Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Energy Transfer Mediated Carbonylimination of Alkenes Using Bifunctional Reagent

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Supporting information

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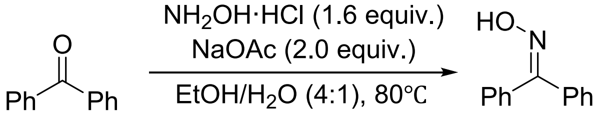
1. General Informations

All commercial reagents were used without addition6al purification. Reactions were monitored by thin-layer chromatography (TLC) on commercial silica gel plates (GF 254) using UV light as a visualizing agent. Products were purified by flash chromatography on 200 – 300 mesh silica gels, SiO_2 was carried out with silica gel (200−300 mesh). ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded with 400 MHz, 101 MHz and 377 MHz spectrometers in $CDCl_3$ by using tetramethylsilane (TMS) as the internal standard, respectively. High-resolution mass spectra (HRMS) were recorded using a positive-ion electrospray ionization (ESI^+) source. The Blue LED strips were purchased from https://m.tb.cn/h.g93DRei7jdhoc4G?tk=rziq32u0dh0

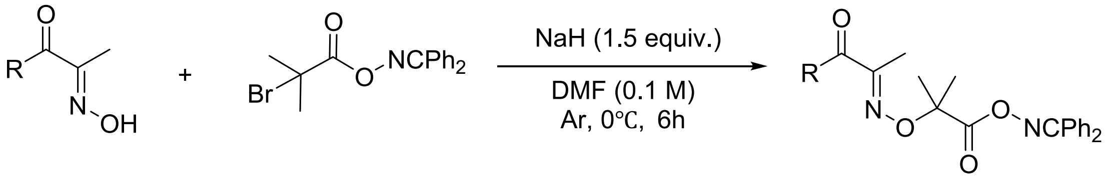
2. Methods for the synthesis of substrates

2.1 Preparation method of benzophenone oxime



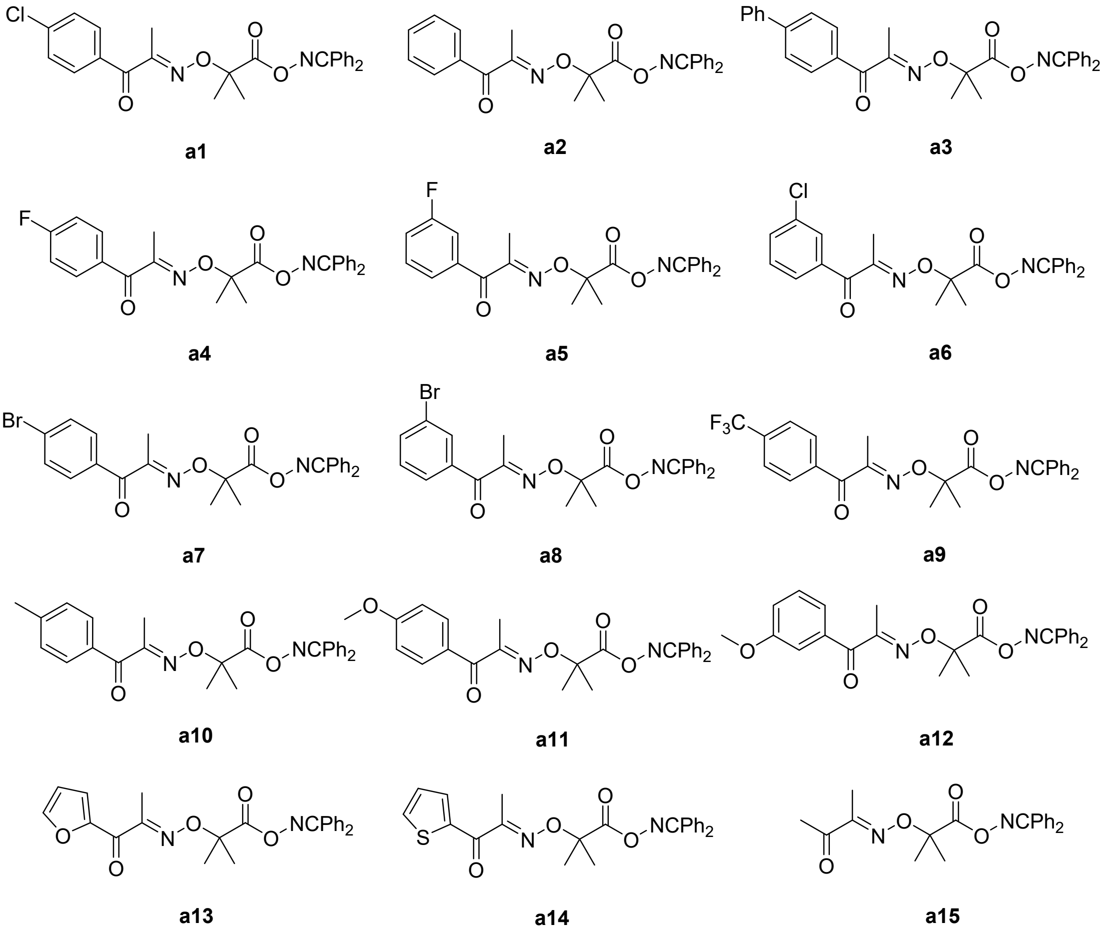
In a 250 mL round bottom flask equipped with a condenser, aromatic ketones (50.0 mmol, 1.0 equiv.) were dissolved in the mixture of EtOH/H_2O (v/v, 4:1, 125 mL). Then, hydroxylamine hydrochloride (80.0 mmol, 1.6 equiv.) and NaOAc (100.0 mmol, 2.0 equiv.) were added in one portion After the reaction mixture was refluxed in an oil bath at 80°C overnight, the consumption of starting material was monitored by TLC. In order to remove as much ethanol as possible, the reaction was then cooled to room temperature and added 50 mL saturated $NaHCO_3$ carefully. Then extracted with ethyl acetate 3 times and then dried over anhydrous Na_2SO_4. Evaporation of the solvent afforded the product as a white solid in quantitative yield.

2.2 Prepared method of bifunctional reagent



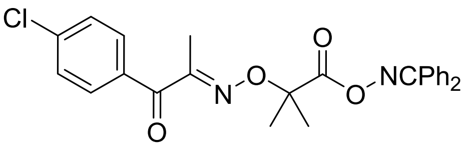
Added acyl oxime[1] (2.0 mmol) and DMF (20 ml) to a Schlenk tube under Argon atmosphere. Added NaH (3.0 mmol, 60% in oil) to the reaction mixture under Argon atmosphere. The mixture was stirred at 0 °C for additional 30 min. Then, O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) was added in one portion and the mixture was stirred at room temperature overnight. The reaction was quenched with water. Extracted with ethyl acetate 3 times and then dried over anhydrous Na_2SO_4. The resulting crude product was concentrated under reduced pressure and subsequently purified via column chromatography to yield the bifunctional reagents.

2.3 Scope of bifunctional reagents



Scheme S1 Scope of bifunctional reagents

Characterization data of substrates



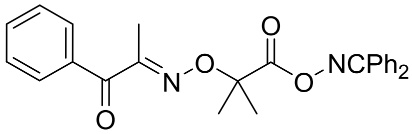
*9-(4-chlorophenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione **(a1)***

Synthesized by following General Procedure using 1-(4-chlorophenyl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (614 mg, 66%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.79 (m, 2H), 7.60 (dd, J = 7.9, 1.4 Hz, 2H), 7.46 – 7.32 (m, 8H), 7.21 – 7.11 (m, 2H), 1.99 (s, 3H), 1.47 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 189.73, 170.37, 166.29, 155.36, 139.14, 134.55, 134.29, 132.47, 132.16, 131.20, 129.63, 129.05, 128.49, 128.47, 128.27, 128.13, 83.09, 24.08, 10.60.;

HRMS (ESI) m/z calcd for $C_{26}H_{24}ClN_2O_4^+$ (M+H)$^+$ 463.1419, found 463.1414.



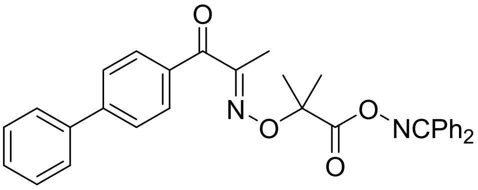
*5,5,8-trimethyl-1,1,9-triphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione (**a2**)*

Synthesized by following General Procedure using 2-(hydroxyimino)-1-phenylpropan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (421mg, 49%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (dd, J = 6.9, 1.4 Hz, 2H), 7.59 (d, J = 7.7 Hz, 2H), 7.48 – 7.32 (m, 9H), 7.14 (dd, J = 7.4, 2.0 Hz, 2H), 1.98 (s, 3H), 1.48 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 191.03, 170.46, 166.11, 155.44, 136.26, 134.42, 132.66, 132.50, 131.11, 130.75, 129.58, 129.03, 128.50, 128.45, 128.11, 127.95, 82.94, 24.07, 10.70.;

HRMS (ESI) m/z calcd for $C_{26}H_{25}N_2O_4^+$ (M+H)$^+$ 429.1809, found 429.1812.



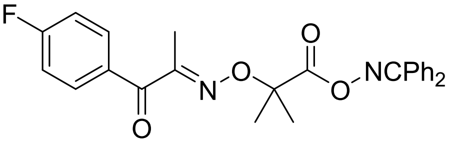
*9-([1,1'-biphenyl]-4-yl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione (**a3**)*

Synthesized by following General Procedure using 1-([1,1'-biphenyl]-4-yl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (577 mg, 57%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.66 – 7.48 (m, 6H), 7.43 – 7.26 (m, 9H), 7.16 – 7.04 (m, 2H), 2.03 (s, 3H), 1.48 (d, J = 1.1 Hz, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 190.54, 170.54, 166.57, 155.57, 145.35, 139.90, 134.97, 133.91, 132.44, 131.47, 131.13, 129.61, 129.06, 128.89, 128.53, 128.49, 128.13, 128.09, 127.25, 126.64, 83.06, 24.15, 10.84.;

HRMS (ESI) m/z calcd for $C_{32}H_{29}N_2O_4^+$ (M+H)$^+$ 505.2111, found 505.2109.



*9-(4-fluorophenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione **(a4)***

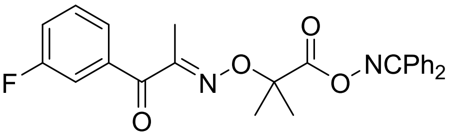
Synthesized by following General Procedure using 1-(4-fluorophenyl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (554 mg, 62%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 – 7.87 (m, 2H), 7.60 (dd, J = 7.7, 2.1 Hz, 2H), 7.44 – 7.05 (m, 10H), 1.99 (s, 3H), 1.48 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 189.34, 170.40, 166.26, 165.58 (d, J =254.4 Hz), 155.42, 134.33, 133.43 (d, J =9.3 Hz), 132.47, 131.19, 129.65, 129.03, 128.50, 128.14, 115.10 (d, J =21.8 Hz), 83.00, 24.05, 10.72.;

^{19}F NMR (376 MHz, CDCl$_3$) δ -105.69.

HRMS (ESI) m/z calcd for $C_{26}H_{24}FN_2O_4^+$ $(M+H)^+$ 447.1715, found 447.1719.



*9-(3-fluorophenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione **(a5)***

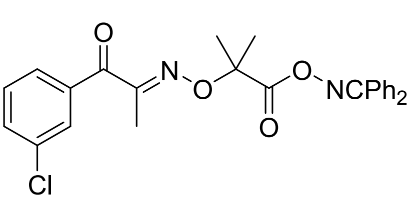
Synthesized by following General Procedure using 1-(3-fluorophenyl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (548 mg, 61%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (dt, J = 7.8, 1.3 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.43 – 7.30 (m, 7H), 7.22 – 7.13 (m, 3H), 1.98 (s, 3H), 1.49 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 189.54, 170.32, 166.19, 162.19 (d, J=246.7 Hz), 155.32, 138.17 (d, J =6.8 Hz), 134.37, 132.52, 131.14, 129.63, 129.51 (d, J =8.1 Hz), 129.05, 128.50, 128.45, 128.13, 127.73, 126.64 (d, J =3.0 Hz), 119.59 (d, J =21.8 Hz), 117.32 (d, J =23.5 Hz), 83.11, 24.04, 10.60.

^{19}F NMR (376 MHz, CDCl$_3$) δ -112.60.

HRMS (ESI) m/z calcd for $C_{26}H_{24}FN_2O_4^+$ $(M+H)^+$ 447.1715, found 447.1715.



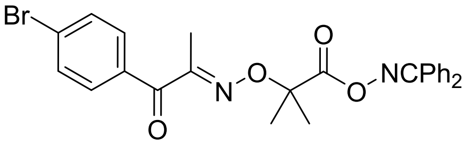
*9-(3-chlorophenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione **(a6)***

Synthesized by following General Procedure using 1-(3-chlorophenyl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (366 mg, 40%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 2.0 Hz, 1H), 7.75 (dq, *J* = 7.7, 1.2 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.43 – 7.30 (m, 8H), 7.20 – 7.14 (m, 2H), 1.97 (d, *J* = 0.8 Hz, 3H), 1.49 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 189.58, 170.30, 166.12, 155.26, 137.78, 134.37, 134.07, 132.51, 132.46, 131.13, 130.60, 129.62, 129.21, 129.05, 128.93, 128.51, 128.44, 128.12, 83.15, 24.14, 10.53.;

HRMS (ESI) m/z calcd for $C_{26}H_{24}ClN_2O_4^+$ $(M+H)^+$ 463.1419, found 463.1418.



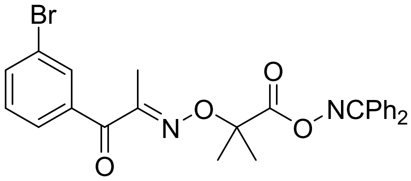
*9-(4-bromophenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dion*e ***(a**7)*

Synthesized by following General Procedure using 1-(4-bromophenyl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (526 mg, 52%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.30 (m, 10H), 7.16 (d, *J* = 8.9 Hz, 2H), 1.99 (s, 3H), 1.47 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 189.90, 170.75, 166.30, 155.34, 134.99, 134.29, 132.48, 132.28, 131.25, 131.20, 129.64, 129.06, 128.50, 128.47, 128.14, 127.90, 83.11, 24.12, 10.58.;

HRMS (ESI) m/z calcd for $C_{26}H_{24}BrN_2O_4^+$ $(M+H)^+$ 507.0914, found 507.0917.



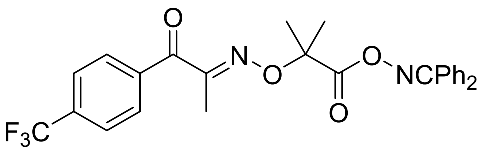
*9-(3-bromophenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione (**a8**)*

Synthesized by following General Procedure using 1-(3-bromophenyl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (207 mg, 20%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (t, *J* = 1.9 Hz, 1H), 7.79 (dd, *J* = 7.8, 2.7 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.43 – 7.19 (m, 9H), 1.97 (s, 3H), 1.49 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 189.46, 170.29, 166.11, 155.24, 137.99, 135.36, 134.01, 133.52, 132.50, 131.13, 129.37, 129.05, 128.51, 128.44, 128.12, 122.05, 83.16, 24.11, 10.52.;

HRMS (ESI) m/z calcd for $C_{26}H_{24}BrN_2O_4^+$ $(M+H)^+$ 507.0914, found 507.0911.



*5,5,8-trimethyl-1,1-diphenyl-9-(4-(trifluoromethyl)phenyl)-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dion*e ***(a9)***

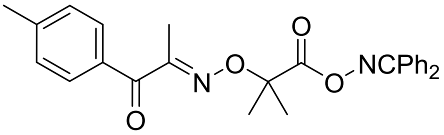
Synthesized by following General Procedure using 2-(hydroxyimino)-1-(4-(trifluoromethyl)phenyl)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (365 mg, 37%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.66 – 7.56 (m, 4H), 7.46 – 7.32 (m, 6H), 7.16 (dd, J = 7.5, 2.3 Hz, 2H), 2.01 (s, 3H), 1.47 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 190.01, 170.25, 166.39, 155.35, 140.17, 134.21,133.73 (q, J = 32.5 Hz), 132.48, 131.24, 130.97, 129.65, 129.02, 128.49, 128.42, 128.13, 124.86 (q, J = 3.8 Hz), 123.7 (q, J = 272.7 Hz), 83.25, 24.07, 9.97.;

^{19}F NMR (376 MHz, CDCl$_3$) δ -63.09.

HRMS (ESI) m/z calcd for $C_{27}H_{24}F_3N_2O_4^+$ $(M+H)^+$ 497.1683, found 497.1683.



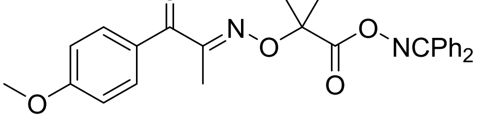
*5,5,8-trimethyl-1,1-diphenyl-9-(p-tolyl)-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dion*e ***(a10)***

Synthesized by following General Procedure using 2-(hydroxyimino)-1-(p-tolyl)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (723 mg, 82%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.78 (m, 2H), 7.60 (dd, J = 7.7, 2.2 Hz, 2H), 7.48 – 7.31 (m, 6H), 7.20 – 7.08 (m, 4H), 2.31 (s, 3H), 1.97 (d, J = 1.2 Hz, 3H), 1.48 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 190.62, 170.52, 166.02, 155.48, 143.52, 134.43, 133.58, 132.50, 131.11, 130.94, 129.55, 129.03, 128.74, 128.47, 128.44, 128.11, 82.87, 24.06, 21.56, 10.82..

HRMS (ESI) m/z calcd for $C_{27}H_{27}N_2O_4^+$ $(M+H)^+$ 443.1965, found 443.1966.



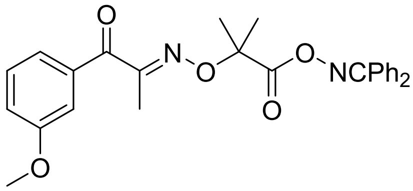
(4-methoxyphenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione ***(a11)***

Synthesized by following General Procedure using 2-(hydroxyimino)-1-(4-methoxyphenyl)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (506 mg, 55%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 – 7.91 (m, 2H), 7.61 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.46 – 7.32 (m, 6H), 7.15 (dt, *J* = 8.3, 1.2 Hz, 2H), 6.90 – 6.83 (m, 2H), 3.74 (d, *J* = 1.0 Hz, 3H), 1.97 (d, *J* = 1.0 Hz, 3H), 1.53 – 1.43 (m, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 189.32, 170.62, 166.05, 163.50, 155.56, 134.45, 133.24, 132.45, 131.11, 129.58, 129.04, 128.82, 128.51, 128.45, 128.12, 113.36, 82.76, 55.34, 24.08, 11.04.;

HRMS (ESI) m/z calcd for $C_{27}H_{27}N_2O_5^+$ $(M+H)^+$ 459.1914, found 459.1918.



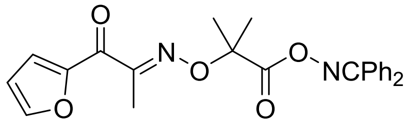
*9-(3-methoxyphenyl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione **(a12)***

Synthesized by following General Procedure using diphenylmethanone oxime (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a white solid (687 mg, 75%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.52 – 7.24 (m, 9H), 7.21 – 7.11 (m, 2H), 7.03 (dd, *J* = 8.2, 3.5 Hz, 1H), 3.81 (s, 3H), 1.99 (s, 3H), 1.54 – 1.43 (m, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 190.69, 170.48, 166.11, 159.21, 155.56, 137.47, 134.39, 132.47, 131.12, 129.57, 129.00, 128.96, 128.49, 128.43, 128.12, 123.47, 119.83, 114.53, 82.83, 55.09, 24.18, 10.85.;

HRMS (ESI) m/z calcd for $C_{29}H_{31}N_2O_3^+$ $(M+H)^+$ 459.1914, found 459.1914.



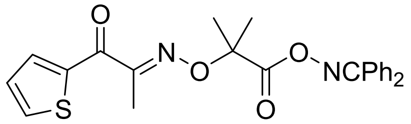
*9-(furan-2-yl)-5,5,8-trimethyl-1,1-diphenyl-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione **(a13)***

Synthesized by following General Procedure using 1-(furan-2-yl)-2-(hydroxyimino)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as white solid (576 mg, 69%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.55 (m, 3H), 7.49 – 7.30 (m, 7H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.49 (dd, *J* = 2.6, 1.2 Hz, 1H), 1.92 (d, *J* = 0.9 Hz, 3H), 1.54 (d, *J* = 1.0 Hz, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 176.73, 170.65, 166.35, 155.27, 150.19, 147.51, 134.31, 132.48, 131.15, 129.64, 129.01, 128.44, 128.40, 128.10, 122.91, 112.49, 83.03, 24.66, 9.98.;

HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2O_5^+$ $(M+H)^+$ 419.1601, found 419.1603.



*5,5,8-trimethyl-1,1-diphenyl-9-(thiophen-2-yl)-3,6-dioxa-2,7-diazanona-1,7-diene-4,9-dione **(a14)***

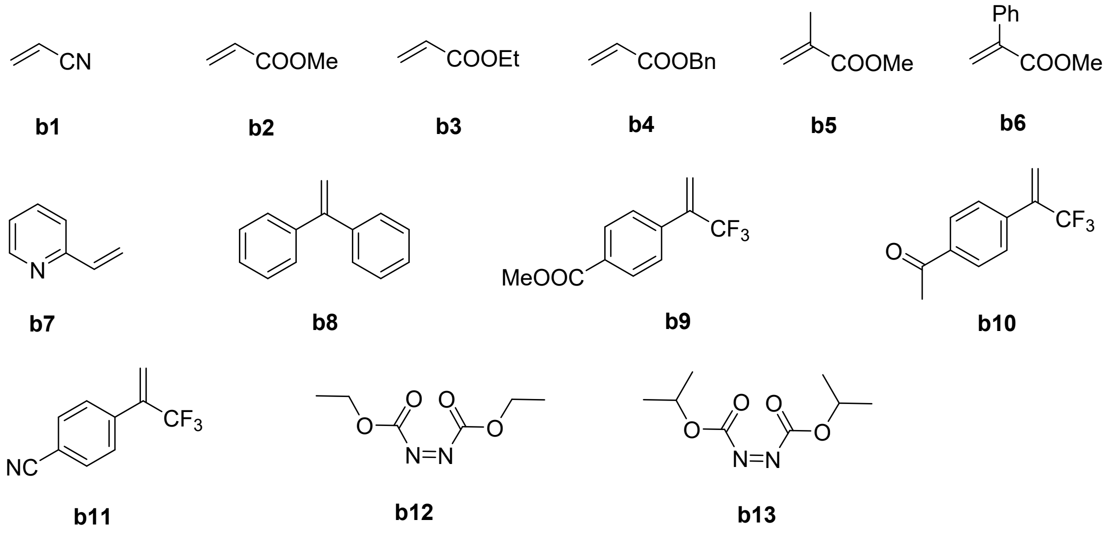
Synthesized by following General Procedure using 2-(hydroxyimino)-1-(thiophen-2-yl)propan-1-one (2.0 mmol) and O-(2-bromo-2-methylpropanoyl) oxime (2.2 mmol) to afford as a yellow oil (597 mg, 69%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (q, *J* = 2.4, 1.9 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.46 – 7.30 (m, 6H), 7.18 – 7.11 (m, 2H), 7.07 (dd, *J* = 5.1, 3.9 Hz, 1H), 1.90 (d, *J* = 1.1 Hz, 3H), 1.59 (s, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 181.01, 170.69, 166.11, 155.51, 139.32, 135.72, 135.52, 134.38, 132.55, 131.09, 129.55, 129.00, 128.41, 128.07, 127.44, 83.21, 24.36, 9.93.;

HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2O_4S^+$ $(M+H)^+$ 435.1373, found 435.1371.

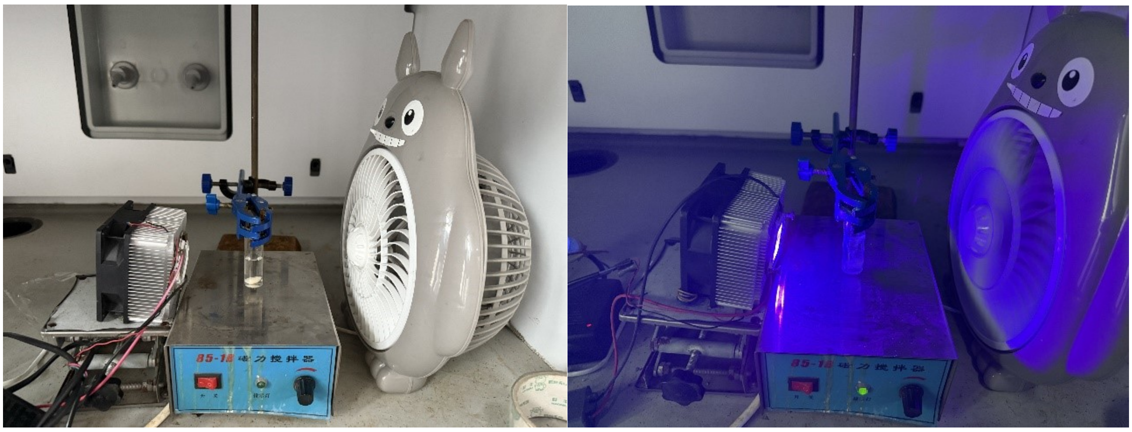
2.4 Scope of alkenes



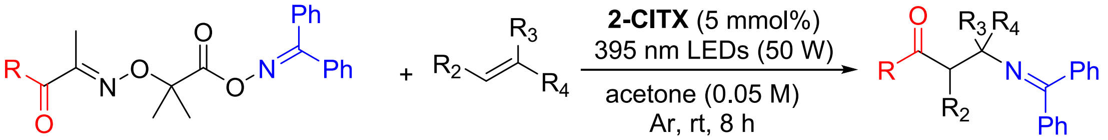
Scheme S2 Scope of alkenes. Alkenes **b1-b8** and **b12-b13** were commercially available and **b9-b11** was prepared using reported method[2].

3. Experimental section

3.1 Reaction set-up

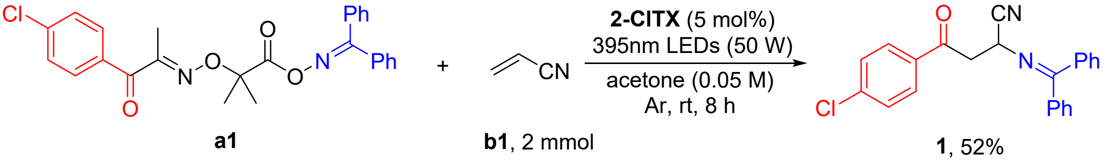


3.2 General produced for synthesis of β-aminoketones



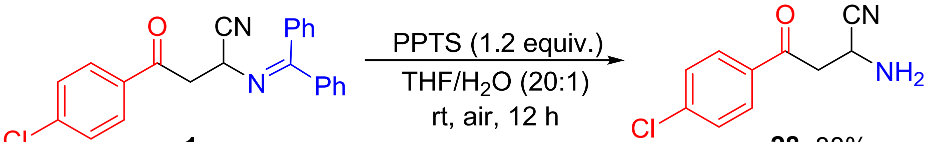
An oven dried 8 mL reaction vial was charged with a stir bar, bifunctional reagent (0.3 mmol, 1.5 equiv.), and 2-ClTX photosensitizer (2.5 mg, 5 mol %) were charged under air. The reaction vial was sealed, evacuated and backfilled three times with Ar. Then under Ar atmosphere, added of acetone (4.0 mL, 0.05 M) and alkenes (0.2 mmol, 1.0 equiv.). The reaction mixture was stirred and irradiated using a 50 W 395 nm LED lamp for 8 h until the reaction was completed. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of EtOAc (2 x 3 mL). NEt_3 (approx. 0.5 mL) and SiO_2 were added to this solution and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO_2, pre-basified with NEt_3 using pentane: EtOAc mixtures afforded the corresponding products.

3.3 Scale-up reaction



An oven dried 50 mL Schlenk tube was charged with a stir bar, bifunctional reagent **a1** (3 mmol, 1.5 equiv.), and 2-ClTX (24.7 mg, 5 mol %) were charged under air. The Schlenk tube was sealed, evacuated and backfilled three times with Ar. Then under Ar atmos, added of acetone (40 mL, 0.05 M) and acrylonitrile **b1** (2 mmol, 1.0 equiv.). The reaction mixture was stirred and irradiated using a 50 W 395 nm LED lamp for 8 h until the reaction was completed. After irradiation, the resulting homogenous solution was transferred to a 50 mL round bottom flask with aid of EtOAc (2 x 5 mL). NEt_3 (approx. 3 mL) and SiO_2 were added to this solution and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO_2, pre-basified with NEt_3 using pentane: EtOAc mixtures afforded the corresponding product **1** as a yellow solid (386.9 mg, 52% yield).

3.4 Products derivatization



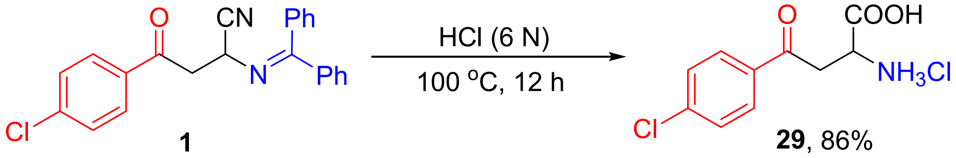
1 **28**, 88%

A 8 mL vial was charged with compound **1** (74.4 mg, 0.2 mmol), THF (2.0 mL) and H_2O (0.2 mL) were added. Pyridinium *p*-toluene sulfonate (0.24 mmol, 1.2 equiv.) was added to the vial. The reaction was stirred at room temperature for 12 h. The reaction was then diluted with EtOAc (5.0 mL) and H_2O (10.0 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (10.0 mL x 2). The combined organic phases were dried (Na_2SO_4), filtered, and evaporated. Crude mixture was purified using column chromatography to give **30** as a yellow solid (36.6 mg, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.83 (m, 2H), 7.56 – 7.41 (m, 2H), 4.30 (t, J = 5.8 Hz, 1H), 3.44 (d, J = 4.3 Hz, 2H), 2.39 (s, 2H).;

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.28, 140.61, 134.15, 129.48, 129.25, 121.26, 43.35, 38.97.;

HRMS (ESI) m/z calcd for $C_{10}H_{10}N_2OCl^+$ $(M+H)^+$ 209.0476, found 209.0478.



1

29, 86%

An oven dried 8 mL reaction vial was charged with a stir bar, compound **1** (74.4 mg, 0.2 mmol) and 6N HCl (2.0 mL) was charged under air. The reaction vial was sealed, the solution was left stirring for 12 h in 100°C. The solution was poured into 1 N HCl (10.0 mL) and extracted with Et_2O (10.0 mL x 3). The water layer was separated and water was evaporated in vacuum to give **31** as a white solid (39.2 mg, 86% yield).

^{1}H NMR (400 MHz, D_2O) δ 7.80 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 4.41 (t, J = 5.0 Hz, 1H), 3.75 (d, J = 5.0 Hz, 2H).;

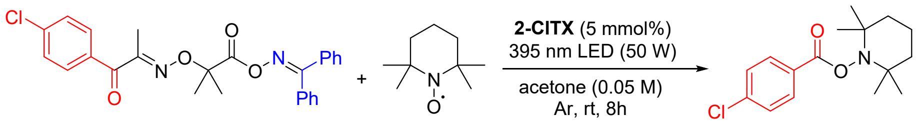
^{13}C NMR (101 MHz, D_2O) δ 197.90, 171.41, 140.44, 133.25, 129.80, 129.05, 48.71, 38.09.;

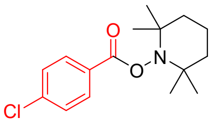
HRMS (ESI) m/z calcd for $C_{10}H_{12}Cl_2NO_3^+$ $(M+H)^+$ 264.0189, found 264.0183.

4. Mechanism Study

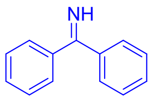
4.1 Tempo trapping experiment

An oven dried 8 mL reaction vial was charged with a stir bar, bifunctional reagent **a1** (0.3 mmol, 1.5 equiv.), **b1** (0.2 mmol, 1.0 equiv.), TEMPO (0.4 mmol, 2.0 equiv.) and 2-ClTX (2.47 mg, 5 mol %) were charged under air. The reaction vial was sealed, evacuated and backfilled three times with Ar. Then under Ar atmosphere, added of acetone (4.0 mL, 0.05 M). The reaction mixture was stirred and irradiated using a 50 W 395 nm LED lamp until the reaction was completed. Intermediates and products of the reaction process was detected by HRMS.

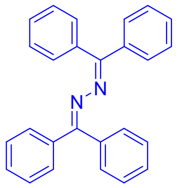




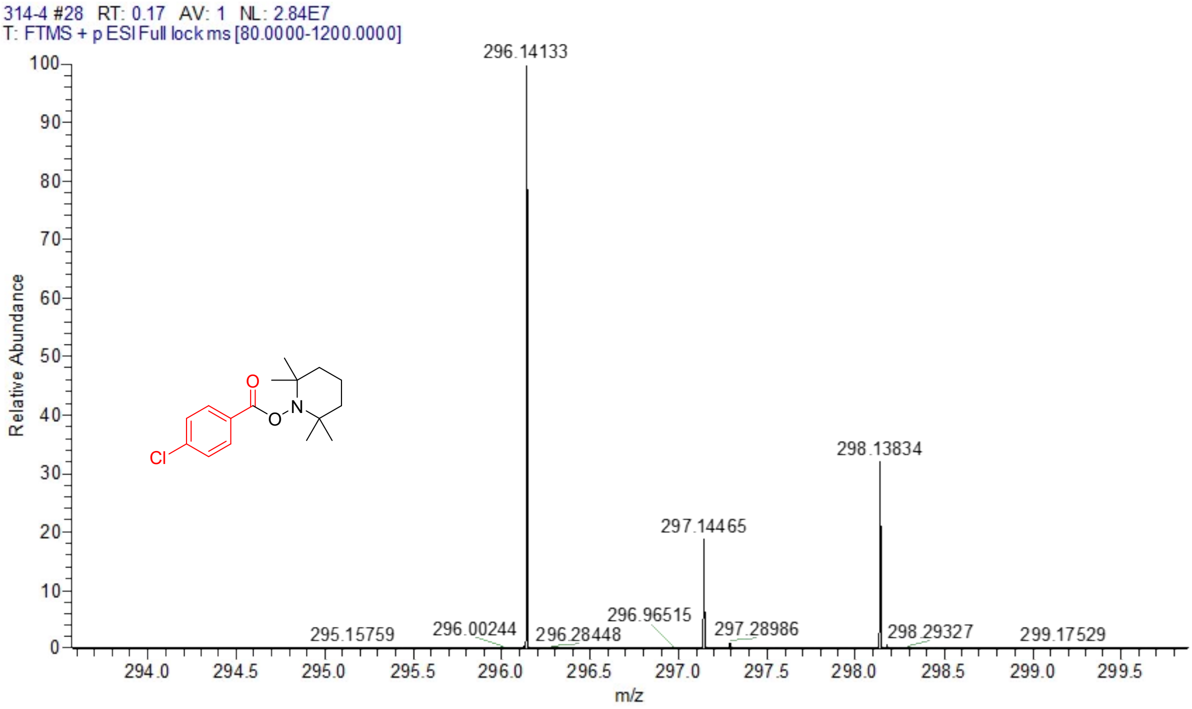
(M+H)$^+$ cals: 296.1412
found 296.1413



(M+H)$^+$ cals: 182.0964
found 182.0966



(M+H)$^+$ cals: 361.1699
found 361.1700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T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
296.14133
298.13834
297.14465
296.96515
295.15759
296.00244
296.28448
297.28986
298.29327
299.17529
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
294.0
294.5
295.0
295.5
296.0
296.5
297.0
297.5
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298.5
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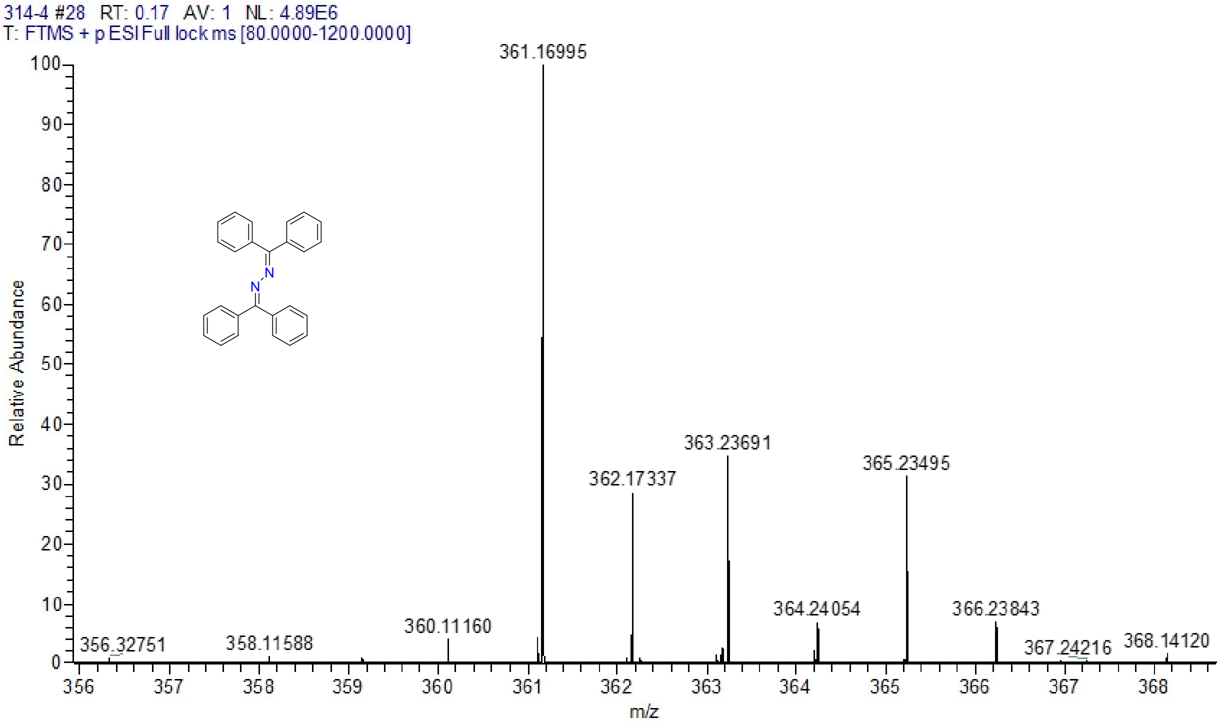
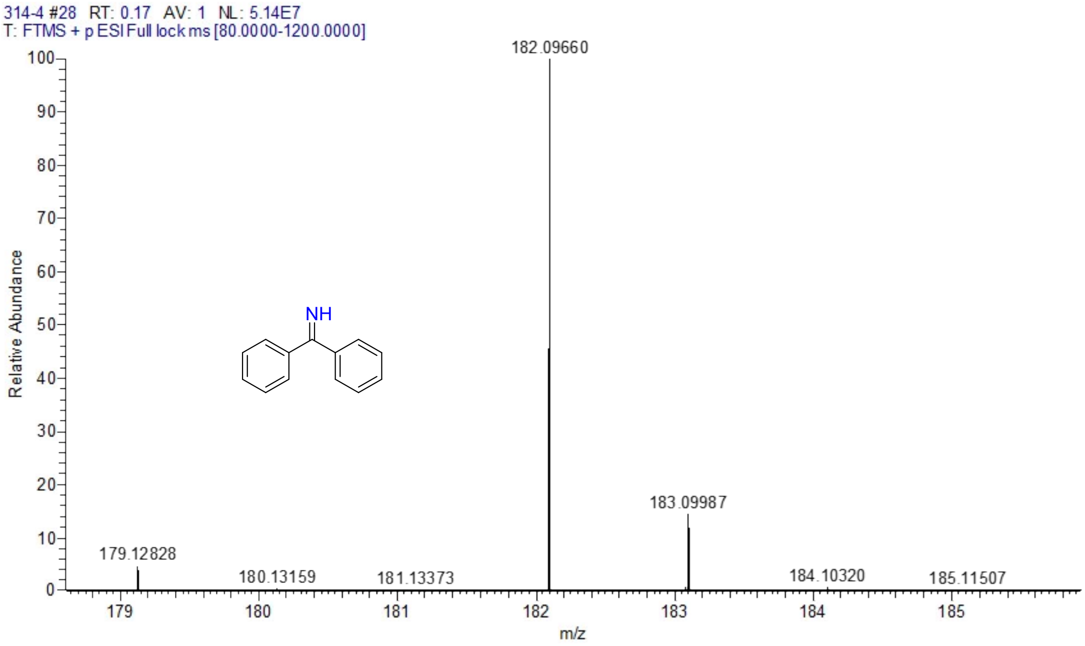
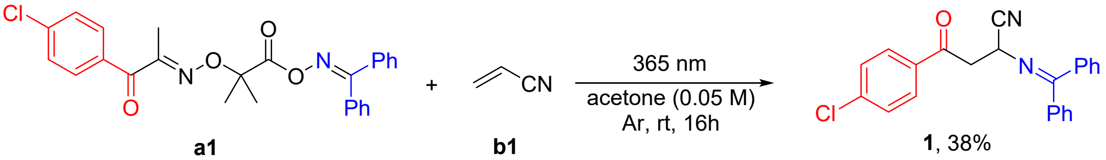
m/z
O
O
N
Cl


314-4 #28 RT: 0.17 AV: 1 NL: 4.89E6
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
361.16995
363.23691
365.23495
362.17337
364.24054
366.23843
360.11160
356.32751
358.11588
367.24216
368.14120
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
356
357
358
359
360
361
362
363
364
365
366
367
368
m/z
N
N



4.2 Direct excitation experiment



An oven dried 8 mL reaction vial was charged with a stir bar, bifunctional reagent **a1** (0.3 mmol, 1.5 equiv.), and **b1** (0.2 mmol, 1.0 equiv.) were charged under air. The reaction vial was sealed, evacuated and backfilled three times with Ar. Then under Ar atmosphere, added of acetone (4.0 mL, 0.05 M). The reaction mixture was stirred and irradiated using a 30 W 365 nm LED lamp for 16 h. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of EtOAc (2 x 3 mL). NEt_3 (approx. 0.5 mL) and SiO_2 were added to this solution and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO_2, pre-basified with NEt_3 using pentane: EtOAc mixtures afforded the corresponding product **1** in 38% yiled.

4.3 Quantum yield of the reactions

Determination of the photon flux

The photon flux was determined by ferrioxalate actinometry similar to a procedure by Xia,[3] the photon flux of the LED (λ_{max}= 395 nm) was first determined by standard ferrioxalate actinometry. For this, a 10 mL 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution). A 20 mL buffered solution of 1,10 phenanthroline was prepared by dissolving 1,10-phenanthroline (20 mg) and sodium acetate (4.5 g) in H_2SO_4 (20 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.00 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90 seconds at 395 nm with excitation and emission slit width of 10 nm on the benchtop under air. After irradiation, 0.35 mL of phenanthroline buffer solution was added to this irradiated ferrioxalate solution, stirred for 1 h to allow the ferrous ions to completely coordinate with the phenanthroline. The absorption of the solution was measured at 510 nm. A non-irradiated sample was also prepared identically and the absorption at 510 nm was also measured. Each sample preparation and measurements were repeated two more times. The average of the absorption of the irradiated and non-irradiated samples were determined and used for the calculation of photon flux.

