4.057
3.312
3.305
3.276
3.268
2.402
1.570
0.000
7.585
7.571
7.556
7.470
7.454
7.450
7.438
7.433
7.333
7.316
7.65
7.55
7.45
7.35
f1 (ppm)
O
N
H
O
O
Cl
10da
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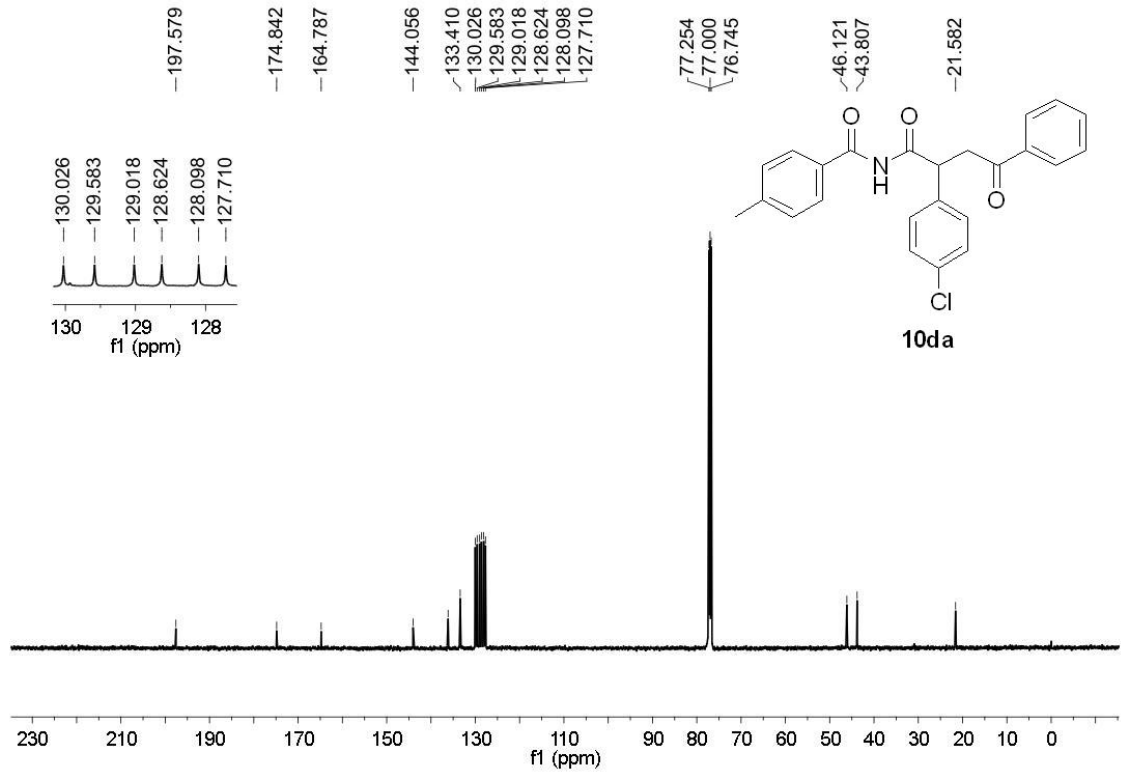
1.99
1.13
0.70
3.75
2.13
1.12
1.00
1.16
1.18
3.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.098
127.710
77.254
77.000
76.745
46.121
43.807
21.582
130.026
129.583
129.018
128.624
128.098
127.710
130
129
128
f1 (ppm)
O
N
H
O
O
Cl
10da
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210
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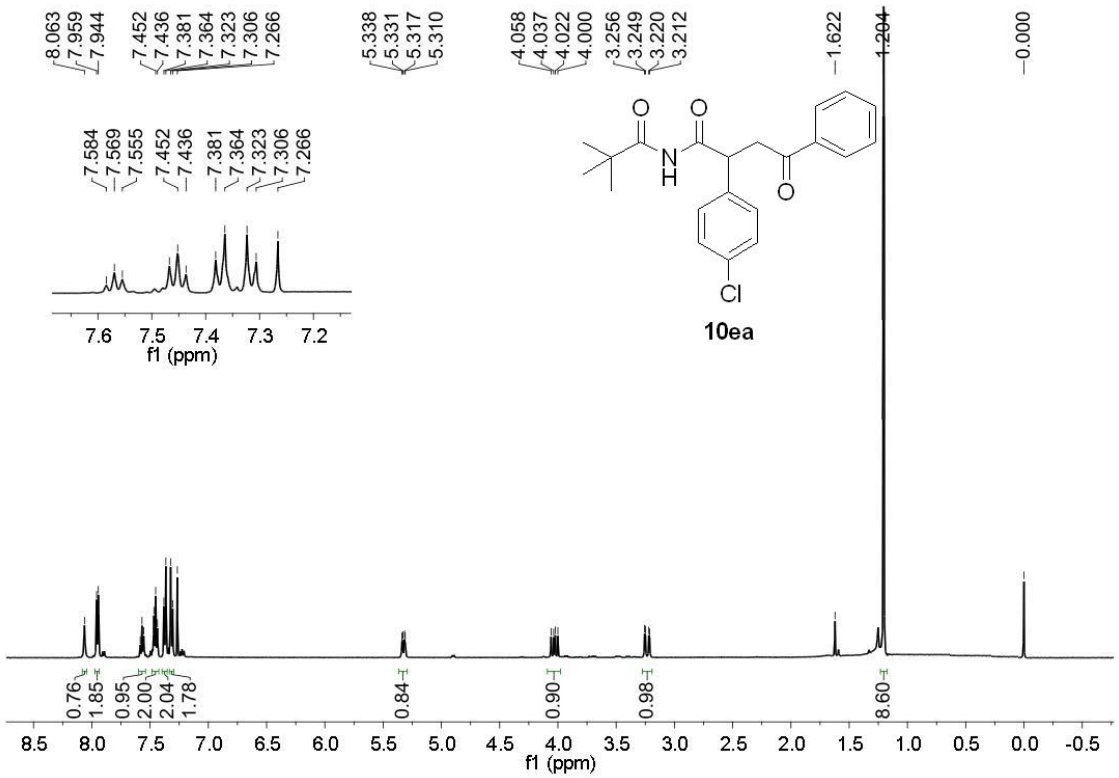
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.381
7.364
7.323
7.306
7.266
5.338
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5.317
5.310
4.058
4.037
4.022
4.000
3.256
3.249
3.220
3.212
1.622
1.264
0.000
7.584
7.569
7.555
7.452
7.436
7.381
7.364
7.323
7.306
7.266
7.6 7.5 7.4 7.3 7.2
f1 (ppm)
Cl
10ea
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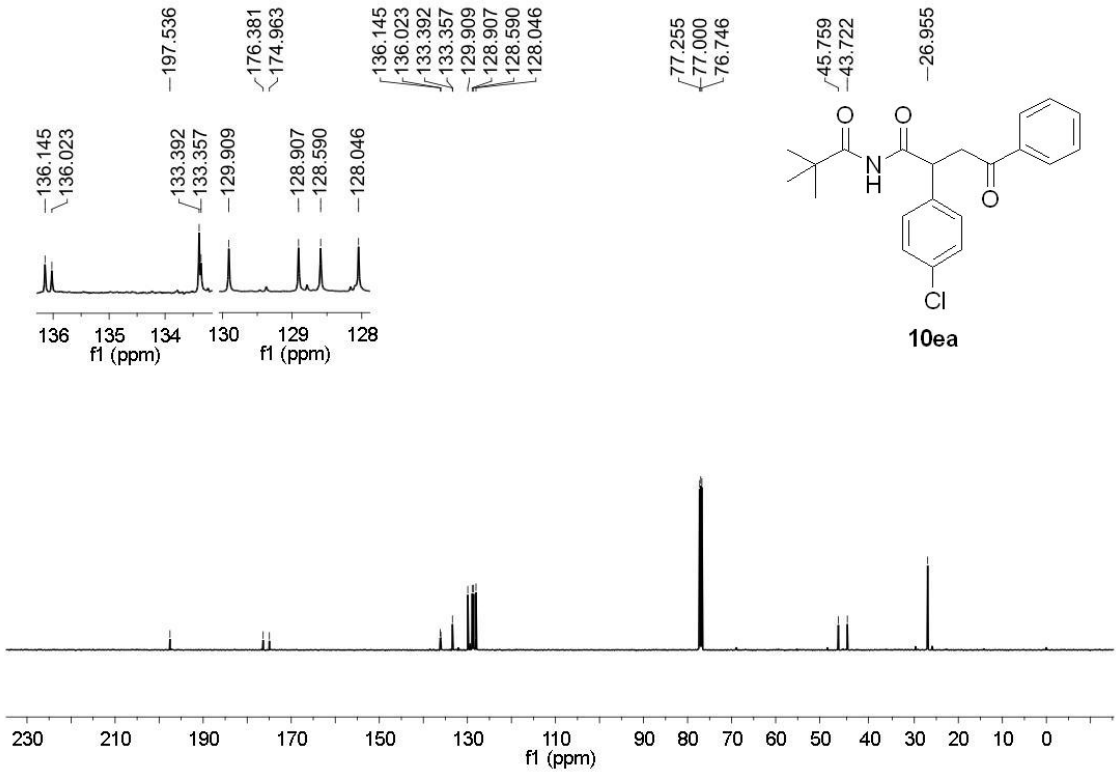
1.85
0.95
2.00
2.04
1.78
0.84
0.90
0.98
8.60
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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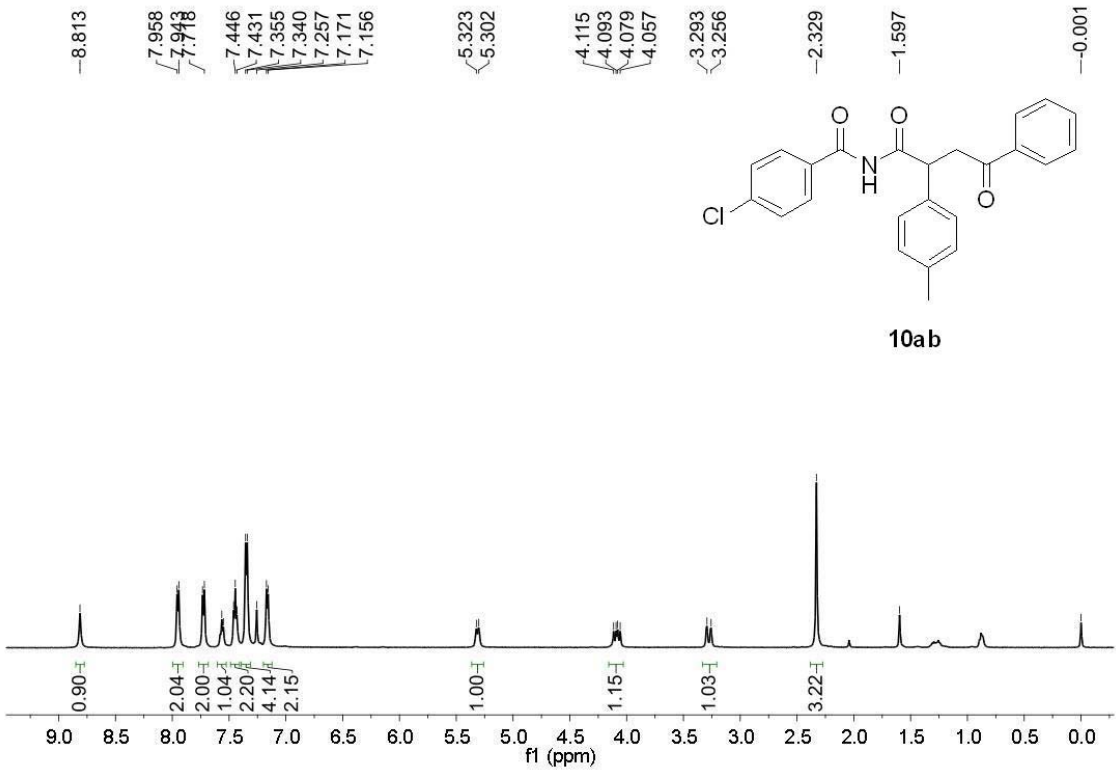
136.023
133.392
133.357
129.909
128.907
128.590
128.046
77.255
77.000
76.746
45.759
43.722
26.955
136.145
136.023
133.392
133.357
129.909
128.907
128.590
128.046
136 135 134
f1 (ppm)
130 129 128
f1 (ppm)
Cl
10ea
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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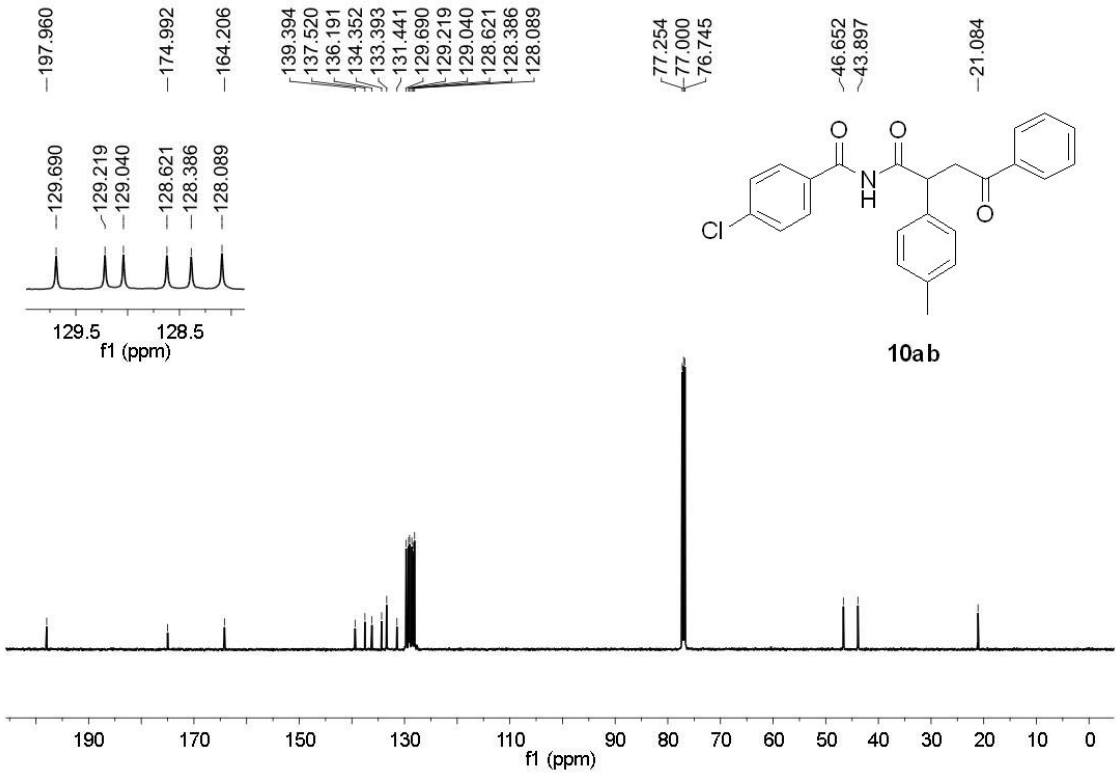
7.156
5.323
5.302
4.115
4.093
4.079
4.057
3.293
3.256
2.329
1.597
0.001
Cl
O
N
H
O
O
10ab
0.90
2.04
2.00
1.04
2.20
4.14
2.15
1.00
1.15
1.03
3.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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137.520
136.191
