Supporting Information

Palladium-Catalyzed Oxidative Cross-Coupling for Synthesis of α-Amino Ketones

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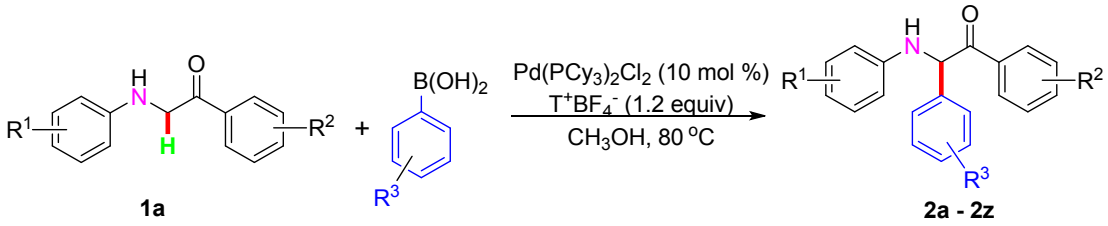
General

All reactions involving air- or moisture-sensitive reagents were carried out under an argon atmosphere. All solvents were distilled under Ar before use. All chemicals were purchased from Aldrich and J&K Chemical and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230 - 400 mesh) was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ solvent on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C) or on a Varian OXFORD 300 spectrometer (300 MHz for ^{1}H and 75.75 MHz for ^{13}C). The chemical shift is given indimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy.

Experimental Section

1. General procedure for synthesis of 2a-2z



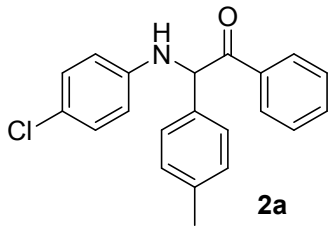
An oven-dried 10 mL screw-capped vial containing **1a** (0.1 mmol, 1.0 equiv), phenyl boric acid (0.12 mmol, 1.2 equiv), $Pd(PCy_3)_2Cl_2$ (0.01 mmol, 0.1 equiv), 2,6,6-tetramethylpiperidine-1-oxoammonium *tetra*-fluoroborate ($T^{+}BF_4^{-}$) (0.12 mmol, 1.2 equiv), and purged with Ar three times. Then, CH_3OH (1 mL) was added *via* syringe, and heated to 80°C in an oil bath until the starting material has disappeared for 20 hours (monitored by TLC). And then the solvent was removed in vacuo and residue was purified on a silica gel column using EA/PE as eluent to afford the desired product **2a**.

2. Synthesis of $T^{+}BF4^{-}$[1]

In a 250 mL round bottom flask, an aqueous solution of HBF_4 (48% aqueous

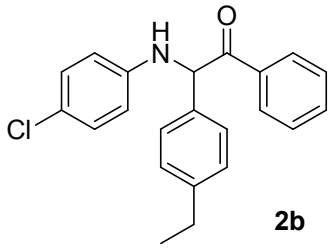
solution, 10.9 mL, 83.2 mmol) was added to the heterogeneous solution of 1 (11.367g, 72.8 mmol) in purified water (31.15 mL). The reaction mixture was stirred at room temperature for 30 min to give a yellow orange mixture. In ice bath, an aqueous solution of NaOCl (5% aqueous solution, 48.5mL, 35.7 mmol) was added to the solution for 2 h. The mixture is filtered with grass filter and the yellow solid was washed with cooled water (4 ^{o}C, 4 × 20 mL) and dichloromethane (3 × 30 mL). After dried under high vacuum at room temperature overnight, the product is obtained as a bright yellow solid.

3. Analytical Data of Products



2a

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 6.8 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.12 – 7.00 (m, 4H), 6.57 (d, J = 8.8 Hz, 2H), 5.94 (d, J = 6.4 Hz, 1H), 5.44 (d, J = 6.4 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.58, 144.55, 138.06, 134.74, 134.05, 133.56, 129.82, 128.99, 128.83, 128.65, 127.93, 122.20, 114.50, 62.25, 21.06. **MS (ESI)**: found $[M+H]^+$ 336.2.



2b

Yellow solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.08 (dd, *J* = 14.6, 8.3 Hz, 4H), 6.57 (d, *J* = 8.6 Hz, 2H), 5.95 (d, *J* = 6.7 Hz, 1H), 5.43 (d, *J* = 6.7 Hz, 1H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.60, 144.60, 144.27, 134.21, 133.57, 129.00, 128.86, 128.66, 128.62, 127.95, 114.47, 62.24, 29.66, 28.37, 15.15. **MS (ESI)**: found $[M+H]^+$ 366.1.

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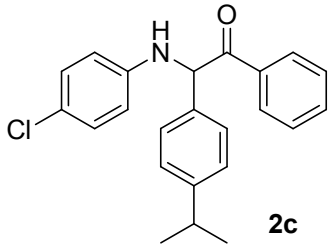
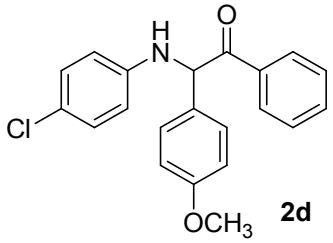
1 Y. Yonekuta, K. Oyaizu and H. Nishide, *Chem. Lett.* **2007***, 36,* 866.



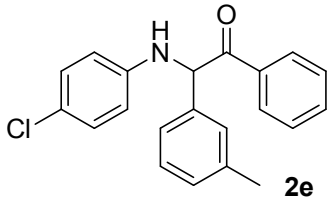
2c

Yellow solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 6.6 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 5.96 (d, *J* = 6.7 Hz, 1H), 5.41 (d, *J* = 6.6 Hz, 1H), 2.81 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.65, 148.86, 144.66, 134.77, 134.27, 133.60, 129.01, 128.90, 128.68, 127.91, 127.25, 122.18, 114.45, 62.21, 33.65, 23.76. **MS (ESI)**: found $[M+H]^+$ 363.4.



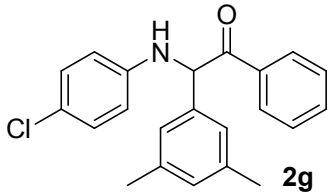
2d

Yellow solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 5.93 (d, *J* = 6.6 Hz, 1H), 5.42 (d, *J* = 6.5 Hz, 1H), 3.71 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.60, 159.30, 144.53, 134.76, 133.54, 129.23, 128.99, 128.90, 128.79, 128.67, 122.20, 114.51, 114.49, 61.86, 55.15. **MS (ESI)**: found $[M+H]^+$ 352.0.



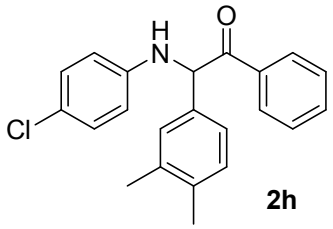
2e

Yellow solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.13 (m, 3H), 7.06 (t, *J* = 7.1 Hz, 3H), 6.58 (d, *J* = 8.7 Hz, 2H), 5.93 (d, *J* = 5.6 Hz, 1H), 5.42 (d, *J* = 4.5 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.63, 144.61, 138.94, 137.02, 134.71, 133.63, 129.10, 129.02, 128.90, 128.86, 128.68, 128.40, 125.38, 122.25, 114.49, 62.57, 21.43. **MS (ESI)**: found $[M+H]^+$ 336.2.



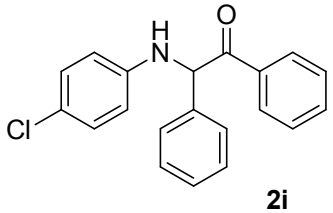
2g

Yellow solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 6.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.13 – 6.97 (m, 4H), 6.84 (s, 1H), 6.58 (d, *J* = 8.8 Hz, 2H), 5.89 (d, *J* = 6.8 Hz, 1H), 5.35 (d, *J* = 6.8 Hz, 1H), 2.24 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.72, 144.74, 138.70, 136.93, 134.74, 133.58, 130.07, 129.01, 128.86, 128.66, 125.78, 122.21, 114.47, 62.60, 21.30. **MS (ESI)**: found $[M+H]^+$ 349.7.



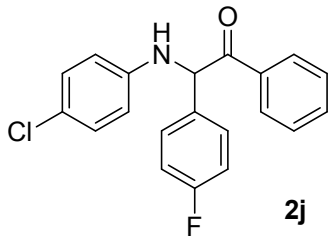
2h

Yellow solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.48 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.05 (t, *J* = 6.8 Hz, 3H), 6.58 (d, *J* = 8.8 Hz, 2H), 5.91 (d, *J* = 6.5 Hz, 1H), 5.40 (d, *J* = 6.7 Hz, 1H), 2.17 (s, 3H), 2.15 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.63, 144.67, 137.54, 136.82, 134.74, 134.38, 133.54, 130.23, 128.99, 128.87, 128.64, 125.72, 122.15, 114.47, 62.30, 29.68, 19.88, 19.45. **MS (ESI)**: found $[M+H]^+$ 349.7.



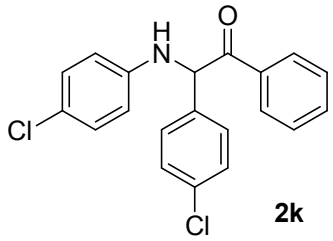
2i

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.28 (t, *J* = 7.4 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 5.97 (d, *J* = 6.6 Hz, 1H), 5.45 (d, *J* = 6.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.63, 144.59, 137.23, 134.86, 133.64, 129.13, 129.06, 128.86, 128.72, 128.26, 128.07, 122.43, 114.60, 62.70. **MS (ESI)**: found $[M+H]^+$ 321.5.



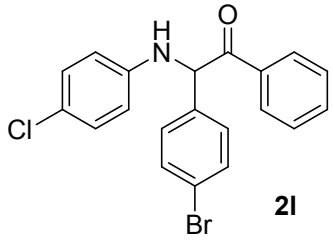
2j

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.97 (t, *J* = 7.9 Hz, 2H), 6.57 (d, *J* = 7.4 Hz, 2H), 5.97 (d, *J* = 6.3 Hz, 1H), 5.47 (d, *J* = 6.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.42, 144.25, 134.55, 133.82, 132.94(d, *J* = 3.6 Hz), 129.67 (d, *J* = 8.4 Hz), 129.09, 128.80, 122.51, 116.16 (d, *J* = 21.7 Hz), 114.52, 61.72. **MS (ESI)**: found $[M+H]^+$ 340.1.



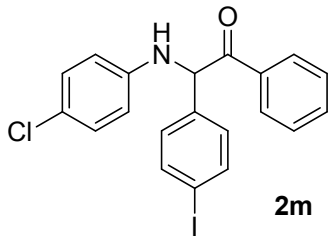
2k

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 5.96 (d, *J* = 6.4 Hz, 1H), 5.50 (d, *J* = 6.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.18, 144.14, 135.75, 134.48, 134.11, 133.90, 129.33, 129.30, 129.11, 128.82, 122.59, 114.52, 61.82. **MS (ESI)**: found $[M+H]^+$ 355.7.



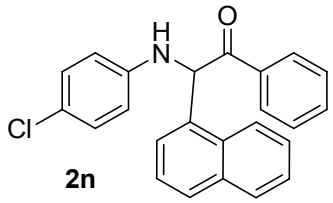
2l

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.33 – 7.24 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 5.94 (d, *J* = 6.4 Hz, 1H), 5.48 (d, *J* = 6.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.15, 144.16, 141.22, 136.34, 134.53, 133.91, 132.28, 129.63, 129.13, 128.83, 122.68, 114.55, 61.94. **MS (ESI)**: found $[M+H]^+$ 399.8.



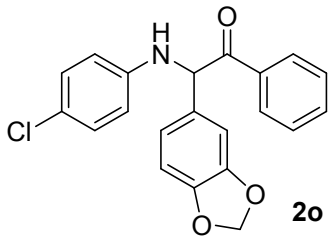
2m

White solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.59 (dd, *J* = 11.1, 7.9 Hz, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.55 (d, *J* = 8.3 Hz, 2H), 5.92 (d, *J* = 6.4 Hz, 1H), 5.49 (d, *J* = 6.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.06, 147.98, 144.11, 138.19, 137.00, 134.45, 133.93, 129.83, 129.12, 128.83, 114.50, 105.16, 61.99. **MS (ESI)**: found $[M+H]^+$ 447.5.



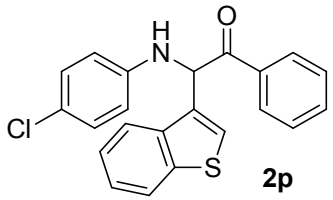
2n

Yellow solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 3H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.67 – 7.43 (m, 3H), 7.45 – 7.27 (m, 4H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.64 (dd, *J* = 12.3, 8.3 Hz, 3H), 4.89 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.96, 145.32, 135.09, 134.29, 133.55, 132.76, 131.01, 129.56, 129.24, 129.16, 128.71, 128.52, 127.25, 126.77, 126.23, 125.48, 122.86, 122.79, 114.55, 60.02. **MS (ESI)**: found $[M+H]^+$ 372.1.



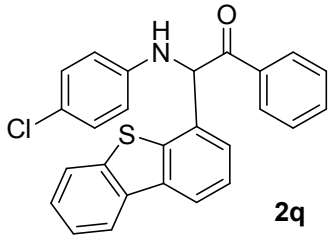
2o

White solid, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 1.7 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.9 Hz, 2H), 5.89 (d, *J* = 5.7 Hz, 3H), 5.45 (d, *J* = 6.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.35, 148.28, 147.52, 144.37, 134.63, 133.66, 130.84, 129.02, 128.81, 128.71, 122.31, 122.02, 114.54, 108.62, 107.85, 101.24, 62.03. **MS (ESI)**: found $[M+H]^+$ 366.1.



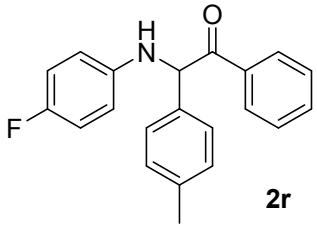
2p

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 7.94 (m, 3H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.30 (m, 5H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.37 (s, 1H), 5.06 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.61, 145.00, 140.74, 136.96, 134.81, 133.76, 131.55, 129.14, 128.79, 128.54, 126.82, 124.92, 124.71, 123.08, 122.95, 121.86, 114.70, 57.69. **MS (ESI)**: found $[M+H]^+$ 337.8.



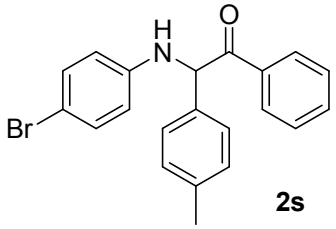
2q

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 – 7.97 (m, 4H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.34 (m, 7H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.23 (d, *J* = 6.2 Hz, 1H), 5.56 (d, *J* = 6.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.66, 144.41, 139.27, 138.00, 137.01, 135.20, 134.85, 133.72, 131.42, 129.09, 128.68, 128.64, 127.15, 126.94, 125.20, 124.61, 122.83, 122.72, 121.66, 114.89, 77.32, 77.00, 76.68, 62.58. **MS (ESI)**: found $[M+H]^+$ 427.8.



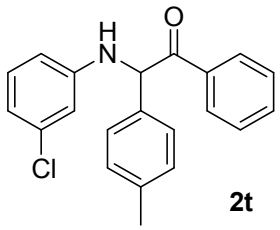
2r

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.83 (t, *J* = 8.7 Hz, 2H), 6.64 – 6.55 (m, 2H), 5.93 (d, *J* = 6.2 Hz, 1H), 5.25 (d, *J* = 5.9 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.91, 155.80 (d, *J* = 235.3 Hz), 142.41, 137.90, 134.87, 134.28, 133.39, 129.72, 128.72, 128.56, 127.86, 115.54 (d, *J* = 22.4 Hz), 114.29 (d, *J* = 7.4 Hz, 1H), 62.89, 20.97. **MS (ESI)**: found $[M+H]^+$ 319.5.



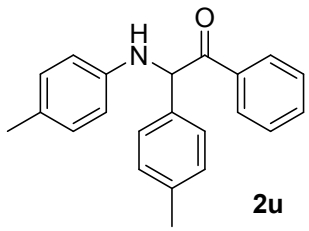
2s

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 – 7.94 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 8.9 Hz, 2H), 5.93 (s, 1H), 5.45 (s, 1H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.58, 145.03, 138.10, 134.85, 134.06, 133.56, 131.89, 129.85, 128.85, 128.67, 127.96, 115.07, 109.36, 62.24, 21.06. **MS (ESI)**: found $[M+H]^+$ 379.3.



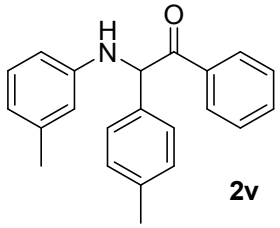
2t

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 6.9 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.53 (d, *J* = 7.5 Hz, 1H), 5.95 (d, *J* = 6.6 Hz, 1H), 5.53 (d, *J* = 6.5 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.44, 147.17, 138.11, 134.86, 134.74, 134.05, 133.59, 130.15, 129.88, 128.88, 128.68, 127.93, 117.55, 113.11, 111.74, 62.04, 21.08. **MS (ESI)**: found $[M+H]^+$ 336.2.



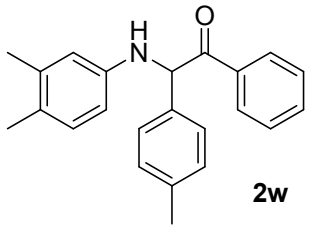
2u

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 6.5 Hz, 1H), 5.21 (d, *J* = 6.4 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.32, 143.88, 137.81, 135.16, 134.70, 133.37, 129.74, 129.69, 128.83, 128.62, 127.99, 126.93, 113.63, 62.68, 21.07, 20.37. **MS (ESI)**: found $[M+H]^+$ 315.6.



