Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Ni-Catalyzed 1,2-Iminoacylation of Alkenes *via* a Reductive Strategy

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1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in $CDCl_3$ at 400 and 101 MHz. ^{19}F NMR were reported as ^{19}F exp. comp. pulse decoupling (F19CPD) unless otherwise noted. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ =($SiMe_4$) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ =($CDCl_3$) = 7.26, ^{13}C: δ =($CDCl_3$) = 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. Flash chromatography was performed using 300-400 mesh silica gel with the indicated solvent system.

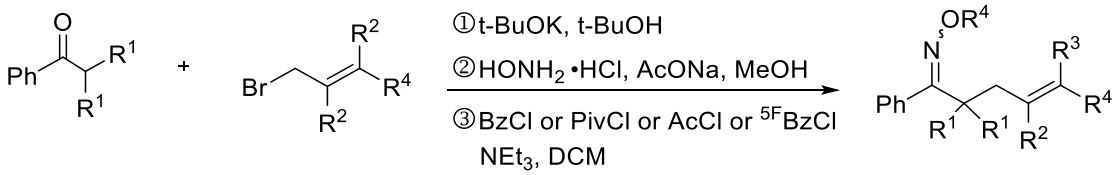
Unless otherwise stated, all reactions were set up on 10mL tube with 14# rubber stopper and carried out under nitrogen. Ni(deme)Cl_2 was purchased from Strem and used as received. 2,2'-Biquinoline, Zinc powder (325 mesh) and all solvents were purchased from Adamas China. Acid chlorides were purchased from Adamas China and Energy Chemical. Other commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Strem, Acros, Energy Chemical and were used as received.

Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Other visualization methods include staining with a basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating.

2. Experimental Procedures and Characterization Data

2.1 Preparation of γ,δ-unsaturated oxime ester

Procedure (A) for the synthesis of **1a-1, 1a-2, 1a-3, 1a-4, 1g, 1i, and 1l.**

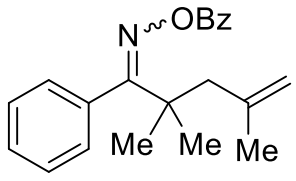


The reactions were performed according to an adapted version of the literature [1].

(1) A mixture of isobutyrophenone or benzoylcyclobutane (10.0 mmol, 1.0 equiv) and potassium *t*-butoxide (15.0 mmol, 1.5 equiv) in *t*-butyl alcohol (30 mL, 3 mL/mmol) was heated under reflux for 10 min, before allyl bromide or (3-bromoprop-1-en-2-yl)benzene (12.0 mmol, 1.2 equiv) (synthesized according to the literature [2]) was added dropwise into the solution. After the reaction was complete according to the TLC analysis, the mixture was cooled to ambient temperature and concentrated in vacuo. The residual was treated with water (20 mL) and extracted with ethyl acetate (30 mL ×3). The combined extracts were washed with saturated brine, dried with $MgSO_4$, filtered, and removed under reduced pressure. The crude product was used in the next step without other purified.

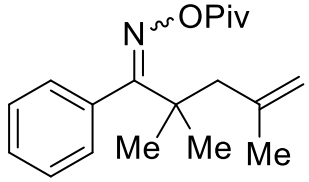
(2) To a MeOH solution (30 mL, 3 mL/mmol) of γ,δ-unsaturated ketone (crude, 10.0 mmol, 1.0 equiv) was added NaOAc (20 mmol, 2.0 equiv) and hydroxylamine hydrochloride (20.0 mmol, 2.0 equiv). The mixture was stirred under reflux a. After the reaction was complete according to the TLC analysis, the mixture was cooled to ambient temperature and concentrated in vacuo. The residual was treated with water (30 mL) and extracted with ethyl acetate (30 mL ×3) and the combined extracts were washed with saturated brine, and dried with $MgSO_4$. The combined extracts were washed with saturated brine, dried with $MgSO_4$, filtered, and removed under reduced pressure. The crude product was used in the next step without other purified.

(3) A mixture of ketoxime (crude, 10.0 mmol, 1.0 equiv) and NEt_3 (20.0 mmol, 2.0 equiv) in DCM (30 mL, 3mL/mmol) at room temperature was added dropwise benzoyl chloride or pivaloyl chloride or acetyl chloride or pentafluorobenzoyl Chloride (12.0 mmol, 1.2 equiv). After stirring overnight, the mixture was concentrated in vacuo until the ketoximes were consumed monitored by TLC. The residual was extracted from water (30ml) with ethyl acetate (30ml ×3) and the combined extracts were washed with saturated brine, and dried with $MgSO_4$. The combined extracts were washed with saturated brine, dried with $MgSO_4$, filtered, and removed under reduced pressure. The crude product was purified through flash chromatography to give the corresponding γ,δ-unsaturated oxime esters.



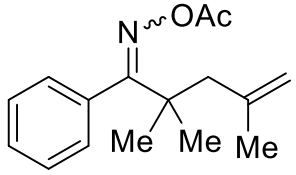
1a-1

2,2,4-Trimethyl-1-phenylpent-4-en-1-one O-benzoyl oxime (1a-1) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a white solid (1.76 g, 55% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ= 7.54 (d, J = 7.7 Hz, 2H), 7.43 (m, 4H), 7.26 (t, J = 7.6 Hz, 2H), 7.22 – 7.07 (m, 2H), 4.96 (s, 1H), 4.86 (s, 1H), 2.40 (s, 2H), 1.83 (s, 3H), 1.33 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ =175.1, 163.6, 142.2, 133.5, 132.9, 129.3, 129.1, 128.3, 128.0, 126.8, 115.2, 46.9, 41.5, 26.4, 25.4 ppm.



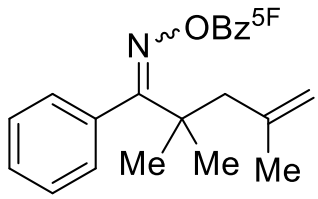
1a-2

2,2,4-Trimethyl-1-phenylpent-4-en-1-one O-pivaloyl oxime (1a-2) was isolated by flash chromatography on silica gel (hexane:EtOAc = 50:1) as a white solid (1.38g, 46% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 7.45 – 7.30 (m, 3H), 7.18 – 7.00 (m, 2H), 4.95 (s, 1H), 4.83 (s, 1H), 2.34 (s, 2H), 1.81 (s, 3H), 1.27 (s, 6H), 0.90 (s, 9H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =176.2, 175.1, 142.1, 133.4, 128.1, 127.8, 126.6, 115.1, 46.7, 41.4, 38.3, 26.7, 26.1, 25.4 ppm.



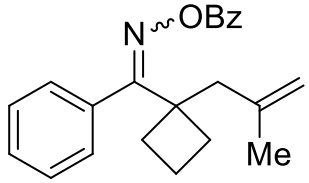
1a-3

2,2,4-Trimethyl-1-phenylpent-4-en-1-one O-acetyl oxime (1a-3) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a colourless oil (1.06g, 41% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 – 7.32 (m, 3H), 7.08 (dt, *J* = 7.4, 1.3 Hz, 2H), 4.94 (s, 1H), 4.82 (s, 1H), 2.32 (s, 2H), 1.91 (s, 3H), 1.79(s, 3H), 1.25 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =174.3, 168.9, 142.2, 133.1, 128.2, 127.9, 126.7, 115.0, 46.9, 41.4, 26.4, 25.3, 19.6 ppm.



1a-4

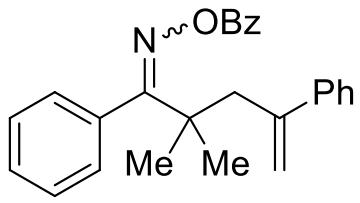
2,2,4-Trimethyl-1-phenylpent-4-en-1-one O-perfluorobenzoyl oxime (1a-4) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a yellow solid (1.23g, 30% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.53 – 7.31 (m, 3H), 7.20 – 6.97 (m, 2H), 4.97 (s, 1H), 4.84 (s, 1H), 2.35 (s, 2H), 1.82 (s, 3H), 1.29 (s, 6H) ppm. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ =-137.17 – -137.82 (m, 2F), -148.26 – -148.72 (m, 1F), -160.36 (m, 2F) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 176.9, 141.9, 132.5, 128.6, 128.0, 126.4, 115.2, 46.8, 41.9, 26.2, 25.3ppm (*Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity*).



1g

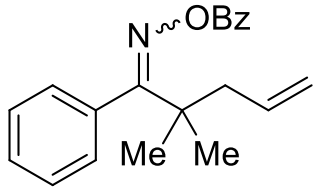
(1-(2-Methylallyl)cyclobutyl)(phenyl)methanone O-benzoyl oxime (1g) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a white solid (1.50g, 45% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.64 (dd, J = 8.3, 1.4 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.43 – 7.35 (m, 3H), 7.29 (t, J = 7.8 Hz, 2H), 7.25 – 7.17 (m, 2H), 4.88(s, 1H), 4.85(s,1H), 3.01 – 2.78 (m, 2H), 2.38 (s, 2H), 2.16 – 1.93 (m, 4H), 1.67 (s, 3H) ppm. **^{13}C NMR** (101

MHz, Chloroform-*d*) δ= 172.2, 163.8, 142.2, 133.0, 132.9, 129.4, 129.2, 128.6, 128.3, 128.0, 126.7, 112.8, 47.2, 43.9, 31.2, 24.3, 15.8 ppm.



1i

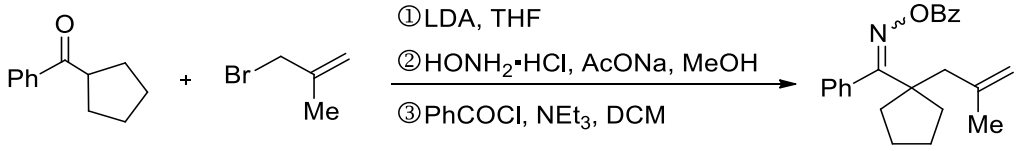
2,2-Dimethyl-1,4-diphenylpent-4-en-1-one O-benzoyl oxime (1i) was isolated by flash chromatography on silica gel (hexane:EtOAc = 50:1) as a white solid (1.53g, 40% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.60 – 7.50 (m, 2H), 7.49 – 7.34 (m, 6H), 7.33 – 7.18 (m, 5H), 7.11 – 7.02 (m, 2H), 5.38 (s, 1H), 5.24 (s, 1H), 2.98 (s, 2H), 1.17 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =175.1, 163.6, 145.7, 143.2, 133.4, 132.9, 129.4, 129.0, 128.3, 128.3, 128.0, 127.3, 126.7, 126.7, 118.1, 44.4, 42.0, 26.2 ppm.



1l

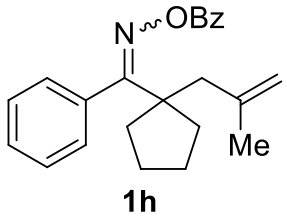
2,2-Dimethyl-1-phenylpent-4-en-1-one O-benzoyl oxime (1l) was isolated by flash chromatography on silica gel (hexane:EtOAc = 50:1) as acolourless oil (1.29g, 42% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.58 – 7.50 (m, 2H), 7.48 – 7.36 (m, 4H), 7.31 – 7.21 (m, 2H), 7.17 – 7.10 (m, 2H), 5.95 (ddt, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.22 – 5.03 (m, 2H), 2.40 (dt, *J* = 7.2, 1.3 Hz, 2H), 1.29 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =174.6, 163.6, 134.2, 133.3, 132.9, 129.3, 129.0, 128.3, 128.0, 126.7, 118.3, 44.2, 41.4, 25.7 ppm.

Procedures for the synthesis of **1h**.



(1) *The reaction was performed according to an adapted version of literature* **[1]**.To a THF solution (60 mL) of diisopropylamine (24.0 mmol, 1.2equiv) contained in 250 ml round bottom flask under the N_2-protection was added *n*-butylithium (24.0 mmol, 2.5 M in *n*-hexane) at -78℃, and the resulting solution was stirred for 0.5 h at this temperature. Then cyclopentyl phenyl ketone (20.0 mmol, 1.0 equiv) was added into the solution. After stirring at -78℃ for 1h allylbromide (24.0 mmol, 1.2 equiv) was added to the mixture, which was then warmed to ambient temperature, and was stirred overnight. The reaction was then quenched with a saturated aqueous solution of NH_4Cl (50 mL), and the organic and aqueous layers were separated. The latter was extracted with ethyl acetate (3×30 mL) and the combined organic layers were dried with $MgSO_4$, filtered and evaporated in vacuum. The residual was used in the next step without other purified.

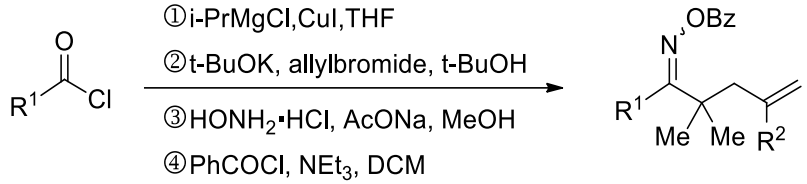
(2) **1h** was prepared from the corresponding γ,δ-unsaturated ketone following the aforementioned procedure (Procedure A-2 and A-3).



1h

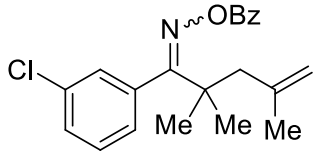
(1-(2-Methylallyl)cyclopentyl)(phenyl)methanone O-benzoyl oxime (1h) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a colourless oil (2.29g, 33% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.56 (dd, J = 8.3, 1.4 Hz, 2H), 7.48 – 7.34 (m, 4H), 7.31 – 7.14 (m, 4H), 5.01 (s, 1H), 4.95 (s, 1H), 2.43 – 2.21 (m, 1H), 2.33(s, 3H), 1.87 – 1.63 (m, 9H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 173.5, 163.6, 142.9, 133.8, 132.9, 129.3,129.2, 128.4, 128.3, 128.0, 126.7, 113.8, 53.0, 44.5, 36.3, 24.8, 23.8 ppm.

Procedures (B) for the synthesis of **1b-1f.**



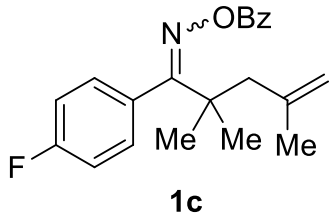
(1) *The reaction was performed according to an adapted version of literature* **[3]**.To a mixture of the acid chlorides (20 mmol, 1.0 equiv) and CuI (191 mg, 1.0 mmol, 5 mol%) in THF (30 mL) was added 0.5M solution of isopropylmagnesium chloride in THF (40.8 mL, 20.4 mmol, 1.02 equiv) at −15℃ dropwise under nitrogen atmosphere. The reaction mixture was stirred at −15℃ for 1h and at room temperature overnight, before it was quenched by adding sat. aq. NH_4Cl solution (50 mL). Then the aqueous solution was extracted with diethyl ether (3×50ml). The combined organic phases were washed with sat. aq. NH_4Cl solution and brine, dried over $MgSO_4$, filtered and removed in vacuo. The residue was roughly purified by column chromatography.

(2) The **1b-1f** were prepared from the corresponding γ,δ-unsaturated ketones according to the aforementioned procedure (Procedure A-1 to A-3)..



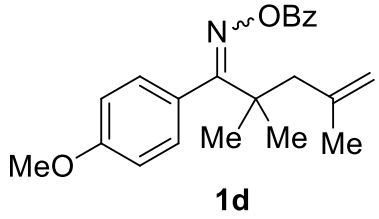
1b

1-(3-Chlorophenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (1b) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a white solid (2.49g, 35% yield, over 4 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 7.64 – 7.54 (m, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.22 – 7.16 (m, 1H), 7.07 (dt, J = 6.8, 1.7 Hz, 1H), 4.98 (s, 1H), 4.87 (s, 1H), 2.38 (s, 2H), 1.83(s, 3H), 1.32 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 173.5, 163.4, 142.0, 135.0, 134.2, 133.1, 129.43, 129.36, 128.8, 128.5, 128.4, 126.8, 125.1, 115.3, 46.9, 41.6, 26.4, 25.4 ppm.



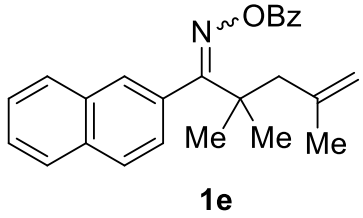
1c

1-(4-Fluorophenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (**1c**) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a colourless oil (2.78g, 41% yield, over 4 steps). **^{1}H NMR** (400 MHz, Chloroform-d) δ= 7.61 – 7.53 (m, 2H), 7.51 – 7.43 (m, 1H), 7.34 – 7.25 (m, 2H), 7.21 – 7.10 (m, 4H), 4.97 (s, 1H), 4.86 (s, 1H), 2.37 (s, 2H), 1.82 (s, 3H), 1.32 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 174.3, 163.7, 162.5 (d, *J*= 246.4 Hz), 142.1, 133.1, 129.3, 129.2 (d, *J*= 3.6 Hz), 128.9, 128.7 (d, *J*= 8.0 Hz), 128.4, 115.3 (d, *J*= 20.3Hz), 115.1, 46.9, 41.6, 26.4, 25.4 ppm.



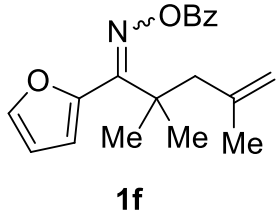
1d

1-(4-Methoxyphenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (1d) was isolated by flash chromatography on silica gel (hexane:EtOAc= 20 : 1) as a white solid (2.32g, 33% yield, over 4 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 7.65 – 7.57 (m, 2H), 7.51 – 7.41 (m, 1H), 7.34 – 7.24 (m, 2H), 7.15 – 7.06 (m, 2H), 7.00 – 6.92 (m, 2H), 4.95 (s, 1H), 4.85 (s, 1H), 3.85 (s, 3H), 2.37 (s, 2H), 1.82 (s, 3H), 1.31 (s, 6H)ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 175.0, 163.8, 159.4, 142.3, 132.9, 129.4, 129.2, 128.3, 128.2, 125.5, 115. 0, 113.4, 55.3, 47.0, 41.7, 26.7, 25.4 ppm .



1e

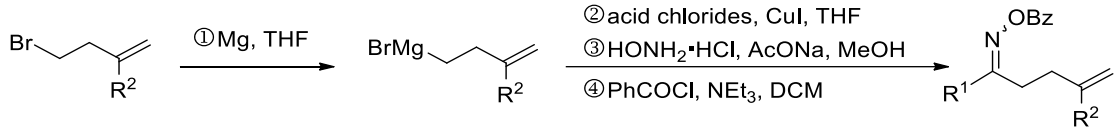
2,2,4-Trimethyl-1-(naphthalen-2-yl)pent-4-en-1-one O-benzoyl oxime (1e) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a white solid (2.67g, 36% yield, over 4 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.95 – 7.82 (m, 3H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.52 – 7.45 (m, 2H), 7.39 – 7.33 (m, 1H), 7.29 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 2H), 4.99 (s, 1H), 4.89 (s, 1H), 2.52 – 2.34 (s, 2H), 1.85 (s, 3H), 1.38 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 175.0, 163.7, 142.2, 132.9, 132.8, 132.6, 131.0, 129.3, 129.0, 128.31, 128.26, 127.8, 127.7, 126.7, 126.6, 125.6, 125.1, 116.3, 47.0, 41.9, 26.5, 25.4 ppm.



1f

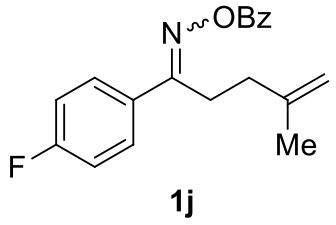
1-(Furan-2-yl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (1f) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a colourless oil (1.25g, 20% yield, over 4 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =8.03 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.65 – 7.54 (m, 2H), 7.53 – 7.41 (m, 2H), 7.15 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.57 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.80 (s, 1H), 4.65 (s, 1H), 2.59 (s, 2H), 1.67 (s, 3H), 1.45 (s, 6H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 163.9, 161.2, 144.7, 142.8, 142.6, 133.2, 129.7, 129.3, 128.6, 118.6, 114.6, 111.5, 48.2, 42.3, 27.3, 24.2 ppm .

Procedures for the synthesis of **1j-1k, 1m.**



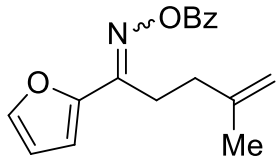
(1) *The reaction was performed according to an adapted version of patent* [4] .The temperature of the mixed solution consisting of magnesium (0.98 g, 40 mmol, 2 equiv), catalytic amount of iodine and 10ml THF was raised to 60°C under nitrogen atmosphere. A solution of 4-bromo-1-butene (2.1 mL, 20 mmol, 1.0 equiv) or 4-bromo-2-methyl-1-butene (synthesized according to a literature [5]) (3.0 g, 20 mmol, 1.0 equiv) in 10 mL THF was added dropwise over 15min. Gentle foaming was observed immediately after dropwise addition. After stirring for 1h. The mixture was cooled after and the corresponding Grignard reagent was obtained.