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133.393
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129.690
129.219
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128.621
128.386
128.089
77.254
77.000
76.745
46.652
43.897
21.084
129.690
129.219
129.040
128.621
128.386
128.089
129.5
128.5
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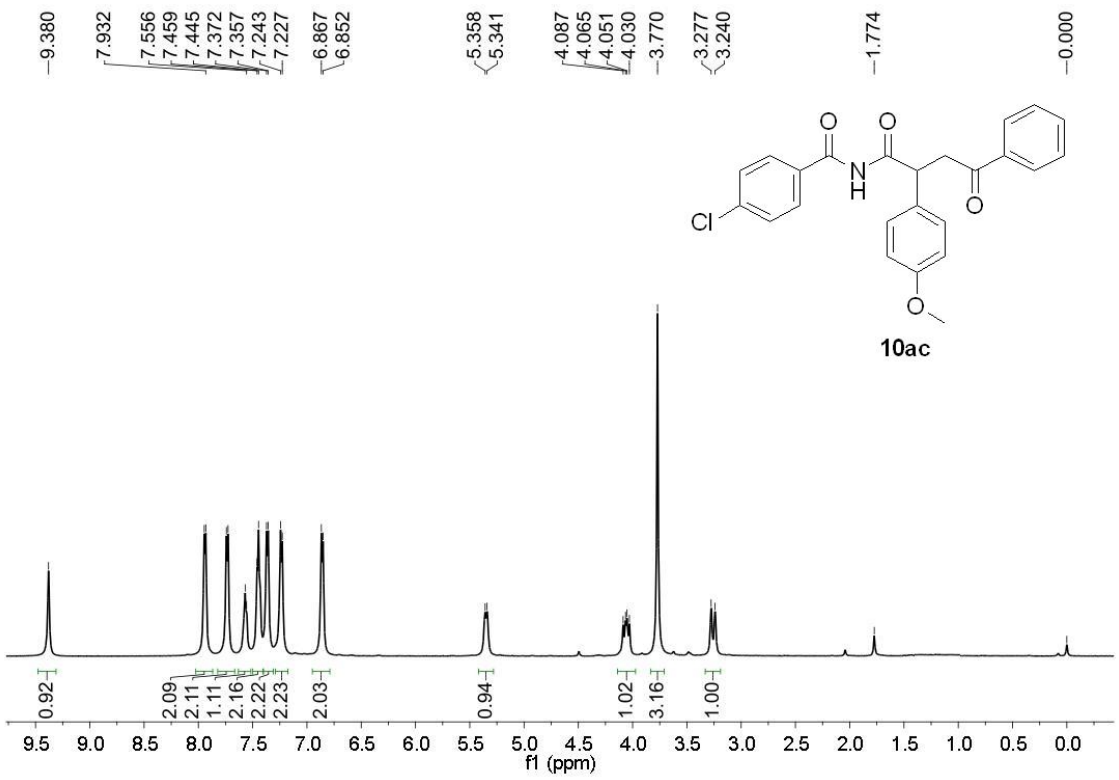
Cl
O
N
H
O
O
10ab
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.372
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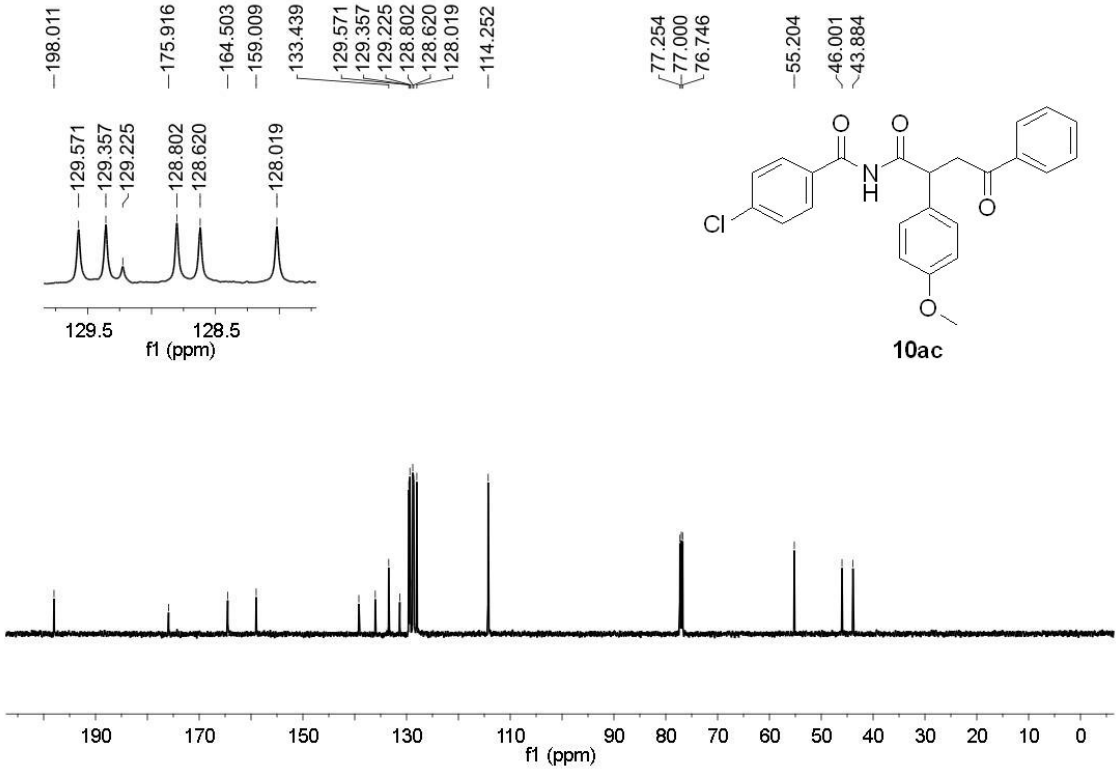
7.243
7.227
6.867
6.852
5.358
5.341
4.087
4.065
4.051
4.030
3.770
3.277
3.240
1.774
0.000
Cl
O
N
H
O
O
O
10ac
0.92
2.09
2.11
1.11
2.16
2.22
2.23
2.03
0.94
1.02
3.16
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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175.916
164.503
159.009
133.439
129.571
129.357
129.225
128.802
128.620
128.019
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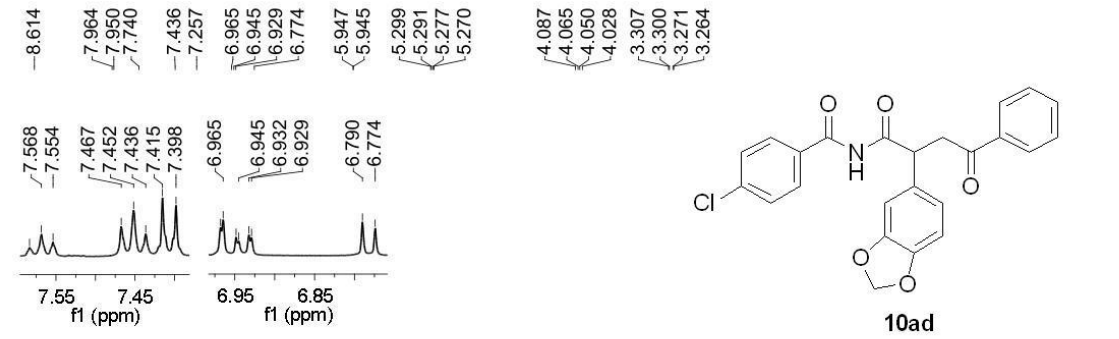
77.254
77.000
76.746
55.204
46.001
43.884
129.571
129.357
129.225
128.802
128.620
128.019
129.5
128.5
f1 (ppm)
Cl
O
N
H
O
O
O
10ac
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.436
7.257
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6.945
6.929
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3.264
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7.55
7.45
f1 (ppm)
6.95
6.85
f1 (ppm)
Cl
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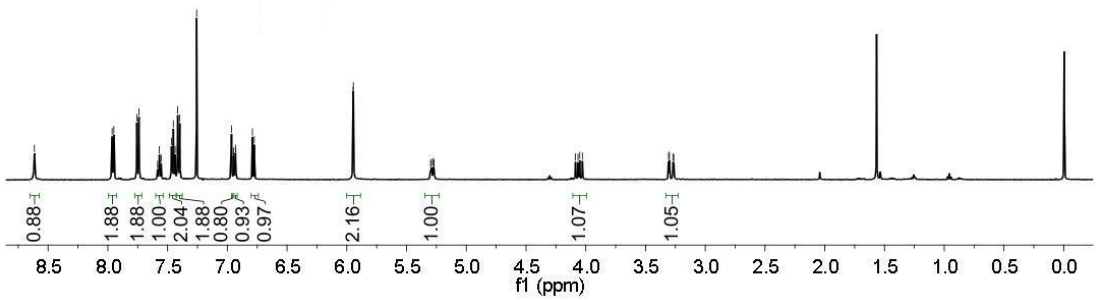
N
H
O
O
O
O
O
10ad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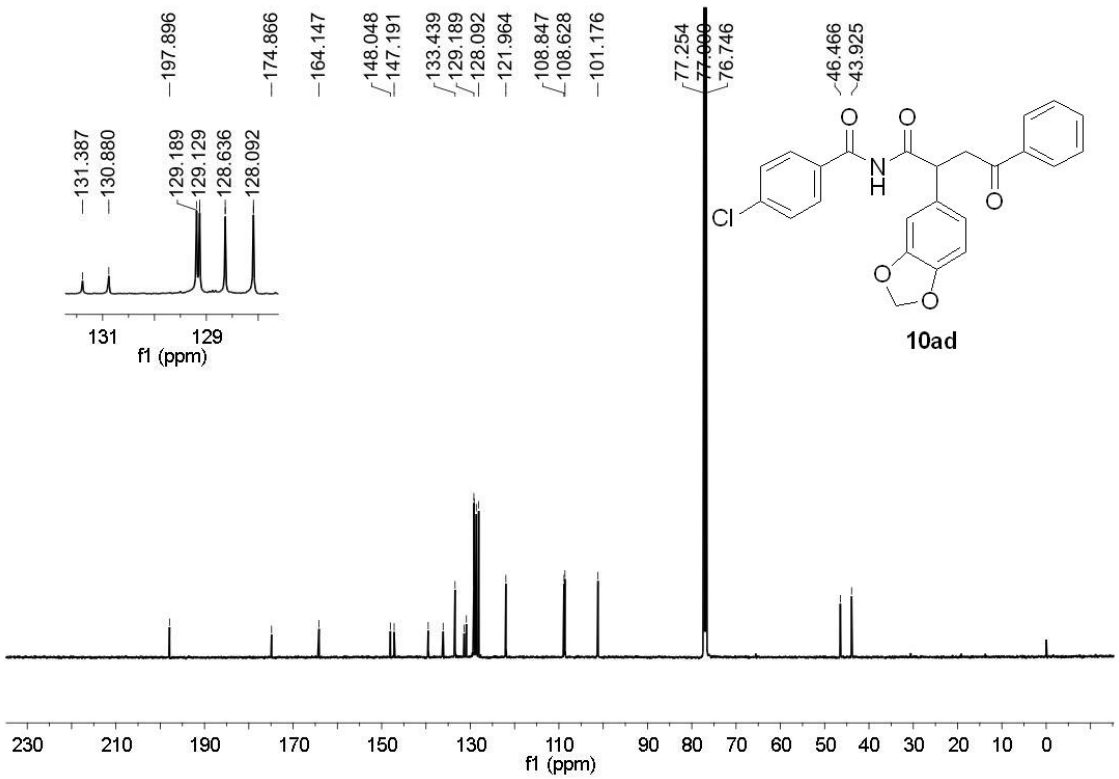
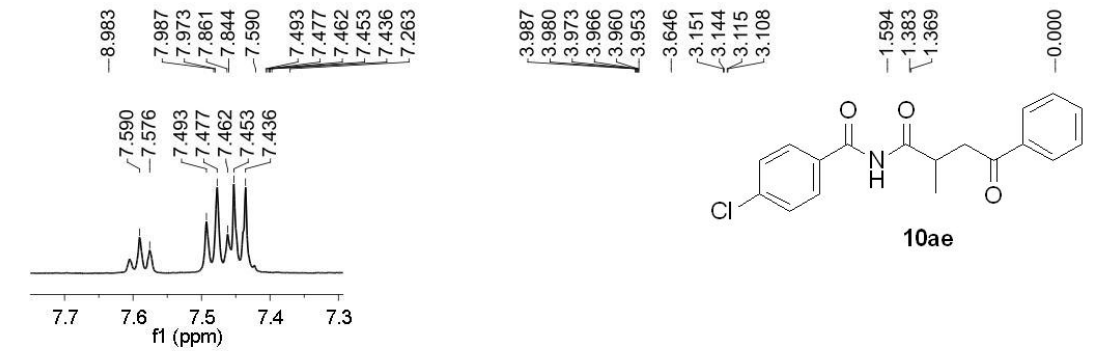
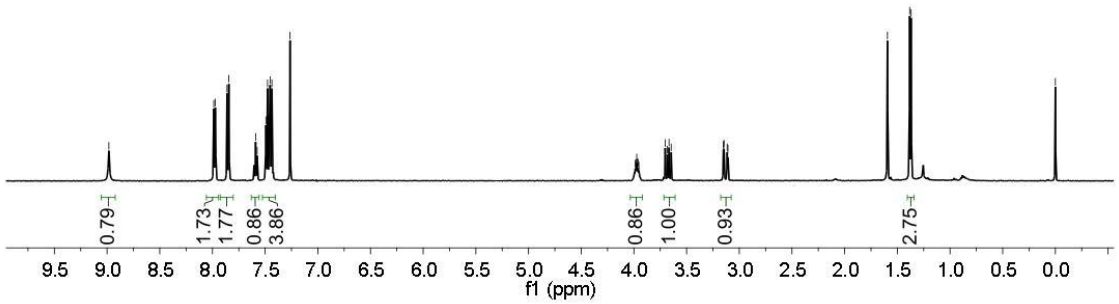
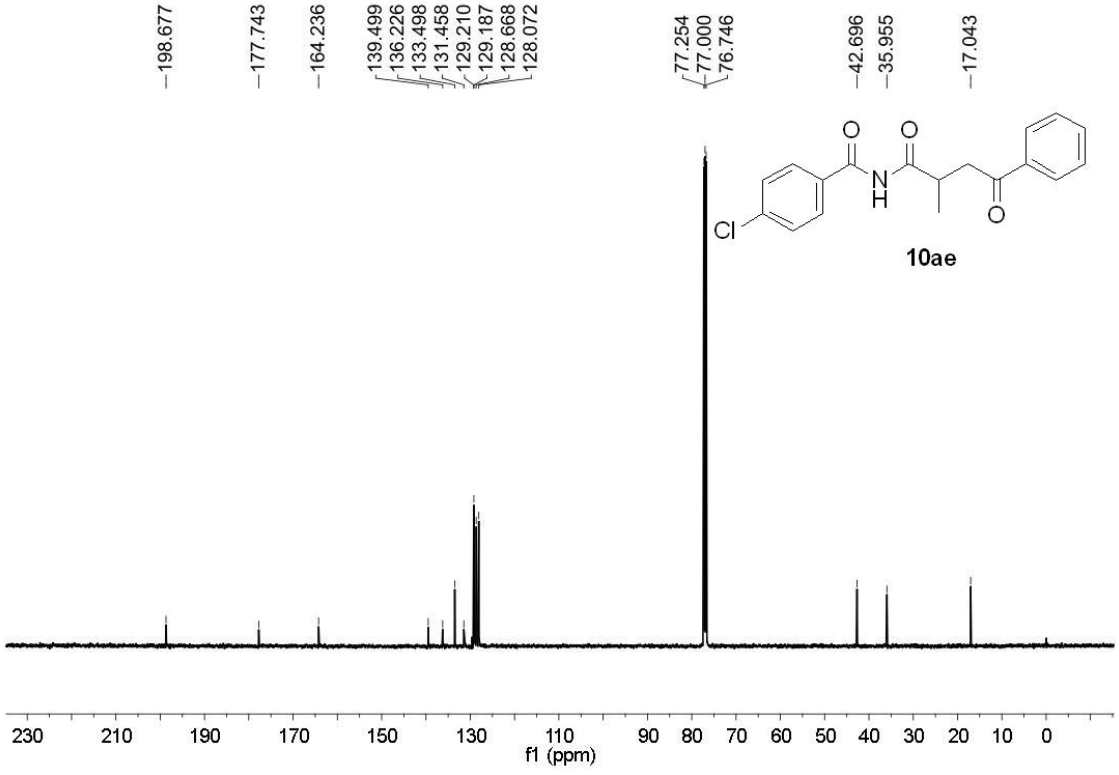
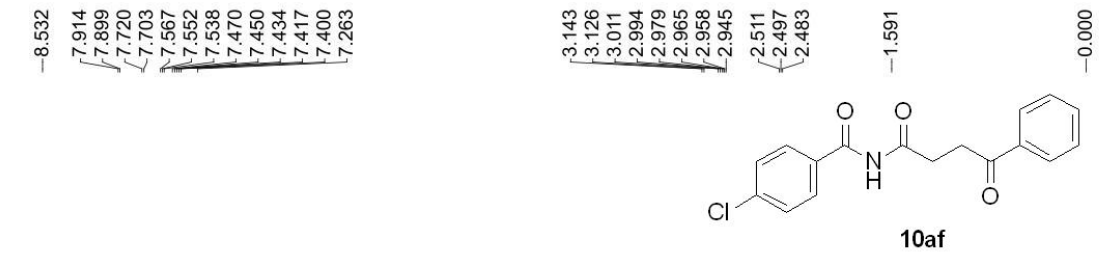
1.88
1.00
2.04
1.88
0.80
0.93
0.97
2.16
1.00
1.07
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