Conversion was calculated using equation 1

$$mol\, Fe^{2+} = \frac{V \times \Delta A(510\, nm)}{l \times \varepsilon} \tag{1}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11100 L $mol^{-1}cm^{-1}$).

The average value of the experiment was 2.05×10^{-7} mol of Fe^{2+}.

The photon flux can be calculated using equation 2.

$$Photon\ flux = \frac{mol\ (Fe^{2+})}{\Phi \times t \times f} \tag{2}$$

Where *Φ* is the quantum yield for the ferrioxalate actinometer (1.13 at 395 nm), t is the irradiation time, and f is the fraction of light absorbed at λ_{max} = 390 nm by the ferrioxalate actinometer. This value is calculated using equation 3 where A (395 nm) is the absorption of the ferrioxalate solution at 395 nm.

$$f = 1 - 10^{-A(395\, nm)} \tag{3}$$

A measured absorbance value of >3 at 395 nm indicates the fraction of absorbed light (f) to be >0.999.

The average photon flux was calculated to be 2.01×10^{-9} einsteins s^{-1}

Determination of the 1,2-carbonylimination reaction quantum yield

An oven dried 8 mL reaction vial was charged with a stir bar, bifunctional reagent **a1** (0.3 mmol, 1.5 equiv.), and 2-ClTX photosensitizer (2.5 mg, 5 mol %) were charged under air. The reaction vial was sealed, evacuated and backfilled three times with Ar. Then under Ar atmosphere, added of acetone (4.0 mL, 0.05 M) and **b1** (0.2 mmol, 1.0 equiv.). The reaction mixture was stirred and irradiated using a 50 W 395 nm LED lamp for 1200s using the same setup as for the photon flux determination. Then, the NMR yield was determined (15%) using CH_2Br_2 as internal standard. The reaction quantum yield was determined using equation 4, where photon flux was determined as above described, t is the reaction time, *f* is determined by using equation 4.

$$\Phi = \frac{mol\ of\ product\ formed}{photo\ flux \times t \times f} \tag{4}$$

$$\Phi = \frac{0.0002 \times 0.15}{2.01 \times 10^{-9} \times 1200 \times 0.981} = 12.68$$

The 1,2-carbonylimination reaction quantum yield (*Φ*) was determined to be 12.68, indicating that a radical chain propagation might be operative in this reaction.

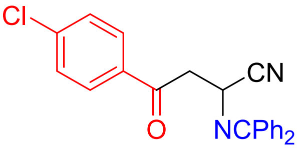
5. Reference

1. P.-Z. Wang, Y. Gao, J. Chen, X.-D. Huan, W.-J. Xiao and J.-R. Chen, *Nat. Commun.*, **2021**, 12, 1815.

2. Luo, X. L, Huang, M. S, Li, S. S, Jiang, Y. S, Chen, L. N, Li, S. H, Xia, P. J, *Org. Lett.*, **2023**, 25, 6407−6412.

3. X.-K. Qi, M.-J. Zheng, C. Yang, Y. Zhao, L. Guo and W. Xia, *J. Am. Chem. Soc.*, **2023**, 145, 16630-16641.

6. Characterization Data



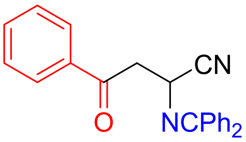
*4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-4-oxobutanenitrile (**1**)*

Compound **1** was prepared following the general procedure as a yellow solid (48.3 mg, 65%)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.32 (m, 12H), 4.92 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.89 (dd, *J* = 17.4, 8.3 Hz, 1H), 3.55 (dd, *J* = 17.4, 4.8 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.74, 174.84, 140.37, 138.35, 135.34, 134.34, 131.80, 129.58, 129.54, 129.18, 129.06, 129.04, 128.23, 127.45, 119.05, 48.94, 43.25.;

HRMS (ESI) m/z calcd for $C_{23}H_{18}ClN_2O^+$ $(M+H)^+$ 373.1102, found 373.1109.



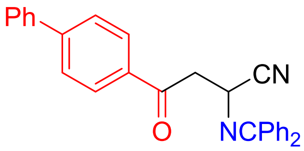
*2-((diphenylmethylene)amino)-4-oxo-4-phenylbutanenitrile (**2**)*

Compound **2** was prepared following the general procedure as a white solid (55.7 mg, 82%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 – 7.87 (m, 2H), 7.61 – 7.28 (m, 13H), 4.91 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.89 (dd, *J* = 17.4, 8.3 Hz, 1H), 3.62 – 3.51 (m, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 194.85, 174.66, 138.45, 136.05, 135.41, 133.80, 131.25, 129.49, 129.06, 129.01, 128.83, 128.20, 128.17, 127.49, 119.22, 48.58, 43.32.;

HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O^+$ $(M+H)^+$ 339.1492, found 339.1490.



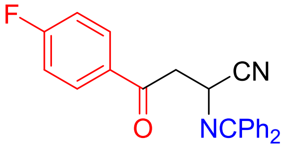
*4-([1,1'-biphenyl]-4-yl)-2-((diphenylmethylene)amino)-4-oxobutanenitrile (**3**)*

Compound **3** was prepared following the general procedure as a white solid (46.1 mg, 65%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.34 (m, 17H), 4.97 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.96 (dd, *J* = 17.3, 8.3 Hz, 1H), 3.62 (dd, *J* = 17.3, 4.8 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 194.45, 174.69, 146.48, 139.64, 138.46, 135.43, 134.74, 131.26, 129.50, 129.08, 129.05, 129.02, 128.79, 128.47, 128.21, 127.50, 127.44, 127.32, 119.25, 48.64, 43.34.;

HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2O^+$ $(M+H)^+$ 415.1805, found 415.1809.



*2-((diphenylmethylene)amino)-4-(4-fluorophenyl)-4-oxobutanenitrile (**4**)*

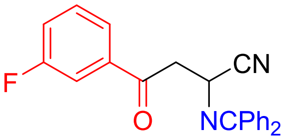
Compound **4** was prepared following the general procedure as a white solid (46.0 mg, 64%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 – 7.89 (m, 2H), 7.60 – 7.30 (m, 10H), 7.20 – 7.10 (m, 2H), 4.89 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.86 (dd, *J* = 17.4, 8.3 Hz, 1H), 3.53 (dd, *J* = 17.4, 4.8 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.30, 174.75, 166.11 (d, *J* = 166.1 Hz), 138.39, 135.36, 132.53 (d, *J* = 3.0 Hz), 131.29, 130.93, 130.84, 129.52, 129.05, 129.02, 128.22, 127.45, 119.10, 116.01 (d, *J* = 22.2 Hz), 48.55, 43.22.;

^{19}F NMR (377 MHz, CDCl$_3$) δ -63.14.

HRMS (ESI) m/z calcd for $C_{23}H_{18}FN_2O^+$ $(M+H)^+$ 357.1398, found 357.1398.



*6-((diphenylmethylene)amino)-6-(4-fluorophenyl)-4-methylhexan-1-ol (**5**)*

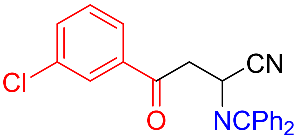
Compound **5** was prepared following the general procedure as a yellow solid (45.4 mg, 64%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.70 – 7.55 (m, 6H), 7.54 – 7.42 (m, 2H), 7.41 – 7.30 (m, 5H), 4.92 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.90 (dd, *J* = 17.5, 8.4 Hz, 1H), 3.57 (dd, J = 17.5, 4.8 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.71, 174.84, 162.92 (d, *J* = 245.9 Hz), 138.35, 138.05 (d, *J* = 6.3 Hz), 135.34, 131.32, 130.57 (d, *J* = 7.6 Hz), 129.54, 129.06, 129.04, 128.23, 127.45, 123.97 (d, *J* = 3.0 Hz), 120.89 (d, *J* = 21.8 Hz) 119.01, 114.89 (d, *J* = 22.9 Hz), 48.47, 43.45.;

^{19}F NMR (377 MHz, CDCl$_3$) δ -111.28.;

HRMS (ESI) m/z calcd for $C_{23}H_{18}FN_2O^+$ $(M+H)^+$357.1398, found 357.1396.



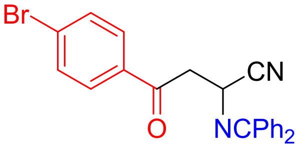
*4-(3-chlorophenyl)-2-((diphenylmethylene)amino)-4-oxobutanenitrile (**6**)*

Compound **6** was prepared following the general procedure as a yellow solid (43.7 mg, 59%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 – 7.58 (m, 2H), 7.43 – 7.20 (m, 10H), 7.03 (ddd, *J* = 13.1, 6.8, 3.1 Hz, 2H), 4.49 – 4.32 (m, 1H), 3.60 – 3.45 (m, 2H), 2.07 – 1.69 (m, 2H), 1.48 – 1.21 (m, 5H), 0.73 (dd, *J* = 37.9, 6.4 Hz, 3H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.30, 174.75, 167.41, 164.86, 138.39, 135.36, 132.54, 132.51, 131.30, 130.93, 130.84, 129.52, 129.05, 129.03, 128.22, 127.45, 119.10, 116.12, 115.90, 48.55, 43.21.;

HRMS (ESI) m/z calcd for $C_{23}H_{18}ClN_2O^+$ $(M+H)^+$ 373.1102, found 373.1101.



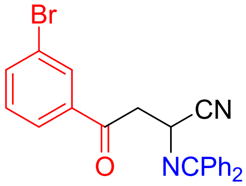
4-(4-bromophenyl)-2-((diphenylmethylene)amino)-4-oxobutanenitrile (7)

Compound **7** was prepared following the general procedure as a white solid (59.4 mg, 71%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, *J* = 6.7 Hz, 2H), 7.61 – 7.32 (m, 12H), 4.88 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.85 (dd, *J* = 17.4, 8.3 Hz, 1H), 3.51 (dd, *J* = 17.4, 4.8 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.95, 174.82, 138.35, 135.34, 134.76, 132.18, 131.33, 129.65, 129.54, 129.06, 129.04, 128.37, 128.23, 127.45, 119.04, 48.50, 43.24.;

HRMS (ESI) m/z calcd for $C_{23}H_{18}BrN_2O^+$ $(M+H)^+$ 417.0597, found 417.0594.



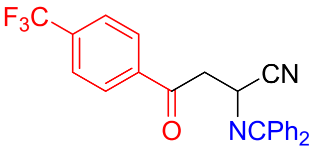
*4-(3-bromophenyl)-2-((diphenylmethylene)amino)-4-oxobutanenitrile (**8**)*

Compound **8** was prepared following the general procedure as a white solid (48.5 mg, 58%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (t, *J* = 1.8 Hz, 1H), 7.90 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.75 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.66 – 7.52 (m, 5H), 7.49 – 7.31 (m, 6H), 4.91 (dd, *J* = 8.4, 4.7 Hz, 1H), 3.90 (dd, *J* = 17.5, 8.4 Hz, 1H), 3.55 (dd, *J* = 17.5, 4.7 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$)δ 193.65, 174.86, 138.31, 137.71, 136.65, 135.33, 131.33, 131.26, 130.42, 129.54, 129.07, 129.03, 128.23, 127.44, 126.69, 123.22, 118.96, 48.46, 43.35.;

HRMS (ESI) m/z calcd for $C_{23}H_{18}BrN_2O$ $^+$ $(M+H)^+$ 417.0597, found 417.0598.



*2-((diphenylmethylene)amino)-4-oxo-4-(4-(trifluoromethyl)phenyl)butanenitrile (**9**)*

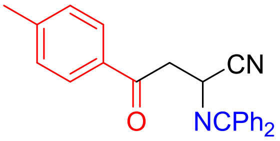
Compound **9** was prepared following the general procedure as a yellow oil (36.7 mg, 45%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.33 (m, 10H), 4.94 (dd, *J* = 8.4, 4.7 Hz, 1H), 3.95 (dd, *J* = 17.5, 8.4 Hz, 1H), 3.60 (dd, *J* = 17.5, 4.7 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 194.07, 175.03, 138.61, 138.28, 135.30, 135.05 (q, *J* = 33.0 Hz), 131.38, 130.42, 129.58, 129.06, 128.53, 128.49, 128.37, 128.24, 125.93 (q, *J* = 3.9 Hz), 123.49 (q, *J* = 273.2 Hz), 118.89, 48.43, 43.55.;

^{19}F NMR (377 MHz, CDCl$_3$) δ -63.18.

HRMS (ESI) m/z calcd for $C_{24}H_{18}F_3N_2O^+$ $(M+H)^+$ 407.1366, found 407.1373.



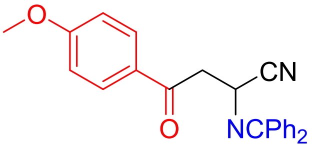
*2-((diphenylmethylene)amino)-4-oxo-4-(p-tolyl)butanenitrile (**10**)*

Compound **10** was prepared following the general procedure as a yellow solid (52.3 mg, 74%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.67 – 7.54 (m, 5H), 7.46 – 7.27 (m, 7H), 4.94 (dd, *J* = 8.3, 4.9 Hz, 1H), 3.90 (dd, *J* = 17.4, 8.3 Hz, 1H), 3.57 (dd, *J* = 17.4, 4.9 Hz, 1H), 2.45 (s, 3H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 194.45, 174.56, 144.76, 138.50, 135.44, 133.63, 131.23, 129.51, 129.48, 129.07, 129.01, 128.30, 128.20, 127.51, 119.32, 48.64, 43.20, 21.75.;

HRMS (ESI) m/z calcd for $C_{27}H_{32}NO^+$ $(M+H)^+$ 353.1648, found 353.1659.



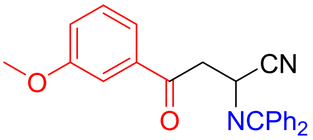
*2-((diphenylmethylene)amino)-4-(4-methoxyphenyl)-4-oxobutanenitrile (**11**)*

Compound **11** was prepared following the general procedure as a yellow oil (63.3 mg, 86%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 – 7.86 (m, 2H), 7.68 – 7.30 (m, 10H), 7.01 – 6.92 (m, 2H), 4.94 (dd, *J* = 8.2, 5.0 Hz, 1H), 3.89 (s, 4H), 3.54 (dd, *J* = 17.2, 4.9 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.32, 174.54, 164.03, 138.50, 135.43, 131.22, 130.52, 129.47, 129.17, 129.06, 129.00, 128.20, 127.49, 119.37, 113.98, 55.58, 48.72, 42.94.;

HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2O_2^+$ $(M+H)^+$ 369.1598, found 369.1600.



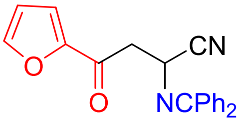
*2-((diphenylmethylene)amino)-4-(3-methoxyphenyl)-4-oxobutanenitrile (**12**)*

Compound **12** was prepared following the general procedure as a white solid (48.9 mg, 66%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 – 7.51 (m, 6H), 7.51 – 7.30 (m, 7H), 7.17 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 4.93 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.98 – 3.81 (m, 4H), 3.58 (dd, *J* = 17.5, 4.9 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 194.70, 174.65, 159.96, 138.44, 137.37, 135.42, 131.27, 129.84, 129.50, 129.07, 129.02, 128.21, 127.49, 120.84, 120.46, 119.22, 112.17, 55.51, 48.59, 43.43.;

HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2O_2^+$ $(M+H)^+$ 369.1598, found 369.1594.



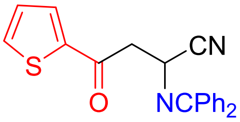
*2-((diphenylmethylene)amino)-4-(furan-2-yl)-4-oxobutanenitrile **(13)***

Compound **13** was prepared following the general procedure as a yellow solid (47.6 mg, 73%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 – 7.53 (m, 6H), 7.48 – 7.23 (m, 7H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.91 (dd, *J* = 8.9, 4.5 Hz, 1H), 3.81 (dd, *J* = 17.0, 8.8 Hz, 1H), 3.41 (dd, *J* = 17.0, 4.5 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 183.71, 174.80, 152.02, 147.06, 138.38, 135.32, 131.26, 129.48, 129.07, 128.98, 128.18, 127.46, 118.93, 118.08, 112.60, 47.56, 42.91.;

HRMS (ESI) m/z calcd for $C_{31}H_{33}N_2O^+$ $(M+H)^+$ 329.1285, found 329.1280.



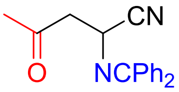
*6-((diphenylmethylene)amino)-7,7,7-trifluoro-4-methyl-6-(quinolin-3-yl)heptan-1-ol **(14)***

Compound **14** was prepared following the general procedure as a yellow oil (39.7 mg, 58%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 (ddd, *J* = 41.3, 4.4, 1.2 Hz, 2H), 7.65 – 7.51 (m, 5H), 7.48 – 7.31 (m, 5H), 7.19 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.93 (dd, *J* = 8.7, 4.5 Hz, 1H), 3.88 (dd, *J* = 16.8, 8.7 Hz, 1H), 3.50 (dd, *J* = 16.8, 4.6 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 187.60, 174.85, 143.21, 138.39, 135.32, 134.68, 132.79, 131.30, 129.52, 129.08, 129.02, 128.41, 128.21, 127.46, 118.98, 48.51, 43.72.;

HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2OS^+$ $(M+H)^+$345.1056, found 345.1055.



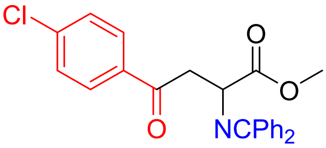
*2-((diphenylmethylene)amino)-7-hydroxy-4-methylheptanenitrile **(15)***

Compound **15** was prepared following the general procedure as a white solid (27.8 mg, 50%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 – 7.57 (m, 2H), 7.53 – 7.39 (m, 4H), 7.35 – 7.28 (m, 4H), 4.68 (ddd, *J* = 8.4, 4.8, 0.9 Hz, 1H), 3.29 (dd, *J* = 17.5, 8.4 Hz, 1H), 3.04 (dd, *J* = 17.5, 4.7 Hz, 1H), 2.19 (d, *J* = 0.8 Hz, 3H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 203.26, 174.66, 138.38, 135.29, 131.27, 129.47, 129.02, 128.97, 128.21, 127.42, 118.89, 48.13, 47.51, 30.39.;

HRMS (ESI) m/z calcd for $C_{21}H_{25}N_2O^+$ $(M+H)^+$277.1335, found 277.1336.



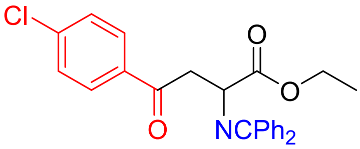
*methyl 4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-4-oxobutanoate (**16**)*

Compound **16** was prepared following the general procedure as a yellow oil (26.9 mg, 33%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 – 7.88 (m, 2H), 7.64 – 7.56 (m, 2H), 7.50 – 7.29 (m, 10H), 4.88 – 4.74 (m, 1H), 3.79 – 3.71 (m, 4H), 3.48 (dd, *J* = 17.1, 7.1 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.06, 171.98, 171.94, 139.67, 139.36, 136.05, 135.10, 130.55, 129.61, 128.92, 128.89, 128.86, 128.51, 128.07, 127.90, 61.69, 52.51, 42.16.;

HRMS (ESI) m/z calcd for $C_{24}H_{21}ClNO_3^+$ $(M+H)^+$ 406.1204, found 406.1205.



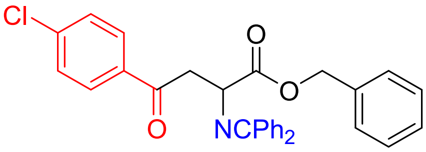
*ethyl 4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-4-oxobutanoate (**17**)*

Compound **17** was prepared following the general procedure as a yellow oil (33.6 mg, 40%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 – 7.89 (m, 2H), 7.65 – 7.57 (m, 2H), 7.55 – 7.30 (m, 10H), 4.84 – 4.71 (m, 1H), 4.27 – 4.13 (m, 2H), 3.74 (dd, *J* = 17.1, 5.8 Hz, 1H), 3.49 (dd, *J* = 17.1, 7.1 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.20, 171.89, 171.35, 139.63, 139.43, 136.14, 135.18, 130.49, 129.62, 128.90, 128.86, 128.81, 128.45, 128.05, 127.95, 61.82, 61.40, 42.10, 14.14.;

HRMS (ESI) m/z calcd for $C_{25}H_{23}ClNO_3^+$ $(M+H)^+$ 420.1361, found 420.1368.



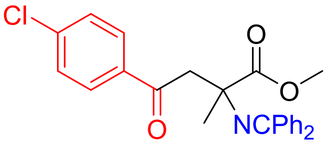
*benzyl 4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-4-oxobutanoate (**18**)*

Compound **18** was prepared following the general procedure as a yellow oil (35.3 mg, 49%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 – 7.88 (m, 2H), 7.59 (dd, *J* = 7.7, 2.1 Hz, 2H), 7.46 – 7.32 (m, 13H), 7.25 – 7.20 (m, 2H), 5.21 (d, *J* = 1.8 Hz, 2H), 4.85 (dd, *J* = 7.1, 5.8 Hz, 1H), 3.77 (dd, *J* = 17.1, 5.8 Hz, 1H), 3.53 (dd, *J* = 17.1, 7.2 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.11, 172.16, 171.15, 139.66, 139.37, 136.05, 135.66, 135.15, 130.54, 129.64, 128.92, 128.89, 128.80, 128.53, 128.46, 128.25, 128.16, 128.07, 127.93, 66.98, 61.84, 42.06.;

HRMS (ESI) m/z calcd for $C_{30}H_{25}ClNO_3^+$ $(M+H)^+$ 482.1517, found 482.1514.



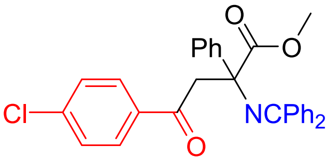
*methyl 4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-2-methyl-4-oxobutanoate (**19**)*

Compound **19** was prepared following the general procedure as a yellow oil (48.2 mg, 56%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 – 7.90 (m, 2H), 7.48 – 7.18 (m, 12H), 3.79 – 3.64 (m, 2H), 3.34 (s, 3H), 1.62 (s, 3H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.83, 174.08, 166.82, 140.81, 139.44, 136.84, 135.88, 130.21, 129.71, 128.81, 128.61, 128.50, 128.45, 127.95, 127.93, 65.72, 51.93, 50.53, 24.46.;

HRMS (ESI) m/z calcd for $C_{26}H_{31}N_2O^+$ $(M+H)^+$ 420.1361, found 420.1366.



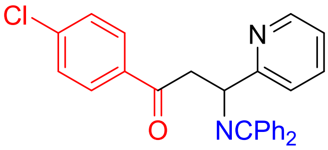
*methyl 4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-4-oxo-2-phenylbutanoate (**20**)*

Compound **20** was prepared following the general procedure as a yellow oil (80.1 mg, 83%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 – 7.52 (m, 6H), 7.41 – 7.16 (m, 11H), 6.87 (dd, J = 7.5, 2.0 Hz, 2H), 3.96 (d, J = 16.5 Hz, 1H), 3.85 (d, J = 16.5 Hz, 1H), 3.64 (s, 3H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 195.39, 173.81, 167.68, 143.02, 141.01, 139.15, 137.74, 135.63, 130.33, 129.50, 128.85, 128.54, 128.43, 128.41, 127.98, 127.89, 127.83, 127.53, 126.69, 70.12, 52.71, 48.36.;

HRMS (ESI) m/z calcd for $C_{30}H_{25}ClNO_3^+$ $(M+H)^+$482.1517, found 482.1517.



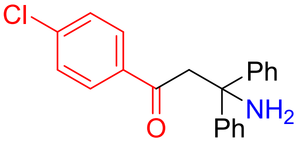
*1-(4-chlorophenyl)-3-((diphenylmethylene)amino)-3-(pyridin-2-yl)propan-1-one (**21**)*

Compound **21** was prepared following the general procedure as a colorless oil (46.2 mg, 54%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, J = 4.8 Hz, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.6 Hz, 3H), 7.36 (dt, J = 26.0, 6.4 Hz, 9H), 7.19 – 7.03 (m, 3H), 5.28 (dd, J = 8.3, 4.6 Hz, 1H), 3.75 (qd, J = 15.9, 6.4 Hz, 2H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.23, 169.65, 162.16, 149.06, 140.19, 139.21, 136.68, 136.47, 135.58, 130.26, 129.77, 128.79, 128.75, 128.58, 128.37, 128.03, 127.64, 121.96, 121.55, 64.26, 46.37.;

HRMS (ESI) m/z calcd for $C_{27}H_{22}ClN_2O^+$ $(M+H)^+$ 425.1415, found 425.1411.



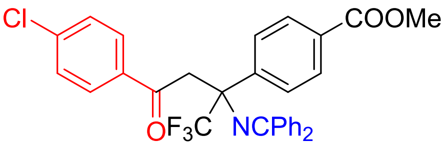
*3-amino-1-(4-chlorophenyl)-3,3-diphenylpropan-1-one (**22**)*

Compound **22** was prepared following the general procedure as a white solid (62.7 mg, 94%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.76 (m, 2H), 7.41 – 7.20 (m, 12H), 3.88 (s, 2H), 2.66 (s, 2H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.57, 147.94, 139.62, 135.82, 129.38, 128.85, 128.28, 126.70, 126.44, 60.79, 50.20.;

HRMS (ESI) m/z calcd for $C_{21}H_{19}ClNO^+$ $(M+H)^+$ 336.1150, found 336.1145.



methyl 4-(4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-1,1,1-trifluoro-4-oxobutan-2-yl)benzoate ***(23)***

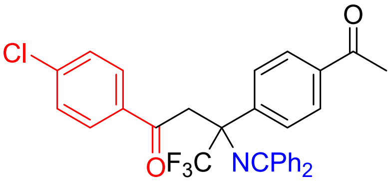
Compound **23** was prepared following the general procedure as a white solid (77.5 mg, 71%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.79 – 7.62 (m, 6H), 7.47 – 7.36 (m, 5H), 7.18 – 7.10 (m, 1H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.72 (s, 2H), 4.11 – 3.93 (m, 4H), 3.22 (d, *J* = 16.8 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 192.69, 169.92, 166.63, 145.68, 140.76, 139.55, 137.75, 135.66, 130.74, 130.11, 129.43, 129.32, 128.98, 128.80, 128.36, 128.13, 128.03, 127.79, 127.66, 126.0 (q, *J* = 286.4 Hz), 68.59 (q, *J* = 25.7 Hz), 52.28, 38.62.;

^{19}F NMR (377 MHz, CDCl$_3$) δ -75.14.;

HRMS (ESI) m/z calcd for $C_{32}H_{37}N_2O^+$ $(M+H)^+$ 550.1391, found 550.1388.



3-(4-acetylphenyl)-1-(4-chlorophenyl)-3-((diphenylmethylene)amino)-4,4,4-trifluorobutan-1-one (24)

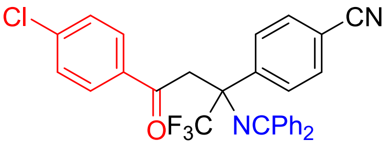
Compound **24** was prepared following the general procedure as a white solid (50.6 mg, 47%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.70 (ddd, *J* = 8.4, 6.0, 1.4 Hz, 6H), 7.58 – 7.33 (m, 6H), 7.19 – 6.94 (m, 3H), 6.74 (s, 2H), 4.01 (d, *J* = 17.0 Hz, 1H), 3.26 (d, *J* = 17.0 Hz, 1H), 2.65 (s, 3H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.65, 192.62, 169.79, 145.79, 140.77, 139.59, 137.73, 136.76, 135.53, 130.75, 129.27, 128.97, 128.78, 128.37, 128.19, 128.13, 127.81, 127.67,125.88 (q, *J* = 283.8 Hz), 68.61 (q, *J* = 26.1 Hz), 38.78, 26.72.;

^{19}F NMR (377 MHz, CDCl$_3$) δ -75.05.

HRMS (ESI) m/z calcd for $C_{31}H_{24}ClF_3NO_2^+$ $(M+H)^+$ 534.1442, found 534.1449.



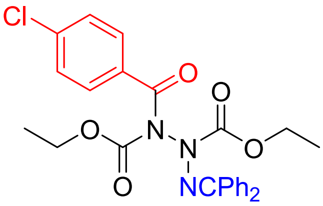
*4-(4-(4-chlorophenyl)-2-((diphenylmethylene)amino)-1,1,1-trifluoro-4-oxobutan-2-yl)benzonitrile (**25**)*

Compound **25** was prepared following the general procedure as a white solid (70.0 mg, 68%).;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 – 7.60 (m, 8H), 7.47 – 7.35 (m, 5H), 7.20 – 6.96 (m, 3H), 6.80 (s, 2H), 3.97 (d, J = 17.3 Hz, 1H), 3.37 (d, J = 17.2 Hz, 1H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 192.40, 170.09, 145.78, 140.62, 139.79, 137.53, 135.21, 131.96, 130.96, 129.26, 128.97, 128.82, 128.75, 128.51, 128.20, 127.85, 127.75, 125.60 (q, J = 285.9 Hz), 118.48, 112.27, 68.61 (q, J = 25.7 Hz), 39.02.;

HRMS (ESI) m/z calcd for $C_{30}H_{20}ClF_3N_2O^+$ (M+H)$^+$ 517.1289, found 517.1287.



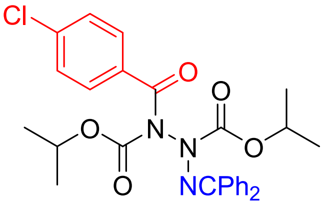
*diethyl 1-(4-chlorobenzoyl)-3-(diphenylmethylene)triazane-1,2-dicarboxylate (**26**)*

Compound **26** was prepared following the general procedure as a white solid (68.7 mg, 75%).;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.28 (m, 14H), 4.36 – 3.99 (m, 4H), 1.33 – 1.04 (m, 6H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 168.72, 152.06, 138.25, 135.80, 133.27, 129.53, 129.03, 128.69, 128.25, 128.08, 64.02, 14.22.;

HRMS (ESI) m/z calcd for $C_{26}H_{25}ClN_3O_5^+$ (M+H)$^+$ 494.1477, found 494.1478.



*diisopropyl 1-(4-chlorobenzoyl)-3-(diphenylmethylene)triazane-1,2-dicarboxylate (**27**)*

Compound **27** was prepared following the general procedure as a yellow oil (73.7 mg, 66%).;

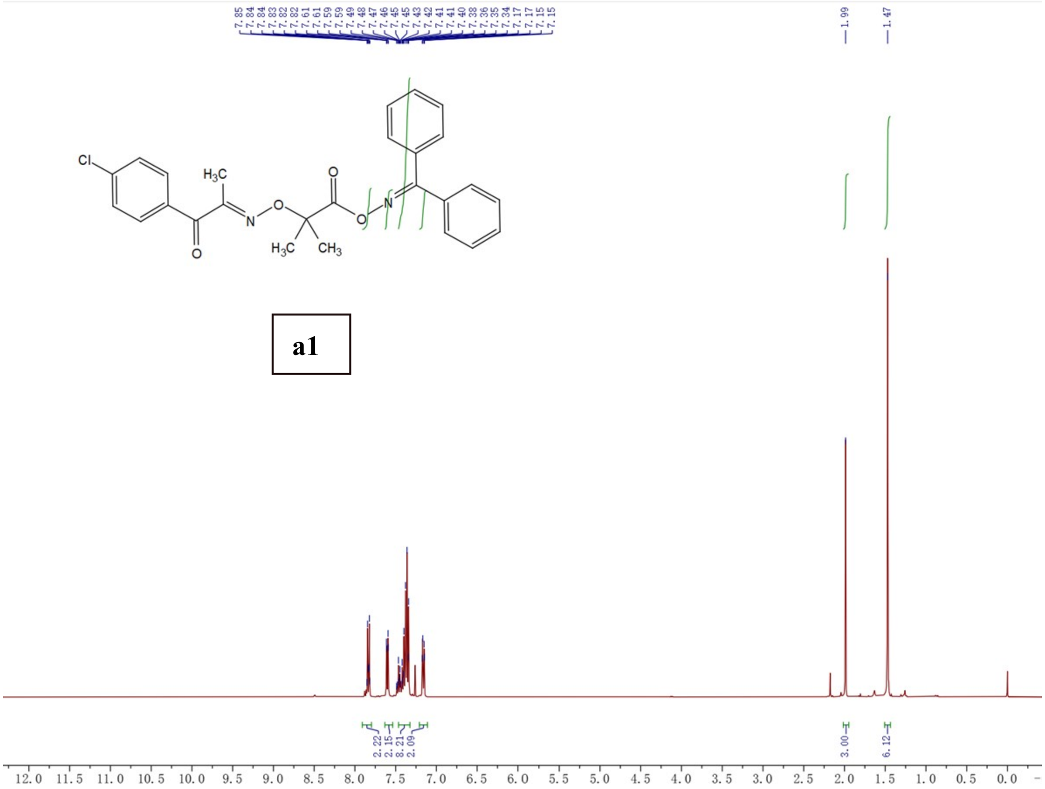
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 – 7.48 (m, 5H), 7.39 (ddt, J = 24.8, 15.1, 7.7 Hz, 9H), 5.04 – 4.74 (m, 2H), 1.16 (q, J = 25.3, 19.3 Hz, 12H).;

^{13}C NMR (101 MHz, CDCl$_3$) δ 168.80, 165.17, 153.63, 152.36, 151.73, 138.15, 133.58, 130.47, 129.59, 129.24, 128.86, 128.31, 128.03, 127.84, 72.64, 46.18, 21.64, 21.55.;

HRMS (ESI) m/z calcd for $C_{29}H_{35}N_2O^+$ (M+H)$^+$ 522.1790, found 522.1787.

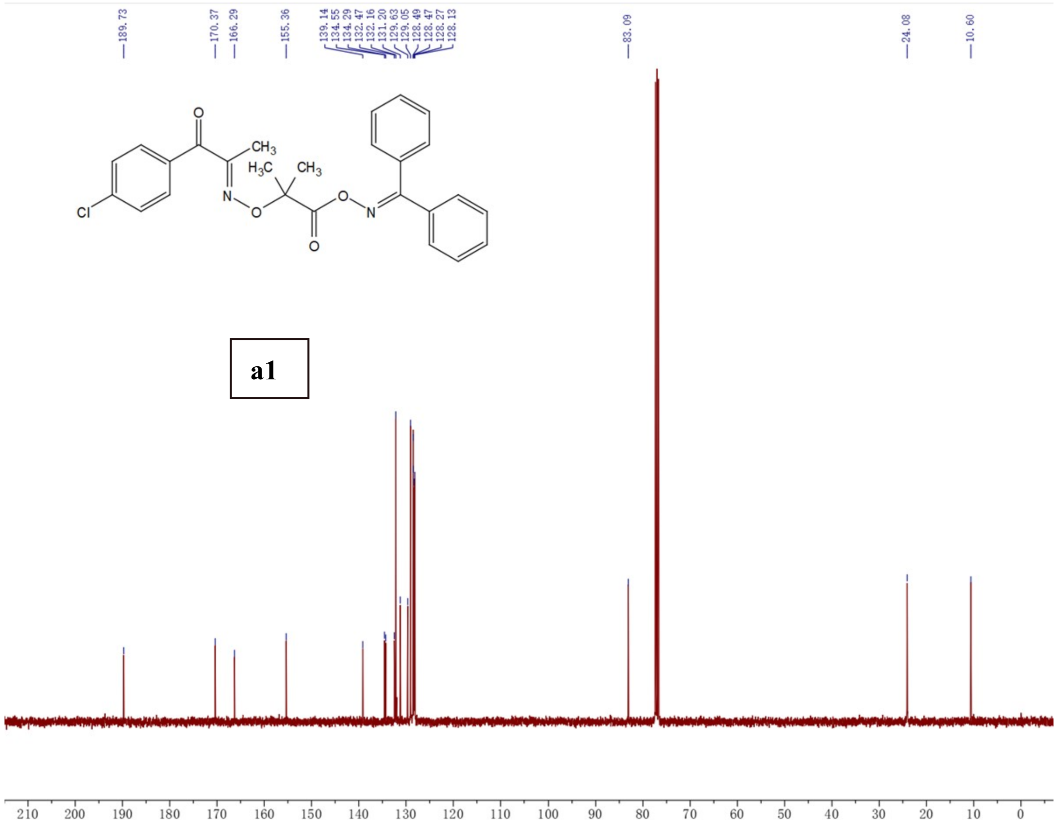
7. NMR Spectrum

^{1}H NMR (400 MHz, $CDCl_3$)

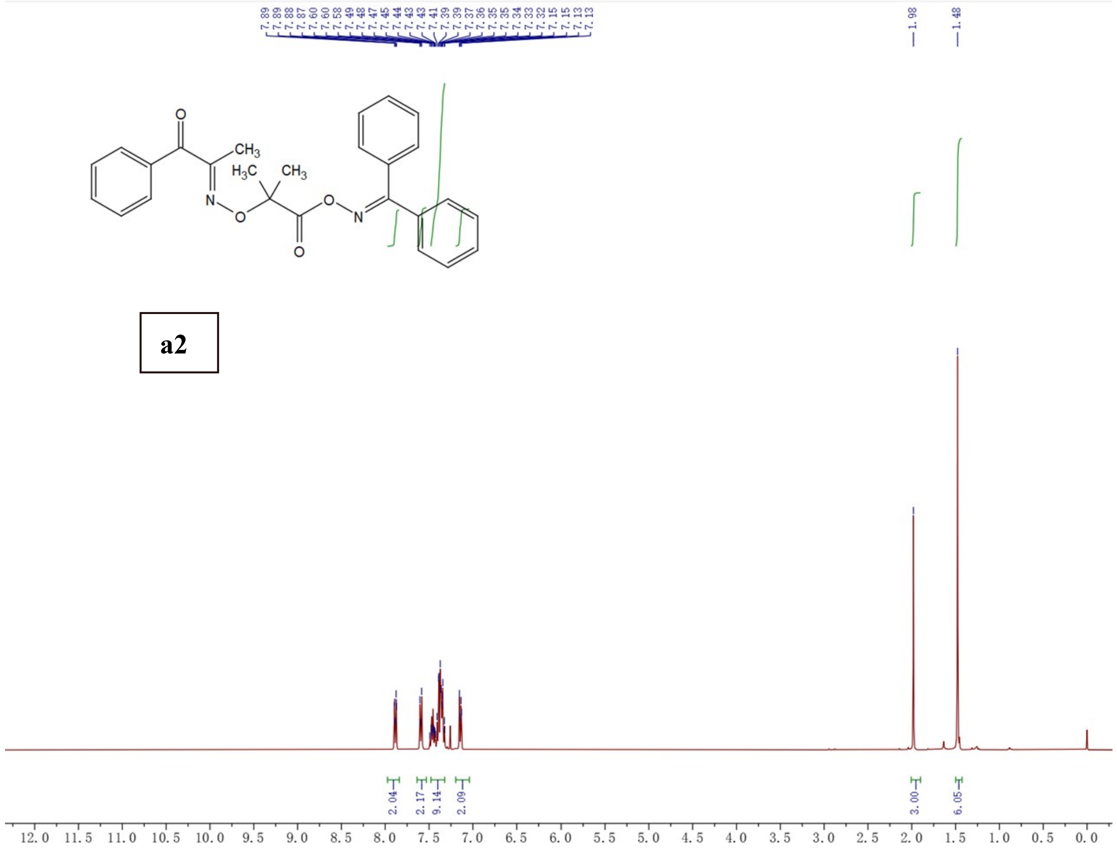


a1

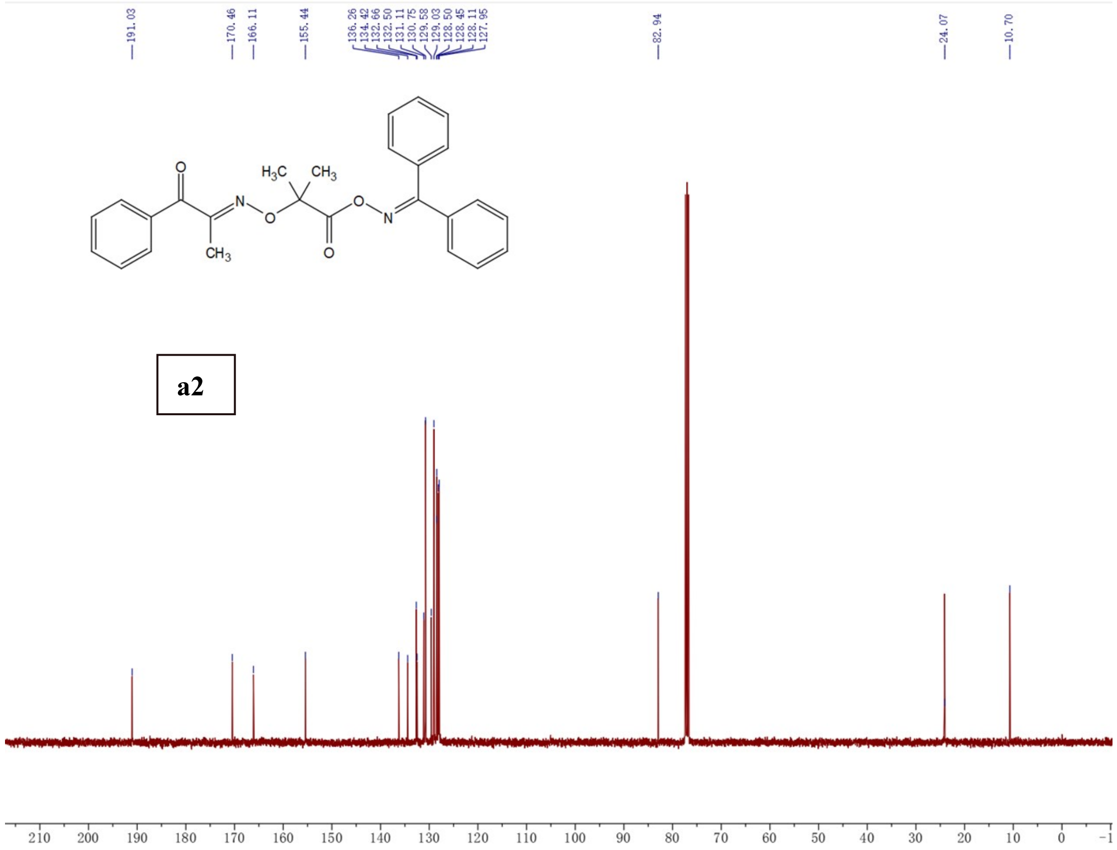
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, CDCl$_3$)