(2) The **1j-1k, 1m** was prepared according to the aforementioned procedure (procedure B-1 and B-2).



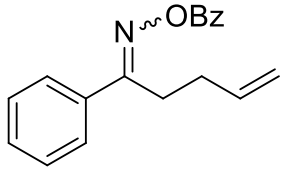
1j

1-(4-Fluorophenyl)-4-methylpent-4-en-1-one O-benzoyl oxime (1j) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a white solid (2.18g, 35% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.20 – 8.01 (m, 2H), 7.91 – 7.56 (m, 3H), 7.50 (dd, J = 8.4, 7.1 Hz, 2H), 7.22 – 6.94 (m, 2H), 4.81 (s, 1H), 4.77 (s, 1H), 3.10 (t, *J*= 8.0 Hz, 2H), 2.34 (t, *J*= 8.0 Hz, 2H), 1.79 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =166.0, 164.3 (d, *J*= 249.6 Hz), 163.7, 143.8, 133.4, 130.0 (d, *J*= 3.3 Hz), 129.6, 129.5 (d, *J*= 8.6 Hz), 129.0, 128.7, 115.8 (d, *J*= 21.6 Hz), 111.3, 34.6, 27.4, 22.4 ppm.



1k

1-(Furan-2-yl)-4-methylpent-4-en-1-one O-benzoyl oxime (1k) was isolated by flash chromatography on silica gel (hexane:EtOAc = 50:1) as a colourless oil (2.43g, 43% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.10 (dt, *J* = 8.4, 1.0 Hz, 2H), 7.67 – 7.56 (m, 2H), 7.55 – 7.37 (m, 2H), 7.00 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.55 - 6.50 (m, 1H), 4.82 (s, 1H), 4.80 (s, 1H), 3.01 (t, *J*=8.0Hz, 2H), 2.40 (t, *J*=8.0Hz, 2H), 1.81 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 163.5, 158.3, 147.8, 145.3, 144.0, 133.4, 129.6, 128.9, 128.6, 113.5, 111.9, 111.3, 35.0, 26.7, 22.3 ppm.

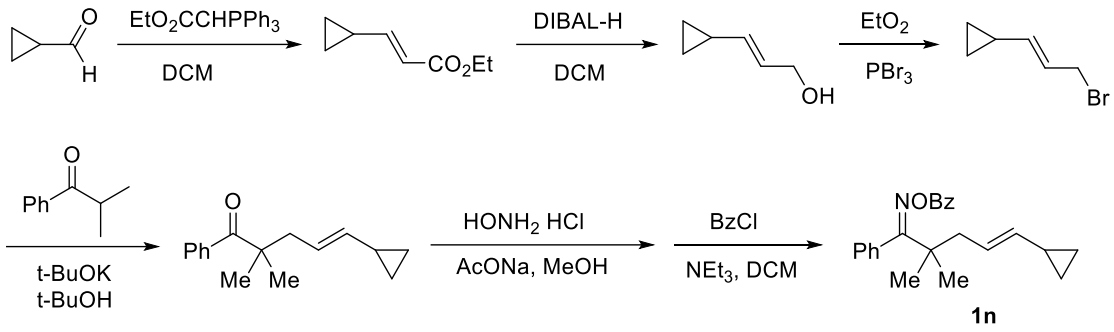


1m

1-Phenylpent-4-en-1-one O-benzoyl oxime (1m) was isolated by flash chromatography on silica gel (hexane:EtOAc = 50:1) as a white solid (2.79g, 50% yield, over 3 steps). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.20 – 8.06 (m, 2H), 7.79 (dd, J = 8.0, 1.7 Hz, 2H), 7.67 – 7.57 (m, 1H), 7.56 – 7.37 (m, 5H), 5.88 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.23 – 4.88 (m, 2H), 3.08 (t, *J*=8.0Hz, 2H), 2.52 – 2.29 (q, *J*=8.0Hz, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ =166.7, 163.8, 136.5, 133.9, 133.4, 130.7, 129.6, 129.2, 128.71, 128.65, 127.4, 116.0, 30.9, 28.2 ppm.

Procedures for the synthesis of 1n



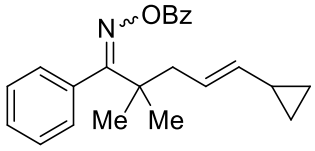
The reaction was performed according to an adapted version of literature [8].

(1) To a solution of cyclopropanecarbaldehyde (2.2 mL, 30 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) was added ethyl (triphenylphosphoranylidene)acetate (12.6 g, 36 mmol , 1.2 equiv) as a solution in CH_2Cl_2 (50 mL) dropwise over 5 minutes at ambient temperature. After being stirred for 5 hours, the solution was poured into saturated aq. NaCl (30 mL). The aqueous phase was extracted with CH_2Cl_2 (2×50 mL). The organic phases were combined, dried over MgSO4, filtered and concentrated in vacuo. Purification of the residue by column chromatography (hexane:EtOAc= 20:1) afforded the ethyl (*E*)-3-cyclopropylacrylate (3.1 g, 78%) as a colorless oil.

(2) To a solution of ethyl (*E*)-3-cyclopropylacrylate (2.8 g, 20 mmol) in CH_2Cl_2 (60 mL) at -78 ˚C was added DIBAL-H (1M in hexane, 42.0 mL, 42.0 mmol) over 5 minutes. The reaction was stirred at this temperature for 15 minutes after which saturated aq. sodium potassium tartrate (50 mL) was added and the mixture was warmed to room temperature with vigorous stirring for 1h. The reaction mixture extracted with EtOAc (3 100 mL). The organic layers were combined, washed with saturated aq. sodium potassium tartrate (50 mL), H_2O (50 mL), brine (50 mL), dried (MgSO4) and filtered. Concentration in vacuo afforded the (*E*)-3-cyclopropylprop-2-en-1-ol (1.6g, 80%) as a yellow oil that was used without further purification.

(3) To a diethyl ether solution (30ml) of (*E*)-3-cyclopropylprop-2-en-1-ol (1.5 g, 15 mmol) was added phosphorus bromide (2.3 mL, 24 mmol, 1.6 equiv) dropwise at 0 ˚C and the mixture was stirred for 3 h. The reaction mixture was then poured into ice-water bath, extracted with Et_2O (3 × 30 mL). The organic layers were combined and concentrated in vacuo to afford the (E)-(3-bromoprop-1-en-1-yl) cyclopropane (crude, 1.6g, 67%) which was unstable and must be subjected to next step immediately.

(4) According to the aforementioned procedure (Procedure A-1 to A-3), the terminal product was prepared from (E)-(3-bromoprop-1-en-1-yl)cyclopropane (10 mmol). The next 3 steps yielded 3 mmol of the terminal product (30% yield, 3 steps).

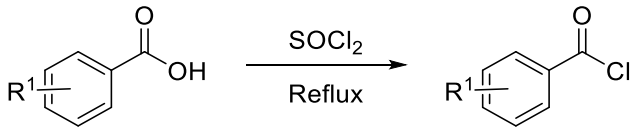


1ab

(4E)-5-cyclopropyl-2,2-dimethyl-1-phenylpent-4-en-1-one O-benzoyl oxime (1ab) was isolated by flash chromatography on silica gel (hexane:EtOAc= 50:1) as a colourless oil. *The NMR Data are in accordance with literature values*[1]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.58 – 7.49 (m, 2H), 7.48 – 7.35 (m, 4H), 7.31 – 7.21 (m, 2H), 7.20 – 7.07 (m, 2H), 5.60 (dt, *J* = 14.8, 7.3 Hz, 1H), 5.02 (ddt, *J* = 15.1, 8.6, 1.4 Hz, 1H), 2.29 (dd, *J* = 7.2, 1.3 Hz, 2H), 1.41 (dtd, *J* = 13.1, 8.3, 4.8 Hz, 1H), 1.27 (s, 6H), 0.71 – 0.62 (m, 2H), 0.34 (dt, *J* = 6.3, 4.4 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 174.9, 163.6, 138.0, 133.5, 132.9, 129.3, 129.1, 128.3, 128.2, 128.0, 126.8, 122.8, 43.0, 41.7, 25.6, 13.8, 6.5 ppm.

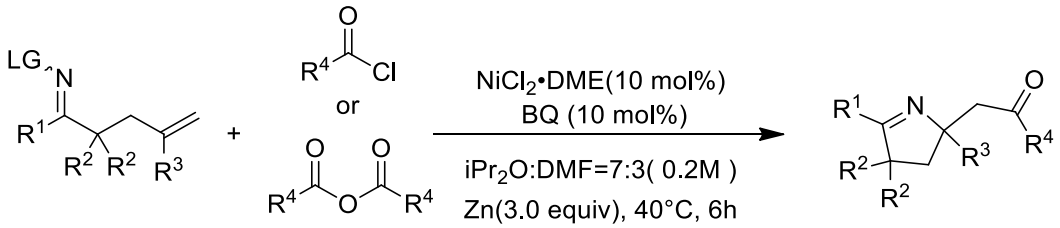
2.2 Preparation of acid chloride

Procedures for the synthesis of **2v, 2w, and 2aa.**



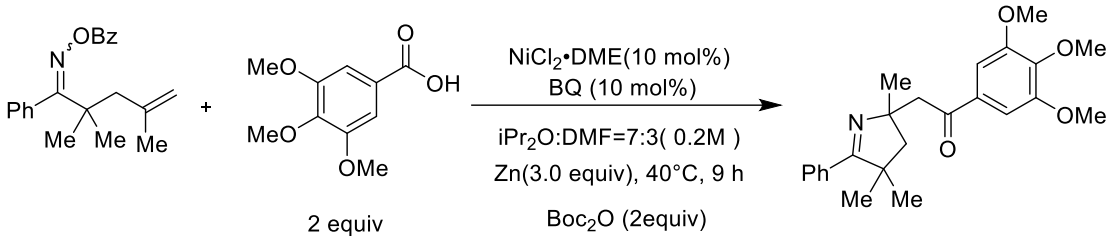
The reaction was performed according to an adapted version of literature [6]. A mixture of aryl carboxyl acid (1.0 equiv) and $SOCl_2$ (5.0 equiv) was refluxed for 4h. Excess $SOCl_2$ was removed under reduced pressure to give a crude aryl chloride that was used for next step without further purification.

2.3 General procedure for the nickel-catalyzed 1,2-iminoacylation of alkenes

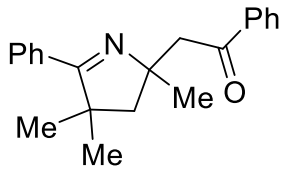


LG=OBz, OPiv, OAc, or OBz[5F]

A mixture of Ni(dme)Cl_2·(10 mol%), 2,2'-biquinoline (10 mol%), Zinc(3.0 equiv), γ,δ-unsaturated oxime esters (0.2 mmol, 1.0 equiv) in dry i-Pr_2O:DMF (0.7 mL:0.3mL) was stirred in a sealed tube at 40 ℃ for 10 min under nitrogen atmosphere. To the resulting solution were added acid chlorides or acid anhydrides (synthesized according to the literature [7]) (0.4 mmol, 2.0 equiv) and the reaction mixture was stirred for 6h at 40 ℃. After cooling to room temperature, the mixture was directly loaded to silica gel and purified by preparative TLC to afford the corresponding products.

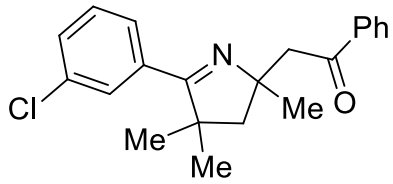


A mixture of Ni(dme)Cl_2·(10 mol%), 2,2'-biquinoline (10 mol%), Zinc(3.0 equiv), γ,δ-unsaturated oxime esters (0.2mmol, 1.0 equiv) , 3,4,5-trimethoxybenzoic acid (2.0 equiv) and Boc_2O (2 equiv) in dry i-Pr_2O:DMF (0.7 mL:0.3 mL) was stirred in a sealed tube at 40 ℃ under nitrogen atmosphere for 9 h. Then the mixture was cooled and directly loaded to silica gel and purified by preparative TLC to afford the corresponding products.



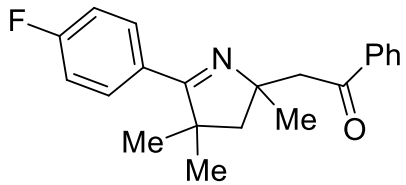
3a

1-Phenyl-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethan-1-one (3a) was isolated by preparative TLC (hexane:EtOAc=5:1) as a colourless oil (47mg, 77% yield (acid chloride); 55mg, 90% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =8.04 – 7.93 (m, 2H), 7.59 – 7.49 (m, 3H), 7.48 -7.41 (m, 2H), 7.40 – 7.29 (m, 3H), 3.51 (d, *J* = 16.0 Hz, 1H), 3.26 (d, *J* = 16.0 Hz, 1H), 2.29 (d, *J* = 13.5 Hz, 1H), 2.07 (d, *J* = 13.5 Hz, 1H), 1.50 (s, 3H), 1.44 (s, 3H), 1.30 (s, 3H)ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.1, 177.7, 137.9, 135.0, 132.9, 129.2, 128.5, 128.4, 128.1, 128.0, 71.1, 51.72, 51.70, 50.5, 29.13, 29.08, 28.5 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1852 , found: 306.1860.



3b

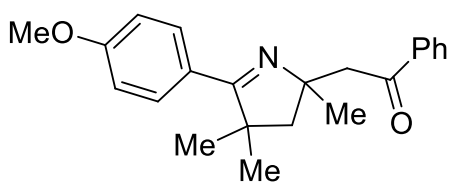
2-(5-(3-Chlorophenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3b) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (39mg, 58% yield (acid chloride); 46 mg, 68% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.03 – 7.96 (m, 2H), 7.60 – 7.53 (m, 1H), 7.51 – 7.39 (m, 4H), 7.34 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.29 – 7.21 (m, 1H), 3.45 (d, *J* = 15.9 Hz, 1H), 3.29 (d, *J* = 15.9 Hz, 1H), 2.30 (d, *J* = 13.6 Hz, 1H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.43 (s, 3H), 1.28 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 199.0, 176.5, 137.9, 136.7, 134.2, 133.1, 129.4, 128.6, 128.4, 128.2, 125.9, 71.3, 51.7, 51.5, 50.3, 29.2, 29.1, 28.3 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{21}H_{23}ClNO$ $[M+H]^+$: 340.1463 , found: 340.1471.



3c

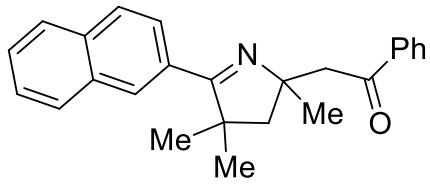
2-(5-(4-Fluorophenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3c) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (36mg, 56% yield (acid chloride); 47mg, 73% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =8.03 – 7.94 (m, 2H), 7.60 – 7.51 (m, 3H), 7.49 – 7.40 (m, 2H), 7.06 – 6.96 (m, 2H), 3.47 (d, *J* = 15.9 Hz, 1H), 3.26 (d, *J* = 15.9

Hz, 1H), 2.29 (d, *J* = 13.5 Hz, 1H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.43 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.0 , 176.4 , 163.4 (d, *J*= 247.6 Hz), 137.9 , 132.9 , 131.0 (d, *J*= 3.4 Hz), 130.0 (d, *J*= 8.2 Hz), 128.5 , 128.3 , 115.1 (d, *J*= 21.3 Hz) , 71.0 , 51.8 , 51.6 , 50.4 , 29.2 , 29.1 , 28.4 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{21}H_{23}FNO$ $[M+H]^+$: 324.1758 , found: 324.1758.



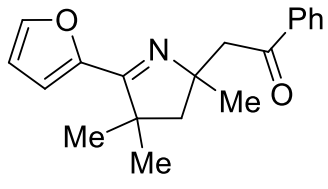
3d

2-(5-(4-Methoxyphenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3d) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (44mg, 65% yield (acid chloride); 62mg, 93% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.07 – 7.93 (m, 2H), 7.65 – 7.50 (m, 3H), 7.45 (m, 2H), 6.90 – 6.78 (m, 2H), 3.81 (s, 3H), 3.50 (d, *J* = 15.9 Hz, 1H), 3.23 (d, *J* = 15.9 Hz, 1H), 2.27 (d, *J* = 13.6 Hz, 1H), 2.05 (d, *J* = 13.5 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.32 (s, 3H)ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.2, 176.5, 160.6, 138.0, 132.9, 129.6, 128.5, 128.4, 127.1, 113.5, 70.7, 55.3, 52.2, 51.3, 50.6, 29.2, 29.1, 28.7 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{22}H_{26}NO_2$ $[M+H]^+$: 336.1958, found: 336.1964.



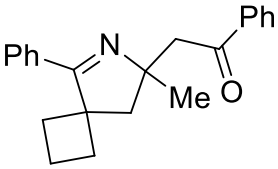
3e

1-Phenyl-2-(2,4,4-trimethyl-5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)ethan-1-one (3e) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (44mg, 62% yield (acid chloride); 54mg, 76% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.14 – 7.94 (m, 3H), 7.86 – 7.76 (m, 3H), 7.72 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.52 – 7.42 (m, 4H), 3.53 (d, *J* = 15.8 Hz, 1H), 3.33 (d, *J* = 15.8 Hz, 1H), 2.34 (d, *J* = 13.5 Hz, 1H), 2.11 (d, *J* = 13.5 Hz, 1H), 1.55 (s, 3H), 1.53 (s, 3H), 1.37 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 199.2, 177.4 , 138.0, 133.6, 133.0, 132.8, 132.3, 128.61, 128.55, 128.45, 127.8, 127.7, 127.6, 126.7, 126.2, 125.7, 71.2, 52.0, 51.8, 50.5, 29.4, 29.3, 28.7 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{26}NO$ $[M+H]^+$: 356.2009 , found: 356.2004.



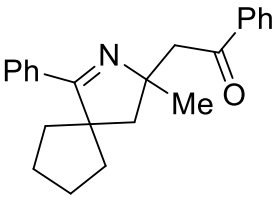
3f

2-(5-(Furan-2-yl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3f) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (44mg, 74% yield (acid chloride); 52mg, 88% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =8.08 – 7.90 (m, 2H), 7.61 – 7.48 (m, 2H), 7.48 – 7.41 (m, 2H), 6.88 – 6.83 (m, 1H), 6.46 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.65 (d, *J* = 16.7 Hz, 1H), 3.16 (d, *J* = 16.6 Hz, 1H), 2.21 (d, *J* = 13.6 Hz, 1H), 2.07 (d, *J* = 13.6 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 198.7, 167.5, 148.9, 144.0, 138.0, 132.9, 128.5, 128.2, 112.9, 111.3, 72.1, 51.3, 51.0, 50.6, 29.0, 28.8, 28.6 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1645 , found: 296.1660.



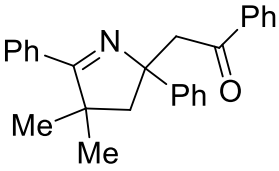
3g

2-(7-Methyl-5-phenyl-6-azaspiro[3.4]oct-5-en-7-yl)-1-phenylethan-1-one (3g) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (42mg, 66% yield (acid chloride); 53mg, 83% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.03 – 7.95 (m, 2H), 7.71 – 7.61 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.35 (m, 5H), 3.53 (d, *J* = 16.0 Hz, 1H), 3.14 (d, *J* = 16.0 Hz, 1H), 2.75 – 2.53 (m, 2H), 2.45 (m, 2H), 2.26 – 2.14 (m, 1H), 2.12 – 2.01 (m, 2H), 1.98 – 1.87 (m, 1H), 1.40 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.1, 176.1, 137.9, 135.2, 133.0, 129.3, 128.5, 128.4, 128.3, 127.8, 71.3, 55.7, 52.1, 49.5, 34.0, 32.4, 27.7, 16.5. **HRMS** (ESI): *m/z* calcd. for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1852 , found: 318.1861.



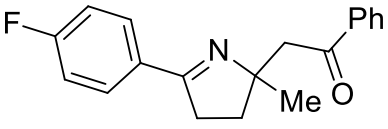
3h

2-(3-Methyl-1-phenyl-2-azaspiro[4.4]non-1-en-3-yl)-1-phenylethan-1-one (3h) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (56mg, 85% yield (acid chloride); 65mg, 98% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.06 – 7.92 (m, 2H), 7.61 – 7.49 (m, 3H), 7.49 – 7.41 (m, 2H), 7.39 – 7.29 (m, 3H), 3.57 (d, *J* = 16.1 Hz, 1H), 3.22 (d, *J* = 16.2 Hz, 1H), 2.20 (d, *J*=11.2Hz, 1H), 2.11 (d, J=11.2Hz, 1H), 2.10 -1.98(m, 2H), 1.83 – 1.53 (m, 6H), 1.48 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 199.2, 177.0, 137.9, 135.0, 133.0, 129.2, 128.5, 128.3, 128.1, 128.0, 71.8, 61.8, 52.3, 50.3, 39.3, 39.1, 28.6, 25.5, 25.4 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{23}H_{26}NO$ $[M+H]^+$: 332.2009, found: 332.2020.