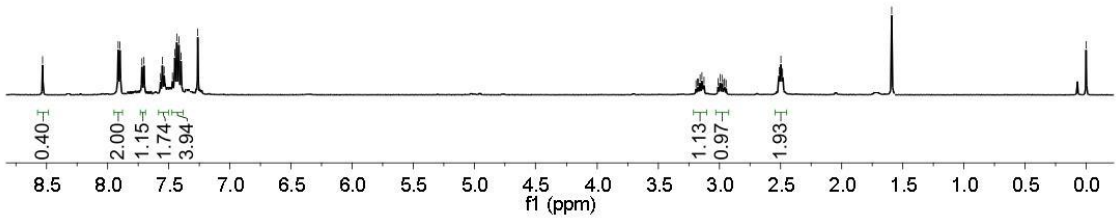

197.896
174.866
164.147
148.048
147.191
133.439
129.189
128.092
121.964
108.847
108.628
101.176
77.254
77.000
76.746
46.466
43.925
131.387
130.880
129.189
129.129
128.636
128.092
131
129
f1 (ppm)
Cl
O
N
H
O
O
O
O
O
10ad
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

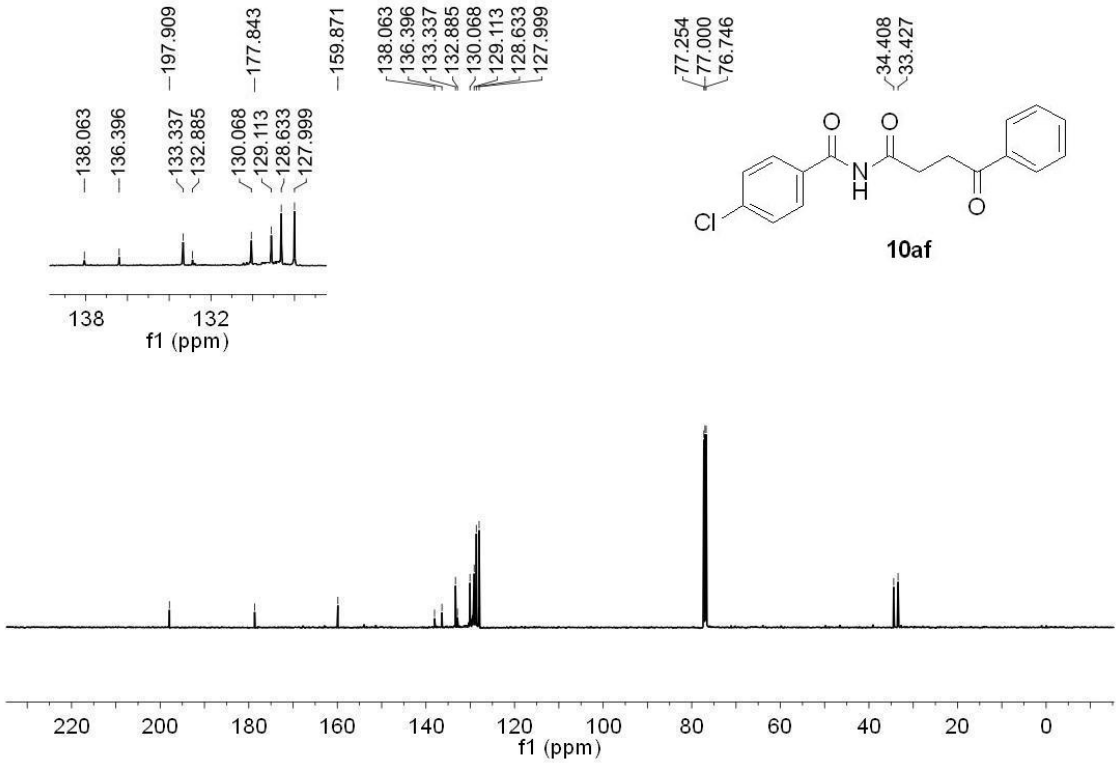

8.983
7.987
7.973
7.861
7.844
7.590
7.493
7.477
7.462
7.453
7.436
7.263
3.987
3.980
3.973
3.966
3.960
3.953
3.646
3.151
3.144
3.115
3.108
1.594
1.383
1.369
0.000
7.590
7.576
7.493
7.477
7.462
7.453
7.436
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
Cl
10ae

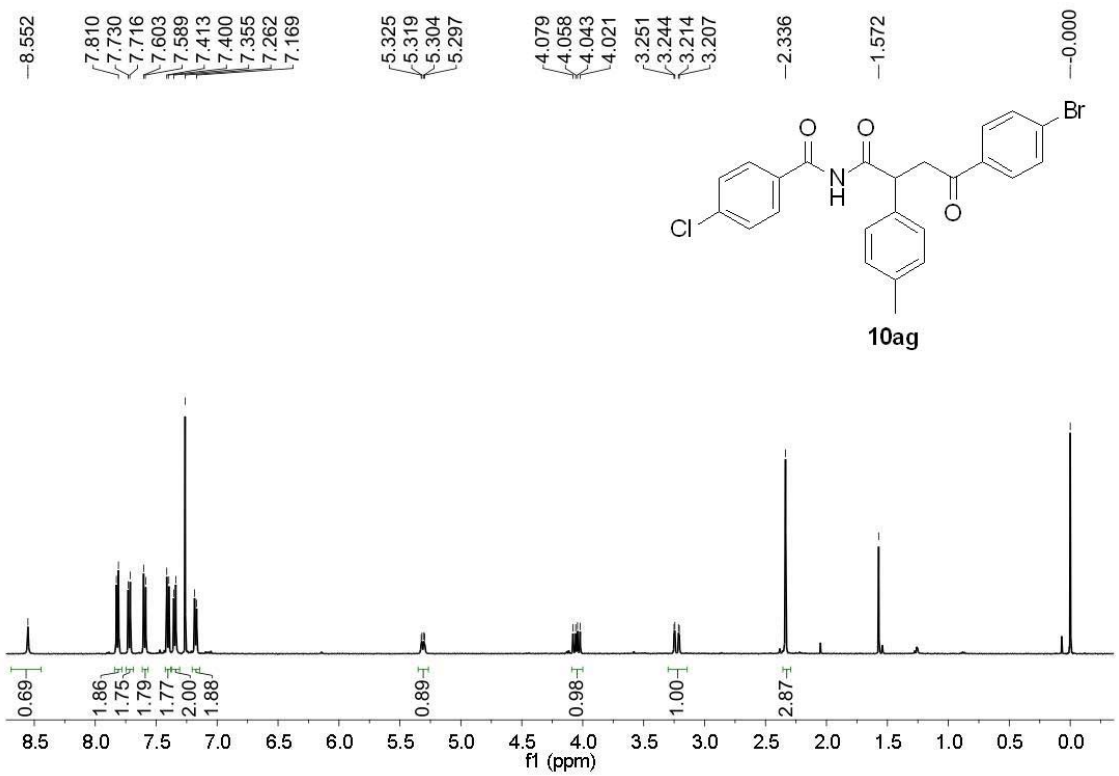

0.79
1.73
1.77
0.86
3.86
0.86
1.00
0.93
2.75
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

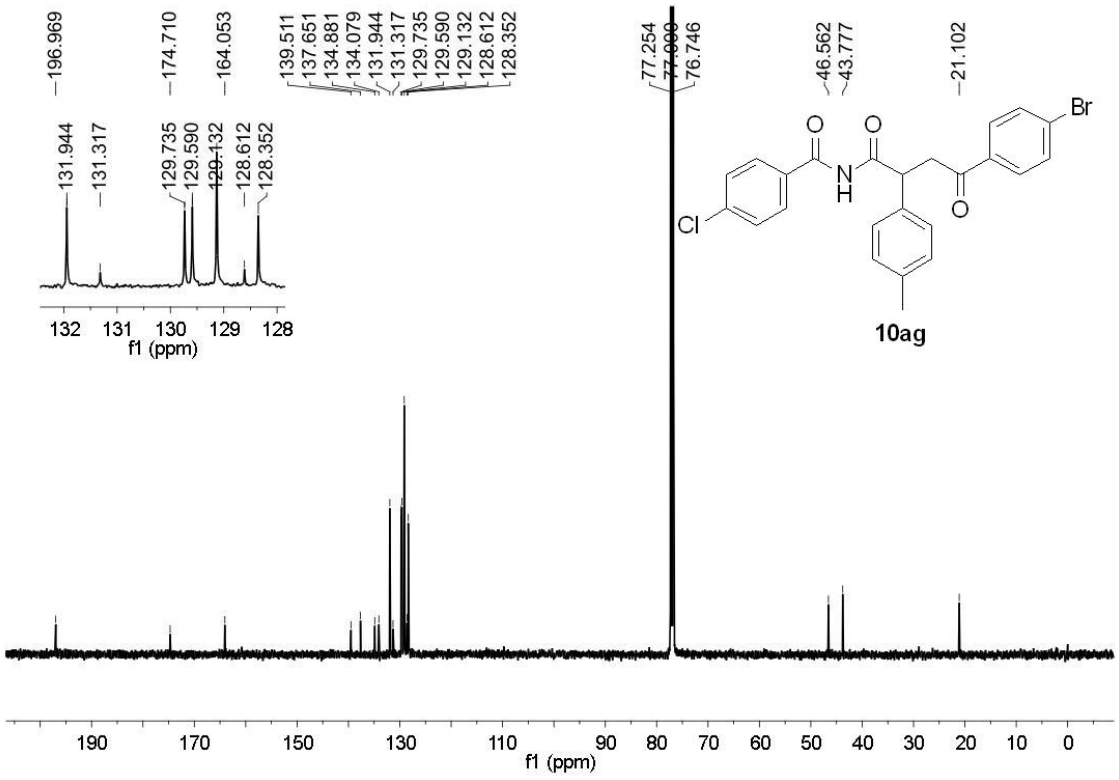

198.677
177.743
164.236
139.499
136.226
133.498
131.458
129.210
129.187
128.668
128.072
77.254
77.000
76.746
42.696
35.955
17.043
Cl
10ae
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

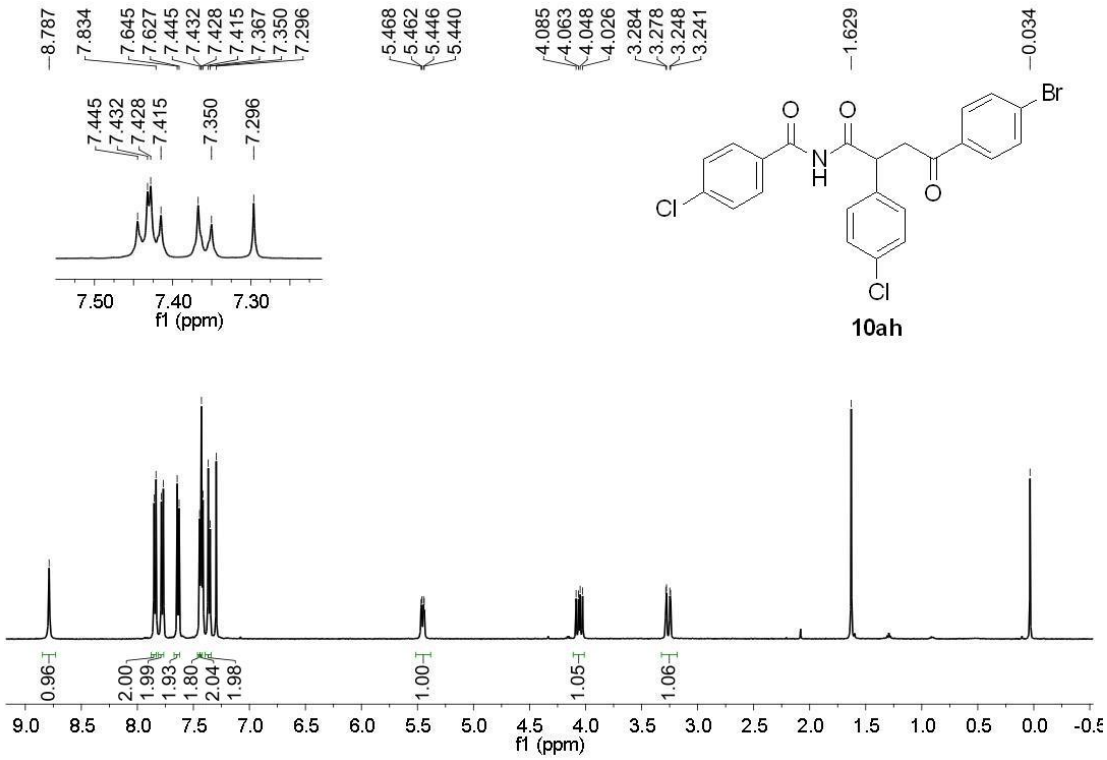

8.532
7.914
7.899
7.720
7.703
7.567
7.552
7.538
7.470
7.450
7.434
7.417
7.400
7.263
3.143
3.126
3.011
2.994
2.979
2.965
2.958
2.945
2.511
2.497
2.483
1.591
0.000
Cl
10af