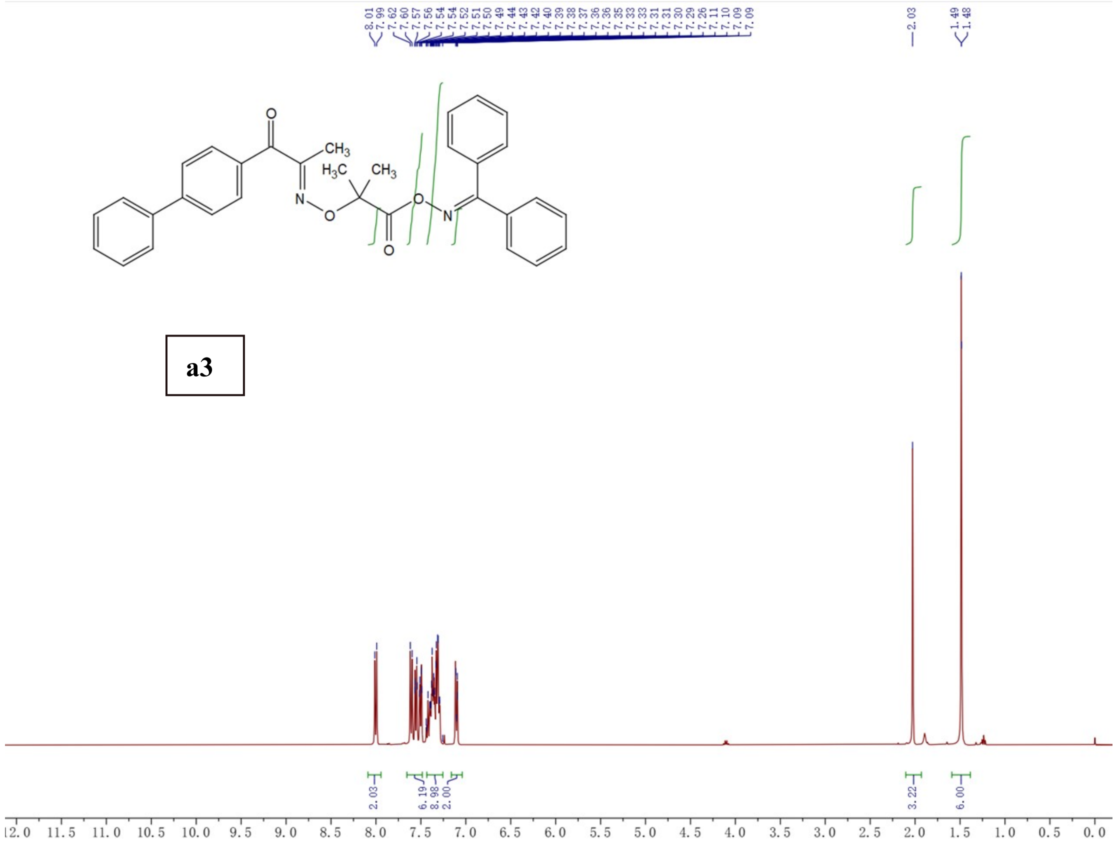


^{13}C NMR (101 MHz, CDCl$_3$)



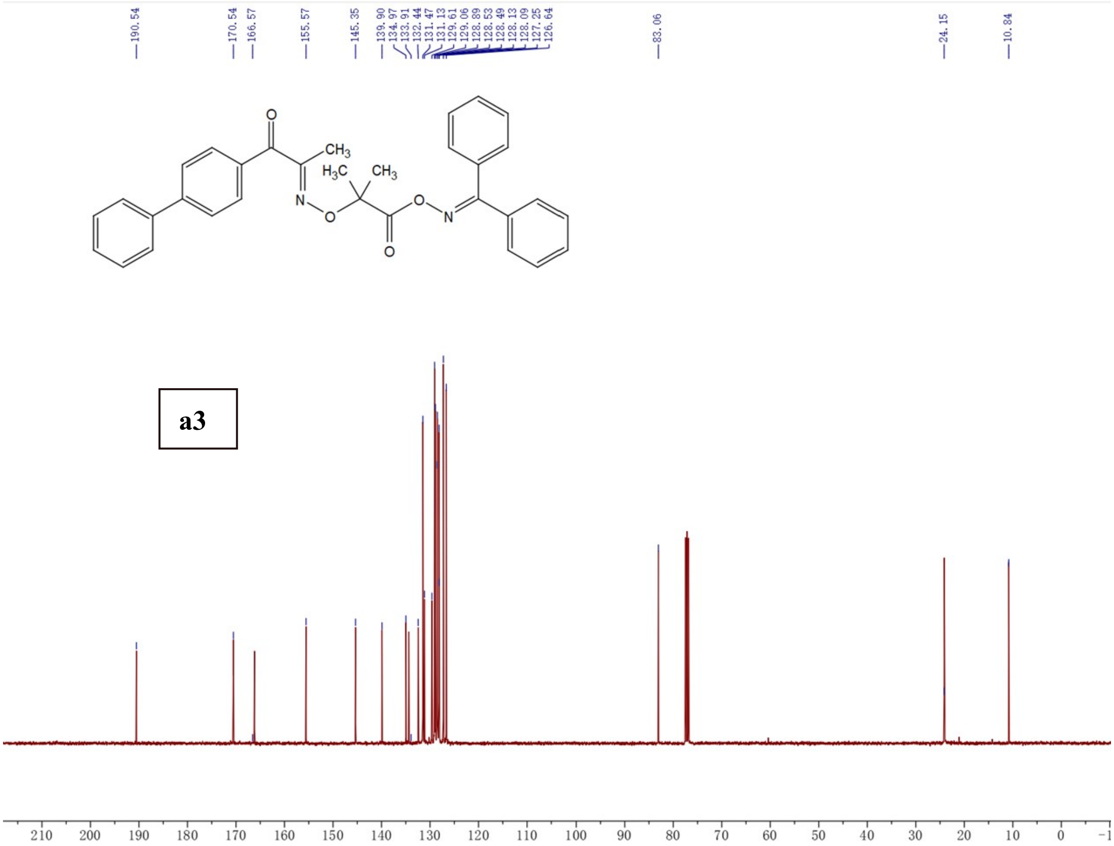
a2

^{1}H NMR (400 MHz, CDCl$_3$)



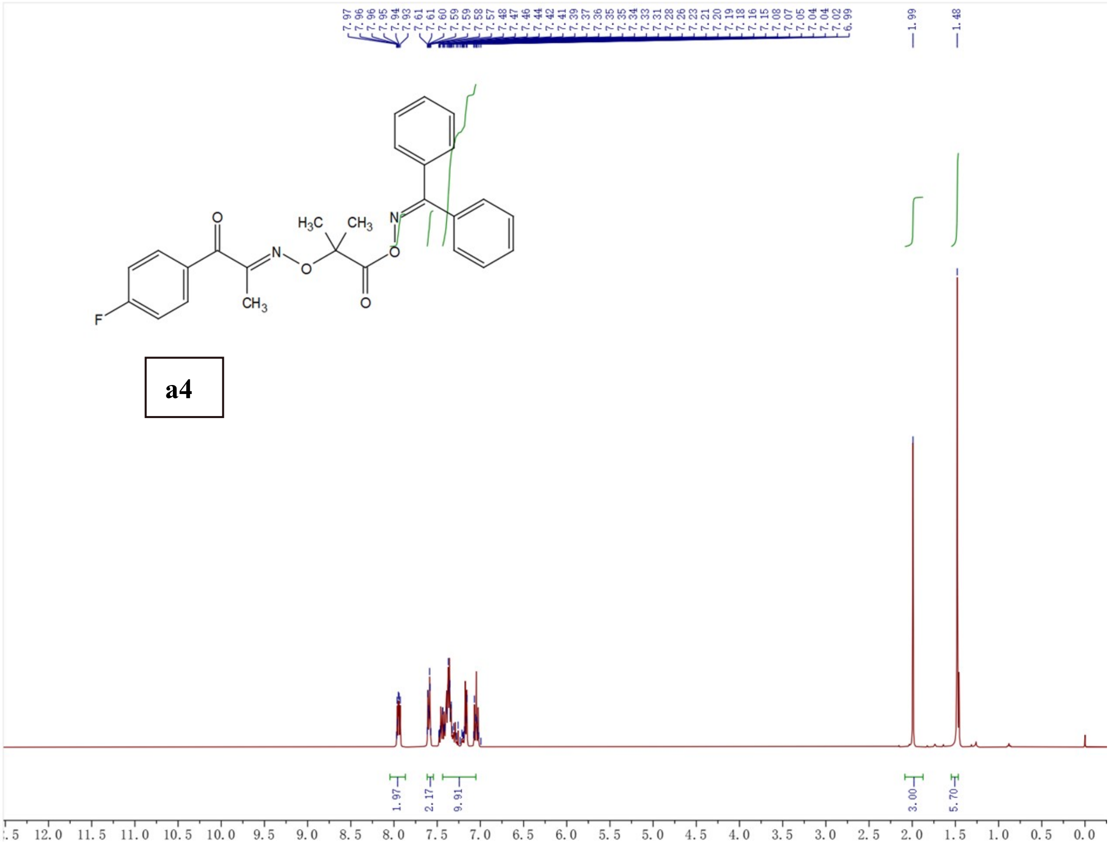
a3

^{13}C NMR (101 MHz, CDCl$_3$)



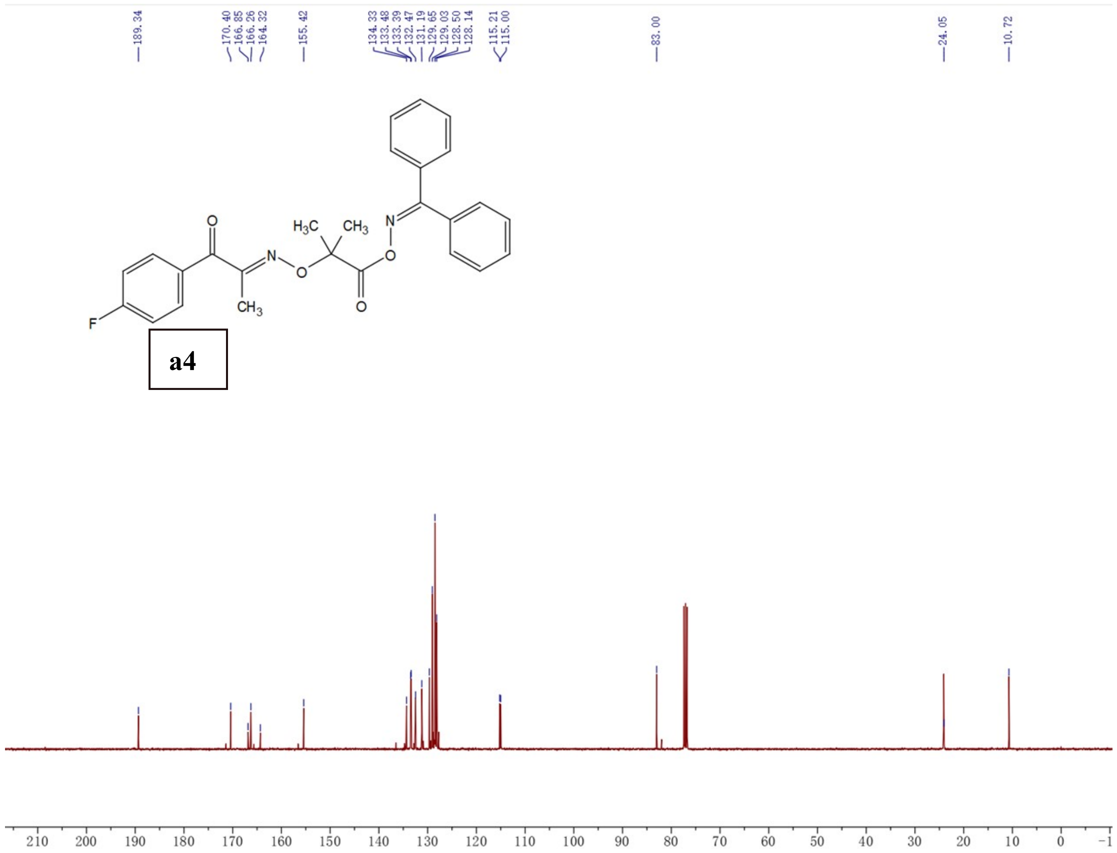
a3

^{1}H NMR (400 MHz, CDCl$_3$)



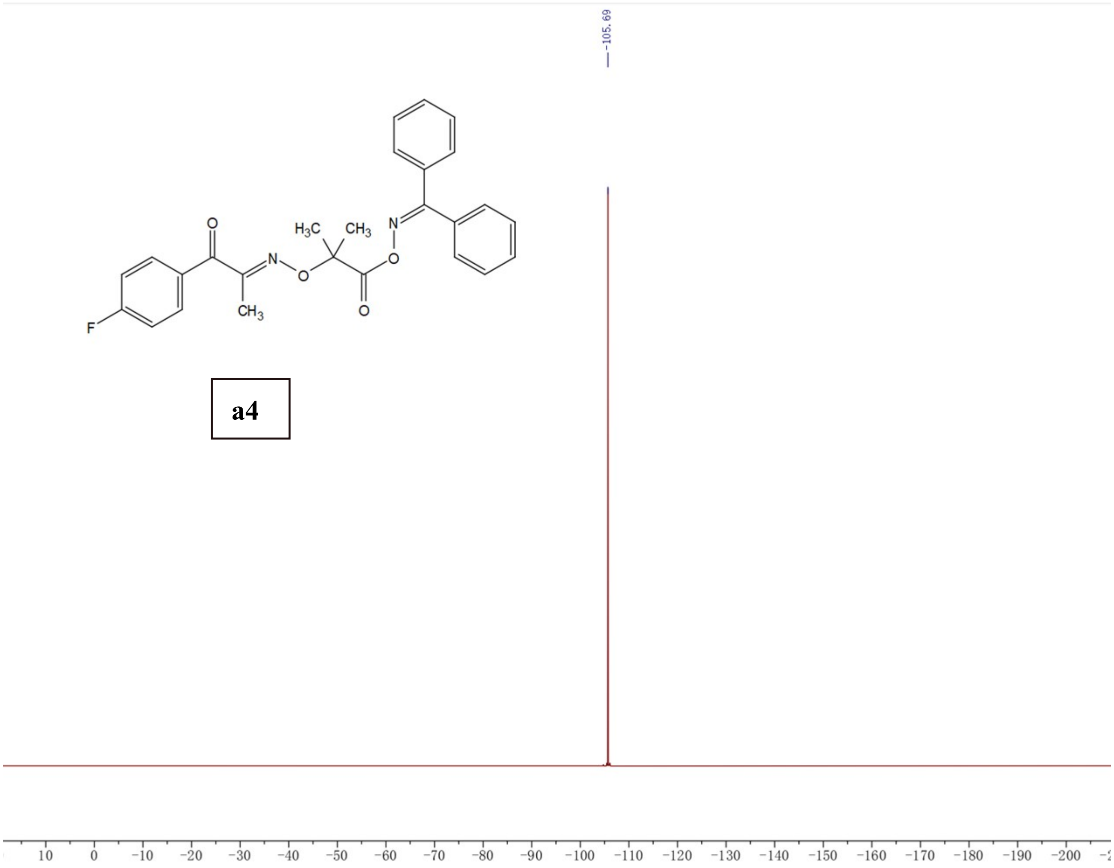
a4

^{13}C NMR (101 MHz, CDCl$_3$)



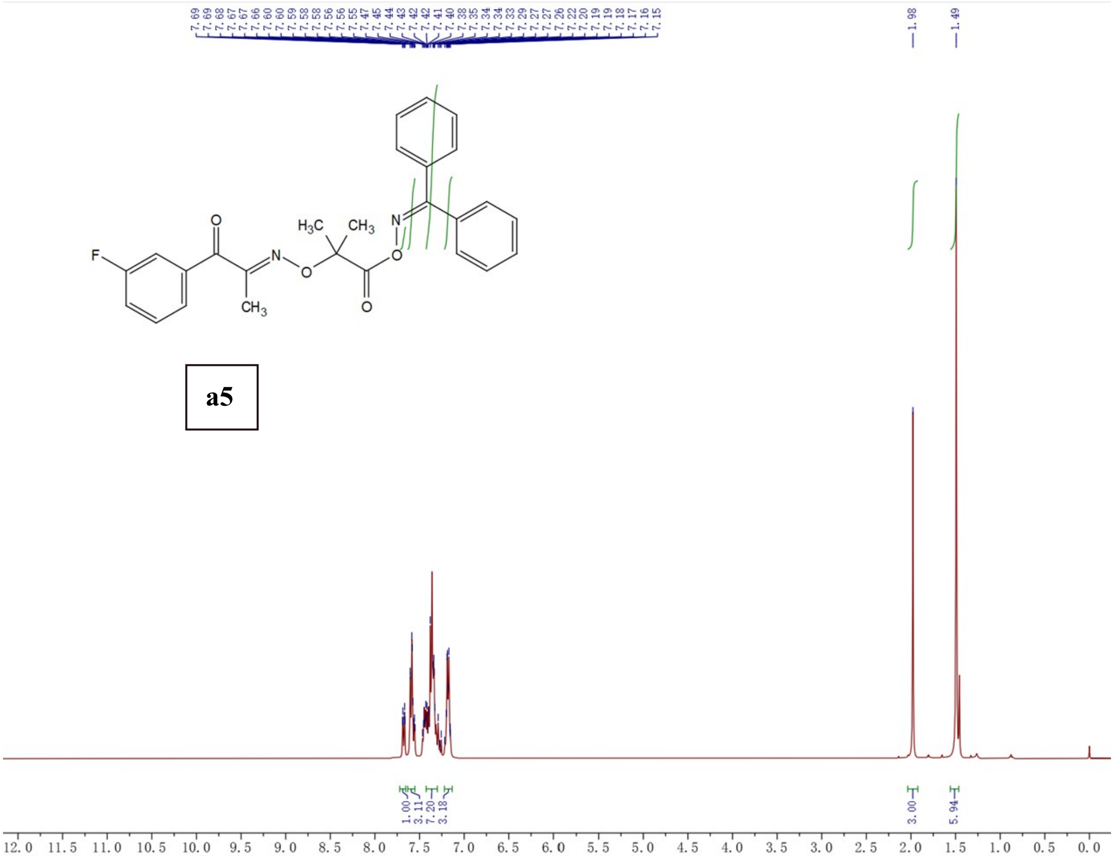
a4

^{19}F NMR (376 MHz, $CDCl_3$)



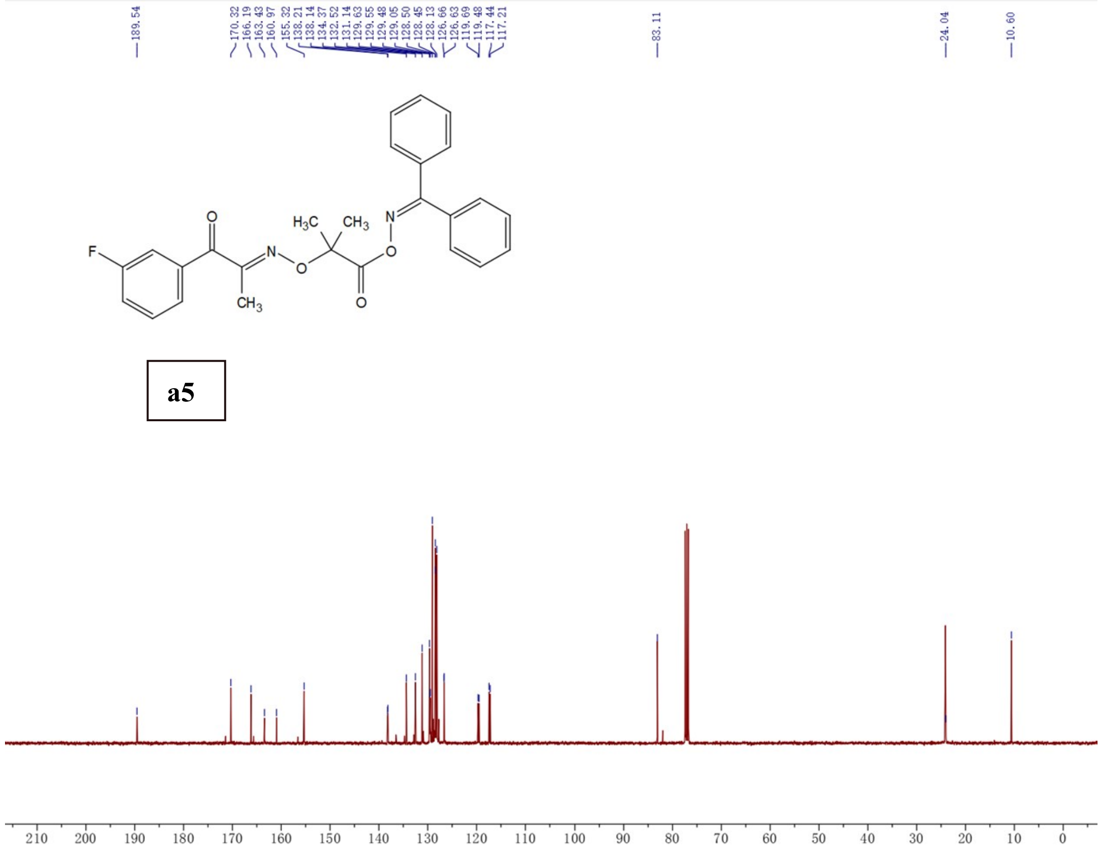
a4

^{1}H NMR (400 MHz, CDCl$_3$)

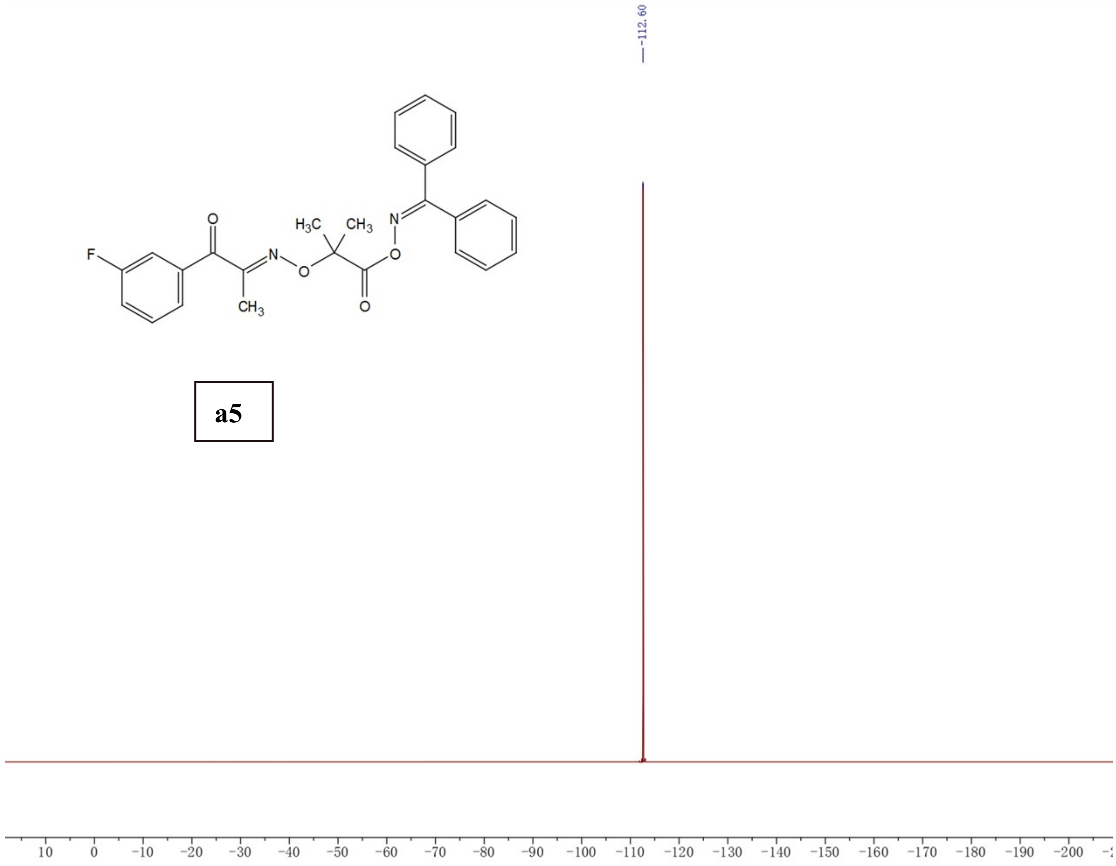


a5

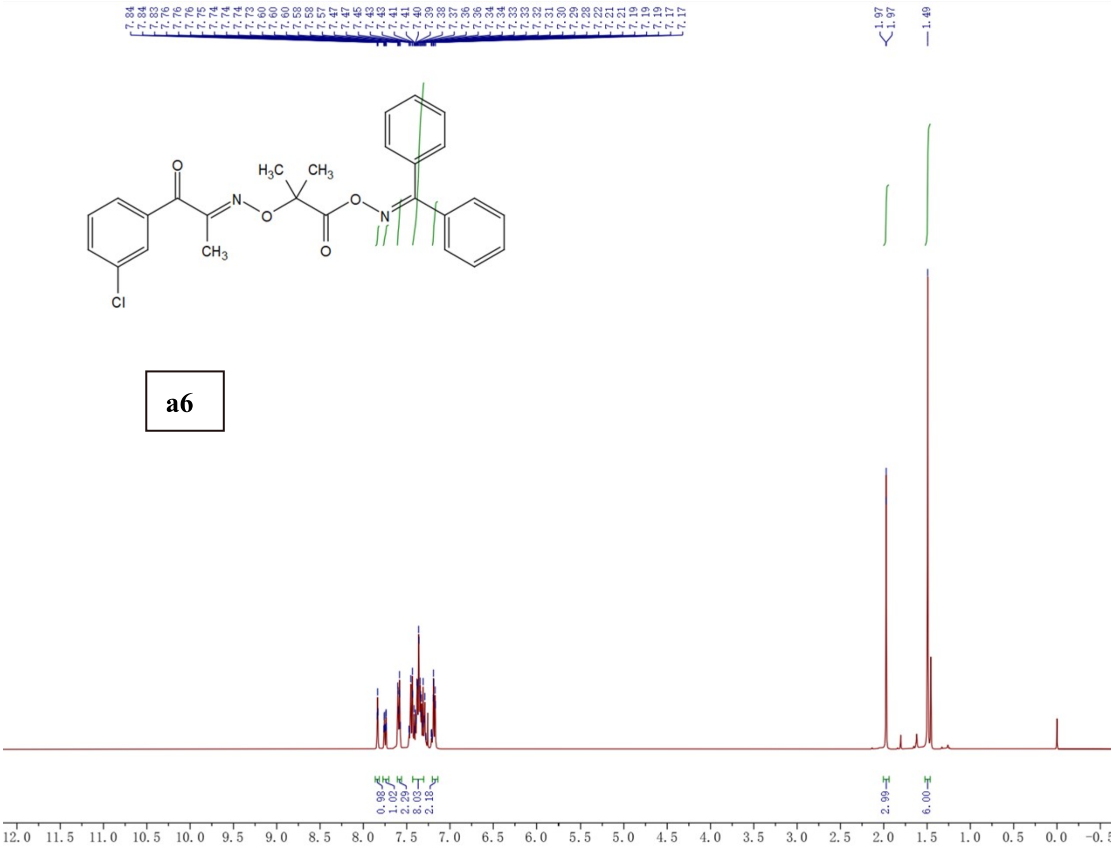
^{13}C NMR (101 MHz, CDCl$_3$)



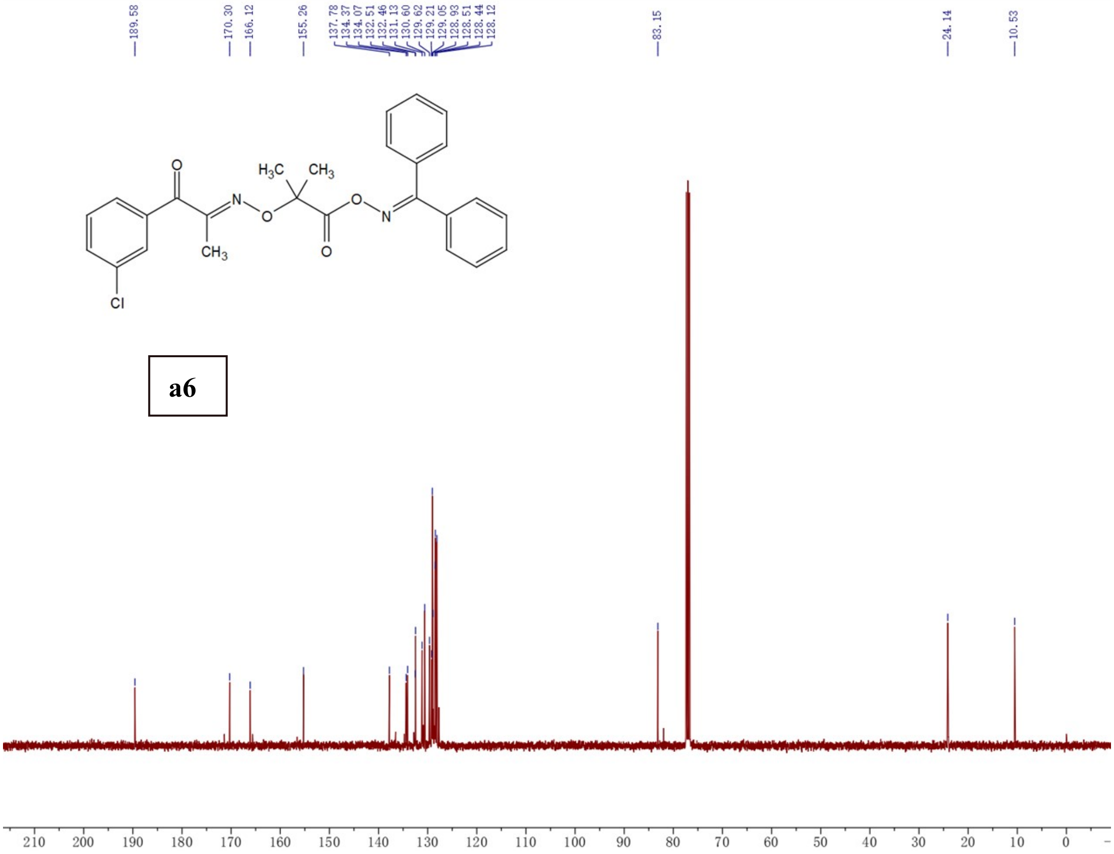
^{19}F NMR (376 MHz, CDCl$_3$)



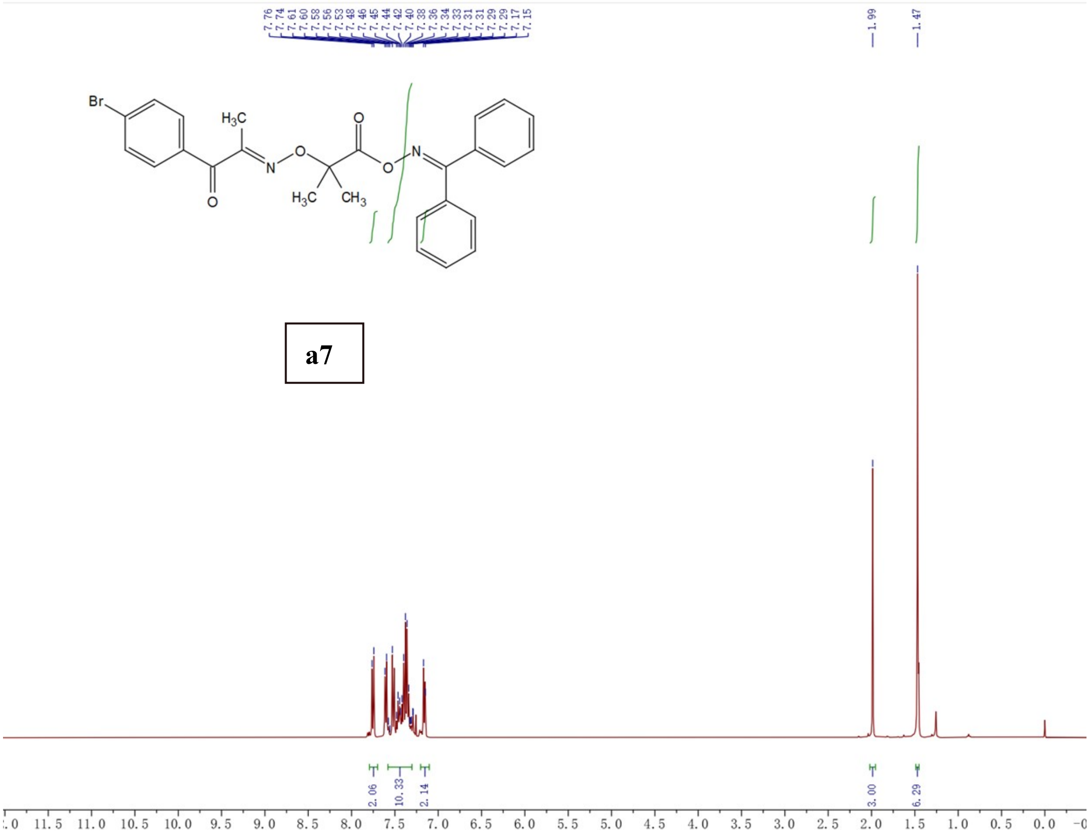
^{1}H NMR (400 MHz, CDCl$_3$)



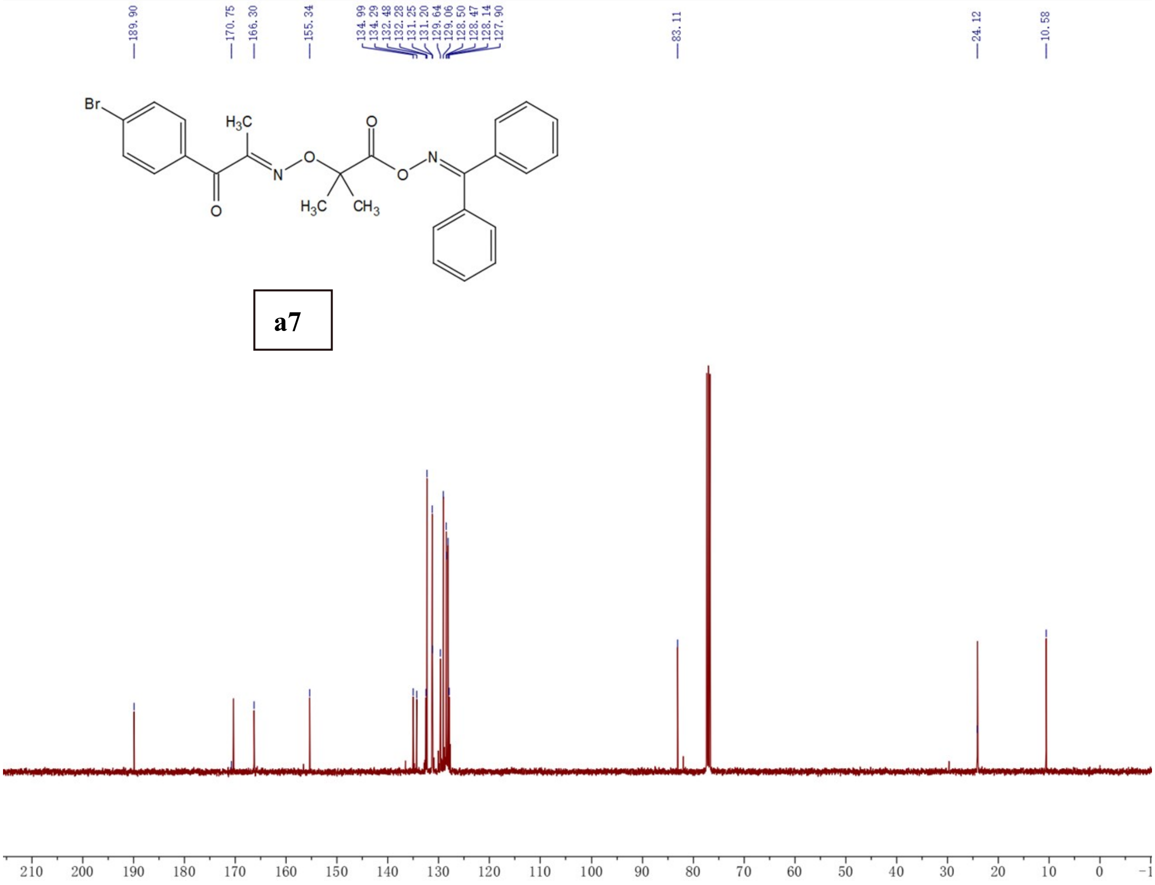
^{13}C NMR (101 MHz, $CDCl_3$)



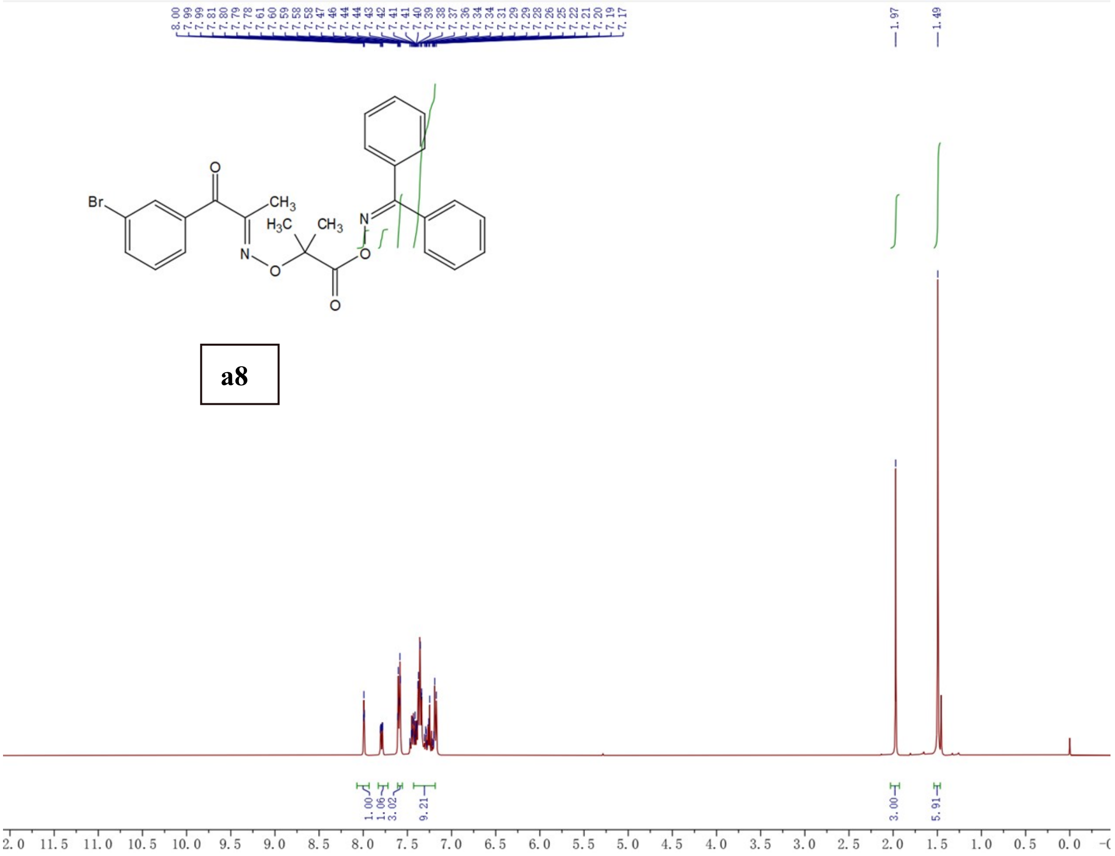
^{1}H NMR (400 MHz, $CDCl_3$)



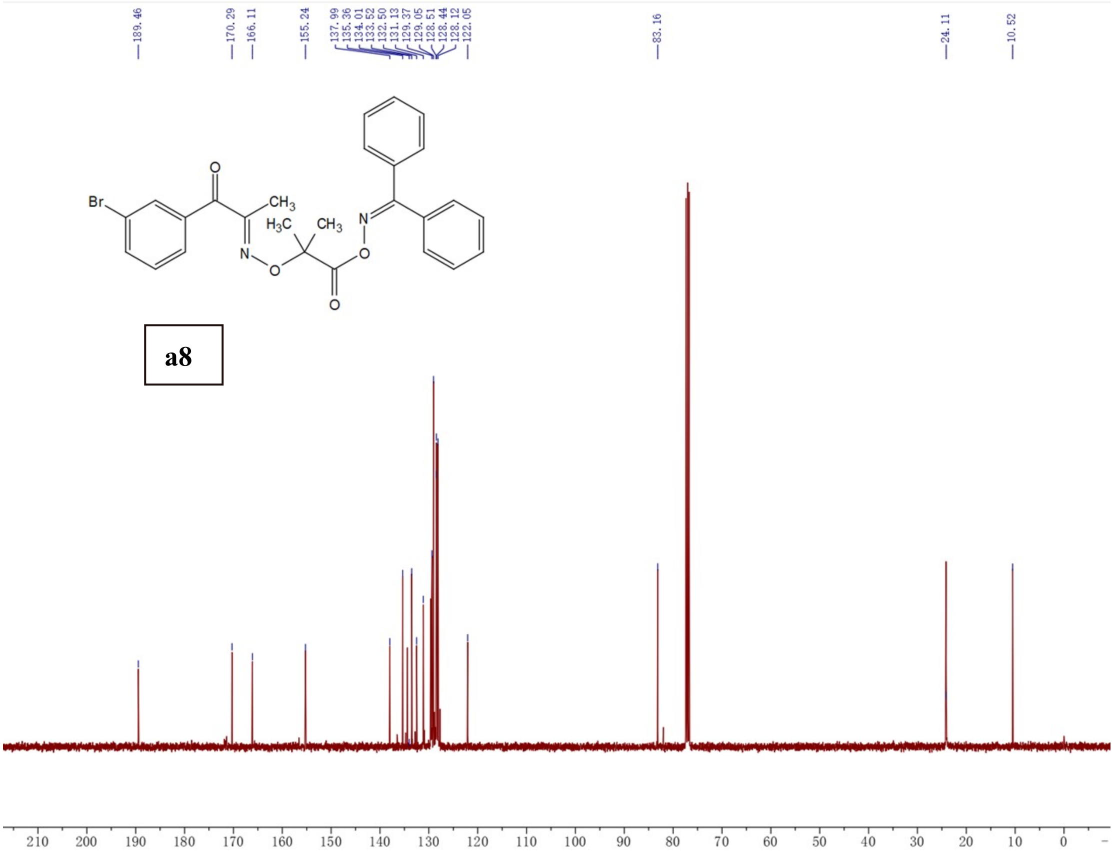
^{13}C NMR (101 MHz, CDCl$_3$)



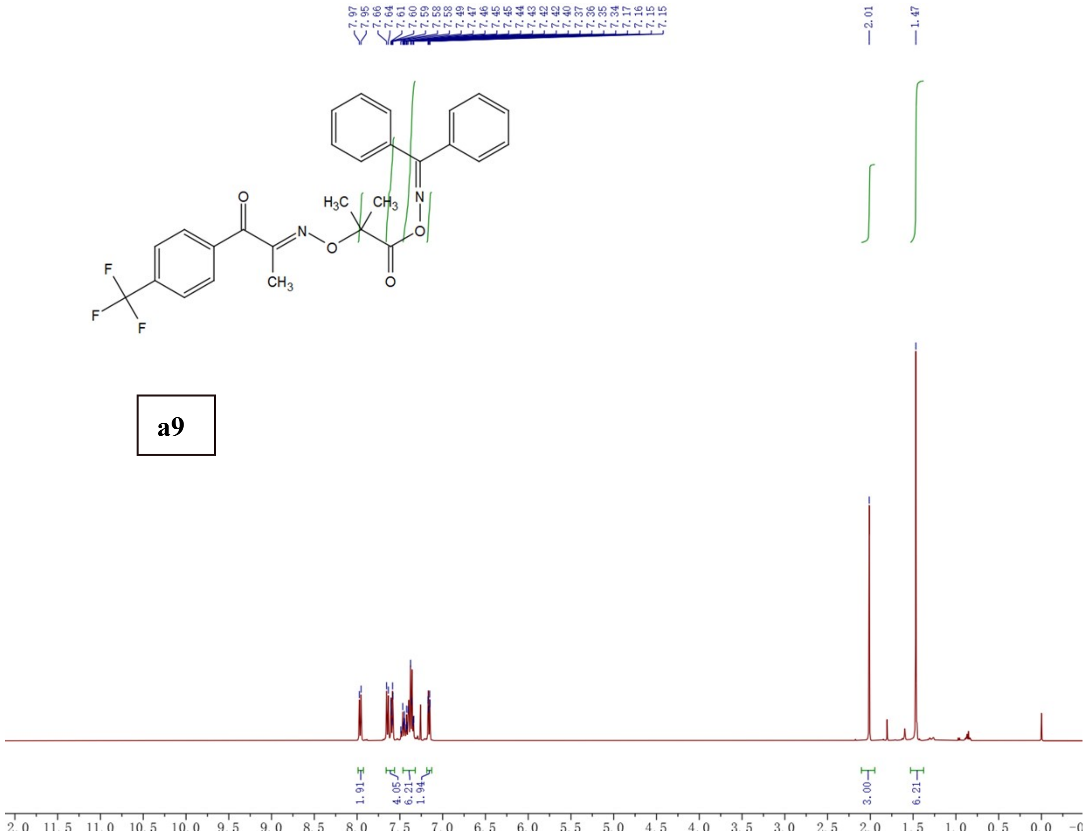
^{1}H NMR (400 MHz, CDCl$_3$)