3i

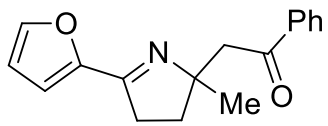
2-(4,4-Dimethyl-2,5-diphenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3i) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (43mg, 59% yield (acid chloride); 60mg, 81% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.93 – 7.83 (m, 2H), 7.60 – 7.52 (m, 4H), 7.53 – 7.45 (m, 1H), 7.42 – 7.23 (m, 7H), 7.23 – 7.12 (m, 1H), 3.69-3.59 (m, 2H), 2.79 (d, *J* = 13.2 Hz, 1H), 2.55 (d, *J* = 13.2 Hz, 1H), 1.37 (s, 3H), 1.11 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =199.0, 178.8, 148.2, 138.1, 134.8, 132.7, 129.4, 128.6, 128.3, 128.2, 128.11, 128.07, 126.5, 126.1, 75.9, 51.7, 51.5, 51.4, 27.4, 27.4 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{26}H_{26}NO$ $[M+H]^+$: 368.2009 , found: 368.2025.



3j

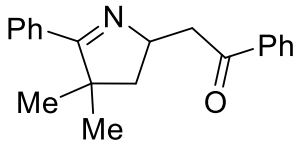
2-(5-(4-Fluorophenyl)-2-methyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3j) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (36mg, 60% yield (acid chloride); 18mg, 30% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ=8.04 – 7.93 (m, 2H), 7.79 – 7.68 (m, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.38 (m, 2H), 7.11 – 6.97 (m, 2H), 3.46 (d, *J* = 15.7 Hz, 1H), 3.28 (d, *J* = 15.7 Hz, 1H), 3.13 – 2.86 (m, 2H), 2.26 (ddd, *J* = 13.2, 9.5, 7.3 Hz, 1H), 2.05 (ddd, *J* = 13.1, 9.1, 5.9 Hz, 1H), 1.44 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.2, 169.8, 164.1 (d, *J*= 248.8 Hz), 137.9, 132.9, 130.8 (d, *J*= 3.0 Hz), 129.8 (d, *J*= 8.5 Hz), 128.43, 128.37, 115.3 (d, *J*= 21.5 Hz), 75.3, 49.1,

35.6, 34.1, 27.7 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{19}H_{19}FNO$ $[M+H]^+$: 296.1445 , found: 296.1454.



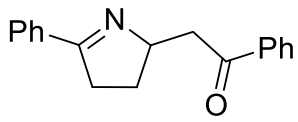
3k

2-(5-(Furan-2-yl)-2-methyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3k) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (33mg, 61% yield (acid chloride); 29mg, 54% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 – 7.90 (m, 2H), 7.60 – 7.48 (m, 2H), 7.47 – 7.39 (m, 2H), 6.76 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.60 (d, *J* = 16.5 Hz, 1H), 3.23 (d, *J* = 16.5 Hz, 1H), 3.04 – 2.90 (m, 2H), 2.29 – 2.14 (m, 1H), 2.06 (ddd, *J* = 13.2, 8.1, 6.8 Hz, 1H), 1.44 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =198.9 , 161.6 , 149.7 , 144.6 , 137.7 , 132.9 , 128.5 , 128.2 , 113.5 , 111.5 , 75.3 , 49.0 , 35.4 , 33.6 , 27.3 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found: 268.1342.



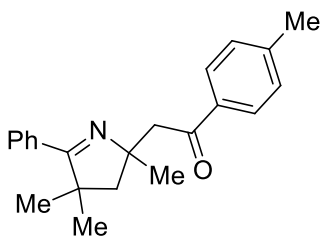
3l

2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (3l) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (31mg, 53% yield (acid chloride); 47mg, 81% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =8.10 – 7.98 (m, 2H), 7.75 – 7.64 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 7.38 (m, 3H), 4.68 – 4.53 (m, 1H), 3.84 (dd, *J* = 16.8, 4.5 Hz, 1H), 3.07 (dd, *J* = 16.8, 9.5 Hz, 1H), 2.36 (dd, *J* = 12.7, 6.7 Hz, 1H), 1.60 (dd, *J* = 12.7, 8.7 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =198.8, 180.3, 137.1, 134.7, 133.2, 129.5, 128.6, 128.22, 128.20, 127.9, 64.4, 50.8, 48.7, 45.9, 27.4, 25.9 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1696 , found: 292.1707.



3m

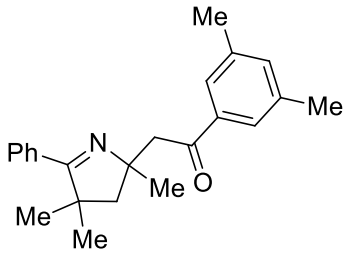
1-Phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethan-1-one (3m) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (24 mg, 46% yield (acid chloride); 11mg, 20% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =8.07 – 7.96 (m, 2H), 7.90 – 7.76 (m, 2H), 7.63 – 7.53 (m, 1H), 7.52 – 7.34 (m, 5H), 4.89 – 4.67 (m, 1H), 3.77 (dd, *J* = 16.8, 4.3 Hz, 1H), 3.23 – 2.85 (m, 3H), 2.52 – 2.40 (m, 1H), 1.74 – 1.58 (m, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 198.8, 173.1, 137.0, 134.4, 133.1, 130.6, 128.6, 128.5, 128.2, 127.7, 69.4, 45.5, 35.2, 29.3 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383 , found: 264.1390.



3n

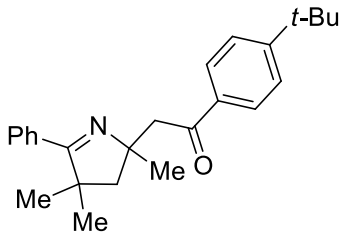
1-(*p*-Tolyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3n) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (33mg, 51% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 7.97 – 7.82 (m, 2H), 7.61 – 7.49 (m, 2H), 7.41 – 7.29 (m, 3H), 7.29 – 7.18 (m, 2H), 3.50 (d, *J* = 16.0 Hz, 1H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.41 (s, 3H), 2.29 (d, *J* = 13.5 Hz, 1H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.43 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-d) δ =198.7, 177.6,

143.7, 135.5, 135.0, 129.22, 129.19, 128.5, 128.1, 128.0, 71.1, 51.71, 51.69, 50.3, 29.11, 29.07, 28.5, 21.6 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{22}H_{26}NO$ $[M+H]^+$: 320.2009, found: 320.2021.



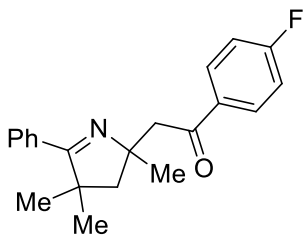
3o

1-(3,5-Dimethylphenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3o) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (40mg, 60% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.67 – 7.55 (m, 4H), 7.42 – 7.30 (m, 3H), 7.23 – 7.11 (m, 1H), 3.52 (d, *J* = 16.1 Hz, 1H), 3.20 (d, *J* = 16.1 Hz, 1H), 2.36 (s, 6H), 2.28 (d, *J* = 13.5 Hz, 1H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.5, 177.5, 138.10, 138.07, 135.0, 134.5, 129.3, 128.1, 128.0, 126.2, 71.1, 51.8, 51.7, 50.6, 29.1, 29.0, 28.5, 21.3 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{23}H_{28}NO$ $[M+H]^+$: 334.2165 , found: 334.2175.



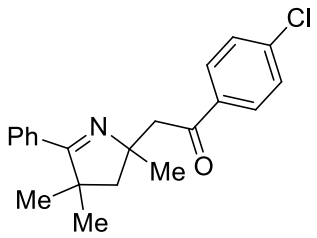
3p

1-(4-(tert-Butyl)phenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3p) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (49mg, 68% yield (acid chloride); 67mg, 93% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =8.01 – 7.89 (m, 2H), 7.56 – 7.42 (m, 4H), 7.40 – 7.28 (m, 3H), 3.48 (d, *J* = 15.8 Hz, 1H), 3.25 (d, *J* = 15.8 Hz, 1H), 2.29 (d, *J* = 13.6 Hz, 1H), 2.06 (d, *J* = 13.6 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.34 (s, 9H), 1.28 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-d) δ =198.8, 177.6, 156.7, 135.4, 135.0, 129.2, 128.4, 128.1 , 127.9, 125.4, 71.2, 51.7, 51.6, 50.4, 35.1, 31.1, 29.2, 29.1, 28.5 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{32}NO$ $[M+H]^+$: 362.2478 , found: 362.2493.



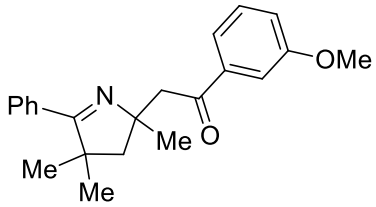
3q

1-(4-Fluorophenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3q) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (38mg, 58% yield (acid chloride); 51mg, 78% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.10 – 7.96 (m, 2H), 7.60 – 7.47 (m, 2H), 7.41 – 7.29 (m, 3H), 7.20 – 7.01 (m, 2H), 3.44 (d, *J* = 15.8 Hz, 1H), 3.25 (d, *J* = 15.8 Hz, 1H), 2.28 (d, *J* = 13.5 Hz, 1H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 197.5 , 177.7, 165.7 (d, *J*= 253.0 Hz), 134.9 , 134.4 (d, *J*= 3.0 Hz) , 131.1 (d, *J*= 9.2 Hz), 129.1, 128.1, 127.9, 115.5 (d, *J*= 21.6 Hz), 71.1, 51.7, 51.6, 50.4, 29.2, 29.1, 28.4 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{21}H_{23}FNO$ $[M+H]^+$: 324.1758 , found: 324.1776.



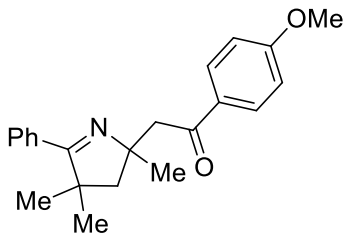
3r

1-(4-Chlorophenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3r) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (25mg, 36% yield (acid chloride); 48mg, 70% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.99 – 7.90 (m, 2H), 7.56 – 7.49 (m, 2H), 7.46 – 7.40 (m, 2H), 7.38 – 7.30 (m, 3H), 3.43 (d, *J* = 15.8 Hz, 1H), 3.26 (d, *J* = 15.8 Hz, 1H), 2.27 (d, *J* = 13.5 Hz, 1H), 2.05 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 197.9, 177.8, 139.4, 136.3, 134.8, 129.9, 129.3, 128.8 , 128.1, 127.9, 71.1, 51.7, 51.6, 50.4, 29.2, 29.1, 28.4 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{21}H_{23}ClNO$ $[M+H]^+$: 340.1463 , found: 340.1471.



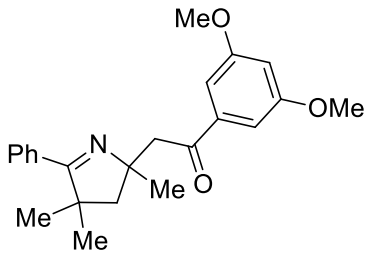
3s

1-(3-Methoxyphenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3s) was isolated by preparative TLC (hexane:EtOAc= 3 : 1) as a colourless oil (37mg, 55% yield (acid chloride); 65mg, 96% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.67 – 7.55 (m, 3H), 7.51 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.42 – 7.30 (m, 4H), 7.10 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1H), 3.84 (s, 3H), 3.54 (d, *J* = 16.2 Hz, 1H), 3.21 (d, *J* = 16.2 Hz, 1H), 2.27 (d, *J* = 13.5 Hz, 1H), 2.08 (d, *J* = 13.5 Hz, 1H), 1.50 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 198.8, 177.6, 159.8 , 139.3, 135.0, 129.5, 129.3, 128.1, 128.0, 121.1, 119.6, 112.2, 71.0, 55.4, 51.8, 51.7, 50.6, 29.04, 29.01, 28.5 ppm . **HRMS** (ESI): *m/z* calcd. for $C_{22}H_{26}NO_2$ $[M+H]^+$: 336.1958 , found: 336.1960.



3t

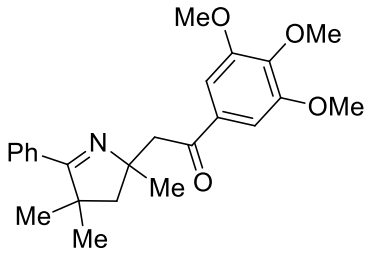
1-(4-Methoxyphenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3t) was isolated by preparative TLC (hexane:EtOAc= 3 : 1) as a colourless oil (24mg, 35% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.10 – 7.83 (m, 2H), 7.64 – 7.45 (m, 2H), 7.44 – 7.28 (m, 3H), 7.01 – 6.86 (m, 2H), 3.87 (s, 3H), 3.46 (d, *J* = 15.7 Hz, 1H), 3.20 (d, *J* = 15.7 Hz, 1H), 2.30 (d, *J* = 13.5 Hz, 1H), 2.08–2.10 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.43 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =197.7 , 177.6 , 163.4 , 135.0 , 131.1 , 130.7 , 129.2 , 128.1 , 128.0 , 113.6 , 71.2 , 55.5 , 51.7 , 51.6 , 50.1 , 29.2 , 29.1 , 28.5 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{22}H_{26}NO_2$ $[M+H]^+$: 336.1958 , found: 336.1973.



3u

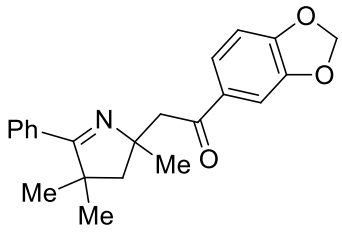
1-(3,5-Dimethoxyphenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3u) was isolated by preparative TLC (hexane:EtOAc= 2 : 1) as a colourless oil (43mg, 59% yield (acid chloride); 62mg, 85% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 7.73 – 7.50 (m, 2H), 7.46 – 7.30 (m, 3H), 7.14 (d, *J* = 2.3 Hz, 2H), 6.65 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 6H), 3.55 (d, *J* = 16.4 Hz, 1H), 3.16 (d, *J* = 16.4 Hz, 1H), 2.25 (d, *J* = 13.5 Hz, 1H), 2.08 (d, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 198.6 ,

177.6 , 160.8 , 139.9 , 135.0, 129.3 , 128.1 , 128.0 , 105.9 , 105.6 , 71.0 , 55.6 , 51.9 , 51.7 , 50.7 , 29.0 , 28.9 , 28.6 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{23}H_{28}NO_3$ $[M+H]^+$: 366.2064 , found: 366.2065.



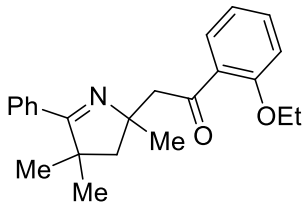
3v

1-(3,4,5-Trimethoxyphenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3v) was isolated by preparative TLC (hexane:EtOAc= 1:1) as a colourless oil (38mg, 48% yield (acid chloride); 38mg, 48% yield (acid); 47.4mg, 81% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.71 – 7.52 (m, 2H), 7.47 – 7.32 (m, 3H), 7.27 (s, 2H), 3.92 (s, 3H), 3.89 (s, 6H), 3.58 (d, *J* = 16.2 Hz, 1H), 3.15 (d, *J* = 16.2 Hz, 1H), 2.28 (d, *J* = 13.6 Hz, 1H), 2.10 (d, *J* = 13.6 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 197.7 , 177.8 , 152.9 , 142.4 , 135.0 , 133.1 , 129.4 , 128.2 , 128.0 , 105.7 , 71.1 , 61.0 , 56.2 , 51.9 , 51.8 , 50.4 , 29.0 , 28.9 , 28.7 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{24}H_{30}NO_4$ $[M+H]^+$: 396.2169 , found: 396.2179.



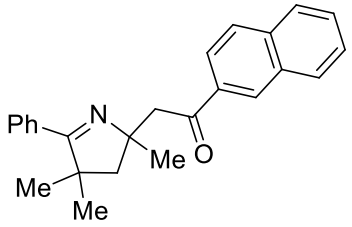
3w

1-(Benzo[d][1,3]dioxol-5-yl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3w) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (25mg, 35% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 7.67 – 7.55 (m, 3H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.42 – 7.30 (m, 3H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 2H), 3.42 (d, *J* = 15.8 Hz, 1H), 3.16 (d, *J* = 15.8 Hz, 1H), 2.28 (d, *J* = 13.5 Hz, 1H), 2.04 (d, *J* = 13.5 Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 197.1, 177.6, 151.6, 148.1, 135.0, 132.9, 129.3, 128.1, 128.0, 124.9, 108.1, 107.8, 101.8, 71.1, 51.7, 50.2, 29.1, 29.1, 28.5 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{22}H_{24}NO_3$ $[M+H]^+$: 350.1751 , found: 350.1760.



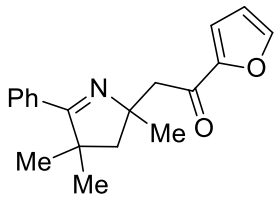
3x

1-(2-Ethoxyphenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3x) was isolated by preparative TLC (hexane:EtOAc= 3 : 1) as a colourless oil (22mg, 32% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ =7.63 – 7.52 (m, 3H), 7.44 – 7.29 (m, 4H), 7.00 – 6.82 (m, 2H), 4.12 (q, *J*=7.2Hz, 2H), 3.59 (d, *J* = 16.6 Hz, 1H), 3.31 (d, *J* = 16.7 Hz, 1H), 2.24 (d, *J* = 13.4 Hz, 1H), 2.02 (d, *J* = 13.4 Hz, 1H), 1.461 (t, *J*=7.2Hz, 3H), 1.459(s, 3H), 1.43 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 202.1 , 177.2 , 157.5 , 135.2 , 132.8 , 130.3 , 129.8 , 129.1 , 128.1 , 128.0 , 120.5 , 112.3 , 71.2 , 64.1 , 55.6 , 52.0 , 51.6 , 29.1 , 28.9 , 28.4 , 14.8 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{23}H_{28}NO_2$ $[M+H]^+$: 350.2115 , found: 350.2131.



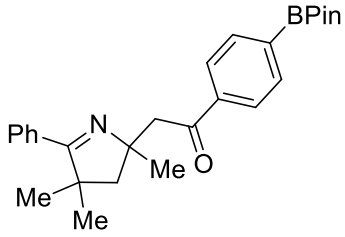
3y

1-(Naphthalen-2-yl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3y) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (39mg, 55% yield (acid chloride); 63mg, 88% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.61 – 8.45 (m, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.95 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.91 – 7.80 (m, 2H), 7.65 – 7.46 (m, 4H), 7.40 – 7.15 (m, 3H), 3.66 (d, *J* = 15.8 Hz, 1H), 3.38 (d, *J* = 15.8 Hz, 1H), 2.35 (d, *J* = 13.5 Hz, 1H), 2.10 (d, *J* = 13.5 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H)ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.1, 177.7, 135.5, 135.3, 134.9, 132.5, 130.4, 129.7, 129.3, 128.4, 128.3, 128.1, 128.0, 127.7, 126.7, 124.0, 71.2, 51.77, 51.75, 50.5, 29.2, 29.1, 28.5 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{26}NO$ $[M+H]^+$: 356.2009 , found: 356.2022.



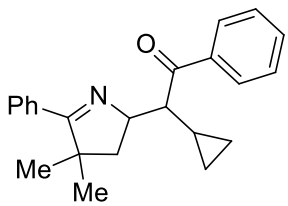
3z

1-(Furan-2-yl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3z) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (21mg, 35% yield (acid chloride); 27mg, 46% yield (acid anhydride)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.53 (m, 3H), 7.41 – 7.29 (m, 3H), 7.22 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.53 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.31 (d, *J* = 14.9 Hz, 1H), 3.08 (d, *J* = 14.9 Hz, 1H), 2.35 (d, *J* = 13.5 Hz, 1H), 1.97 (d, *J* = 13.5 Hz, 1H), 1.47 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ =187.9, 177.8, 153.5, 146.4, 135.0, 129.2, 128.1, 128.0, 117.7, 112.2, 71.1, 51.8, 51.5, 50.2, 29.3, 29.1, 28.4 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1645 , found: 296.1644.



