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Copper-Catalyzed Oxidative Cross-coupling of *α*-Aminocarbonyl Compounds with Aliphatic Primary Amines and Other Amines toward 2-Oxo-E acetamidines

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1. General Information.

Chemicals were either purchased or purified by standard techniques. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Column chromatography separations were performed on silica gel (200−300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-400 spectrometer (400MHz for ^{1}H, 100 MHz for ^{13}C). NMR chemical shifts were measured relative to the signals of residual $CHCl_3$ (δ_H 7.26 ppm and δ_C 77.16 ppm) or DMSO-d_6 (δ_H 2.50 ppm) and DMSO-d_6 (δ_C 39.520 ppm). LRMS was performed on a GC-MS instrument and HRMS was measured on an electrospray ionization (EI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

2. Preparation of *α*-Amino Carbonyl Compounds[1-2]

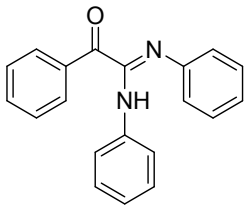
The synthesis of *α*-amino carbonyl compounds is carried out in two steps. The first step, synthesis of α-bromoacetophenone: to a solution of the acetophenone (15.0 mmol, 1 equiv) in 8 mL of acetonitrile were added NBS (2.72 g, 15.3 mmol, 1.02 equiv) and p-toluenesulfonic acid (2.85 g, 15.0 mmol, 1 equiv). The reaction mixture was stirred for 24 h at 50 °C. After that time, the solvent was evaporated under reduced pressure. A water solution of saturated $NaHCO_3$ (30 mL) was then added, and the solution was extracted with dichloromethane (3 × 30 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1, V/V) to afford the desired product in 82% yield as a white solid. After that, the next step is that a solution of *α*-bromoacetophenone (5 mmol) with aniline (5 mmol) and $NaHCO_3$ (5 mmol) in EtOH (20mL) was stirred at room temperature for 12 h and the crude products could be obtained as yellow precipitates, which was recrystallized by EtOH and the yellow solid **1a** was isolated in 81% yield.

3. General Procedure for the Synthesis of Product 3aa

To a flame-dried Round-bottomed flask with a magnetic stirring bar were charged 1a (63.3 mg, 0.3 mmol), aniline 2a (55.8 mg, 0.6 mmol), $Cu(OAc)_2 \cdot H_2O$ (6 mg, 0.03 mmol), TBHP (38.5 mg, 0.3 mmol) in DCE (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 60 °C until complete consumption of the starting material as detected by TLC or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8:1, V/V) to afford the desired product **3aa** in 91% yield (82 mg) as a yellow solid.

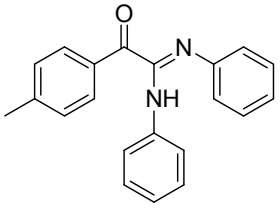
4. All Products

2-oxo-N,N',2-triphenylacetimidamide (3aa). Yellow solid, mp 111-112 °C. Yield 82 mg (91%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (s, 1H), 7.82 (dd, J = 14.8, 7.8 Hz, 4H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.04 (t, J = 7.2 Hz, 3H), 6.78 (t, J = 7.2 Hz, 1H), 6.70 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.1, 152.1, 148.4, 140.1, 134.7, 133.7, 129.3, 129.1, 128.7, 128.5, 122.7, 122.4, 121.8, 119.5. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{16}N_2O$ 300.1246; found 300.1257.



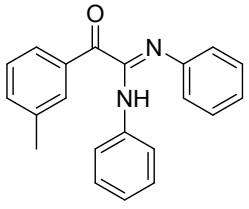
3aa

2-oxo-N,N'-diphenyl-2-(p-tolyl)acetimidamide (3ba). Yellow solid, mp 107-108 °C. Yield 88 mg (93%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.76 (s, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H), 7.31 (dd, J = 19.4, 7.6 Hz, 4H), 7.04 (s, 3H), 6.79 (t, J = 7.0 Hz, 1H), 6.71 (d, J = 7.2 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.5, 152.2, 148.5, 145.5, 140.2, 131.3, 129.7, 129.5, 128.7, 128.5, 122.7, 122.4, 121.8, 119.5, 21.4. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{18}N_2O$ 314.1411; found 314.1422.



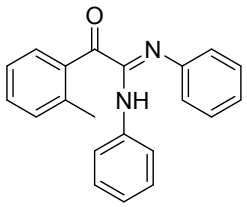
3ba

2-oxo-N,N'-diphenyl-2-(m-tolyl)acetimidamide (3ca). Yellow oil. Yield 69 mg (73%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 (s, 1H), 7.84 (d, J = 7.0 Hz, 2H), 7.61 (d, J = 10.4 Hz, 2H), 7.44 (d, J = 7.2 Hz, 1H), 7.36 (dd, J = 15.0, 7.3 Hz, 3H), 7.05 (s, 3H), 6.79 (s, 1H), 6.71 (d, J = 6.8 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.1, 152.1, 148.5, 140.2, 138.6, 135.4, 133.7, 129.4, 129.1, 128.8, 128.6, 126.9, 122.6 (d, J = 25.5 Hz), 122.5 – 122.1 (m), 121.9, 119.5, 20.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{18}N_2O$ 314.1411; found 314.1421.



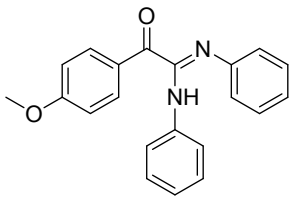
3ca

2-oxo-N,N'-diphenyl-2-(o-tolyl)acetimidamide (3da). Yellow oil. Yield 58 mg (62%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.80 (s, 1H), 7.85 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.37 – 7.26 (m, 3H), 7.16 (d, J = 7.4 Hz, 1H), 7.03 (dd, J = 16.8, 7.8 Hz, 3H), 6.77 (t, J = 7.0 Hz, 1H), 6.62 (d, J = 7.4 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.3, 153.1, 148.4, 140.3, 139.5, 133.3 (d, J = 8.8 Hz), 131.9, 128.8, 128.4, 126.2, 122.7, 122.4, 121.7, 119.5, 20.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{18}N_2O$ 314.1411; found 314.1421.



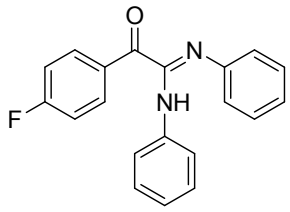
3da

2-(4-methoxyphenyl)-2-oxo-N,N'-diphenylacetimidamide (3ea). Yellow oil. Yield 84 mg (85%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 (s, 1H), 7.84 (d, J = 7.4 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.0 Hz, 2H), 7.03 (dd, J = 15.6, 8.0 Hz, 5H), 6.80 (t, J = 6.8 Hz, 1H), 6.72 (d, J = 7.2 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.2, 164.2, 152.4, 148.6, 140.3, 131.9, 128.7, 128.5, 126.7, 122.6, 122.4, 121.8, 119.5, 114.5, 55.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{18}N_2O_2$ 330.1356; found 330.1364.



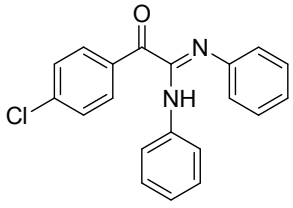
3ea

2-(4-fluorophenyl)-2-oxo-N,N'-diphenylacetimidamide (3fa). Yellow solid, mp 145-146 °C. Yield 72 mg (75%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.86 (dd, J = 17.6, 7.2 Hz, 4H), 7.32 (dd, J = 19.8, 8.4 Hz, 4H), 7.05 (t, J = 7.0 Hz, 3H), 6.80 (t, J = 7.0 Hz, 1H), 6.70 (d, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.6, 151.9, 148.4, 140.1, 132.5 (d, J = 9.7 Hz), 130.7, 128.8, 128.6, 122.9, 122.6, 121.9, 119.6, 116.6, 116.4. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{15}FN_2O$ 318.1176; found 318.1163.



3fa

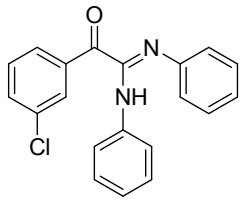
2-(4-chlorophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ga).



3ga

Yellow solid, 139-140 °C. Yield 79 mg (79%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.86 (dd, J = 18.2, 7.2 Hz, 4H), 7.32 (dd, J = 19.6, 8.4 Hz, 4H), 7.05 (t, J = 7.2 Hz, 3H), 6.80 (t, J = 7.2 Hz, 1H), 6.70 (d, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.3, 148.8, 140.5, 132.9 (d, J = 10.2 Hz), 131.0, 129.2, 128.9, 123.2, 122.9, 122.2, 119.9, 116.9, 116.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{15}ClN_2O$ 334.0864; found 334.0875.

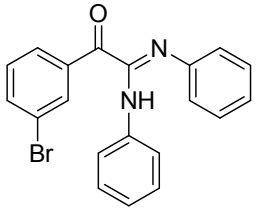
2-(3-chlorophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ha). Yellow solid, mp 101-102 °C.



3ha

Yield 84 mg (84%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.06 (t, J = 6.8 Hz, 3H), 6.81 (t, J = 6.8 Hz, 1H), 6.69 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.1, 151.4, 148.2, 134.0, 135.5, 134.4, 133.9, 131.4, 128.9, 128.7, 128.3, 128.1, 123.0, 122.7, 121.9, 119.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{15}ClN_2O$ 334.0864; found 334.0876.

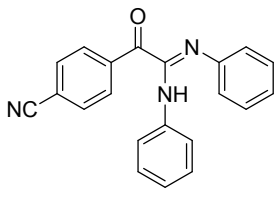
2-(3-bromophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ia). Yellow solid, mp 118-119 °C.



3ia

Yield 87 mg (77%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.80 (d, J = 9.0 Hz, 5H), 7.46 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.06 (s, 3H), 6.81 (t, J = 7.0 Hz, 1H), 6.70 (d, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.0, 151.4, 148.2, 134.0, 137.3, 135.6, 131.6, 131.1, 128.8, 128.7, 122.9, 122.7, 122.3, 121.8, 119.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{15}BrN_2O$ 378.0359; found 378.0366.

2-(4-cyanophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ja).

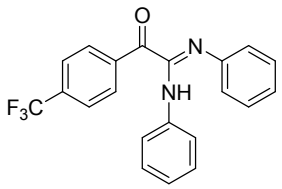


3ja

Yellow oil. Yield 61 mg (63%) at 0.3 mmol scale. ^{1}H NMR (400 MHz,

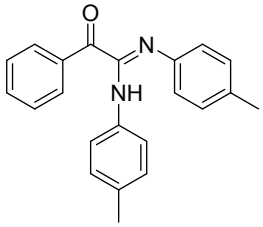
DMSO-d_6) δ 9.89 (s, 1H), 7.93 (q, J = 7.8 Hz, 4H), 7.82 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 6.8 Hz, 2H), 7.12 – 6.99 (m, 3H), 6.81 (d, J = 7.0 Hz, 1H), 6.68 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.6, 151.3, 148.0, 139.9, 136.8, 133.2, 129.7, 128.8, 128.7, 123.0, 122.8, 121.9, 119.6, 117.9, 116.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{15}N_3O$ 325.1221; found 325.1212.

2-oxo-N,N'-diphenyl-2-(4-(trifluoromethyl)phenyl)acetimidamide (3ka). Yellow oil. Yield 79 mg (72%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (s, 1H), 7.98 (d, J = 7.8 Hz, 2H), 7.91 – 7.77 (m, 4H), 7.35 (t, J = 7.2 Hz, 2H), 7.12 – 6.99 (m, 3H), 6.79 (t, J = 6.8 Hz, 1H), 6.70 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.6, 151.5, 148.1, 134.0, 136.8, 133.4, 130.1, 128.75 (d, J = 19.2 Hz), 126.2, 122.88 (d, J = 25.5 Hz), 122.2, 121.9, 119.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{15}F_3N_2O$ 368.1129; found 368.1141.



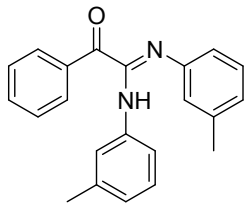
3ka

2-oxo-2-phenyl-N,N'-di-p-tolylacetimidamide (3ab).Yellow solid, mp 140-141 °C. Yield 81 mg (82%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.62 (s, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 6.84 (d, J = 7.4 Hz, 2H), 6.59 (d, J = 7.4 Hz, 2H), 2.27 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.4, 152.0, 145.9, 137.7, 134.7, 133.7, 131.5, 131.0, 129.3, 129.21 – 128.91 (m), 121.7, 119.5, 20.5, 20.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{20}N_2O$ 328.1563; found 328.1579.



3ab

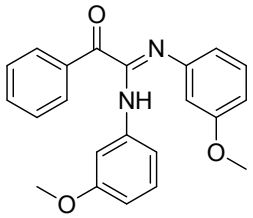
2-oxo-2-phenyl-N,N'-di-m-tolylacetimidamide (3ac). Yellow oil. Yield 79 mg (80%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.67 (s, 1H), 7.61 (d, J = 7.0 Hz, 2H), 7.49 (t, J = 7.0 Hz, 2H), 7.21 (s, 1H), 6.97 – 6.79 (m, 2H), 6.66 – 6.41 (m, 3H), 2.29 (s, 3H),



3ac

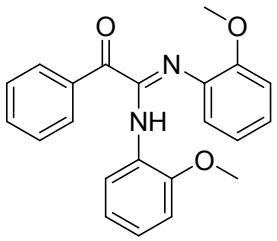
2.09 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.1, 151.9, 148.4, 140.1, 137.9, 137.6, 128.6, 128.3, 123.4, 123.2, 122.7, 119.9, 118.9, 116.8, 21.4, 20.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{20}N_2O$ 328.1563; found 328.1577.

N,N'-bis(3-methoxyphenyl)-2-oxo-2-phenylacetimidamide (3ad). Yellow oil. Yield 81 mg (75%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (s, 1H), 7.81 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.58 (s, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 6.36 (d, J = 7.8 Hz, 1H), 6.29 (d, J = 6.8 Hz, 2H), 3.73 (s, 3H), 3.55 (s, 3H).^{13}C NMR (100 MHz, DMSO-d_6) δ 192.0, 159.6, 159.4, 152.1, 149.7, 141.2, 134.7, 133.8, 129.6, 129.4, 129.3, 129.2, 114.4, 112.0, 108.5, 107.9, 107.5, 105.7, 55.1, 54.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{20}N_2O_3$ 360.1466; found 360.1479.

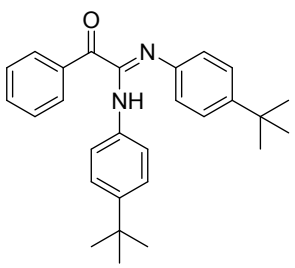


3ad

N,N'-bis(2-methoxyphenyl)-2-oxo-2-phenylacetimidamide (3ae). Yellow oil. Yield 72 mg (67%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (s, 1H), 7.78 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 6.4 Hz, 1H), 7.43 (t, J = 6.8 Hz, 2H), 7.11 – 6.85 (m, 4H), 6.79 – 6.49 (m, 4H), 3.81 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.4, 152.6, 134.4 (d, J = 8.0 Hz), 129.5, 128.9, 124.3 – 123.7 (m), 122.7 (d, J = 14.7 Hz), 122.4 (d, J = 5.8 Hz), 120.6, 111.5, 55.4. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{20}N_2O_3$ 360.1467; found 360.1478.



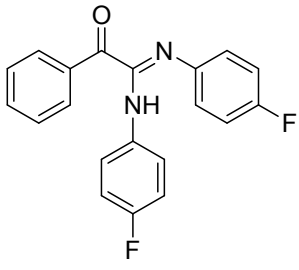
N,N'-bis(4-(tert-butyl)phenyl)-2-oxo-2-phenylacetimidamide (3af). Yellow solid, mp 118-119 °C. Yield 105 mg (85%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.80 (d, J = 7.4 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.34 (d, J =



3ae

7.8 Hz, 2H), 7.05 (d, J = 7.6 Hz, 2H), 6.63 (d, J = 7.6 Hz, 2H), 1.27 (s, 9H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.4, 151.8, 145.8, 144.9, 144.4, 137.6, 134.5, 134.0, 129.3, 129.1, 125.3, 125.1, 34.0, 33.8, 31.3, 31.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{28}H_{32}N_2O$ 412.2502; found 412.2519.

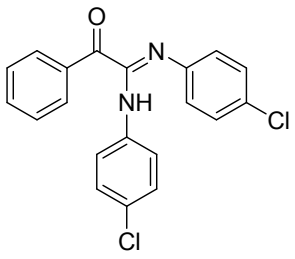
N,N'-bis(4-fluorophenyl)-2-oxo-2-phenylacetimidamide (3ag). Yellow solid, mp 115-116 °C.



3af

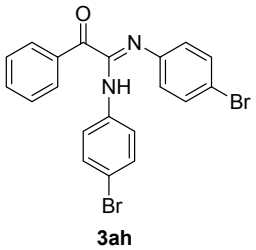
Yield 71 mg (70%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 1H), 7.86 (s, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.19 (t, J = 8.2 Hz, 2H), 6.87 (t, J = 8.2 Hz, 2H), 6.71 (d, J = 4.8 Hz, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 192.1, 159.2, 152.5, 144.8, 136.4, 134.9, 133.6, 129.3, 129.2, 123.24 (d, J = 7.7 Hz), 121.24 (d, J = 7.5 Hz), 115.4, 115.2, 115.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{14}F_2N_2O$ 336.1082; found 336.1069.

N,N'-bis(4-chlorophenyl)-2-oxo-2-phenylacetimidamide (3ah). Yellow solid, mp 129-130 °C.Yield 102 mg(92%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 7.86 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.5, 152.4, 147.2, 138.8, 135.0, 133.4, 129.4, 129.3, 128.7, 128.5, 126.7, 126.5, 123.5, 121.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{14}Cl_2N_2O$ 368.0495; found 368.0486.



3ag

N,N'-bis(4-bromophenyl)-2-oxo-2-phenylacetimidamide (3ai). Yellow solid, mp 126-127 °C.

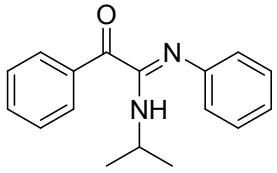


3ah

Yield 100 mg (73%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 7.80 (d, J = 6.8 Hz, 4H), 7.66 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 8.4 Hz, 4H), 7.22 (d, J = 7.8 Hz, 2H), 6.66 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.5, 152.3, 147.6, 139.2, 135.1, 133.4,

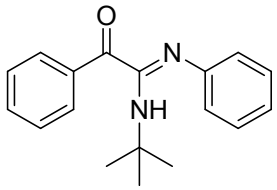
131.6, 131.4, 129.4, 129.3, 124.0, 121.6, 114.8, 114.5. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{14}Br_2N_2O$ 455.9462; found 455.9475.