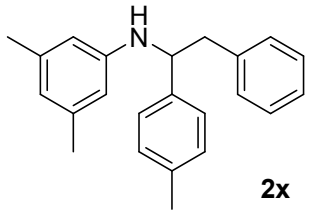
2v

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.48 (dd, *J* = 14.2, 7.2 Hz, 3H), 5.99 (s, 1H), 5.33 (s, 1H), 2.24 (s, 1H), 2.23 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.11, 146.11, 138.90, 137.76, 134.97, 134.64, 133.38, 129.71, 129.02, 128.81, 128.58, 127.93, 118.64, 114.34, 110.30, 62.26, 29.63, 21.58, 21.04. **MS (ESI)**: found $[M+H]^+$ 315.5.



2w

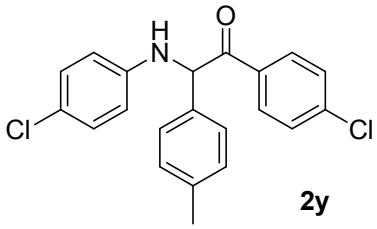
Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 6.9 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.51 (s, 1H), 6.41 (d, *J* = 10.6 Hz, 1H), 5.97 (s, 1H), 5.14 (s, 1H), 2.23 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.41, 144.32, 137.70, 137.21, 135.22, 134.84, 133.29, 130.17, 129.70, 128.80, 128.57, 127.95, 125.73, 115.51, 110.71, 62.64, 29.67, 21.03, 20.00, 18.65. **MS (ESI)**: found $[M+H]^+$ 329.9.



2x

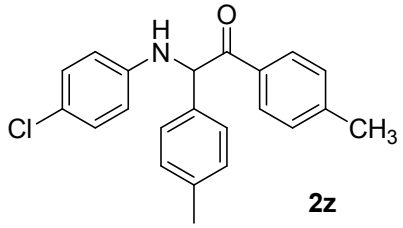
Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.34 (s, 1H), 6.30 (s, 2H), 5.98 (s, 1H), 5.24 (s, 1H), 2.25 (s, 3H), 2.18 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.31, 146.28, 138.79, 137.74, 135.19, 134.87, 133.34, 129.73, 128.84, 128.61, 127.95, 119.82, 111.41, 62.40, 29.69, 21.48, 21.06. **MS (ESI)**:

found $[M+H]^+$ 329.9.



2y

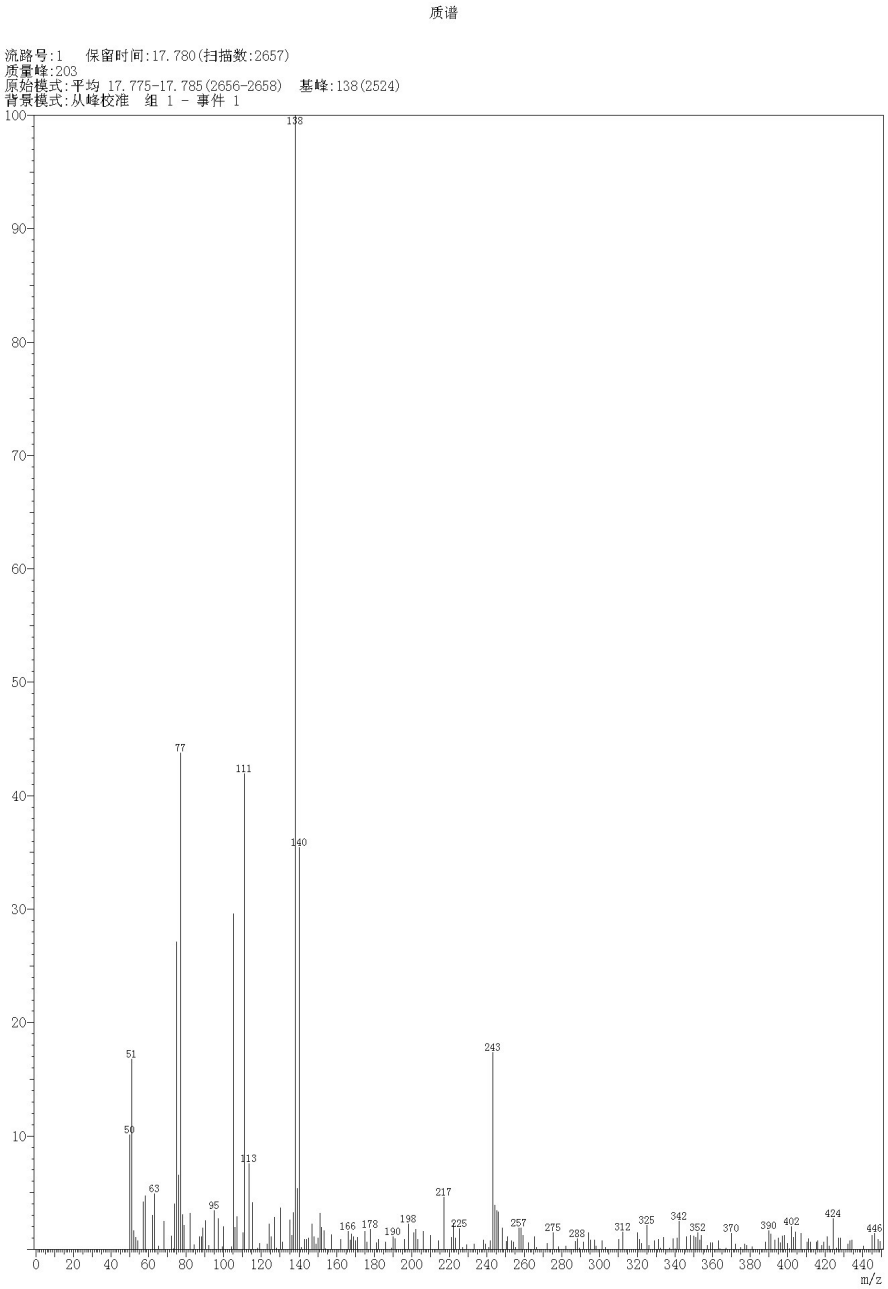
White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 3H), 7.08 (dd, *J* = 14.3, 8.4 Hz, 4H), 6.56 (d, *J* = 8.8 Hz, 2H), 5.87 (d, *J* = 3.7 Hz, 1H), 5.38 (s, 1H), 2.26 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.47, 144.52, 140.08, 138.35, 133.88, 133.16, 130.22, 129.98, 129.07, 129.05, 127.94, 122.51, 114.62, 62.56, 21.08. **MS (ESI)**: found $[M+H]^+$ 369.4.



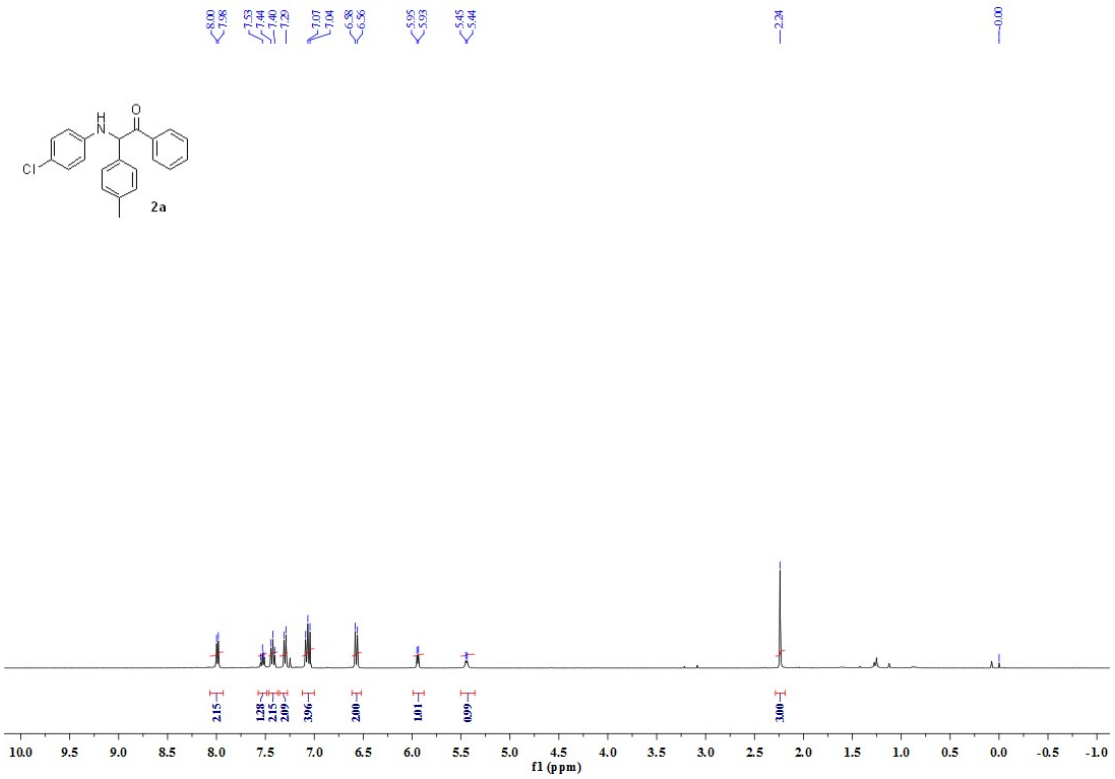
2z

Yellow solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.56 – 7.48 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.98 (s, 1H), 5.21 (s, 1H), 2.24 (s, 3H), 2.19 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.30, 143.87, 137.79, 135.14, 134.69, 133.36, 129.73, 129.67, 128.82, 128.61, 127.97, 126.91, 113.62, 62.66, 21.06, 20.36. **MS (ESI)**: found $[M+H]^+$ 349.7.