3aa

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethanone (3aa) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (36mg, 42% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.00 – 7.92 (m, 2H), 7.92 – 7.84 (m, 2H), 7.61 – 7.52 (m, 2H), 7.42 – 7.30 (m, 3H), 3.55 (d, *J* = 16.2 Hz, 1H), 3.24 (d, *J* = 16.2 Hz, 1H), 2.27 (d, *J* = 13.6 Hz, 1H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.36 (s, 12H), 1.31 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 199.4, 177.7, 139.8, 135.0, 134.9, 129.3, 128.1, 128.0, 127.3, 84.2, 71.0, 51.8, 51.7, 50.6, 29.1, 29.0, 28.5, 24.9 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{27}H_{35}BNO_3$ $[M+H]^+$: 432.2705 , found: 432.2711.

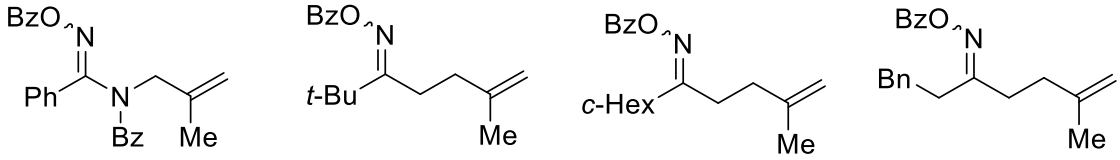


3ab

2-cyclopropyl-2-(4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethanone (3ab) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (17mg, 25% yield, dr=2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 8.02 – 7.95 (m, 3H), 7.64 – 7.54 (m, 3.5H), 7.53 – 7.43 (m, 4H), 7.39 – 7.26 (m, 4.5H), 4.65 – 4.45 (m, 1.5H), 3.29 (dd, *J* = 9.3, 7.4 Hz, 0.5H), 2.99 (dd, *J* = 9.6, 8.2 Hz, 1H), 2.20 (dd, *J* = 12.7, 6.6 Hz, 1H), 2.06 (dd, *J* = 12.6, 6.7 Hz, 0.5H), 1.93 (dd, *J* = 12.7, 9.5 Hz, 1H), 1.81 (dd, *J* = 12.6, 9.4 Hz, 0.5H), 1.41 (s,

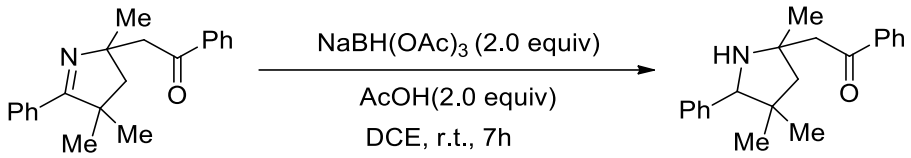
3H), 1.40 (s, 1.5H), 1.37 (s, 3H), 1.23 (s, 1.5H), 1.15 (m, 1H), 0.72 (m, 0.5H), 0.66 – 0.57 (m, 1H), 0.56 – 0.49 (m, 0.5H), 0.49 – 0.31 (m, 2H), 0.22 (ddt, *J* = 9.2, 5.6, 4.7 Hz, 0.5H), 0.15 – 0.05 (m, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = (mixture of two diastereomers) 201.2, 200.9, 177.4, 176.8, 136.3, 136.0, 132.3, 130.6, 130.5, 127.2, 126.4, 126.3, 126.20, 126.18, 125.79, 125.75 , 125.6, 125.5, 68.9, 68.5, 53.7, 53.2, 47.7, 47.6, 44.1, 43.2, 24.7, 24.6, 23.9, 23.6, 10.0, 8.3, 2.5, 2.3, 1.2 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{23}H_{26}NO$ $[M+H]^+$: 332.2009 , found: 332.2006.

2.4 Unsuccessful oxime esters substrates



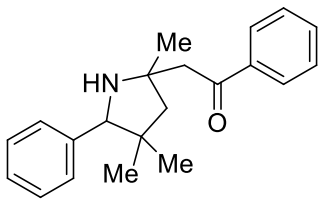
2.5 Derivatizations of 3a

2.5.1 Synthesis of compound 4



3a **4** , d.r= 2:1, Yield: 97%

A mixture of **3a** (0.2 mmol, 61 mg, 1.0 equiv) and $NaBH(OAc)_3$ (0.4 mmol, 85 mg, 2.0 equiv), in AcOH (23 μL, 0.4 mmol, 2.0 equiv) in 1,2-DCE (1.5 mL) was stirred at r.t. for 7h. The solvent was then removed in vacuo, and the crude product was purified by column chromatography using petroleum ether: ethyl acetate 1:1 as eluent.

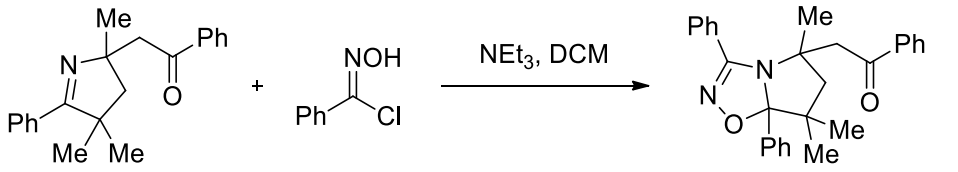


4

1-phenyl-2-(2,4,4-trimethyl-5-phenylpyrrolidin-2-yl)ethanone (5) was isolated by preparative TLC (hexane:EtOAc= 5:1) as a colourless oil (60mg, 97% yield, dr=2:1). The diastereomers were separable. ***Major diastereomer***: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 2H), 7.60 – 7.52 (m, 1H), 7.50 – 7.42 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.21 (m, 3H), 4.05 (s, 1H), 3.33 (d, *J* = 15.4 Hz, 1H), 3.10 (d, *J* = 15.4 Hz, 1H), 1.87 (d, J = 13.3 Hz, 1H), 1.80 (d, J = 13.2 Hz, 1H), 1.39 (s, 3H), 1.04 (s, 3H), 0.70 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 200.5, 140.3, 138.1, 133.1, 128.6, 128.2, 127.7, 127.6, 126.9, 70.4, 57.6, 55.1, 48.8, 42.1, 30.0, 27.5, 24.6 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{21}H_{26}NO$ $[M+H]^+$: 308.2009 , found: 308.2017. ***Minor diastereomer***: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.08 – 7.99 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.18 (m, 3H), 4.09 (s, 1H), 3.35 (d, *J* = 16.0 Hz, 1H), 3.23 (d, *J* = 16.0 Hz, 1H), 1.91 (d, *J* = 13.2 Hz, 1H), 1.78 (d, *J* = 13.3 Hz, 3H), 1.41 (s, 3H), 1.07 (s, 3H), 0.64 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ= 200.0, 140.7, 138.2,

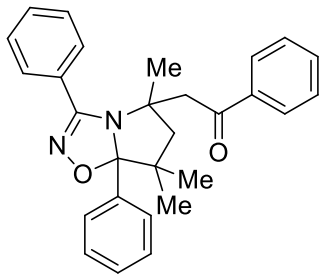
132.8, 128.5, 128.3, 127.7, 127.6, 126.8, 69.6, 56.6, 54.4, 52.1, 41.8, 28.6, 27.8, 25.0 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{21}H_{26}NO$ $[M+H]^+$: 308.2009 , found: 308.2007.

2.5.2 Synthesis of compound 5



3a **5** , d.r.=2:1, yield: 80%

The reaction was performed according to an adapted version of literature [9]. A mixture of **3a** (0.20 mmol, 61 mg, 1.0 equiv), N-hydroxybenzimidoyl chloride (synthesized according to the literature [10]) (0.5 mmol, 77.8 mg, 2.5 equiv) and Et_3N (1.0 mmol, 148 μL 5.0 equiv) in CH_2Cl_2 (2.0 mL) was stirred at r.t. for 2 h. The solvent was then removed in vacuo, and the crude product was purified by column chromatography using petroleum ether:ethyl acetate 10:1 as eluent.



5

1-phenyl-2-(5,7,7-trimethyl-3,7a-diphenyl-5,6,7,7a-tetrahydropyrrolo[1,2-d][1,2,4]oxadiazol-5-yl)ethanone (4) was isolated by preparative TLC (hexane:EtOAc= 1 : 1) as a colourless oil (68mg, 80% yield, dr=1.5:1). ***Major diastereomer***: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ= 8.00 – 7.90 (m, 3H), 7.89 – 7.82 (m, 1H), 7.81- 7.73 (m, 3H), 7.38 – 7.25 (m, 8H), 3.19 (dd, *J* = 16.8, 1.1 Hz, 1H), 2.96 (d, *J* = 16.8 Hz, 1H), 2.44 (d, *J* = 13.4 Hz, 1H), 2.33 (d, *J* = 13.4 Hz, 1H), 1.79 (s, 3H), 1.30 (s, 3H), 0.88 (s, 3H) ppm ***Minor diastereomer***: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ=7.64 – 7.57 (m, 3H), 7.57 – 7.53 (m, 1H), 7.52 – 7.43 (m, 8H), 7.43 – 7.38 (m, 3H), 3.77 (d, *J* = 16.7 Hz, 1H), 3.67 (d, *J* = 16.7 Hz, 1H), 2.58 (d, *J* = 13.5 Hz, 1H), 2.25 (d, *J* = 13.6 Hz, 1H), 1.34 (s, 3H), 1.23 (s, 3H), 0.81 (s, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = (mixture of two diastereomers) 198.1, 196.6, 160.5, 160.3, 140.7, 140.4, 137.6, 137.1, 133.3, 133.2, 130.9, 130.6, 129.5, 129.4, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 127.77, 127.70, 127.65, 127.61, 127.5, 126.3, 126.1, 113.6, 65.9, 65.4, 54.4, 53.0, 50.7, 50.4, 44.0, 43.7, 29.8, 28.7, 28.5, 27.5, 24.8, 24.7 ppm. **HRMS** (ESI): *m/z* calcd. for $C_{28}H_{29}N_2O_2$ $[M+H]^+$: 425.2224 , found: 425.2223.

3. References

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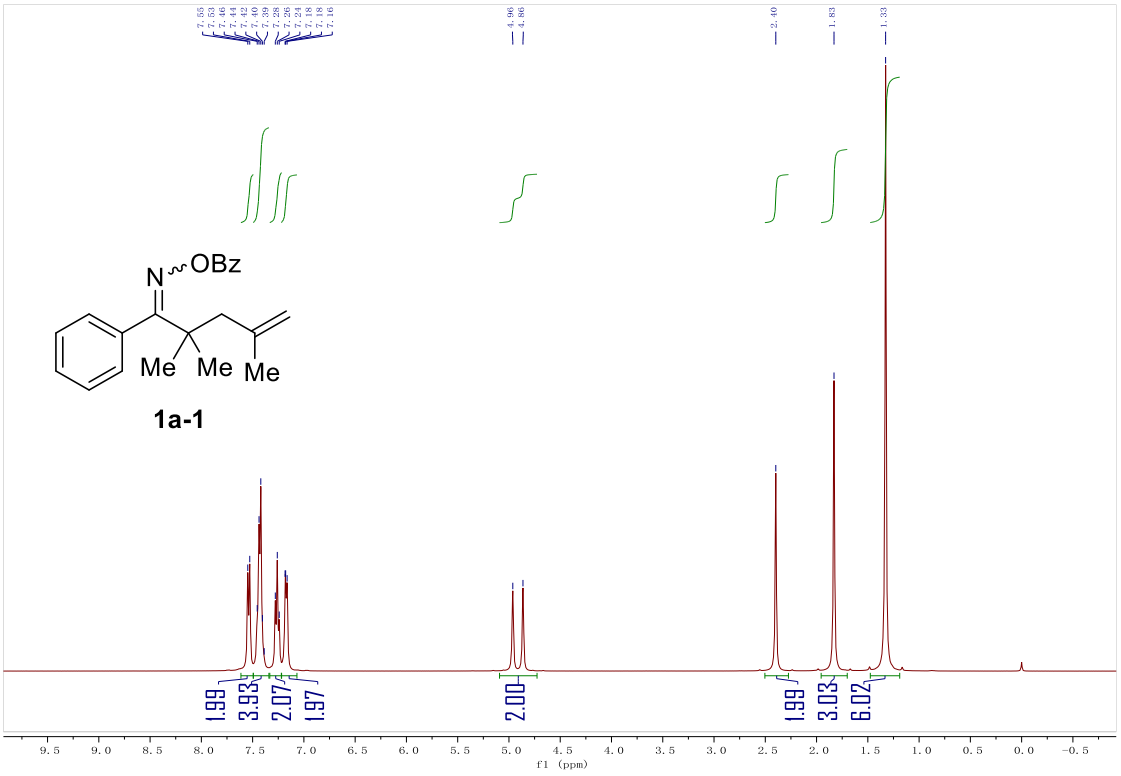
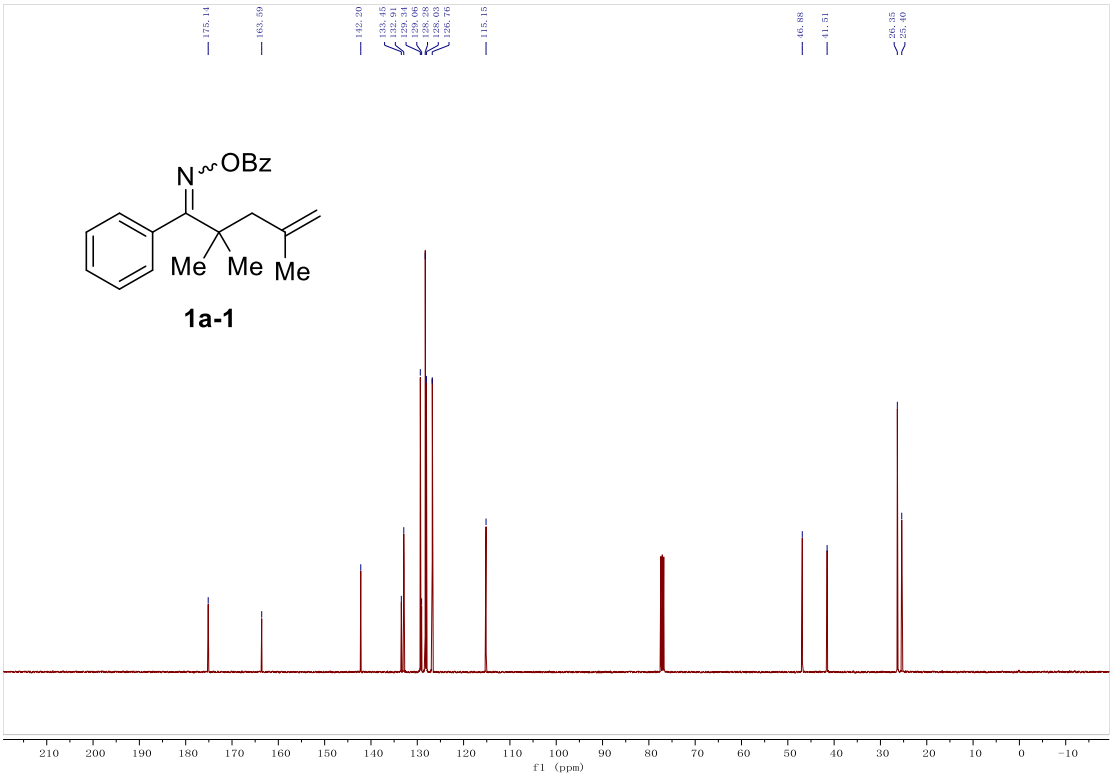
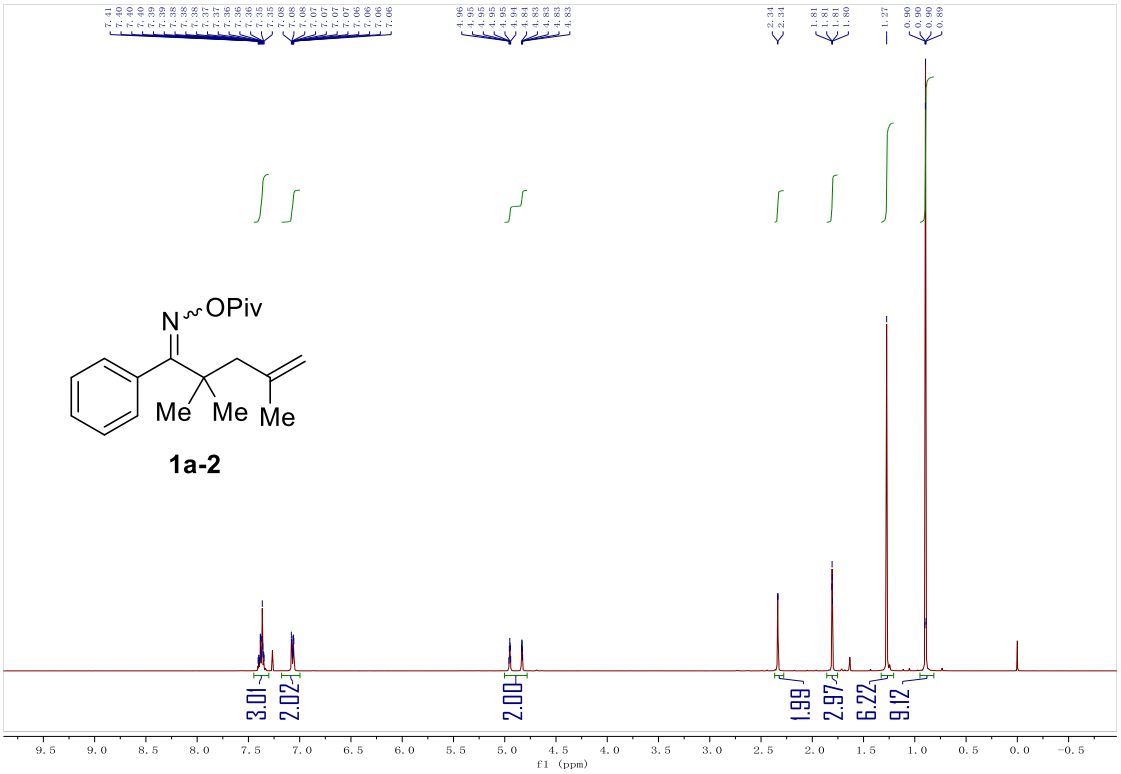
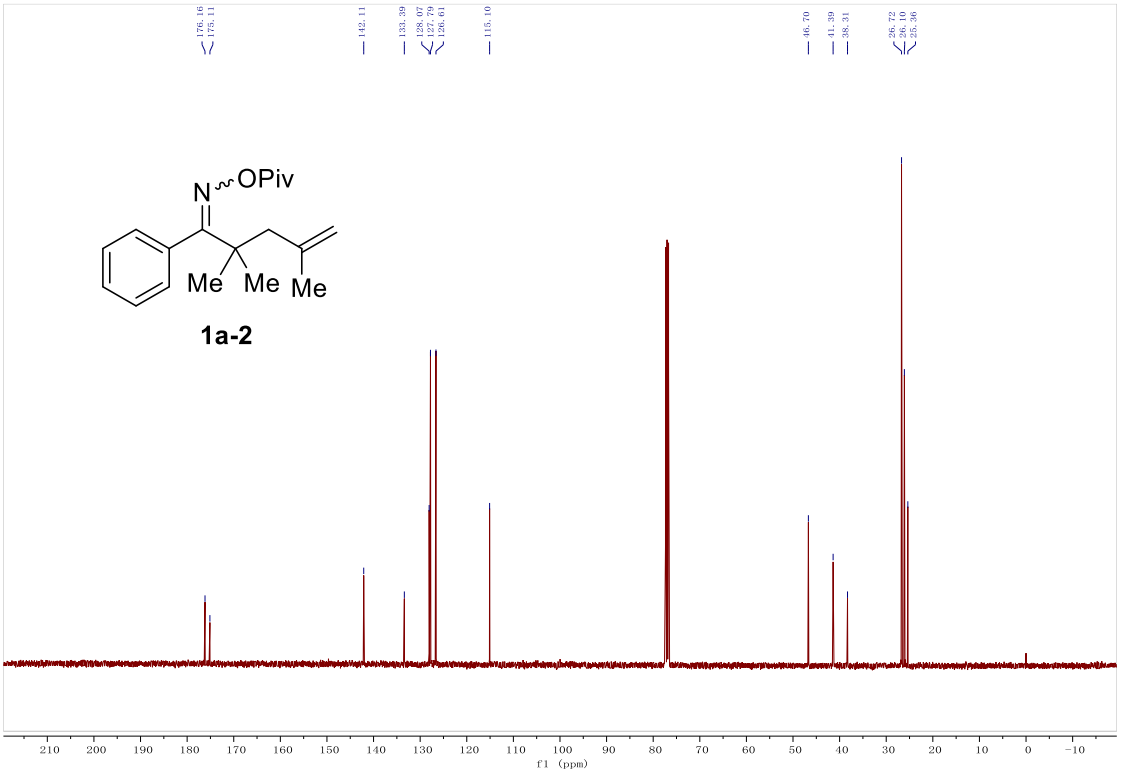
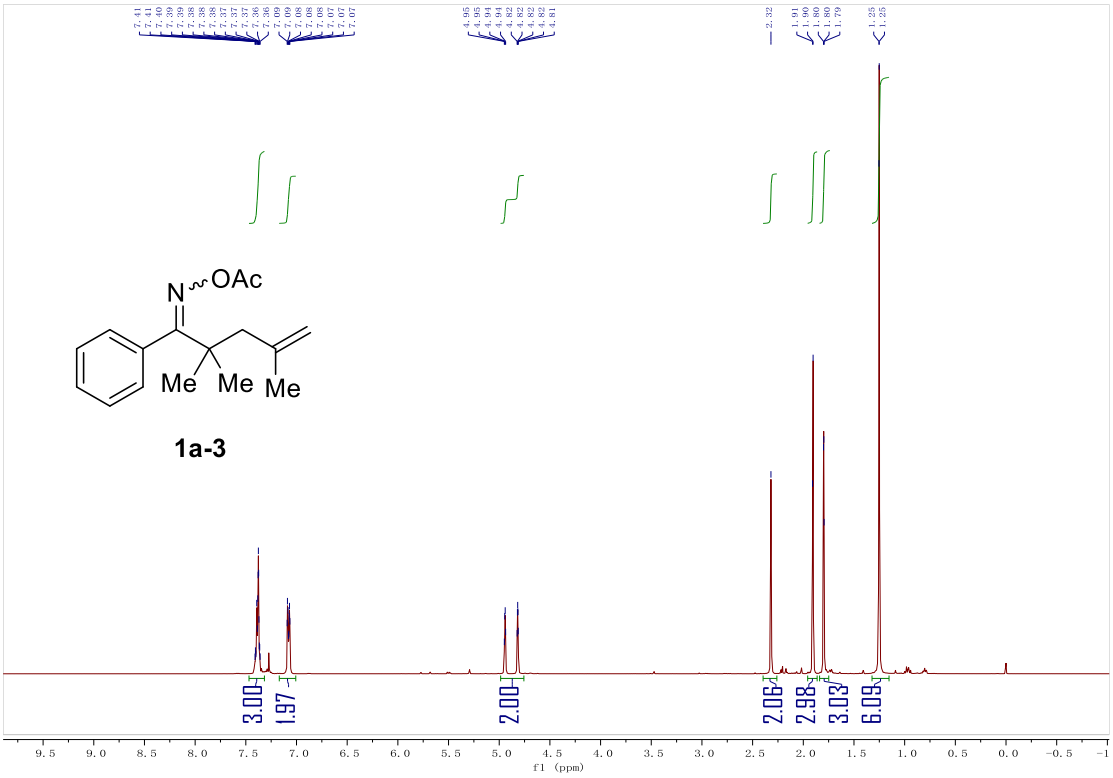
4. NMR Spectra