N-isopropyl-2-oxo-N',2-diphenylacetimidamide (3ak). Yellow solid, mp 144-145 °C. Yield 49 mg (62%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 – 7.36 (m, 3H), 6.97 (t, J = 7.2 Hz, 2H), 6.70 (t, J = 7.0 Hz, 1H), 6.60 (d, J = 7.4 Hz, 2H), 4.16 (s, 1H), 1.22 (d, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.6, 154.2, 149.6, 134.4, 134.0, 129.2, 129.0, 128.4, 122.3, 121.7, 42.0, 22.1. HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{18}N_2O$ 266.1407; found 266.1416.



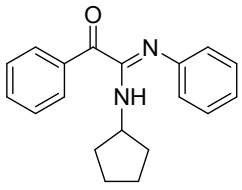
3aj

N-(tert-butyl)-2-oxo-N',2-diphenylacetimidamide (3al). Yellow solid, mp 131-132 °C. Yield 47 mg (56%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.10 (s, 1H), 6.96 (t, J = 7.6 Hz, 2H), 6.68 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 7.8 Hz, 2H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.6, 153.7, 149.6, 134.2, 134.1, 129.1, 128.8, 128.2, 122.1, 121.4, 51.8, 28.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{20}N_2O$ 280.1563; found 280.1581.



3ak

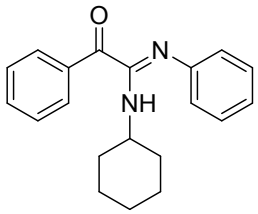
N-cyclopentyl-2-oxo-N',2-diphenylacetimidamide (3am). Yellow solid, mp 115-116 °C. Yield 42 mg (48%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 6.97 (t, J = 7.4 Hz, 2H), 6.69 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 7.6 Hz, 2H), 4.29 (s, 1H), 1.97 (s, 2H), 1.62 (d, J = 44.2 Hz, 7H).^{13}C NMR (100 MHz, DMSO-



3al

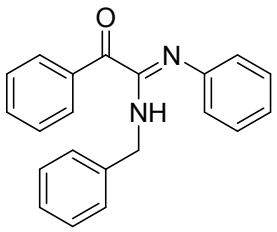
d_6) δ 193.6, 154.5, 149.6, 134.3, 134.0, 129.1, 129.0, 128.3, 122.2, 121.6, 51.9, 32.1, 23.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{20}N_2O$ 292.1589; found 292.1573.

N-cyclohexyl-2-oxo-N',2-diphenylacetimidamide (3an). Yellow solid, mp 104-105 °C. Yield 36 mg (39%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 6.96 (t, J = 7.2 Hz, 2H), 6.69 (t, J = 7.0 Hz, 1H), 6.58 (d, J = 7.6 Hz, 2H), 3.87 (s, 1H), 2.04 (d, J = 9.8 Hz, 2H), 1.73 (d, J = 10.8 Hz, 2H), 1.59 (d, J = 11.8 Hz, 1H), 1.24 (tt, J = 23.2, 12.2 Hz, 6H).^{13}C NMR (100 MHz, DMSO-d_6) δ 193.5, 154.0, 149.5, 134.3, 134.0, 129.2, 129.0, 128.3, 122.2, 121.5, 49.0, 32.0, 25.5, 24.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{22}N_2O$ 306.1719; found 306.1728.



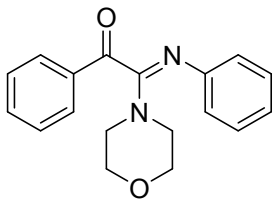
3am

N-benzyl-2-oxo-N',2-diphenylacetimidamide (3ao). Yellow solid, mp 111-112 °C. Yield 34 mg (36%) at 0.3 mmol scale. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (s, 1H), 7.73 (d, J = 7.3 Hz, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.52 – 7.41 (m, 3H), 7.38 (t, J = 7.2 Hz, 2H), 7.33 – 7.22 (m, 1H), 6.98 (t, J = 7.2 Hz, 2H), 6.71 (t, J = 7.0 Hz, 1H), 6.61 (d, J = 7.4 Hz, 2H), 4.59 (d, J = 4.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.0, 155.3, 149.6, 139.7, 134.9, 134.2, 129.6, 129.4, 128.8 (d, J = 4.5 Hz), 128.1 (s), 127.3, 122.6, 122.4 (d, J = 29.4 Hz), 44.1. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{18}N_2O$ 314.1415; found 314.1421.



3ao

2-morpholino-1-phenyl-2-(phenylimino)ethanone (3aq). Yellow oil. Yield 52 mg (57%) at 0.3 mmol scale.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.00 (t, J = 7.6 Hz, 2H), 6.77 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.8 Hz, 2H), 3.75 (s, 4H), 3.52 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 156.1, 148.1, 134.6,



3ao

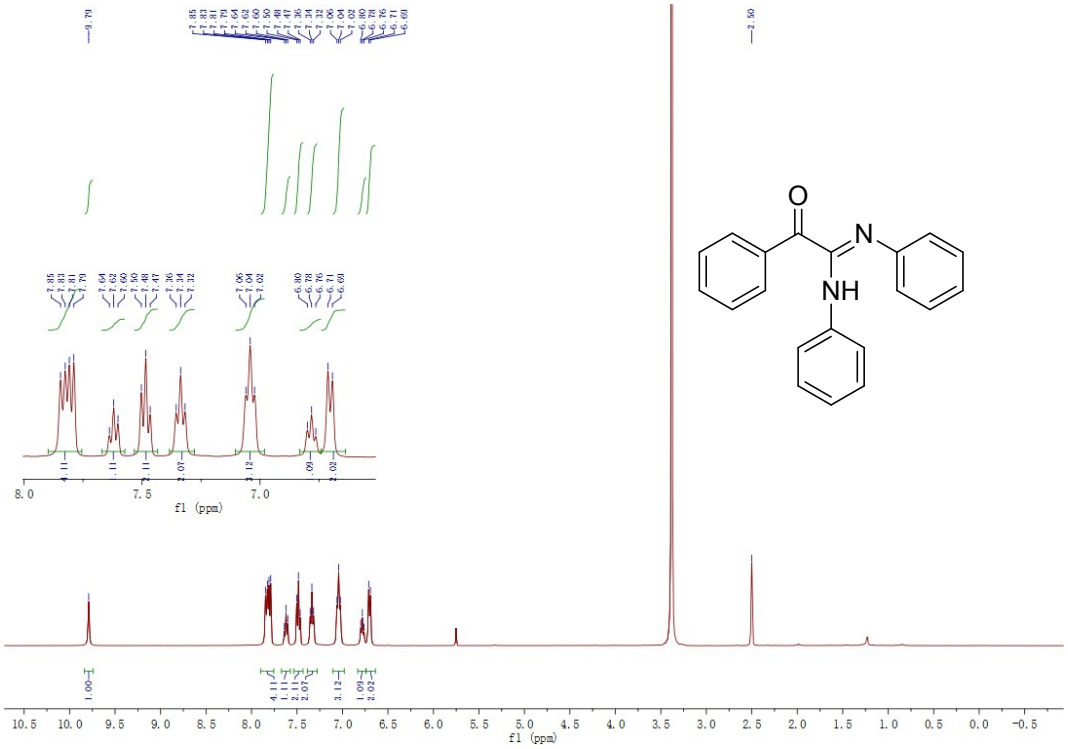
134.5, 129.2, 128.9, 128.4, 122.6, 122.2, 66.6, 45.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{18}N_2O_2$ 294.1381; found 294.1364.

5. Reference

[1] Borzecka, W.; Lavandera, I.; Gotor, V. *J. Org. Chem.* **2013**, *78*, 7312.

[2] Pal, M.; Swamy, N. K.; Hameed, P. S.; Padakanti, S.; Yeleswarapu, K. R. *Tetrahedron* **2004**, *60*, 3987.