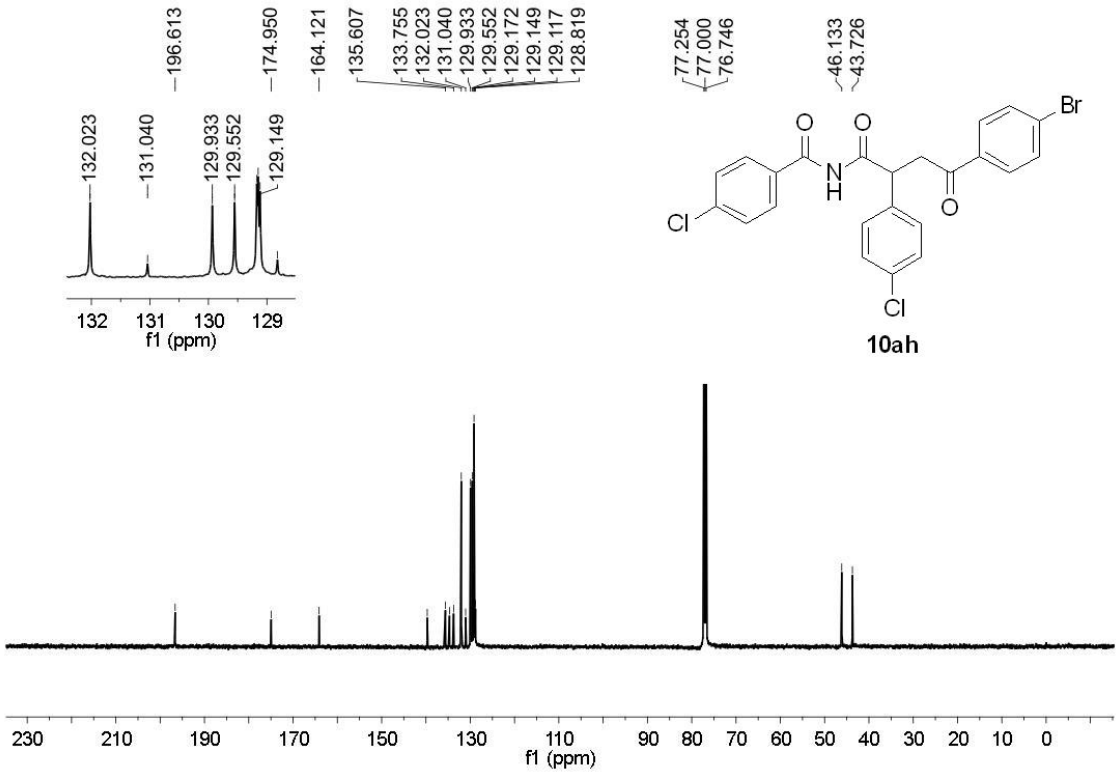

0.40
2.00
1.15
1.74
3.94
1.13
0.97
1.93
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

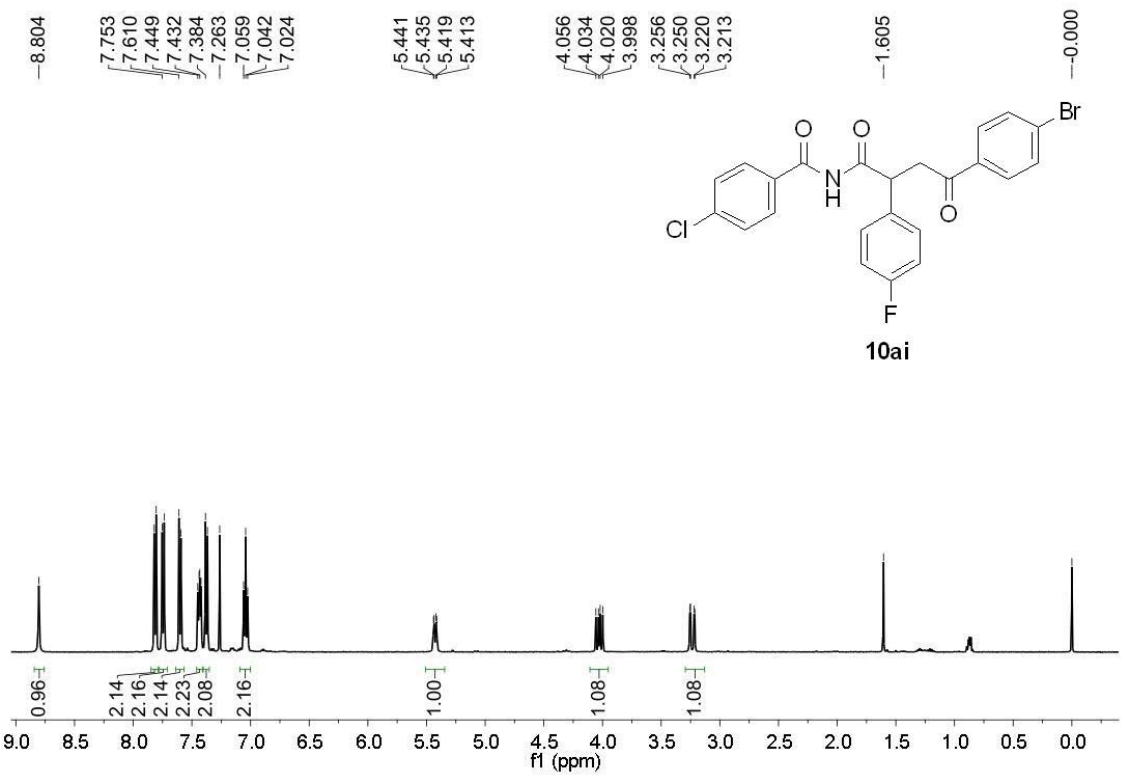

197.909
177.843
159.871
138.063
136.396
133.337
132.885
130.068
129.113
128.633
127.999
77.254
77.000
76.746
34.408
33.427
Cl
10af
138
132
f1 (ppm)
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

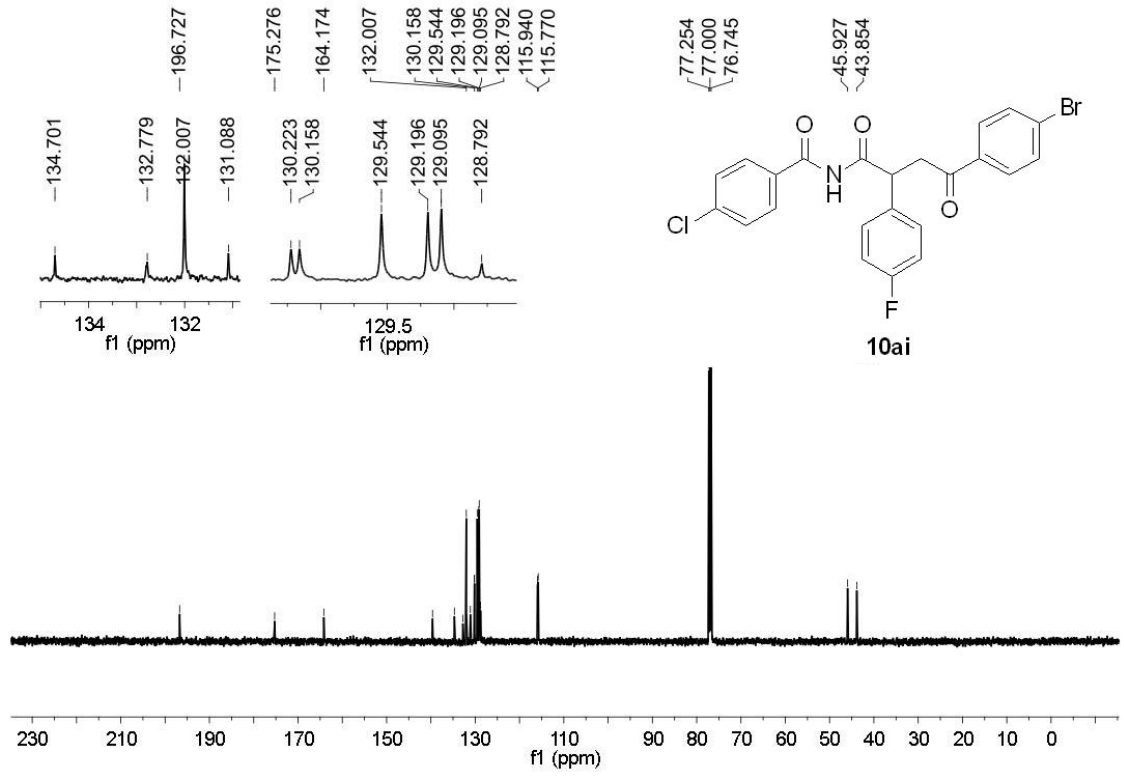

8.552
7.810
7.730
7.716
7.603
7.589
7.413
7.400
7.355
7.262
7.169
5.325
5.319
5.304
5.297
4.079
4.058
4.043
4.021
3.251
3.244
3.214
3.207
2.336
1.572
0.000
Br
Cl
O
N
H
10ag
0.69
1.86
1.75
1.79
1.77
2.00
1.88
0.89
0.98
1.00
2.87
f1 (ppm)

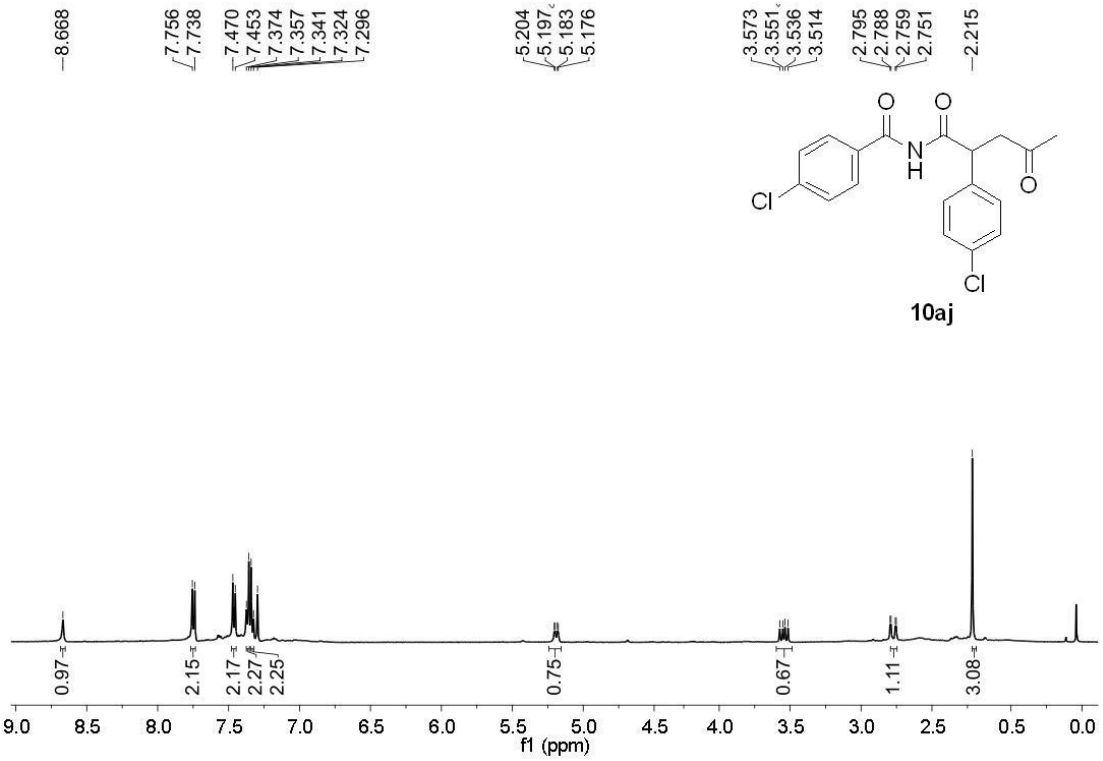

196.969
174.710
164.053
139.511
137.651
134.881
134.079
131.944
131.317
129.735
129.590
129.132
128.612
128.352
77.254
77.000
76.746
46.562
43.777
21.102
Br
Cl
10ag
f1 (ppm)


8.787
7.834
7.645
7.627
7.445
7.432
7.428
7.415
7.367
7.350
7.296
5.468
5.462
5.446
5.440
4.085
4.063
4.048
4.026
3.284
3.278
3.248
3.241
1.629
0.034
7.445
7.432
7.428
7.415
7.350
7.296
7.50
7.40
7.30
f1 (ppm)
Br
Cl
Cl
10ah
0.96
2.00
1.99
1.93
1.80
2.04
1.98
1.00
1.05
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