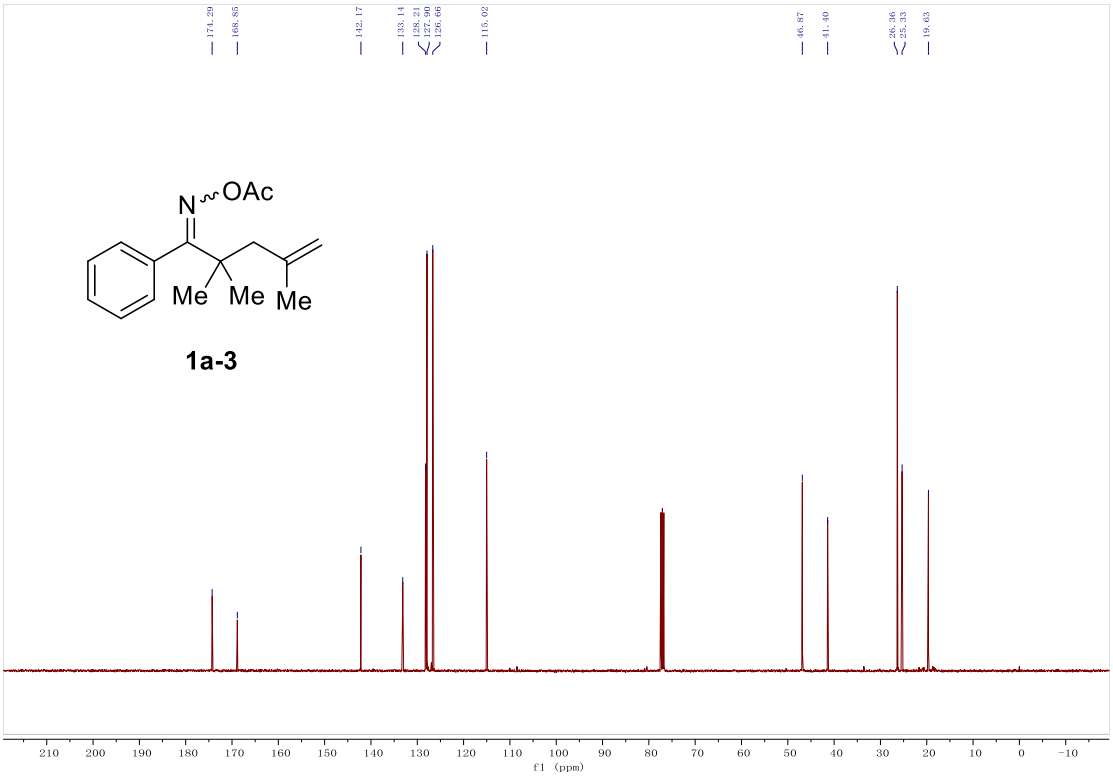


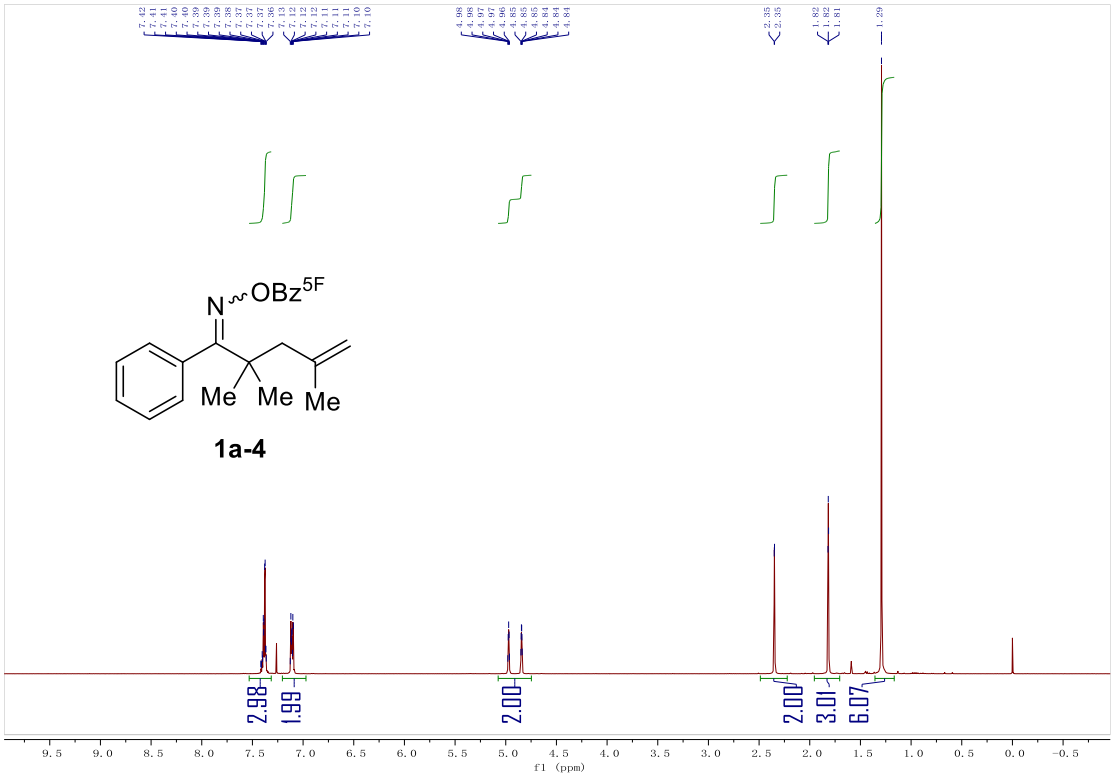


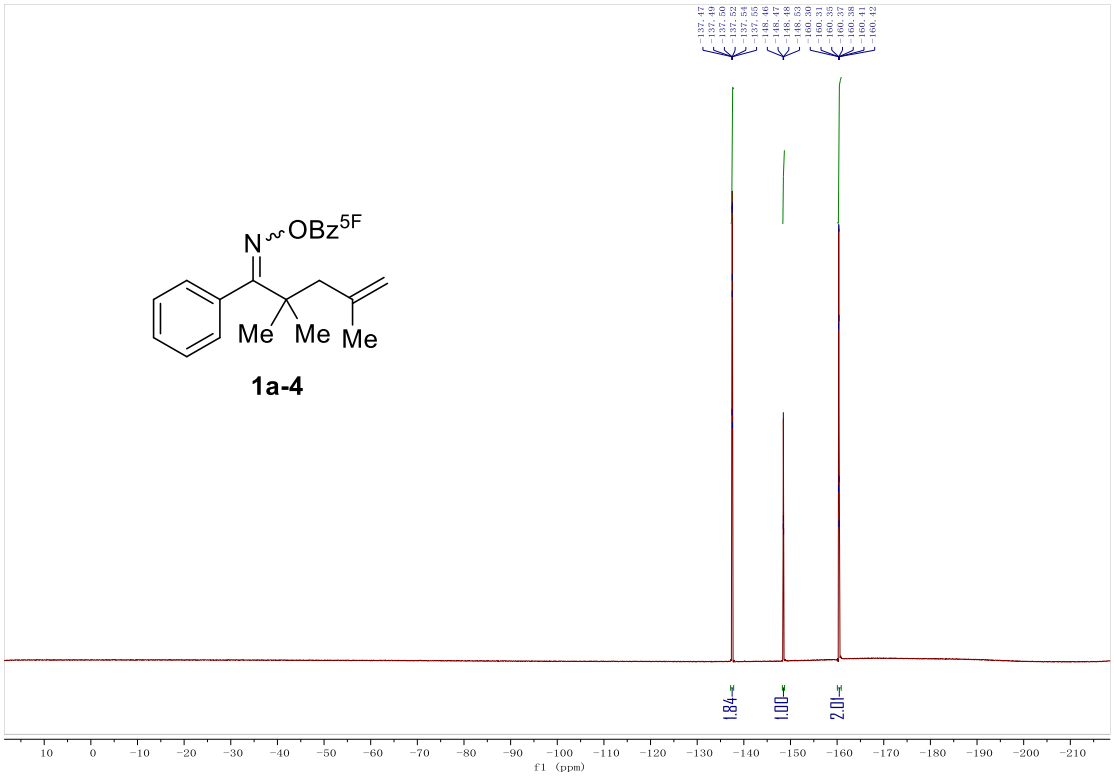

N
OPiv
Me
Me
Me
1a-2
3.01
2.02
2.00
1.99
2.97
6.22
9.12
f1 (ppm)

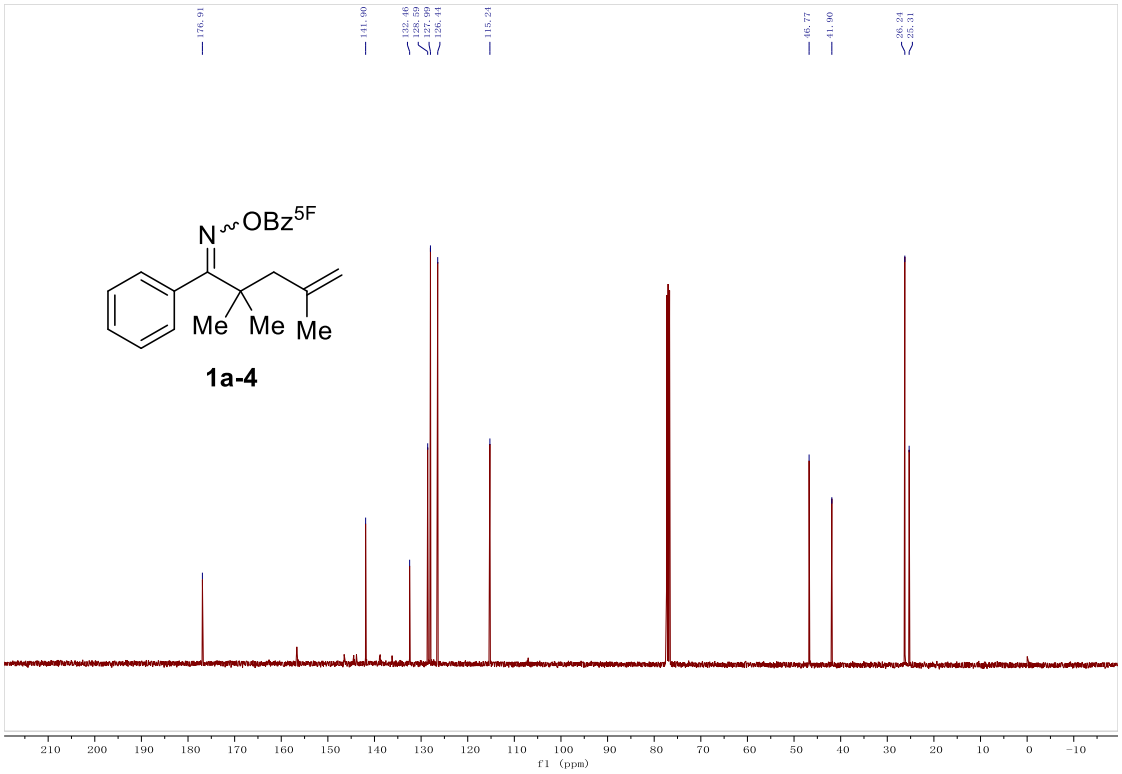

N
OPiv
Me
Me
Me
1a-2
f1 (ppm)

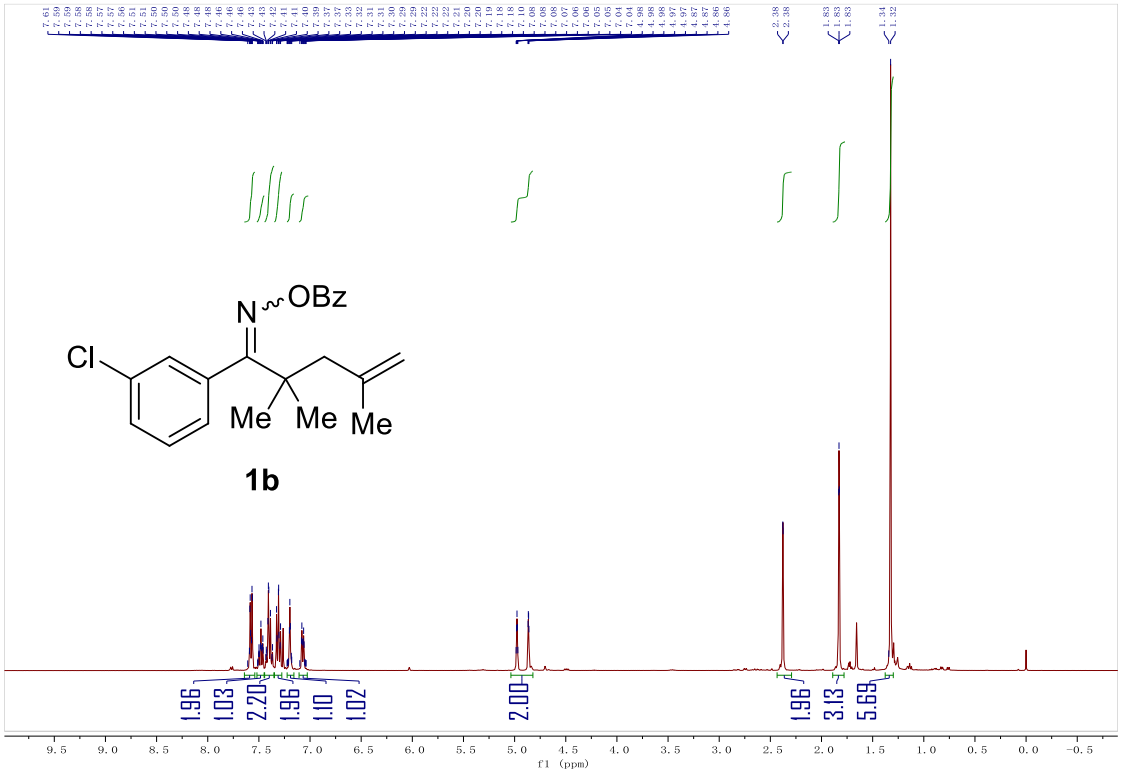

N
OAc
Me
Me
Me
1a-3
3.00
1.97
2.00
2.06
2.98
3.03
6.09
f1 (ppm)

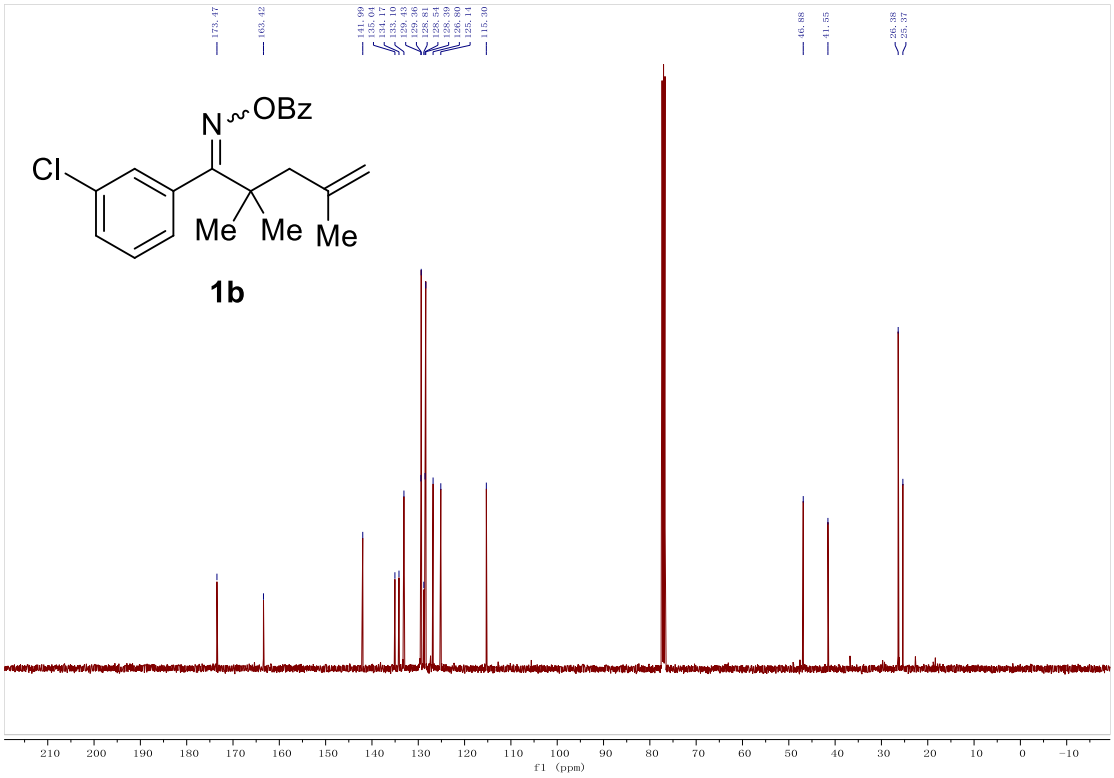

N
OAc
Me
Me
Me
1a-3
f1 (ppm)