6. ^{1}H and ^{13}C NMR Spectra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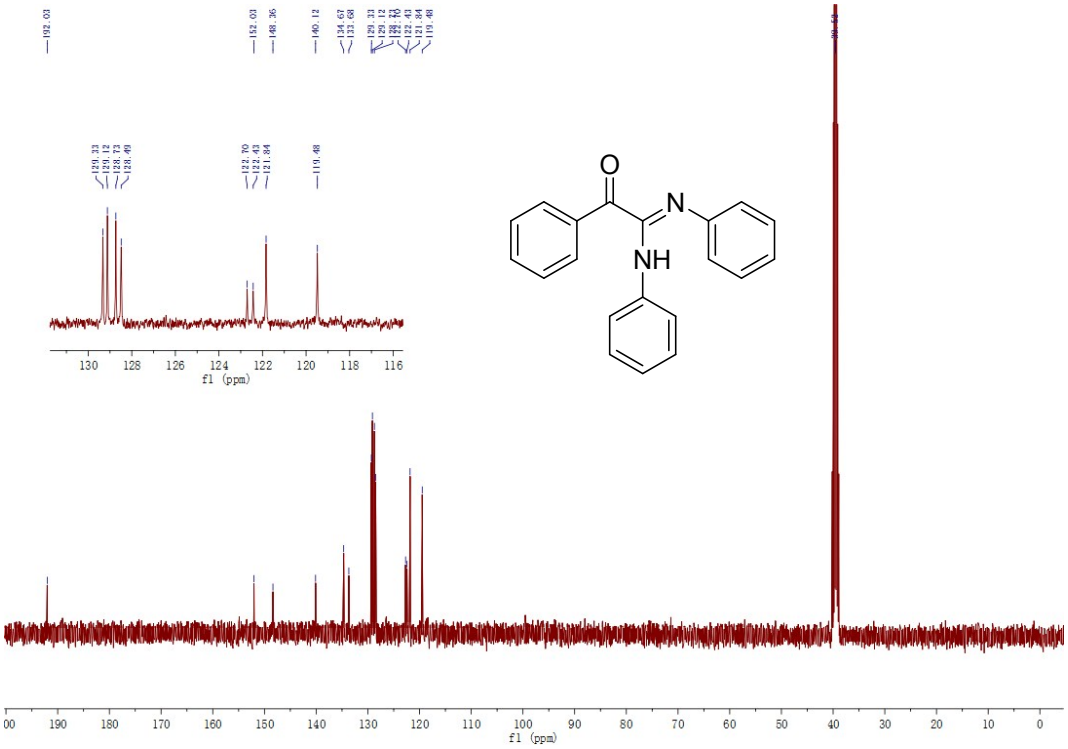
N
NH
fl (ppm)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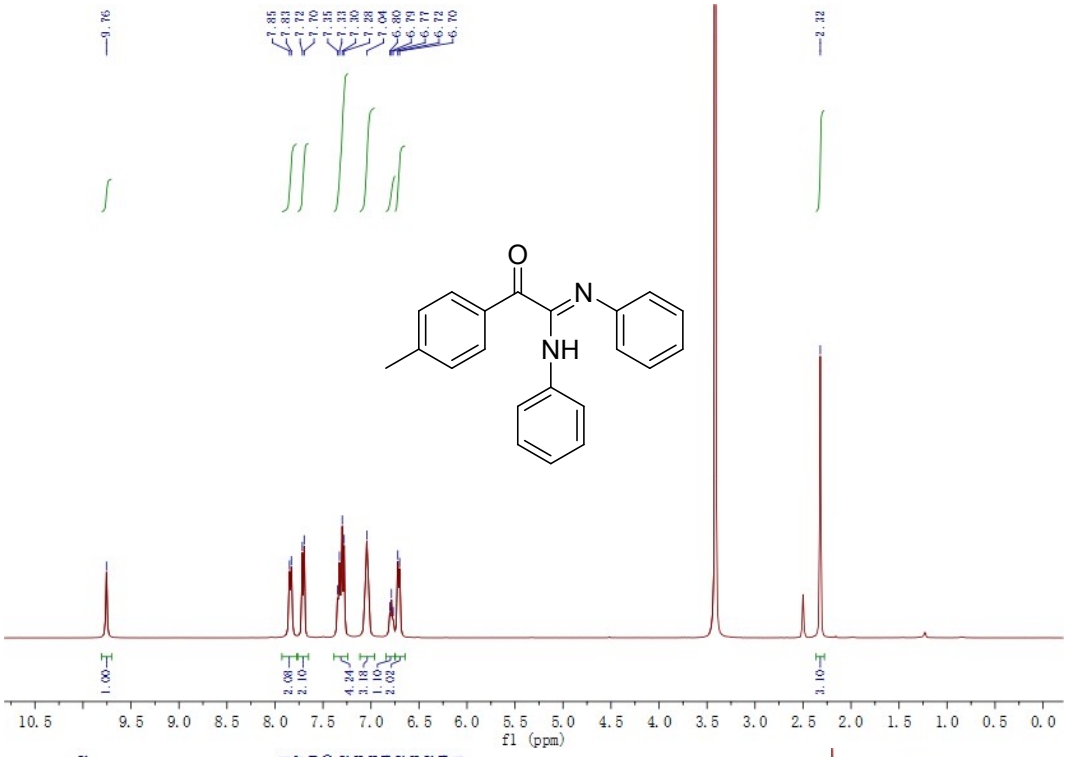
NH
fl (ppm)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6.72
6.70
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O
N
NH
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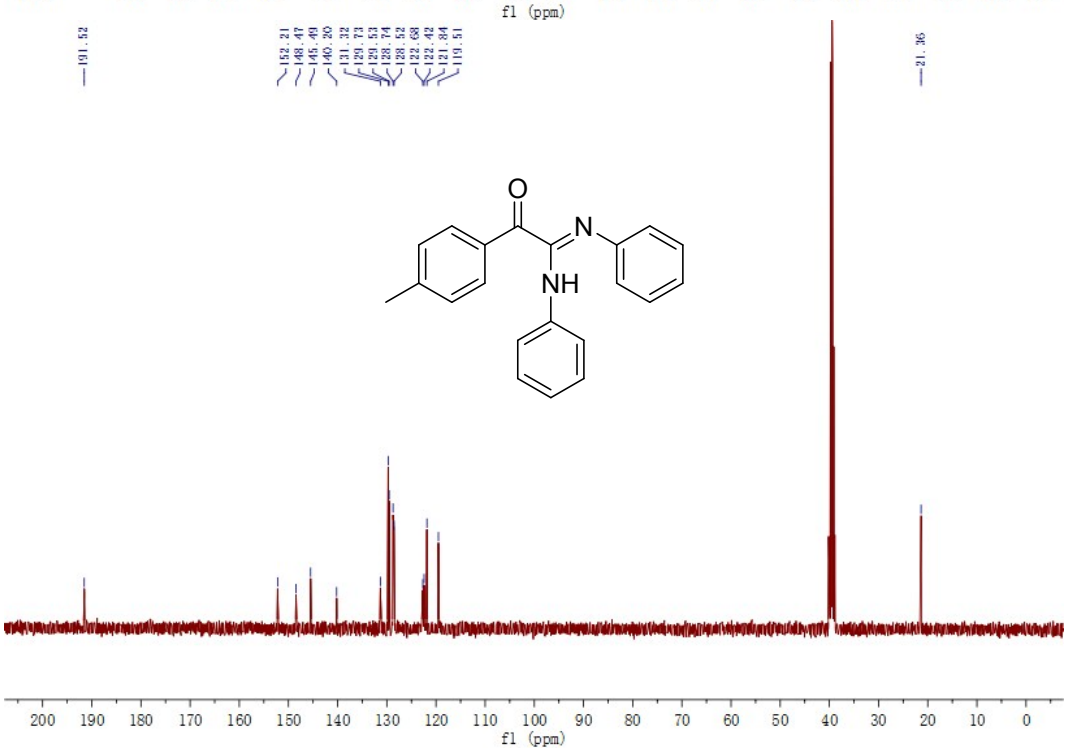
2.08
2.10
4.24
3.18
1.10
2.02
3.10
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.53
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128.52
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119.51
21.36
O
N
NH
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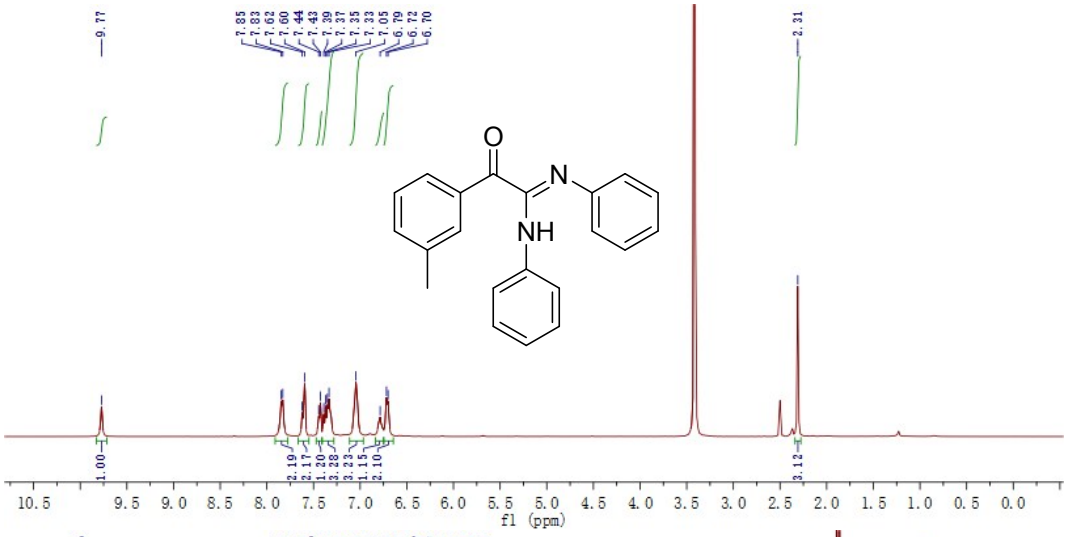
f1 (ppm)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7.05
6.79
6.72
6.70
2.31
O
N
NH
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2.19
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1.20
3.28
3.23
1.15
2.10
3.12
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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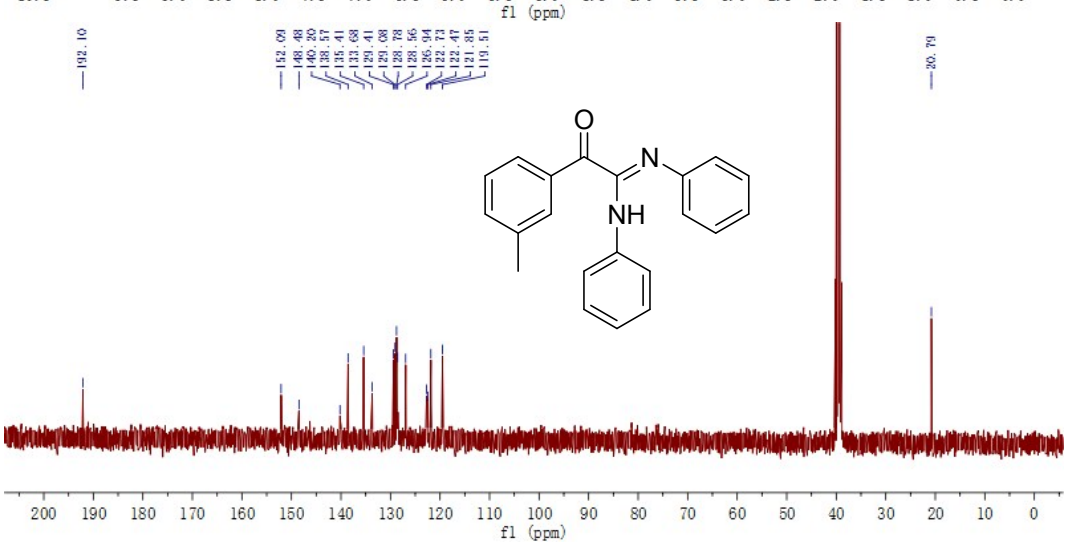
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NH
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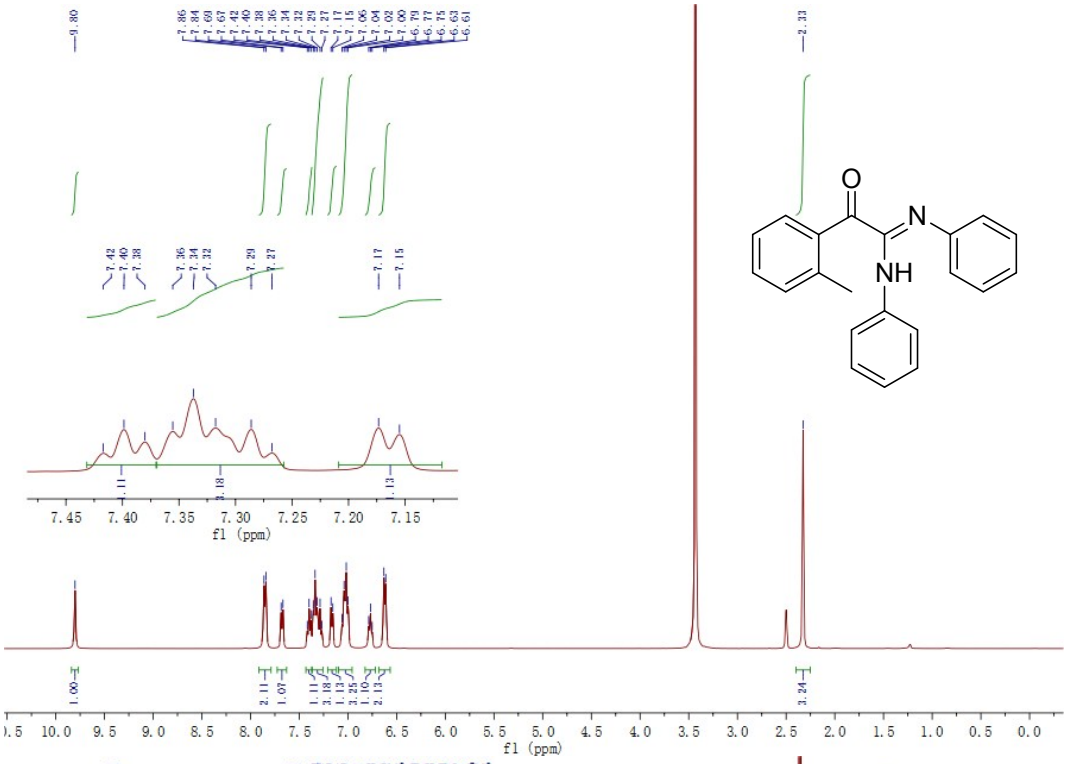
f1 (ppm)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7.17
7.15
7.06
7.04
7.02
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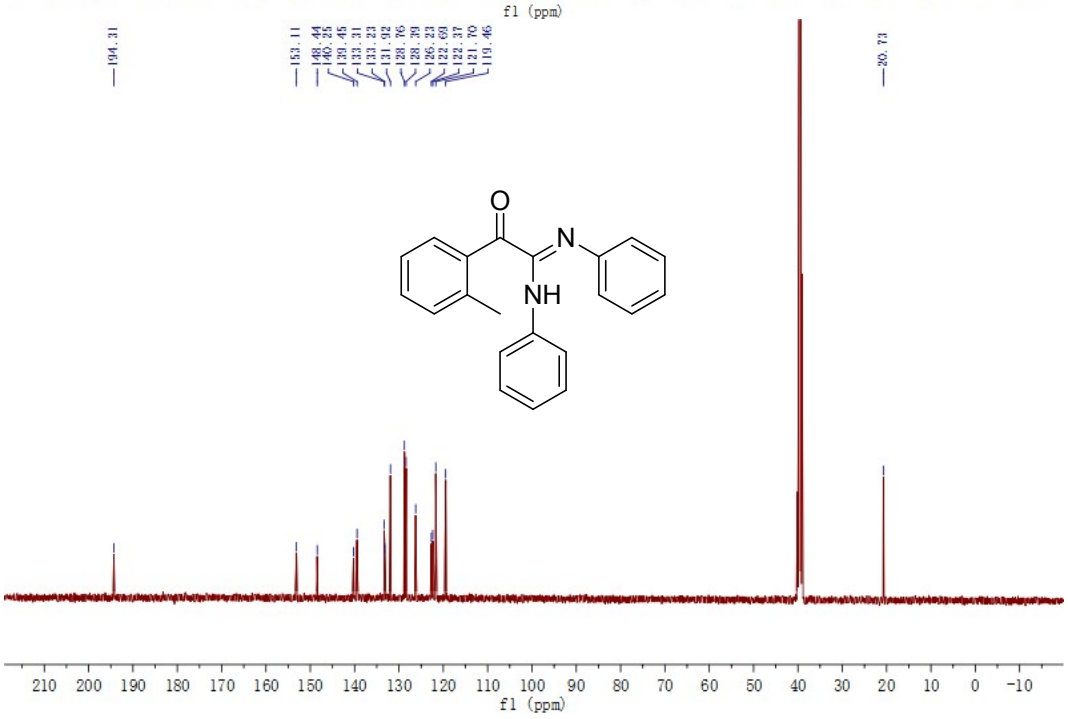
f1 (ppm)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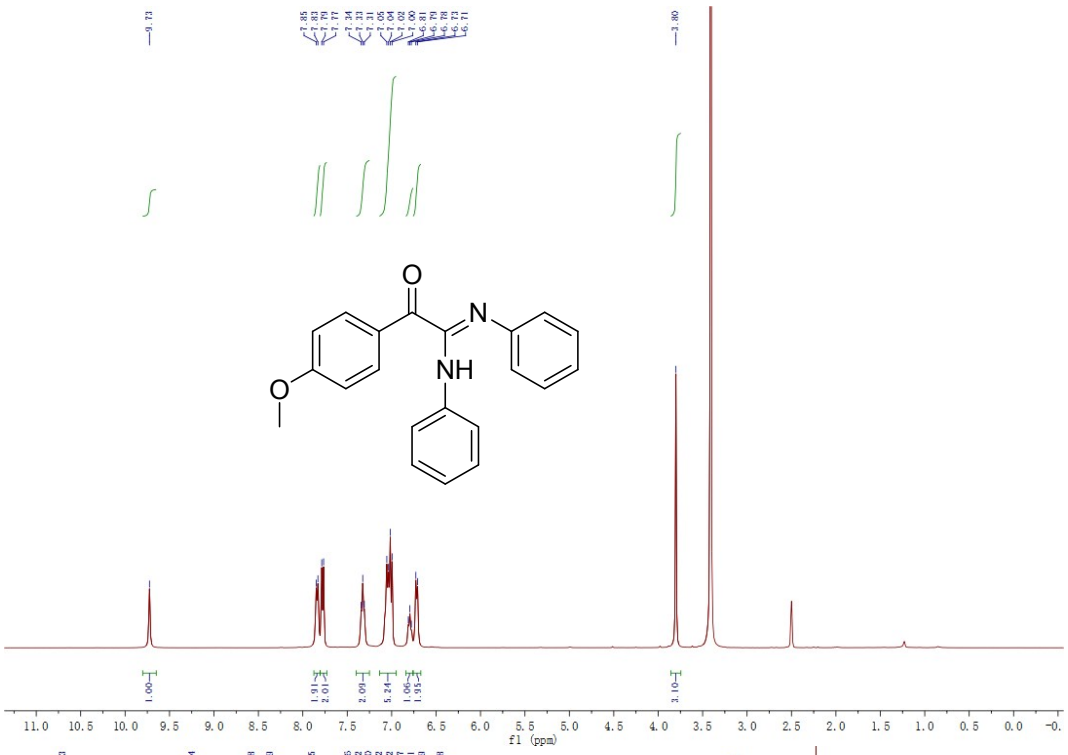
f1 (ppm)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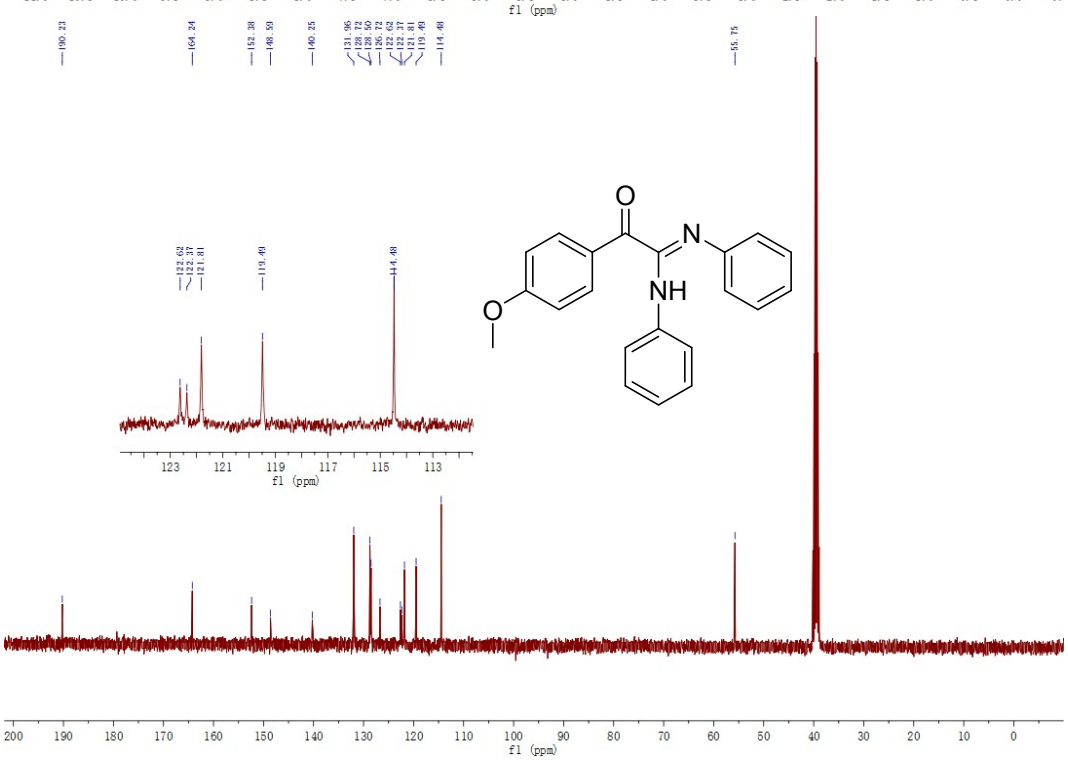
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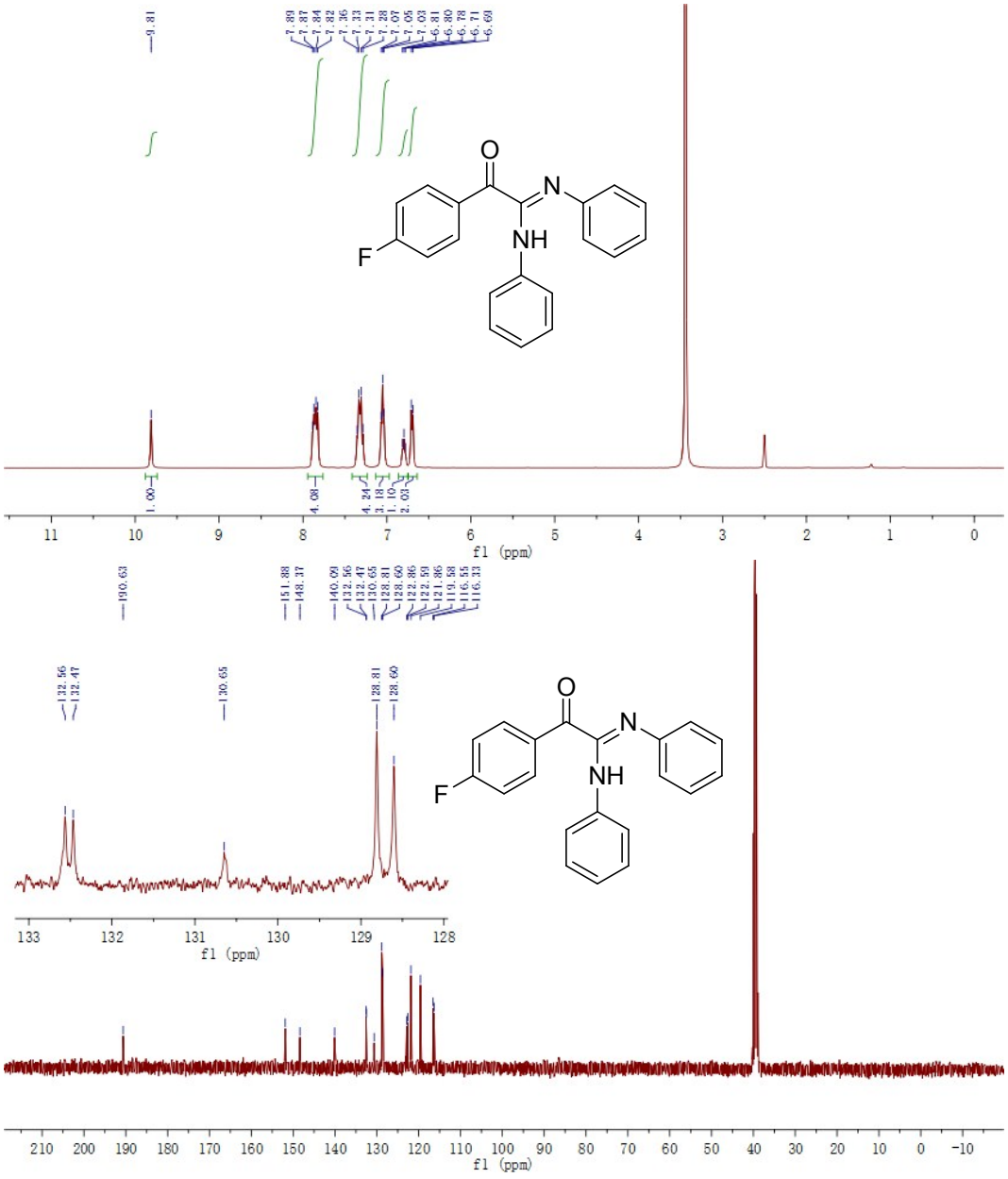
NH
O
f1 (ppm)
f1 (ppm)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N
NH
F
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2.03
f1 (ppm)
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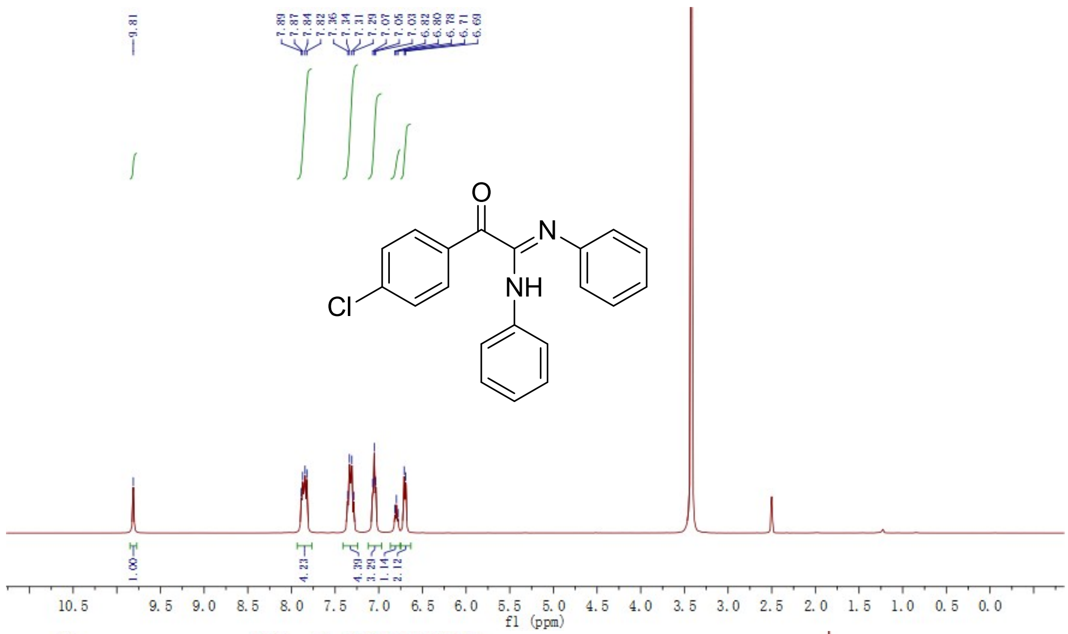
f1 (ppm)
f1 (ppm)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10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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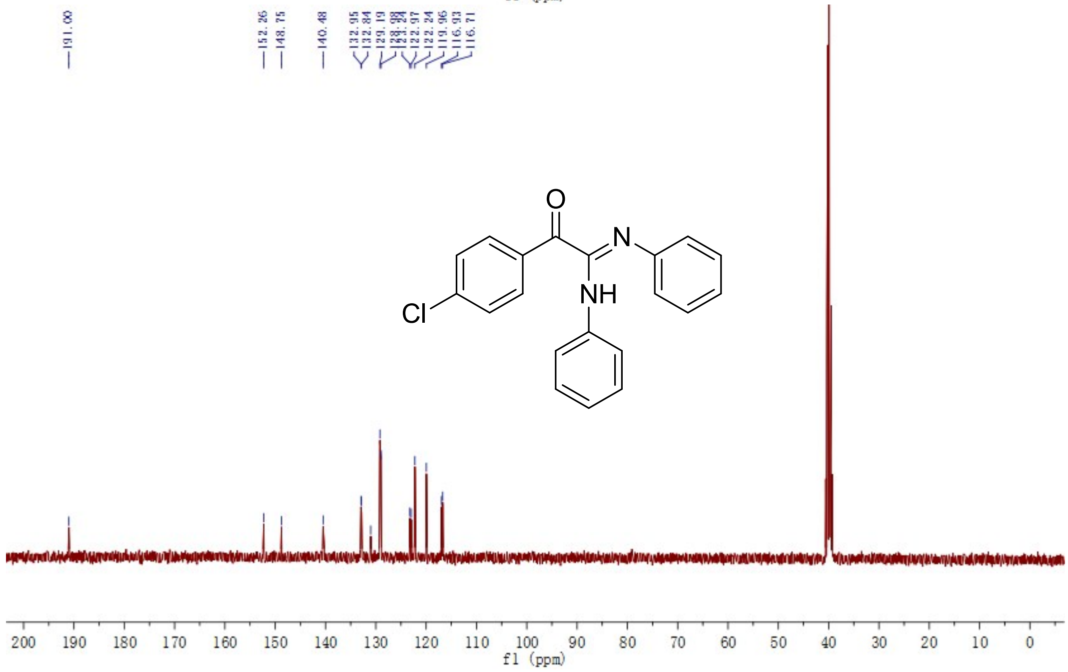
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NH
Cl
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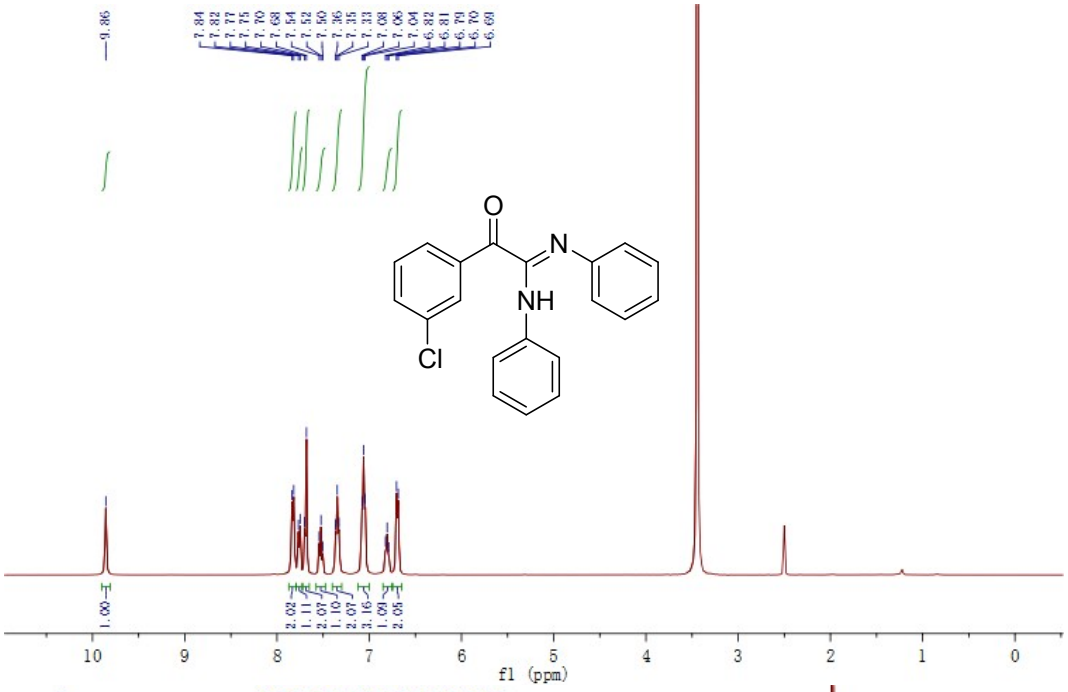
f1 (ppm)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7.33
7.08
7.06
7.04
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6.81
6.79
6.70
6.69
O
N
NH
Cl