196.613
174.950
164.121
135.607
133.755
132.023
131.040
129.933
129.552
129.172
129.149
129.117
128.819
77.254
77.000
76.746
46.133
43.726
132.023
131.040
129.933
129.552
129.149
132
131
130
129
f1 (ppm)
Br
Cl
Cl
10ah
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.804
7.753
7.610
7.449
7.432
7.384
7.263
7.059
7.042
7.024
5.441
5.435
5.419
5.413
4.056
4.034
4.020
3.998
3.256
3.250
3.220
3.213
1.605
0.000
Br
O
O
N
H
O
Cl
F
10ai
0.96
2.14
2.16
2.14
2.23
2.08
2.16
1.00
1.08
1.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.727
175.276
164.174
132.007
130.158
129.544
129.196
129.095
128.792
115.940
115.770
77.254
77.000
76.745
45.927
43.854
134.701
132.779
132.007
131.088
130.223
130.158
129.544
129.196
129.095
128.792
134
132
f1 (ppm)
129.5
f1 (ppm)
Br
O
O
N
H
O
Cl
F
10ai
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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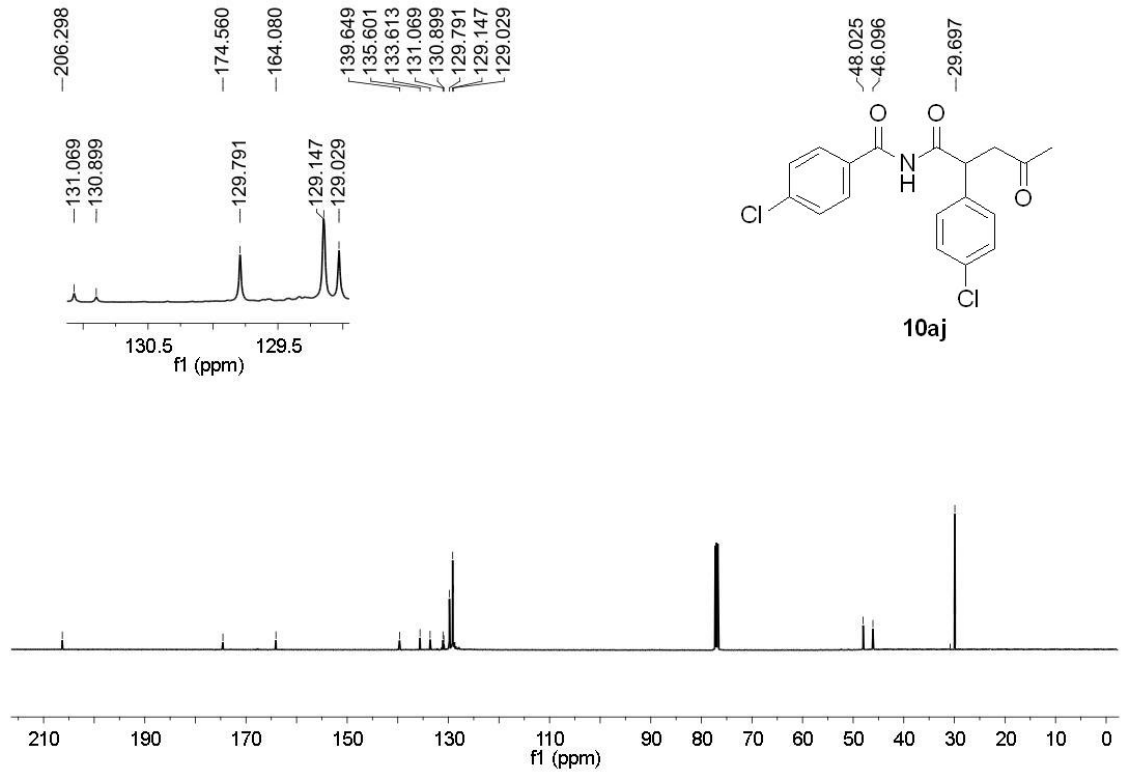
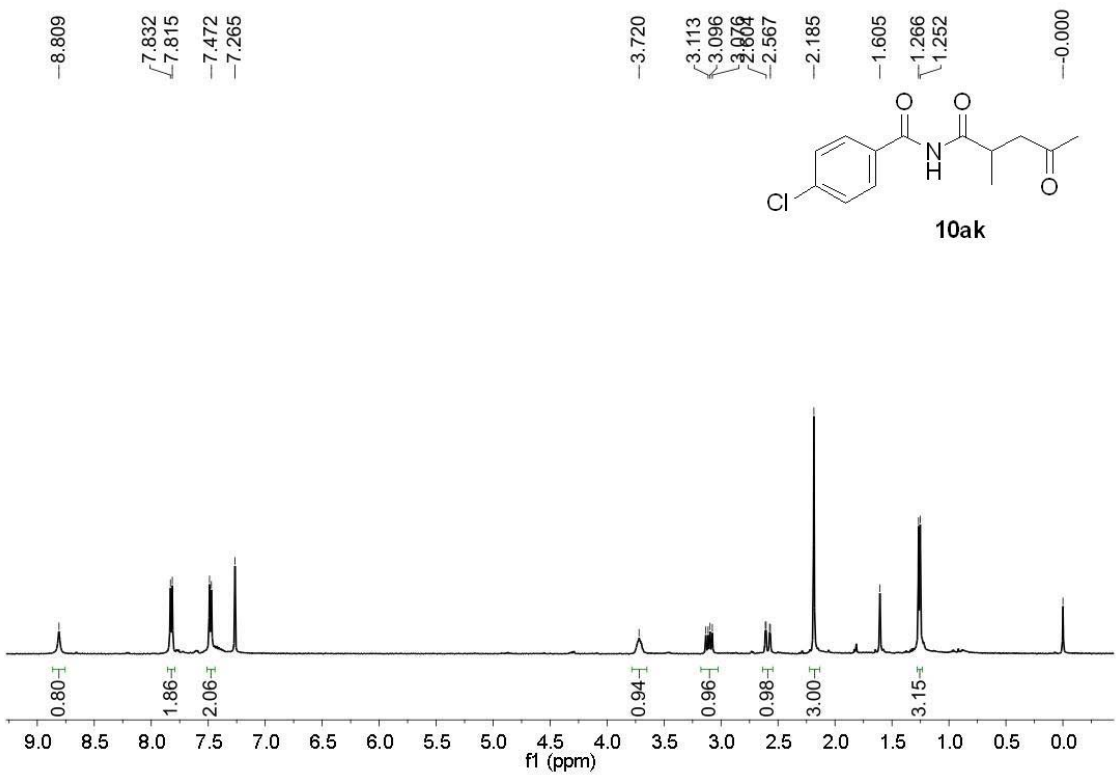
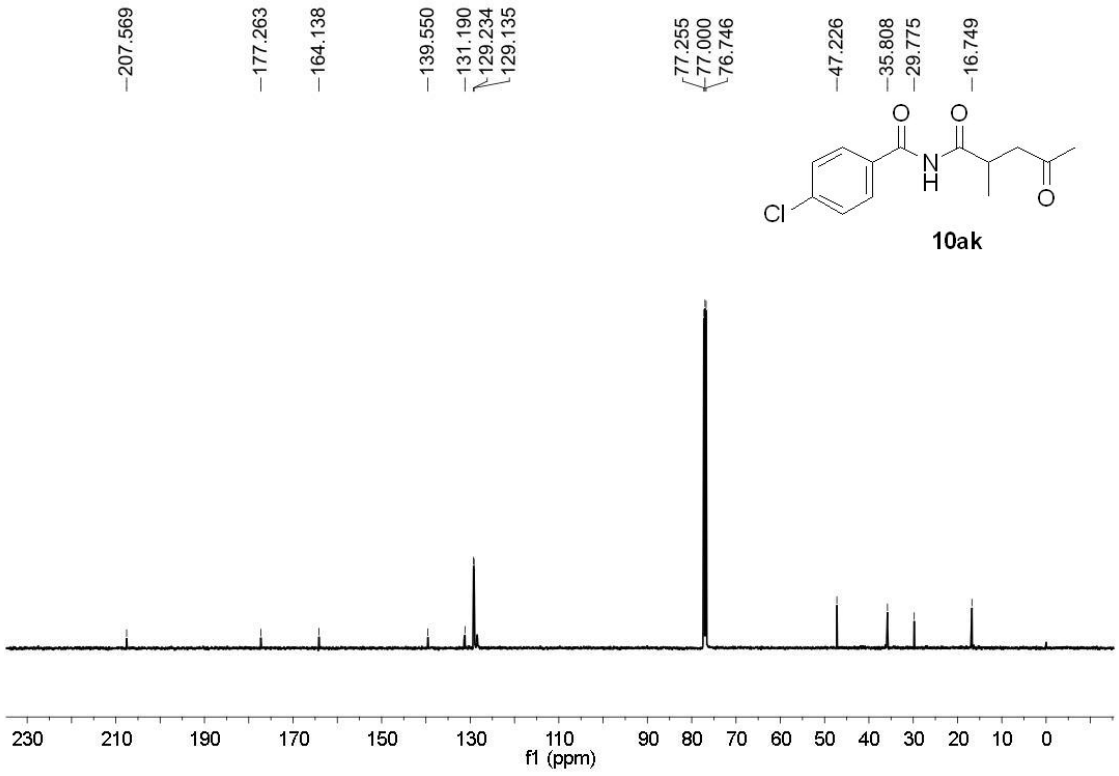
7.756
7.738
7.470
7.453
7.374
7.357
7.341
7.324
7.296
5.204
5.197
5.183
5.176
3.573
3.551
3.536
3.514
2.795
2.788
2.759
2.751
2.215
O
O
N
H
O
Cl
Cl
10aj
0.97
2.15
2.17
2.27
2.25
0.75
0.67
1.11
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
0.5
0.0
f1 (ppm)

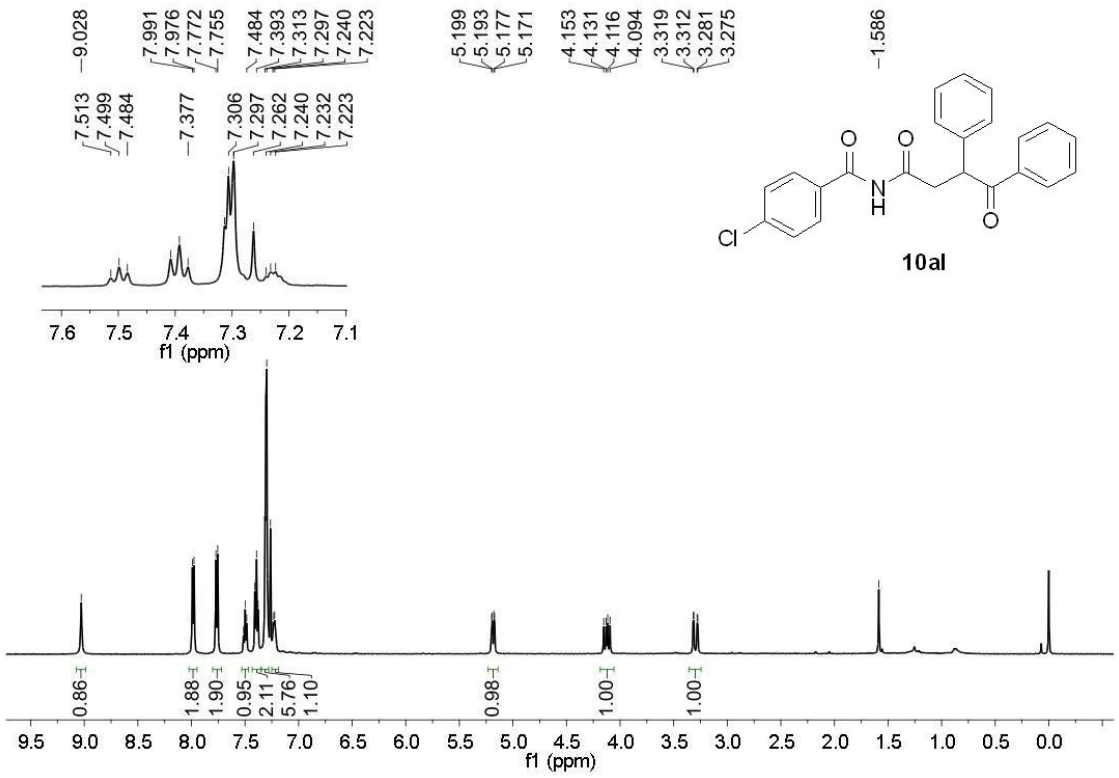

206.298
174.560
164.080
139.649
135.601
133.613
131.069
130.899
129.791
129.147
129.029
48.025
46.096
29.697
131.069
130.899
129.791
129.147
129.029
130.5
129.5
f1 (ppm)
O
O
N
H
O
Cl
Cl
10aj
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

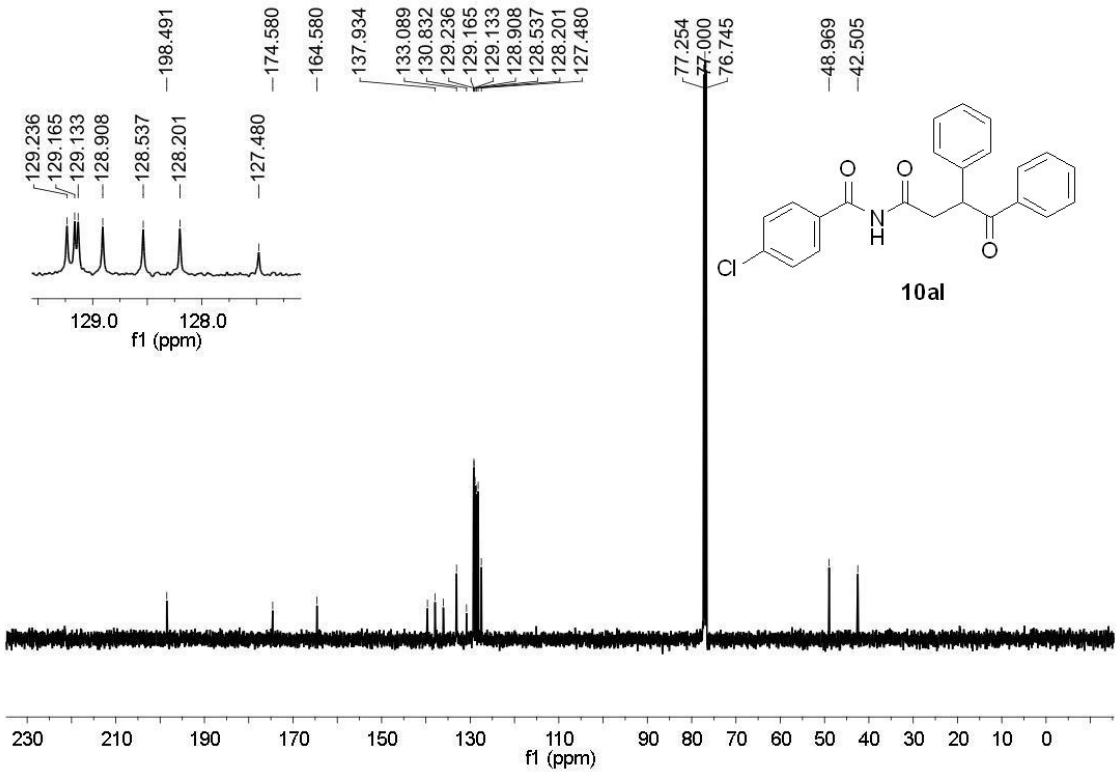

8.809
7.832
7.815
7.472
7.265
3.720
3.113
3.096
2.567
2.185
1.605
1.266
1.252
0.000
0.80
1.86
2.06
0.94
0.96
0.98
3.00
3.15
f1 (ppm)

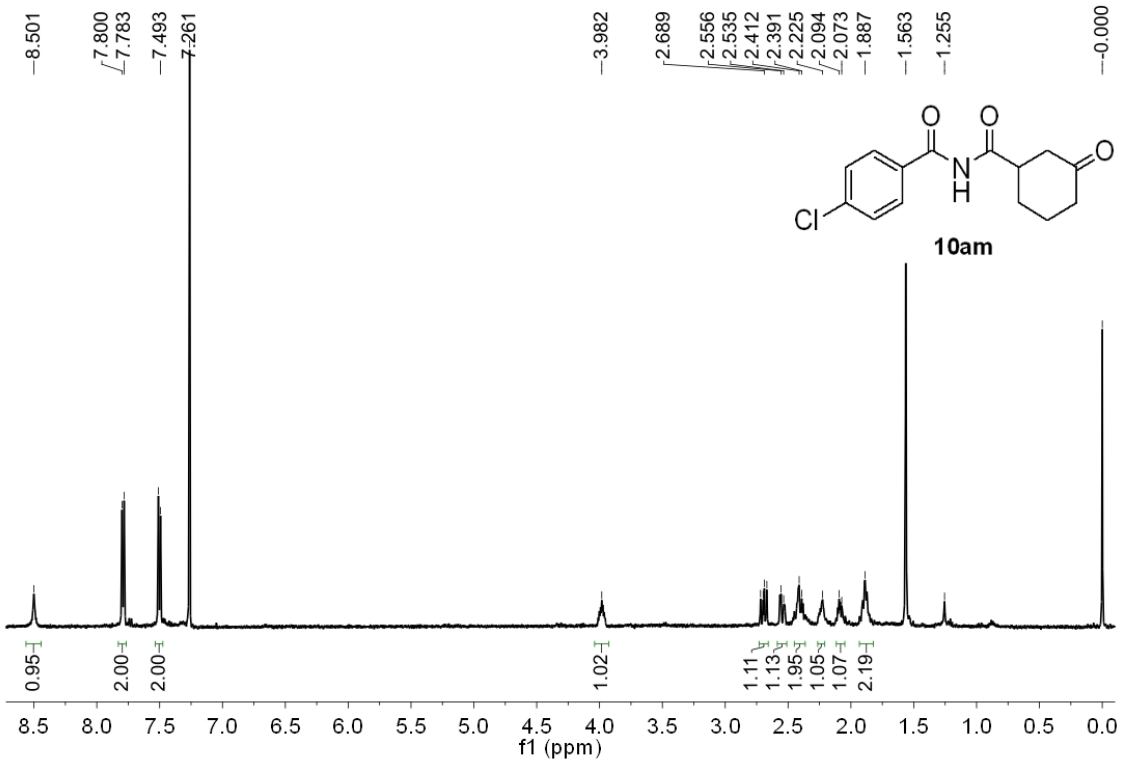
10ak

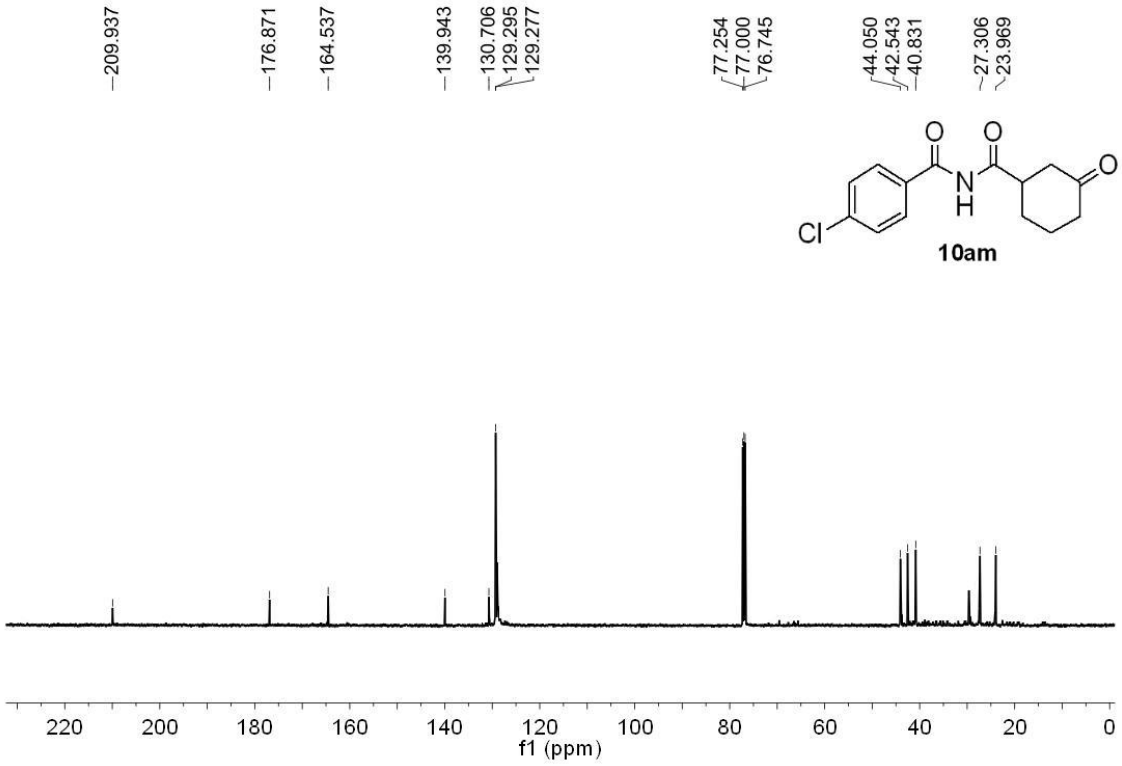

207.569
177.263
164.138
139.550
131.190
129.234
129.135
77.255
77.000
76.746
47.226
35.808
29.775
16.749
f1 (ppm)