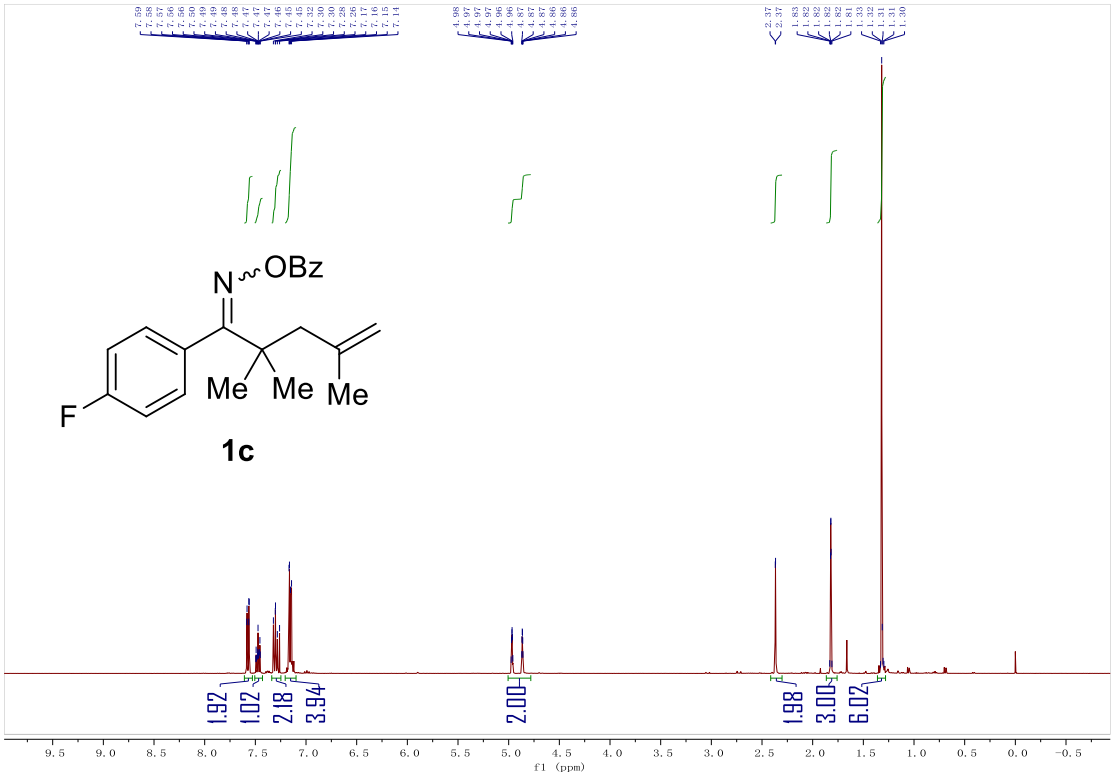

N
OBz5F
Me
Me
Me
1a-4
2.98
1.99
2.00
2.00
3.01
6.07
f1 (ppm)

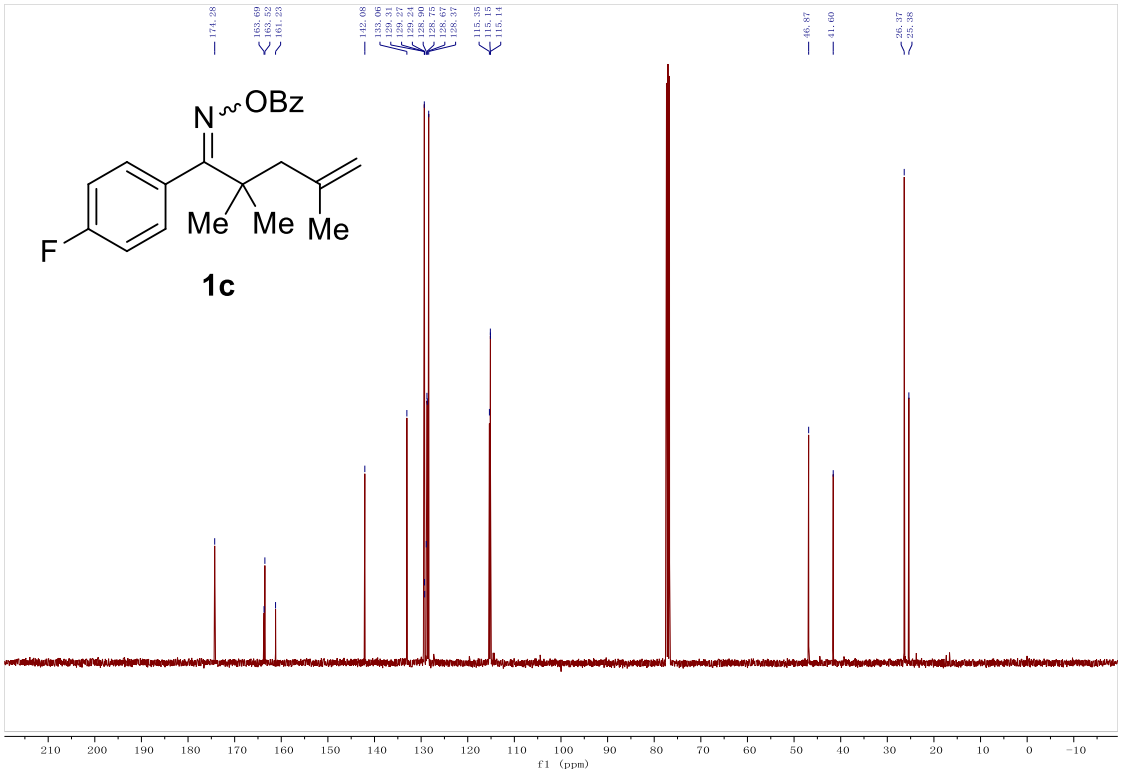

N
OBz5F
Me
Me
Me
1a-4
1.84
1.00
2.01
f1 (ppm)

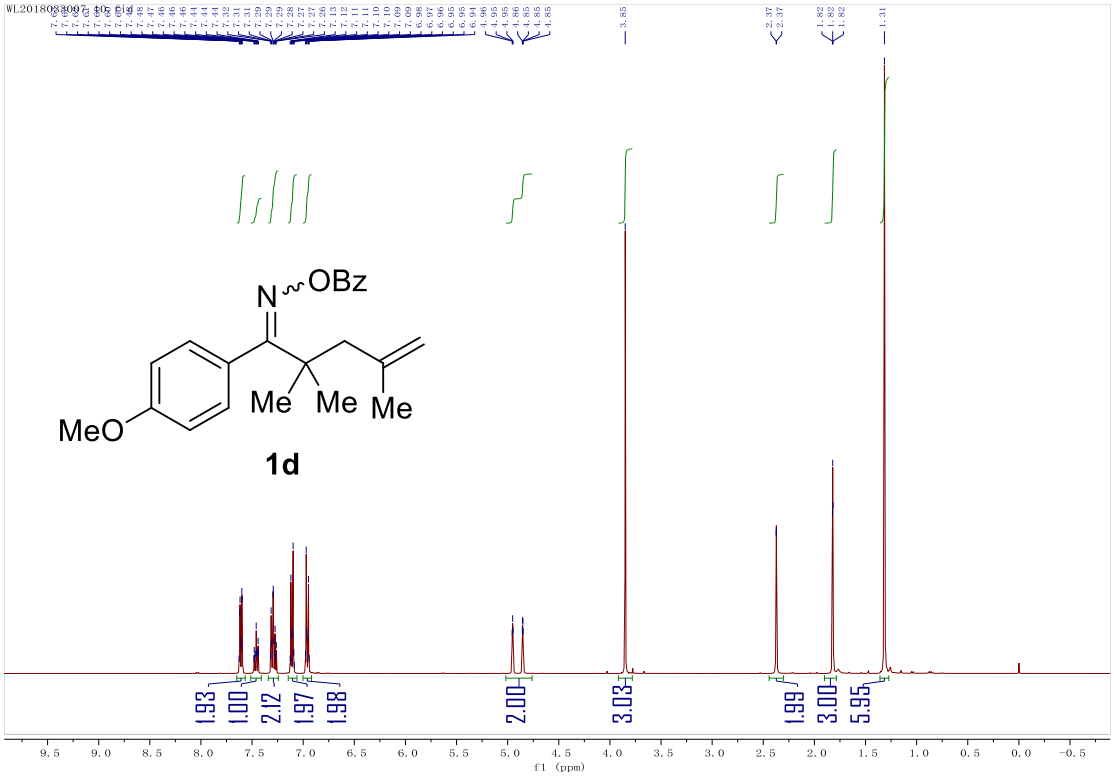

N
OBz5F
Me
Me
Me
1a-4
f1 (ppm)

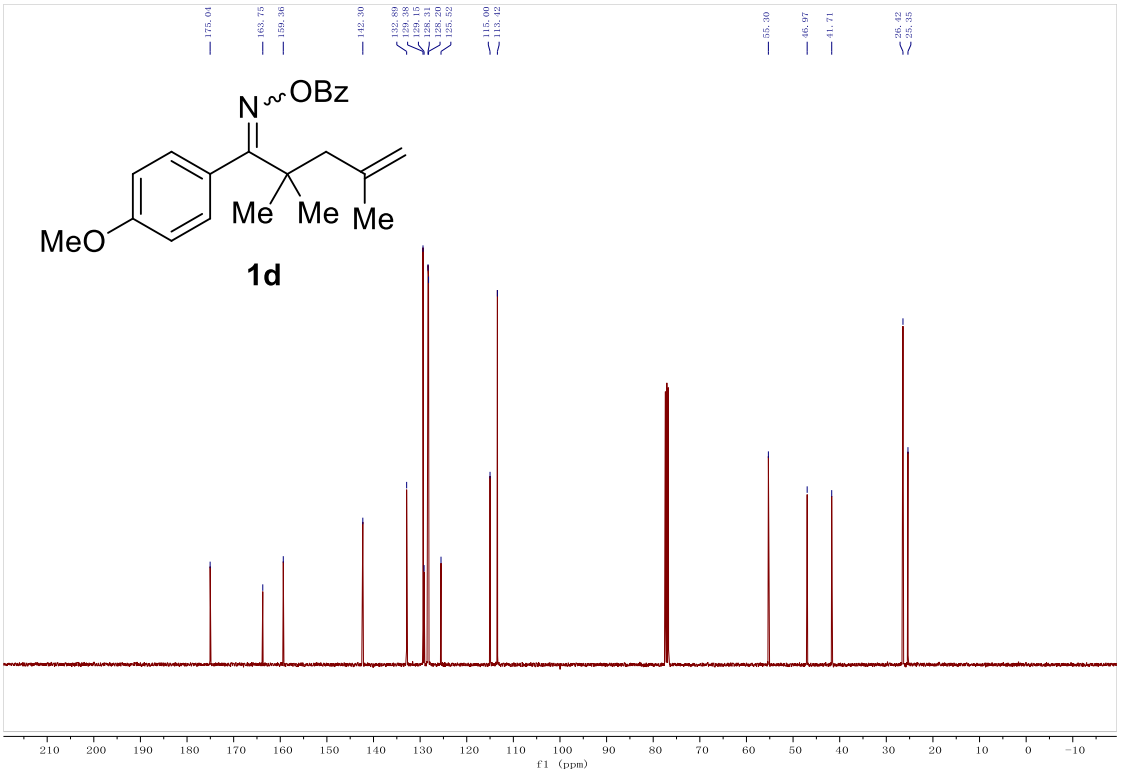

N
OBz
Cl
Me
Me
Me
1b
1.96
1.03
2.20
1.96
1.10
1.02
2.00
1.96
3.13
5.69
f1 (ppm)

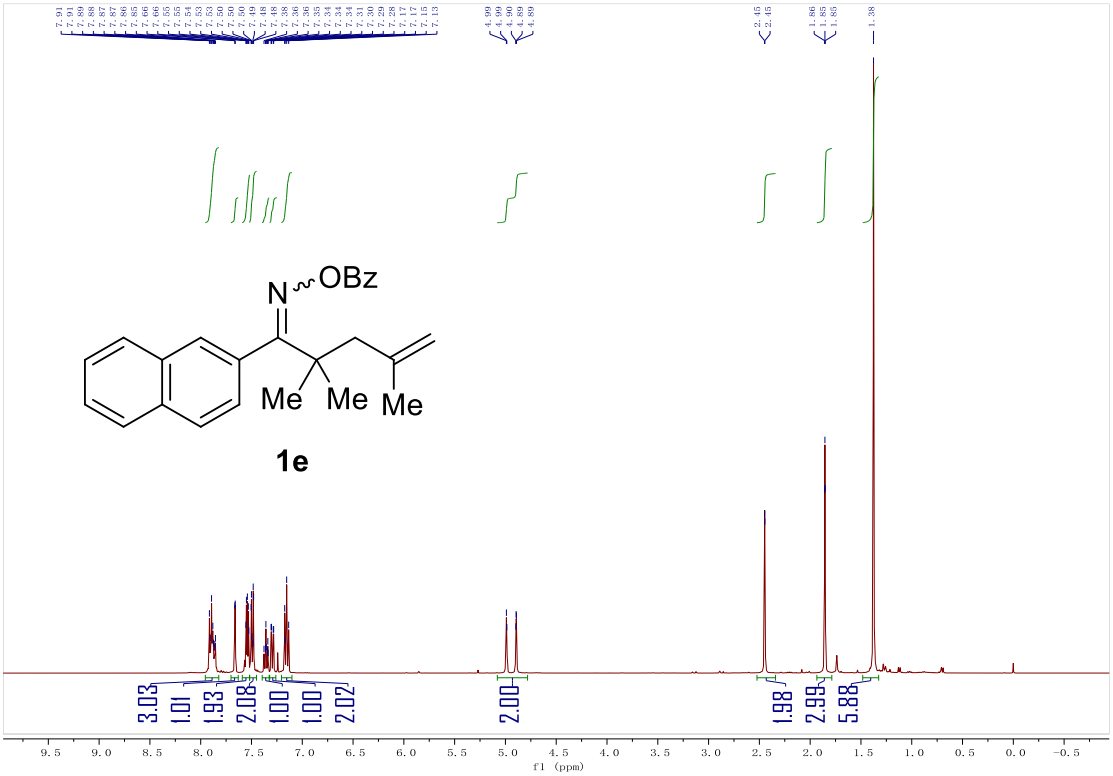

N
OBz
Cl
Me
Me
Me
1b
f1 (ppm)

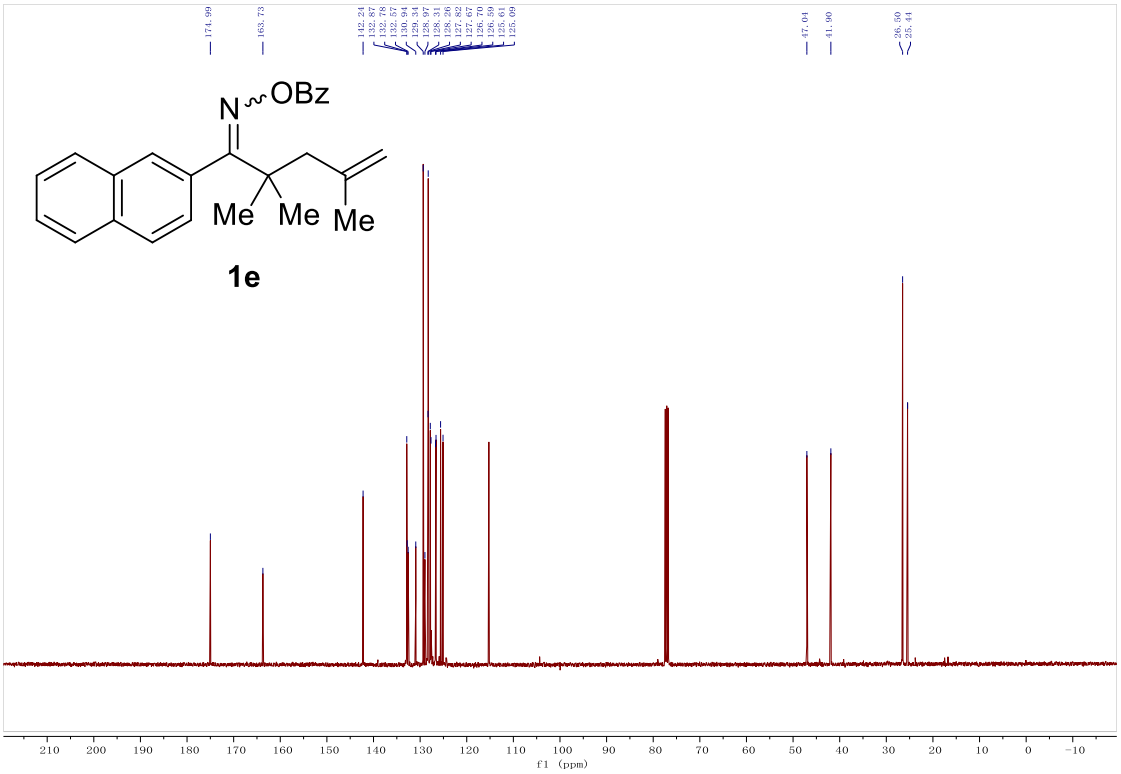

N
OBz
F
Me
Me
Me
1c
1.92
1.02
2.18
3.94
2.00
1.98
3.00
6.02
f1 (ppm)

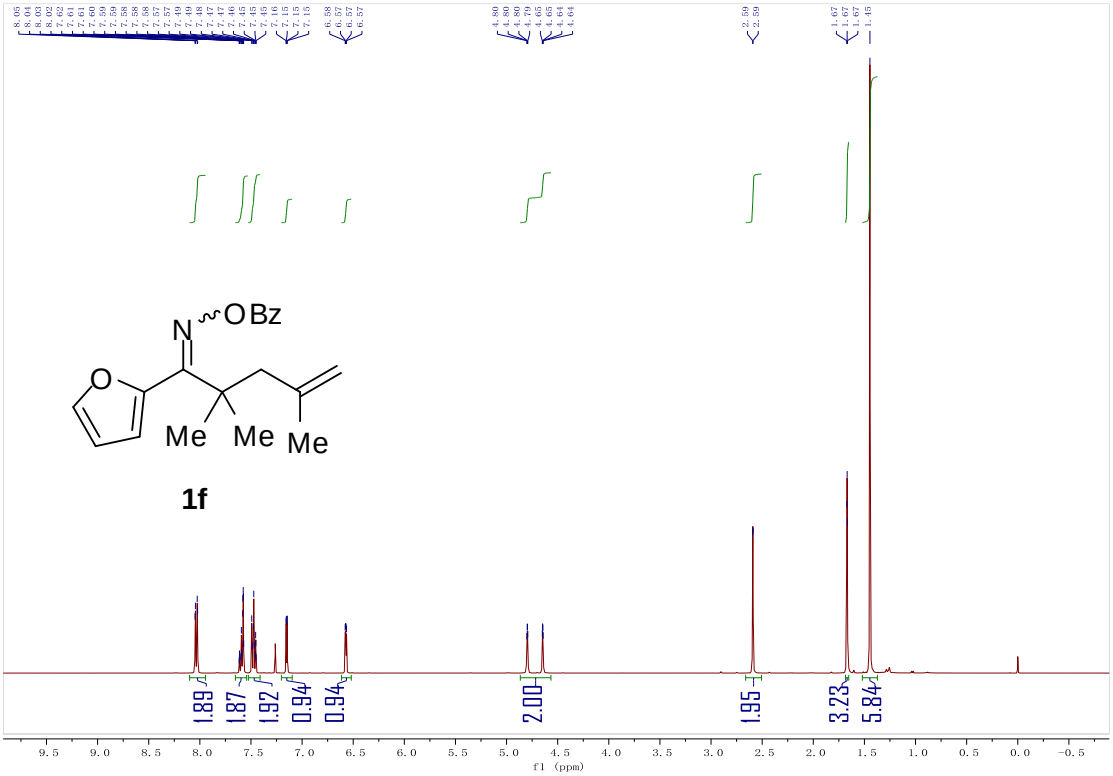

N
OBz
Me
Me
Me
F
1c
f1 (ppm)

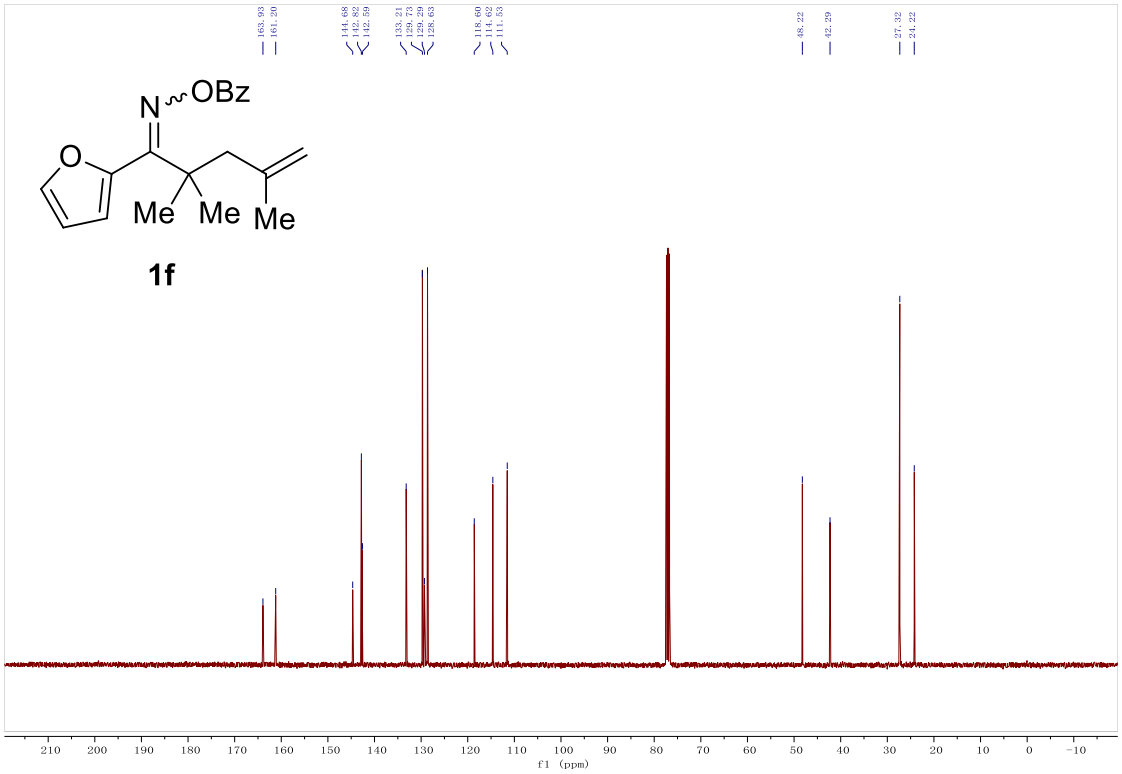

N
OBz
Me
Me
Me
MeO
1d
1.93
1.00
2.12
1.97
1.98
2.00
3.03
1.99
3.00
5.95
f1 (ppm)