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2.07
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2.05
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5
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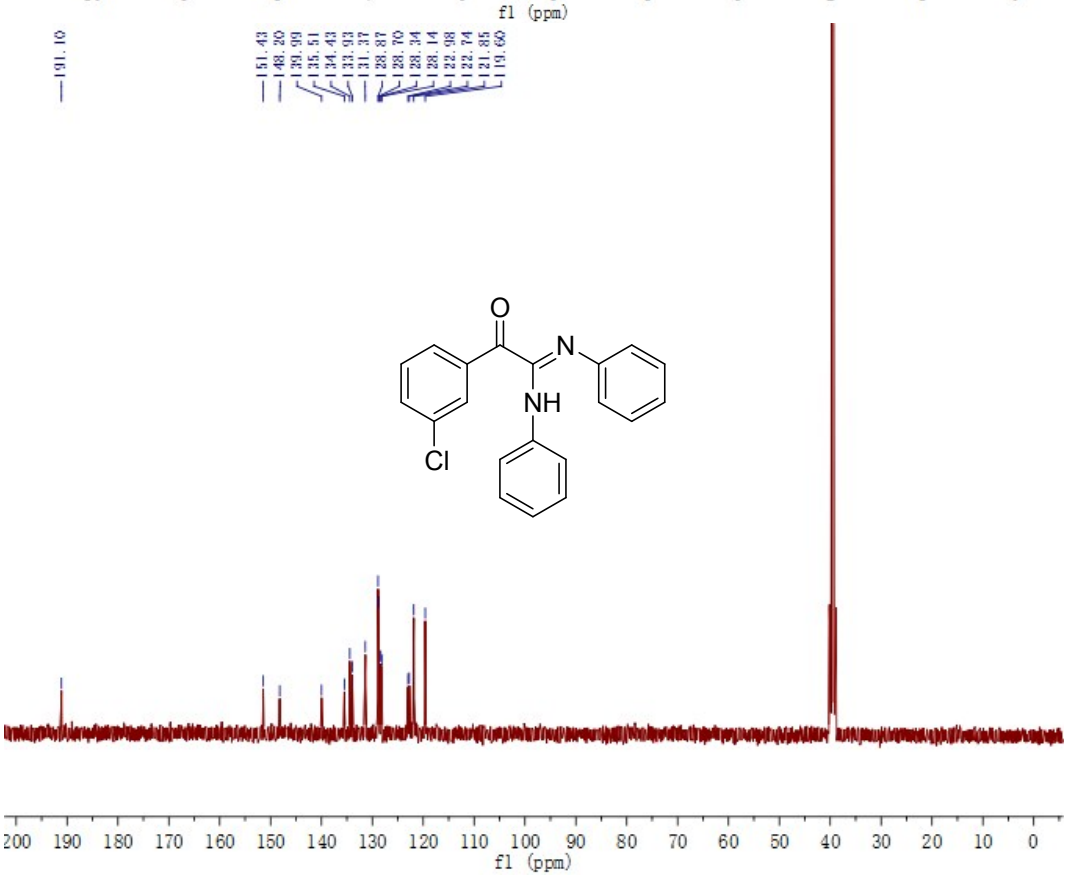
f1 (ppm)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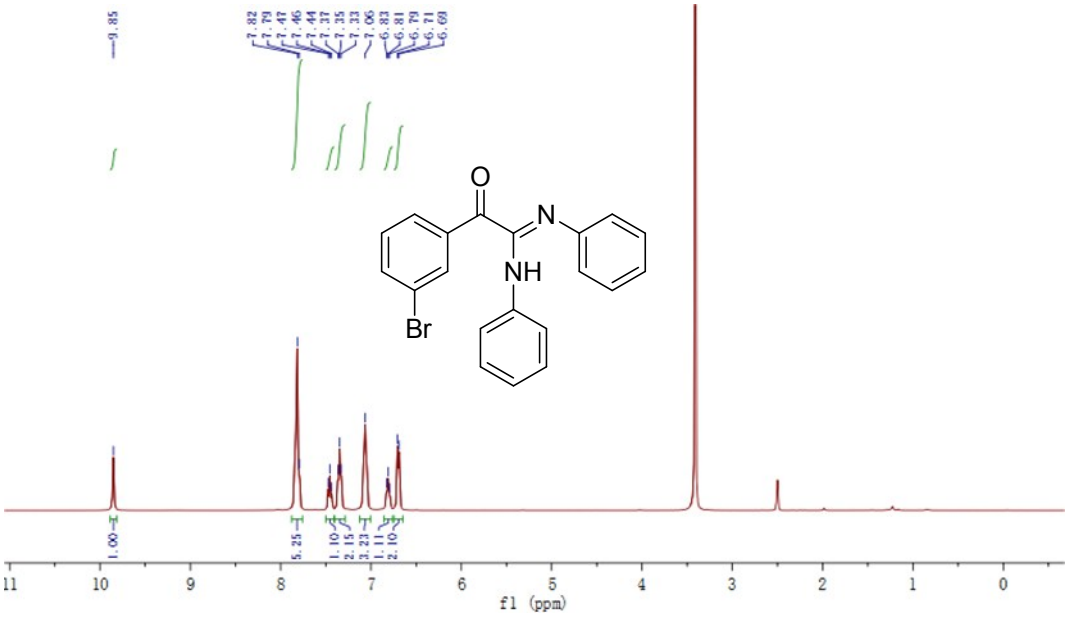
f1 (ppm)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7.79
7.47
7.46
7.44
7.37
7.35
7.33
7.06
6.83
6.81
6.79
6.71
6.69
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5.25
1.10
2.15
3.23
1.11
2.10
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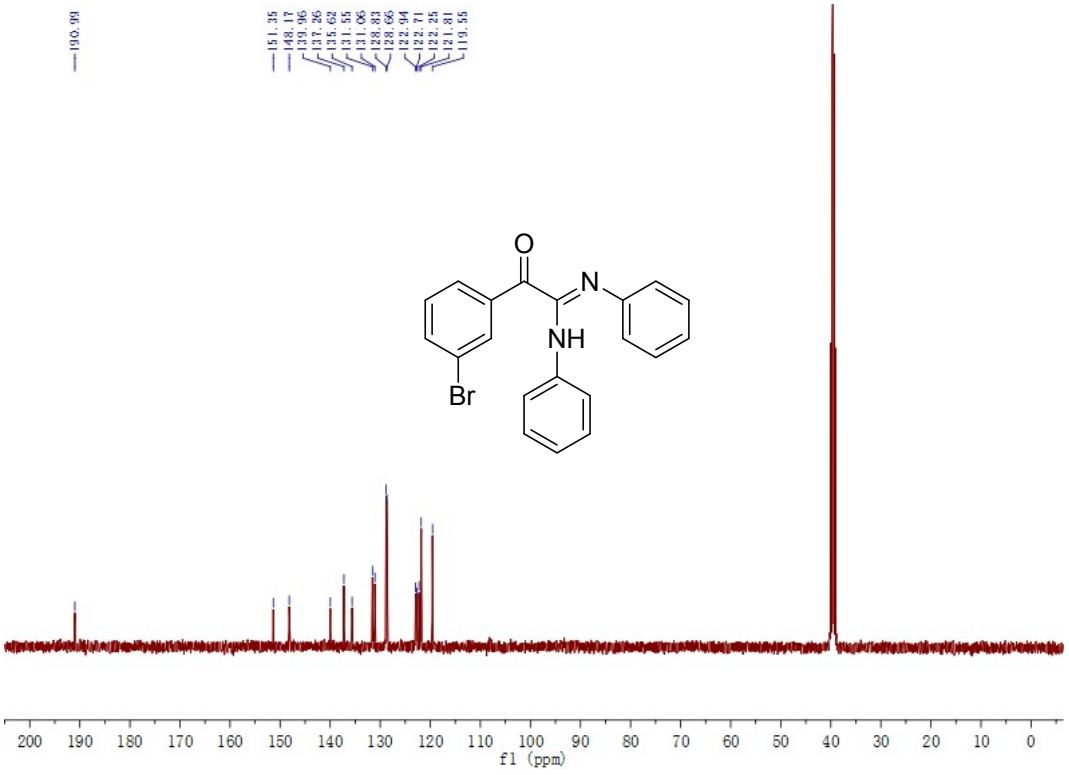
N
NH
Br
f1 (ppm)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137.26
135.62
131.55
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122.71
122.25
121.81
119.55
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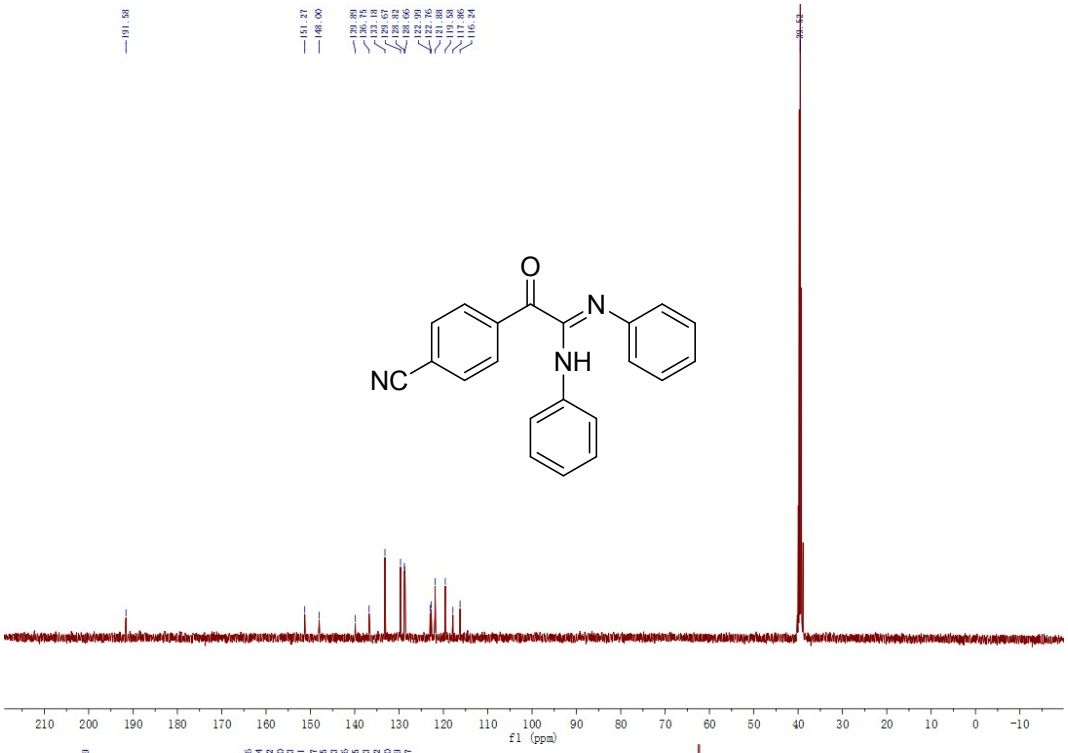
N
NH
Br
f1 (ppm)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128.82
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119.58
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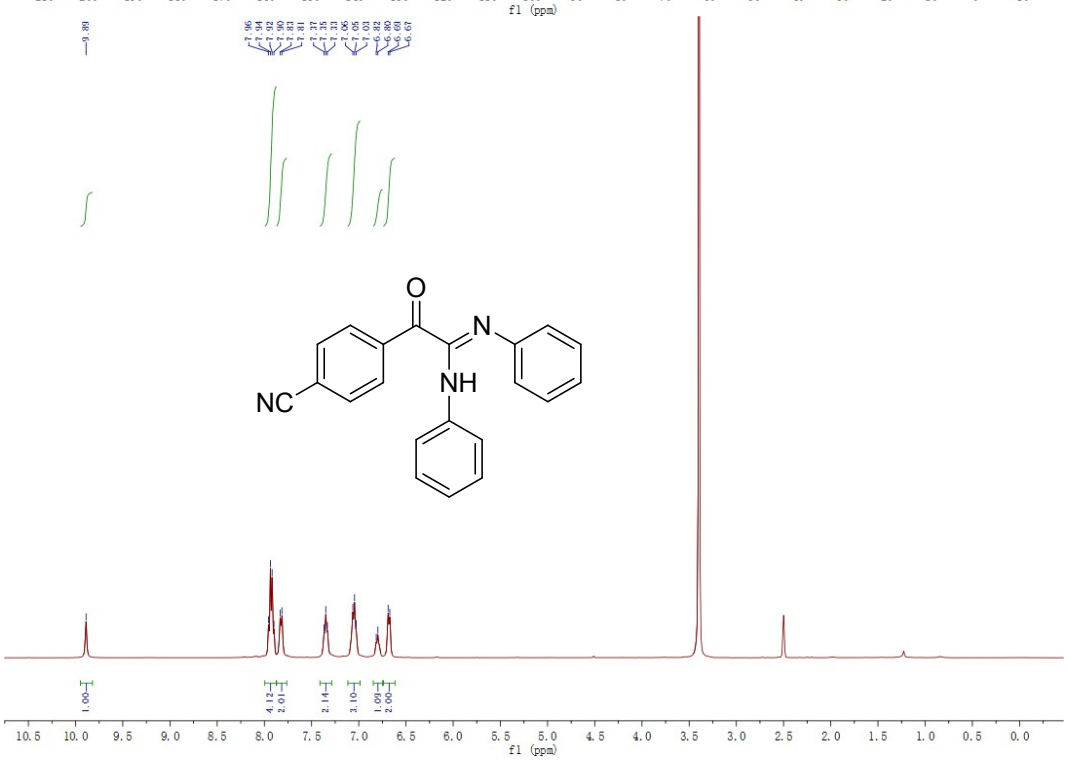
39.52
O
N
NH
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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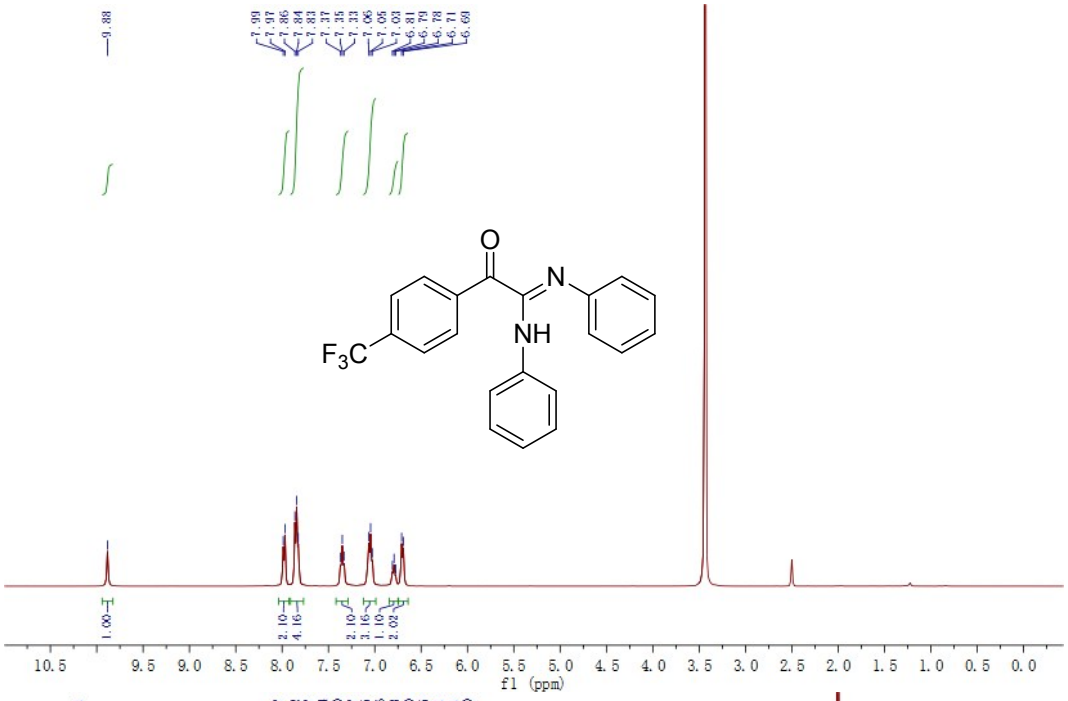
7.92
7.90
7.83
7.81
7.37
7.35
7.33
7.06
7.05
7.03
6.82
6.80
6.69
6.67
O
N
NH
NC
1.00
4.12
2.01
2.14
3.10
1.09
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.37
7.35
7.33
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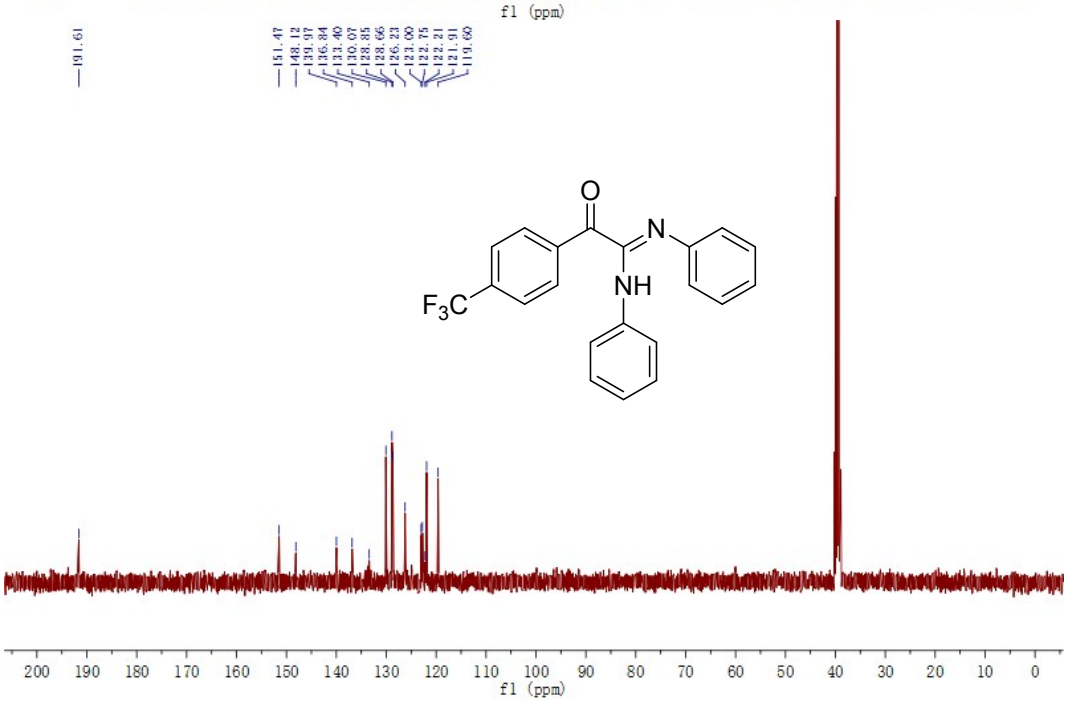
7.05
7.03
6.81
6.79
6.78
6.71
6.69
O
N
NH
F3C
1.00
2.10
4.16
2.10
2.16
1.10
2.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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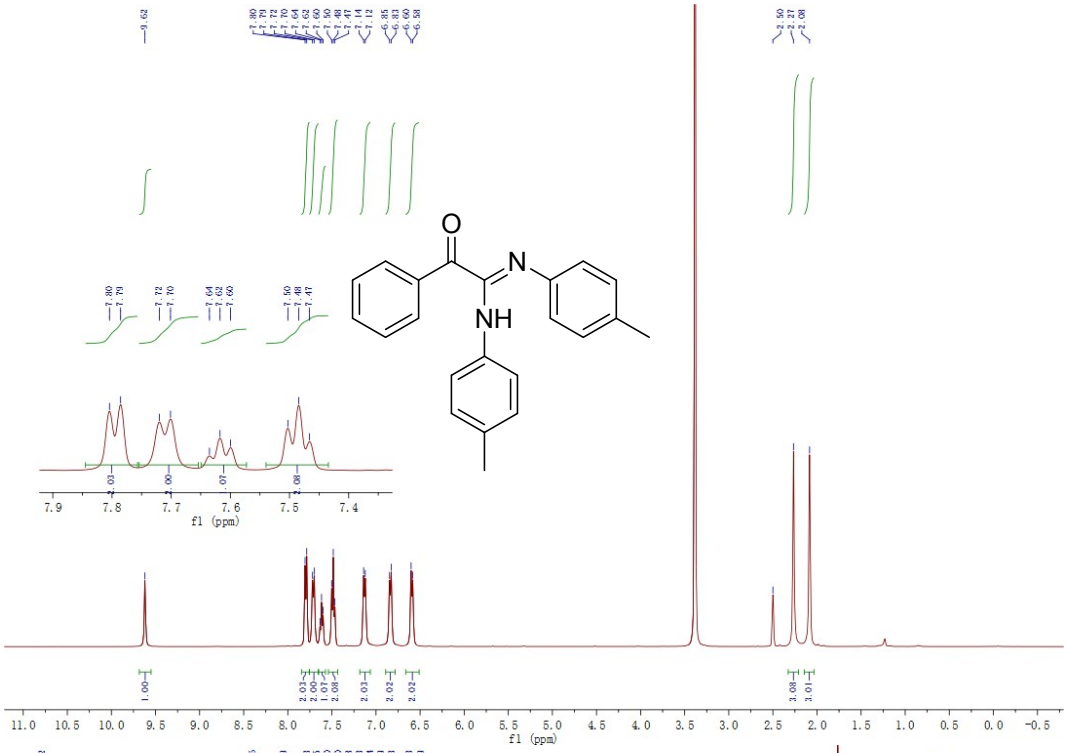
122.75
122.21
121.91
119.60
O
N
NH
F3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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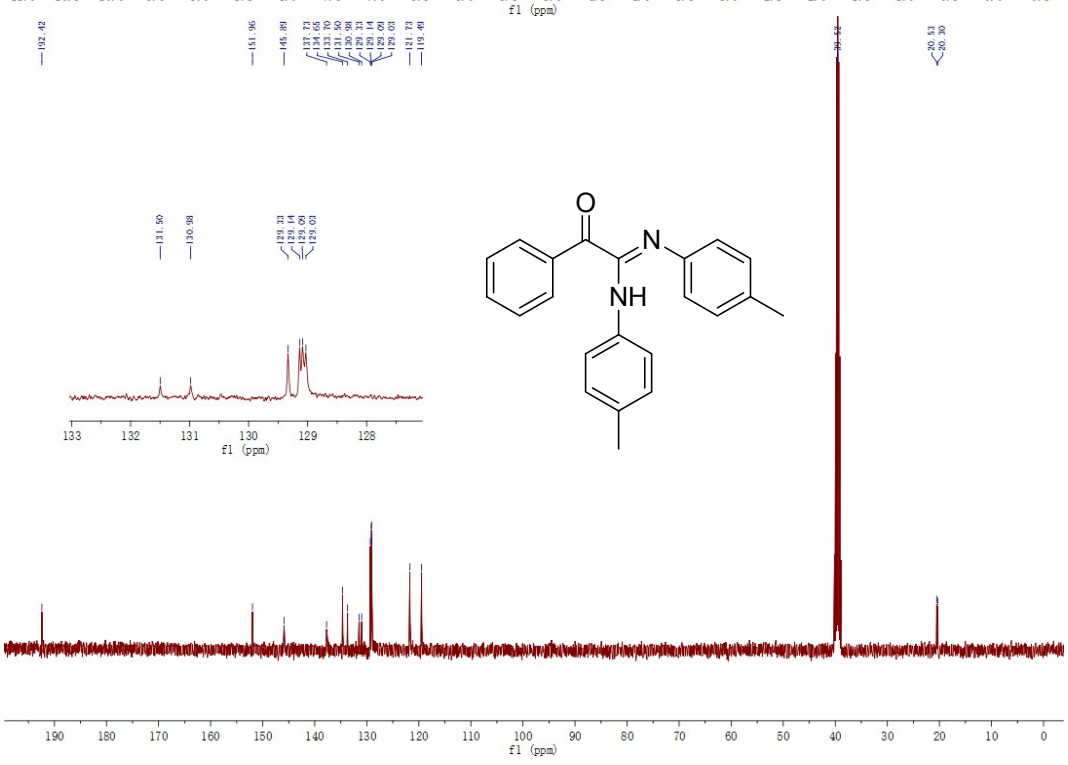
NH
f1 (ppm)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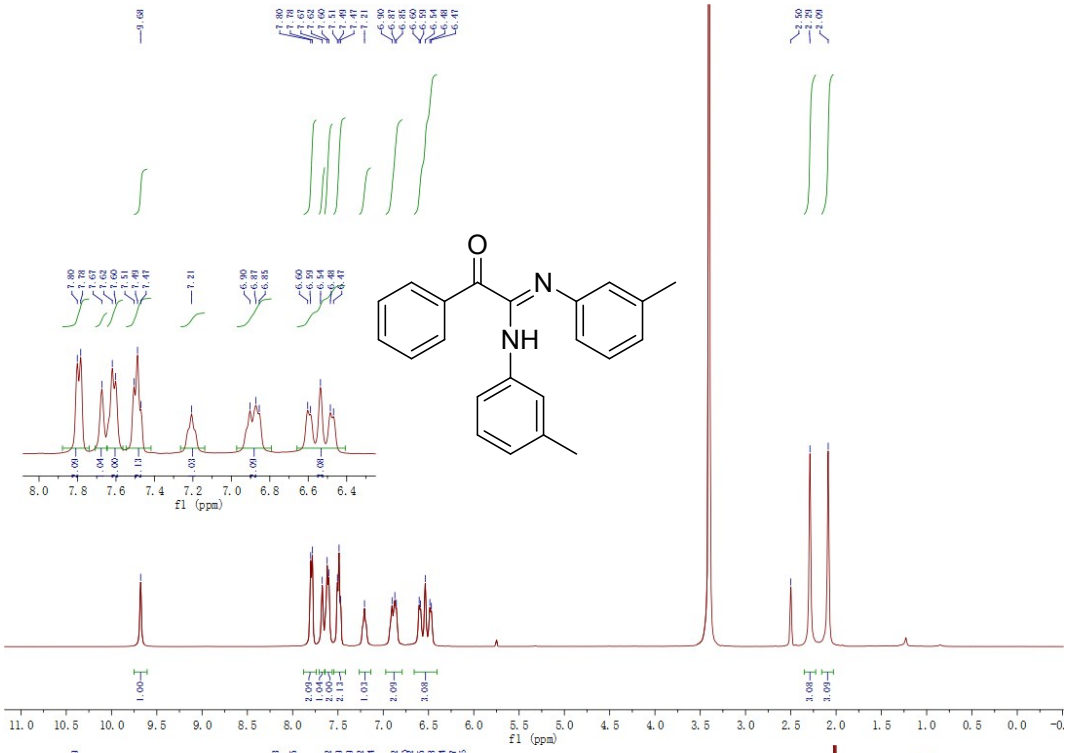
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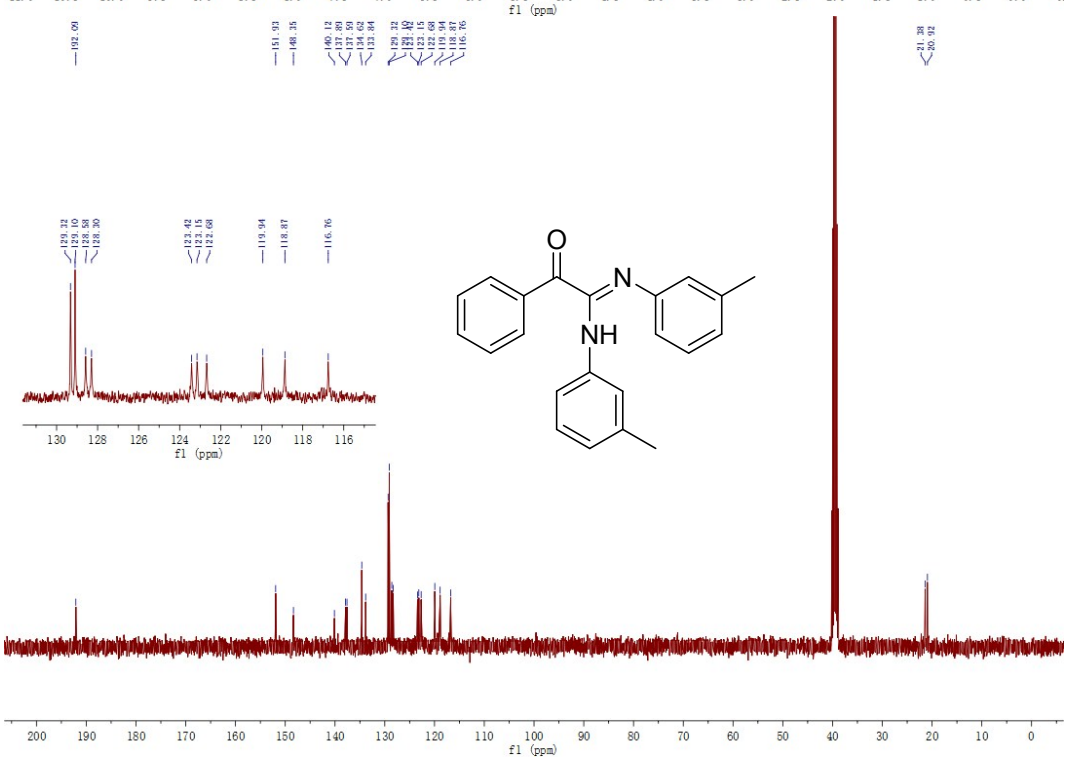
N
NH
f1 (ppm)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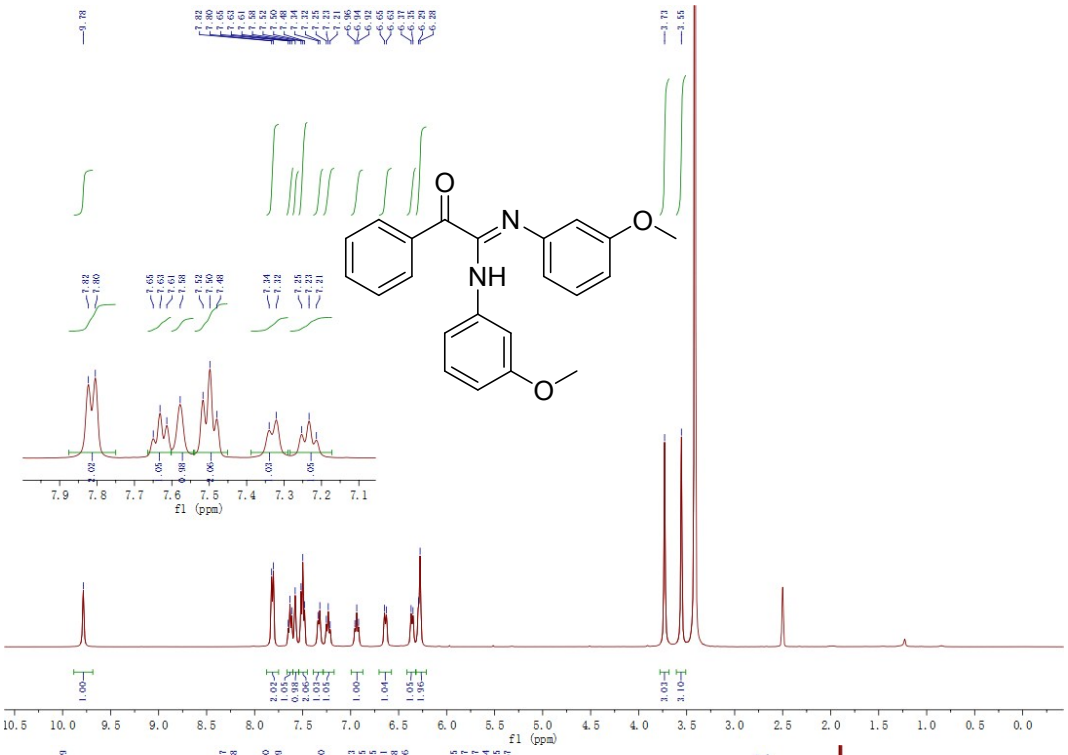
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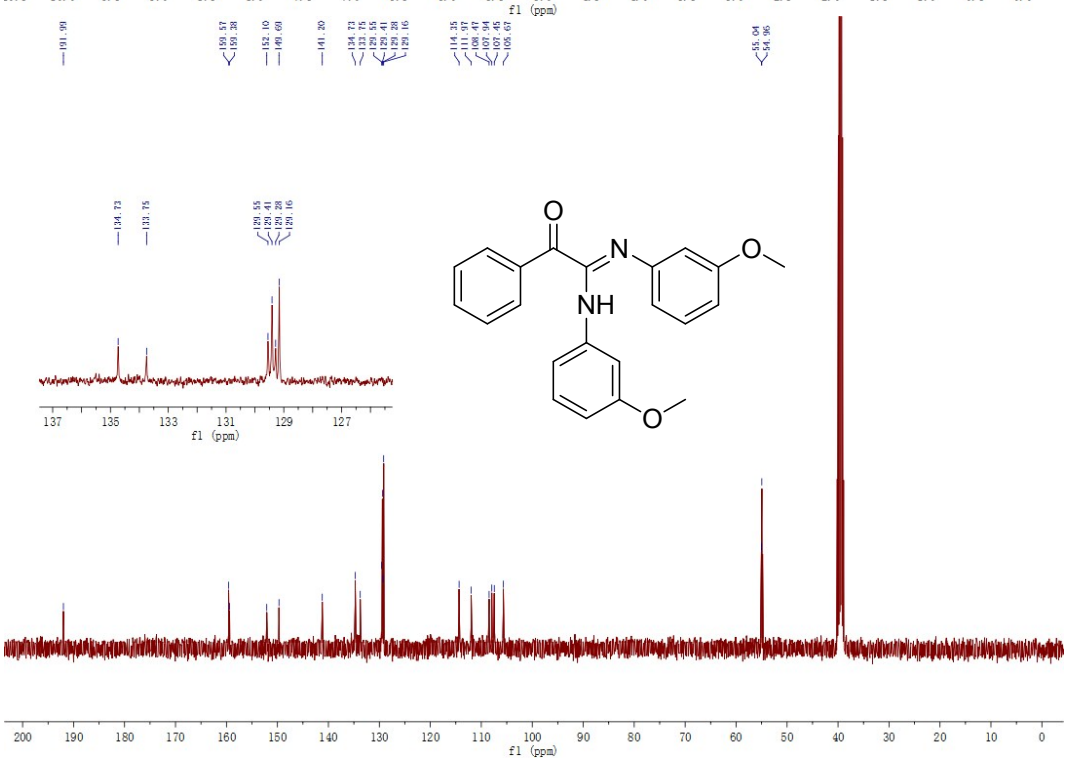
NH
O
O
f1 (ppm)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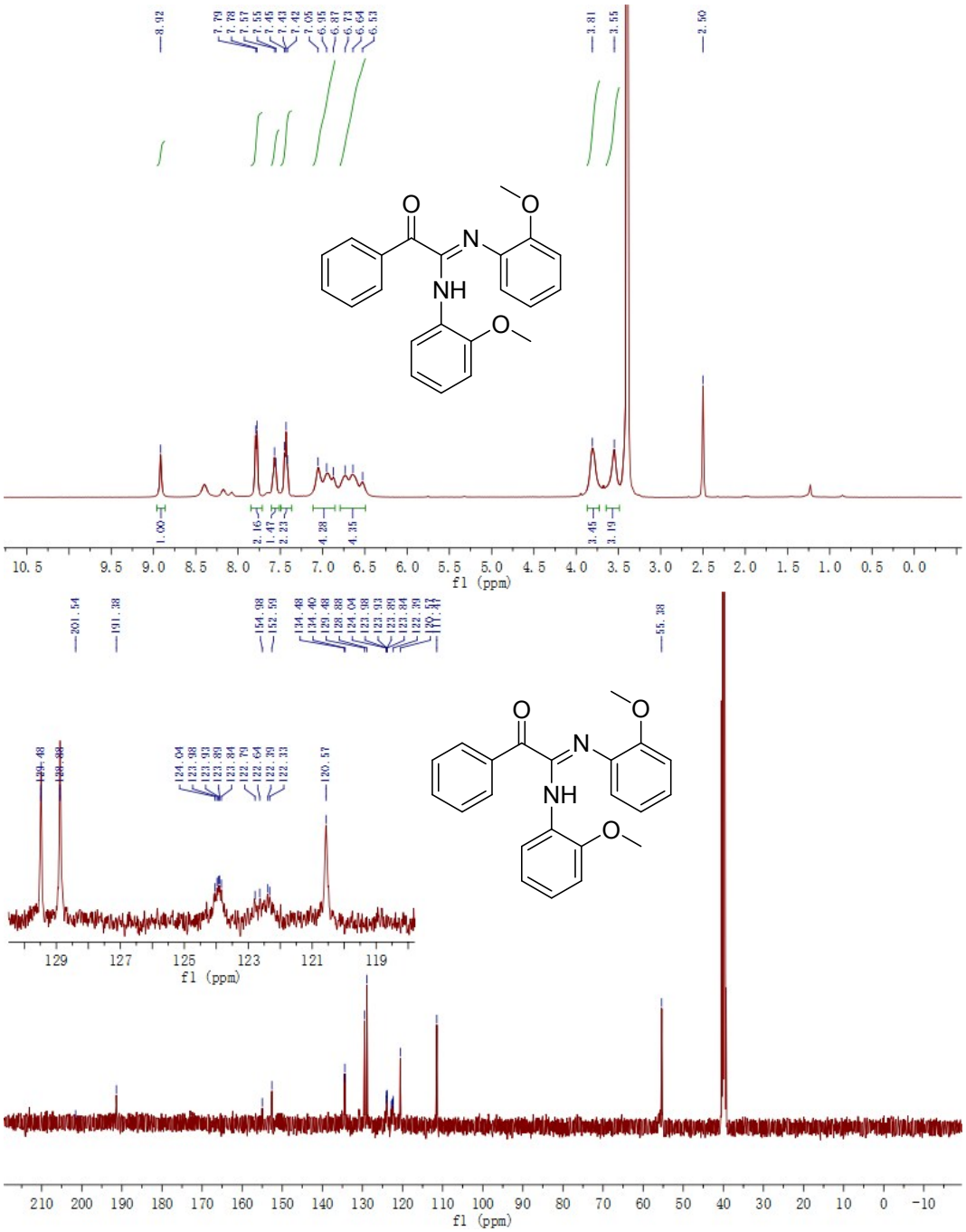
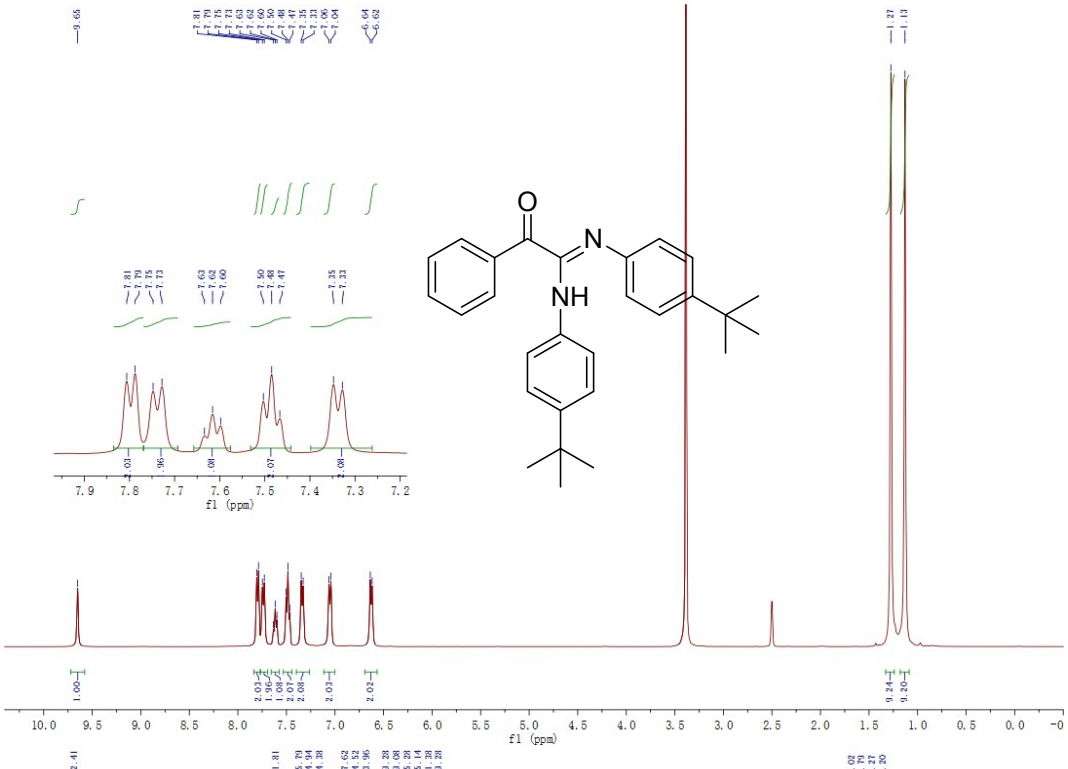
N
NH
O
O
f1 (ppm)