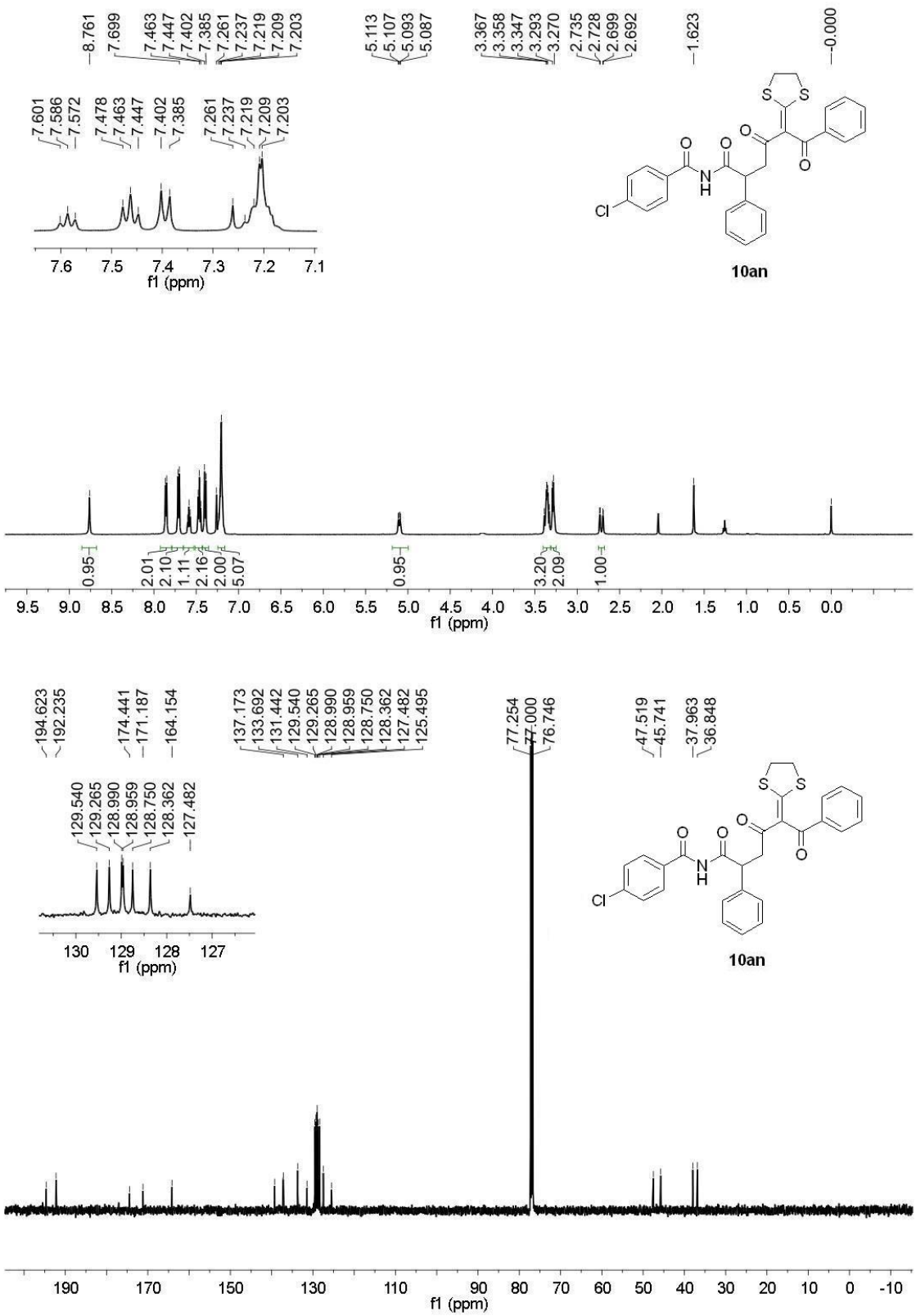
10ak

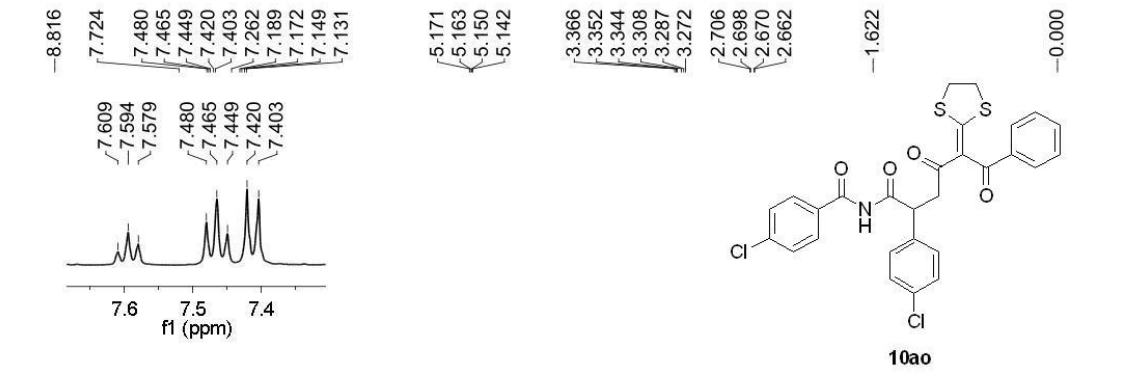

9.028
7.991
7.976
7.772
7.755
7.484
7.393
7.313
7.297
7.240
7.223
5.199
5.193
5.177
5.171
4.153
4.131
4.116
4.094
3.319
3.312
3.281
3.275
1.586
7.513
7.499
7.484
7.377
7.306
7.297
7.262
7.240
7.232
7.223
f1 (ppm)
0.86
1.88
1.90
0.95
2.11
5.76
1.10
0.98
1.00
1.00
f1 (ppm)
10al


198.491
174.580
164.580
137.934
133.089
130.832
129.236
129.165
129.133
128.908
128.537
128.201
127.480
77.254
77.000
76.745
48.969
42.505
129.236
129.165
129.133
128.908
128.537
128.201
127.480
f1 (ppm)
f1 (ppm)
10al


8.501
7.800
7.783
7.493
7.261
3.982
2.689
2.556
2.535
2.412
2.391
2.225
2.094
2.073
1.887
1.563
1.255
0.000
0.95
2.00
2.00
1.02
1.11
1.13
1.95
1.05
1.07
2.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
O
N
H
O
Cl
10am


209.937
176.871
164.537
139.943
130.706
129.295
129.277
77.254
77.000
76.745
44.050
42.543
40.831
27.306
23.969
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)
O
O
N
H
O
Cl
10am


8.761
7.699
7.463
7.447
7.402
7.385
7.261
7.237
7.219
7.209
7.203
5.113
5.107
5.093
5.087
3.367
3.358
3.347
3.293
3.270
2.735
2.728
2.699
2.692
1.623
0.000
7.601
7.586
7.572
7.478
7.463
7.447
7.402
7.385
7.261
7.237
7.219
7.209
7.203
f1 (ppm)
10an
0.95
2.01
2.10
1.11
2.16
2.00
5.07
0.95
3.20
2.09
1.00
f1 (ppm)
194.623
192.235
174.441
171.187
164.154
137.173
133.692
131.442
129.540
129.265
128.990
128.959
128.750
128.362
127.482
125.495
77.254
77.000
76.746
47.519
45.741
37.963
36.848
129.540
129.265
128.990
128.959
128.750
128.362
127.482
f1 (ppm)
10an
f1 (ppm)


8.816
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7.609
7.594
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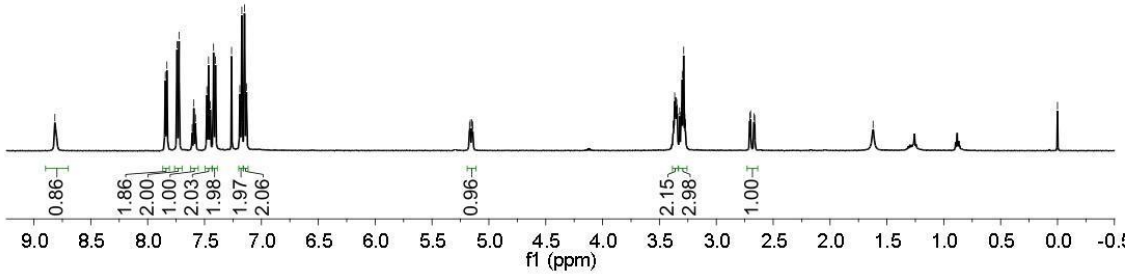
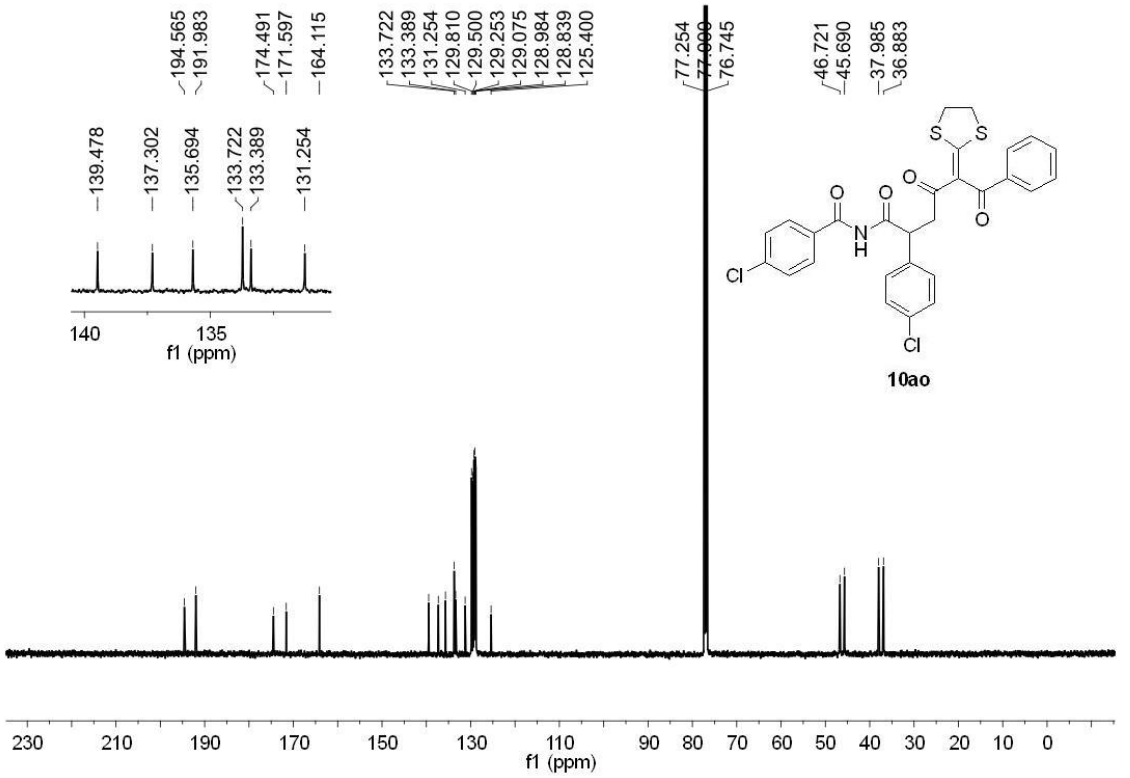
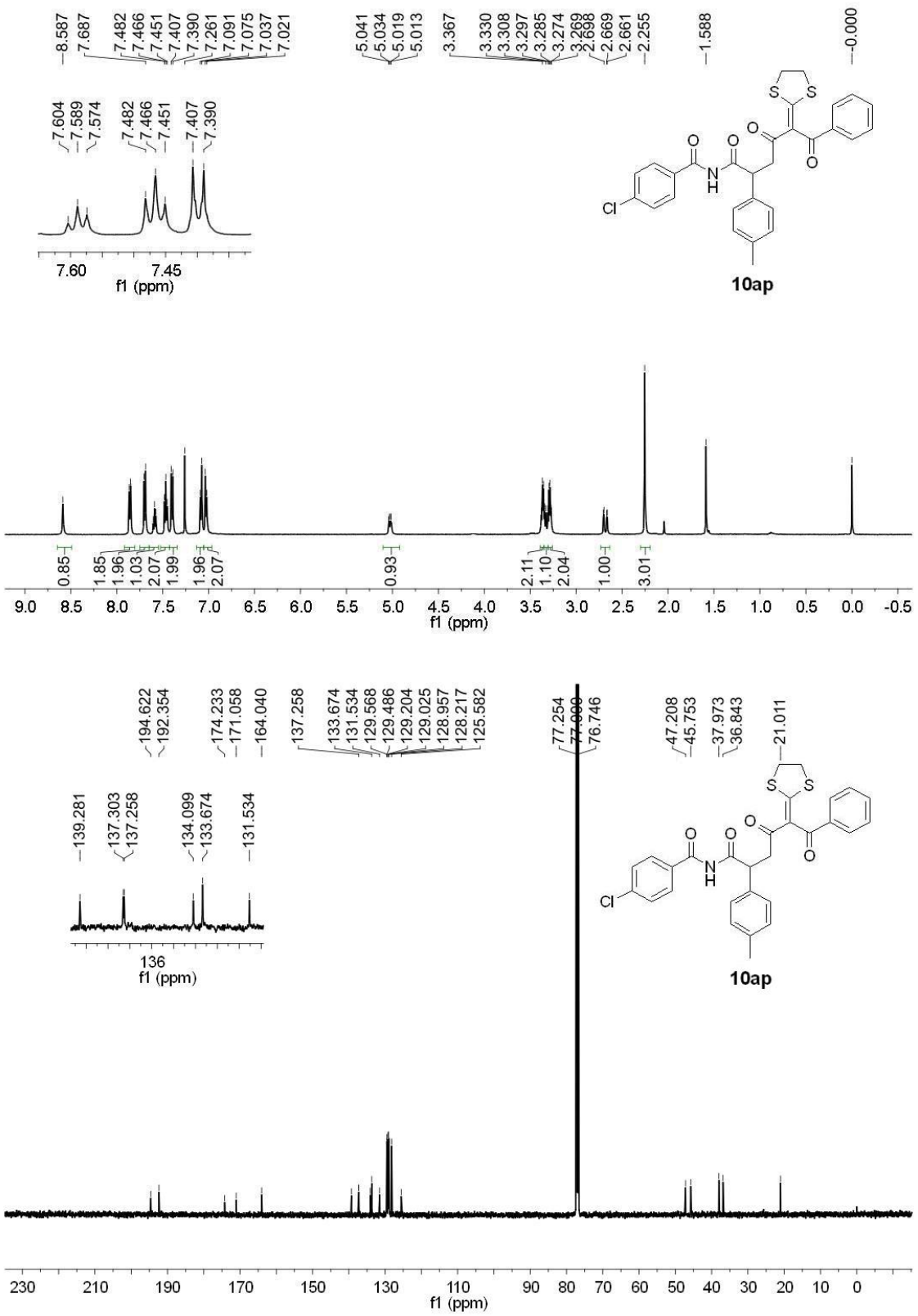
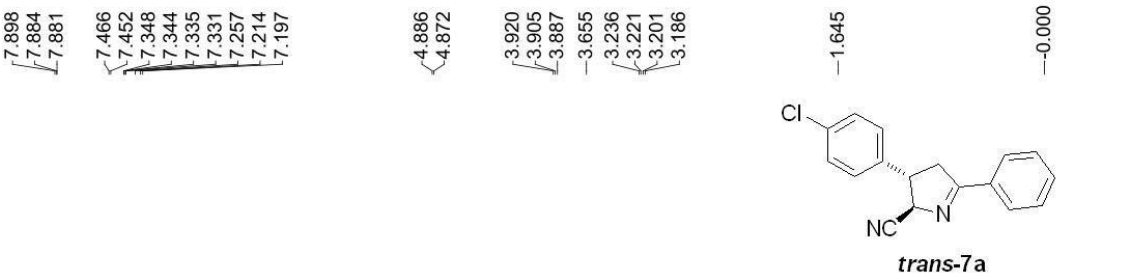
7.480
7.465
7.449
7.420
7.403
7.262
7.189
7.172
7.149
7.131
5.171
5.163
5.150
5.142
3.366
3.352
3.344
3.308
3.287
3.272
2.706
2.698
2.670
2.662
1.622
0.000
7.6
7.5
7.4
f1 (ppm)
10ao