Key intermediate A was detected by GC-MS



^{1}H and ^{13}C NMR spectra of Products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7.29
7.07
7.04
6.58
6.56
5.95
5.93
5.45
5.44
2.24
0.00
Cl
N
H
O
2a
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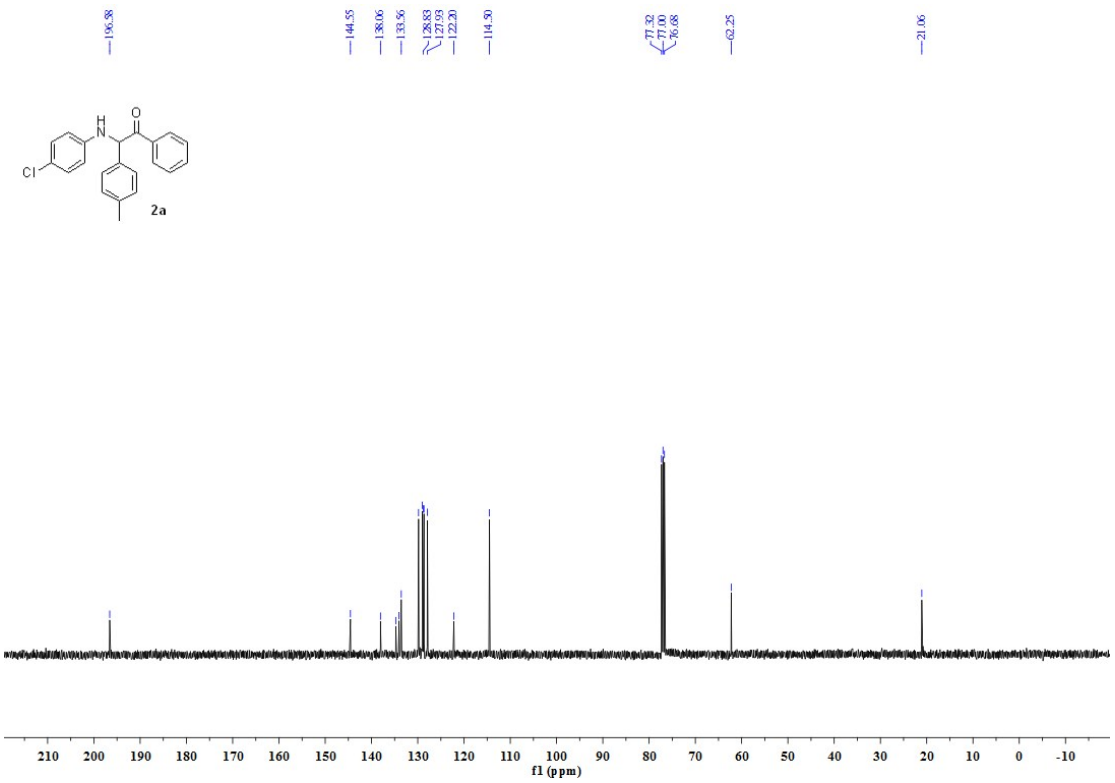
1.28
2.15
2.09
3.06
2.00
1.01
0.99
3.00
f1 (ppm)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Cl
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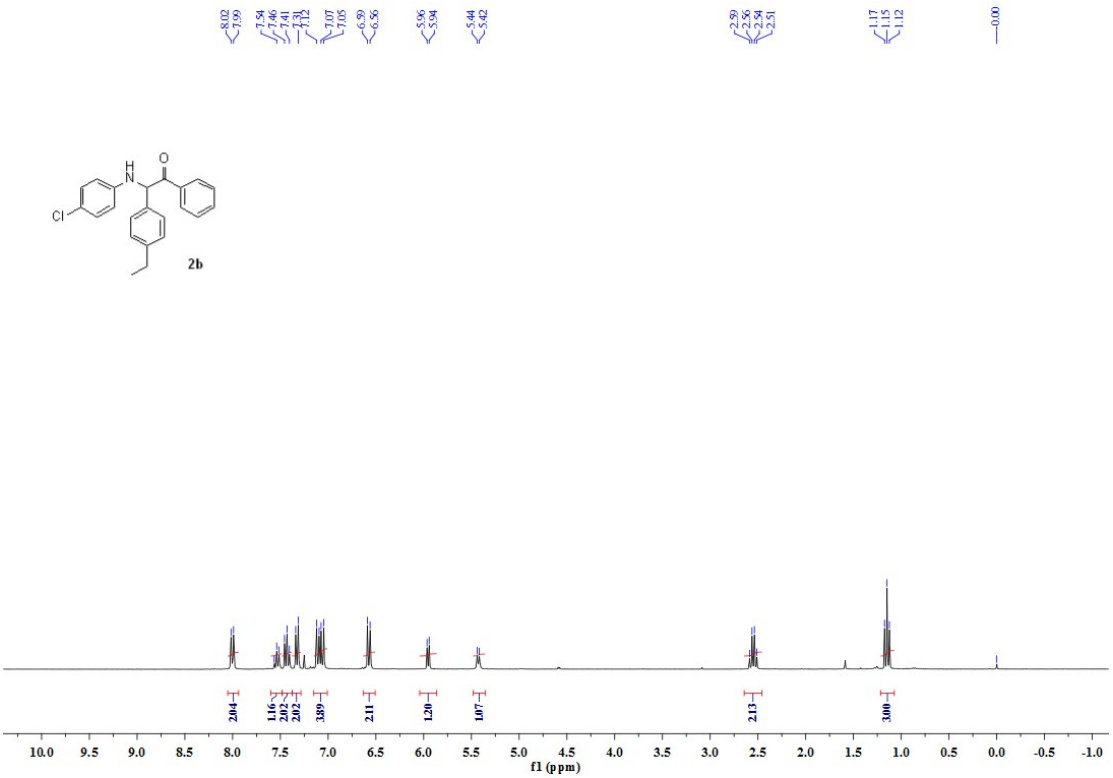
H
O
2a
f1 (ppm)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5.84
5.44
5.42
2.59
2.56
2.54
2.51
1.17
1.15
1.12
0.00
Cl
N
H
O
2b
2.04
1.16
2.02
2.02
3.89
2.11
1.20
1.07
2.13
3.00
10.0
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9.0
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7.0
6.5
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4.0
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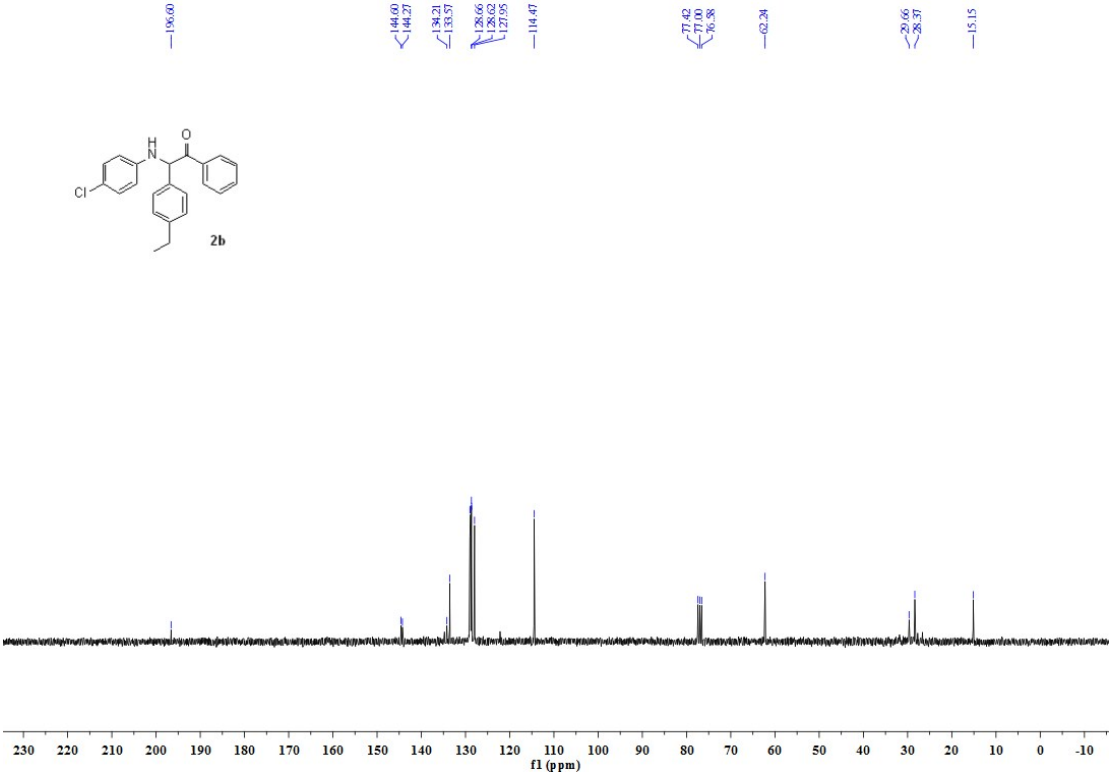
f1 (ppm)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76.58
62.24
29.66
28.37
15.15
Cl
N
H
O
2b
230
220
210
200
190
180
170
160
150
140
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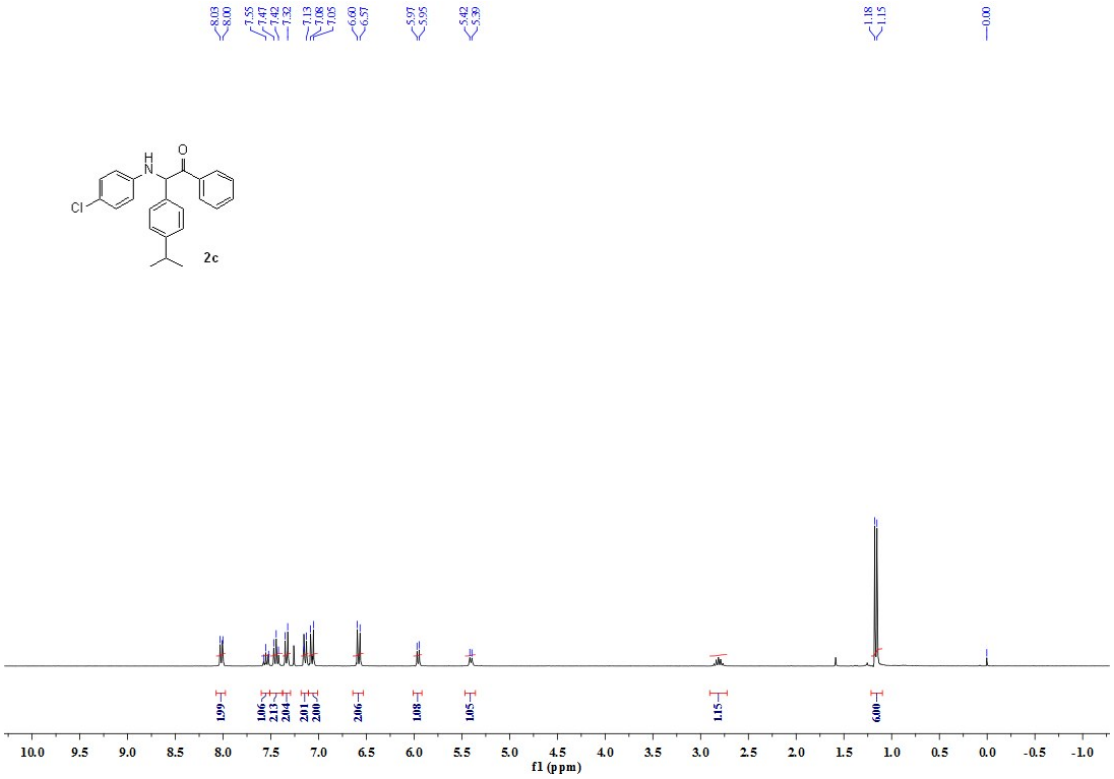
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.32
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7.08
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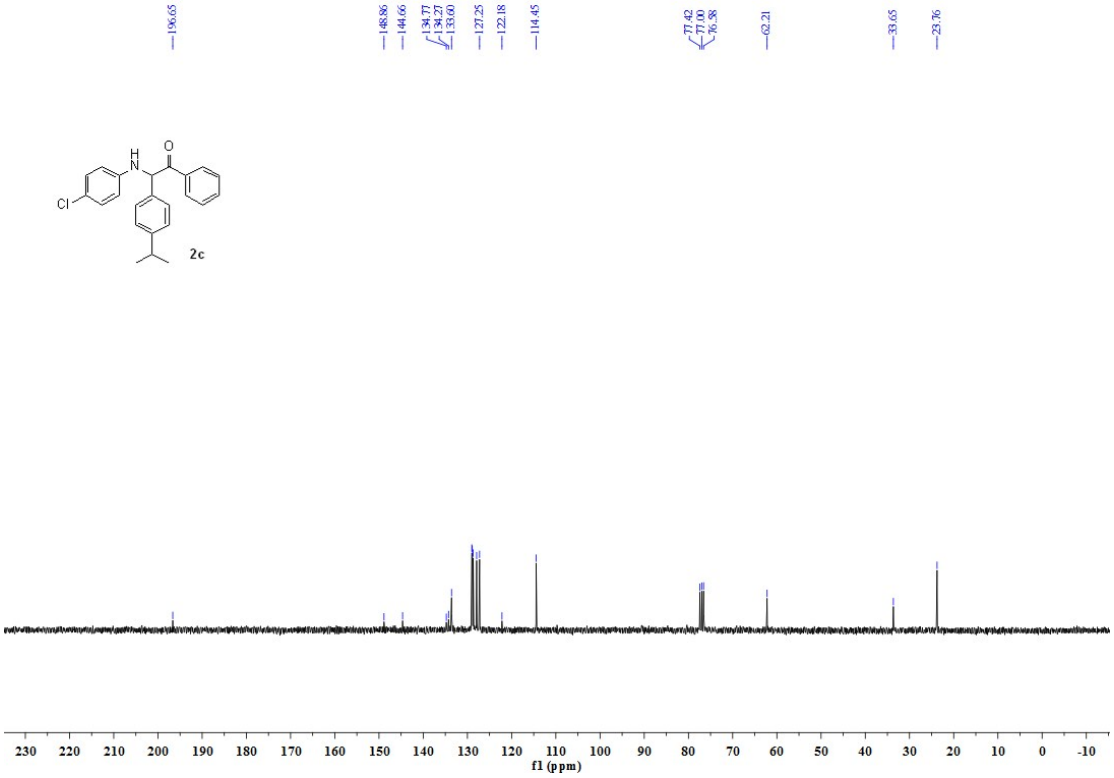
6.60
6.57
5.97
5.95
5.42
5.39
1.18
1.15
0.00
Cl
N
H
O
2c
1.99
1.06
2.13
2.04
2.01
2.00
2.06
1.08
1.05
1.15
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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133.60
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122.18
114.45
77.42
77.00
76.58
62.21
33.65
23.76
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N
H
O
2c
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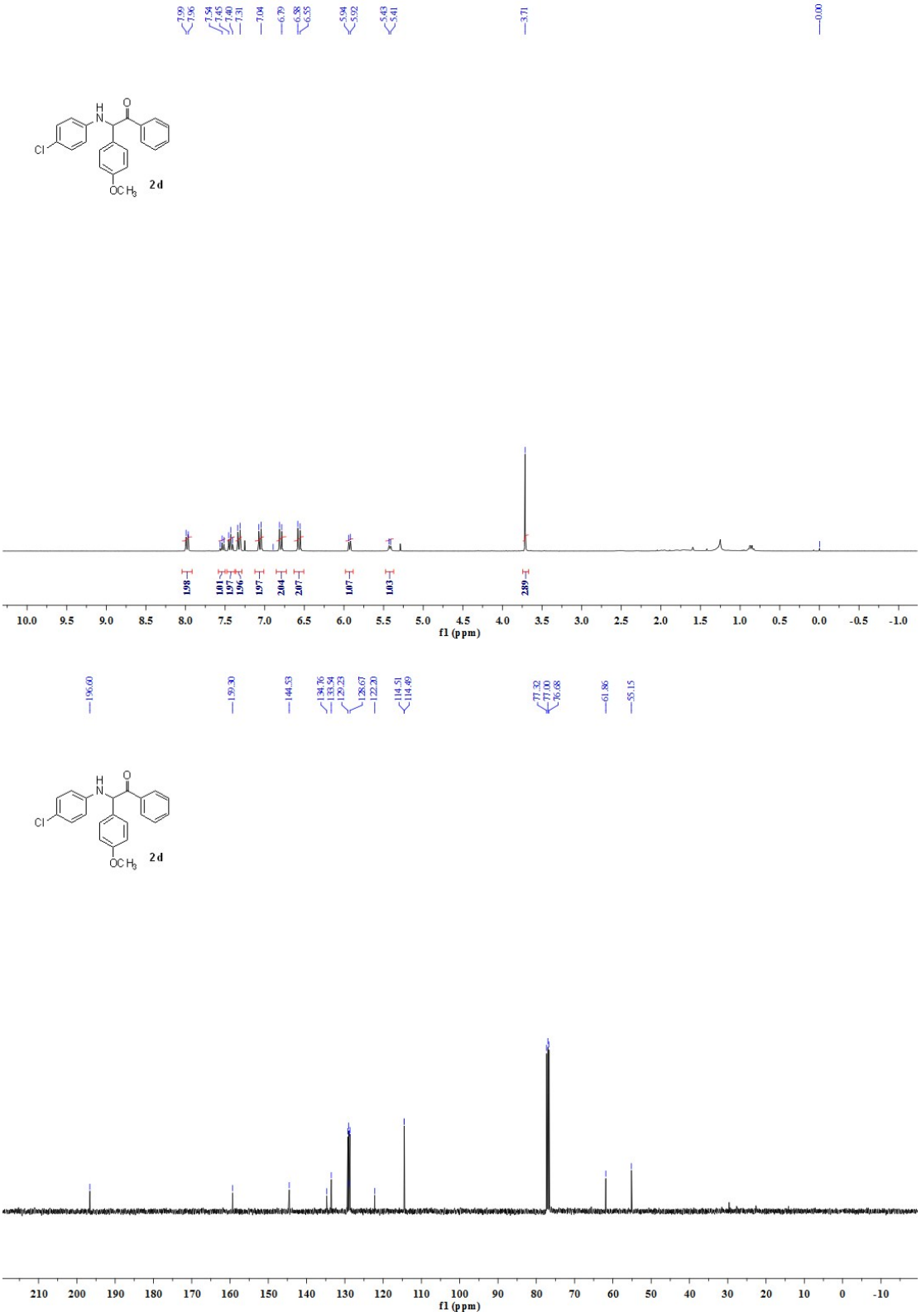
f1 (ppm)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7.31
7.04
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6.55
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5.43
5.41
3.71
0.00
Cl
N
H
O
OCH3
2d
1.98
1.01
1.97
1.96
1.97
2.04
2.07
1.07
1.03
2.89
f1 (ppm)
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159.30
144.53
134.76
133.54
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114.51
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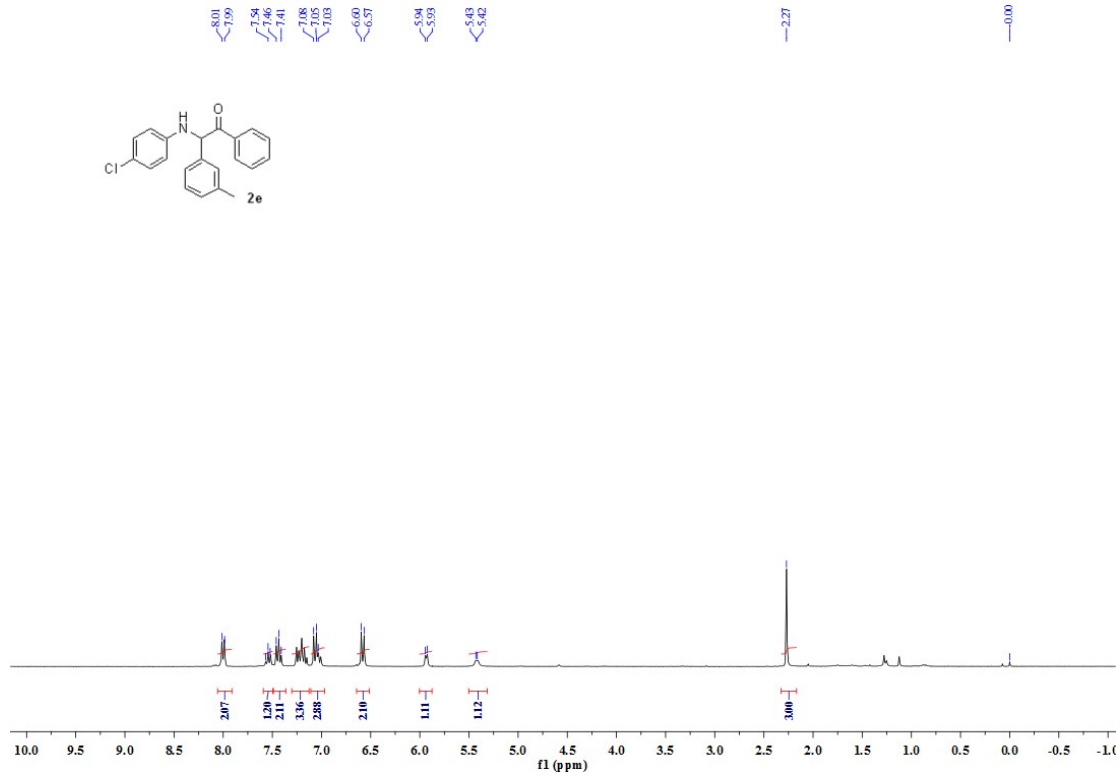
2d
f1 (ppm)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5.42
2.27
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H
O
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1.20
2.11
3.36
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1.11
1.12
3.00
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9.5
9.0
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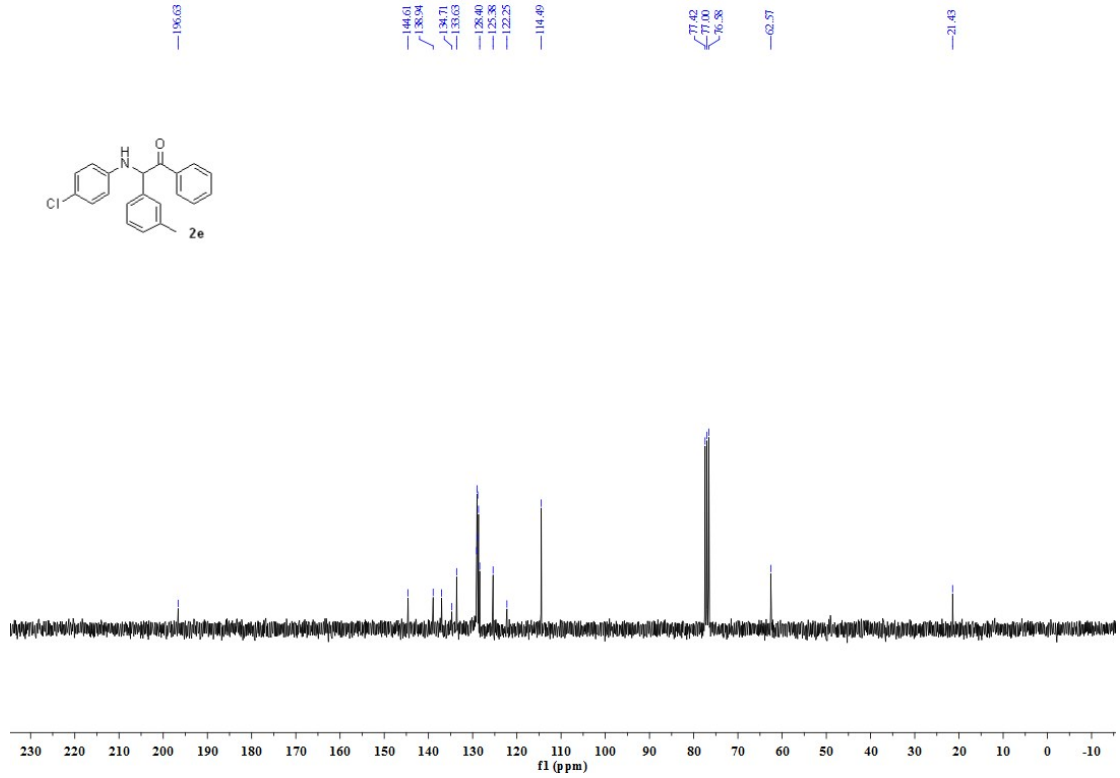
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21.43
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H
O
2e
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200
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180
170
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100
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80
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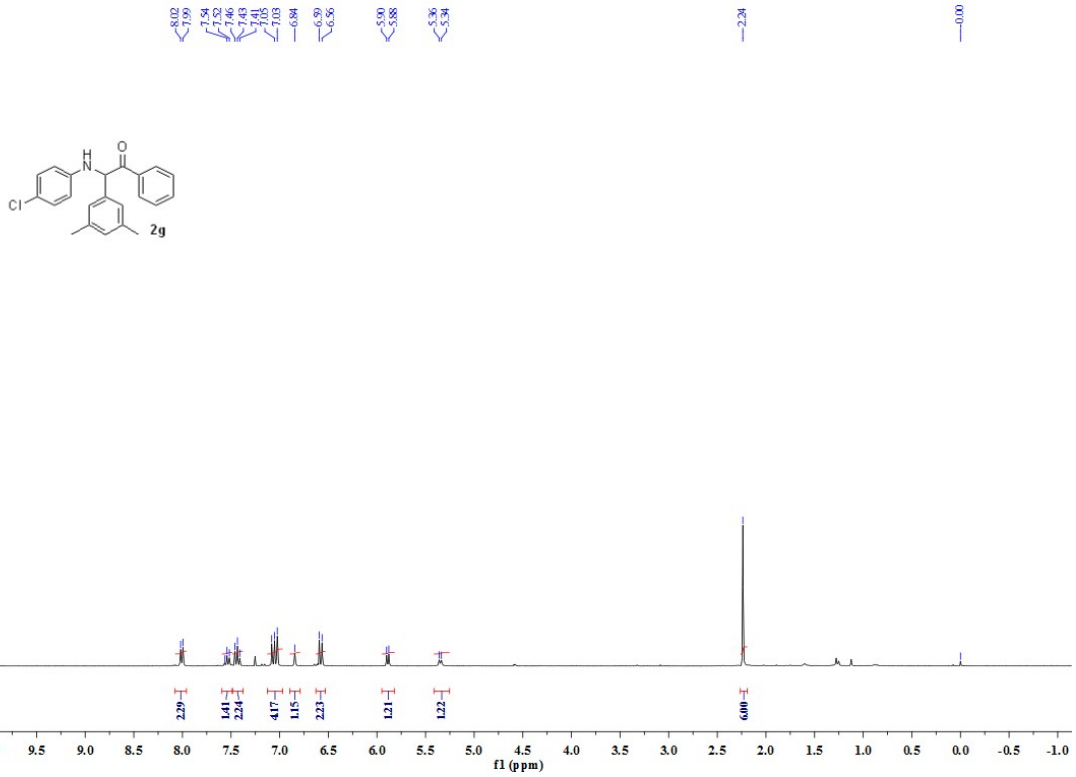
f1 (ppm)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5.90
5.88
5.36
5.34
2.24
0.00
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2.24
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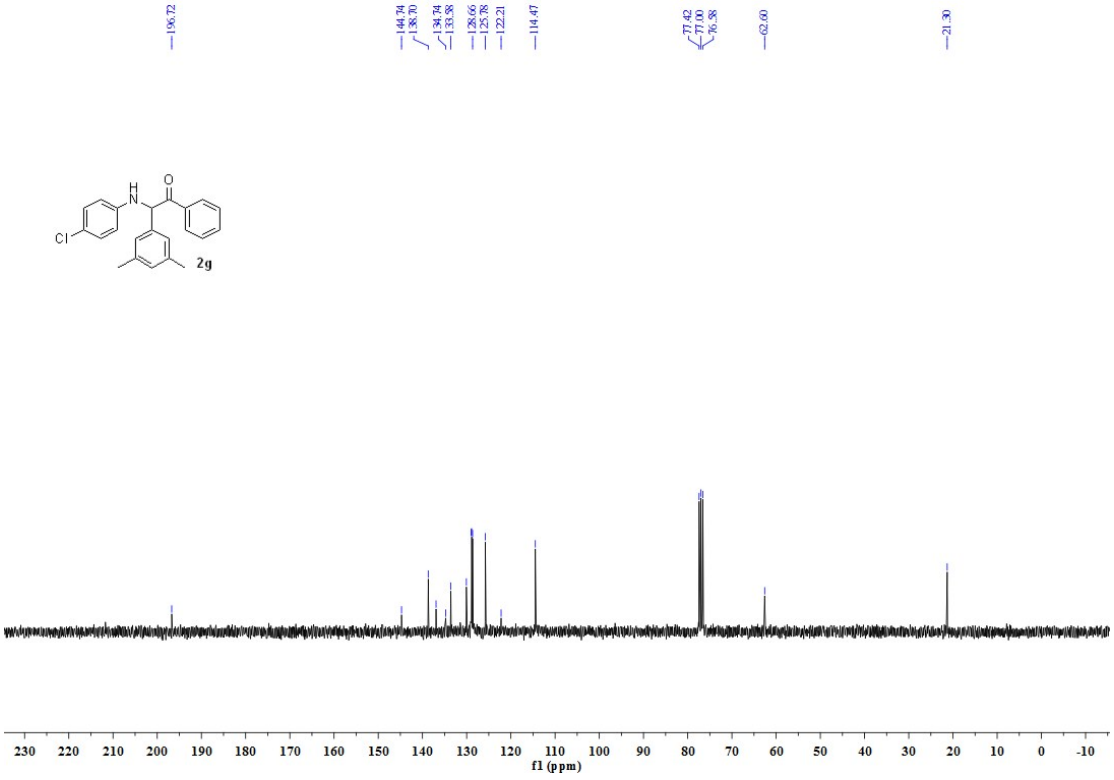
1.21
1.22
6.00
f1 (ppm)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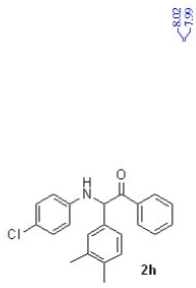
Cl
2g
f1 (ppm)