f1 (ppm)
f1 (ppm)
f1 (ppm)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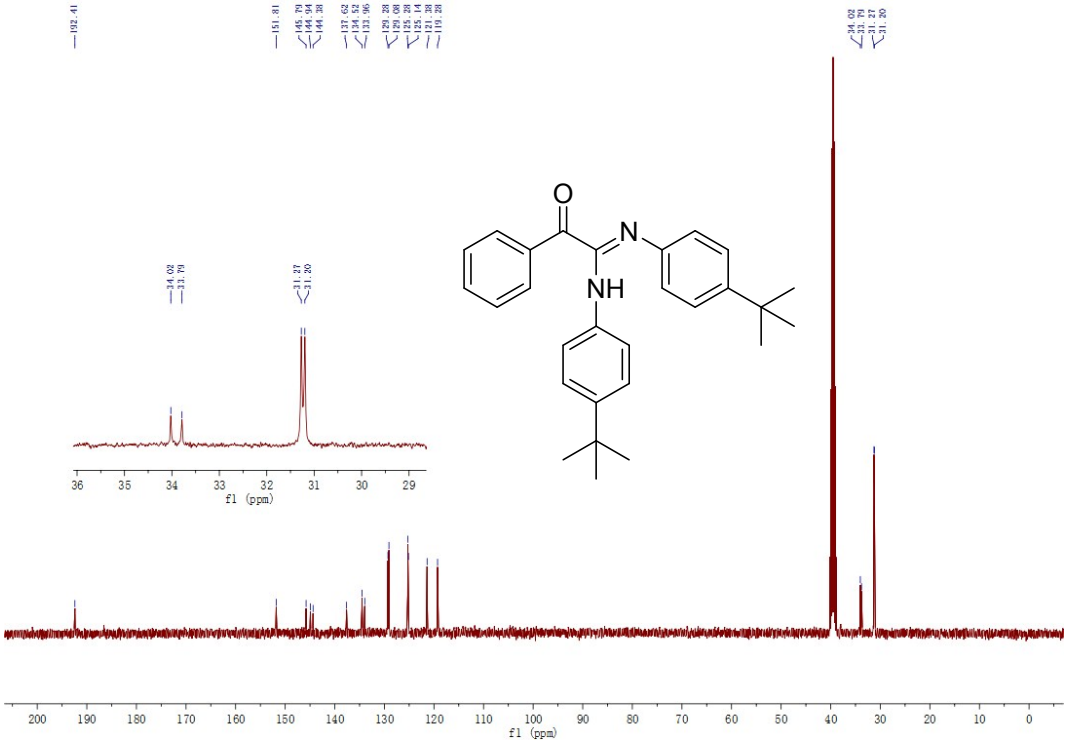
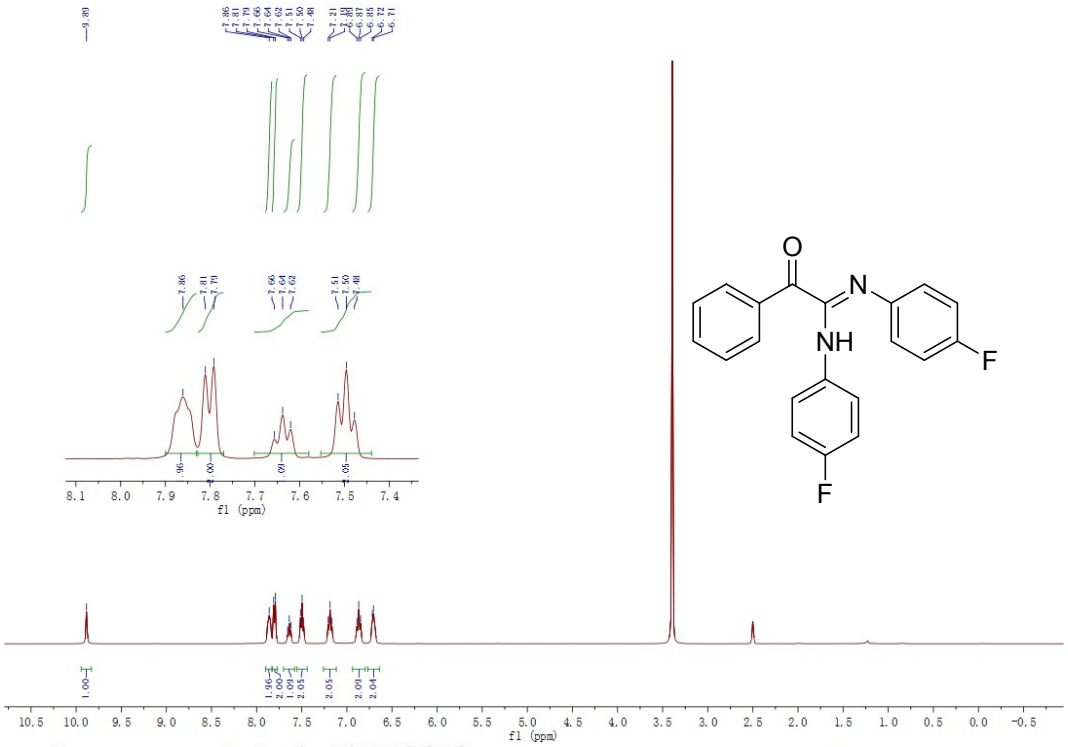
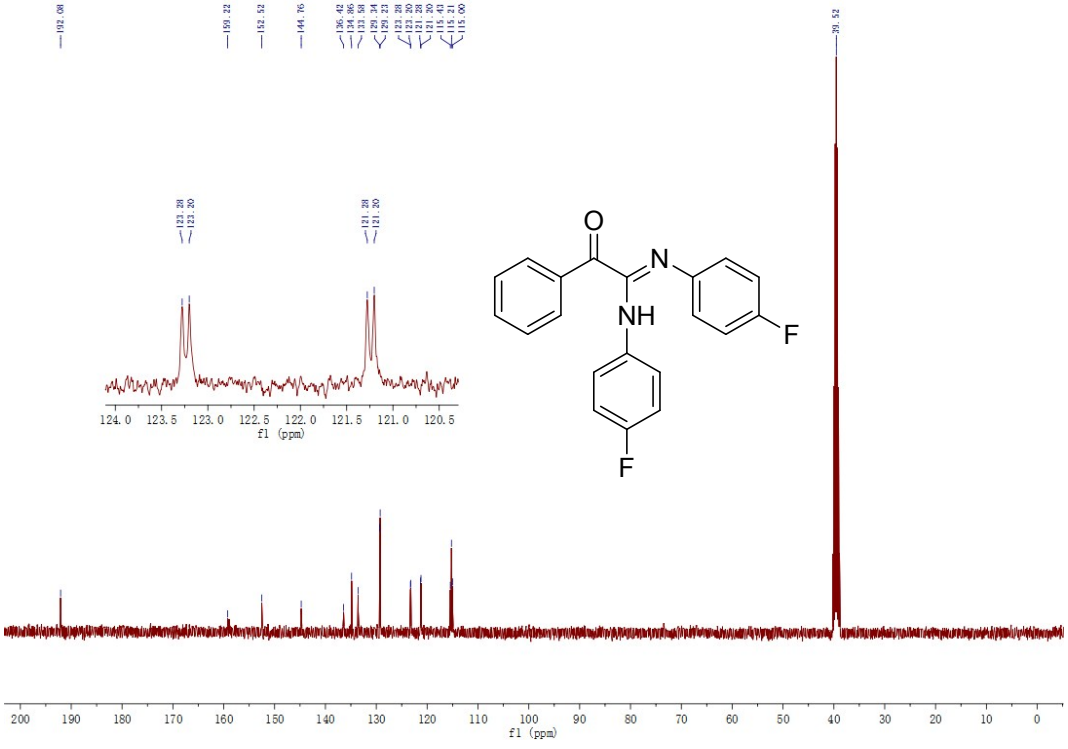
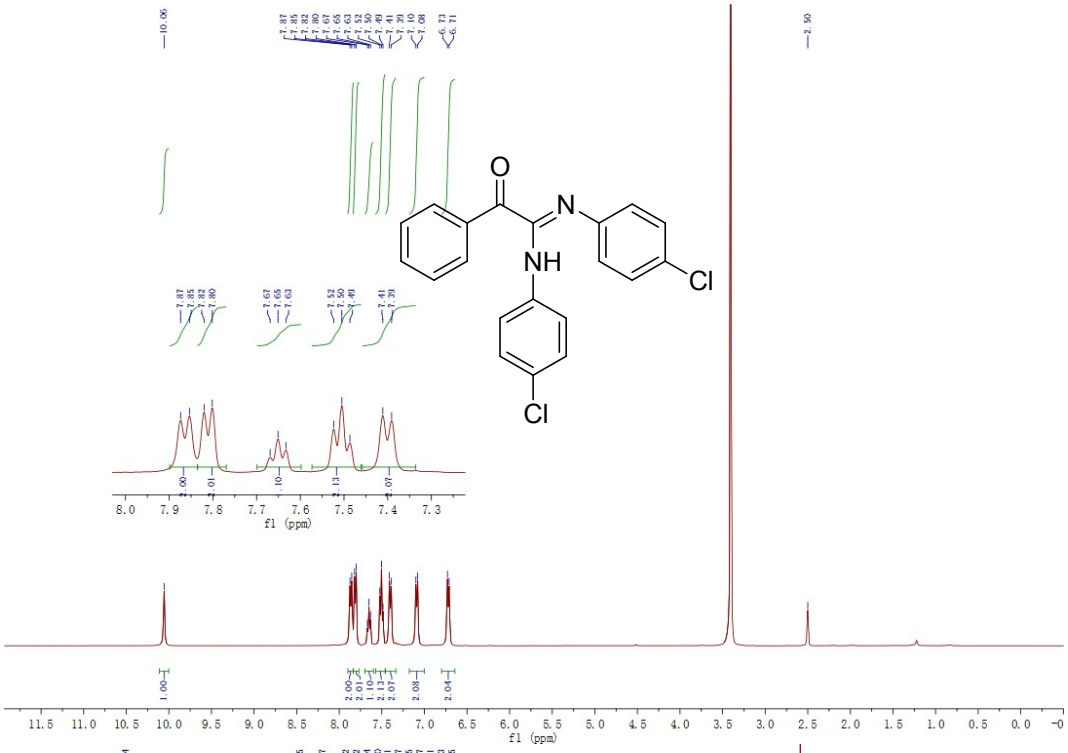
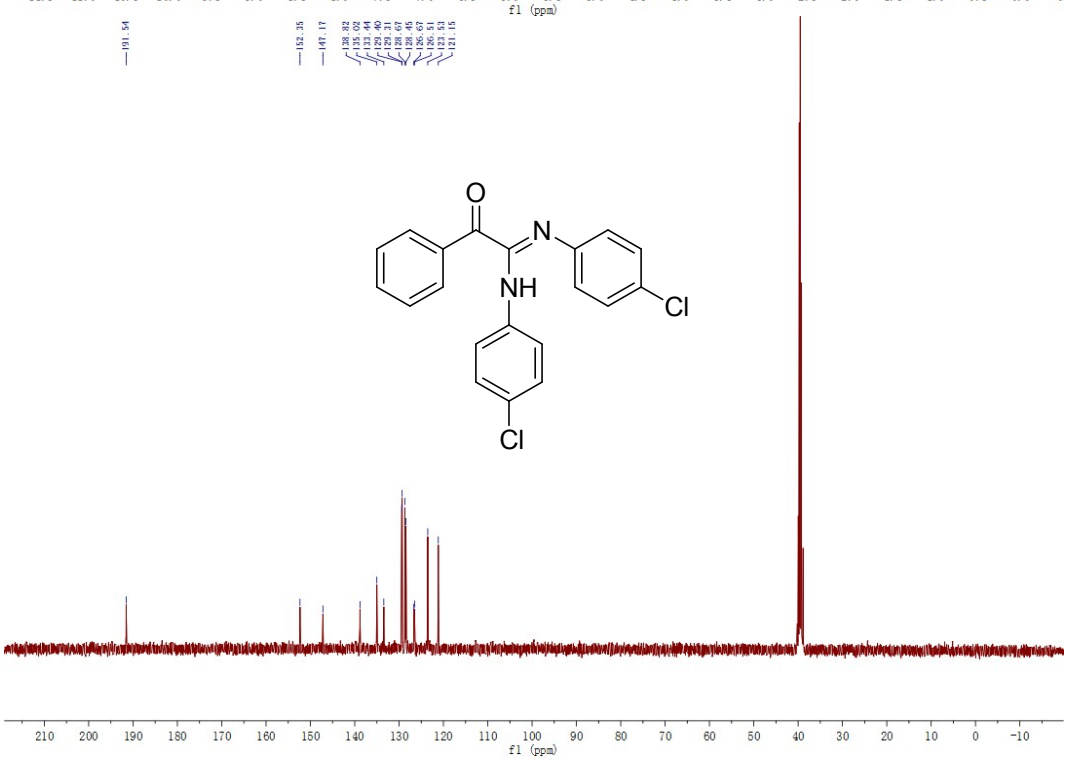
N
NH
f1 (ppm)