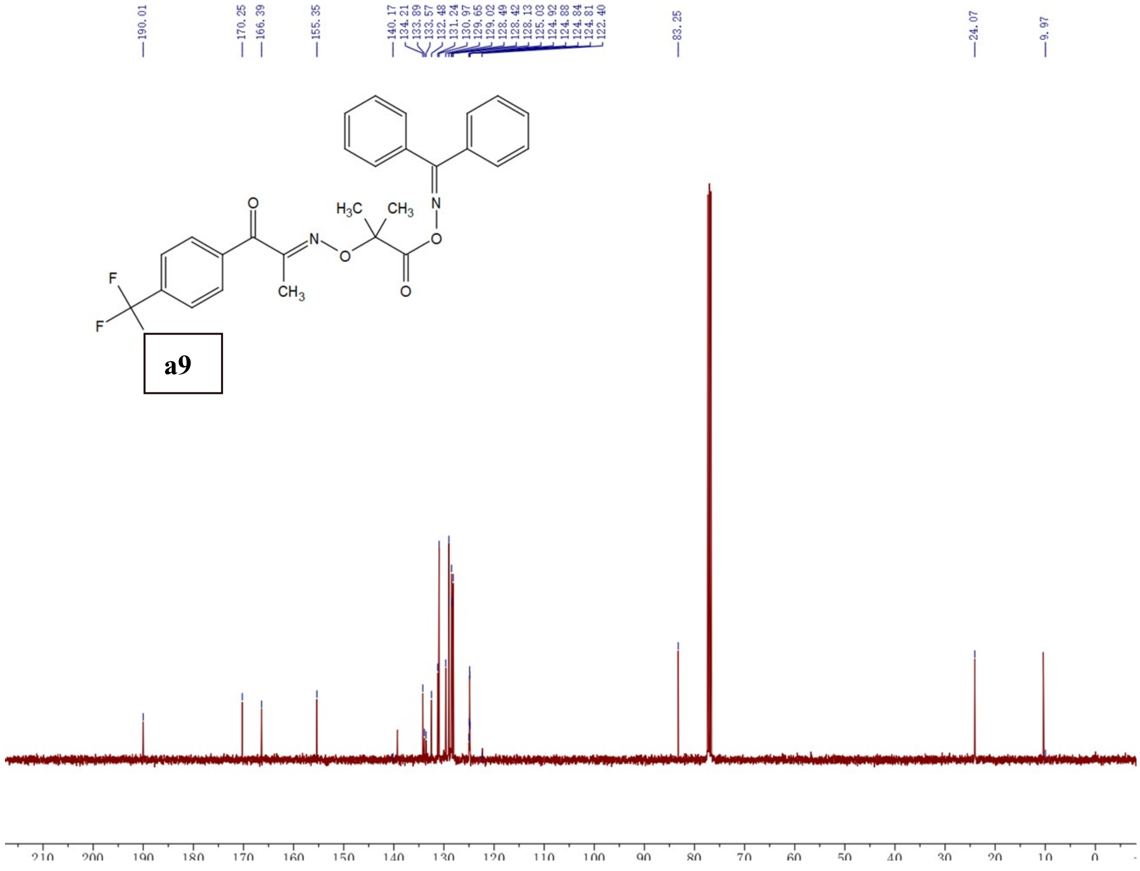
^{13}C NMR (101 MHz, $CDCl_3$)



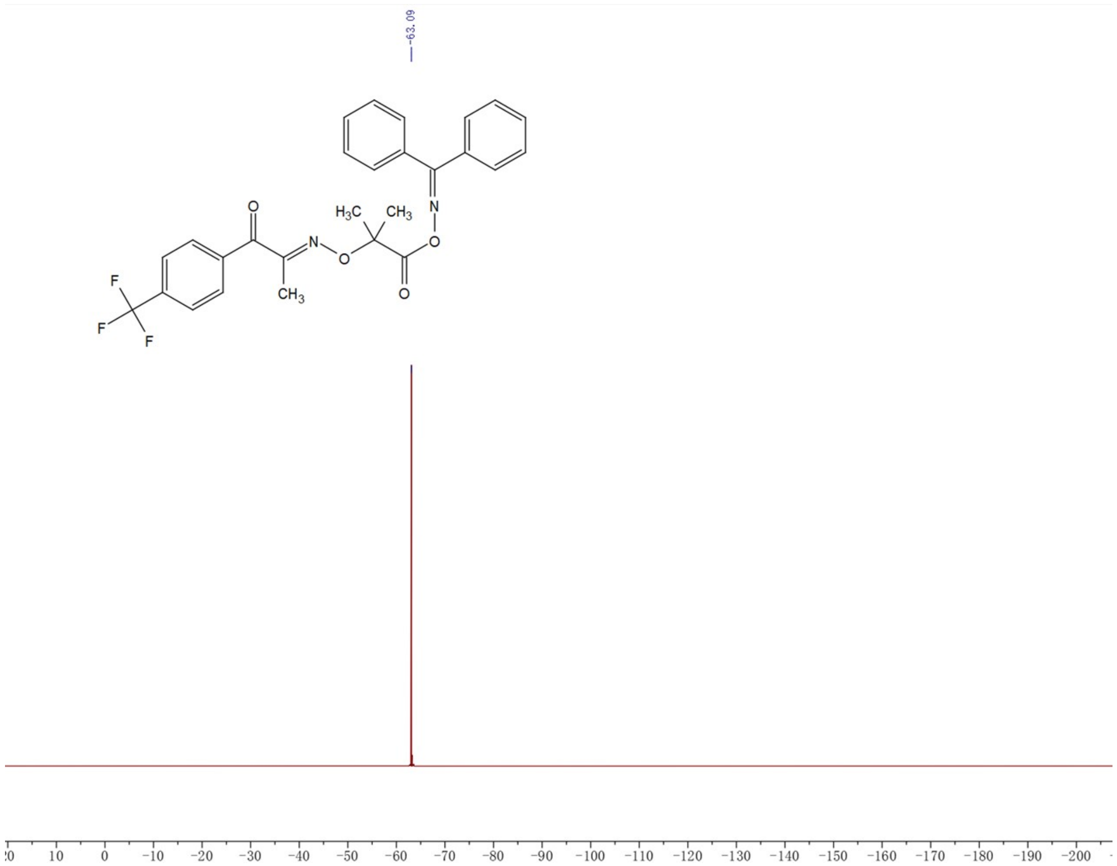
^{1}H NMR (400 MHz, $CDCl_3$)



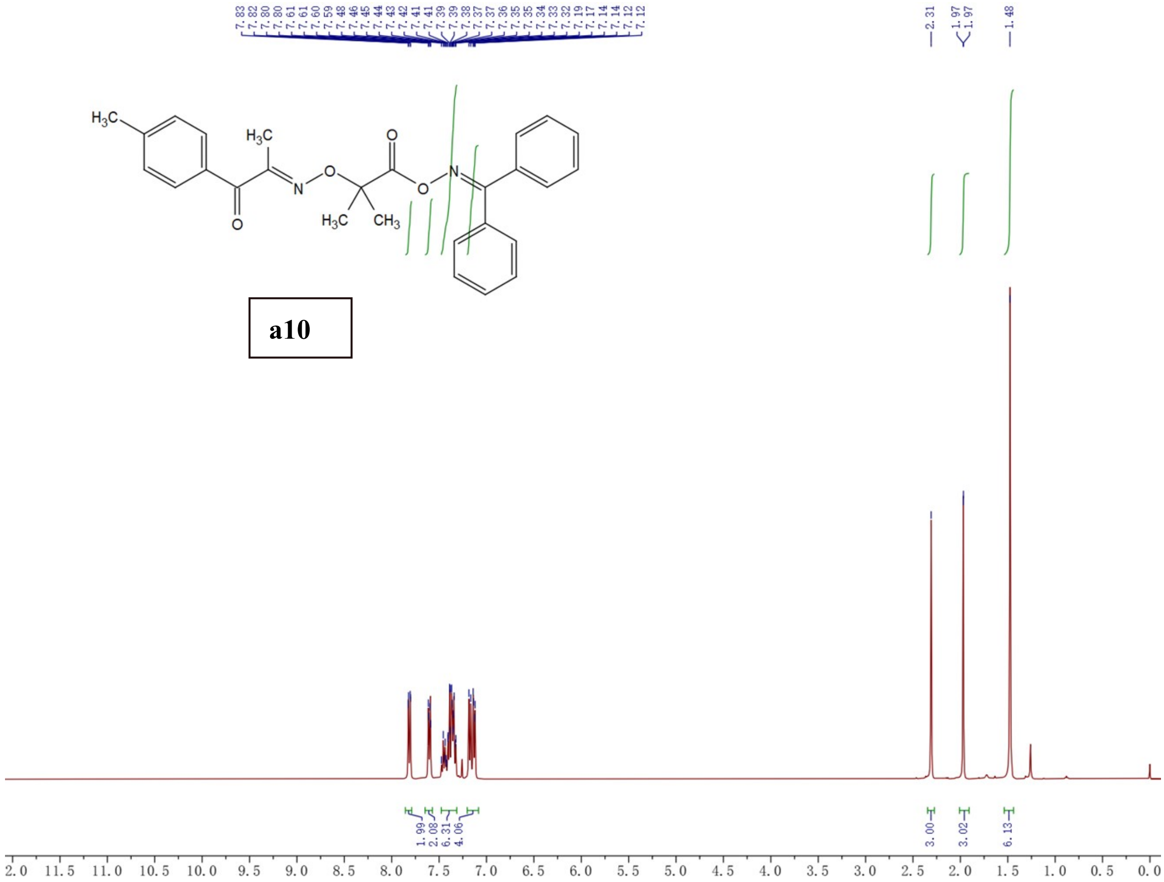
^{13}C NMR (101 MHz, CDCl$_3$)



^{19}F NMR (376 MHz, CDCl$_3$)

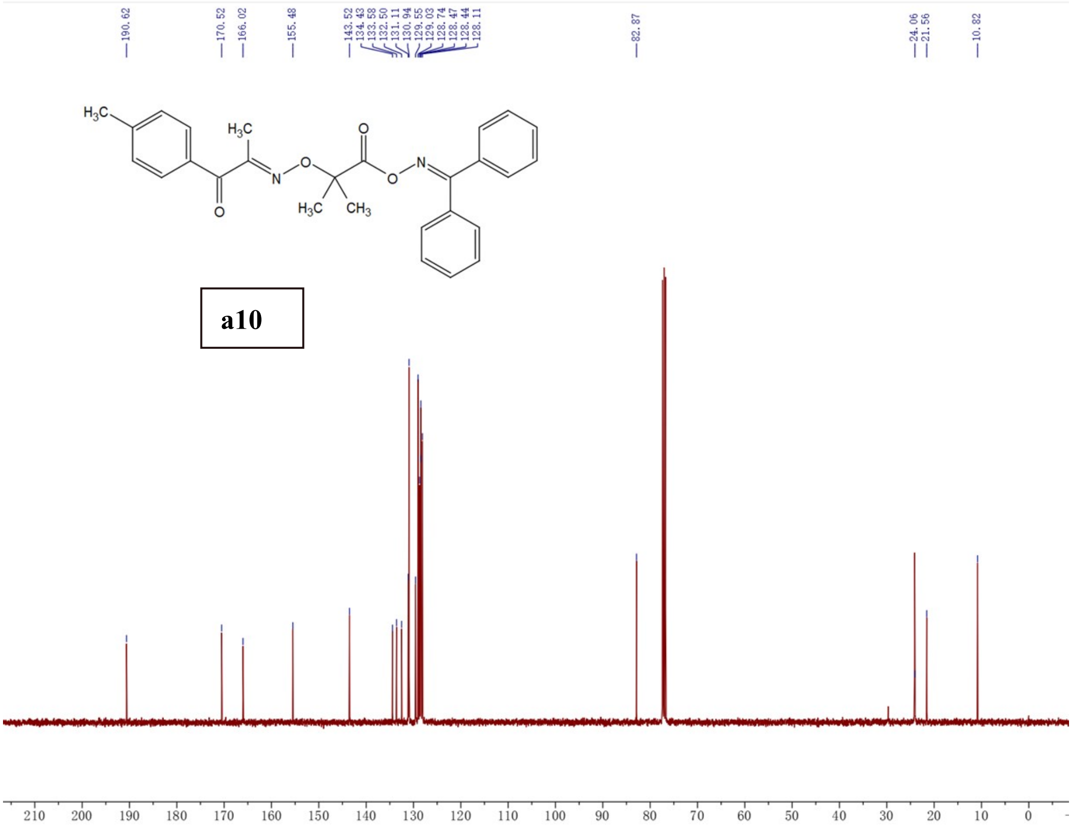


^{1}H NMR (400 MHz, CDCl$_3$)



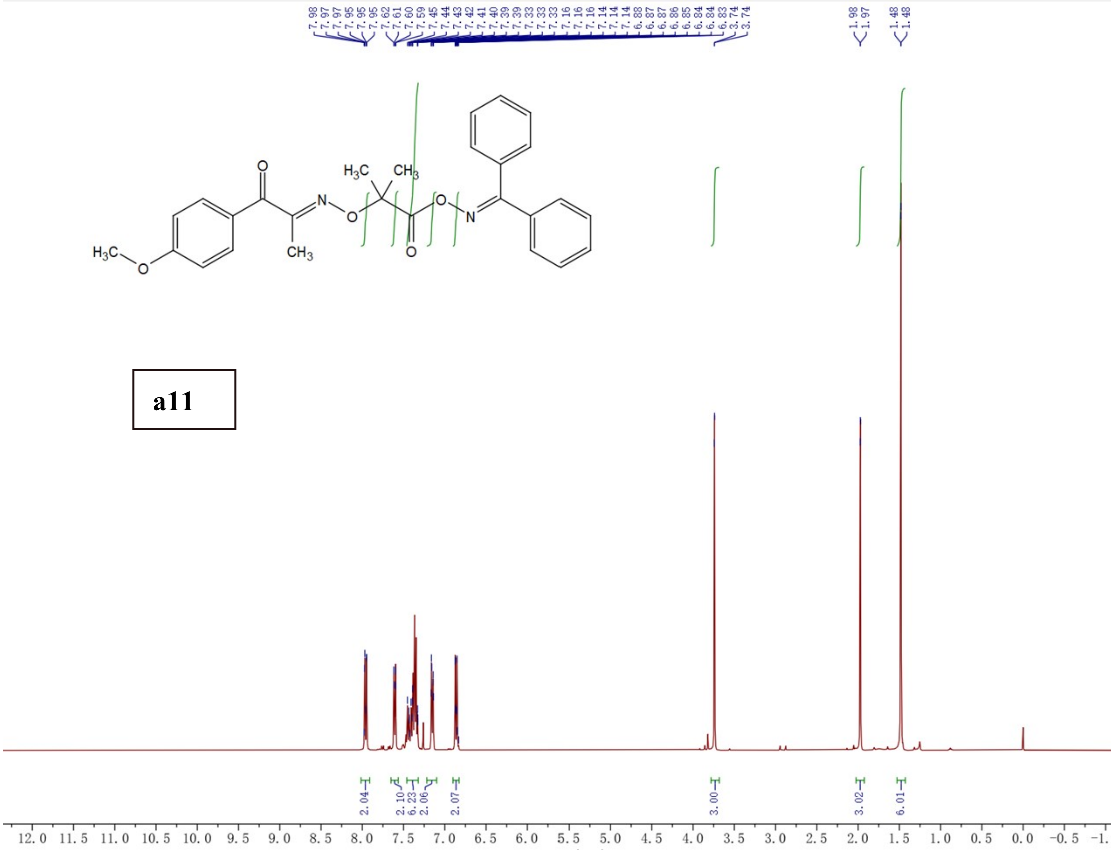
a10

^{13}C NMR (101 MHz, CDCl$_3$)



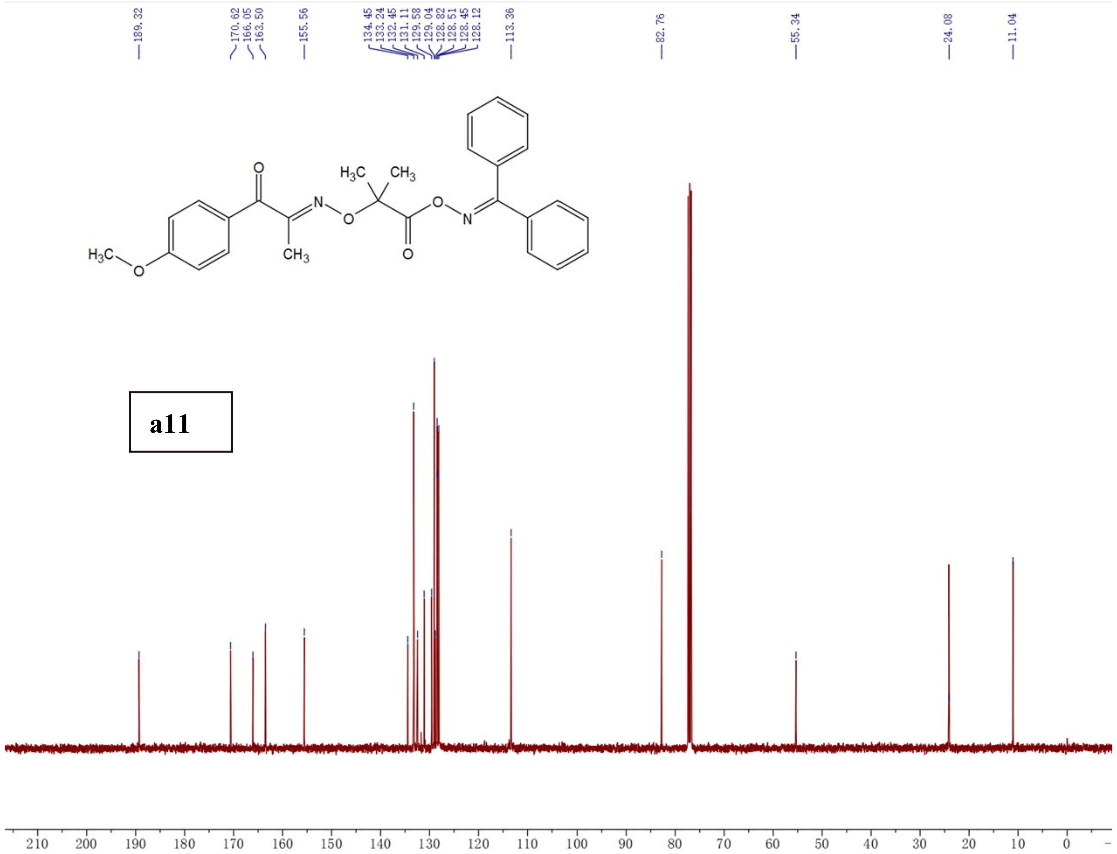
a10

^{1}H NMR (400 MHz, CDCl$_3$)



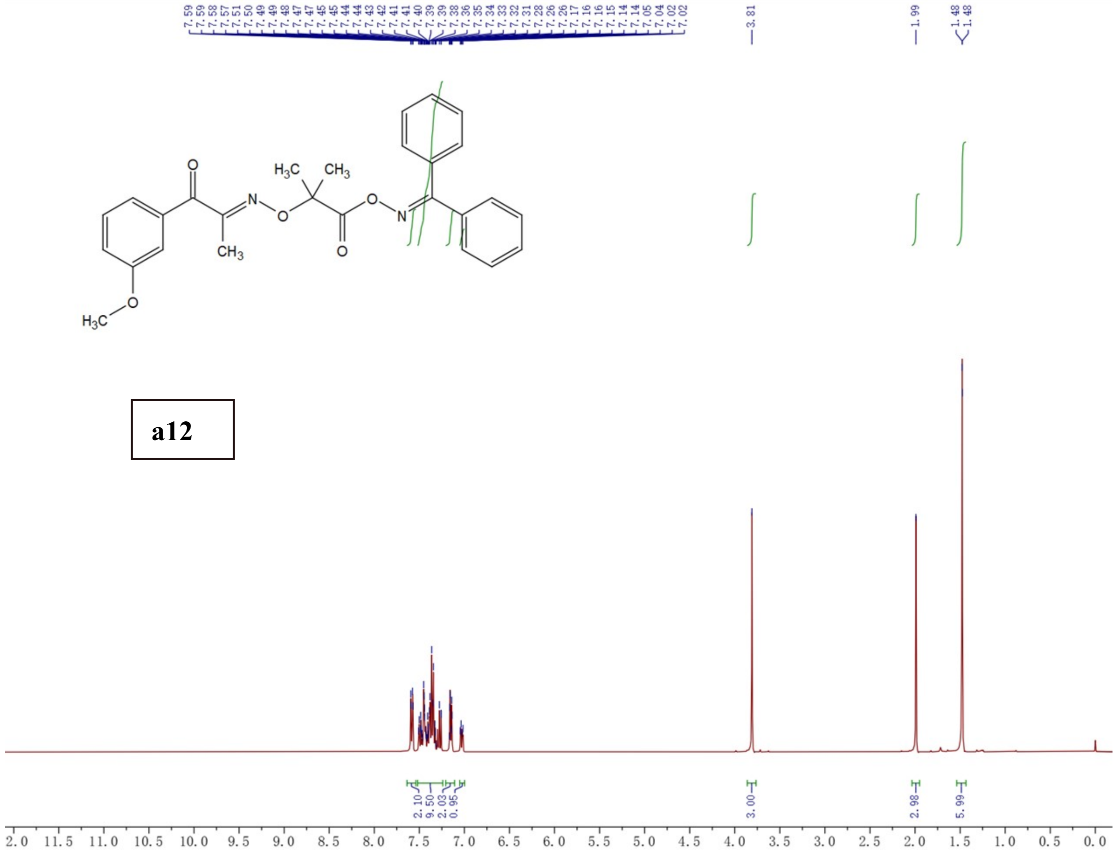
a11

^{13}C NMR (101 MHz, CDCl$_3$)



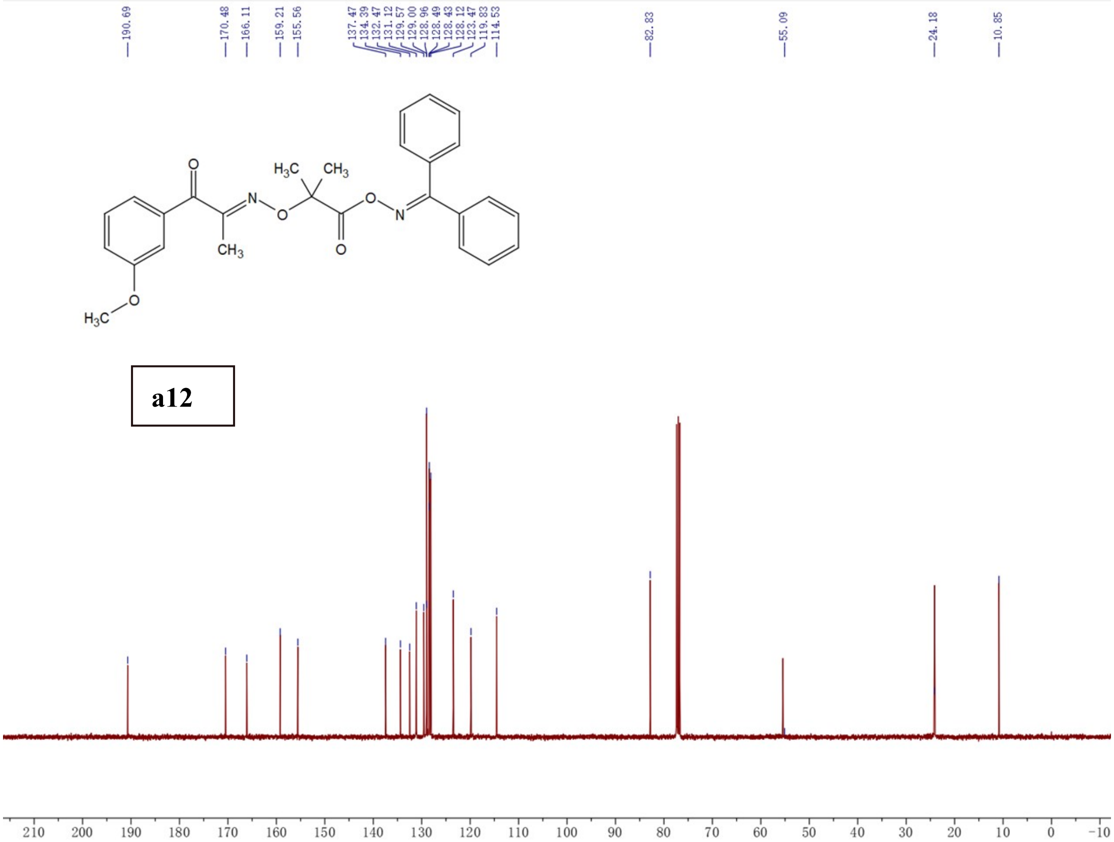
a11

^{1}H NMR (400 MHz, CDCl$_3$)



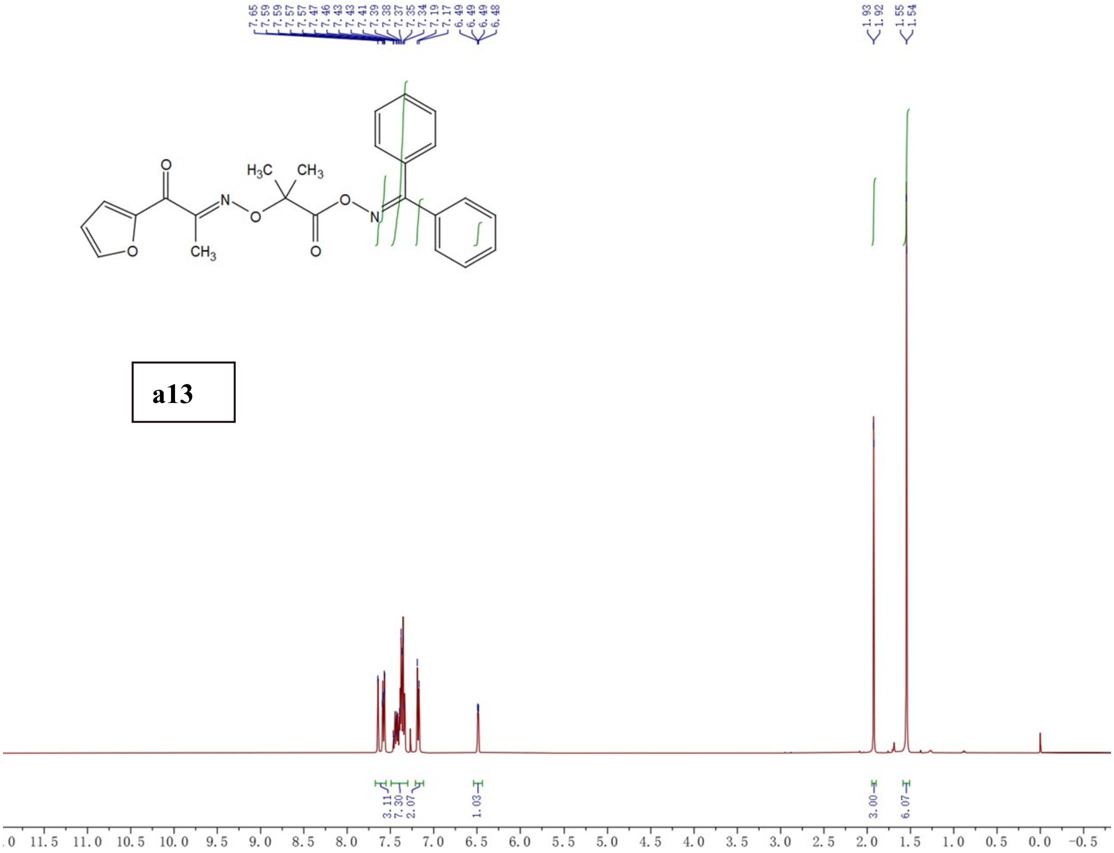
a12

^{13}C NMR (101 MHz, CDCl$_3$)



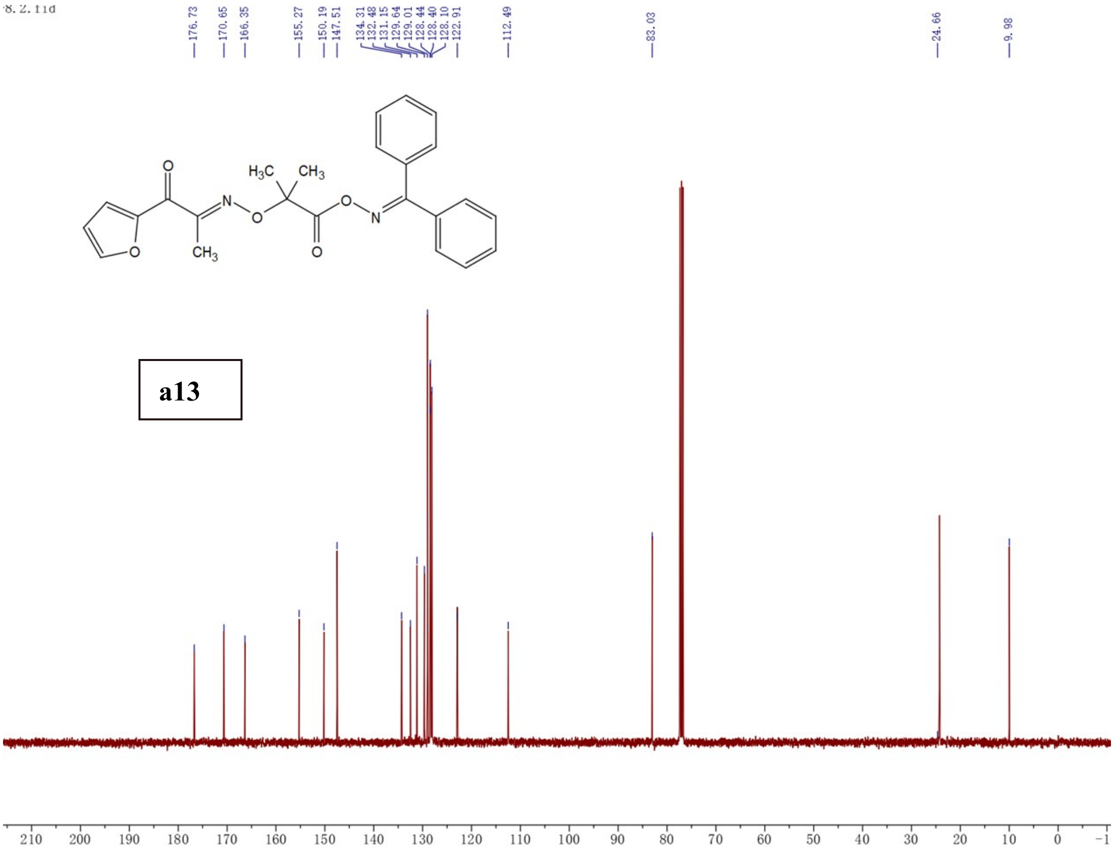
a12

^{1}H NMR (400 MHz, CDCl$_3$)



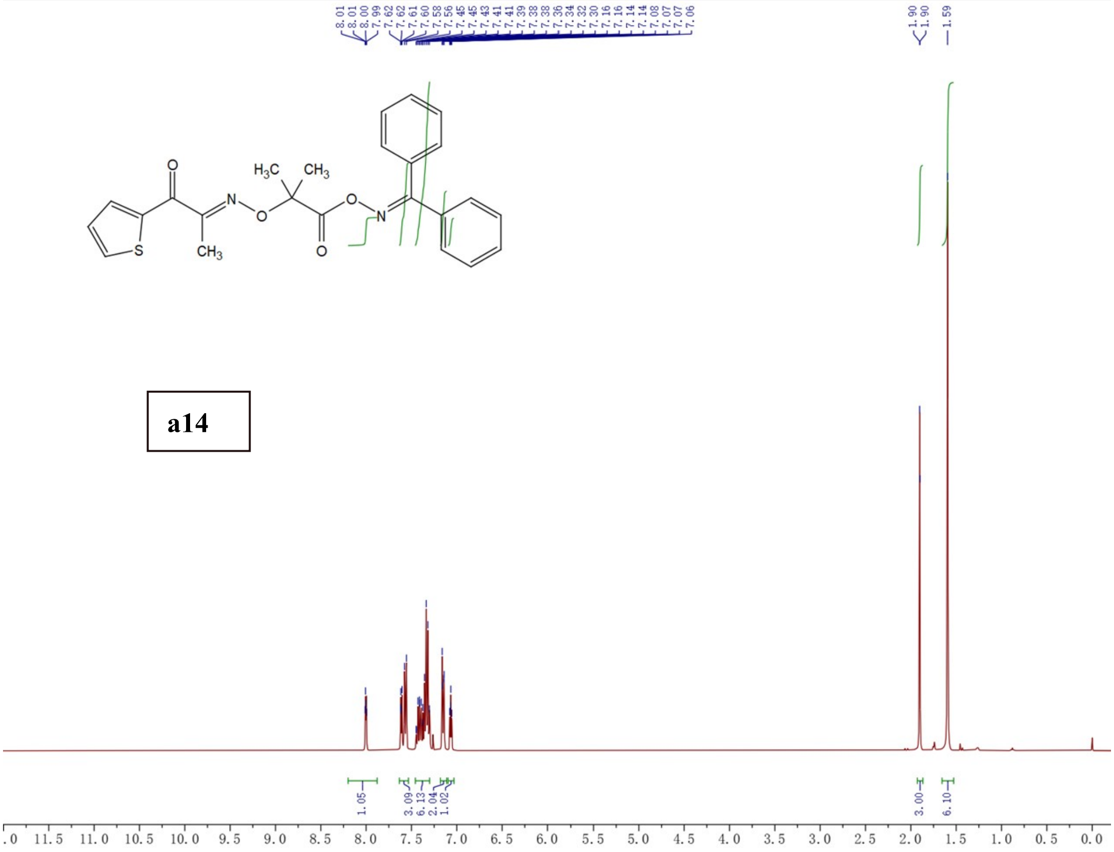
a13

^{13}C NMR (101 MHz, CDCl$_3$)



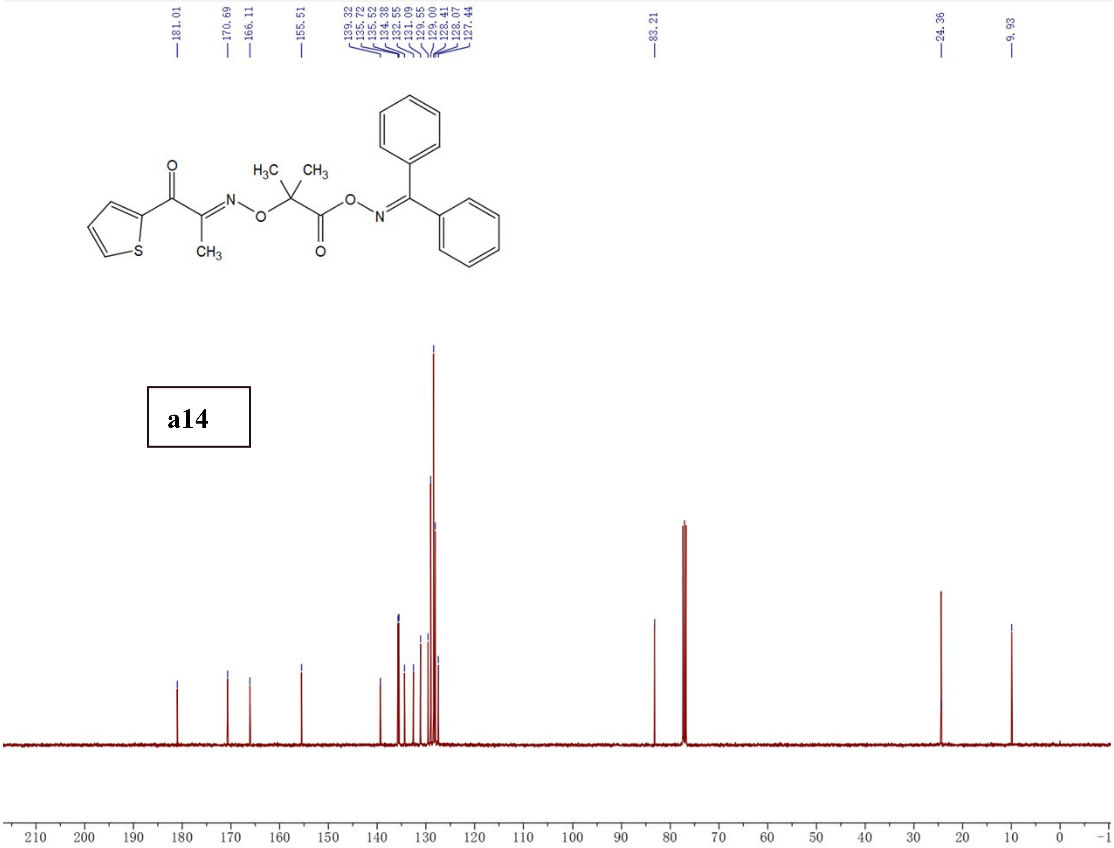
a13

^{1}H NMR (400 MHz, CDCl$_3$)



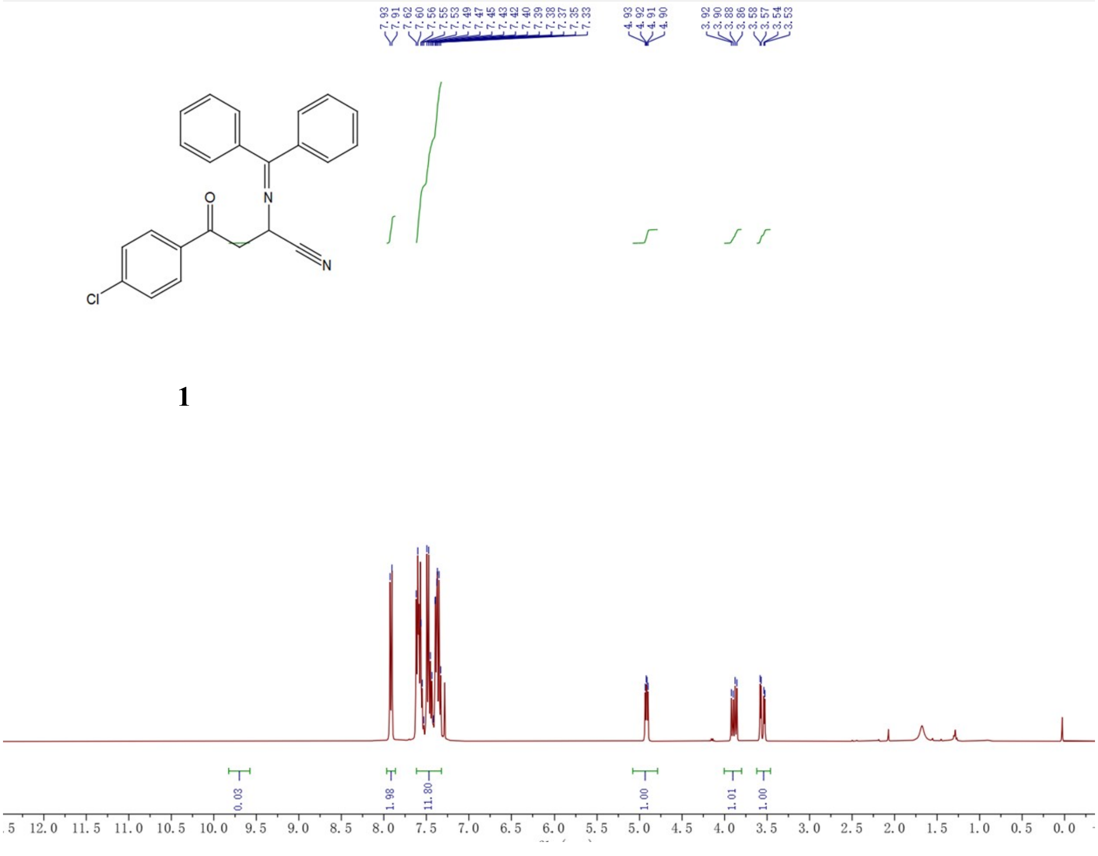
a14

^{13}C NMR (101 MHz, CDCl$_3$)



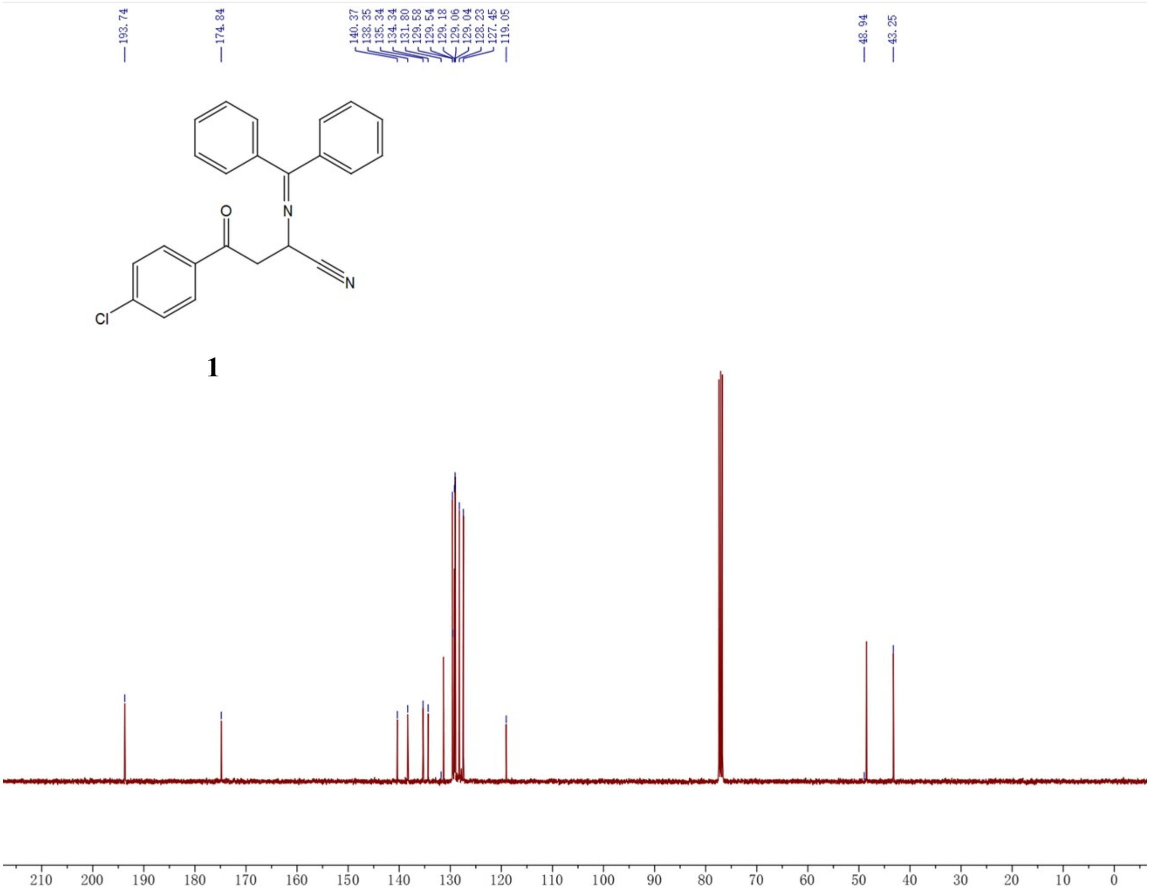
a14

^{1}H NMR (400 MHz, CDCl$_3$)