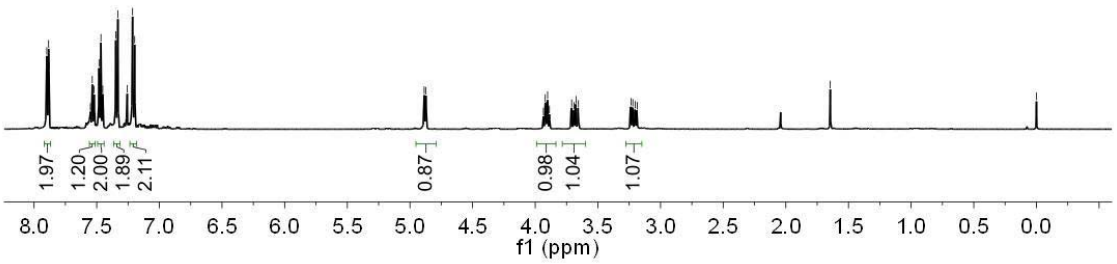

0.86
1.86
2.00
1.00
2.03
1.98
1.97
2.06
0.96
2.15
2.98
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

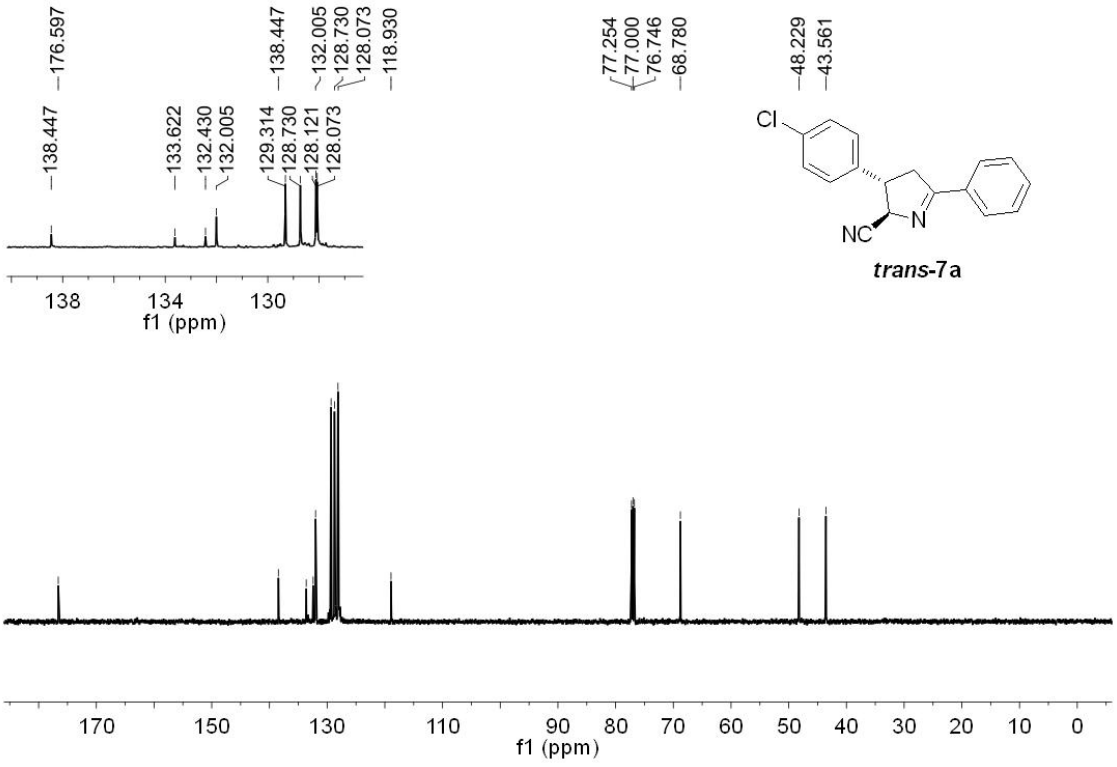

194.565
191.983
174.491
171.597
164.115
139.478
137.302
135.694
133.722
133.389
131.254
133.722
133.389
131.254
129.810
129.500
129.253
129.075
128.984
128.839
125.400
77.254
77.000
76.745
46.721
45.690
37.985
36.883
140
135
f1 (ppm)
10ao
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.587
7.687
7.604
7.589
7.574
7.482
7.466
7.451
7.407
7.390
7.261
7.091
7.075
7.037
7.021
5.041
5.034
5.019
5.013
3.367
3.330
3.308
3.297
3.285
3.274
3.269
2.698
2.669
2.661
2.255
1.588
0.000
7.60
7.45
f1 (ppm)
10ap
0.85
1.85
1.96
1.03
2.07
1.99
1.96
2.07
0.93
2.11
1.10
2.04
1.00
3.01
f1 (ppm)
194.622
192.354
174.233
171.058
164.040
137.258
133.674
131.534
129.568
129.486
129.204
129.025
128.957
128.217
125.582
77.254
77.000
76.746
47.208
45.753
37.973
36.843
21.011
139.281
137.303
137.258
134.099
133.674
131.534
136
f1 (ppm)
10ap
f1 (ppm)