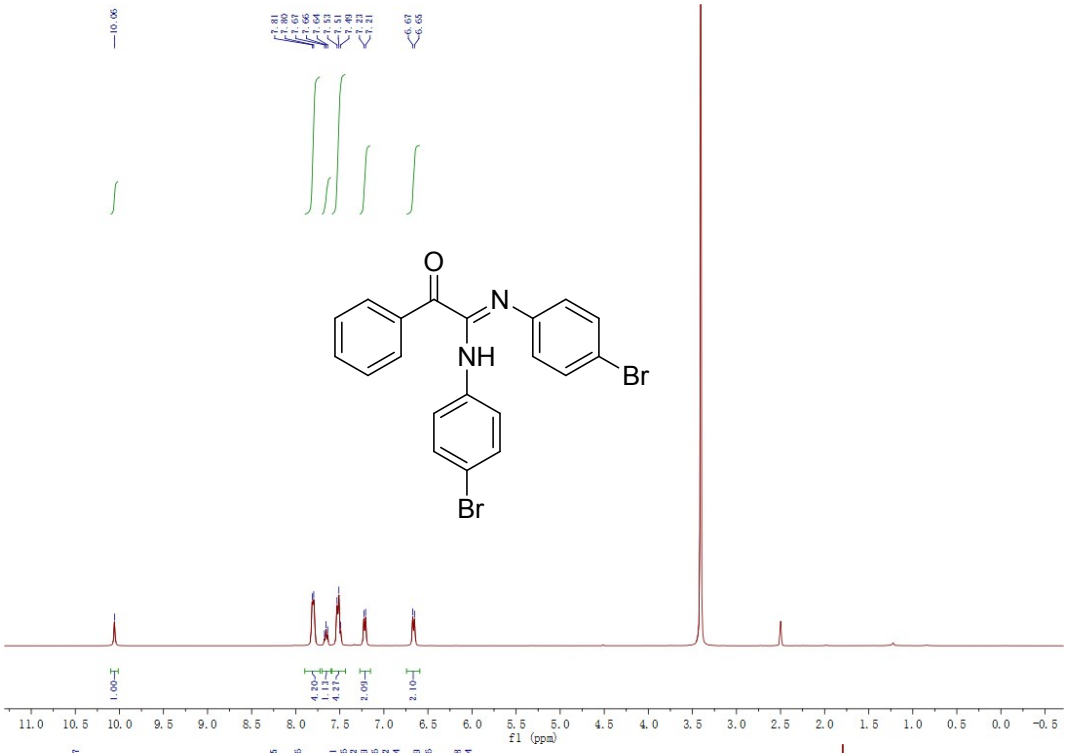

O
N
NH
f1 (ppm)