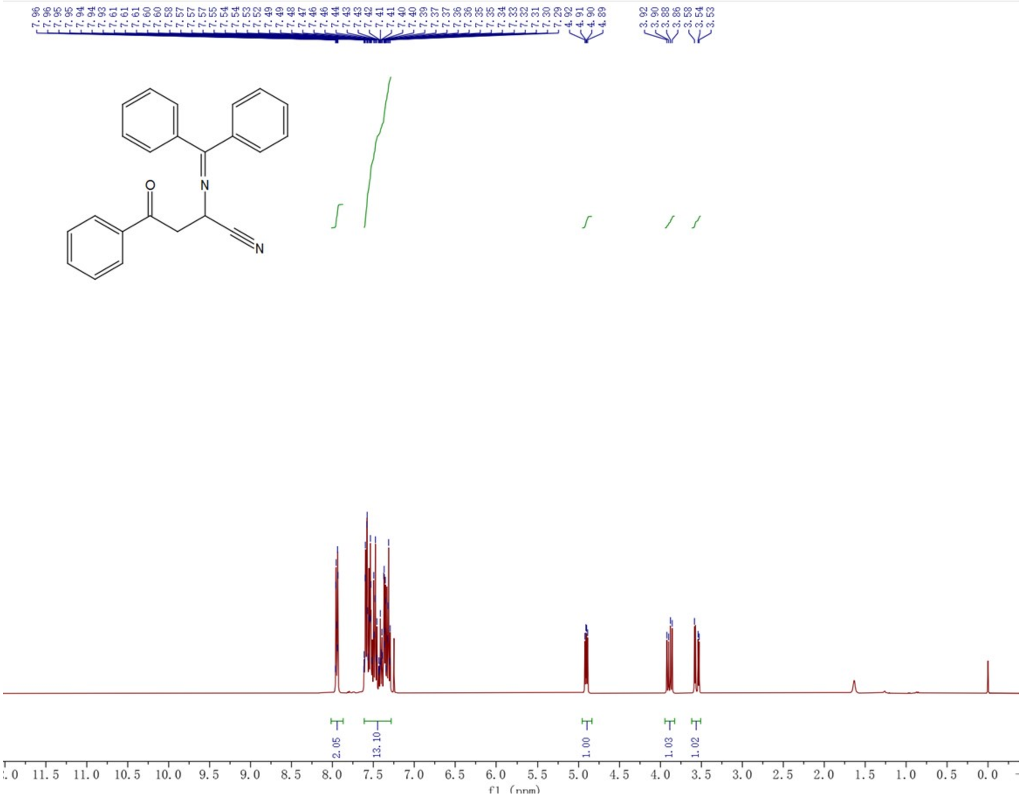
1

^{13}C NMR (101 MHz, $CDCl_3$)

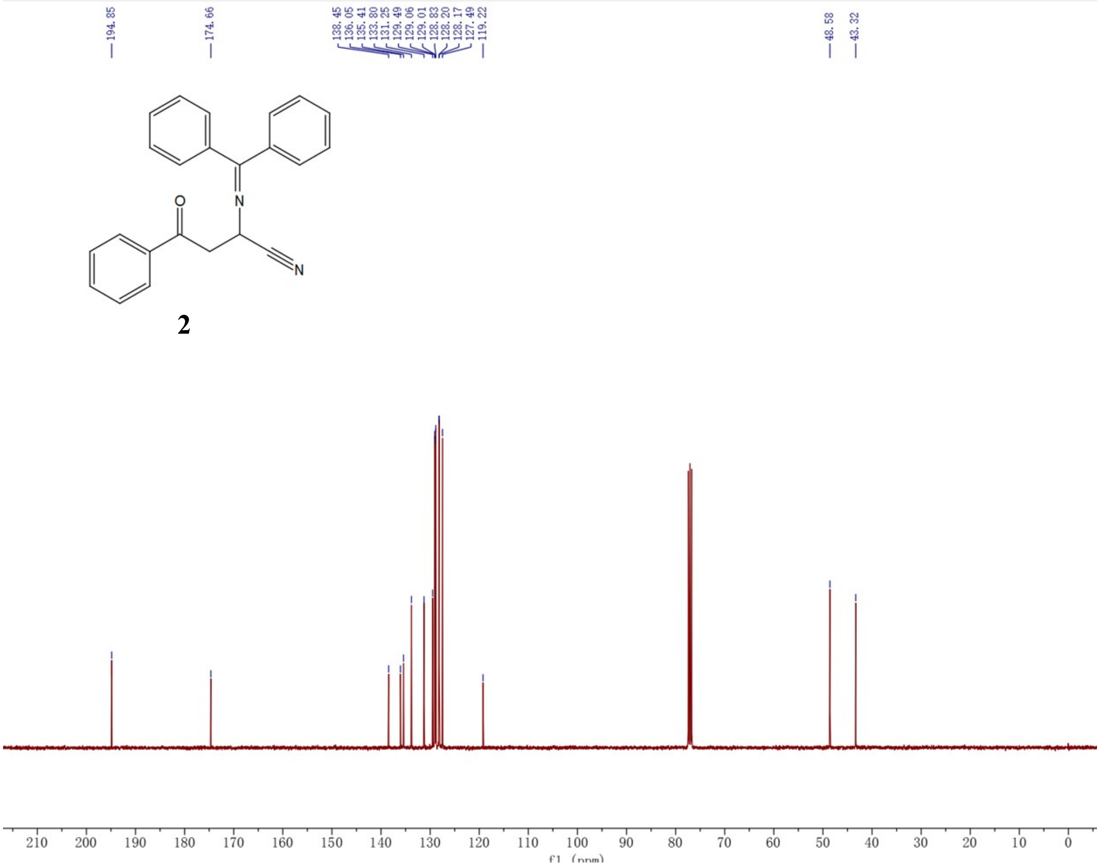


1

^1H NMR (400 MHz, $CDCl_3$)

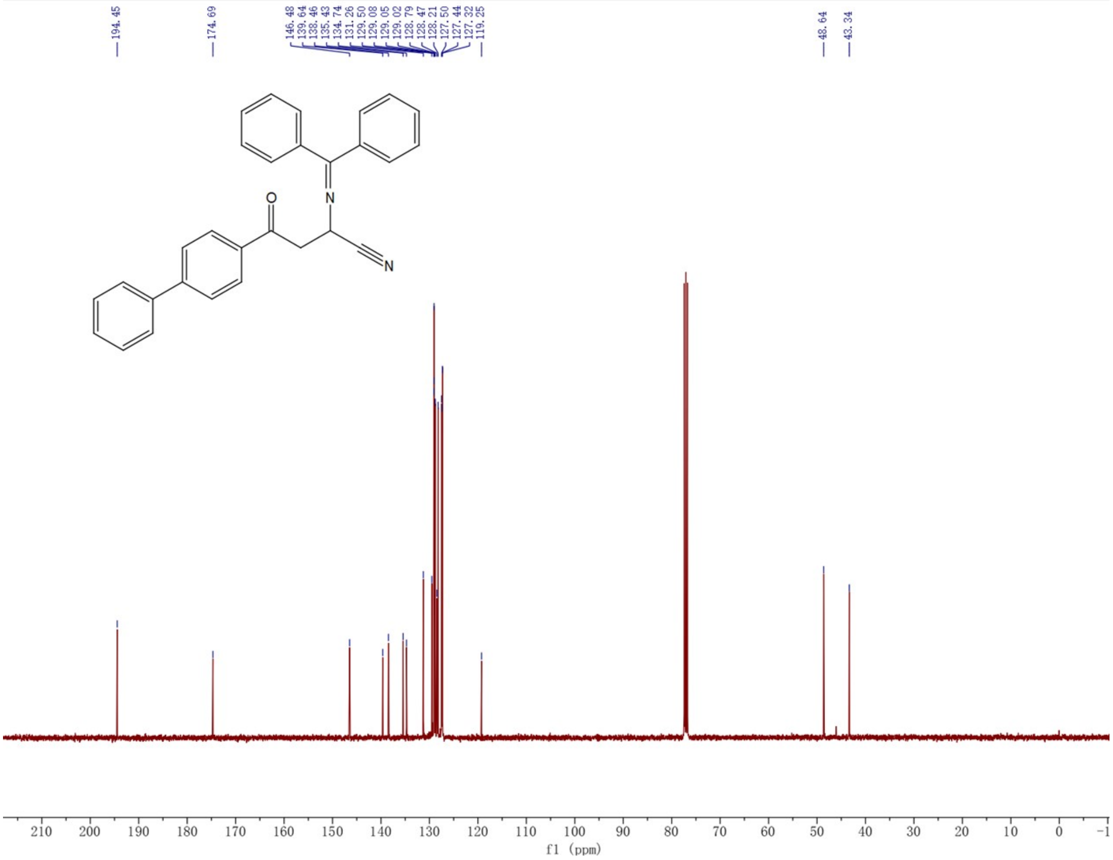


^{13}C NMR (101 MHz, CDCl$_3$)

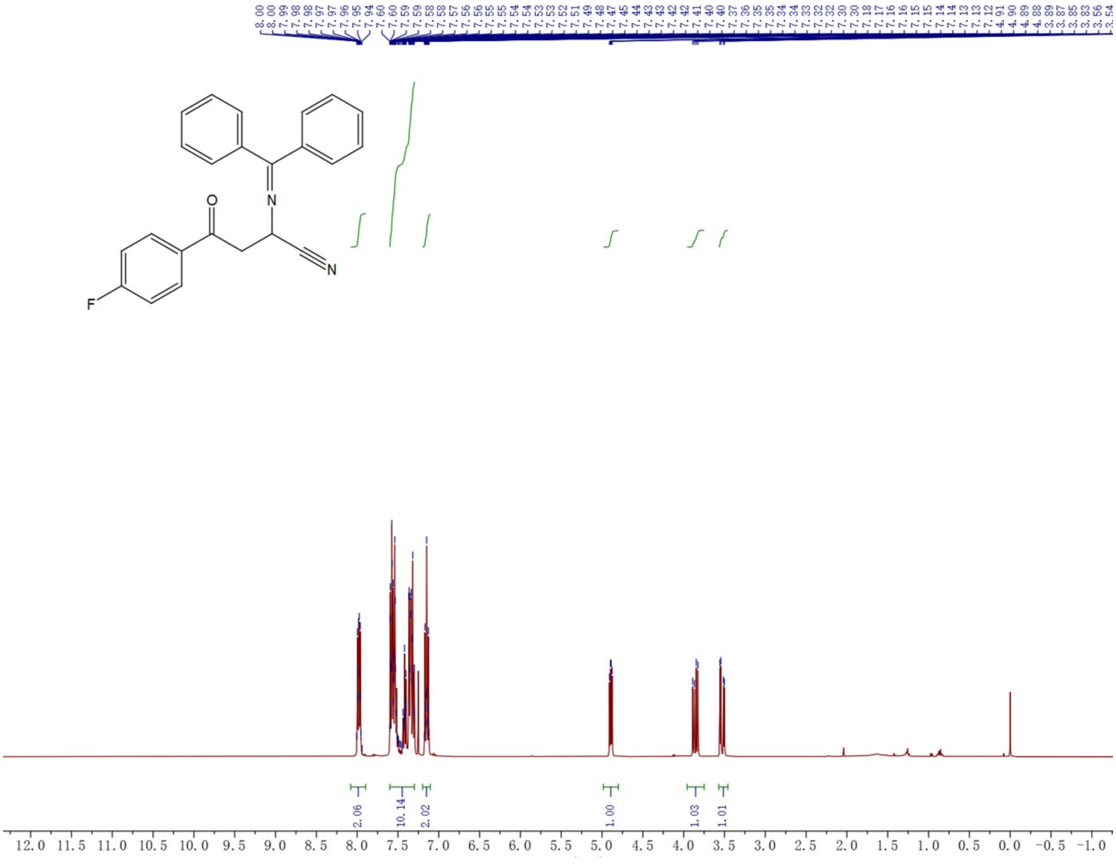


^{1}H NMR (400 MHz, CDCl$_3$)

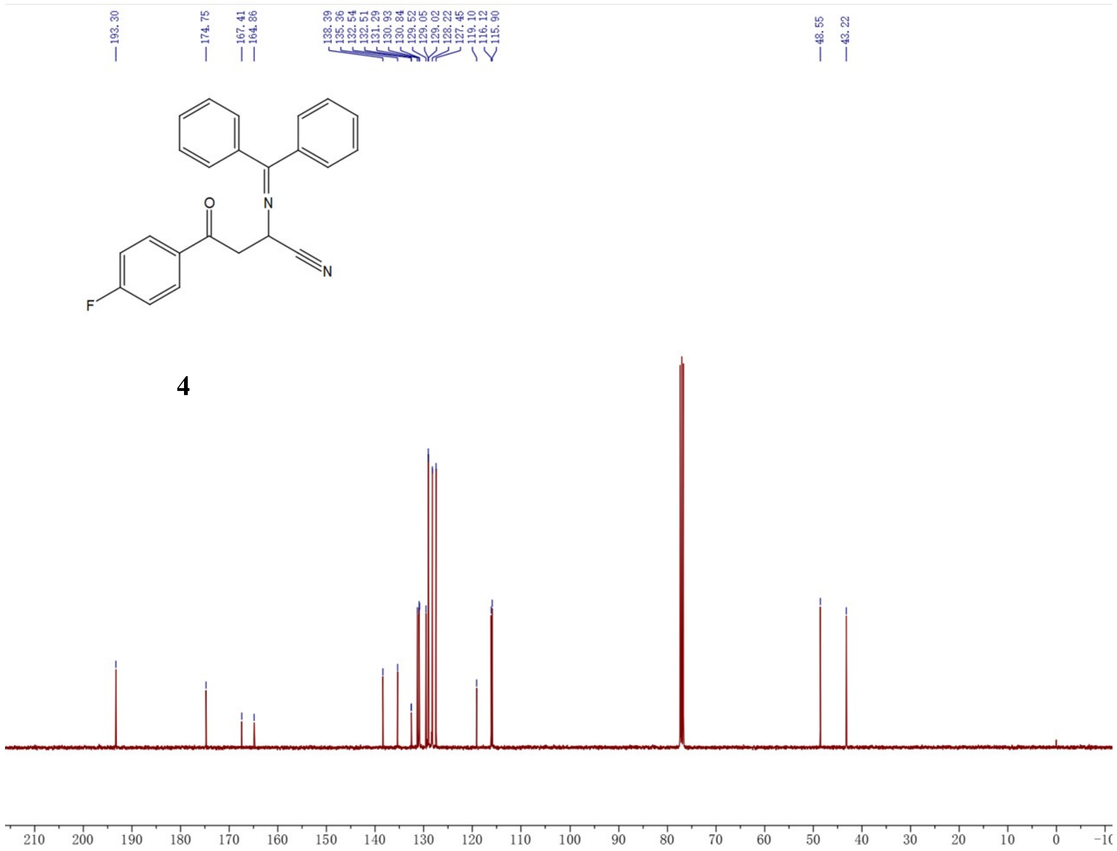
^{13}C NMR (101 MHz, CDCl$_3$)



^{1}H NMR (400 MHz, CDCl$_3$)

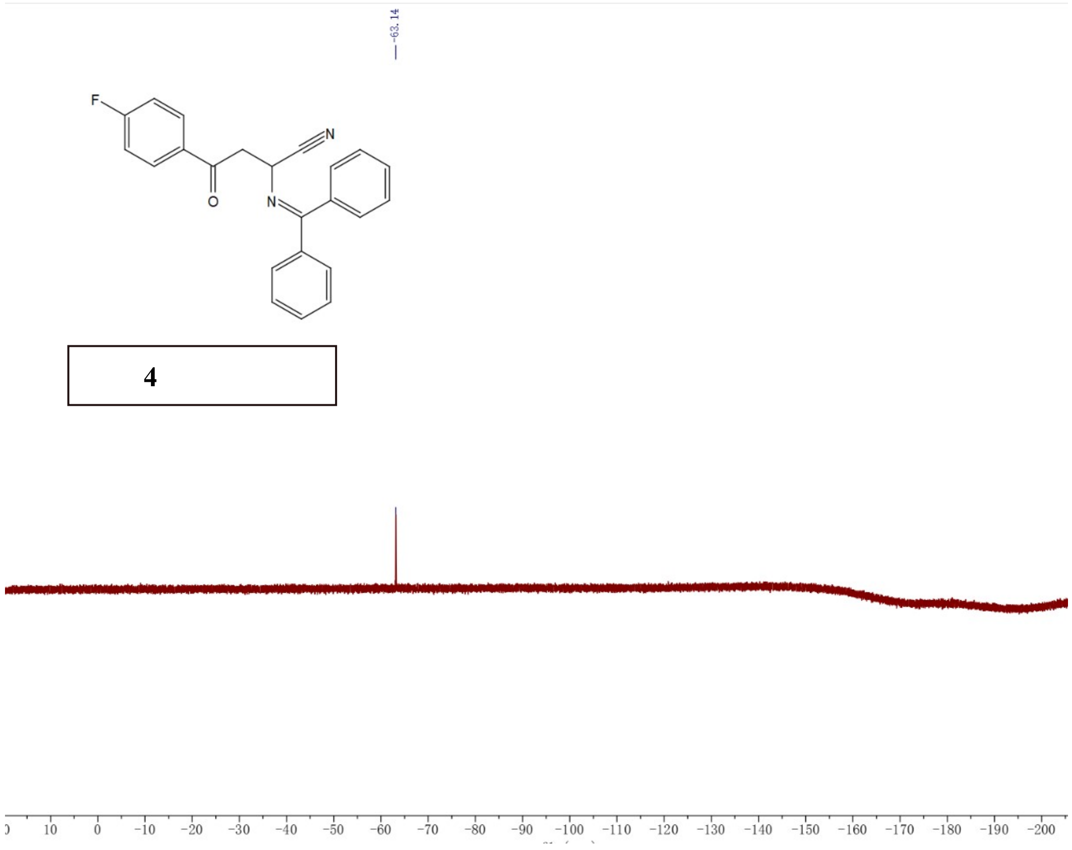


^{13}C NMR (101 MHz, $CDCl_3$)



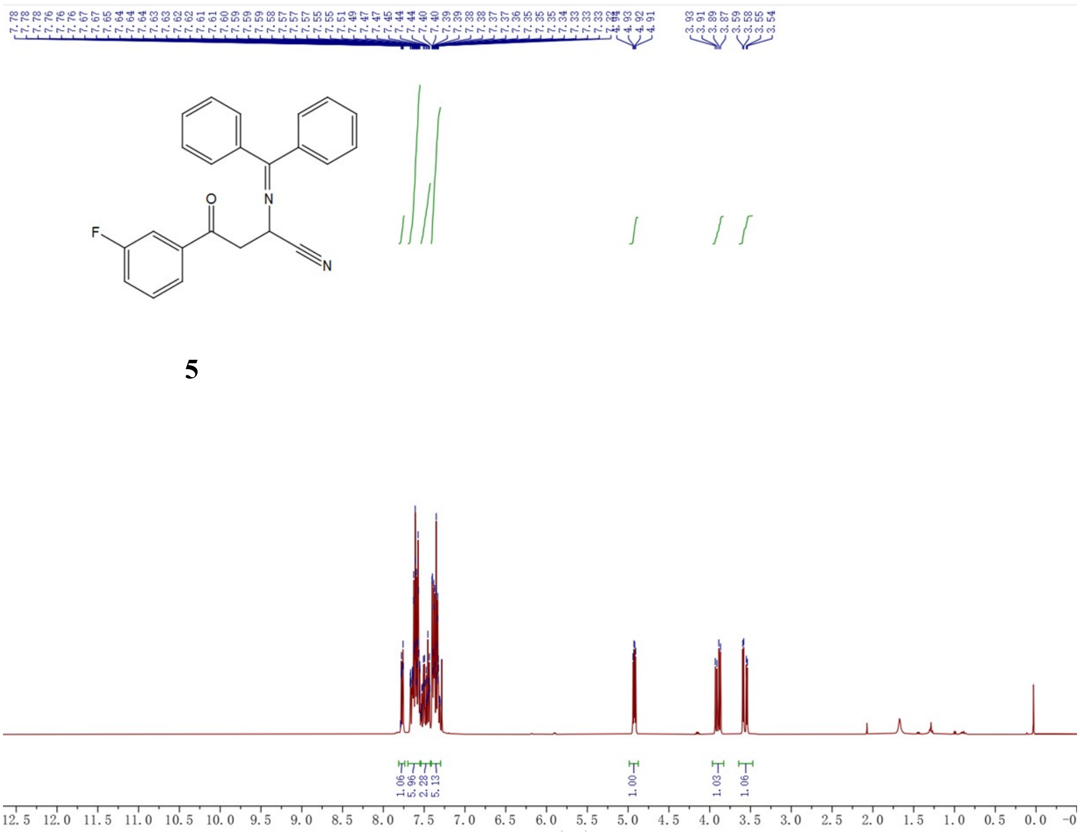
4

^{1}F NMR (377 MHz, $CDCl_3$)



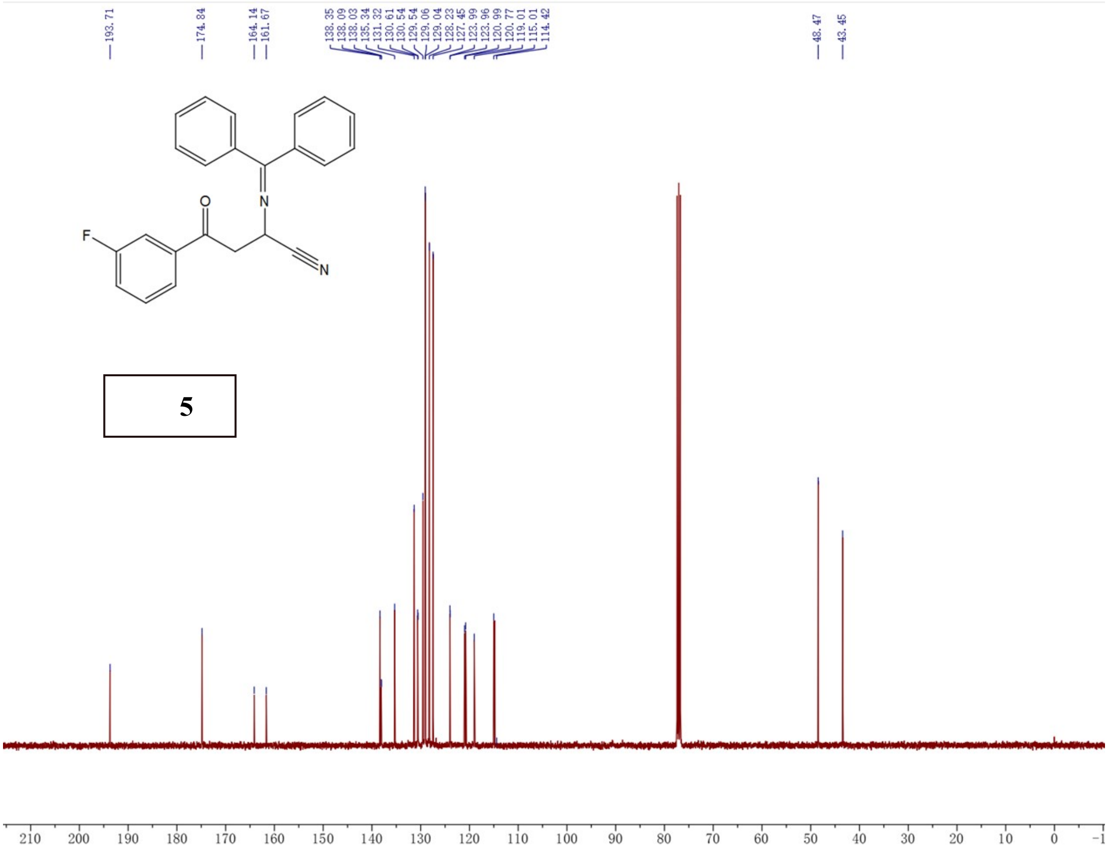
4

^{1}H NMR (400 MHz, CDCl$_3$)



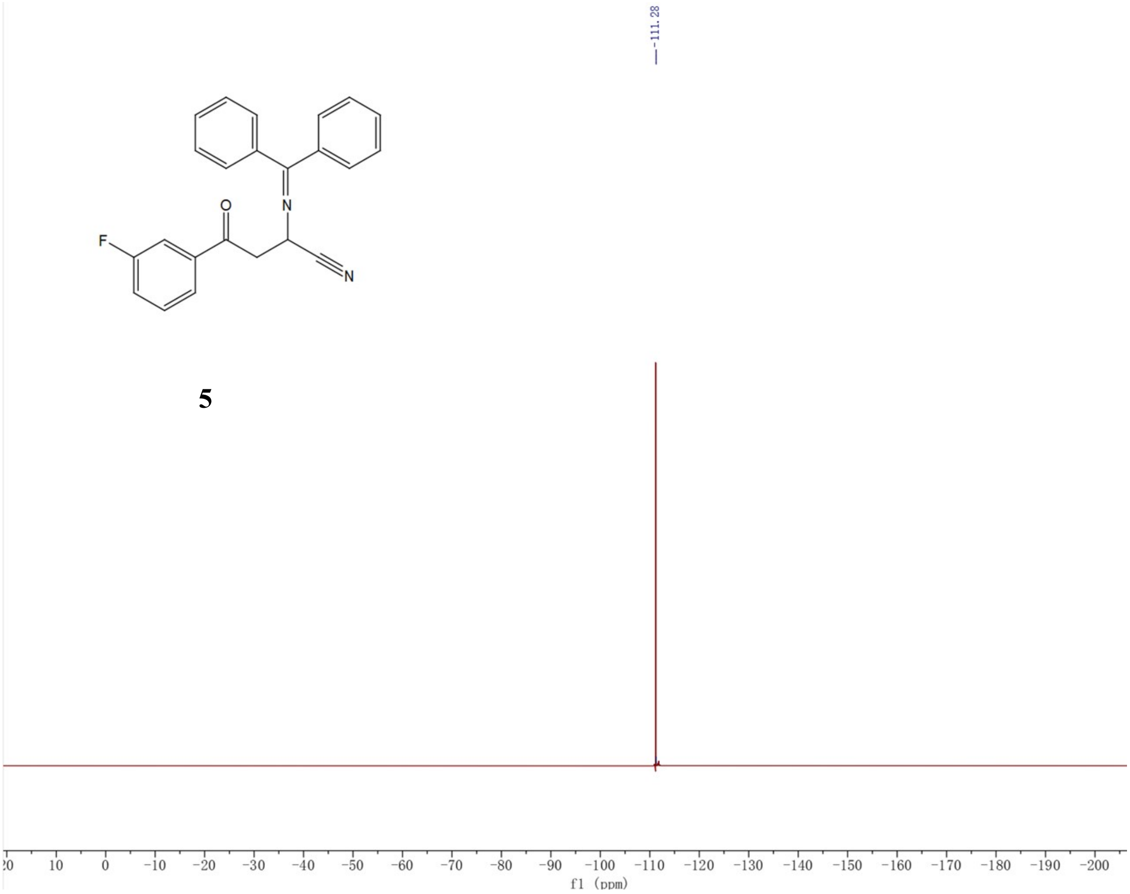
5

^{13}C NMR (101 MHz, CDCl$_3$)



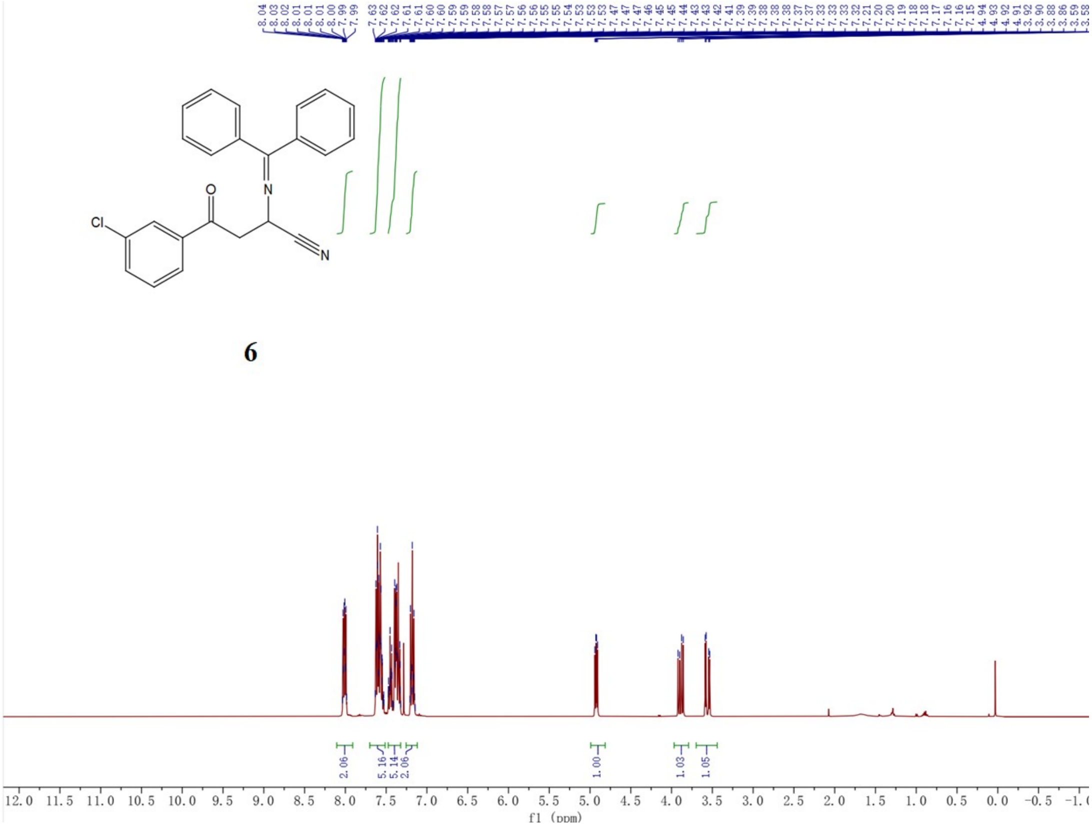
5

^{1}F NMR (377 MHz, CDCl$_3$)



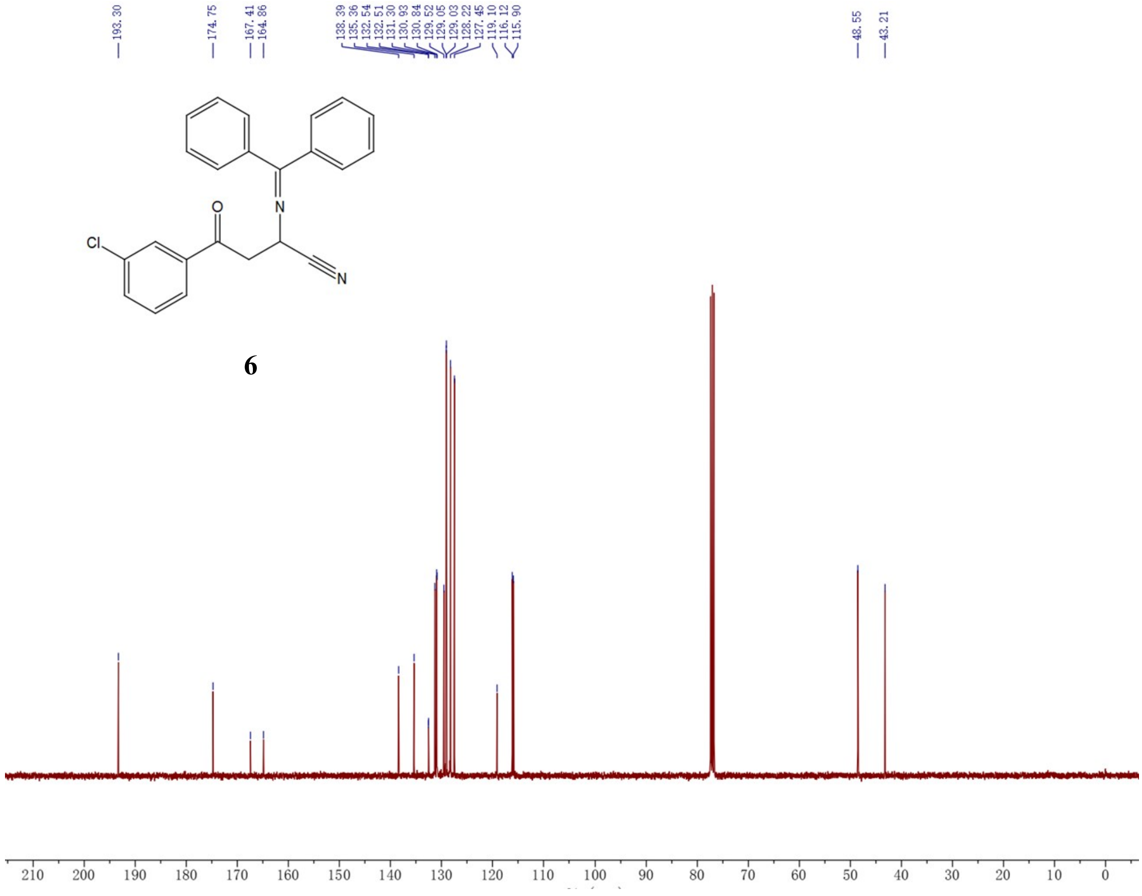
5

^{1}H NMR (400 MHz, CDCl$_3$)



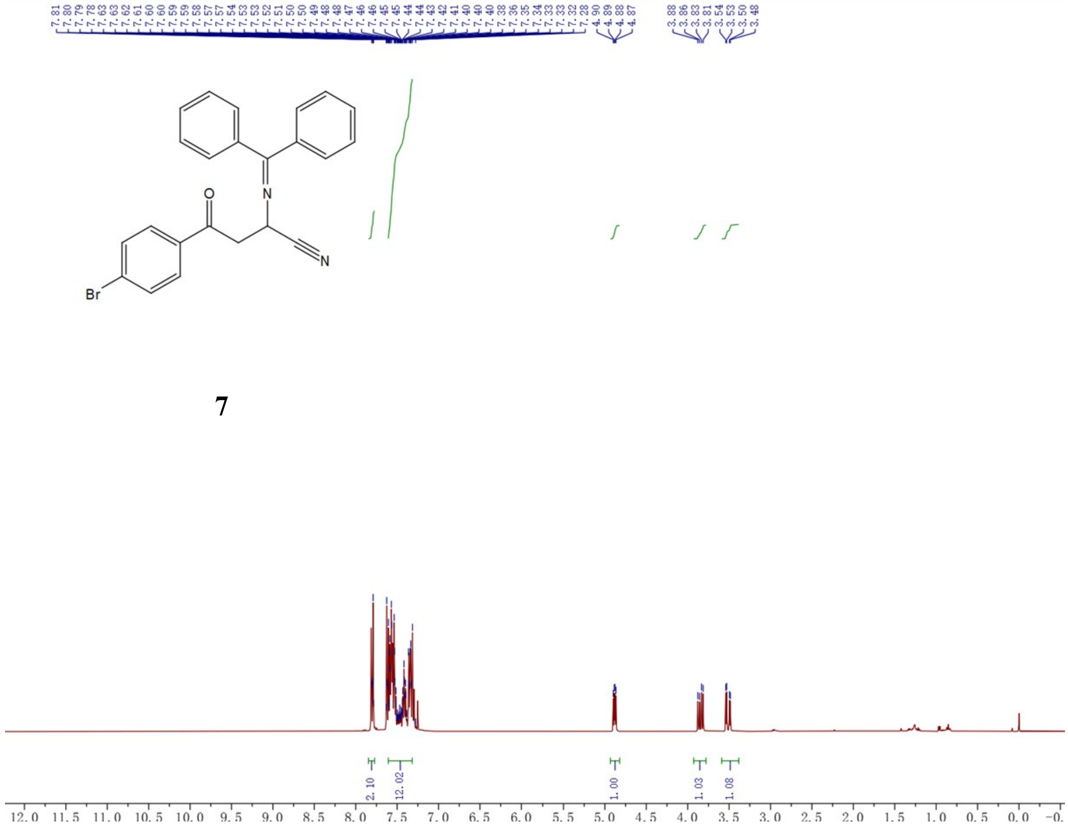
6

^{13}C NMR (101 MHz, CDCl$_3$)



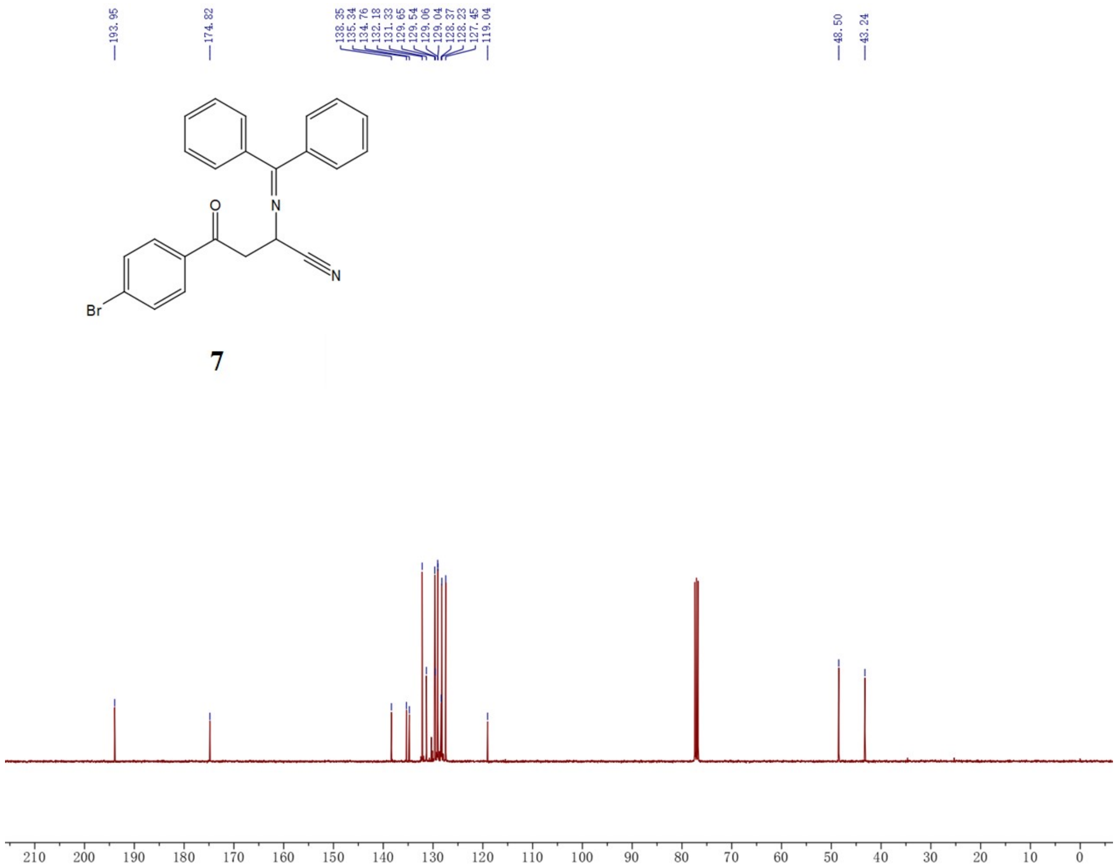
6

^{1}H NMR (400 MHz, CDCl$_3$)



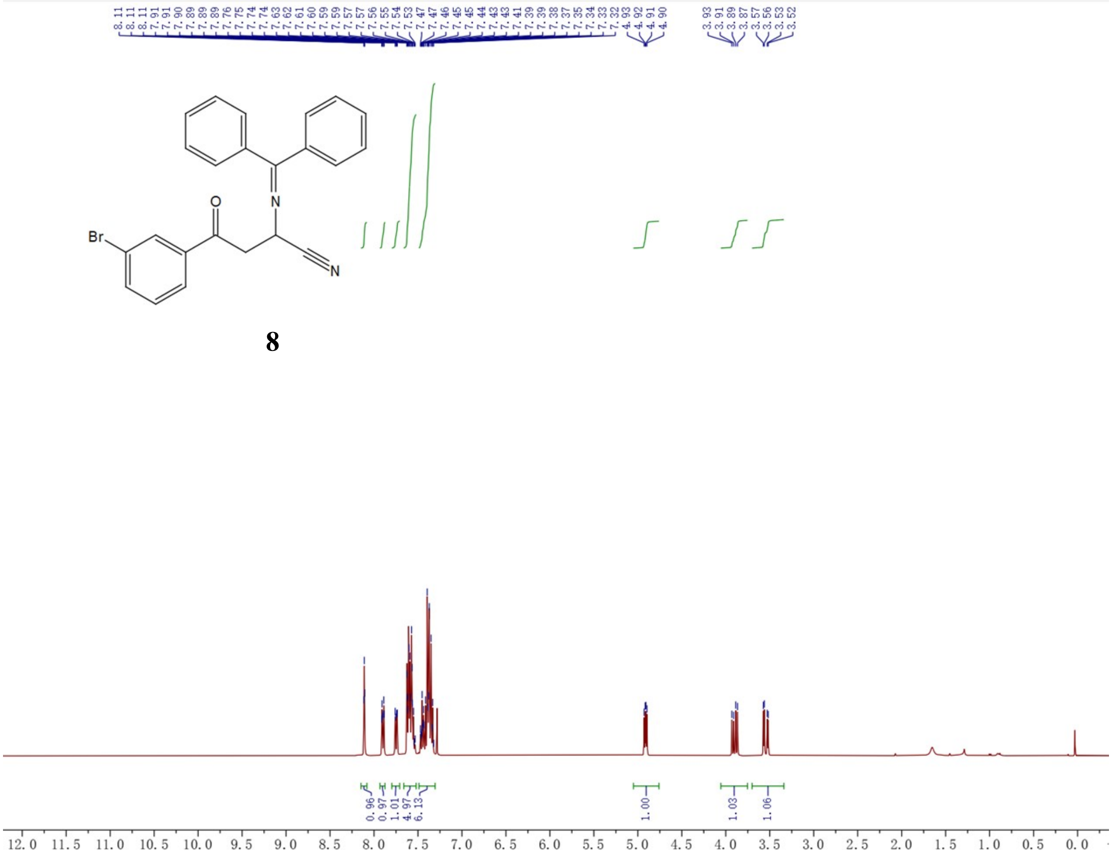
7

^{13}C NMR (101 MHz, $CDCl_3$)