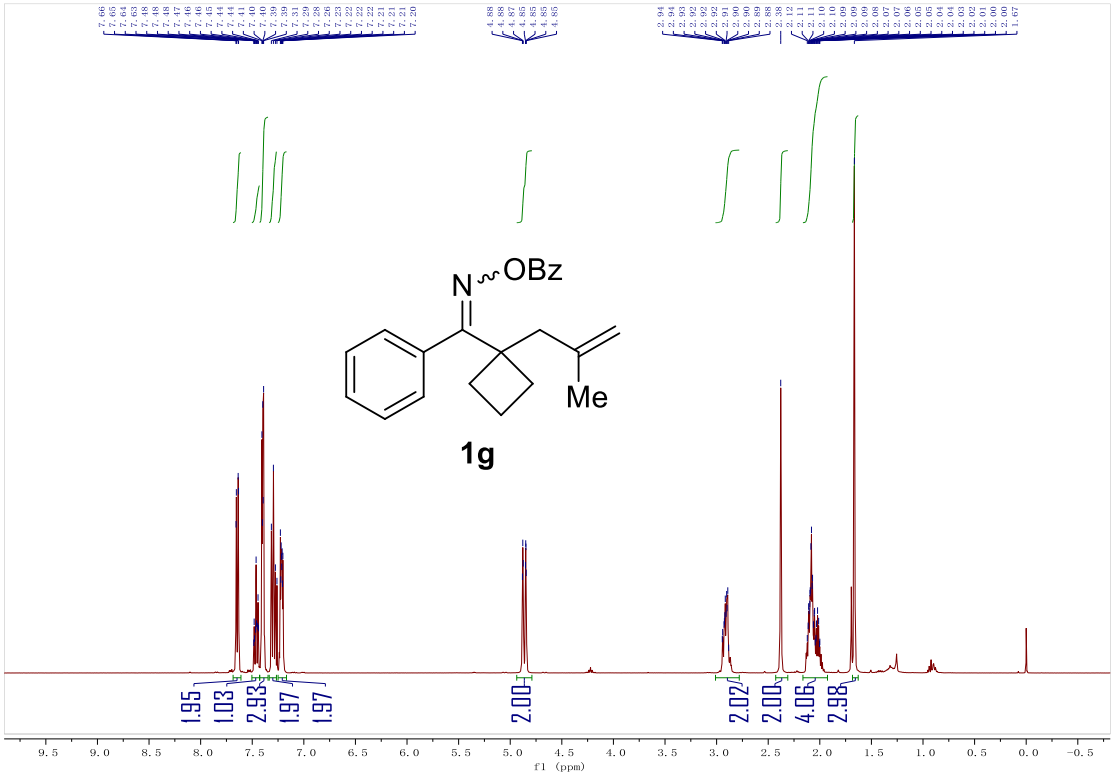

N
OBz
Me
Me
Me
MeO
1d
f1 (ppm)

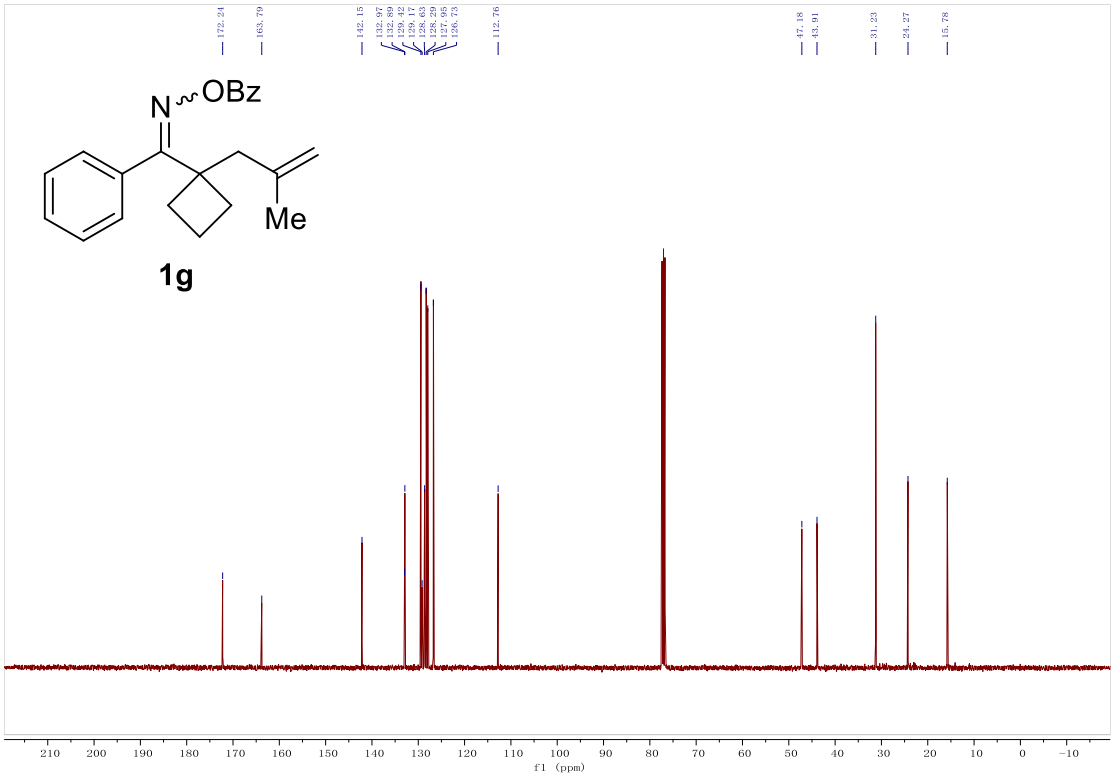

N
OBz
Me
Me
Me
1e
3.03
1.01
1.93
2.08
1.00
1.00
2.02
2.00
1.98
2.99
5.88
f1 (ppm)

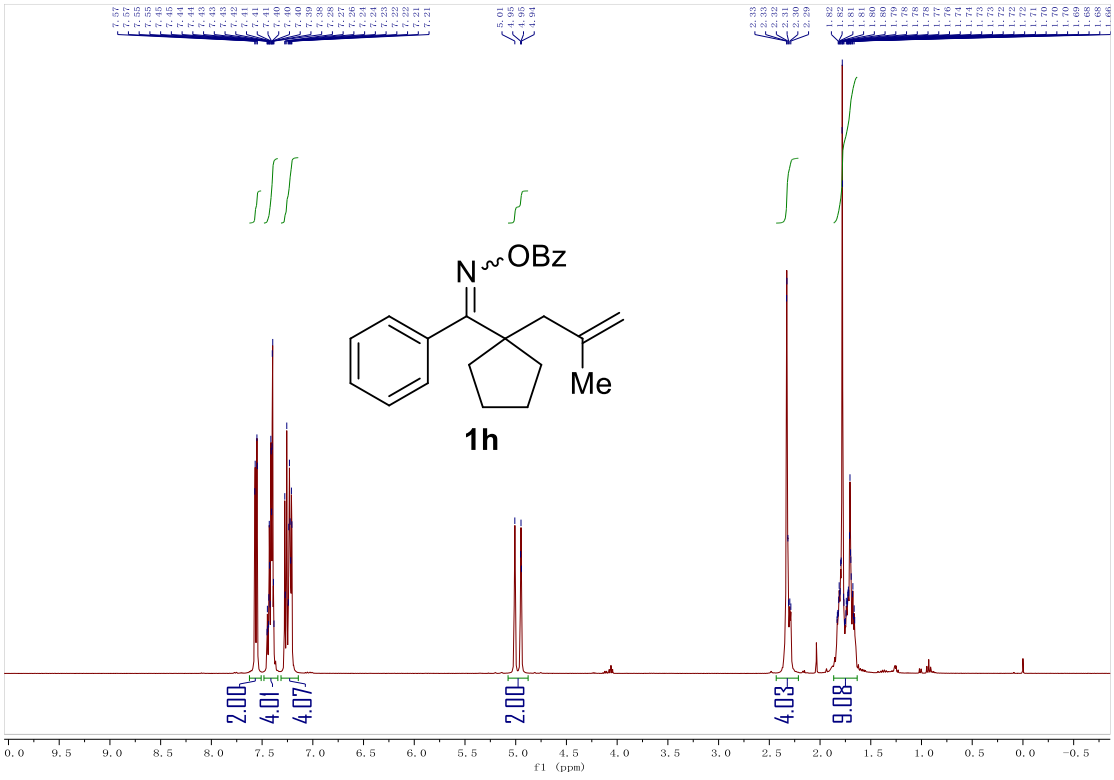

N
OBz
Me
Me
Me
1e
f1 (ppm)

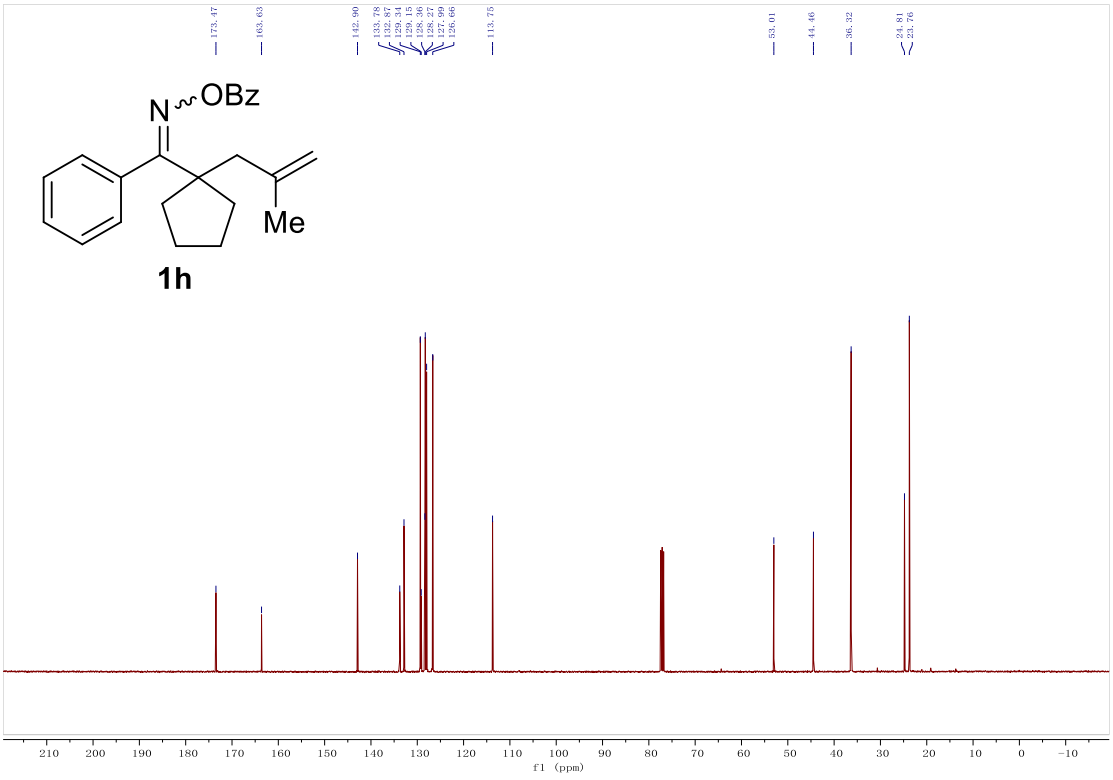

N
OBz
O
Me
Me
Me
1f
1.89
1.87
1.92
0.94
0.94
2.00
1.95
3.23
5.84
f1 (ppm)


163.93
161.20
144.68
142.82
142.59
133.21
129.73
129.29
128.63
118.60
114.62
111.53
48.22
42.29
27.32
24.22
N
OBz
O
Me
Me
Me
1f
f1 (ppm)

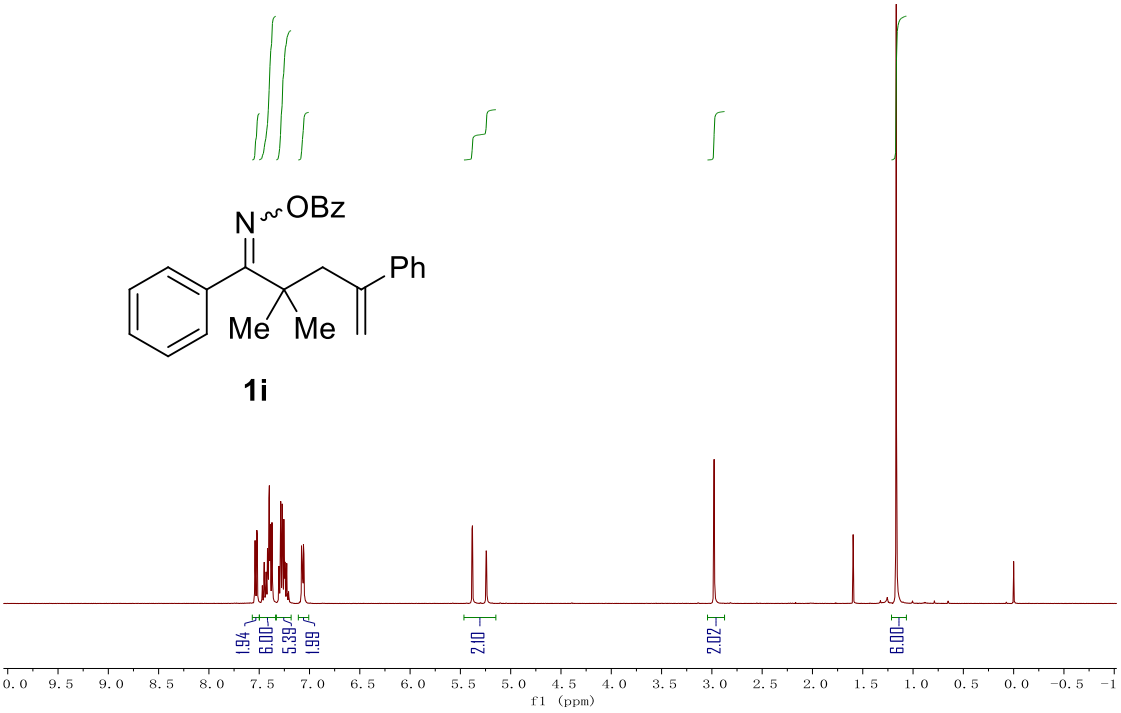

N
OBz
Me
1g
1.95
1.03
2.93
1.97
1.97
2.00
2.02
2.00
4.06
2.98
f1 (ppm)

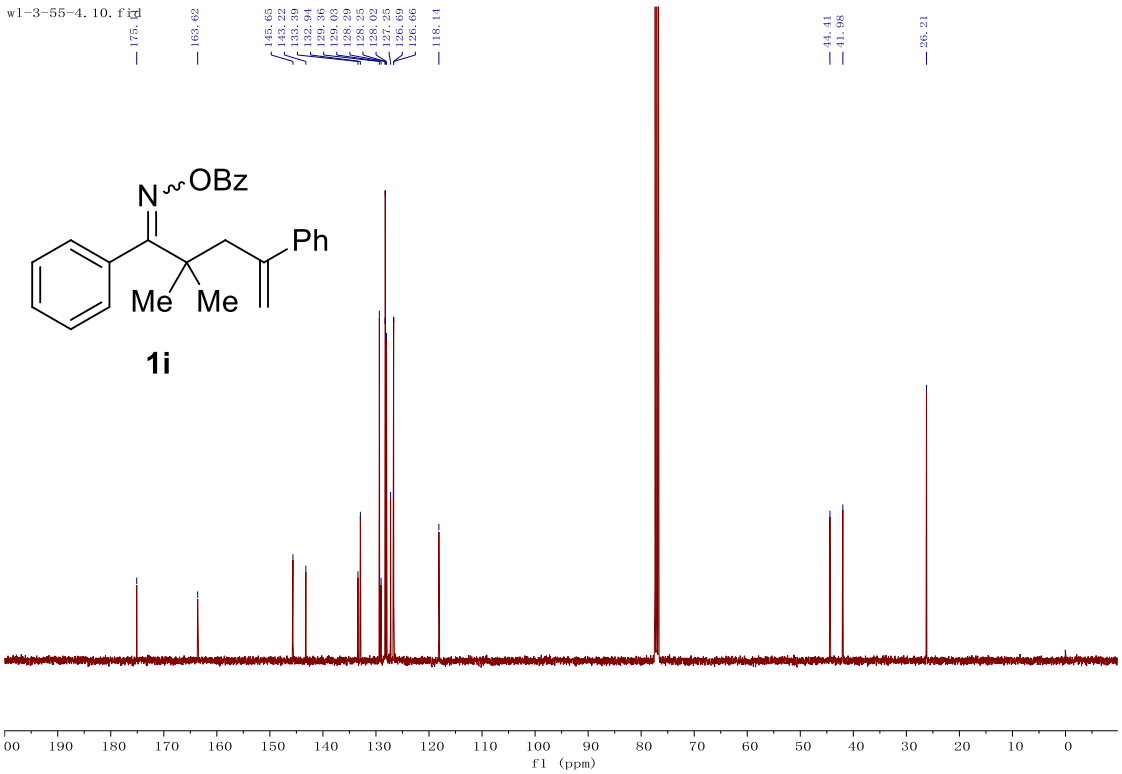

N
OBz
Me
1g
f1 (ppm)

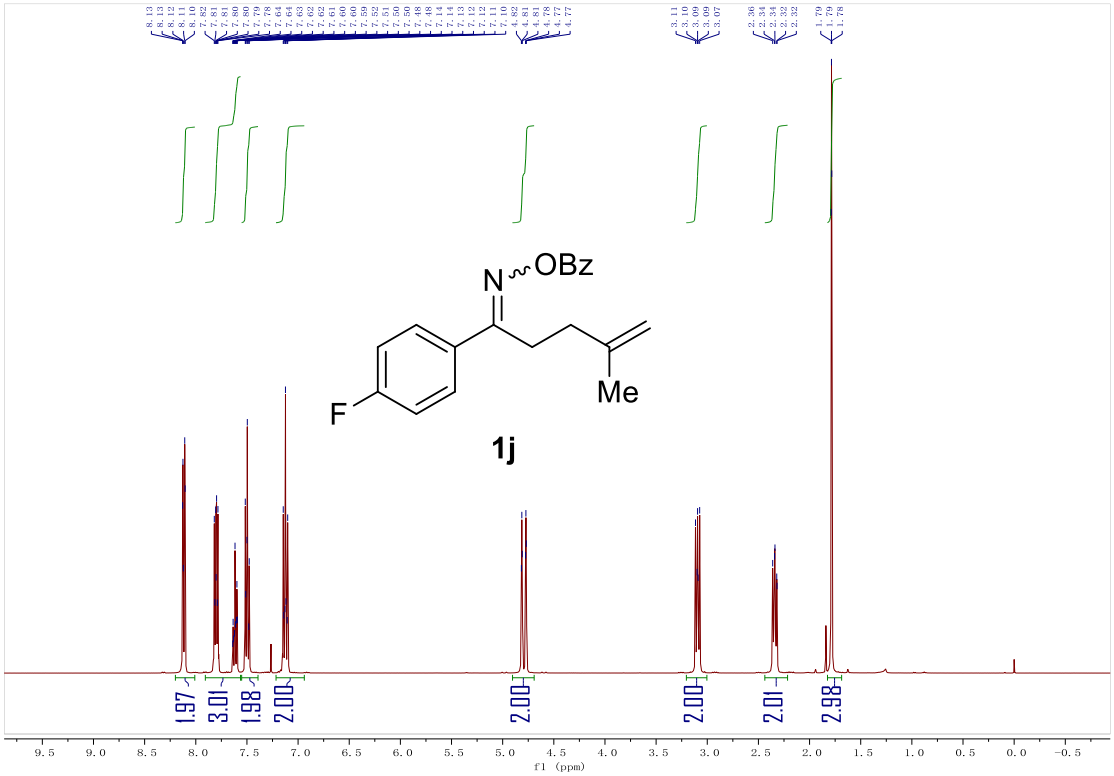

N
OBz
Me
1h
2.00
4.01
4.07
2.00
4.03
9.08
f1 (ppm)