Cl
N
H
O
2h

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7.04
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6.56
5.92
5.90
5.41
5.38
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2.15
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2.19
1.48
2.24
2.38
3.09
2.33
1.25
1.24
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3.00
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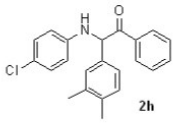
f1 (ppm)


Cl
N
H
O
2h

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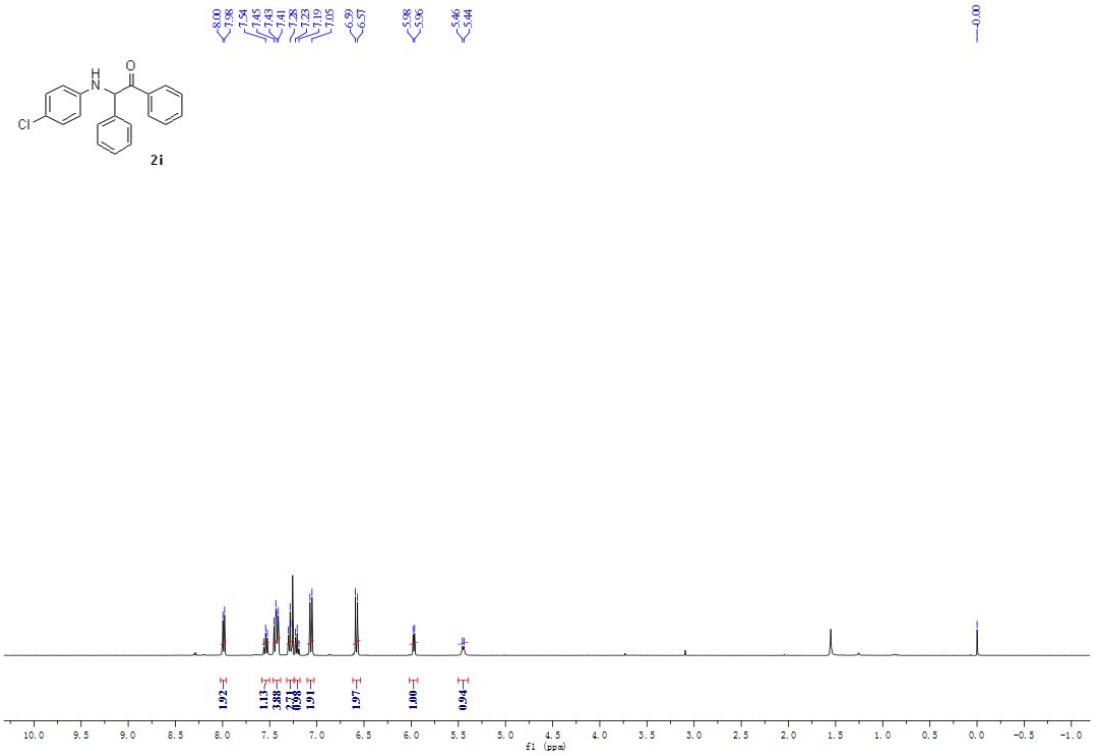
f1 (ppm)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5.98
5.96
5.46
5.44
0.00
1.92
1.13
3.88
0.94
1.91
1.97
1.00
0.94
f1 (ppm)
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144.59
137.23
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128.07
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114.60
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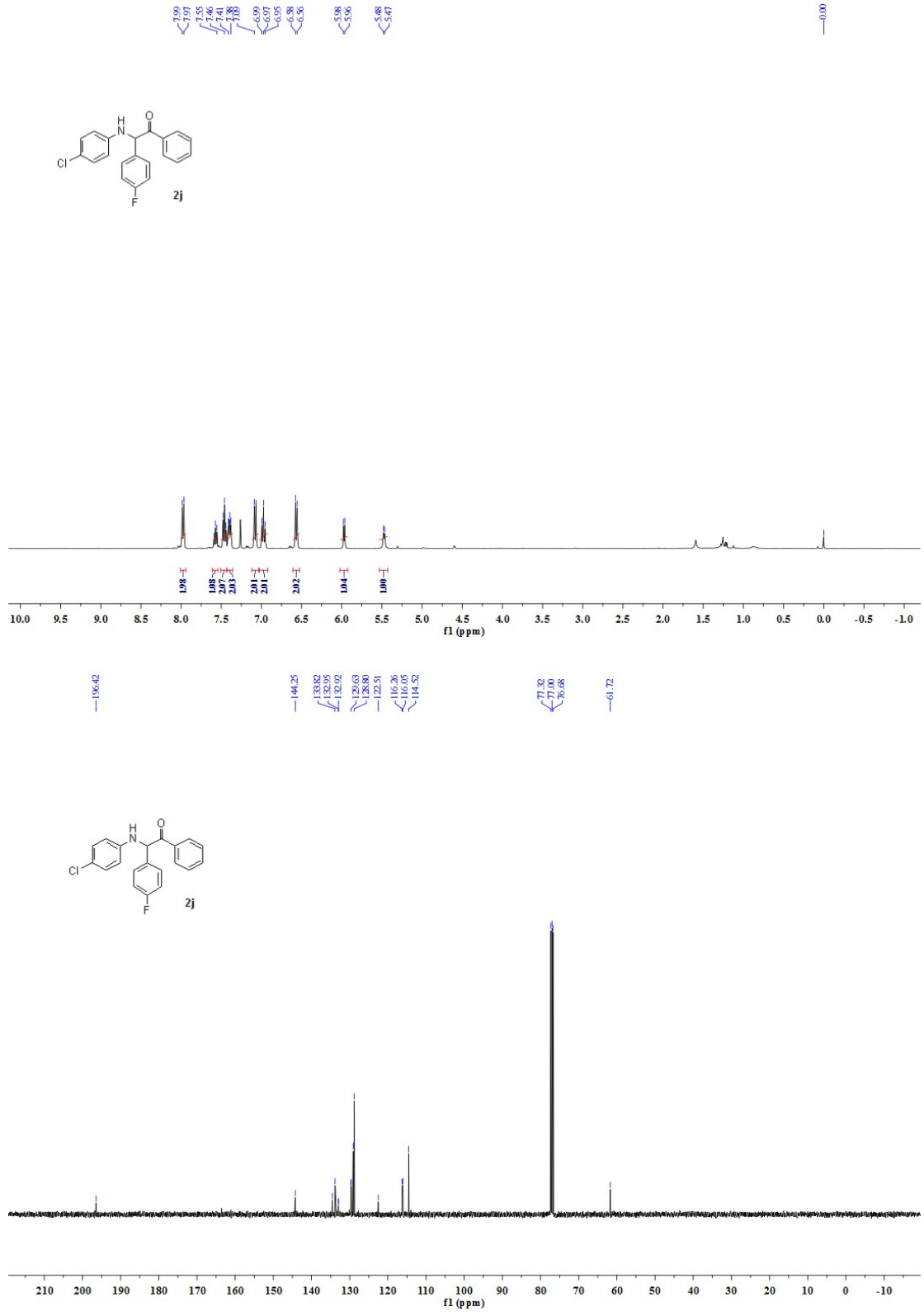
62.70
f1 (ppm)