O
N
NH
F
F
fl (ppm)


O
N
NH
F
F
fl (ppm)


O
N
NH
Cl
Cl
f1 (ppm)


O
N
NH
Cl
Cl
f1 (ppm)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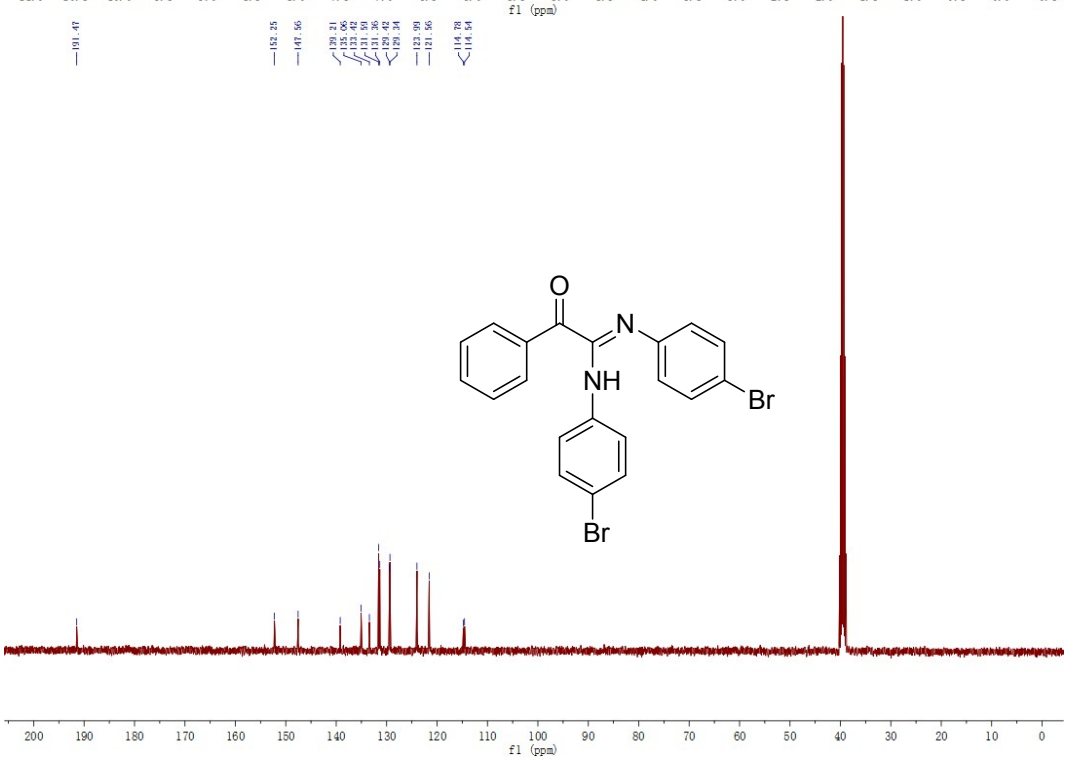
7.81
7.80
7.67
7.66
7.64
7.53
7.51
7.40
7.23
7.21
6.67
6.65
O
N
NH
Br
Br
1.00
4.20
1.12
4.27
2.09
2.10
f1 (ppm)