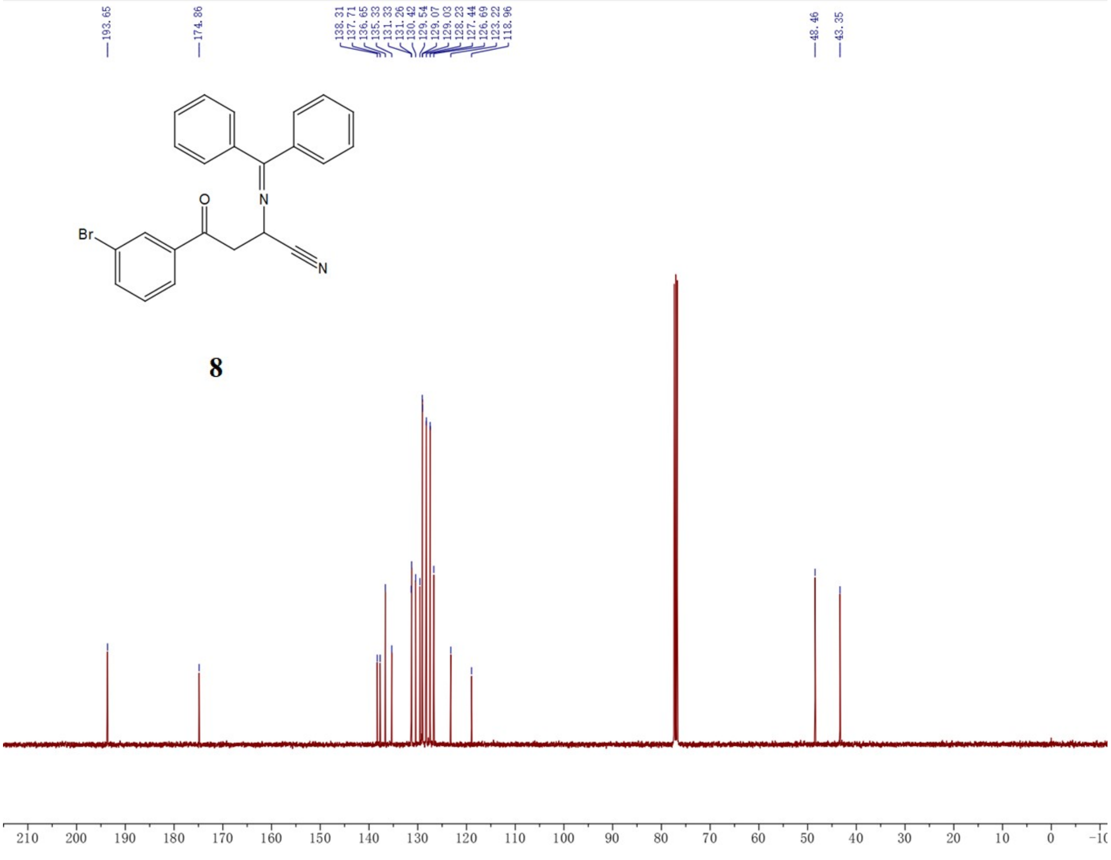
7

^{1}H NMR (400 MHz, $CDCl_3$)



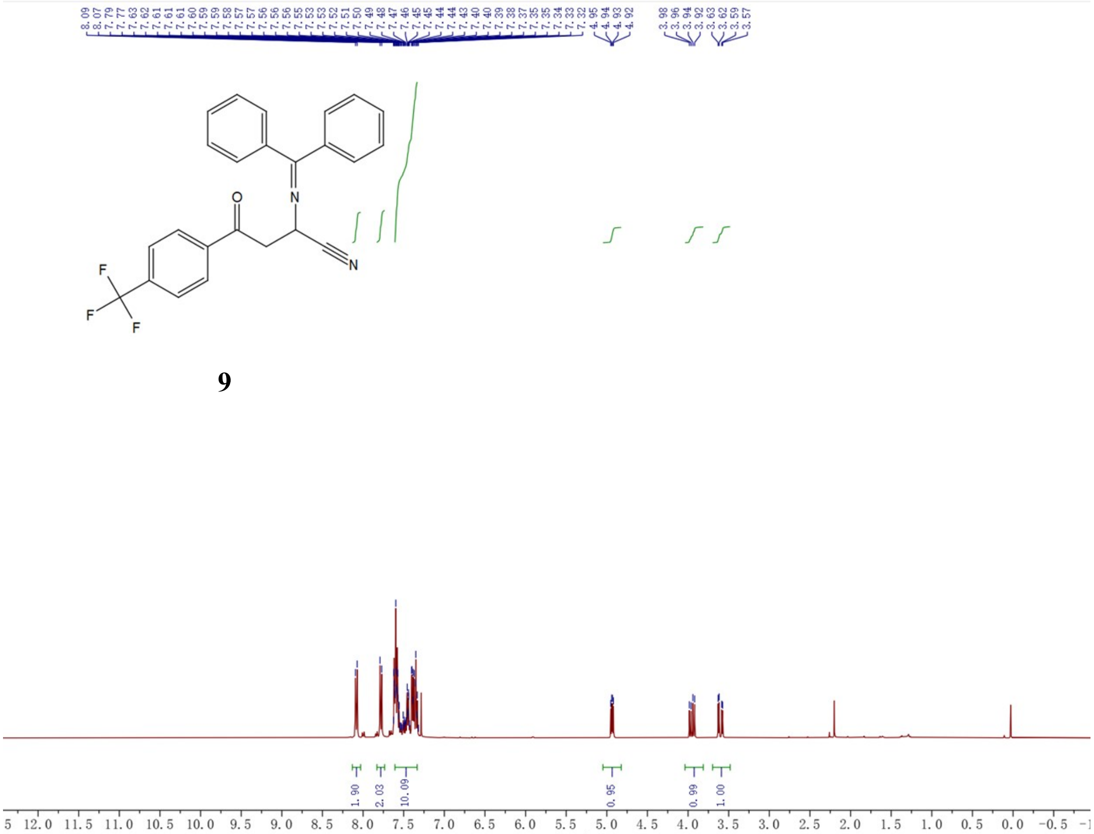
8

^{13}C NMR (101 MHz, CDCl$_3$)



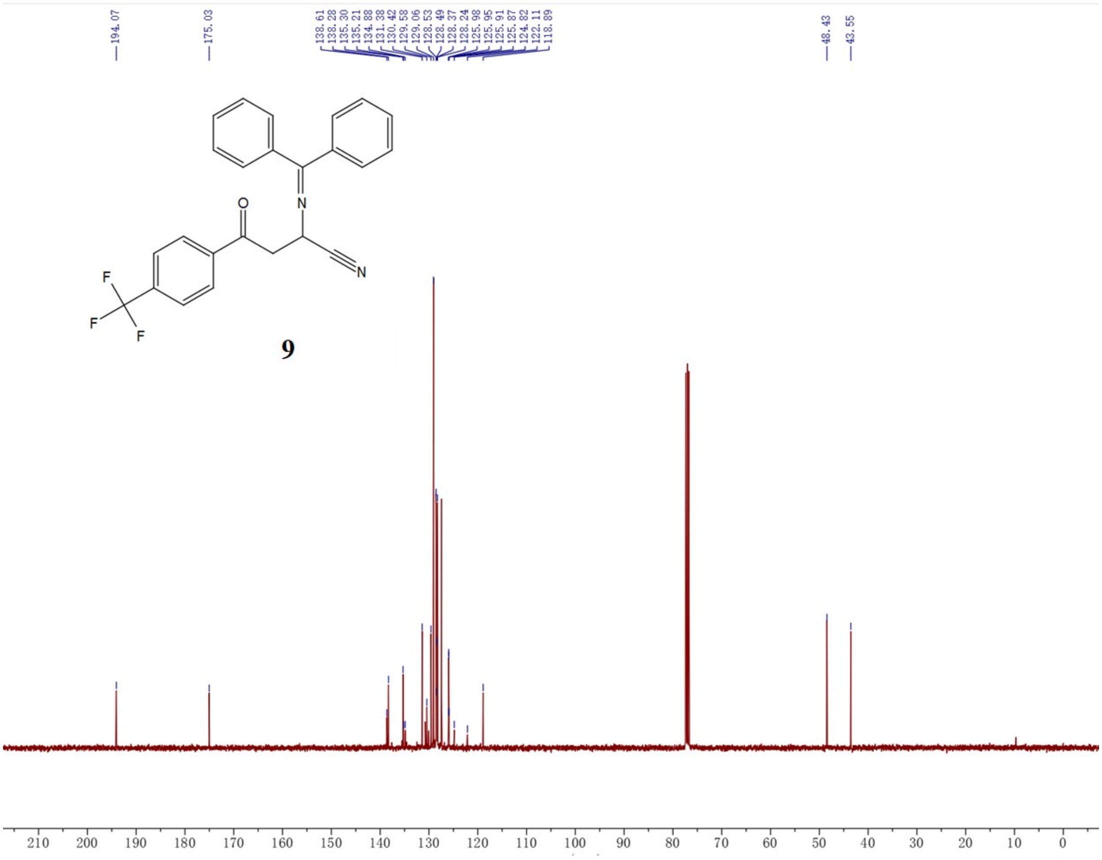
8

^1H NMR (400 MHz, $CDCl_3$)



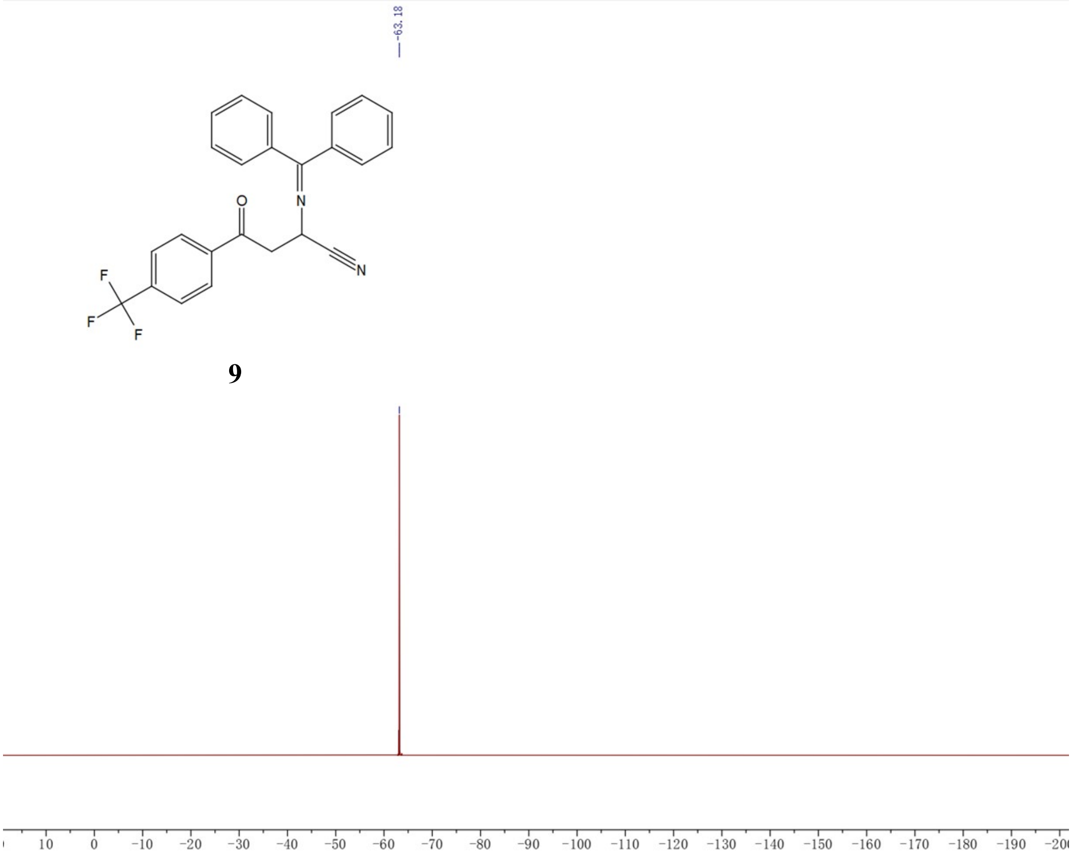
9

^{13}C NMR (101 MHz, $CDCl_3$)



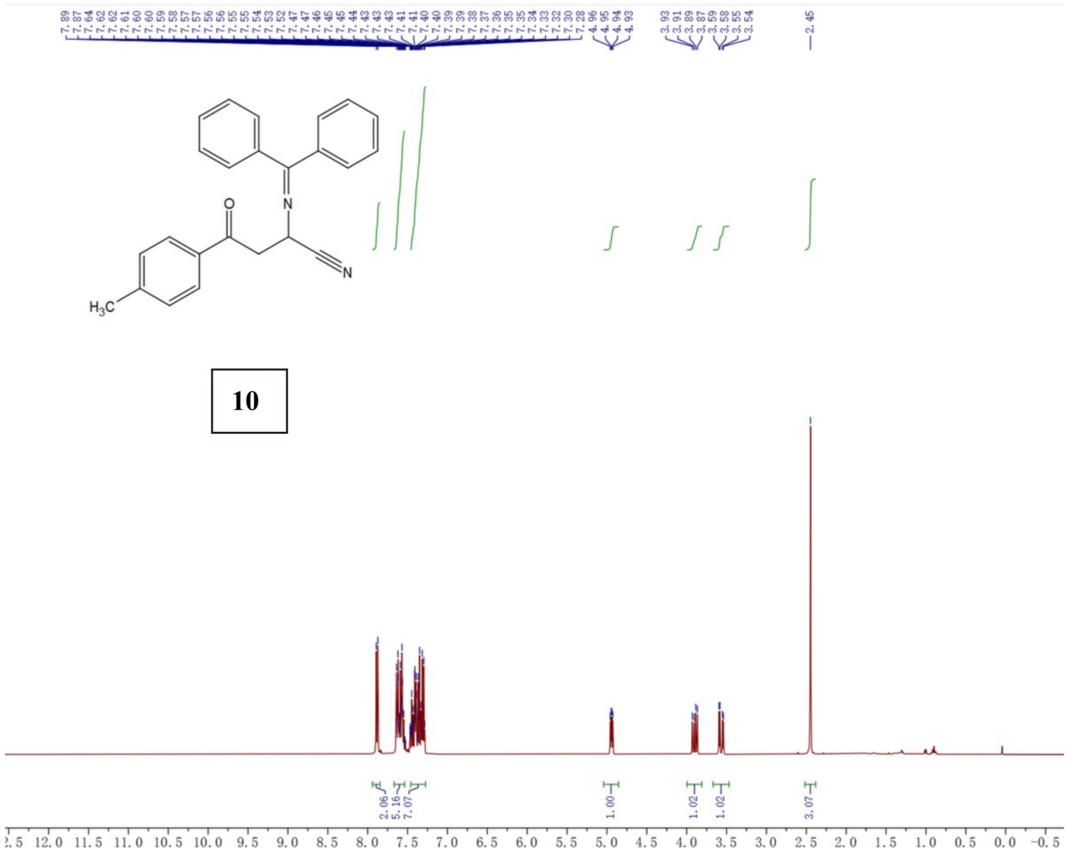
9

^{19}F NMR (337 MHz, $CDCl_3$)



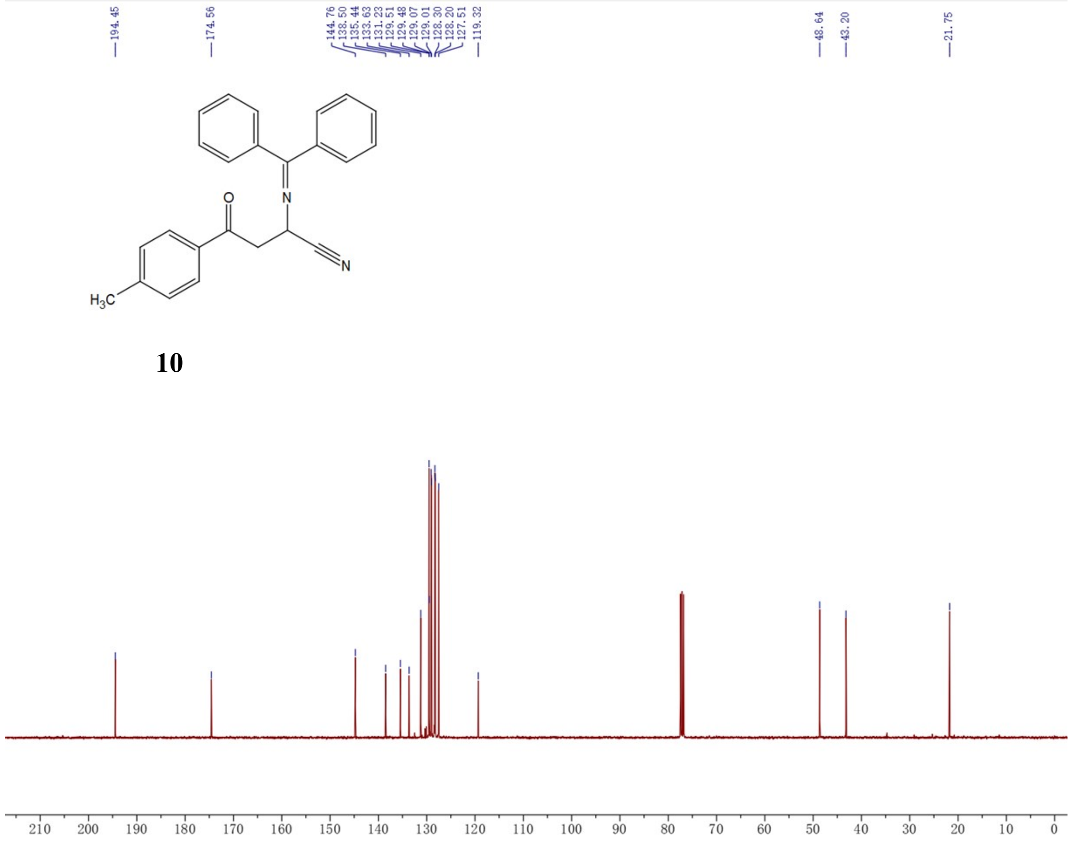
9

^{1}H NMR (400 MHz, CDCl$_3$)



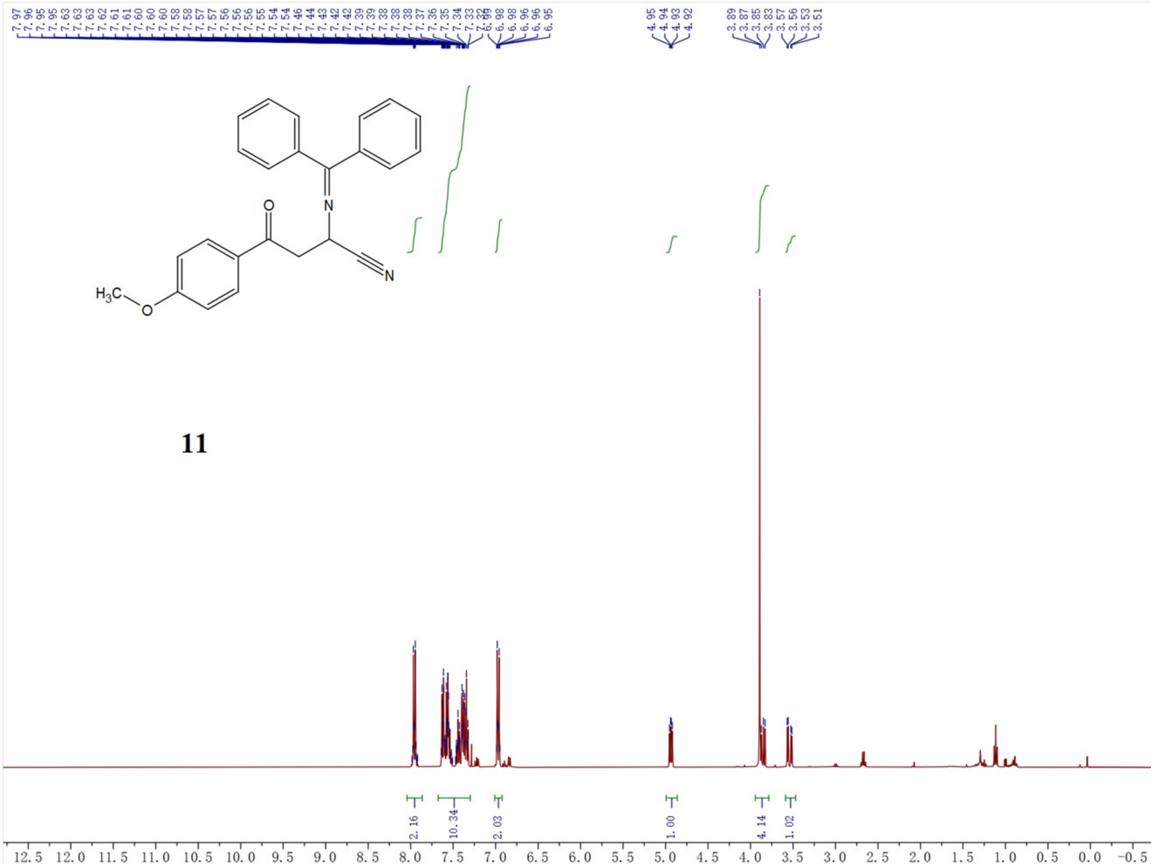
10

^{13}C NMR (101 MHz, CDCl$_3$)



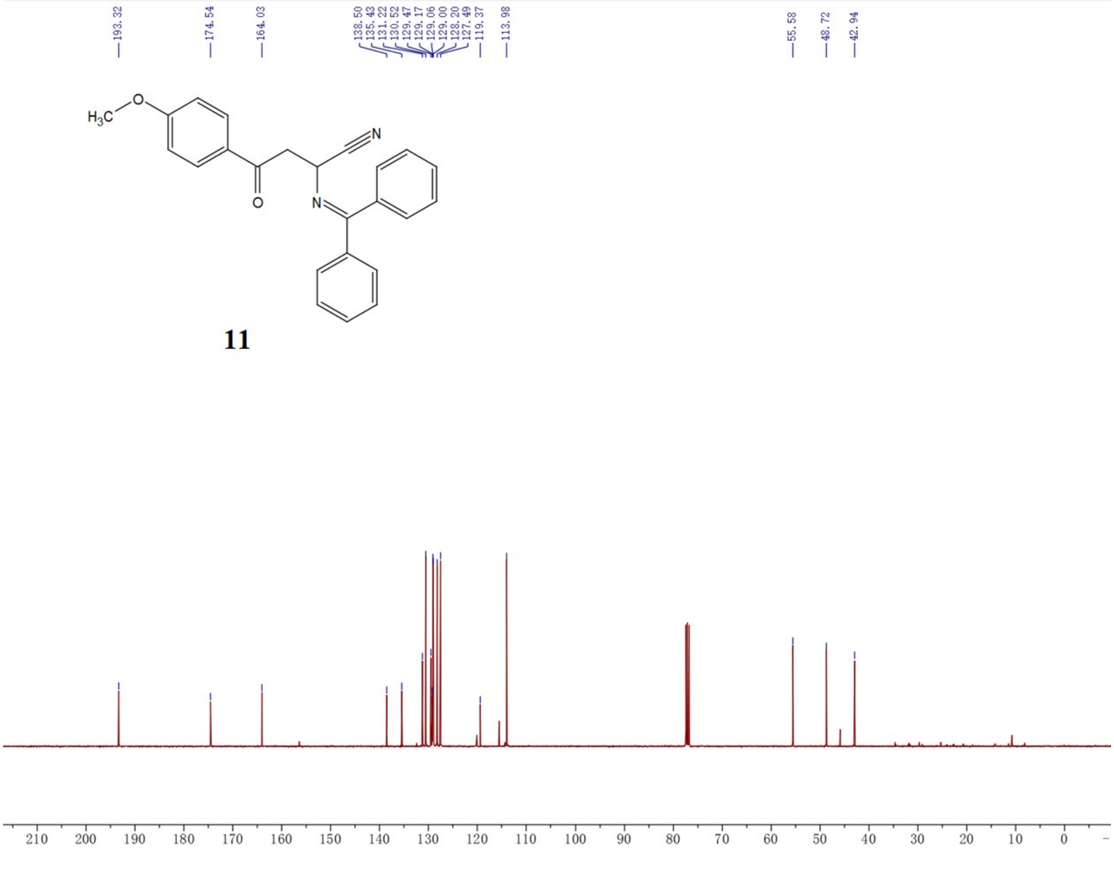
10

^{1}H NMR (400 MHz, $CDCl_3$)



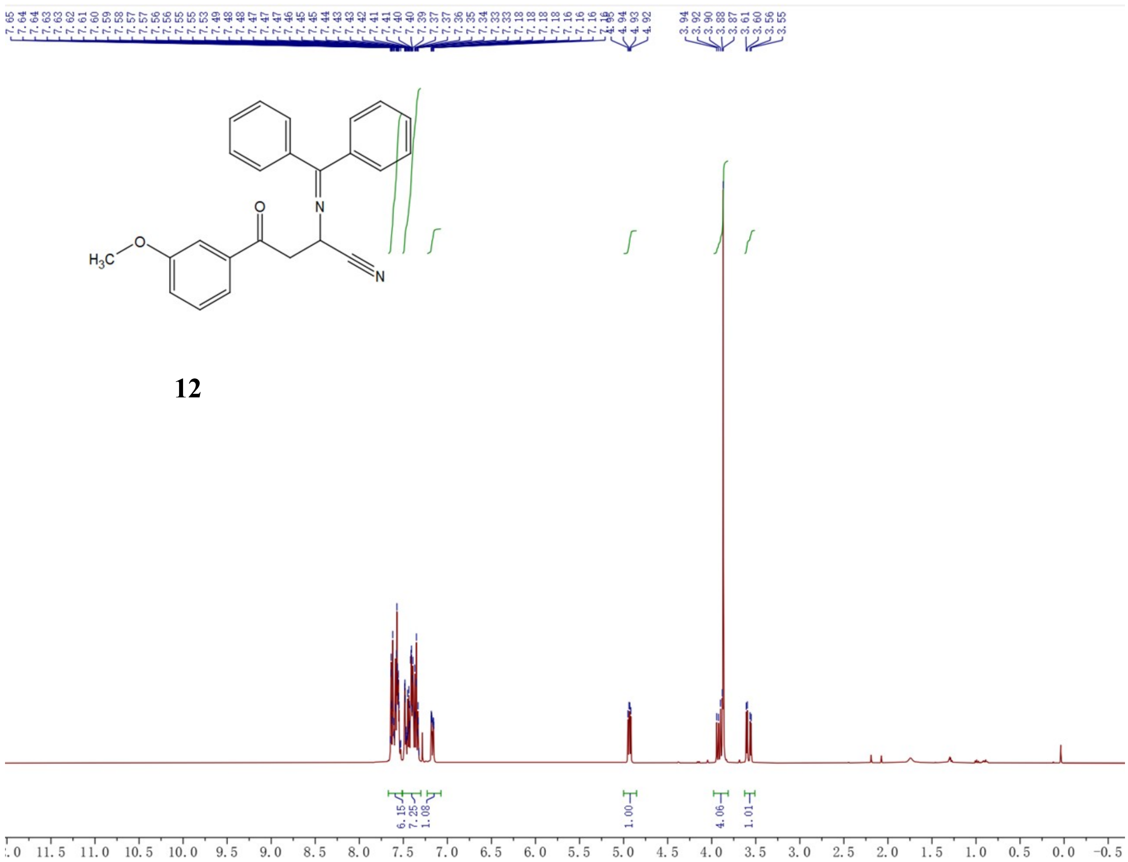
11

^{13}C NMR (101 MHz, $CDCl_3$)



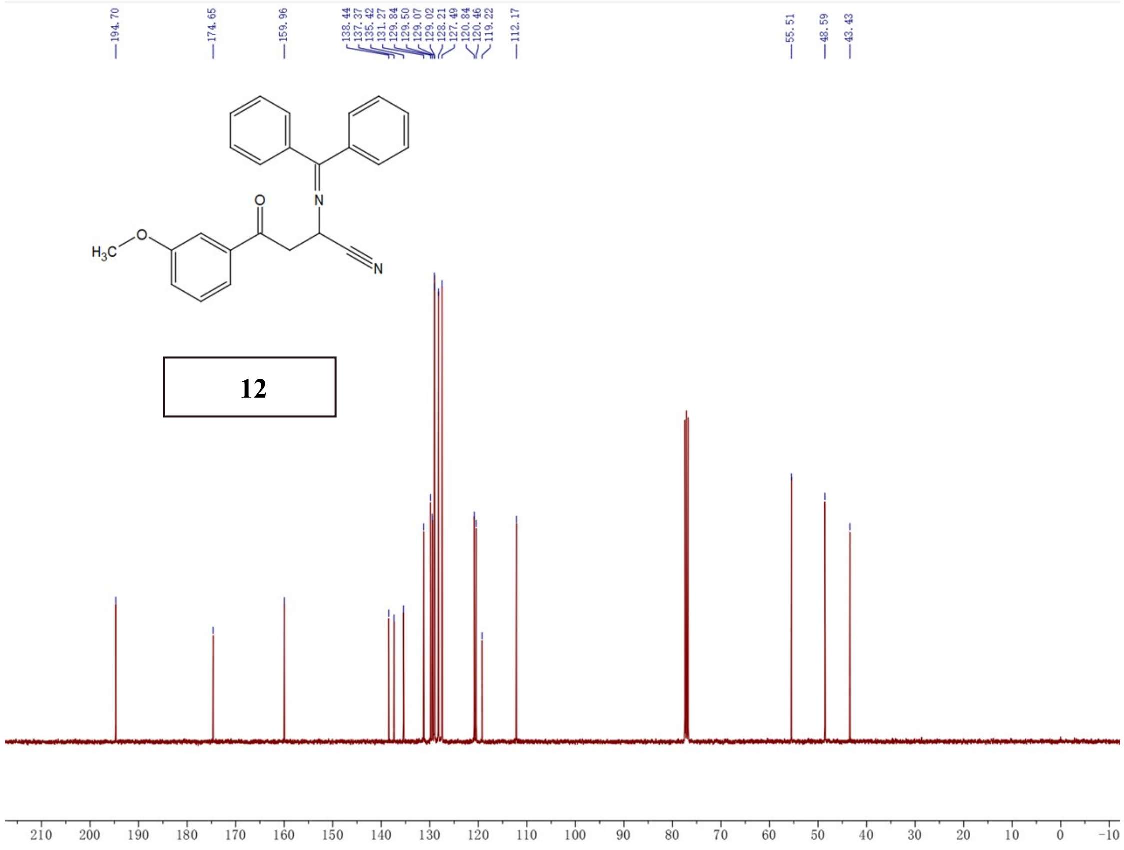
11

^{1}H NMR (400 MHz, CDCl$_3$)



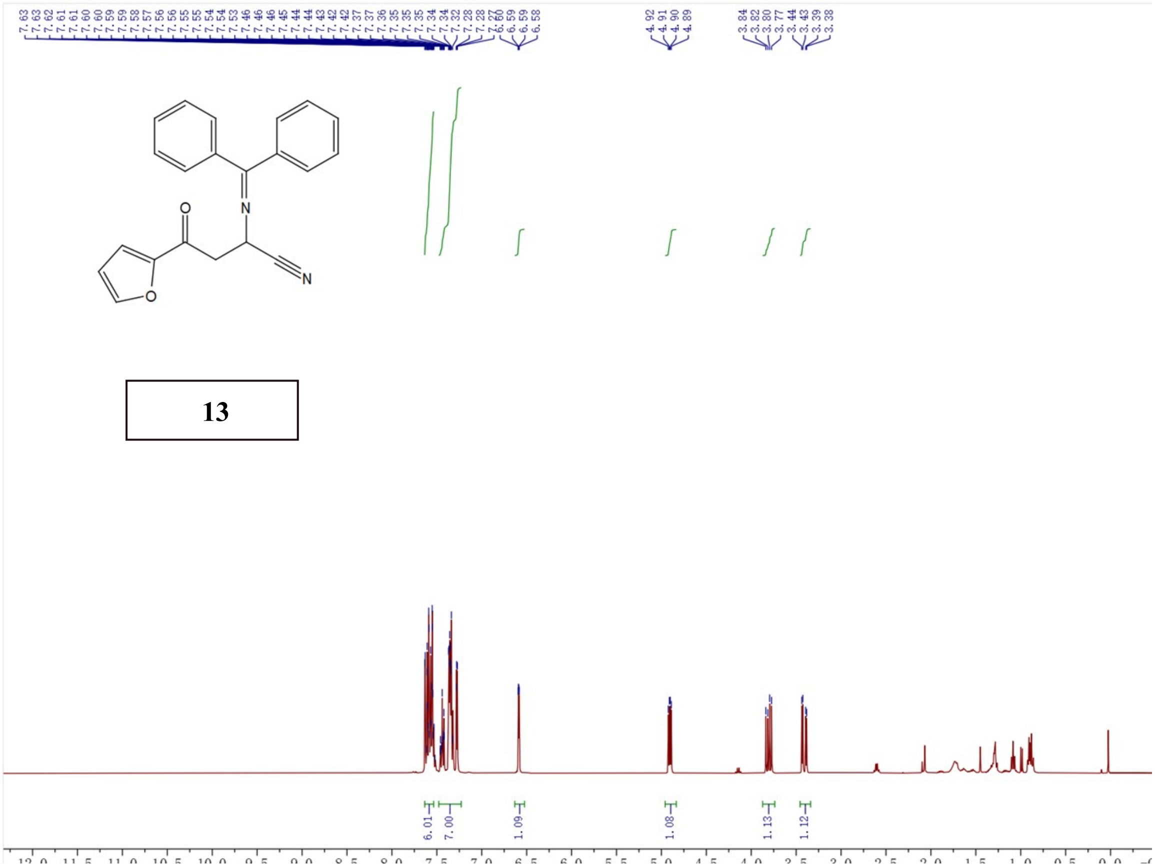
12

^{13}C NMR (101 MHz, CDCl$_3$)



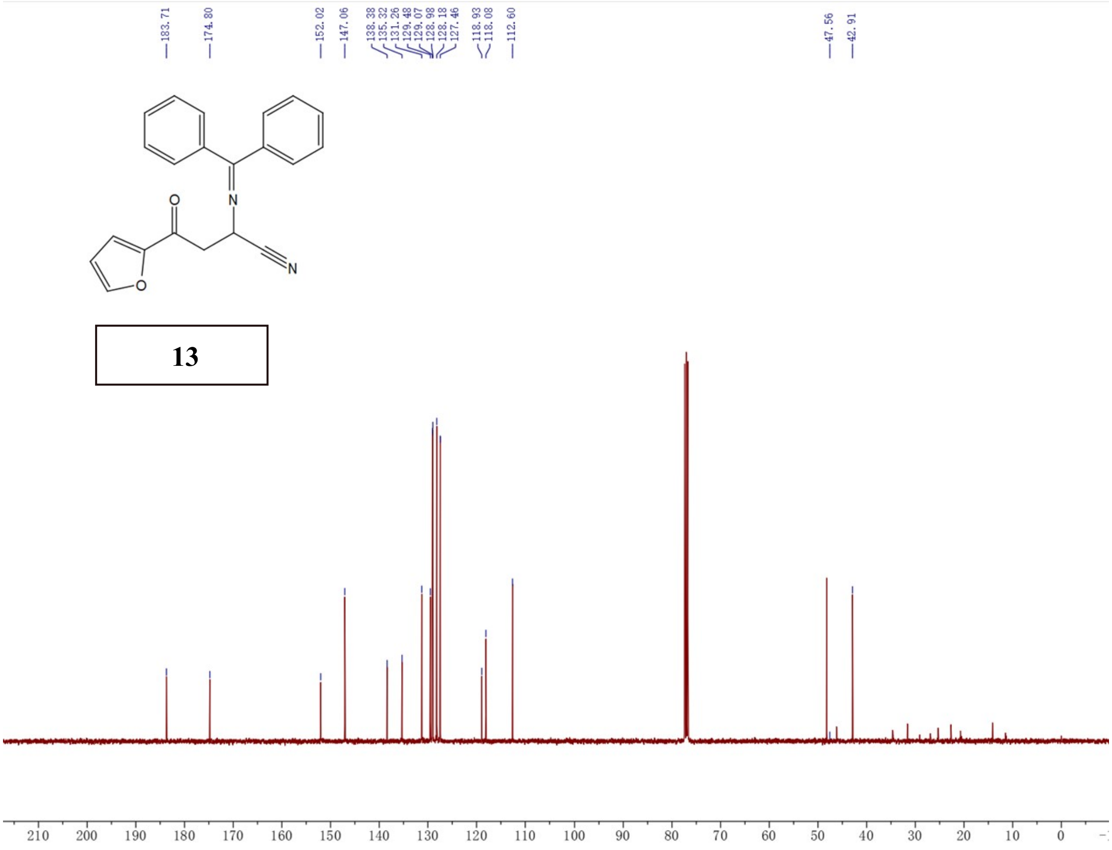
12

^1H NMR (400 MHz, $CDCl_3$)



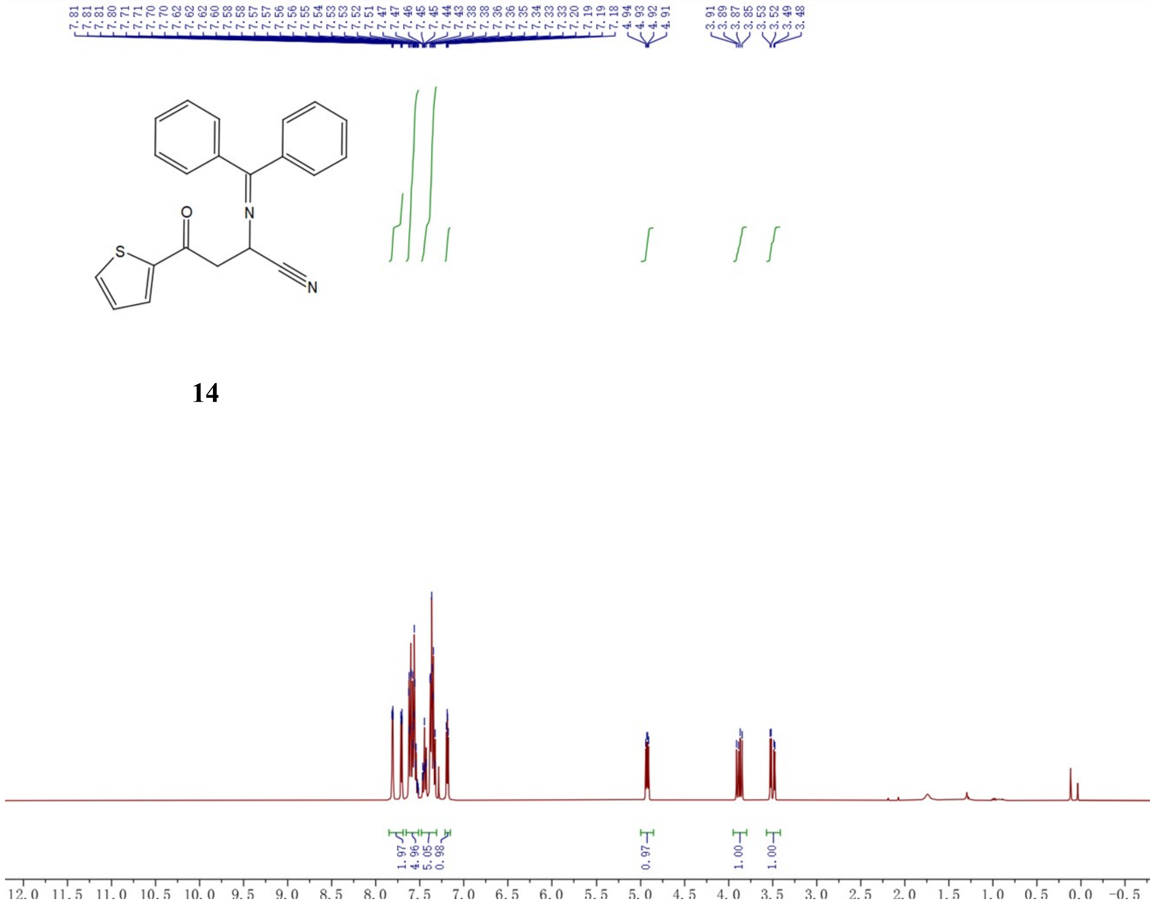
13

^{13}C NMR (101 MHz, $CDCl_3$)



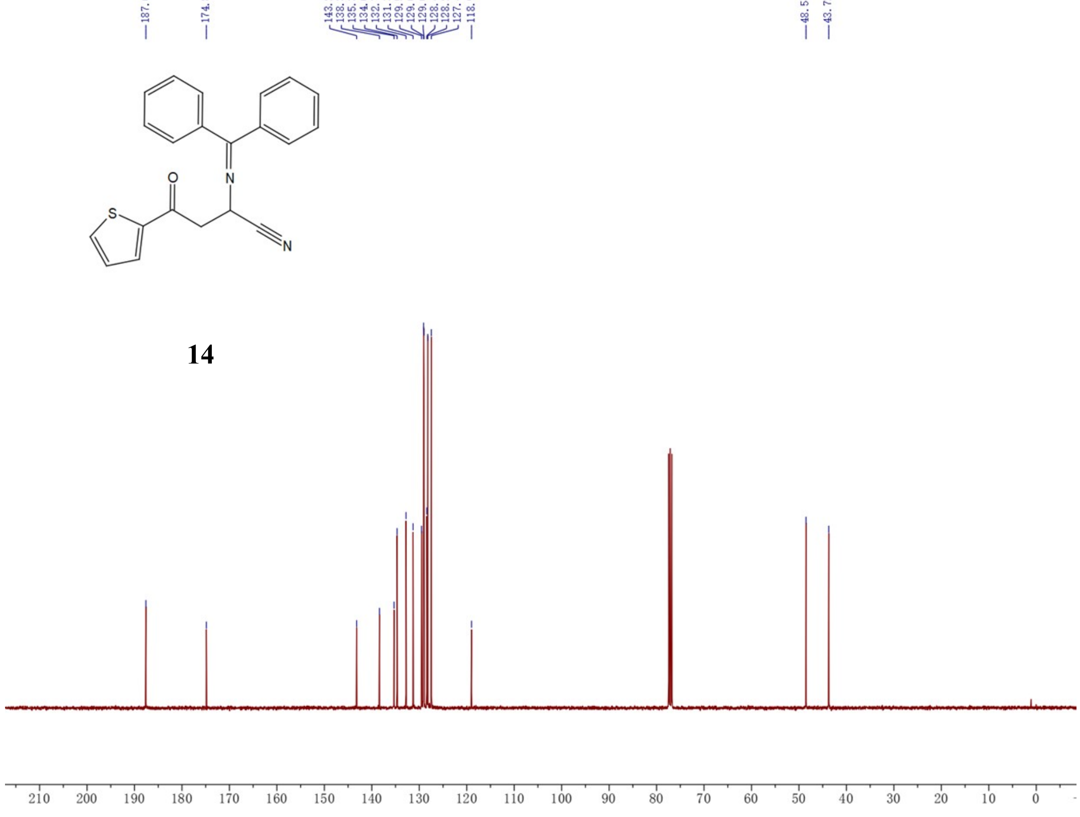
13

^1H NMR (400 MHz, $CDCl_3$)