2i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7.38
7.03
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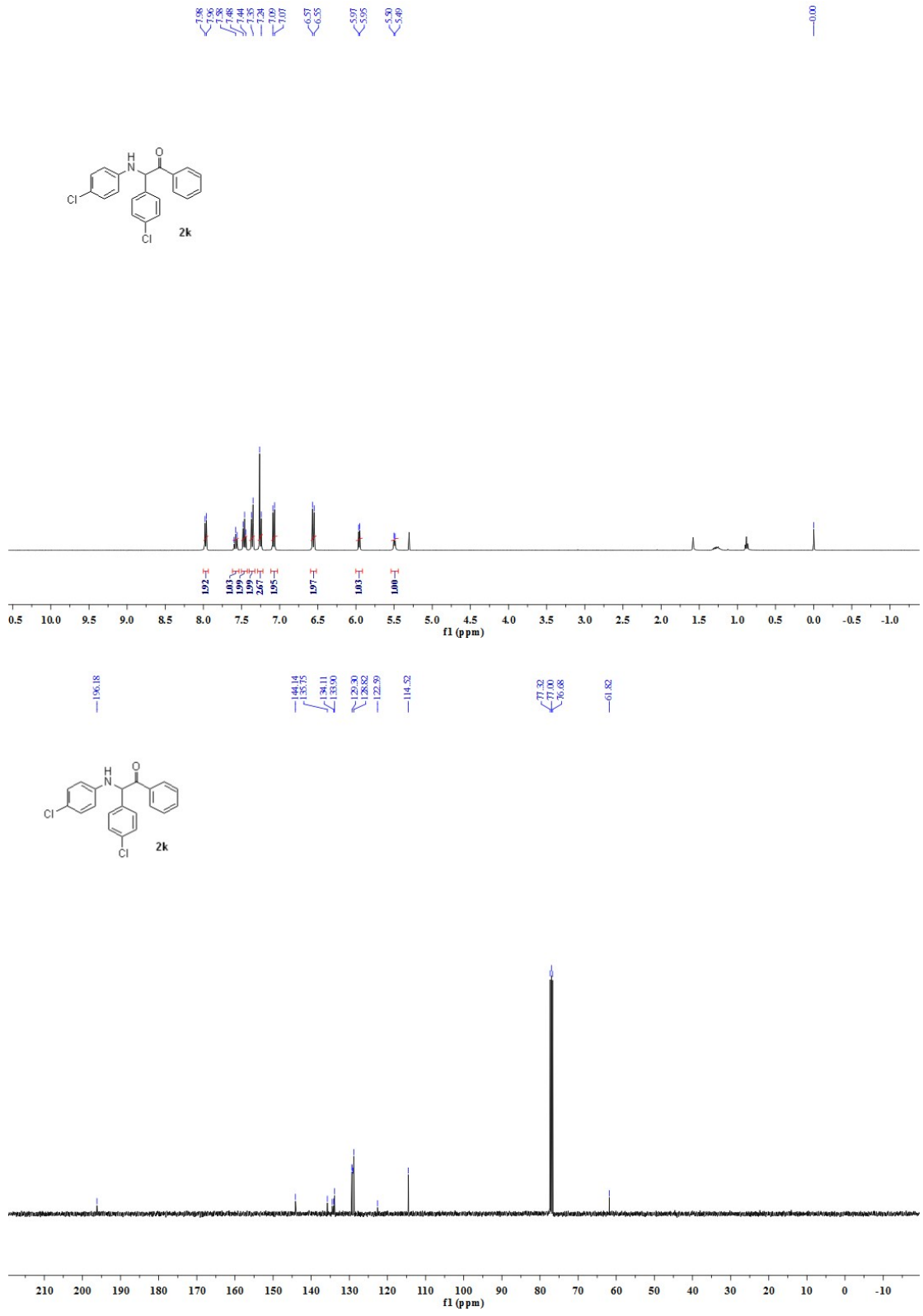
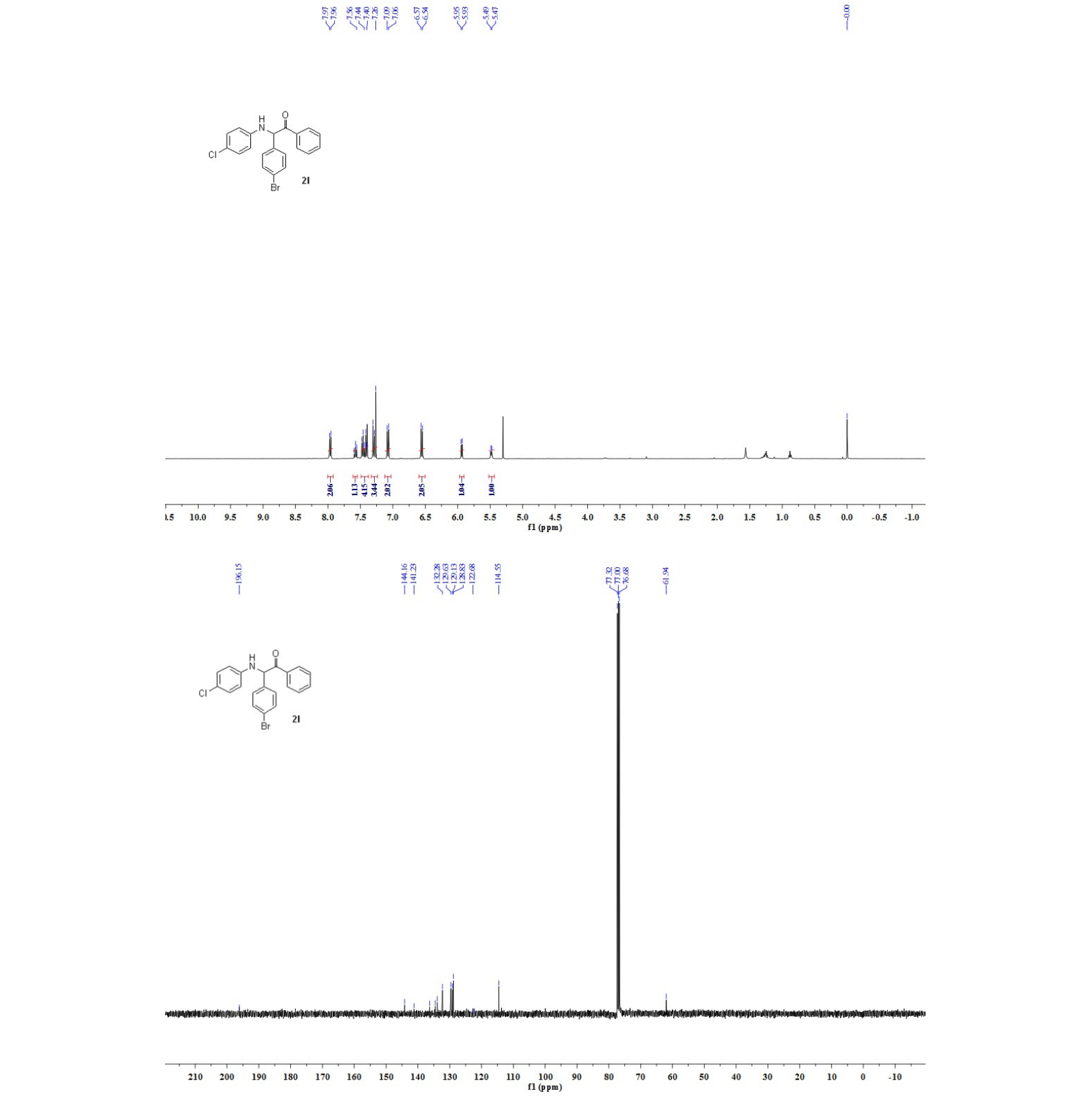
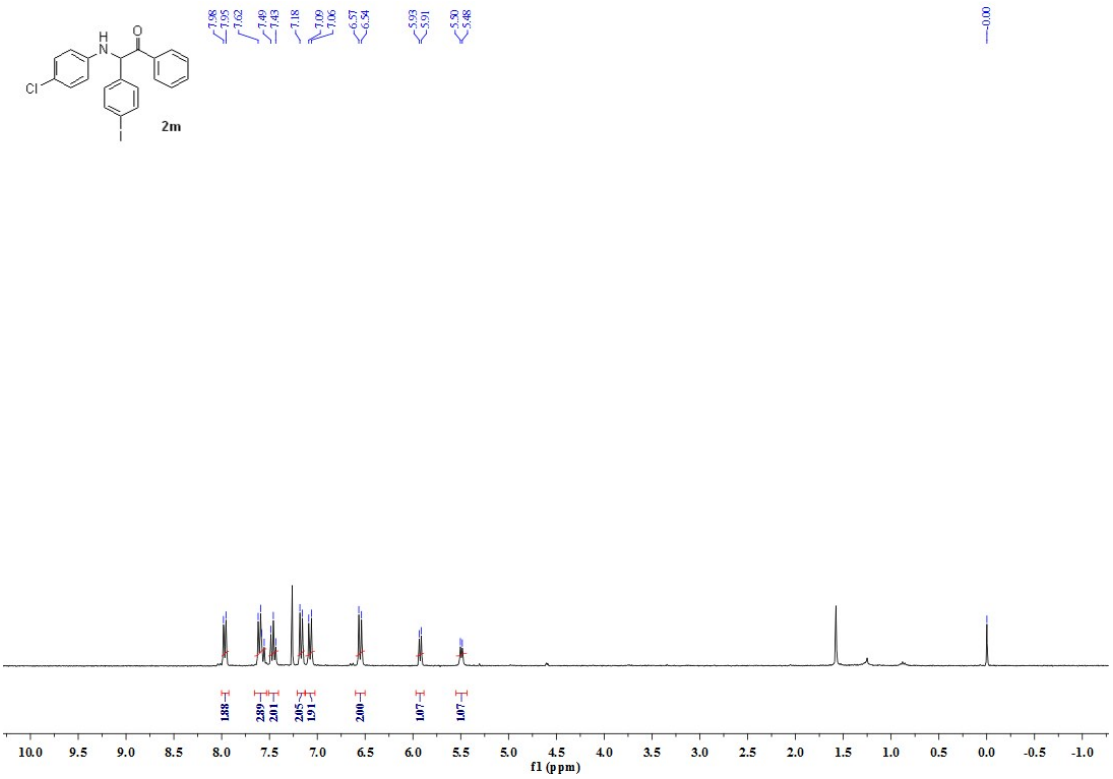
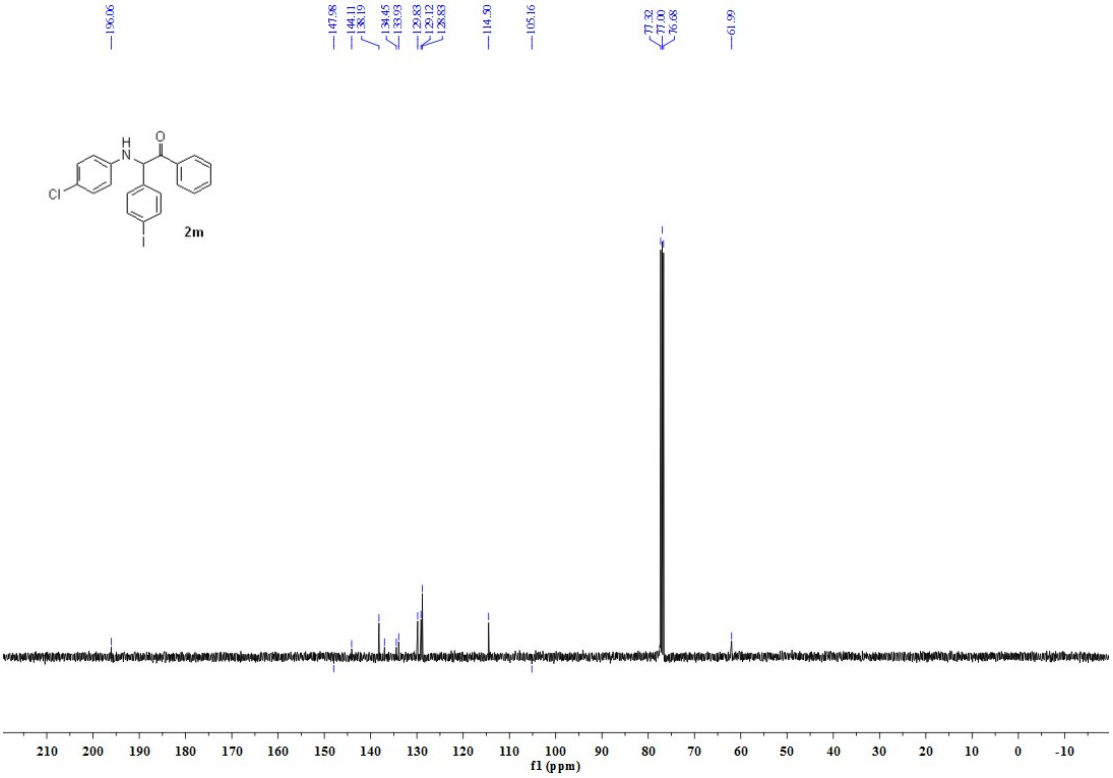
6.97
6.95
6.88
6.86
5.98
5.96
5.48
5.47
0.00
Cl
F
2j
1.98
1.08
2.07
2.03
2.01
2.01
2.02
1.04
1.00
f1 (ppm)
196.42
144.25
133.82
132.95
132.92
129.63
128.80
122.51
116.26
116.05
114.52
77.32
77.00
76.68
61.72
Cl
F
2j
f1 (ppm)


7.98
7.96
7.58
7.48
7.44
7.35
7.24
7.09
7.07
6.57
6.55
5.97
5.95
5.50
5.49
0.00
2k
1.02
1.03
1.99
1.99
2.07
1.05
1.97
1.03
1.00
f1 (ppm)
196.18
144.14
135.75
134.11
133.90
129.30
128.82
122.59
114.52
77.32
77.00
76.68
61.82
2k
f1 (ppm)


7.97
7.96
7.56
7.44
7.40
7.28
7.09
7.06
6.57
6.54
5.95
5.93
5.49
5.47
0.00
2l
2.06
1.13
4.15
3.44
2.02
2.05
1.04
1.00
f1 (ppm)
196.15
144.16
141.23
132.28
129.63
129.13
128.83
122.68
114.55
77.32
77.00
76.68
61.94
2l
f1 (ppm)


7.98
7.95
7.62
7.49
7.43
7.18
7.09
7.06
6.57
6.54
5.93
5.91
5.50
5.48
0.00
2m
1.38
2.89
2.01
2.05
1.91
2.00
1.07
1.07
f1 (ppm)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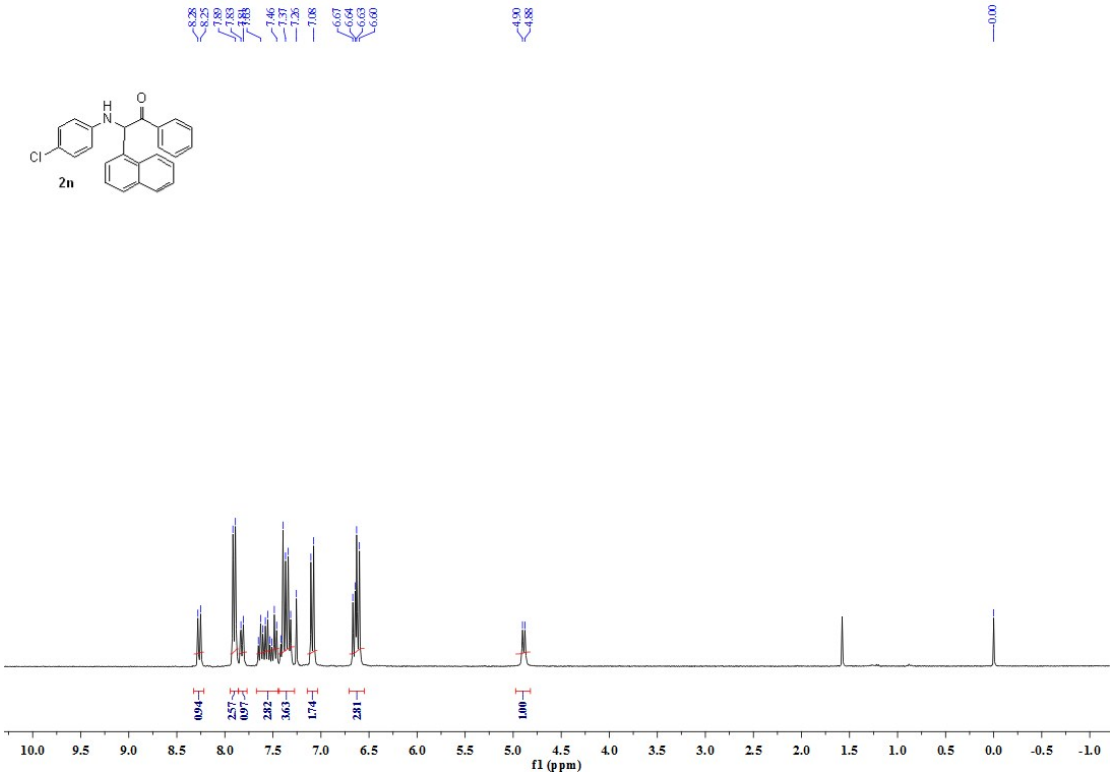
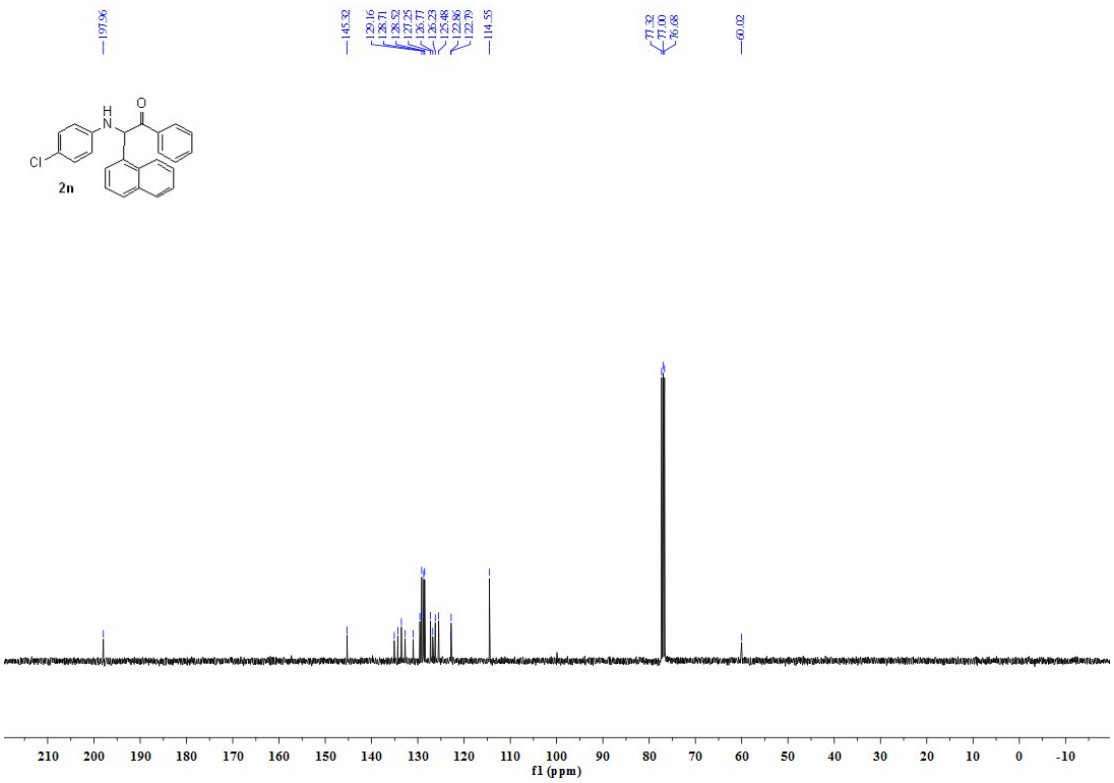
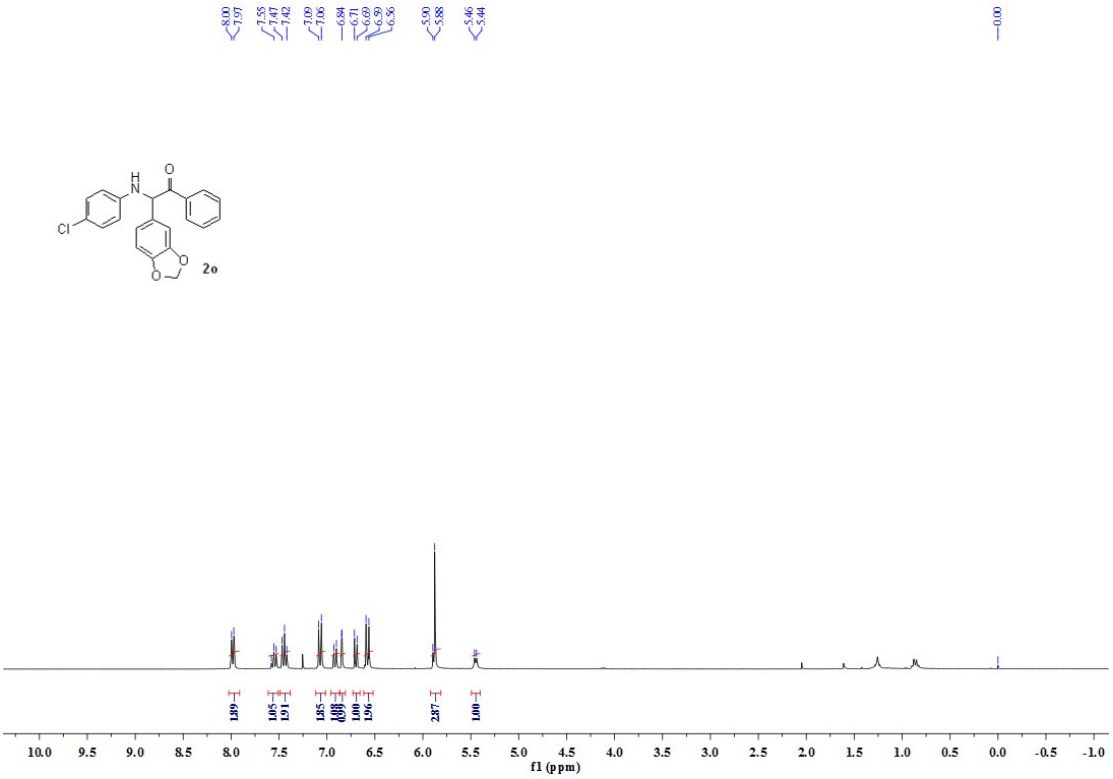
147.98
144.11
138.19
134.45
133.93
129.83
129.12
128.83
114.50
105.16
77.32
77.00
76.68
61.99
2m
f1 (ppm)


8.28
8.25
7.89
7.83
7.81
7.46
7.37
7.25
7.08
6.67
6.64
6.63
6.60
4.90
4.88
0.00
2n
0.94
2.57
0.97
2.82
3.63
1.74
2.81
1.00
f1 (ppm)