191.47
152.25
147.56
139.21
135.06
133.42
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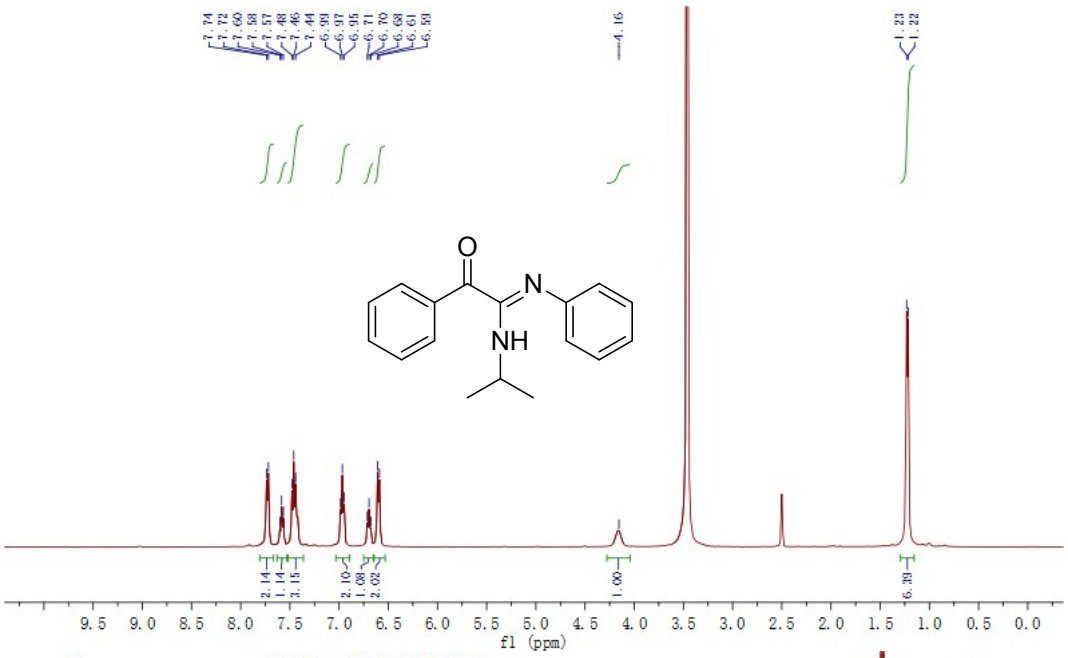
129.34
123.99
121.56
114.78
114.54
O
N
NH
Br
Br
f1 (ppm)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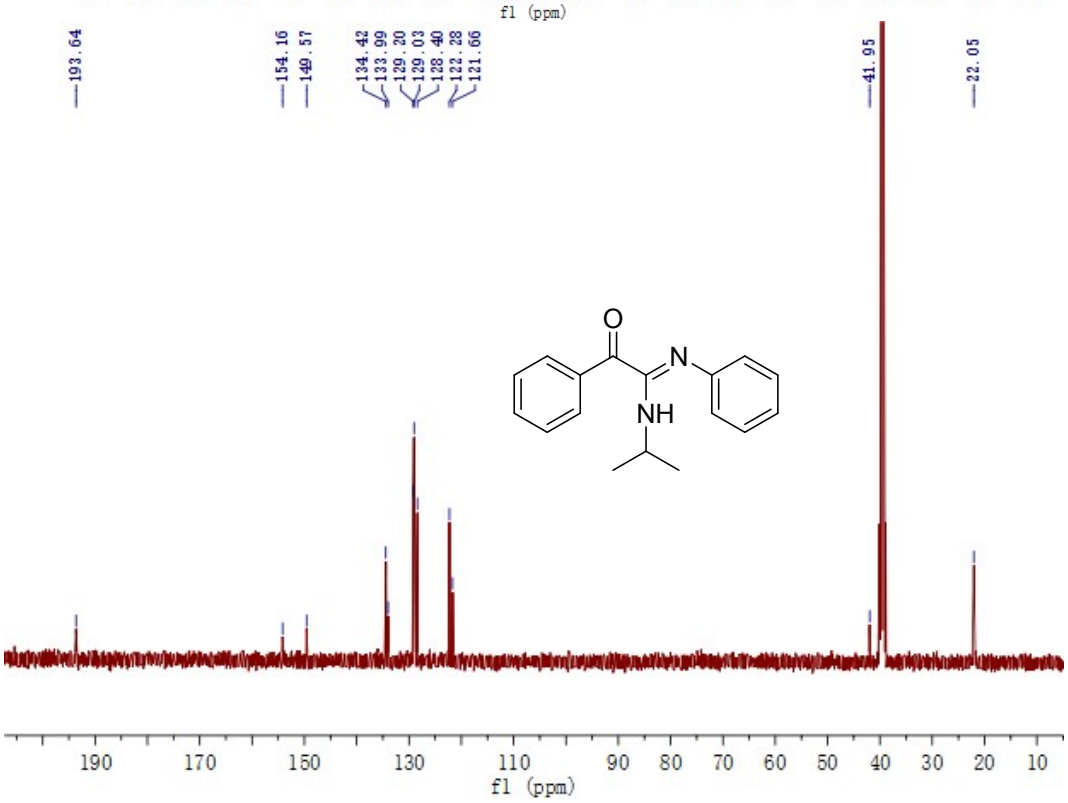
7.72
7.60
7.58
7.57
7.48
7.46
7.44
6.99
6.97
6.95
6.71
6.70
6.68
6.61
6.59
4.16
1.23
1.22
O
N
NH
2.14
1.14
3.15
2.10
1.08
2.02
1.00
6.39
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.42
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128.40
122.28
121.66
41.95
22.05
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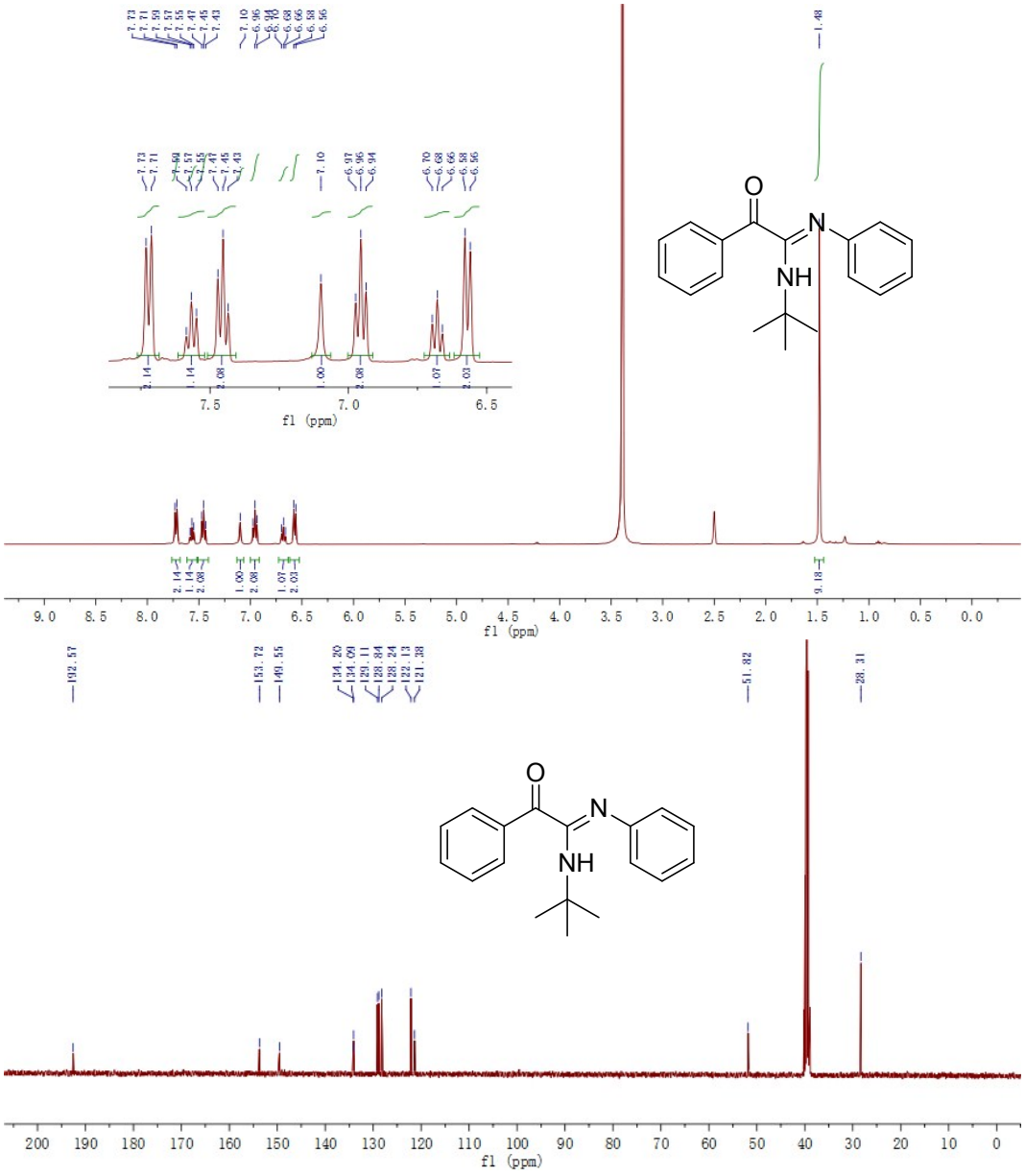
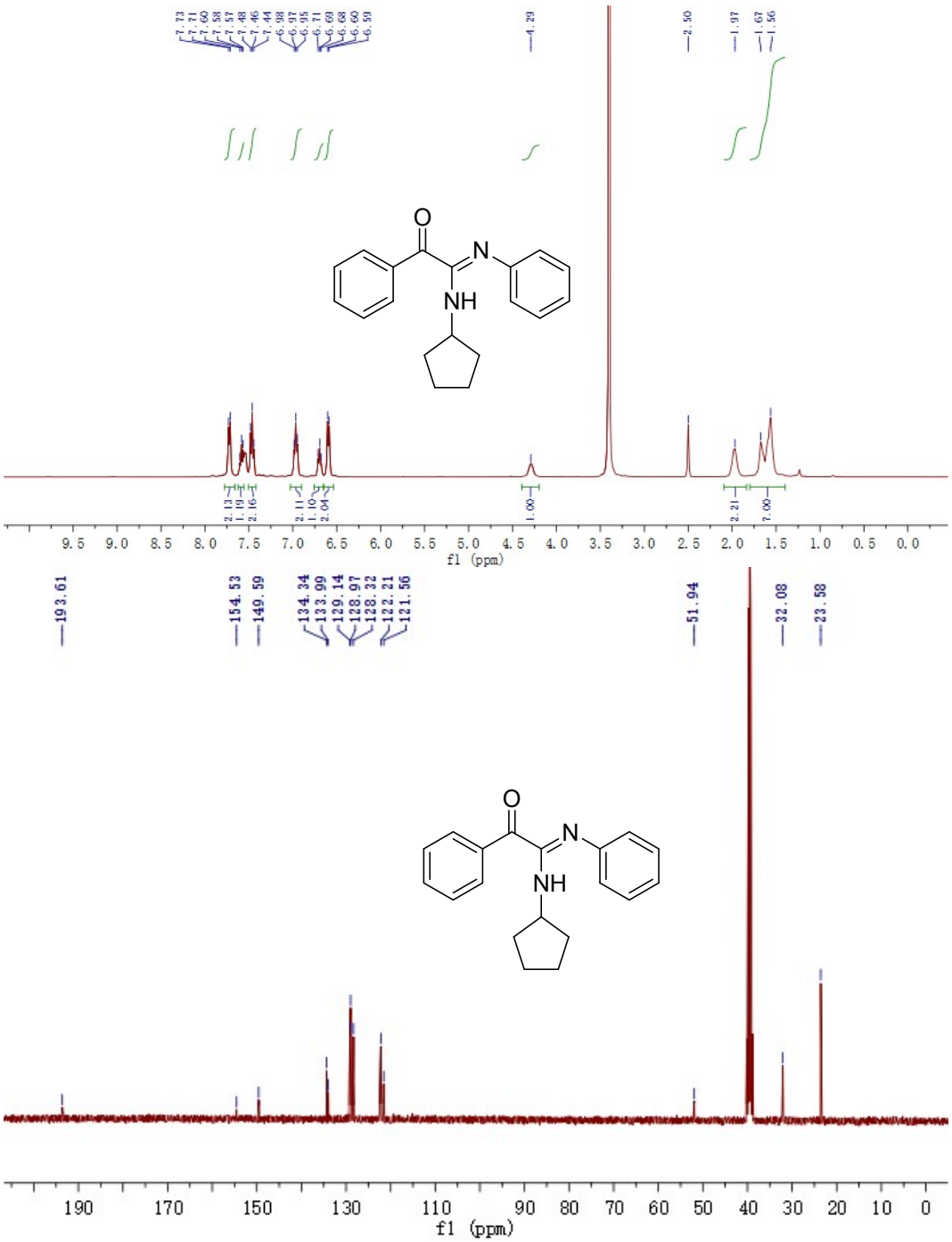
N
NH
190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
N
NH
f1 (ppm)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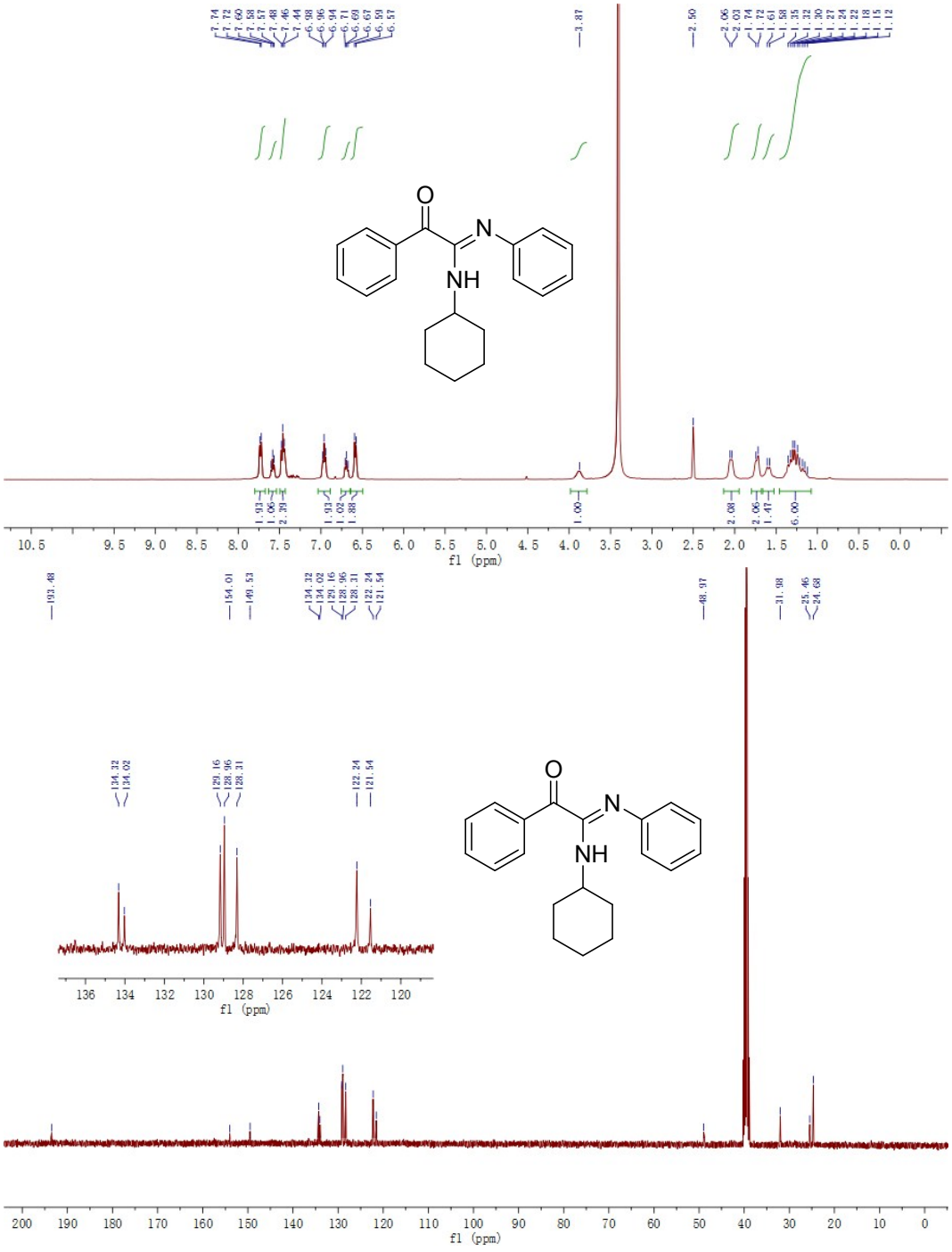
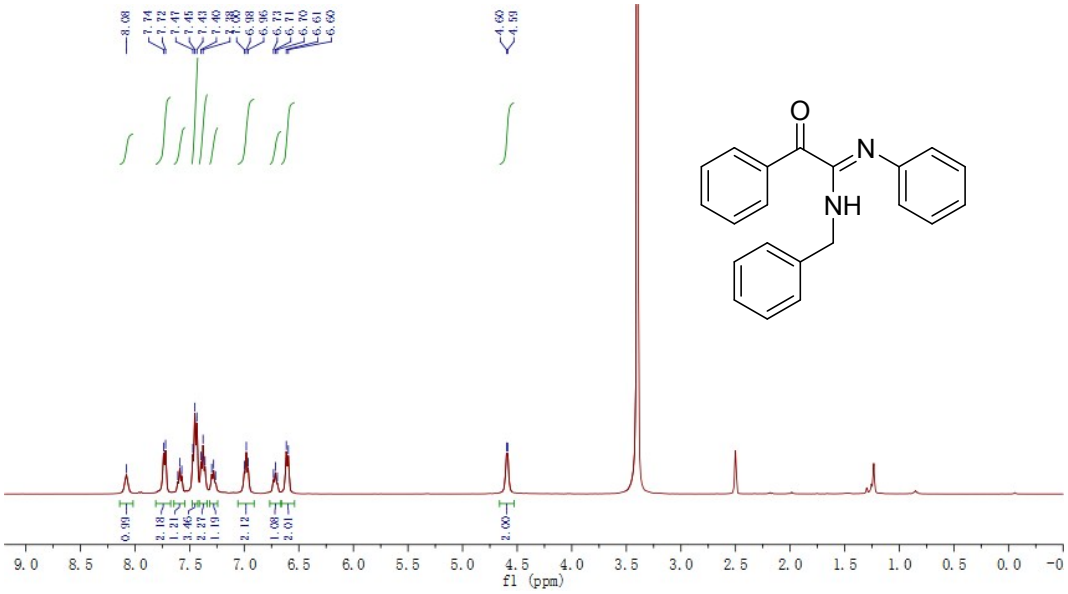
7.44
6.98
6.97
6.95
6.71
6.69
6.68
6.60
6.59
4.29
2.50
1.97
1.67
1.56
O
N
NH
2.13
1.19
2.16
2.11
1.10
2.04
1.00
2.21
7.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
193.61
154.53
149.59
134.34
133.99
129.14
128.97
128.32
122.21
121.56
51.94
32.08
23.58
O
N
NH
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
N
NH
f1 (ppm)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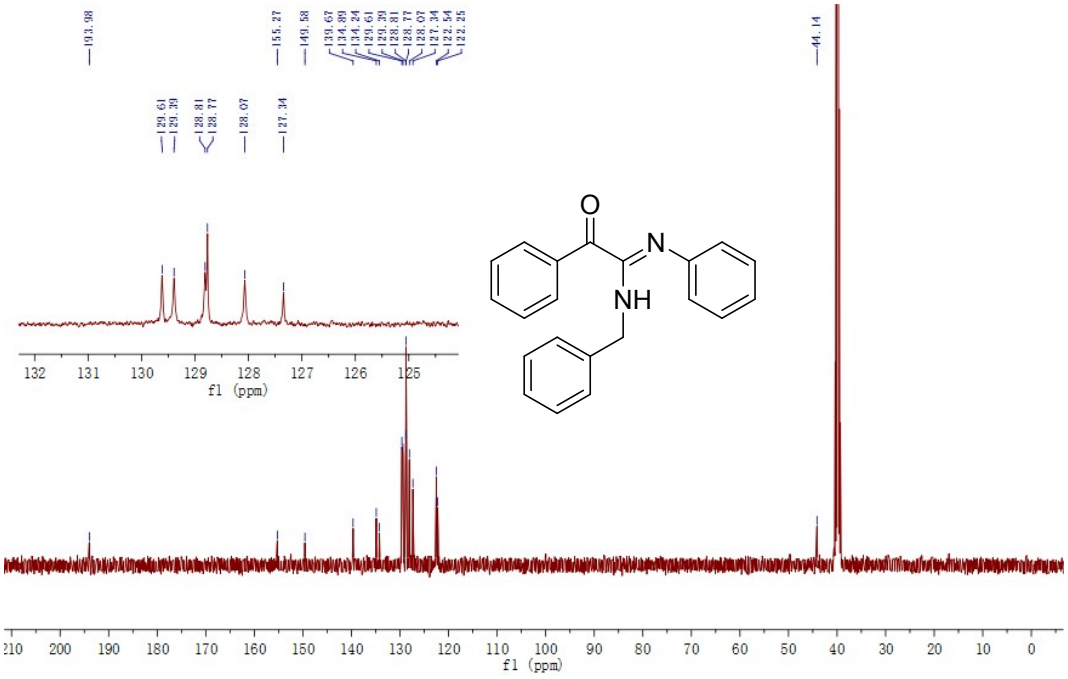
7.43
7.40
6.98
6.96
6.73
6.71
6.70
6.61
6.60
4.60
4.59
O
N
NH
0.99
2.18
1.21
3.46
2.27
1.19
2.12
1.08
2.01
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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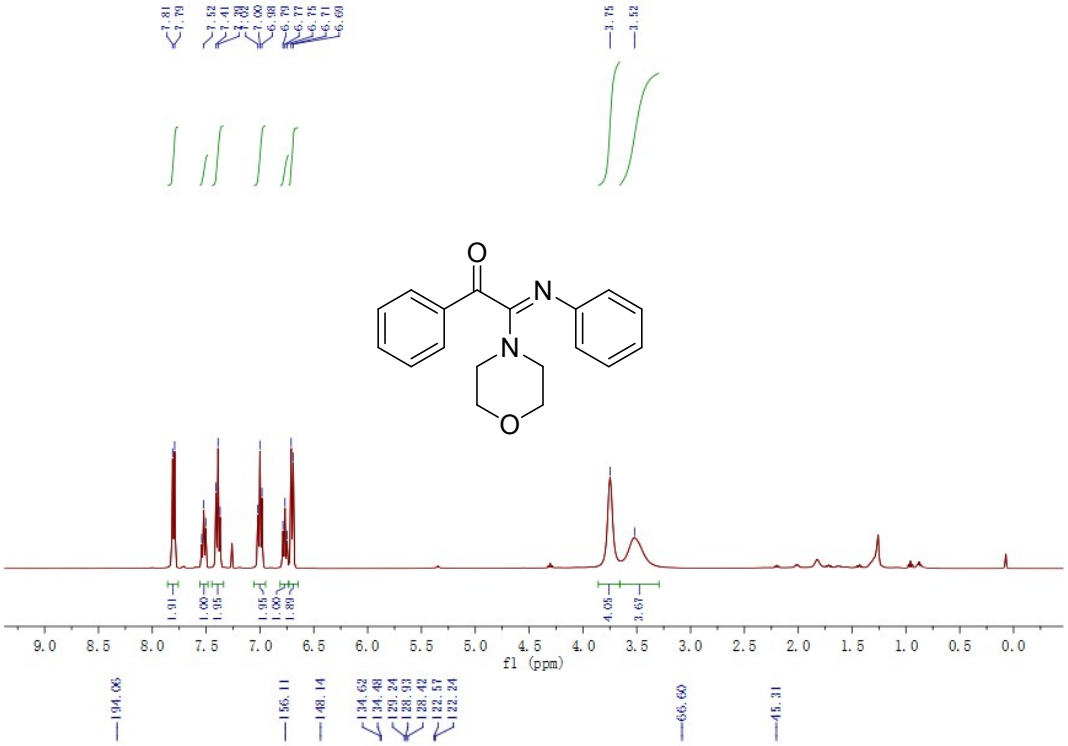
149.58
139.67
134.89
134.24
129.61
129.39
128.81
128.77
128.07
127.34
122.54
122.25
44.14
O
N
NH
132 131 130 129 128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.98
6.79
6.77
6.75
6.71
6.69
3.75
3.52
O
N
N
O
1.91
1.00
1.95
1.95
1.00
1.89
4.05
3.67
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)
194.06
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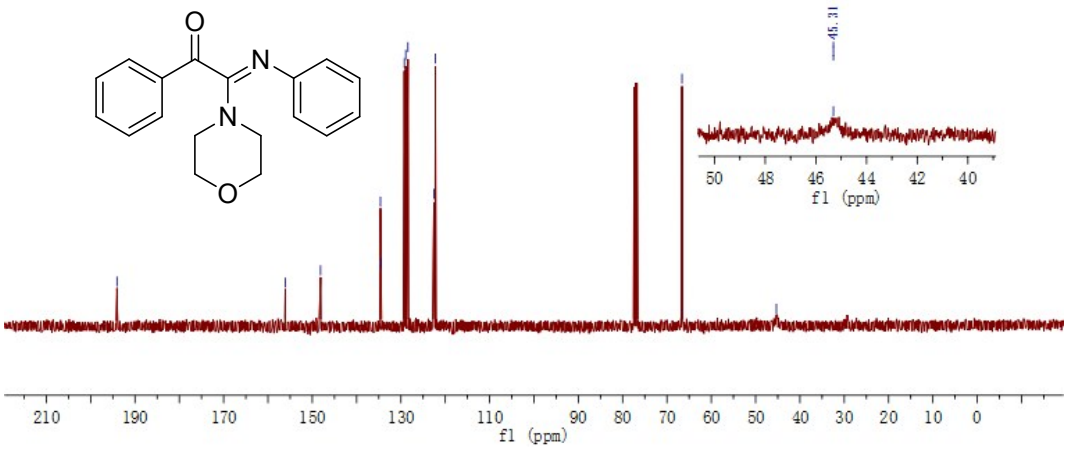
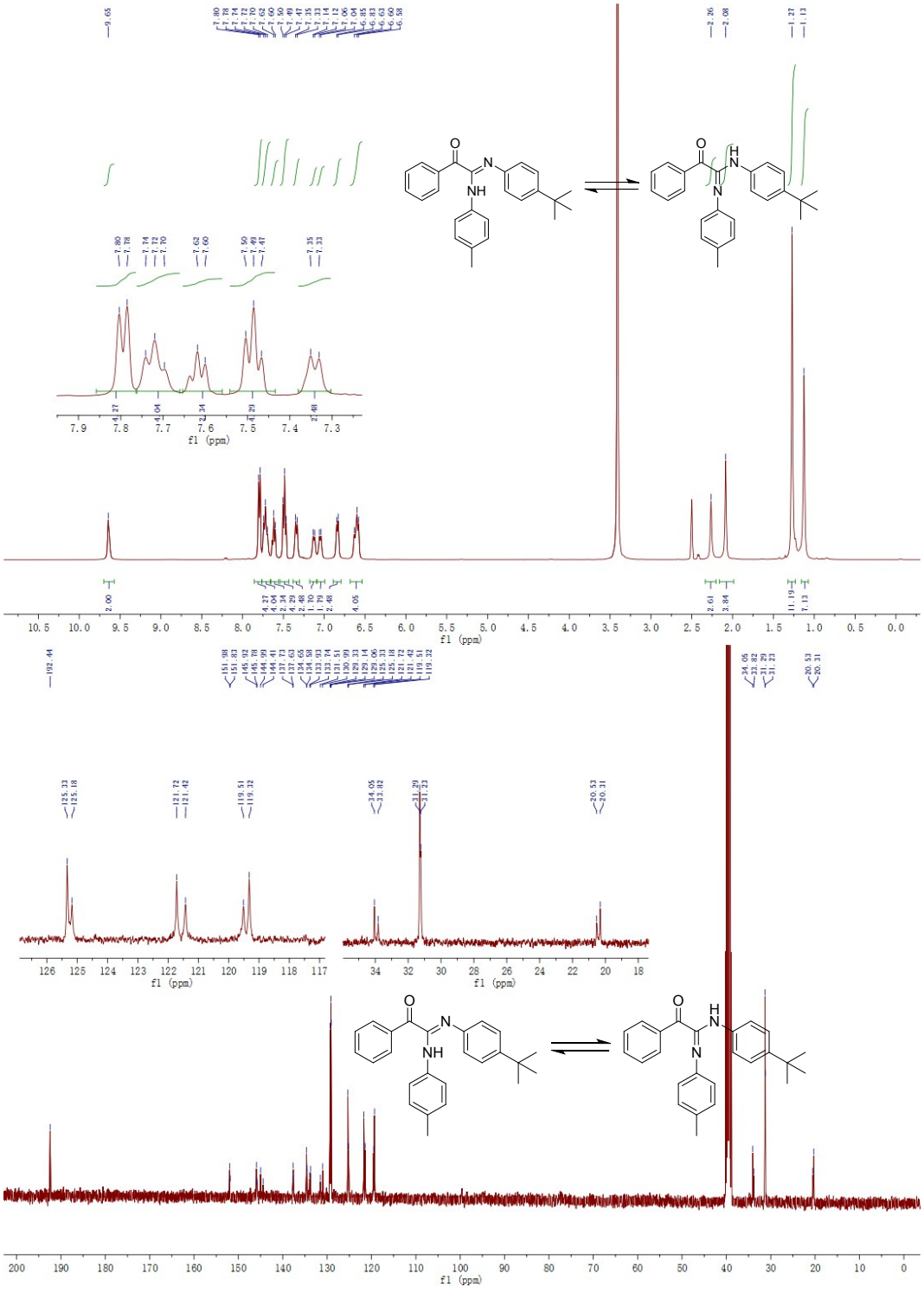
148.14
134.62
134.48
129.24
128.93
128.42
122.57
122.24
66.60
45.31

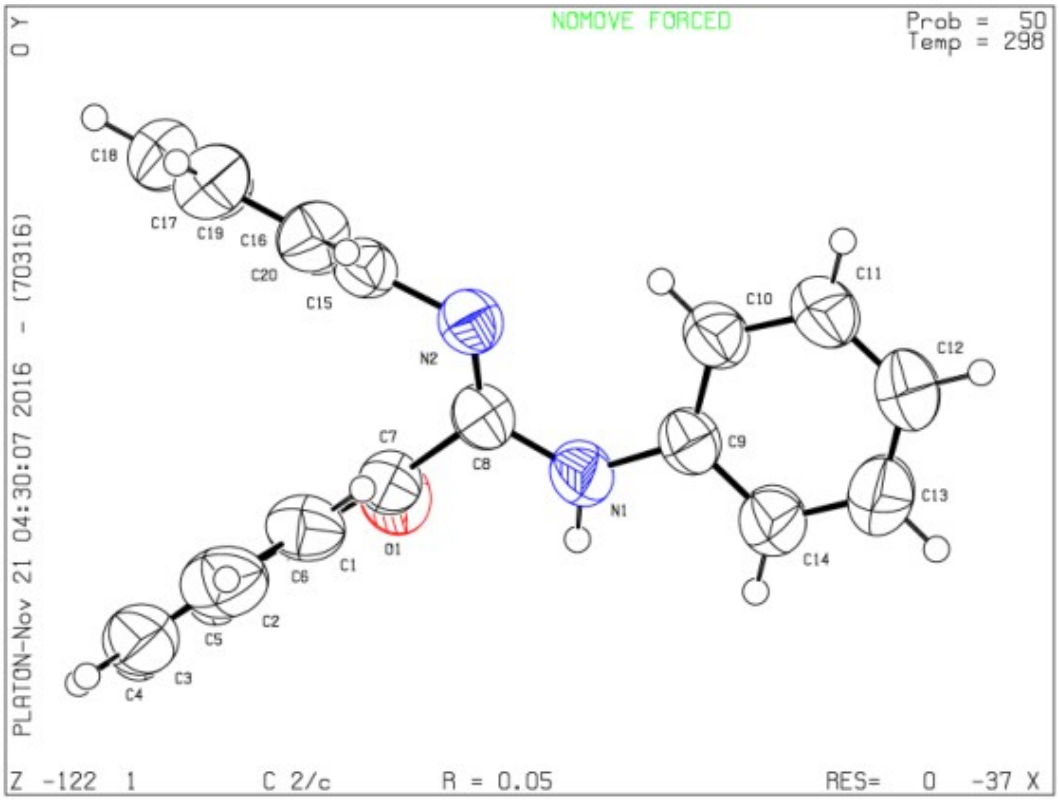

O
N
N
O
45.31
50 48 46 44 42 40
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


f1 (ppm)

6. crystal structure data

A single crystal for X-ray analysis of **3aa** was obtained by recrystallation from EtOAc/petroleumether.

CCDC-1555783 contains the supplementary crystallographic data for this paper. These data canbe obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Compound **3aa**: Displacement ellipsoids are drawn at the 30% probability level.