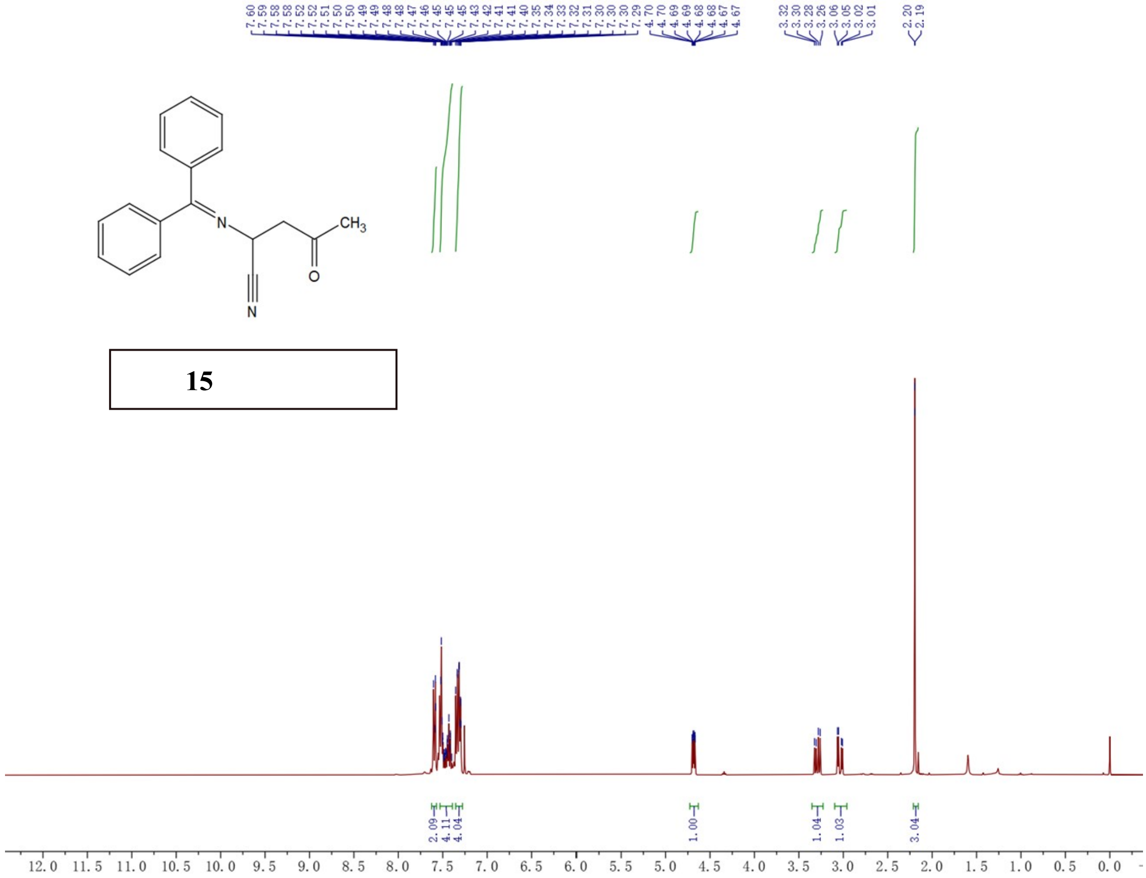
14

^{13}C NMR (101 MHz, $CDCl_3$)

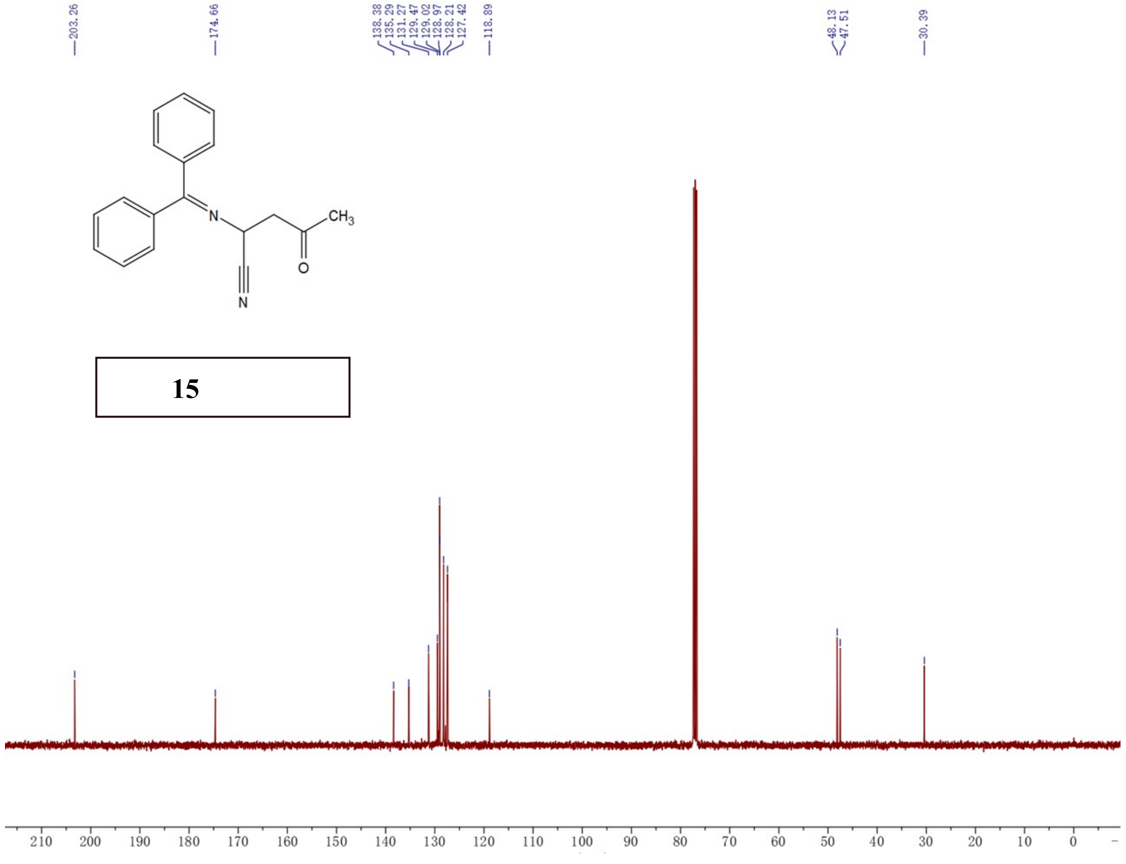


14

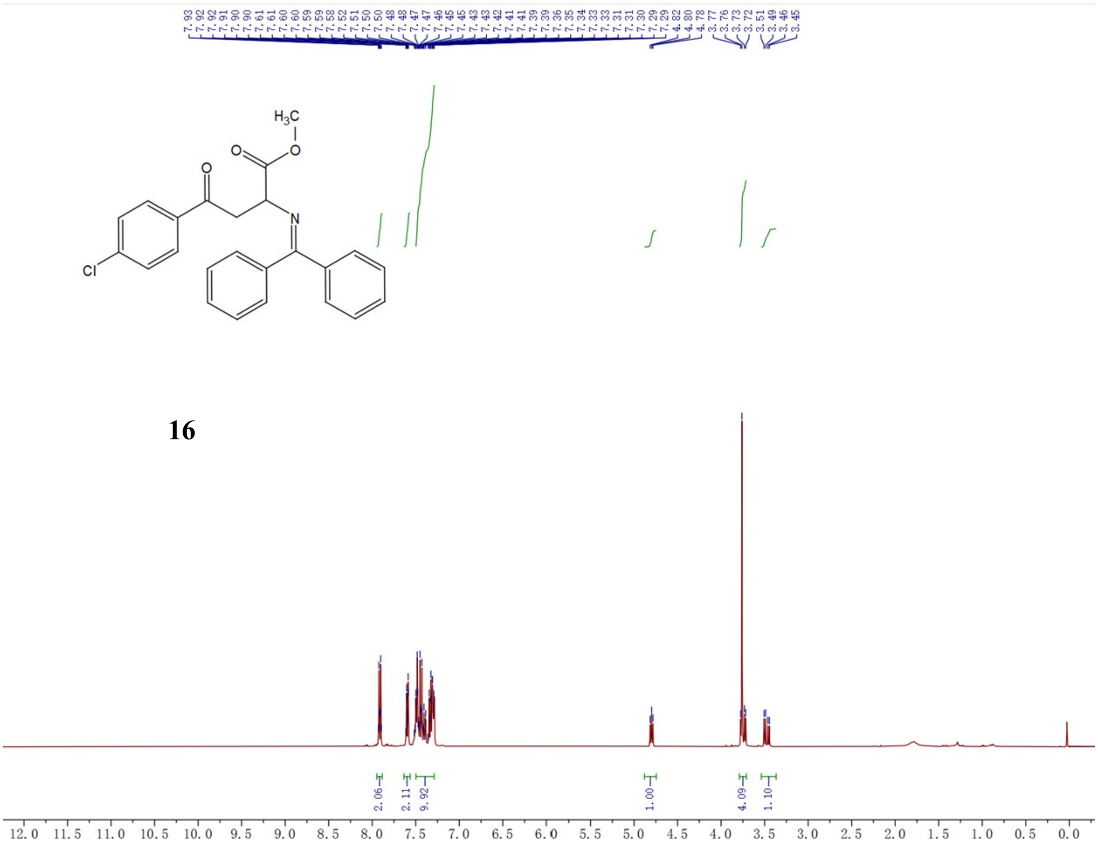
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)

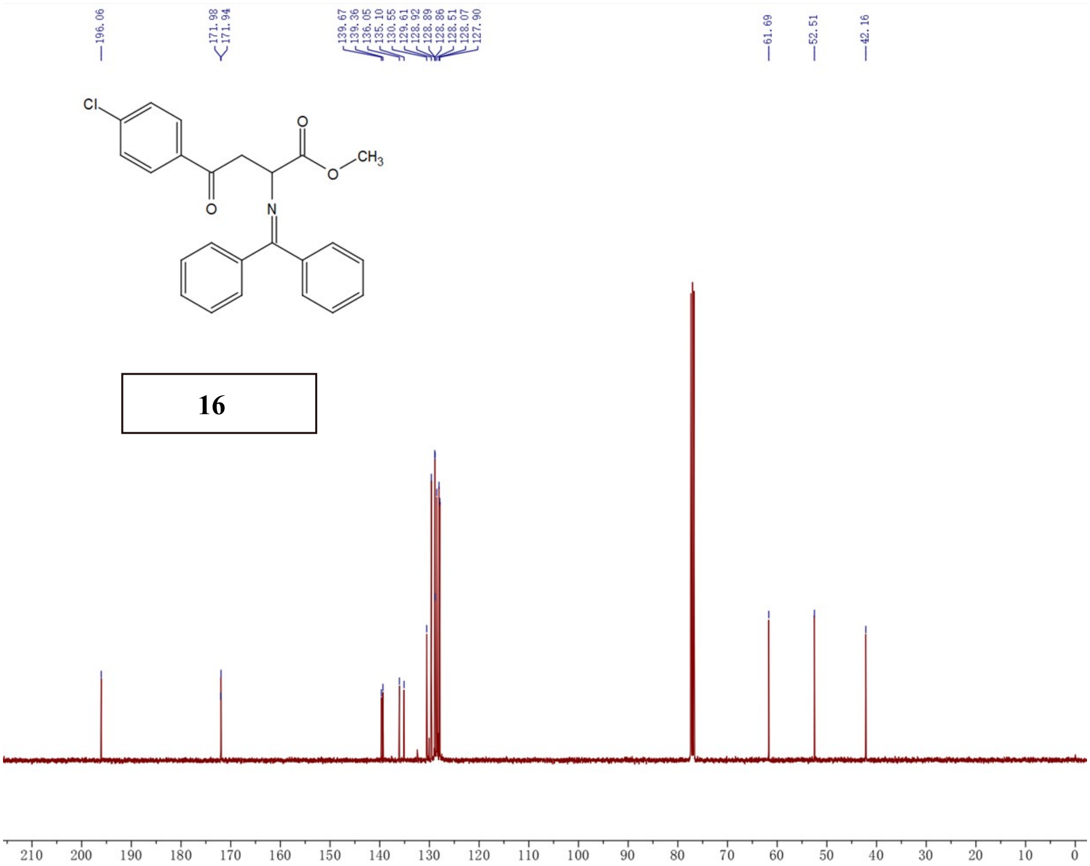


^1H NMR (400 MHz, $CDCl_3$)



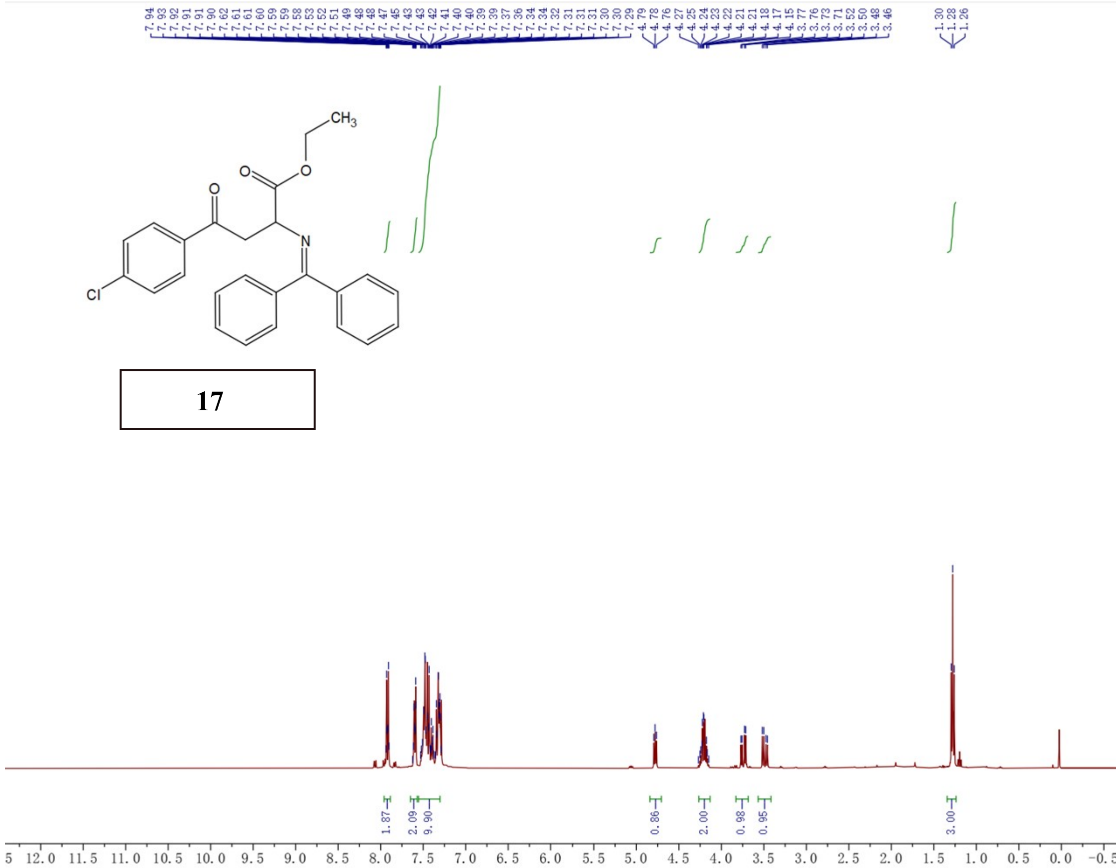
16

^{13}C NMR (101 MHz, $CDCl_3$)



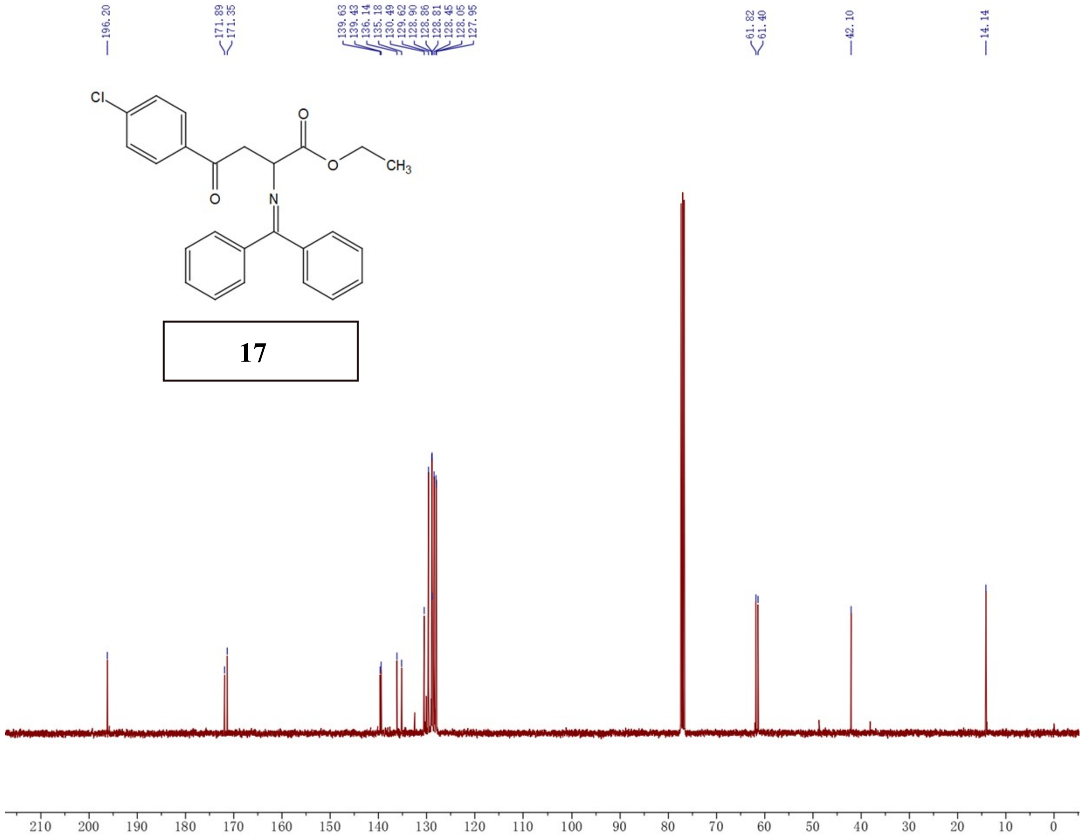
16

^{1}H NMR (400 MHz, $CDCl_3$)



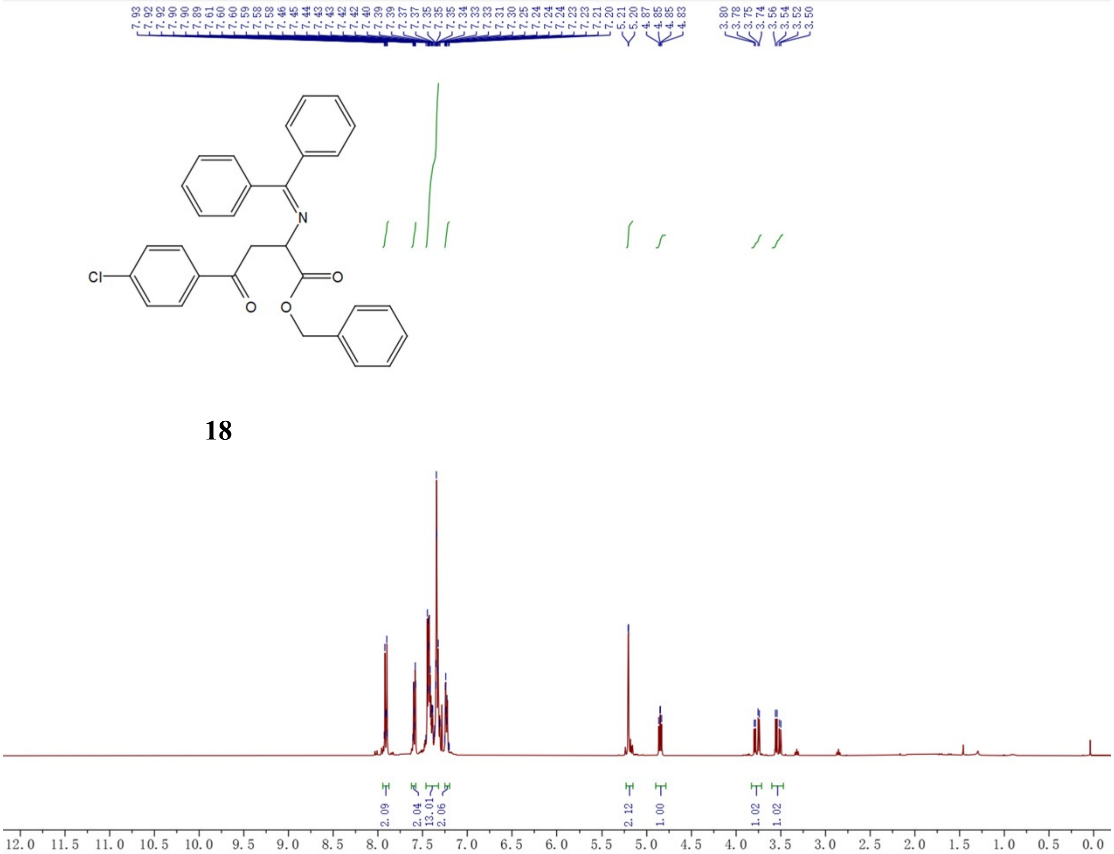
17

^{13}C NMR (101 MHz, $CDCl_3$)



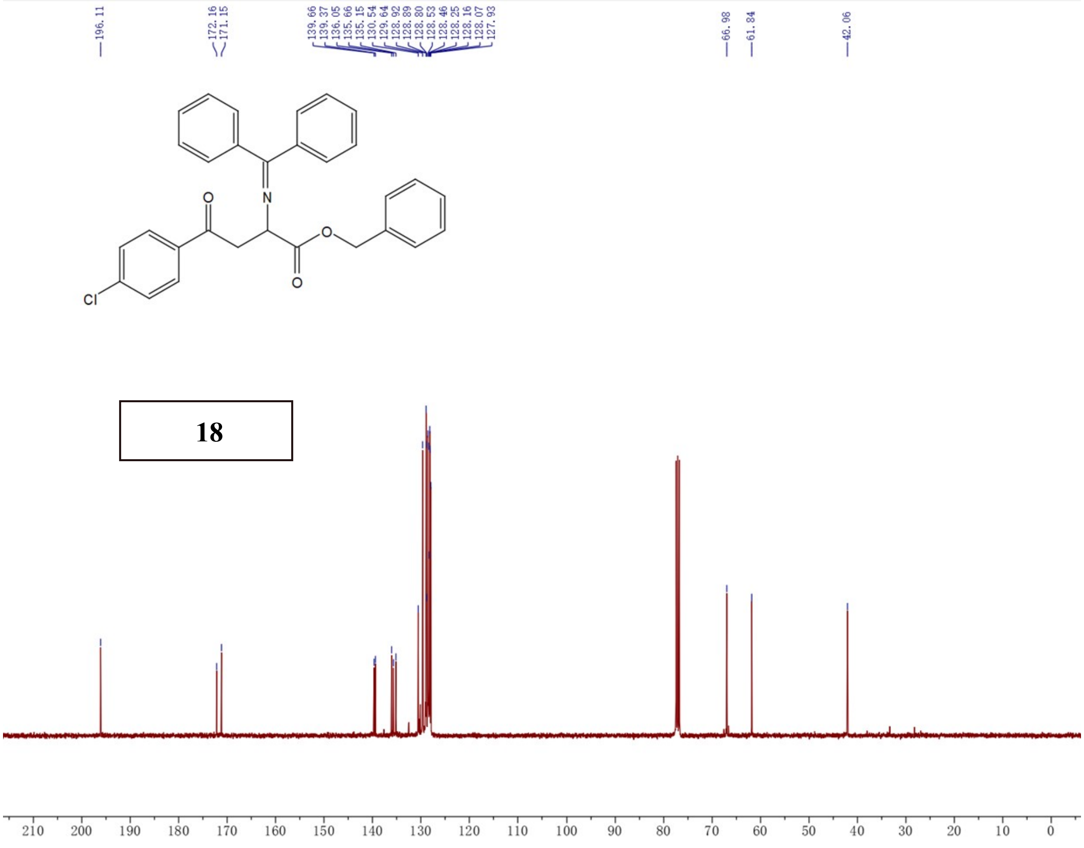
17

^{1}H NMR (400 MHz, CDCl$_3$)



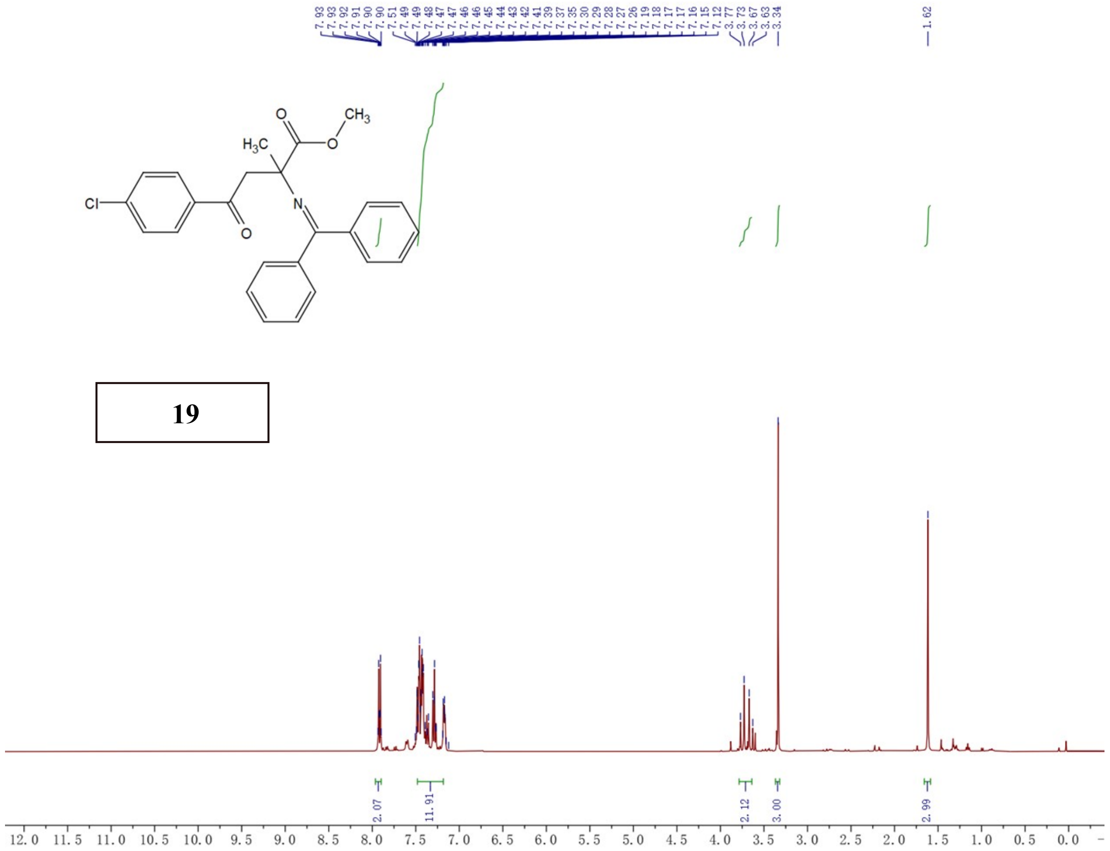
18

^{13}C NMR (101 MHz, CDCl$_3$)



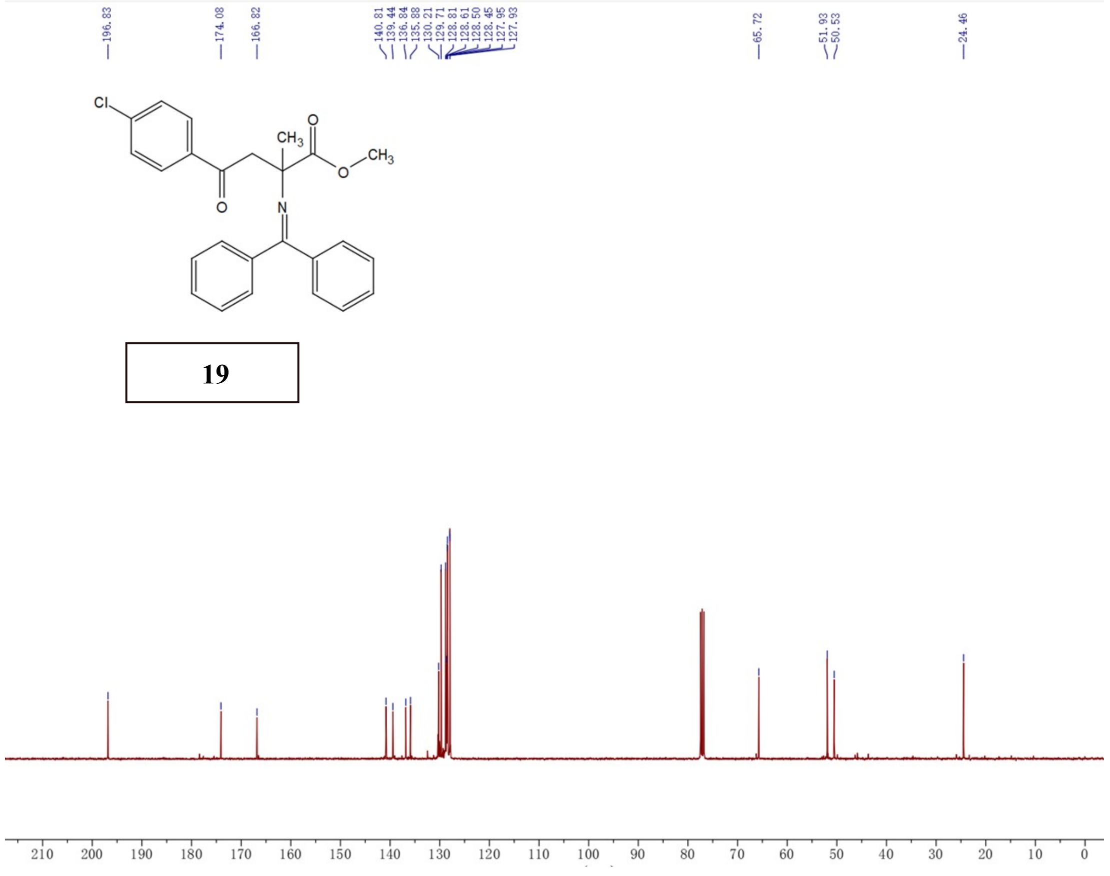
18

^{1}H NMR (400 MHz, $CDCl_3$)



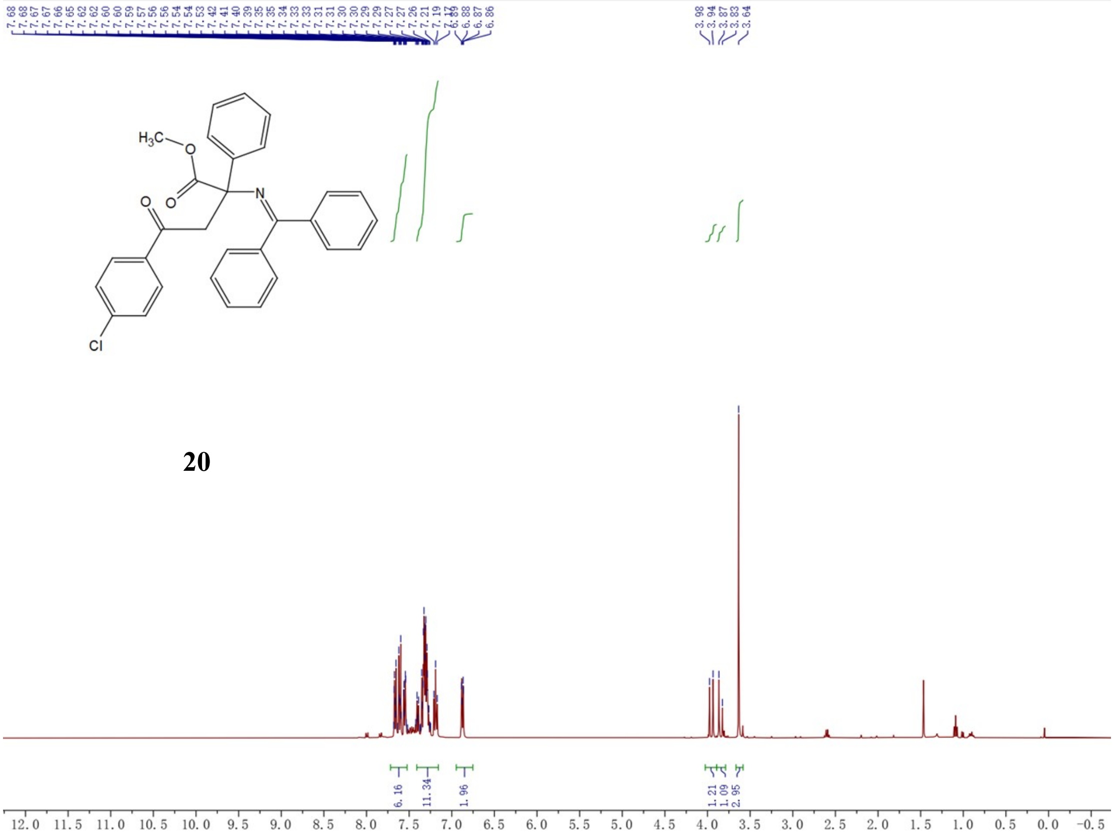
19

^{13}C NMR (101 MHz, $CDCl_3$)



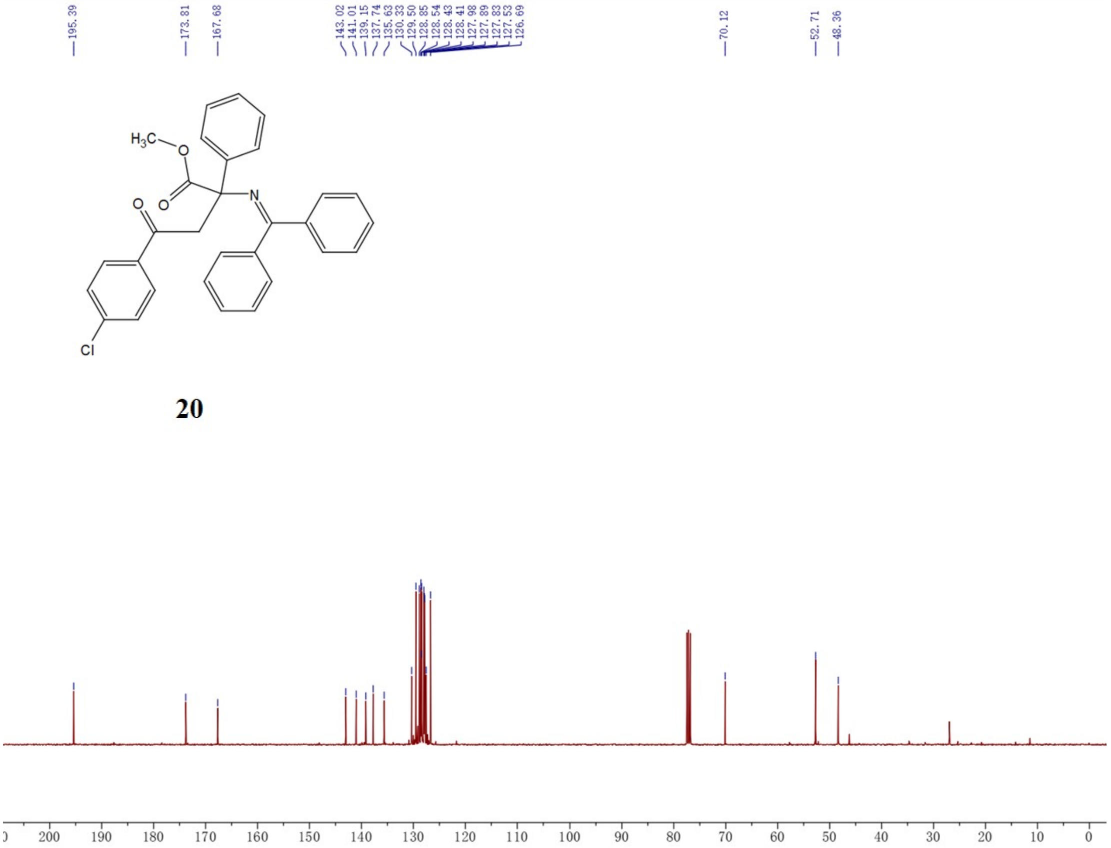
19

^{1}H NMR (400 MHz, CDCl$_3$)



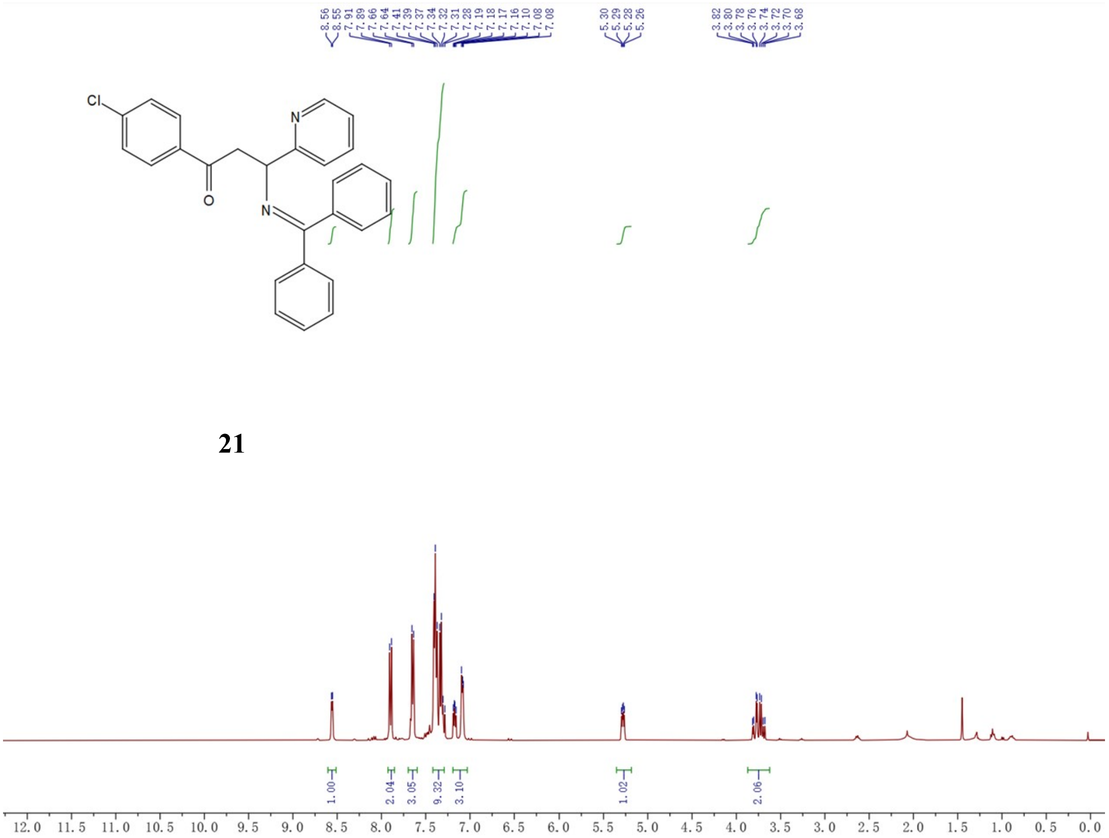
20

^{13}C NMR (101 MHz, CDCl$_3$)



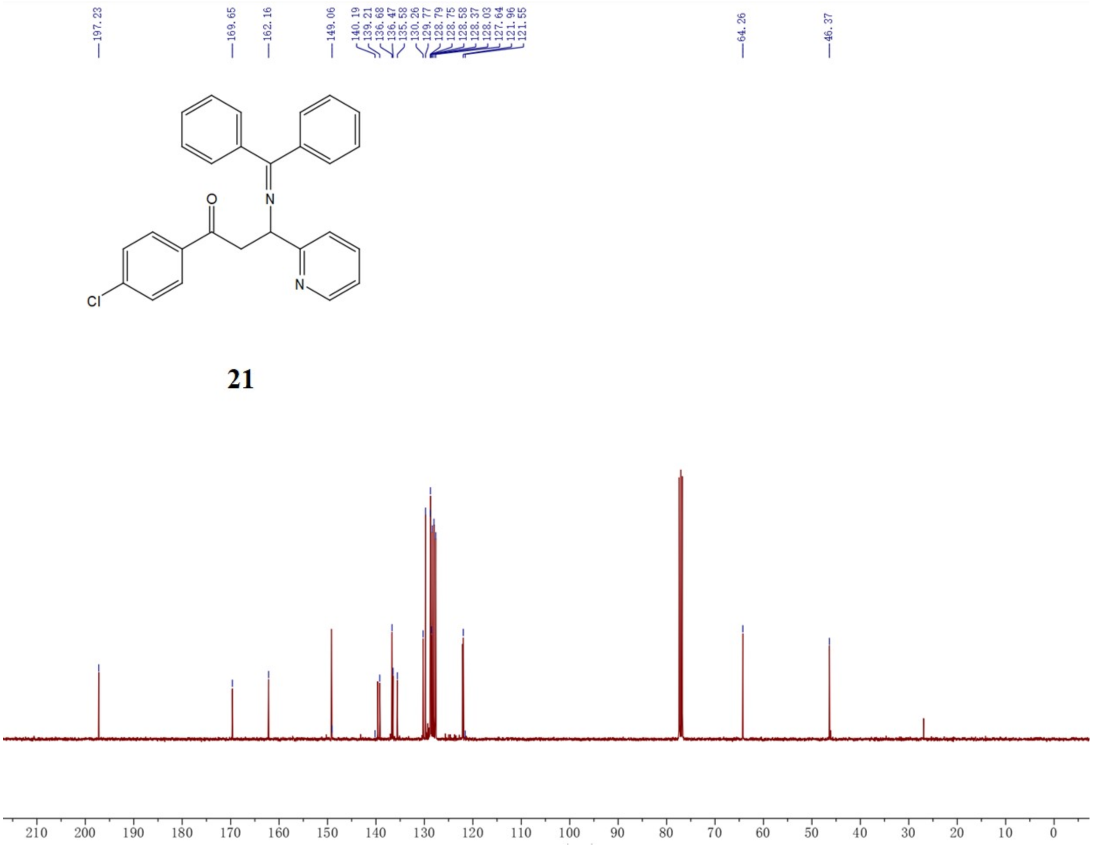
20

^{1}H NMR (400 MHz, CDCl$_3$)



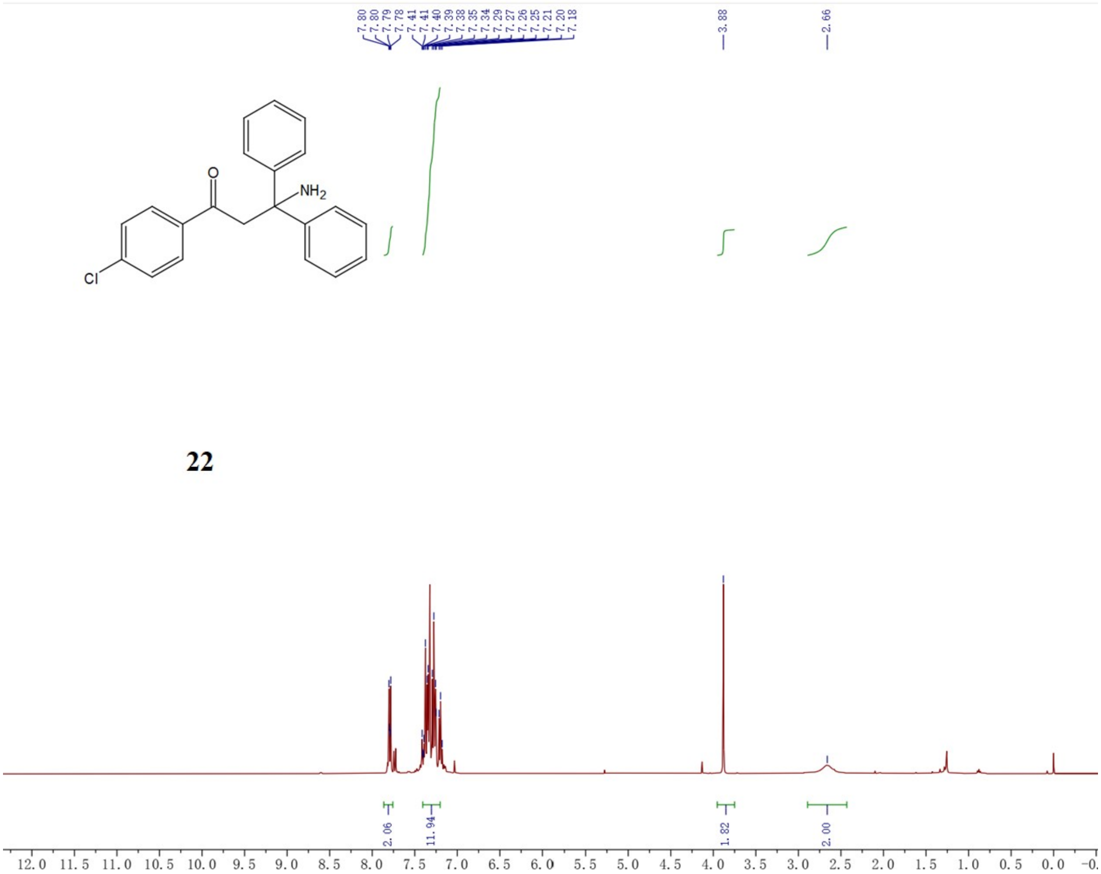
21

^{13}C NMR (101 MHz, CDCl$_3$)