197.96
145.32
129.16
128.71
128.52
127.75
126.77
126.23
125.48
122.86
122.79
114.55
77.32
77.00
76.68
60.02
2n
f1 (ppm)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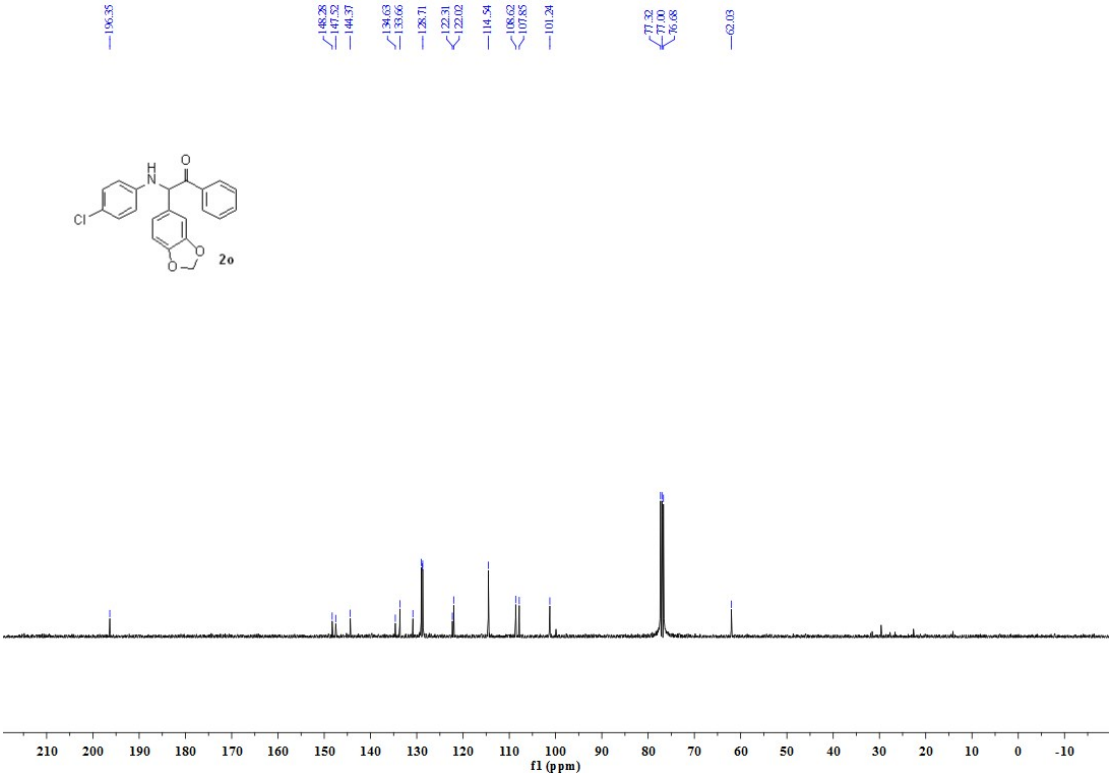
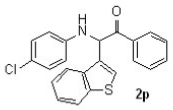
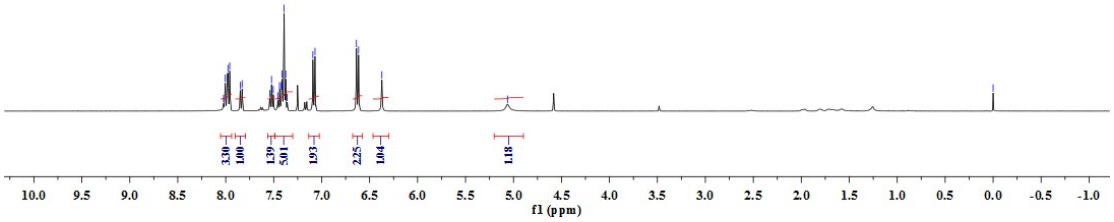
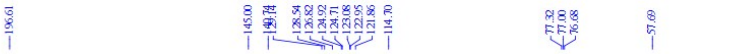
7.55
7.47
7.42
7.09
7.06
6.84
6.71
6.69
6.68
6.56
5.90
5.88
5.46
5.44
0.00
Cl
O
N
H
O
O
2o
1.89
1.05
1.91
1.85
1.03
1.00
1.06
2.87
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

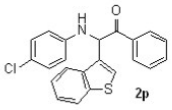

196.35
148.28
147.52
144.37
134.63
133.66
128.71
122.31
122.02
114.54
108.62
107.85
101.24
77.32
77.00
76.68
62.03
Cl
O
N
H
O
O
2o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

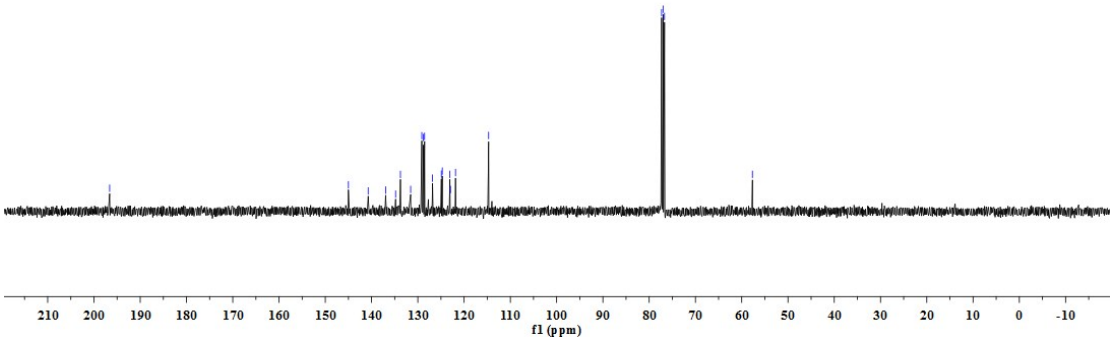

8.02
8.00
7.98
7.98
7.96
7.96
7.85
7.83
7.41
7.36
7.09
7.07
6.64
6.62
6.37
5.06
0.00


H
O
Cl
S
2p

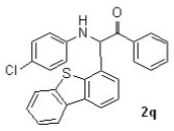

3.10
1.00
1.39
5.01
1.93
2.25
1.04
1.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


196.61
145.00
140.74
140.24
128.54
126.82
126.62
124.92
124.71
123.08
122.95
121.86
114.70
77.32
77.00
76.68
57.69

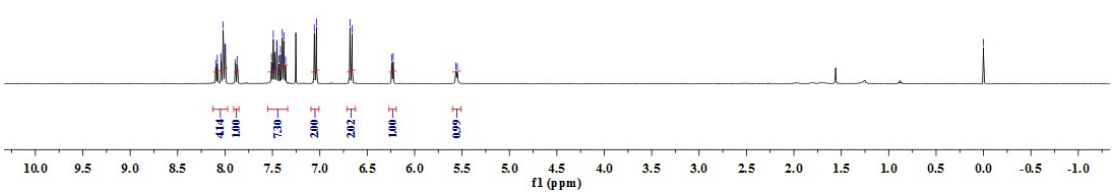

H
O
Cl
S
2p


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

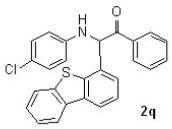

8.10
8.08
8.04
8.02
8.00
7.89
7.43
7.41
7.36
7.06
7.04
6.68
6.66
6.24
6.23
5.57
5.55
0.00


H
N
O
Cl
S

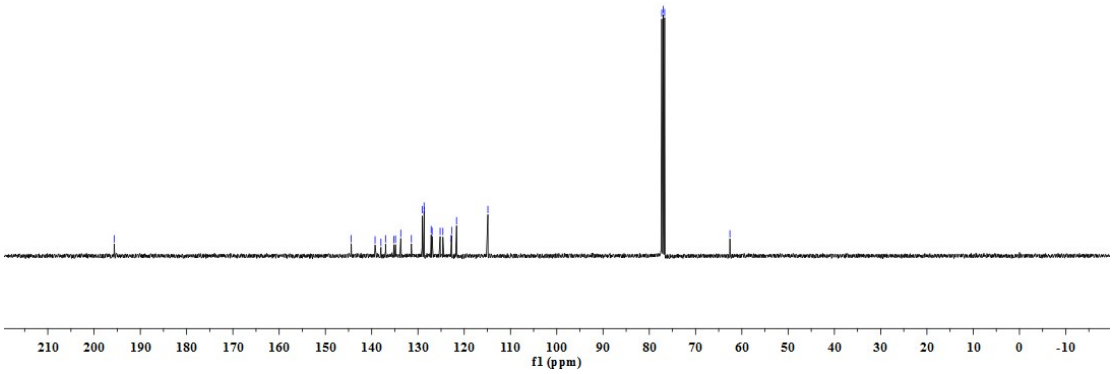
2q

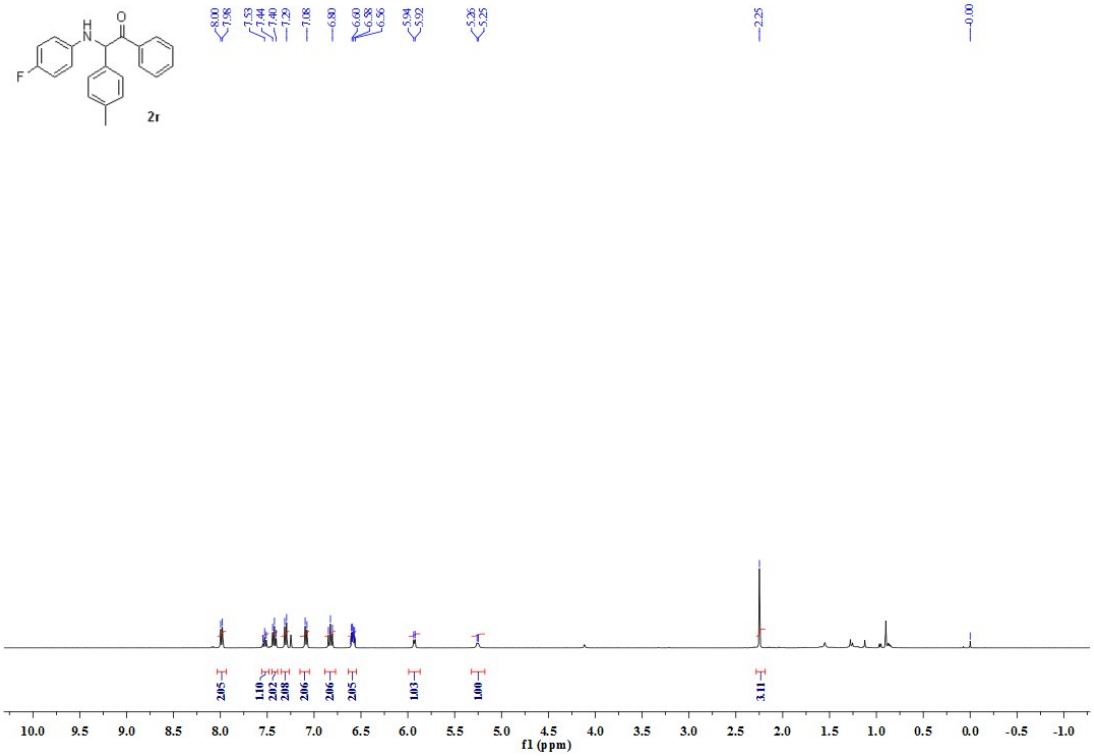

4.14
1.00
7.30
2.00
2.02
1.00
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

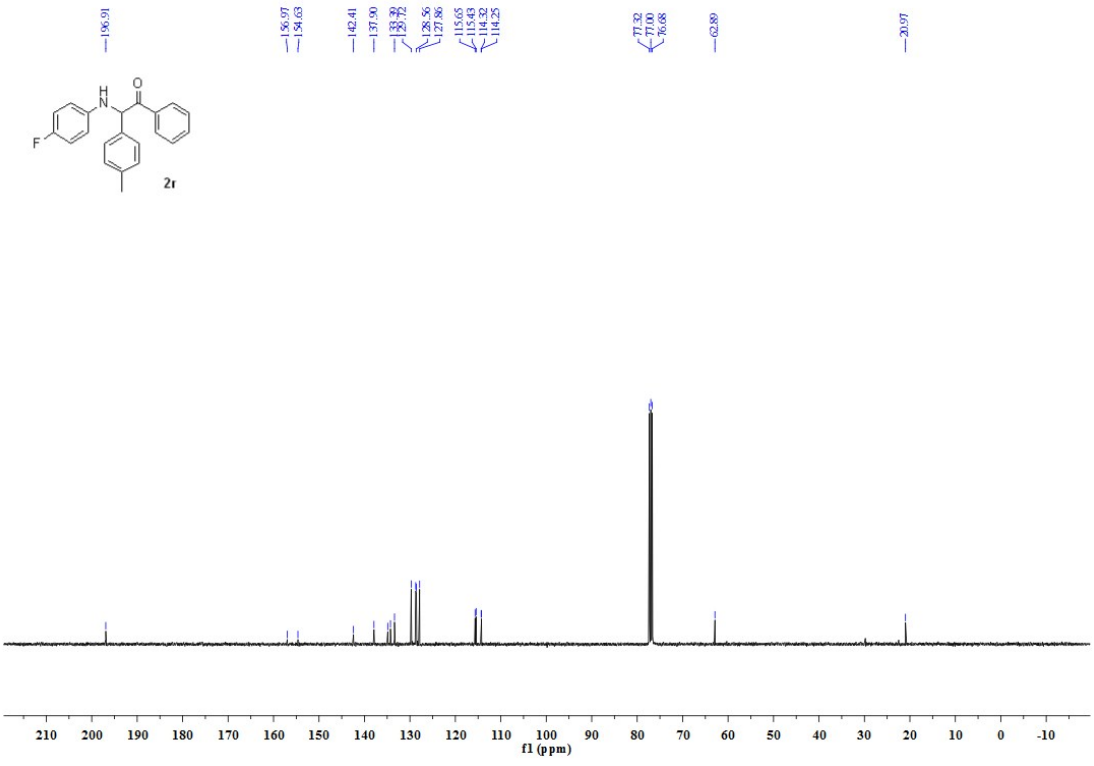

195.66
144.41
137.01
134.85
131.42
129.68
127.15
125.20
122.83
121.66
114.89
77.32
77.00
76.68
62.38