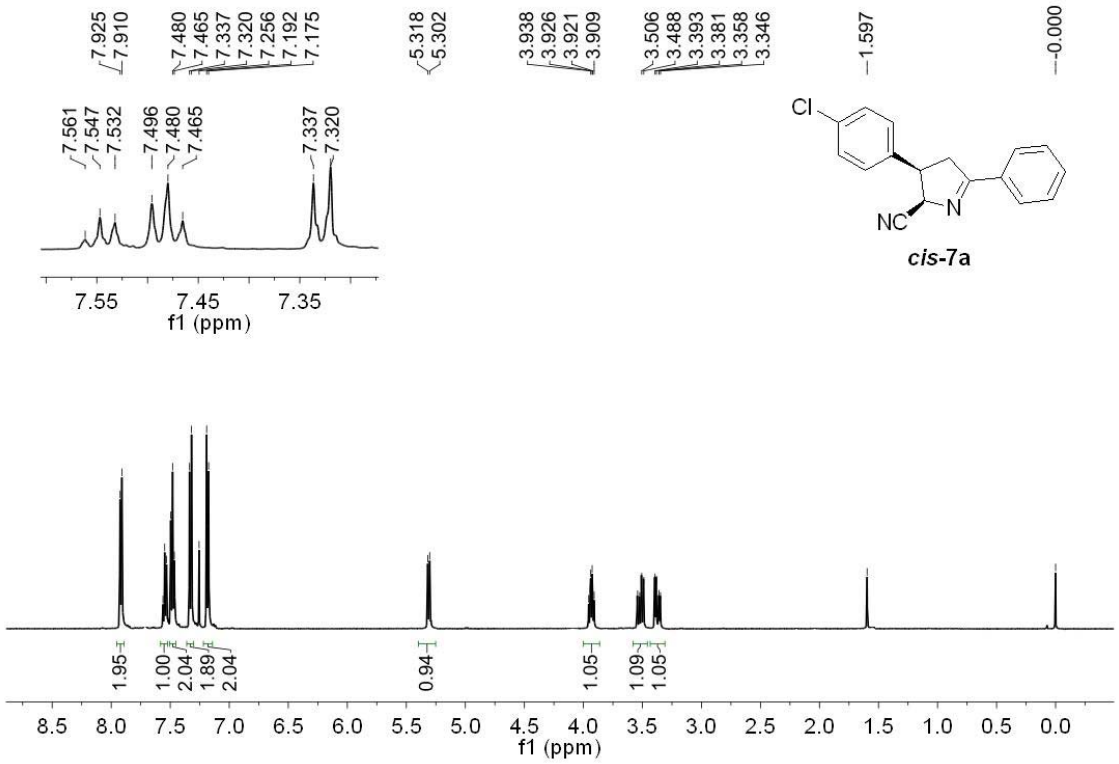


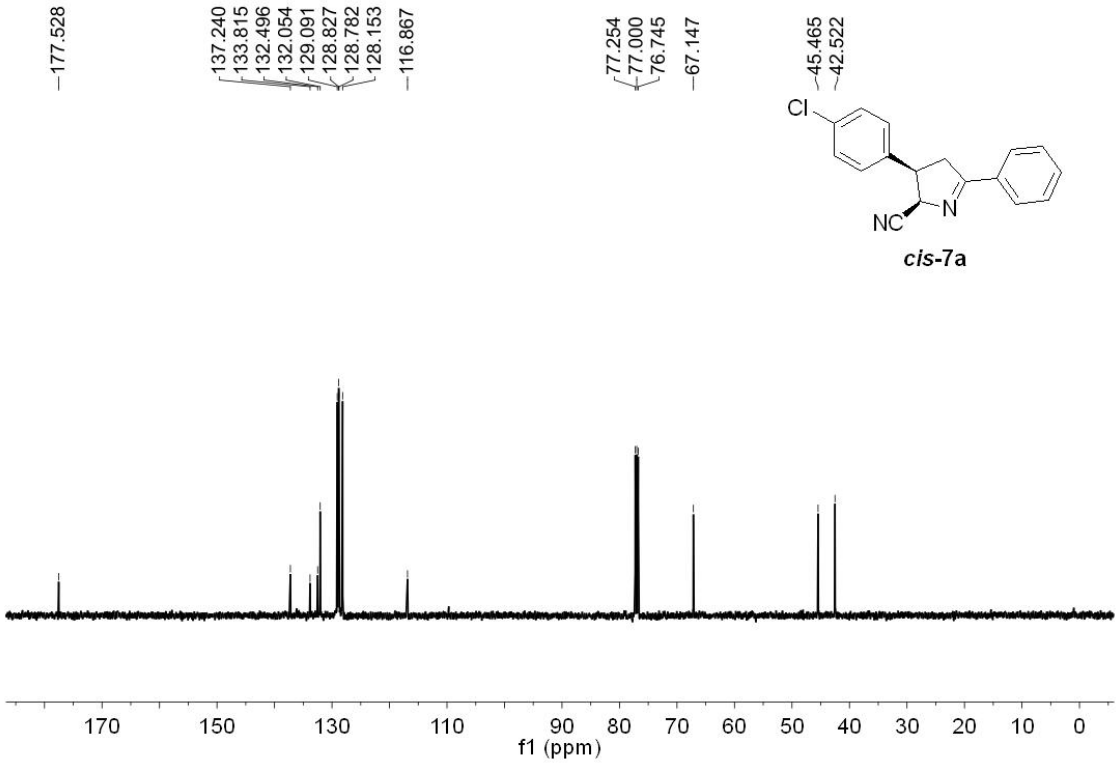
***trans*-7a**

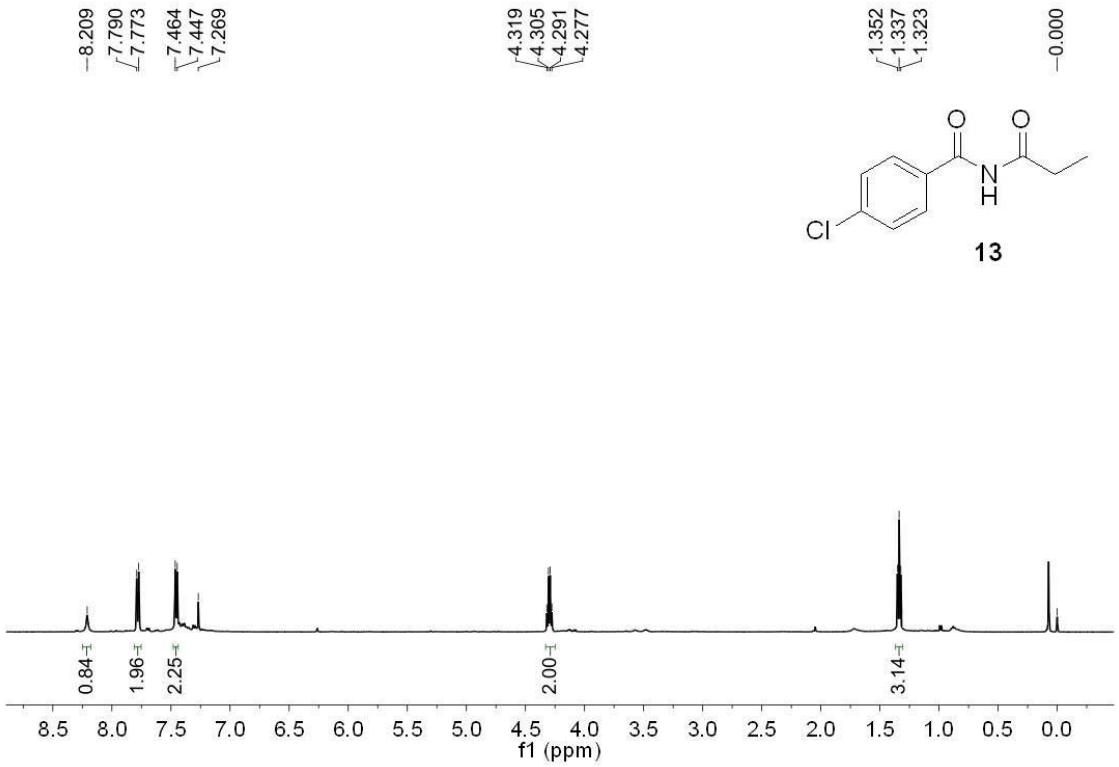


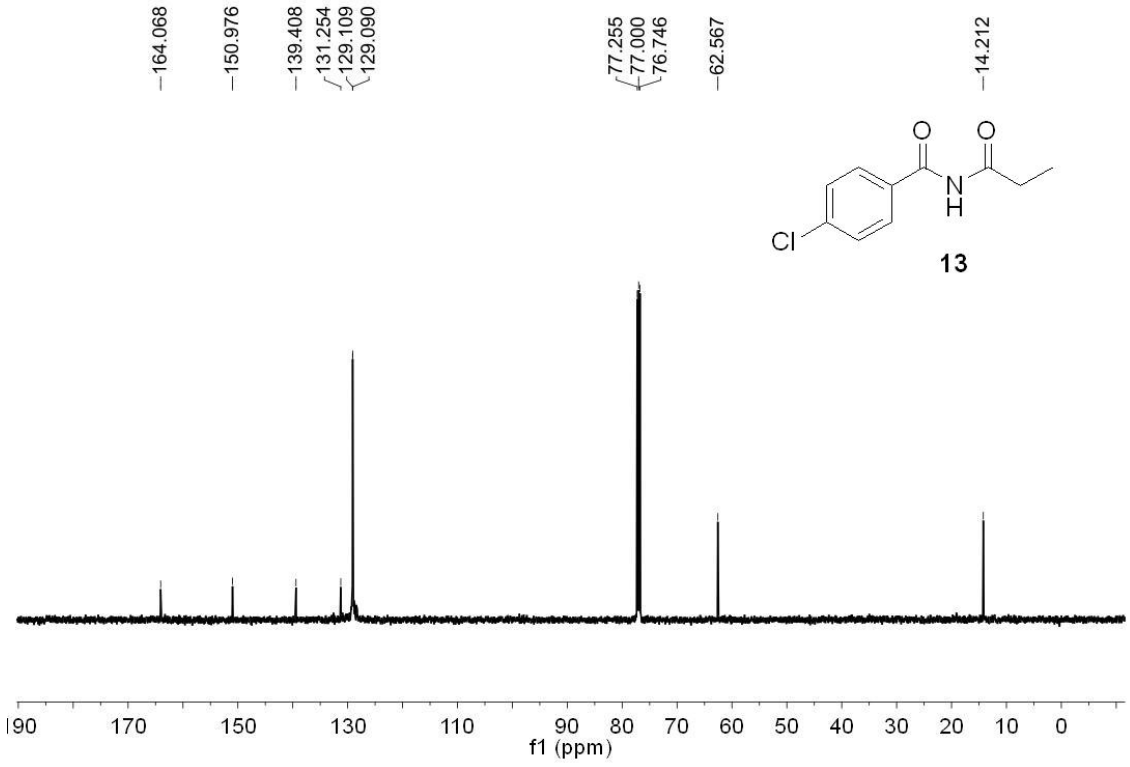


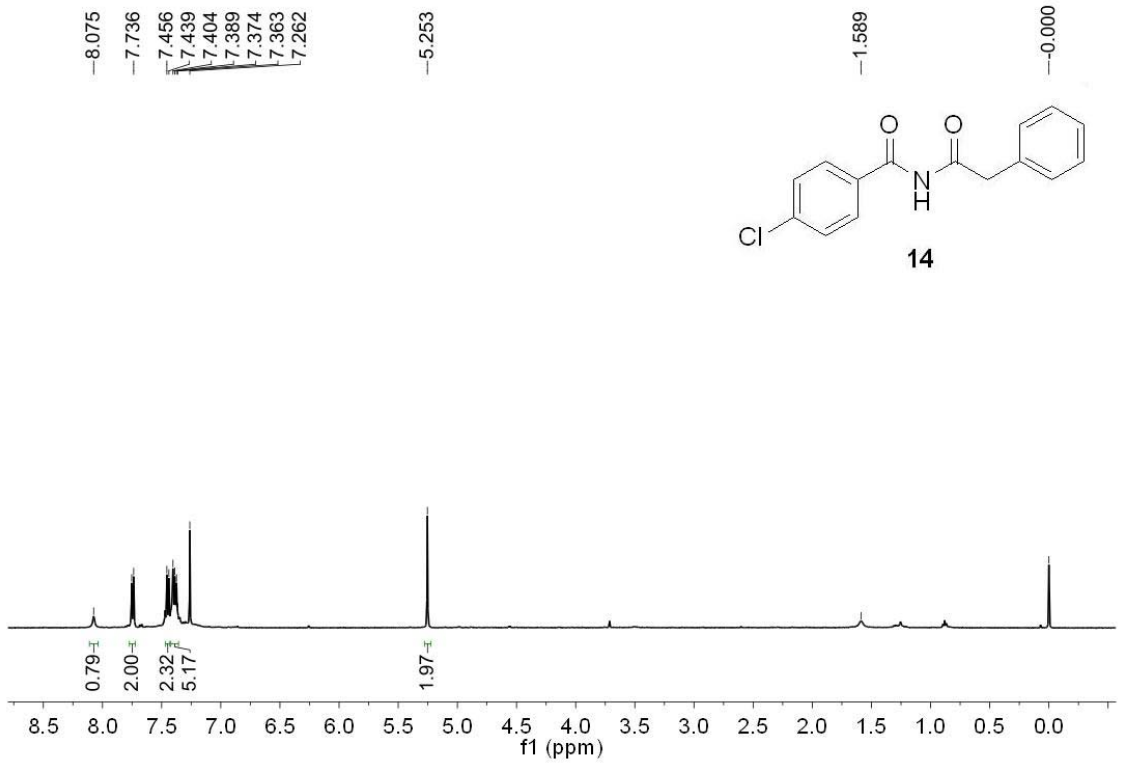
***trans*-7a**

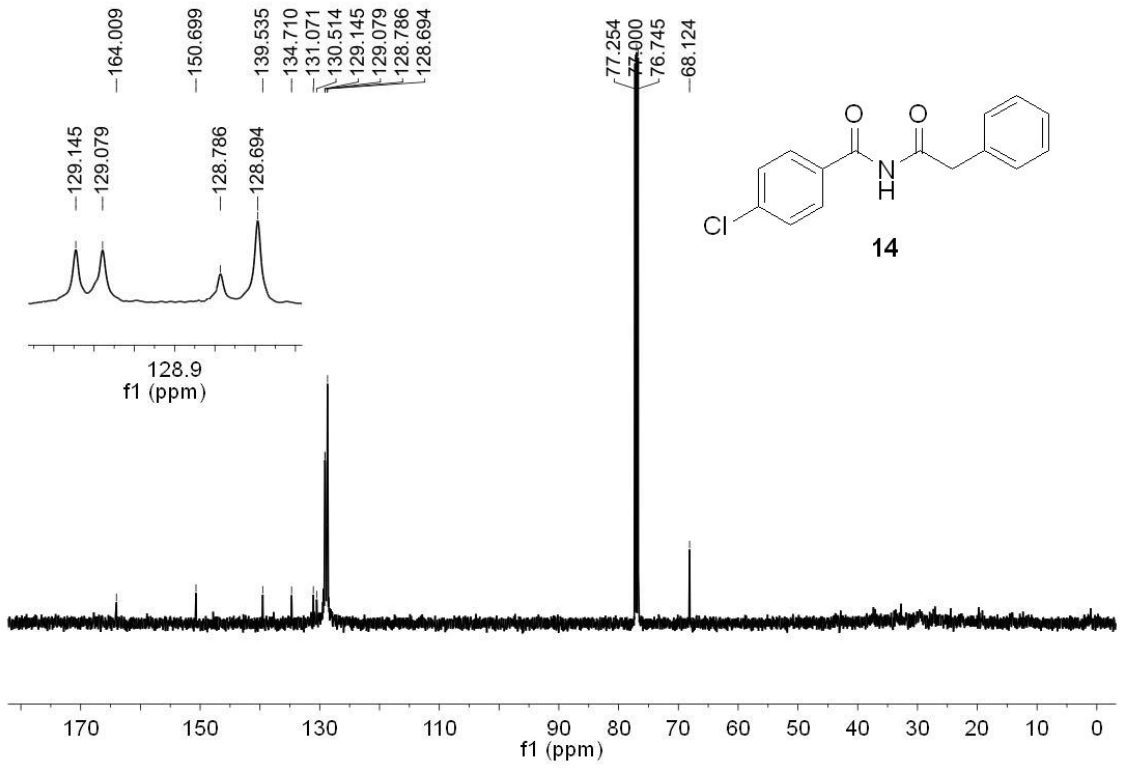

7.925
7.910
7.480
7.465
7.337
7.320
7.256
7.192
7.175
5.318
5.302
3.938
3.926
3.921
3.909
3.506
3.488
3.393
3.381
3.358
3.346
1.597
0.000
7.561
7.547
7.532
7.496
7.480
7.465
7.337
7.320
7.55
7.45
7.35
f1 (ppm)
Cl
NC
N
cis-7a
1.95
1.00
2.04
1.89
2.04
0.94
1.05
1.09
1.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

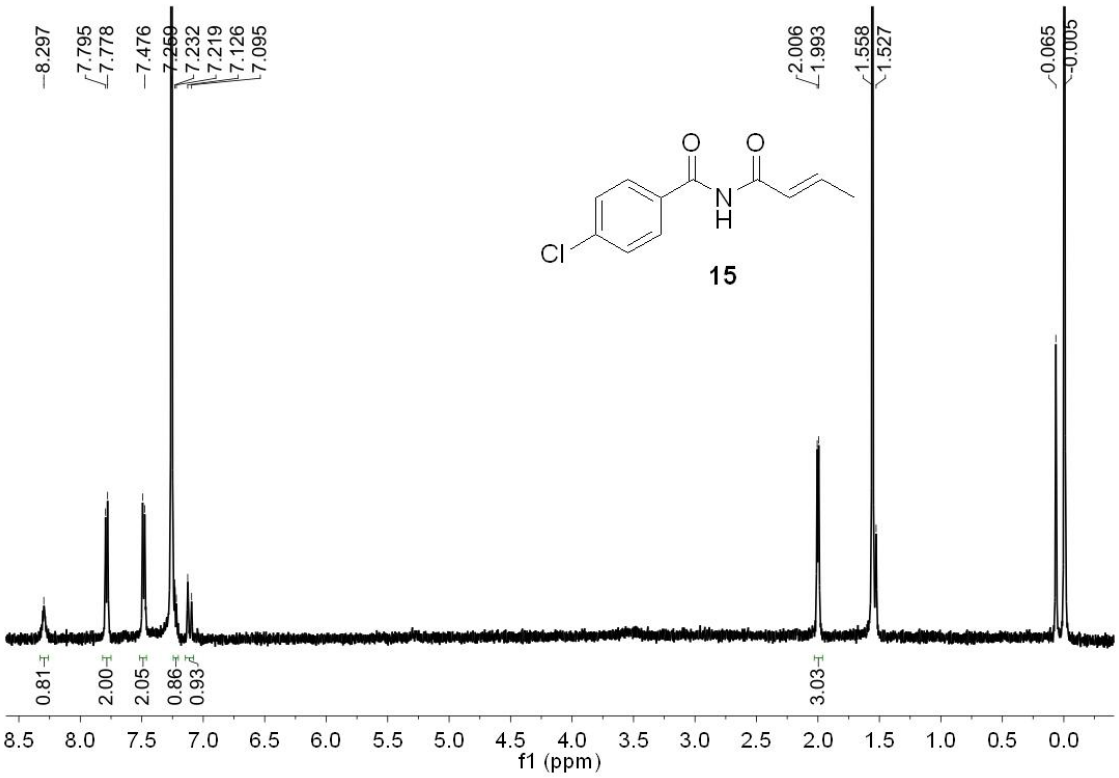

177.528
137.240
133.815
132.496
132.054
129.091
128.827
128.782
128.153
116.867
77.254
77.000
76.745
67.147
45.465
42.522
Cl
NC
N
cis-7a
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

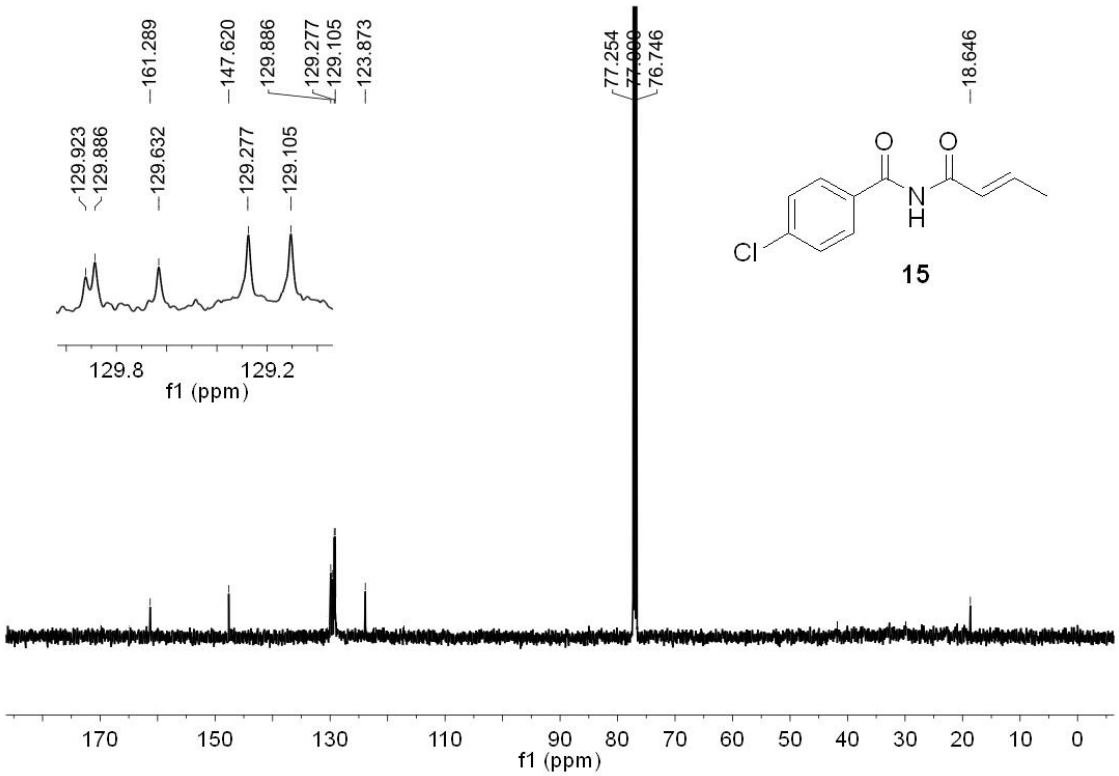

8.209
7.790
7.773
7.464
7.447
7.269
4.319
4.305
4.291
4.277
1.352
1.337
1.323
0.000
O
O
N
H
Cl
13
0.84
1.96
2.25
2.00
3.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.068
150.976
139.408
131.254
129.109
129.090
77.255
77.000
76.746
62.567
14.212
O
O
N
H
Cl
13
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.075
7.736
7.456
7.439
7.404
7.389
7.374
7.363
7.262
5.253
1.589
0.000
O
O
N
H
Cl
14
0.79
2.00
2.32
5.17
1.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.009
150.699
139.535
134.710
131.071
130.514
129.145
129.079
128.786
128.694
77.254
77.000
76.745
68.124
O
O
N
H
Cl
14
128.9
f1 (ppm)
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.297
7.795
7.778
7.476
7.260
7.232
7.219
7.126
7.095
2.006
1.993
1.558
1.527
0.065
0.005
0.81
2.00
2.05
0.86
0.93
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
O
N
H
Cl
15


161.289
147.620
129.886
129.277
129.105
123.873
77.254
77.000
76.746
18.646
129.923
129.886
129.632
129.277
129.105
129.8
129.2
f1 (ppm)
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
O
N
H
Cl
15