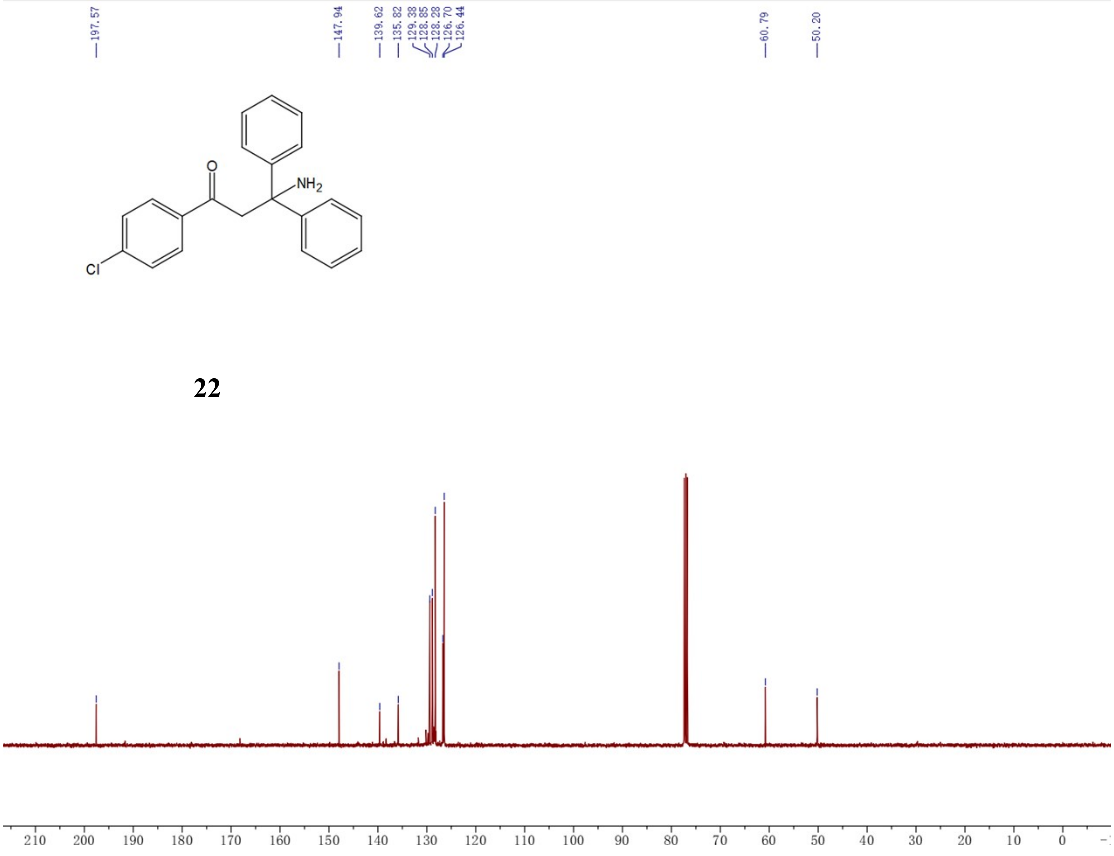
21

^{1}H NMR (400 MHz, $CDCl_3$)



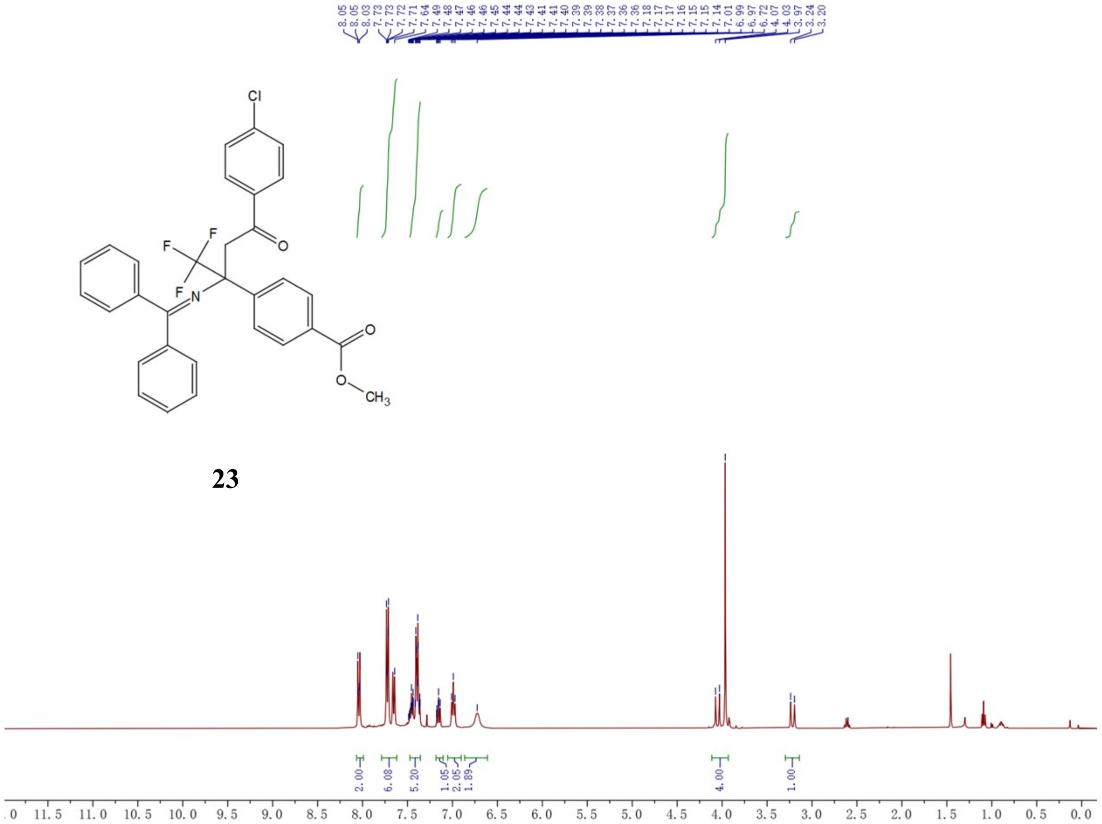
22

^{13}C NMR (101 MHz, $CDCl_3$)



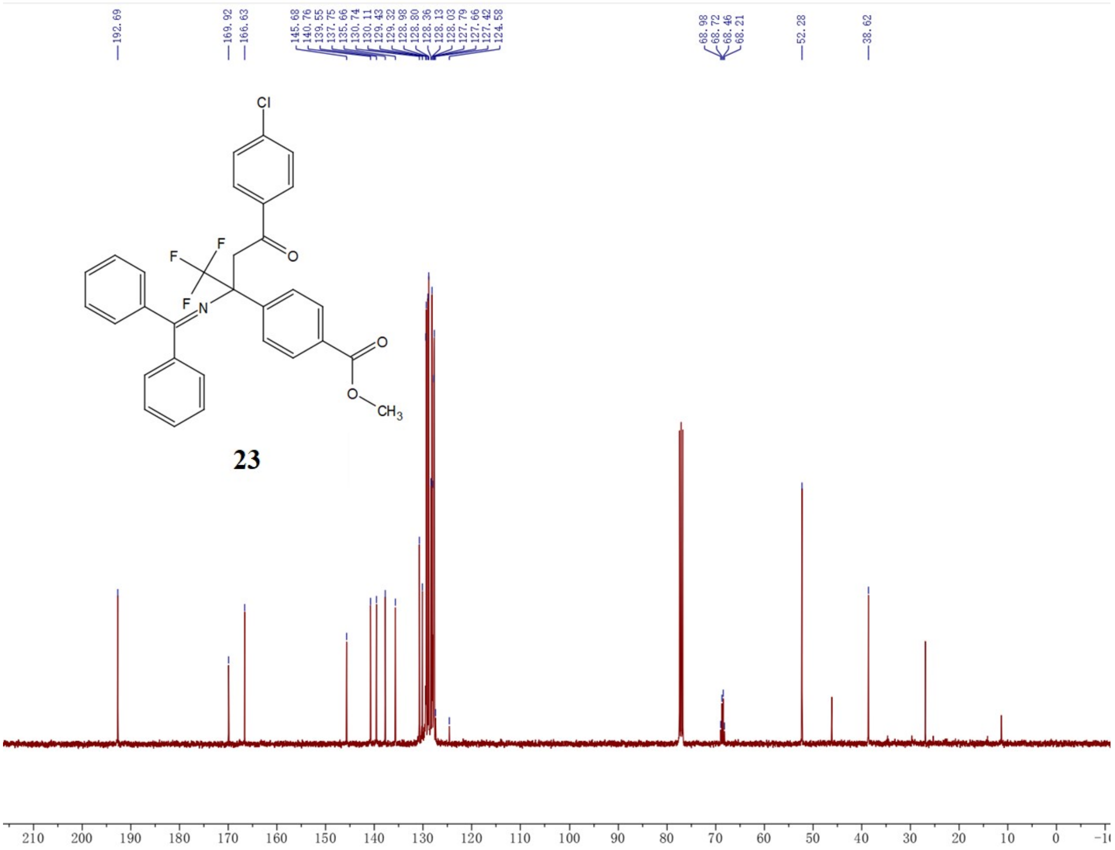
22

^{1}H NMR (400 MHz, CDCl$_3$)



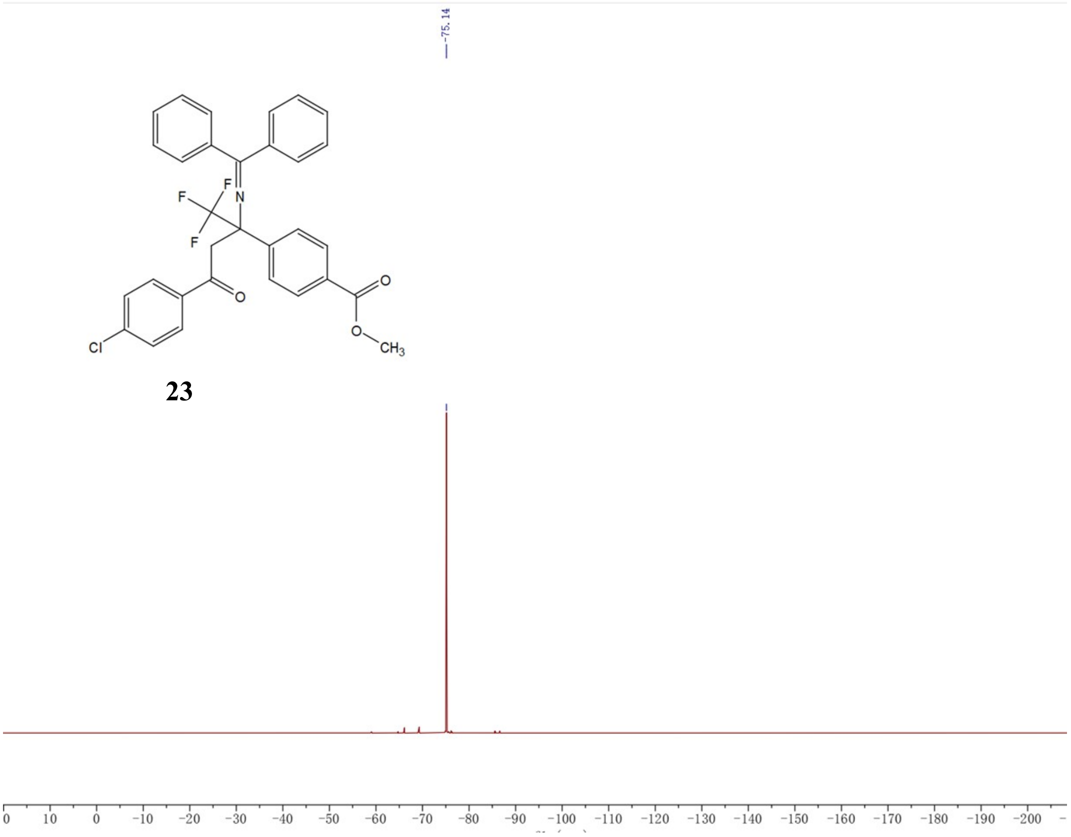
23

^{13}C NMR (101 MHz, CDCl$_3$)



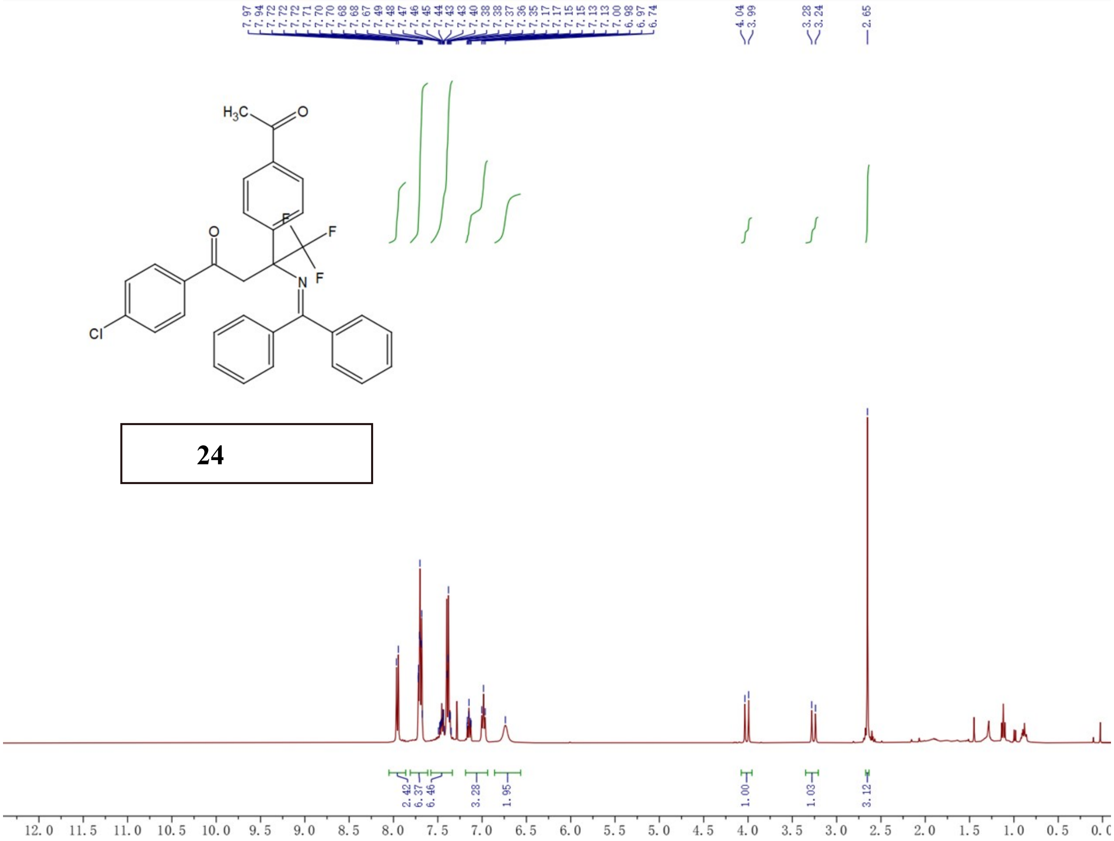
23

^{19}F NMR (337 MHz, $CDCl_3$)



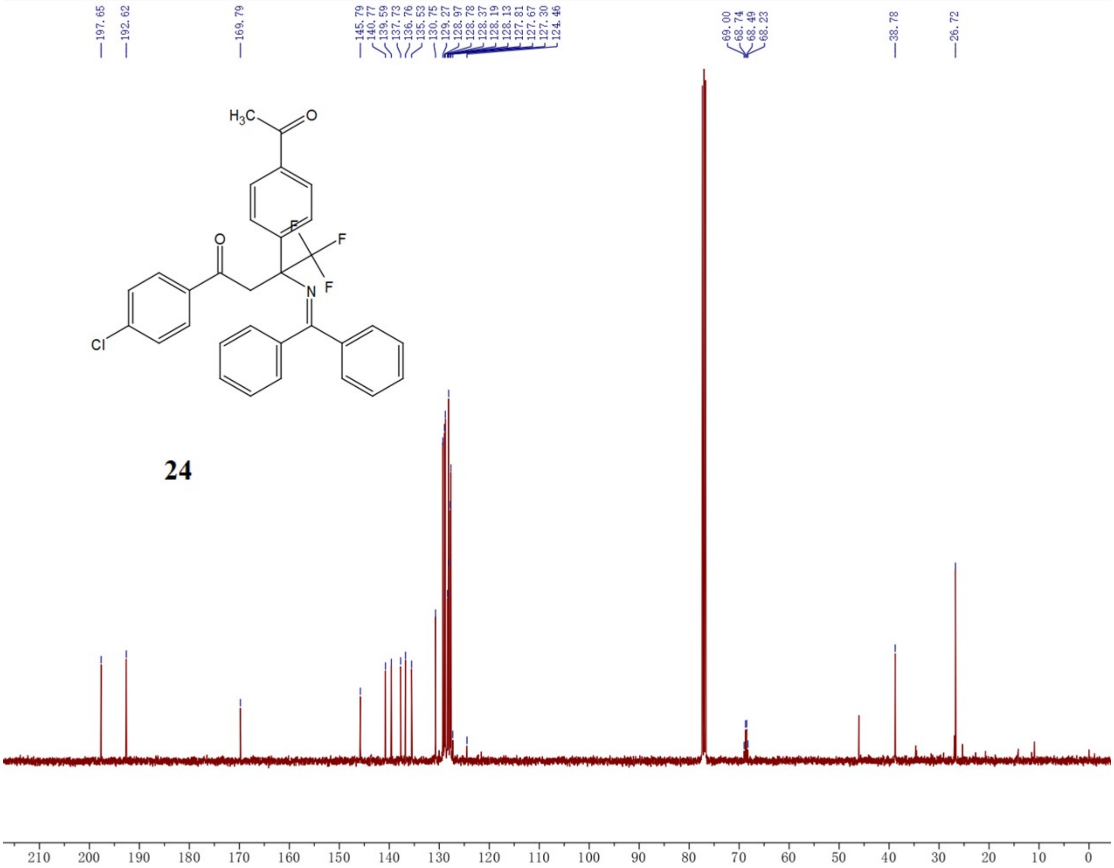
23

^{1}H NMR (400 MHz, $CDCl_3$)

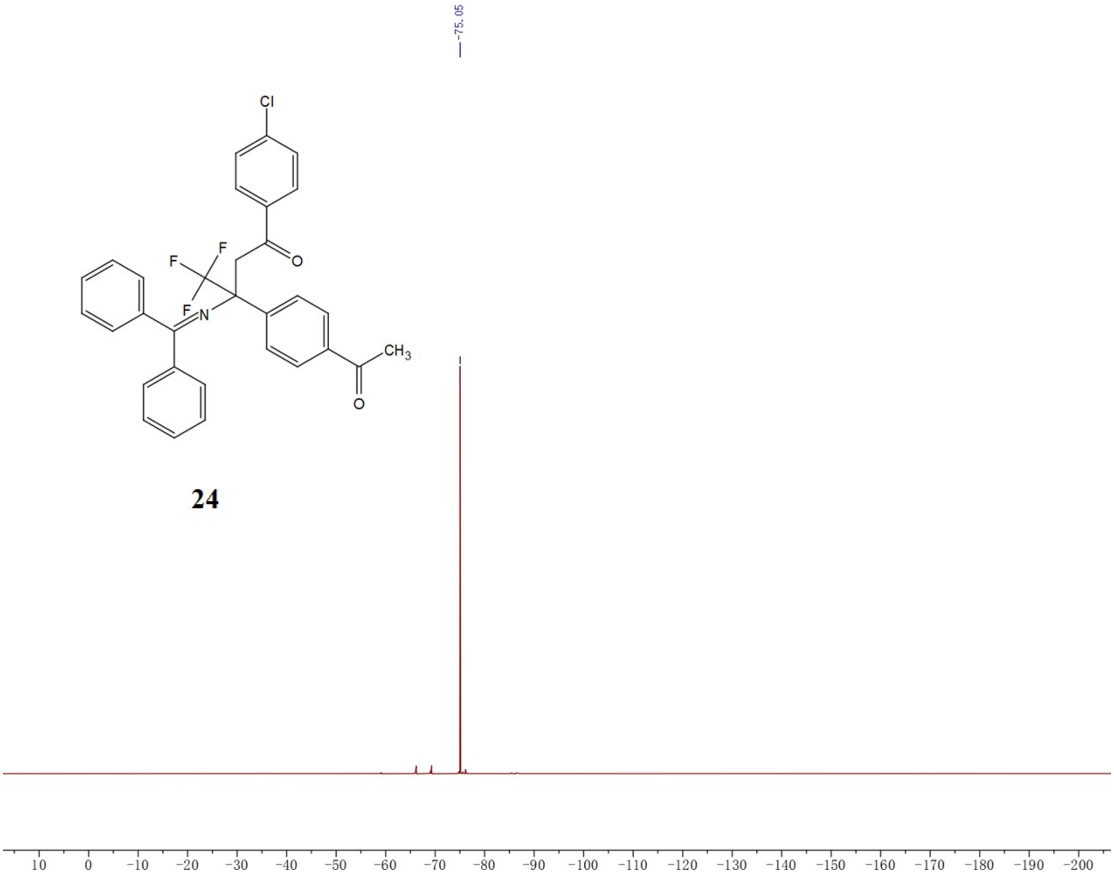


24

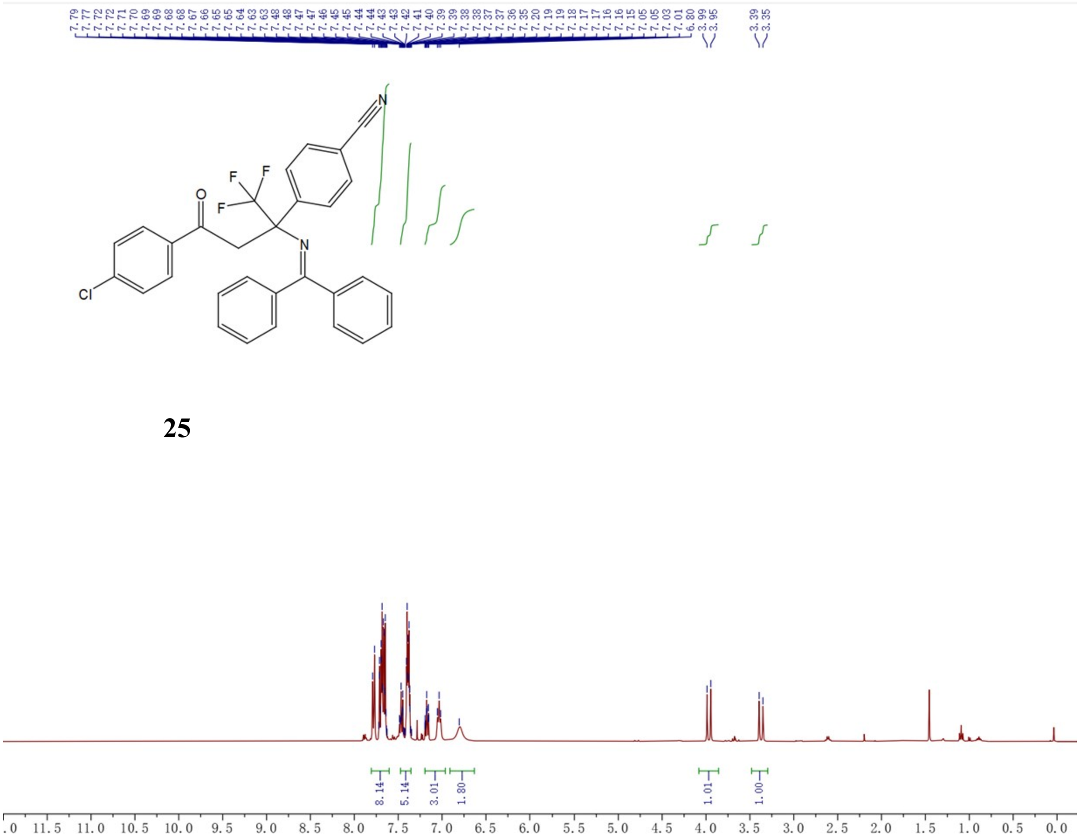
^{13}C NMR (101 MHz, CDCl$_3$)



^{19}F NMR (337 MHz, CDCl$_3$)

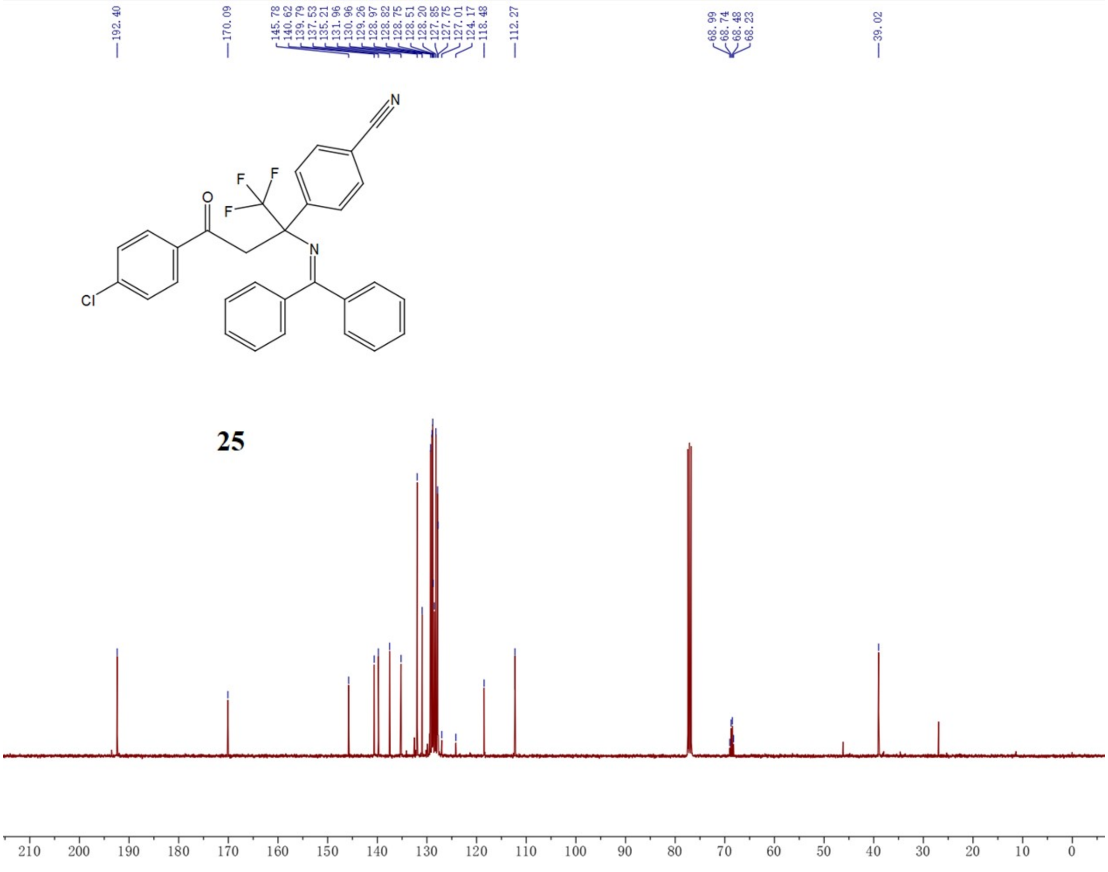


^{1}H NMR (400 MHz, CDCl$_3$)



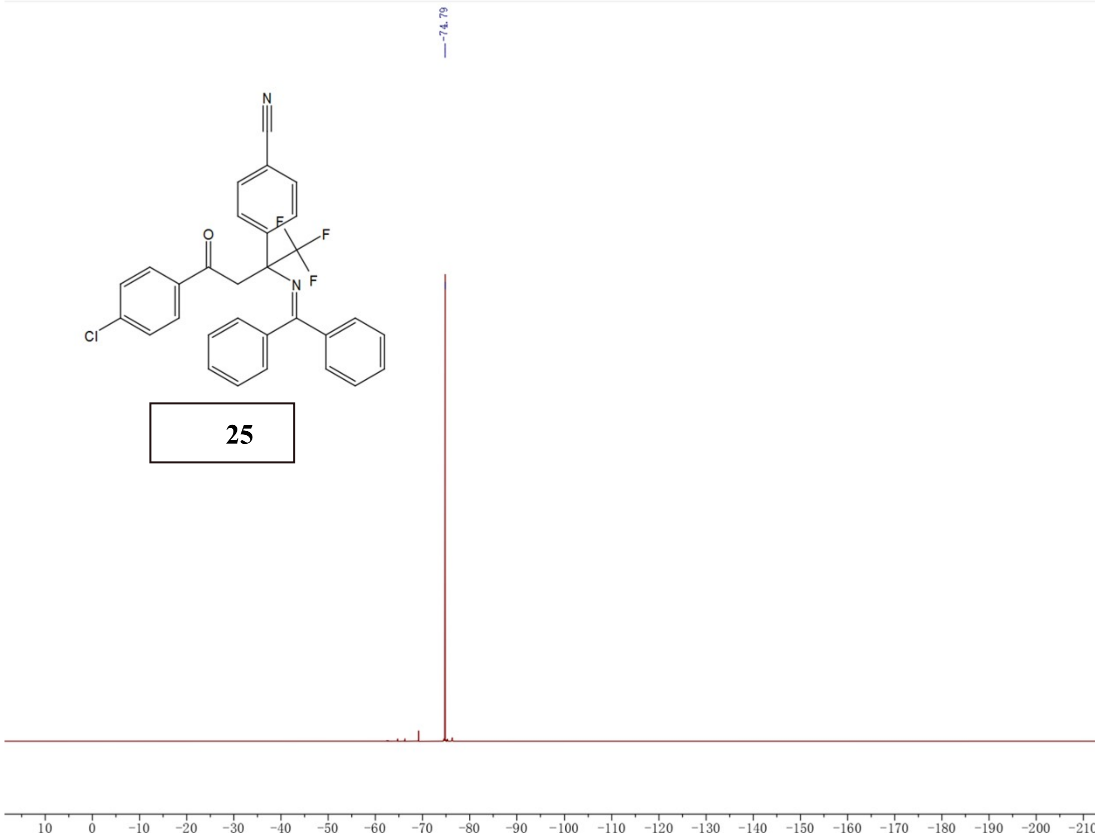
25

^{13}C NMR (101 MHz, CDCl$_3$)



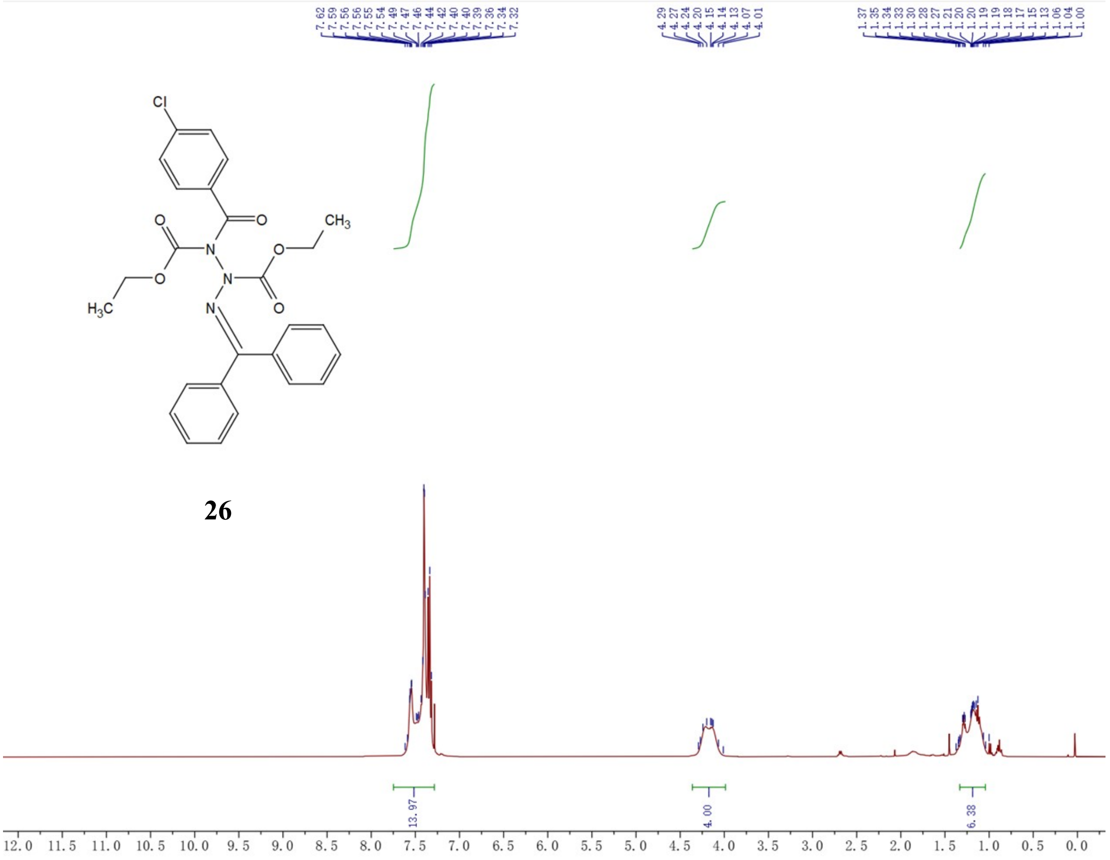
25

^{19}F NMR (337 MHz, $CDCl_3$)



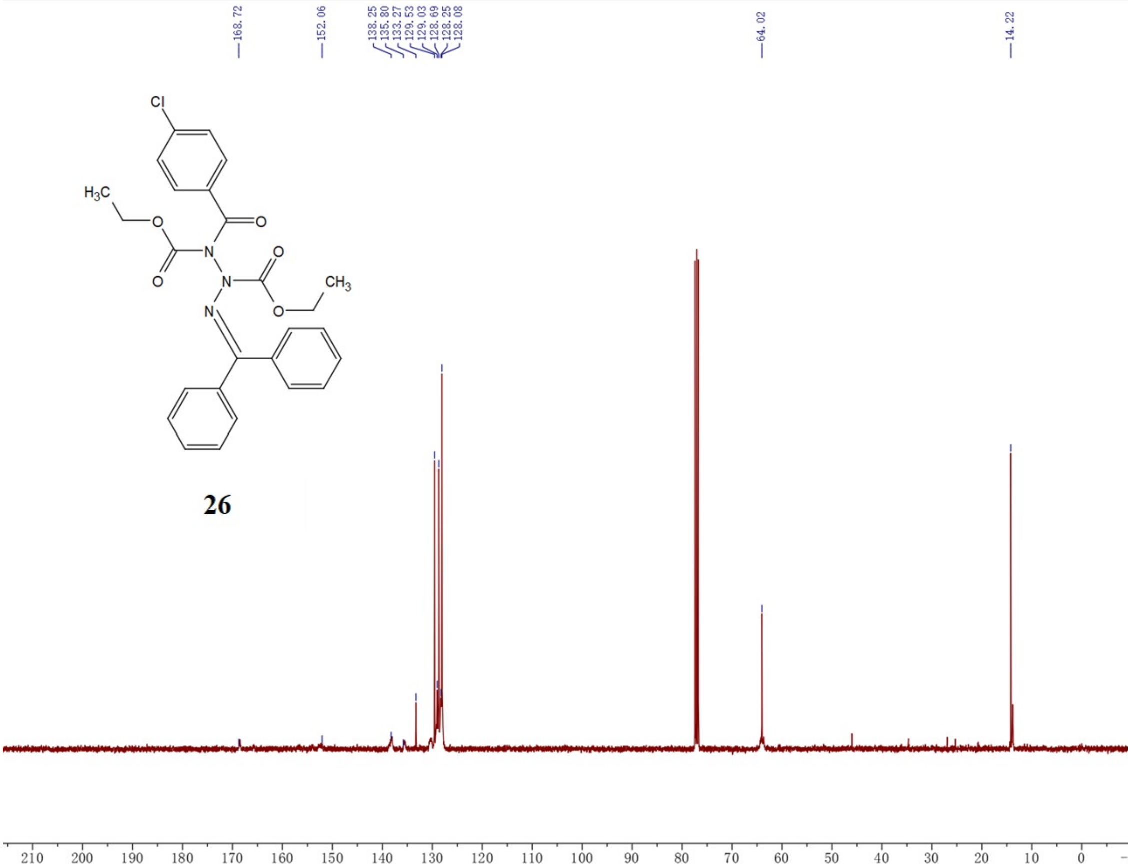
25

^{1}H NMR (400 MHz, $CDCl_3$)



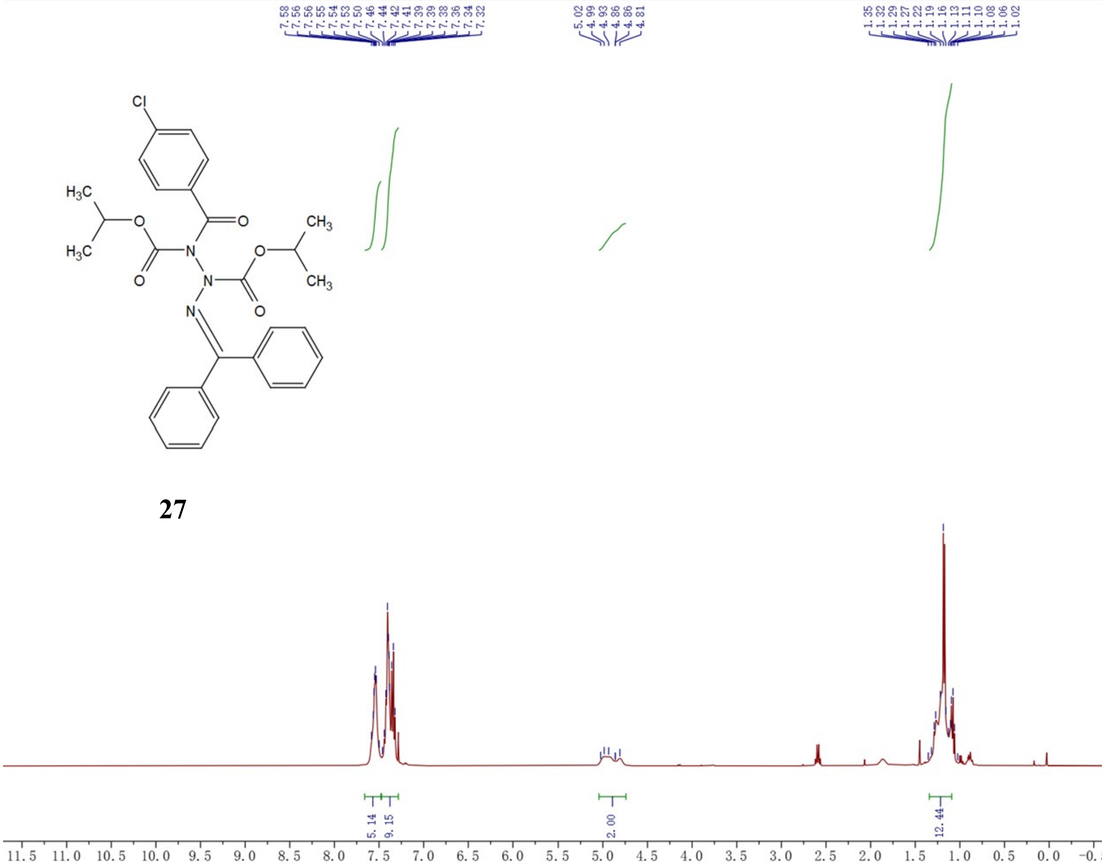
26

^{13}C NMR (101 MHz, CDCl$_3$)



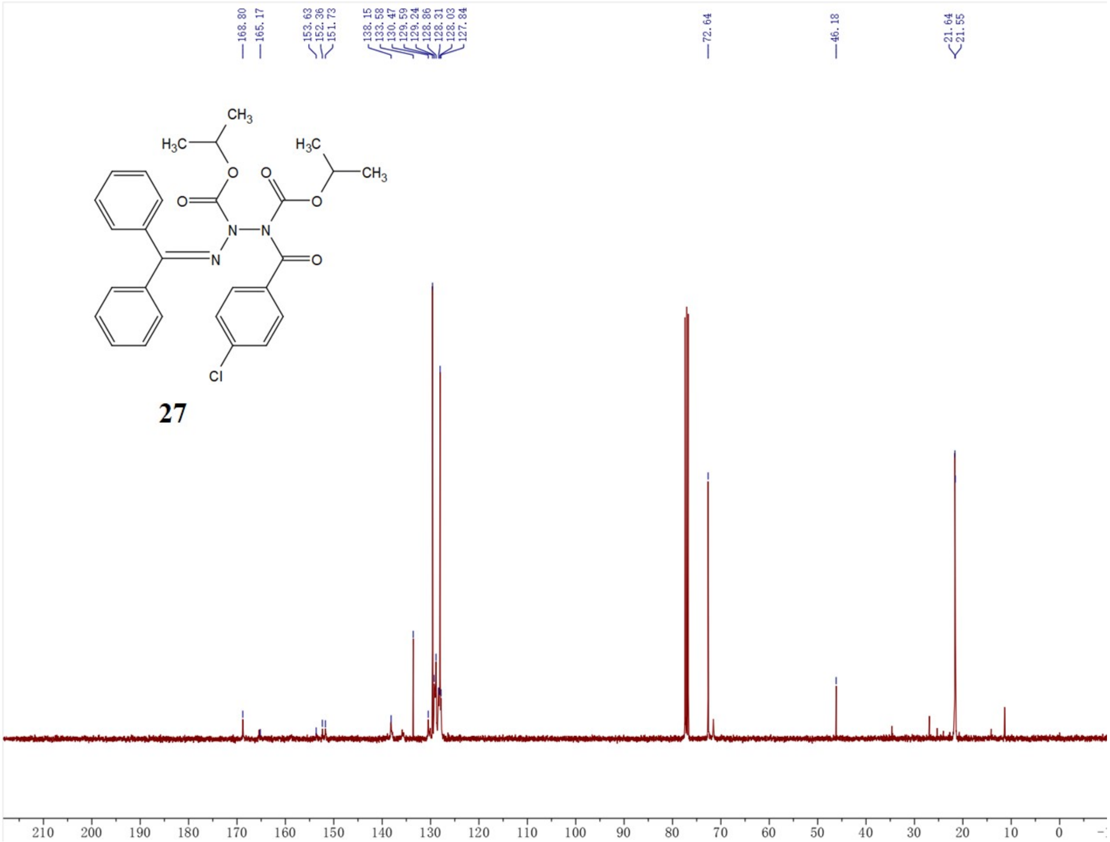
26

^{1}H NMR (400 MHz, CDCl$_3$)



27

^{13}C NMR (101 MHz, $CDCl_3$)



27