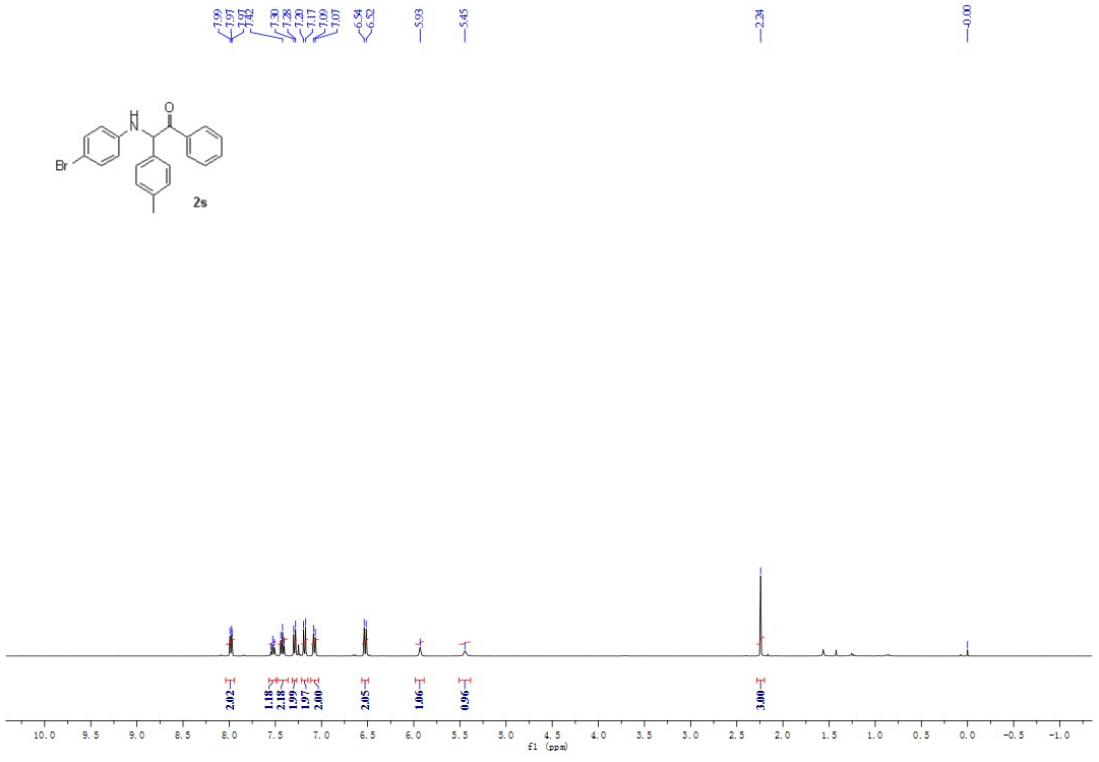

H
N
O
Cl
S

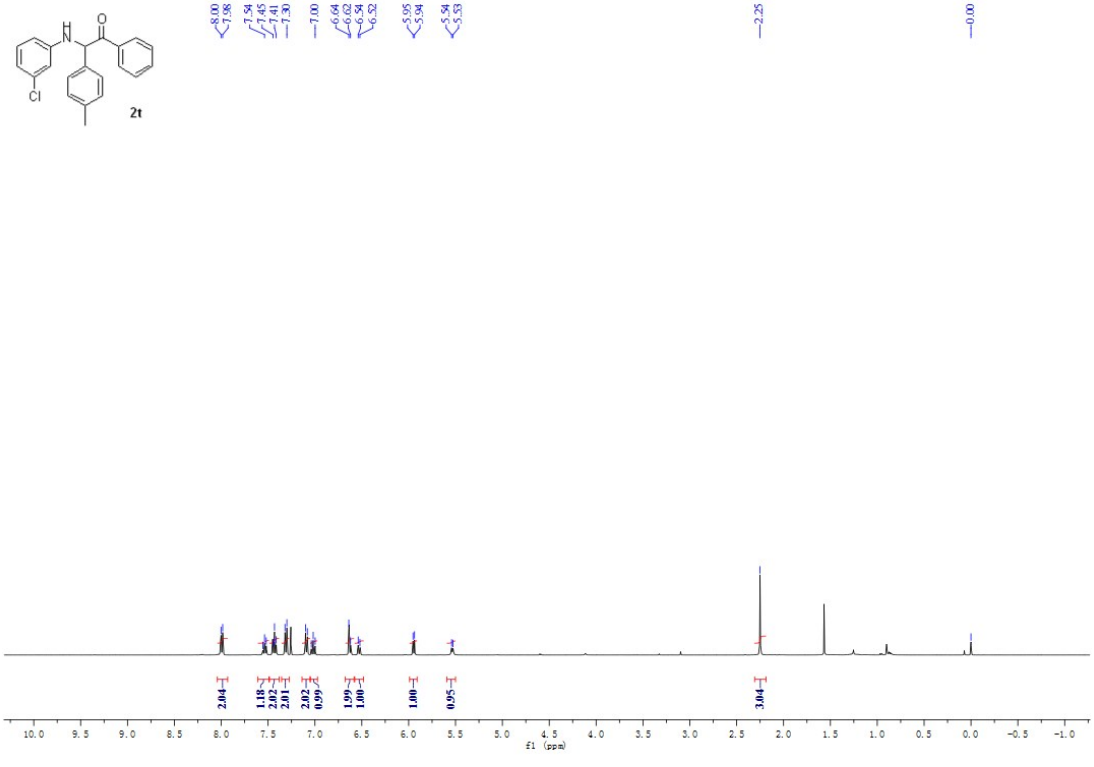
2q

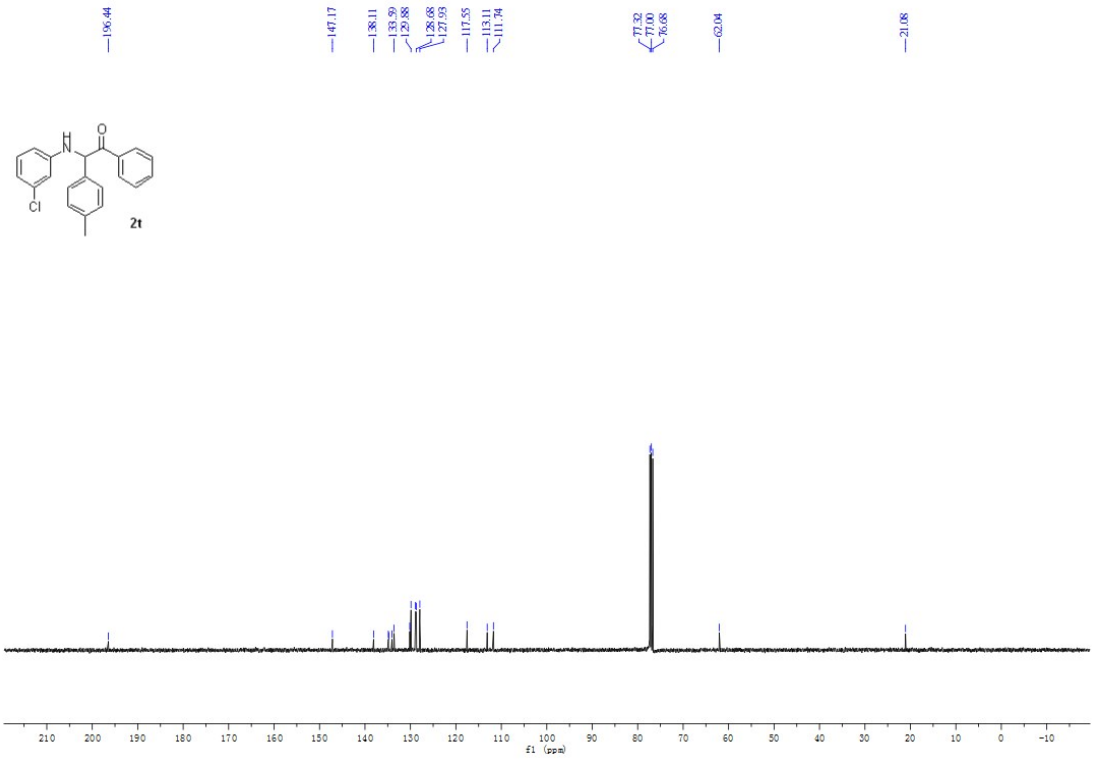

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

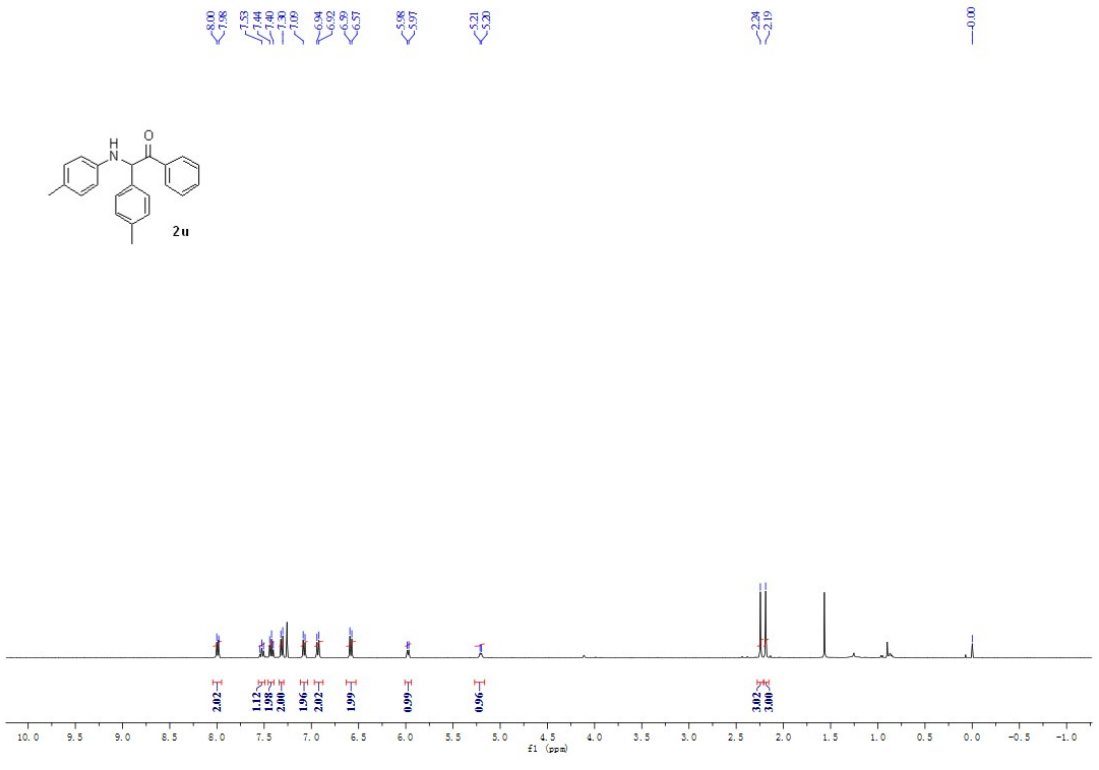

8.00
7.98
7.53
7.44
7.40
7.29
7.08
6.80
6.60
6.58
6.56
5.94
5.92
5.26
5.25
2.25
0.00
2.05
1.10
2.02
2.08
2.06
2.06
2.05
1.03
1.00
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
F
H
N
O
2r

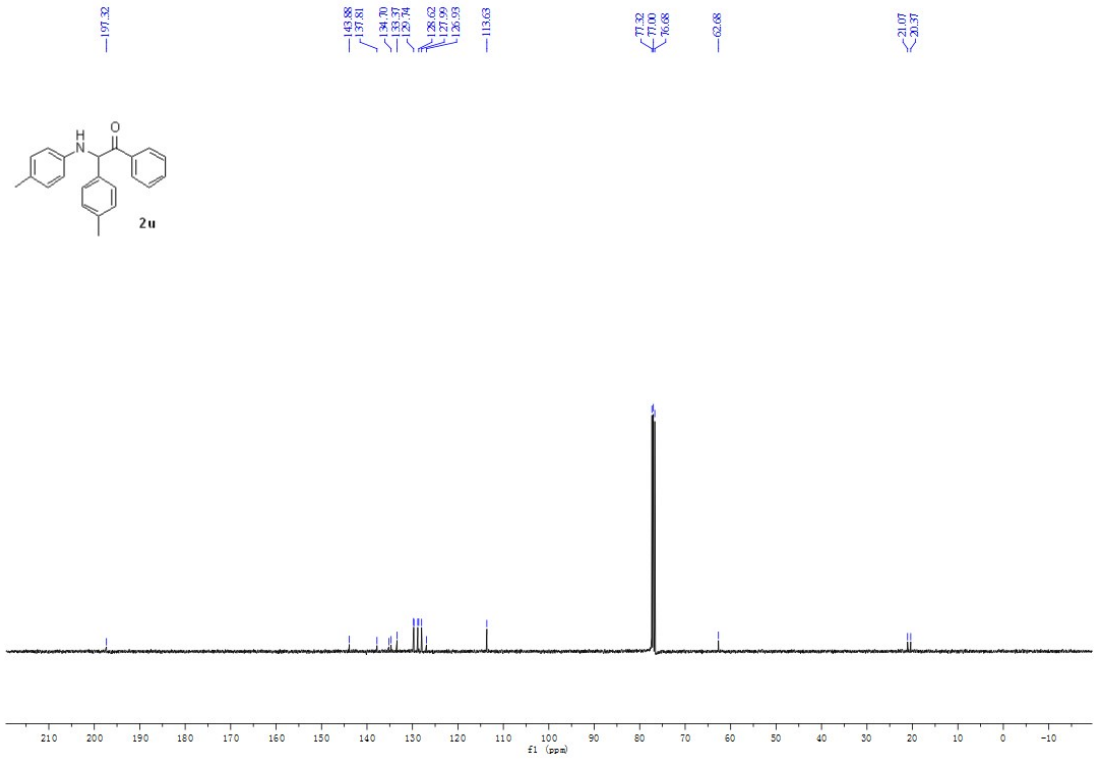

196.91
156.97
154.63
142.41
137.90
133.39
129.72
128.56
127.86
115.65
115.43
114.32
114.25
77.32
77.00
76.68
62.89
20.97
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
F
H
N
O
2r

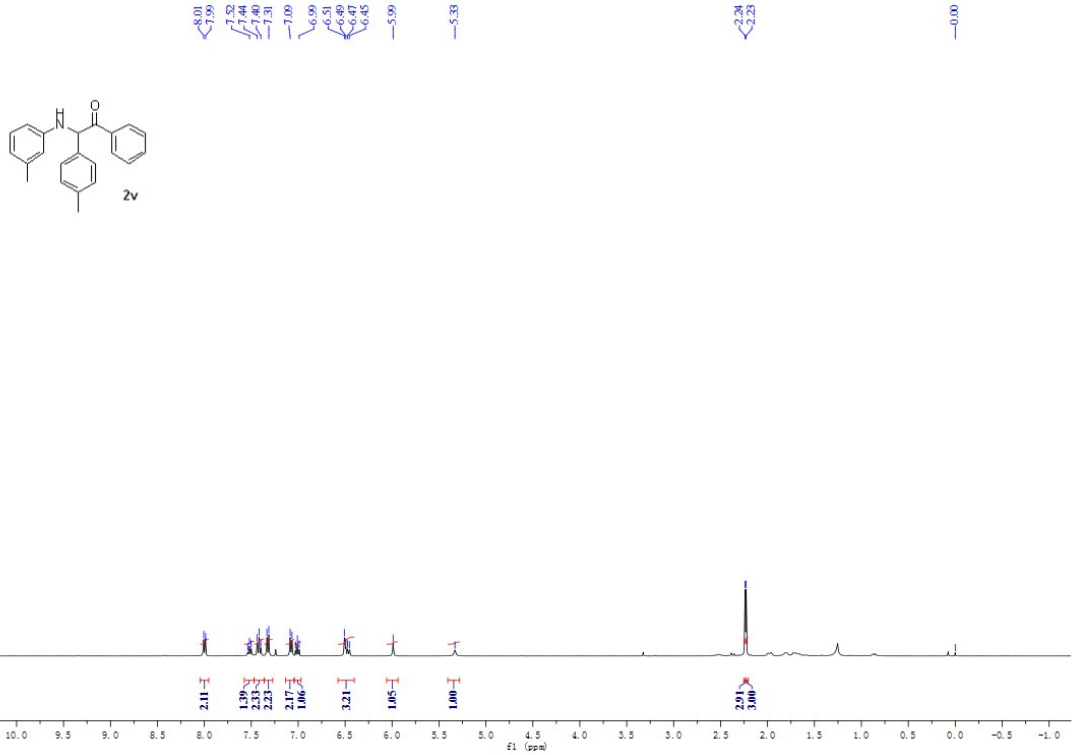

7.99
7.97
7.93
7.42
7.30
7.28
7.20
7.17
7.09
7.07
6.54
6.52
5.93
5.45
2.24
0.00
Br
2s
2.02
1.18
2.18
1.99
1.97
2.00
2.05
1.06
0.96
3.00
f1 (ppm)
196.58
145.03
138.10
131.89
129.85
128.85
128.67
127.96
115.07
109.36
77.32
77.00
76.68
62.24
21.06
Br
2s
f1 (ppm)

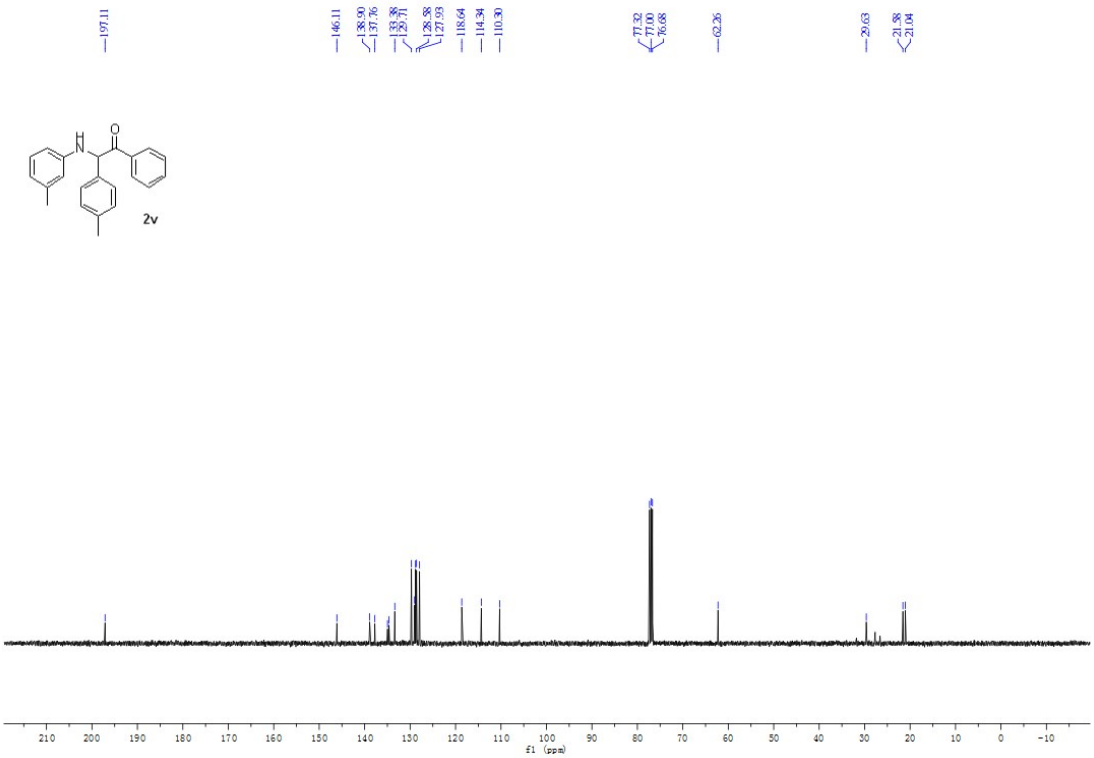

8.00
7.98
7.54
7.45
7.41
7.30
7.00
6.64
6.62
6.54
6.52
5.95
5.94
5.54
5.53
2.25
0.00
2t
2.04
1.18
2.02
2.01
2.02
0.99
1.99
1.00
1.00
0.95
3.04
f1 (ppm)

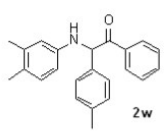

196.44
147.17
138.11
133.59
129.88
128.68
127.93
117.55
113.11
111.94
77.32
77.00
76.68
62.04
21.08
2t
f1 (ppm)


8.00
7.98
7.53
7.44
7.40
7.30
7.09
6.94
6.92
6.89
6.87
5.98
5.97
5.21
5.20
2.24
2.19
0.00
2u
2.02
1.12
1.98
2.00
1.96
2.02
1.99
0.99
0.96
3.02
3.00
f1 (ppm)

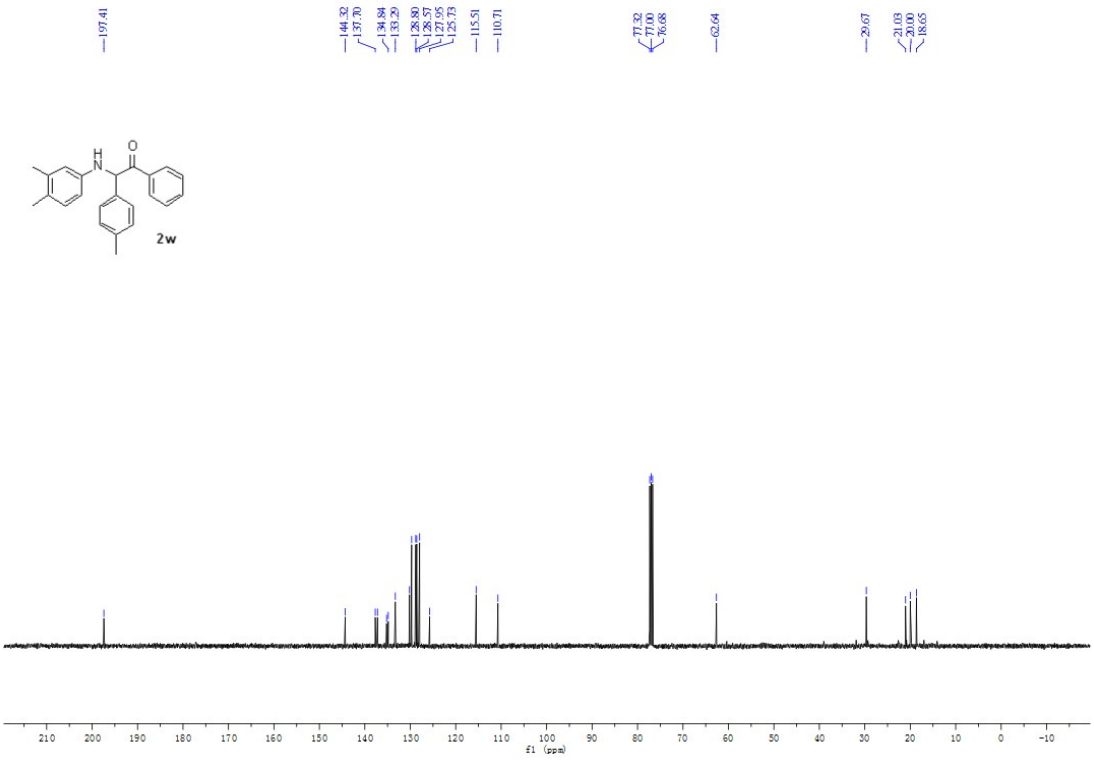

197.32
143.88
137.81
134.70
133.37
129.74
128.62
127.99
126.93
113.63
77.32
77.00
76.68
62.68
21.07
20.37
2u
f1 (ppm)


8.01
7.99
7.52
7.44
7.40
7.31
7.09
6.99
6.51
6.49
6.47
6.45
5.99
5.33
2.24
2.23
0.00
2v
2.11
1.39
2.33
2.23
2.17
1.06
3.21
1.05
1.00
2.91
3.00
f1 (ppm)

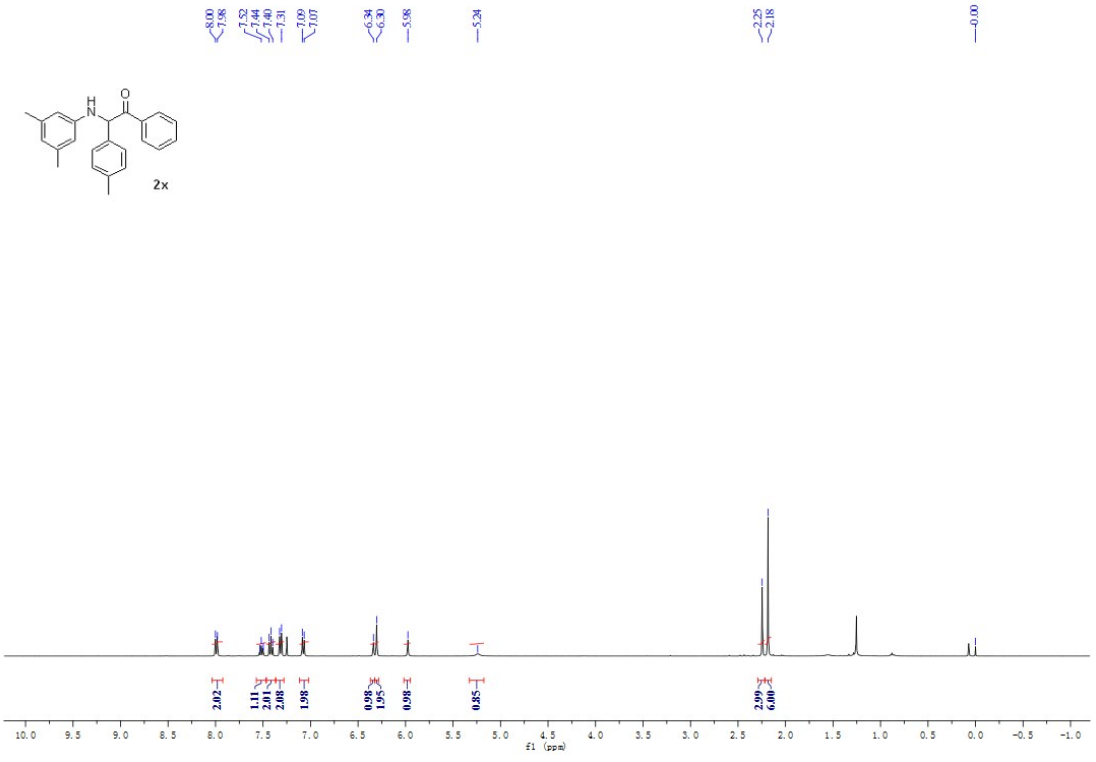

197.11
146.11
138.90
137.76
133.38
129.71
128.58
127.93
118.64
114.34
110.30
77.32
77.00
76.68
62.26
29.63
21.58
21.04
2v
f1 (ppm)

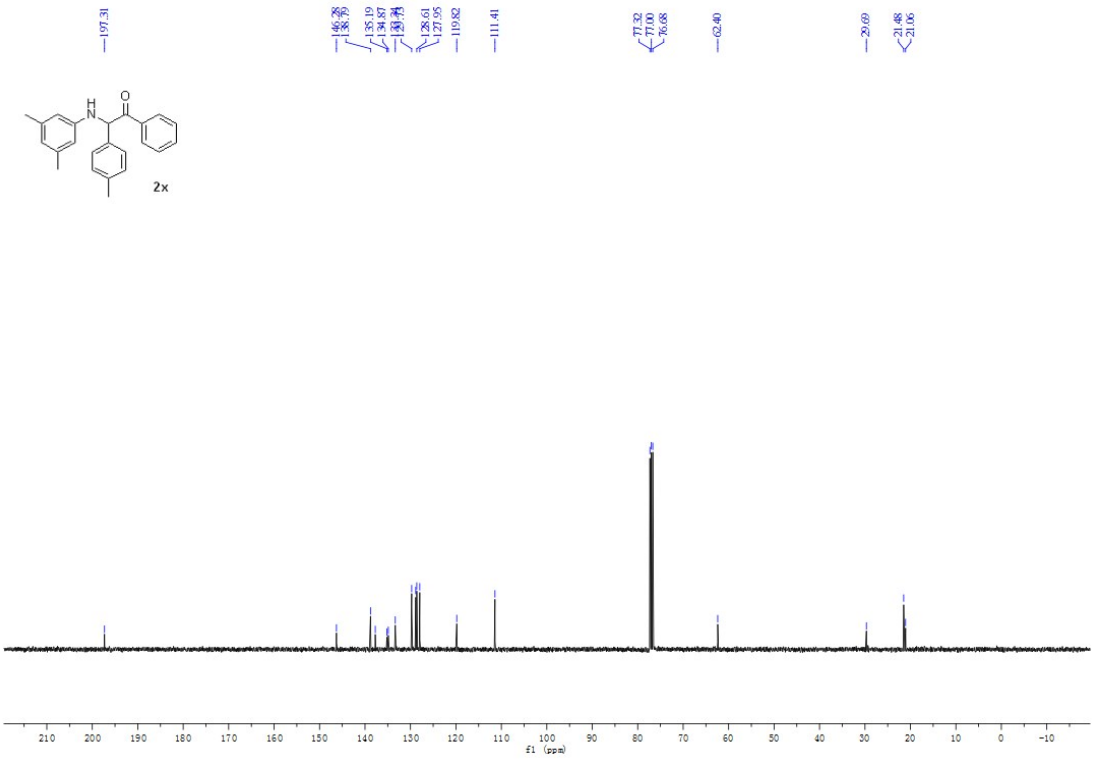

2w

8.00
7.97
7.51
7.42
7.39
7.30
7.06
6.88
6.86
6.51
6.42
6.40
5.97
5.14
2.23
2.14
2.10
0.00
1.90
1.32
2.01
1.90
1.86
0.93
0.94
0.92
0.92
0.76
3.00
2.75
2.89
f1 (ppm)


197.41
144.32
137.70
134.84
133.29
128.80
128.57
127.95
125.73
115.51
110.71
77.32
77.00
76.68
62.64
29.67
21.03
20.00
18.65
f1 (ppm)

2w


8.00
7.98
7.52
7.44
7.40
7.31
7.09
7.07
6.34
6.30
5.98
5.24
2.25
2.18
0.00
2x
2.02
1.11
2.01
2.08
1.98
0.98
1.95
0.98
0.85
2.99
6.00
f1 (ppm)


197.31
146.26
138.79
135.19
134.87
129.74
128.61
127.95
119.82
111.41
77.32
77.00
76.68
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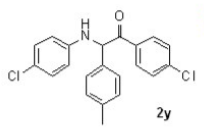
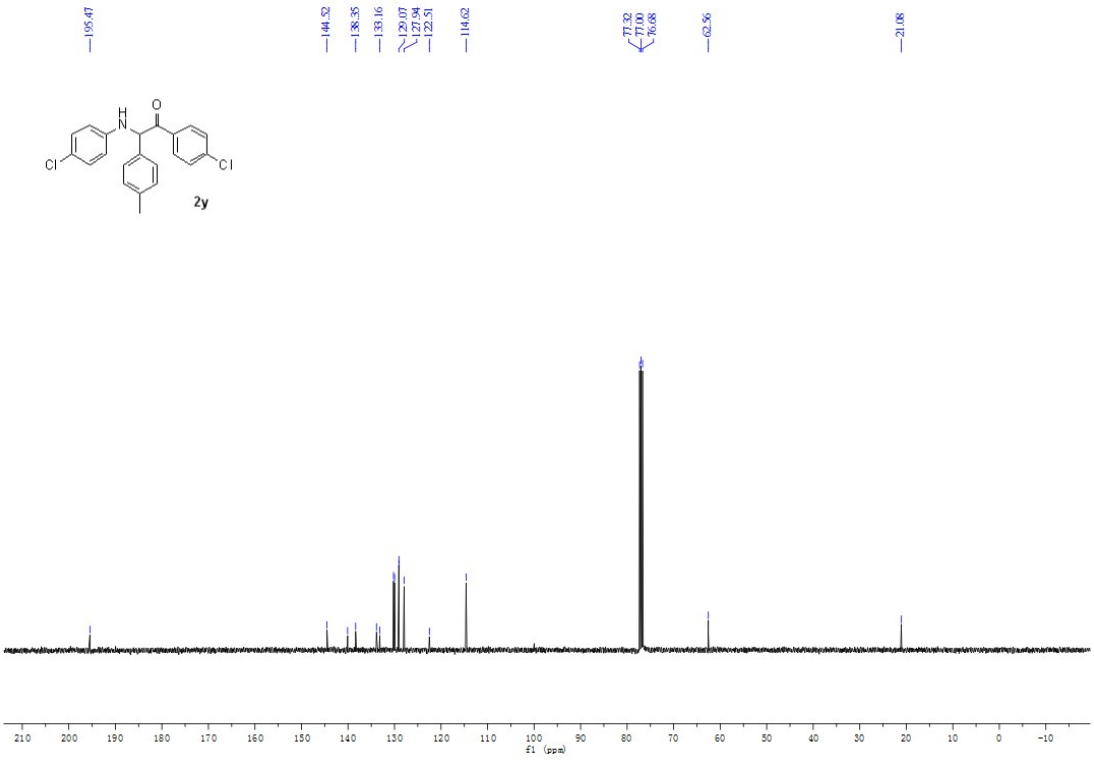
29.69
21.48
21.06
2x
f1 (ppm)

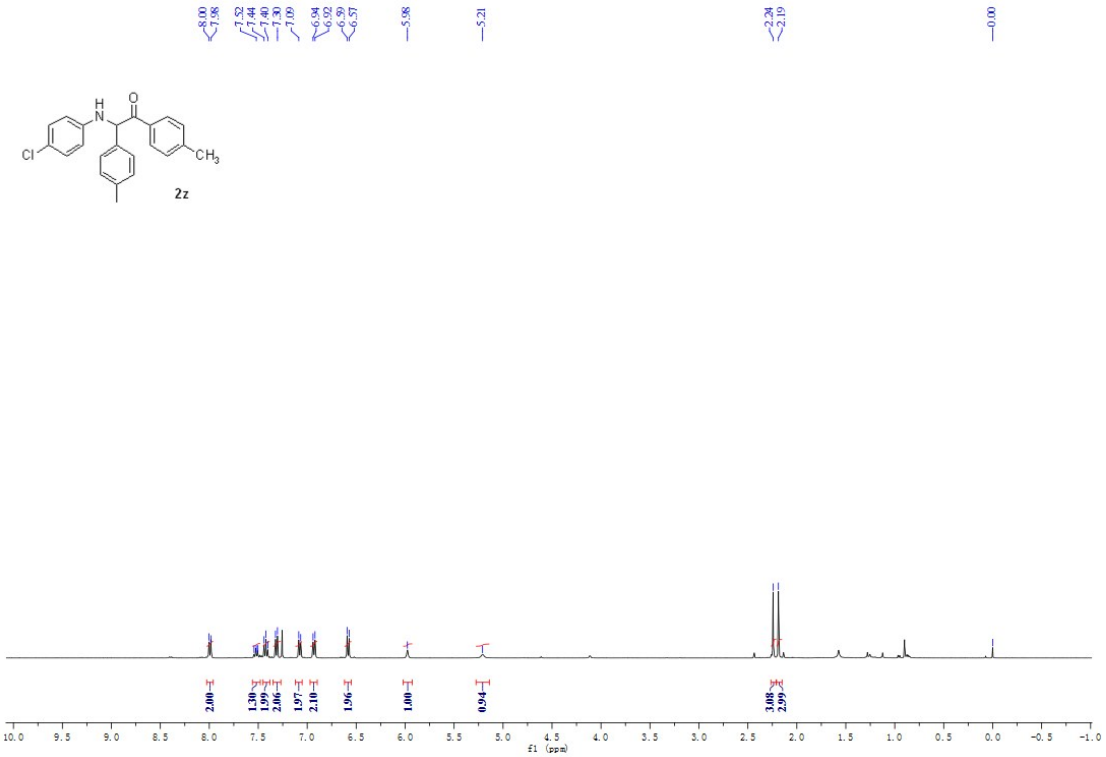

Cl
N
H
O
Cl

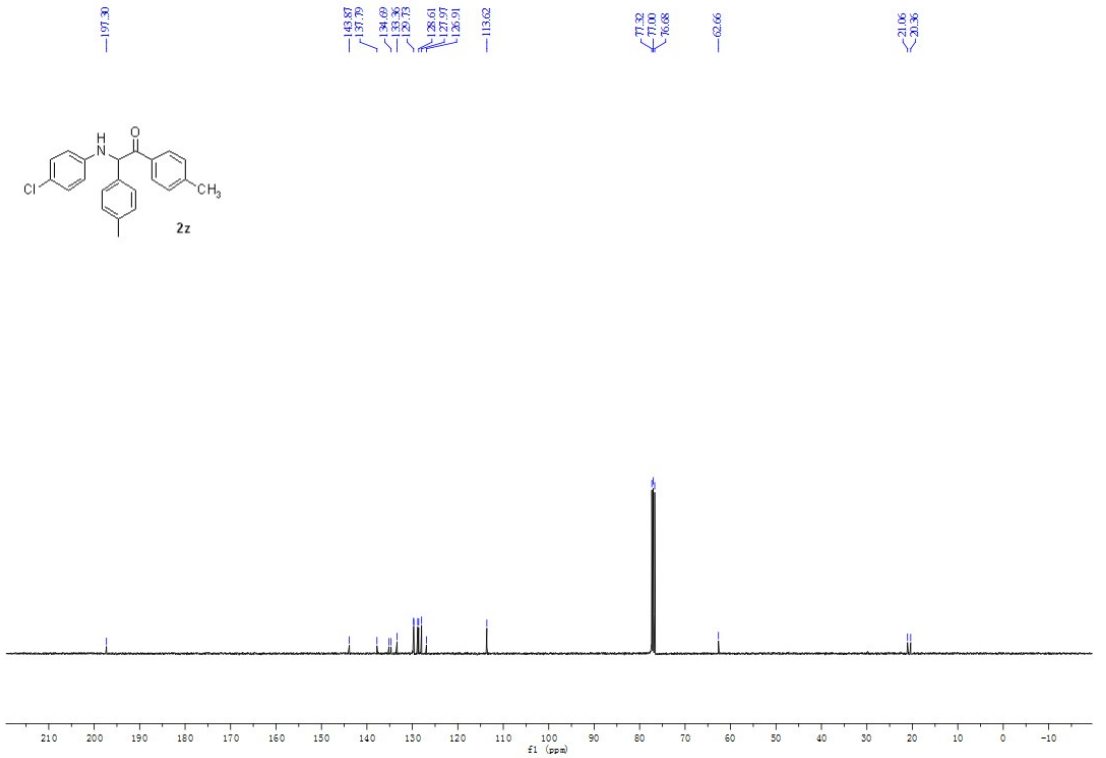
2y

7.93
7.91
7.41
7.39
7.28
7.26
7.07
7.05
6.57
6.55
5.88
5.87
5.38
2.26
0.00
2.01
2.02
2.56
3.89
2.00
1.04
0.98
3.00
f1 (ppm)


195.47
144.52
138.35
133.16
129.07
127.94
122.51
114.62
77.32
77.00
76.68
62.56
21.08
Cl
N
H
O
Cl
f1 (ppm)

2y


8.00
7.98
7.52
7.44
7.40
7.30
7.09
6.94
6.92
6.59
6.57
5.58
5.21
2.24
2.19
0.00
Cl
N
H
O
CH3
2z
2.00
1.30
1.99
2.06
1.97
2.10
1.96
1.00
0.94
3.08
2.99
f1 (ppm)


197.30
143.87
137.79
134.69
133.36
129.73
128.61
127.97
126.91
113.62
77.32
77.00
76.68
62.66
21.06
20.36
Cl
N
H
O
CH3
2z
f1 (ppm)