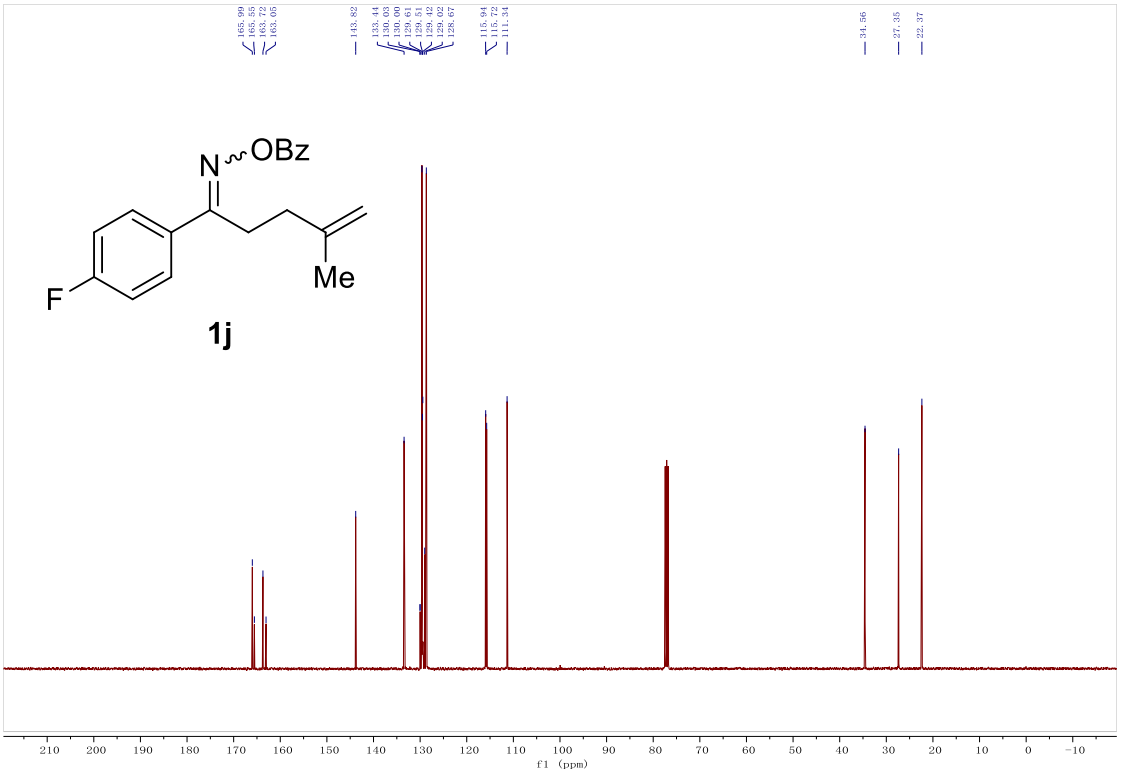

173.47
163.63
142.90
133.78
132.87
129.34
129.15
128.46
128.27
127.99
126.66
113.75
53.01
44.46
36.32
24.81
23.76
N
OBz
Me
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

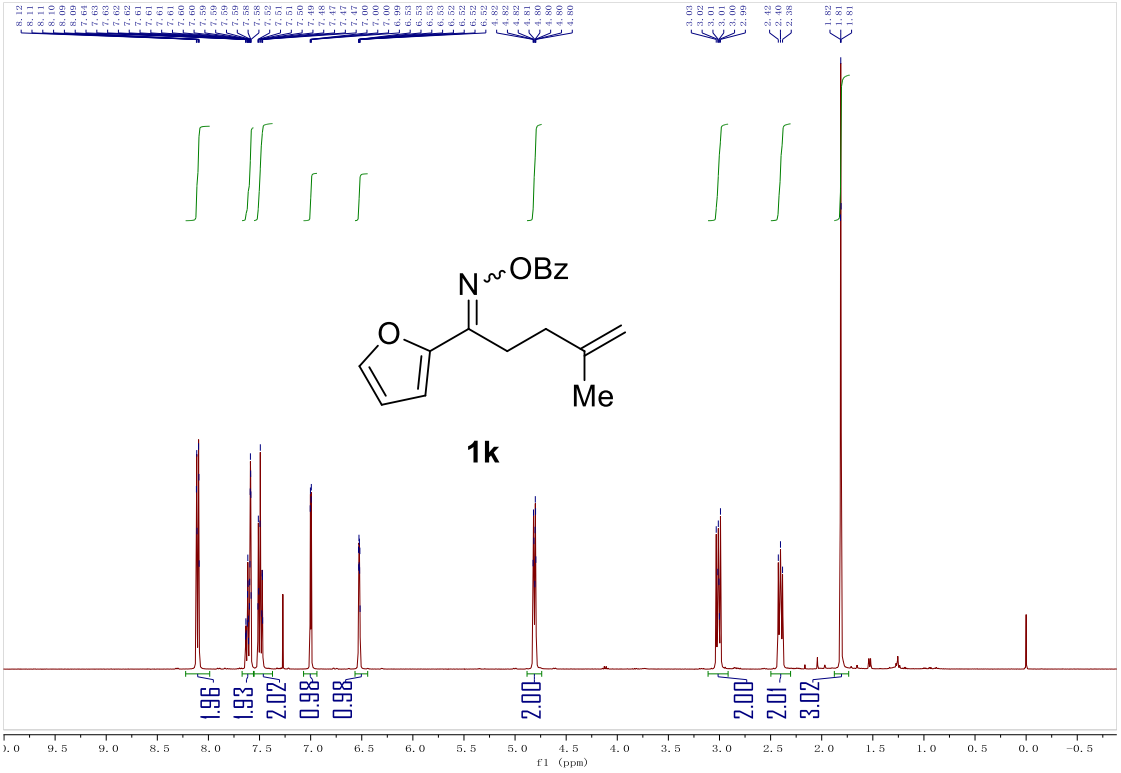
wl-3-55-4.1.fid

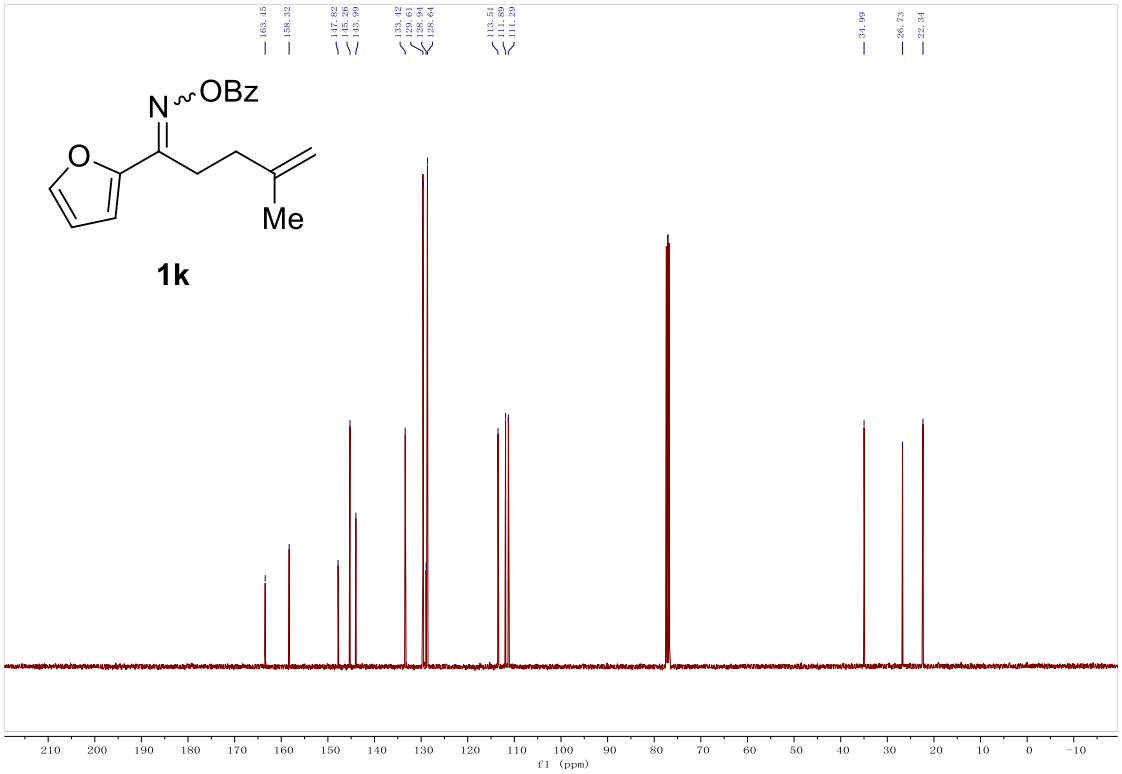

N
OBz
Ph
Me
Me
1i
1.94
6.00
5.39
1.99
2.10
2.02
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

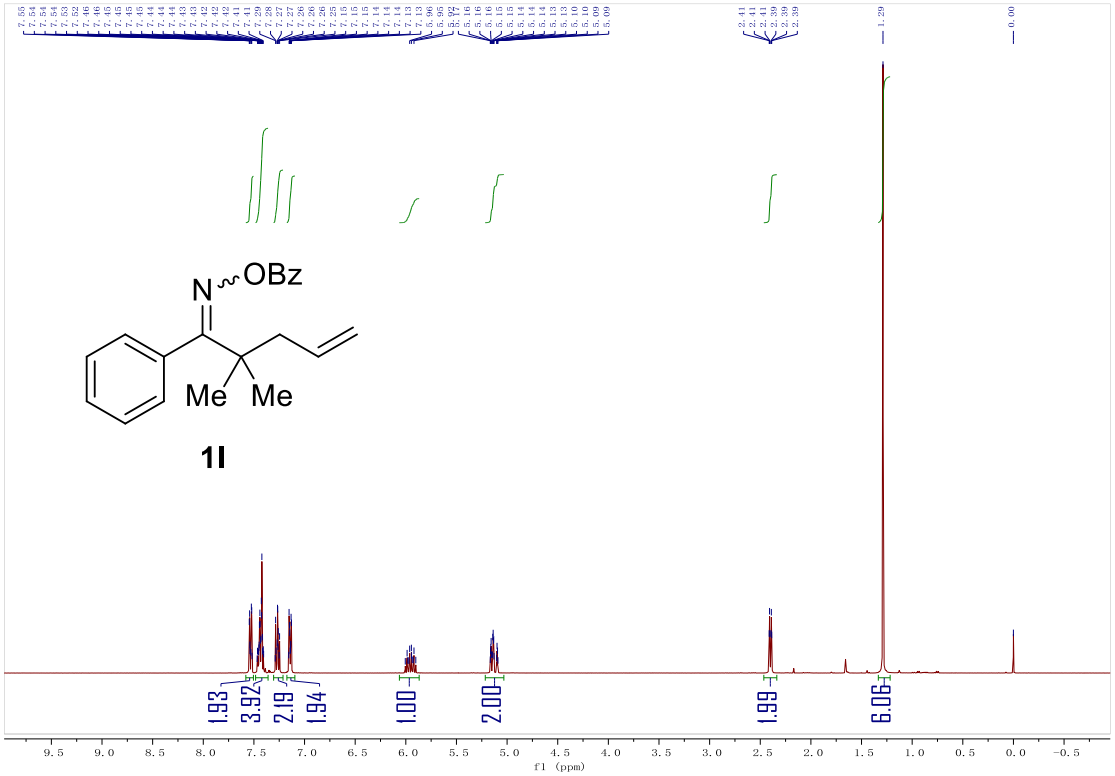

wl-3-55-4.10.fid
175.61
163.62
145.65
143.22
133.39
132.94
129.36
129.03
128.29
128.25
128.02
127.25
126.69
126.66
118.14
44.41
41.98
26.21
N
OBz
Ph
Me
Me
1i
f1 (ppm)

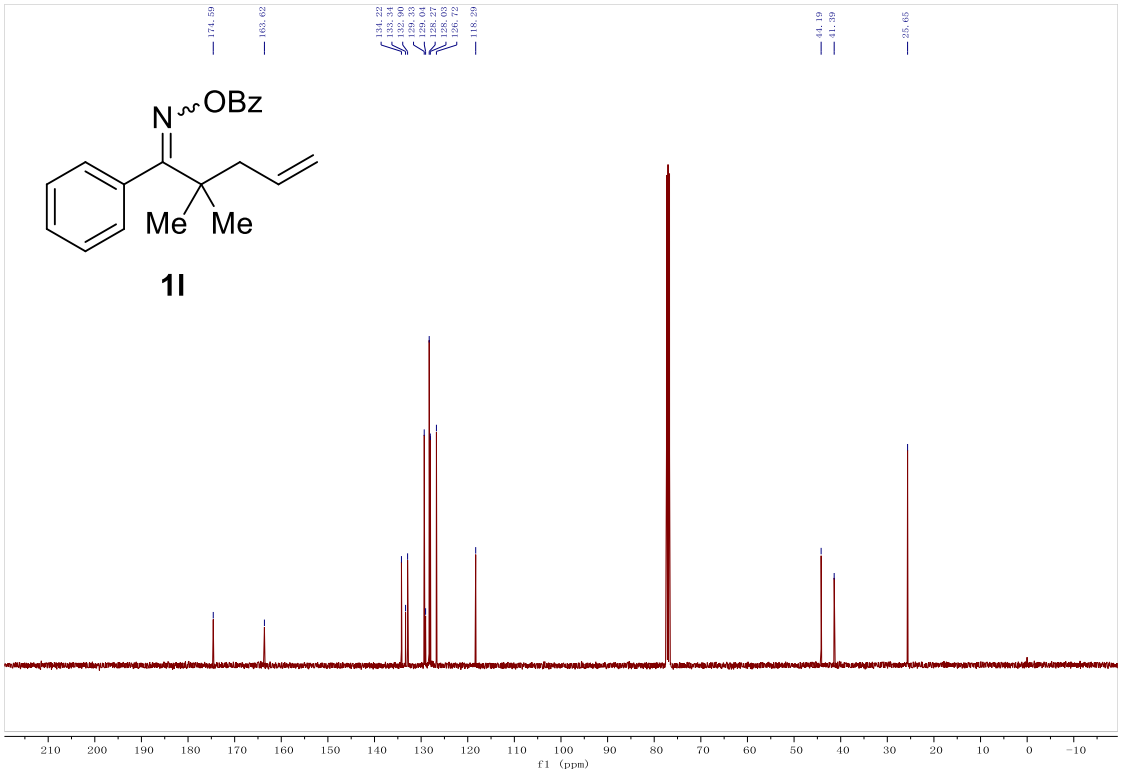

N
OBz
Me
F
1j
1.97
3.01
1.98
2.00
2.00
2.00
2.01
2.98
f1 (ppm)

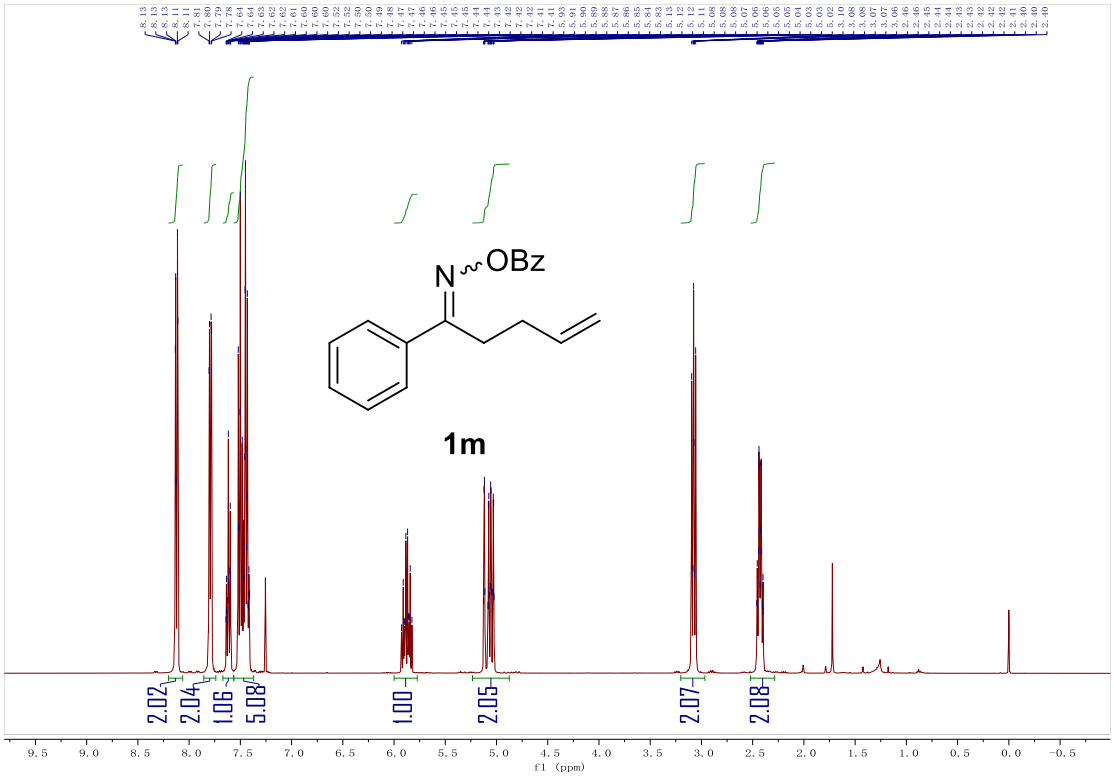

N
OBz
F
Me
1j
f1 (ppm)

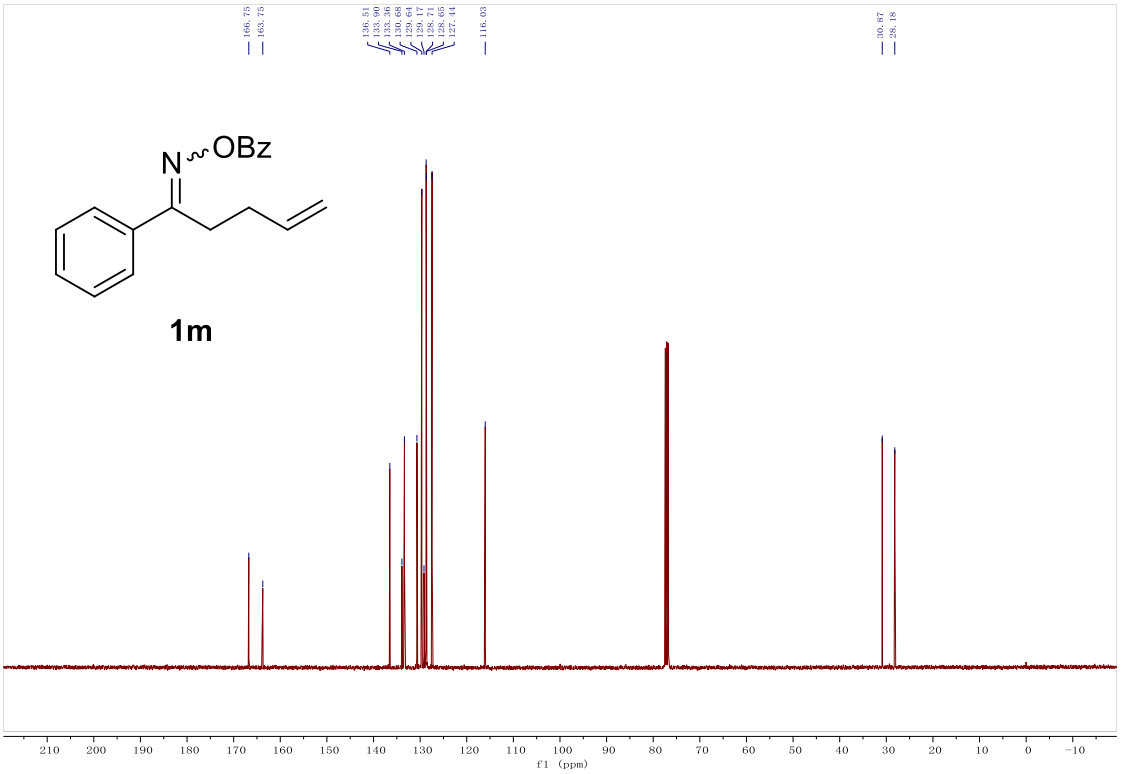

N
OBz
O
Me
1k
1.96
1.93
2.02
0.98
0.98
2.00
2.00
2.01
3.02
f1 (ppm)


163.45
158.32
147.82
145.26
143.99
133.42
129.61
128.94
128.64
113.51
111.89
111.29
34.99
26.73
22.34
N
OBz
O
Me
1k
f1 (ppm)


N
OBz
Me
Me
1l
1.93
3.92
2.19
1.94
1.00
2.00
1.99
6.06
f1 (ppm)


174.59
163.62
134.22
133.34
132.90
129.33
128.64
128.27
128.03
126.72
118.29
84.19
41.39
25.65
N
OBz
Me
Me
1l
f1 (ppm)


N
OBz
1m
2.02
2.04
1.06
5.08
1.00
2.05
2.07
2.08
f1 (ppm)


N
OBz
1m
166.75
163.75
136.51
135.90
133.36
130.68
129.64
129.17
128.71
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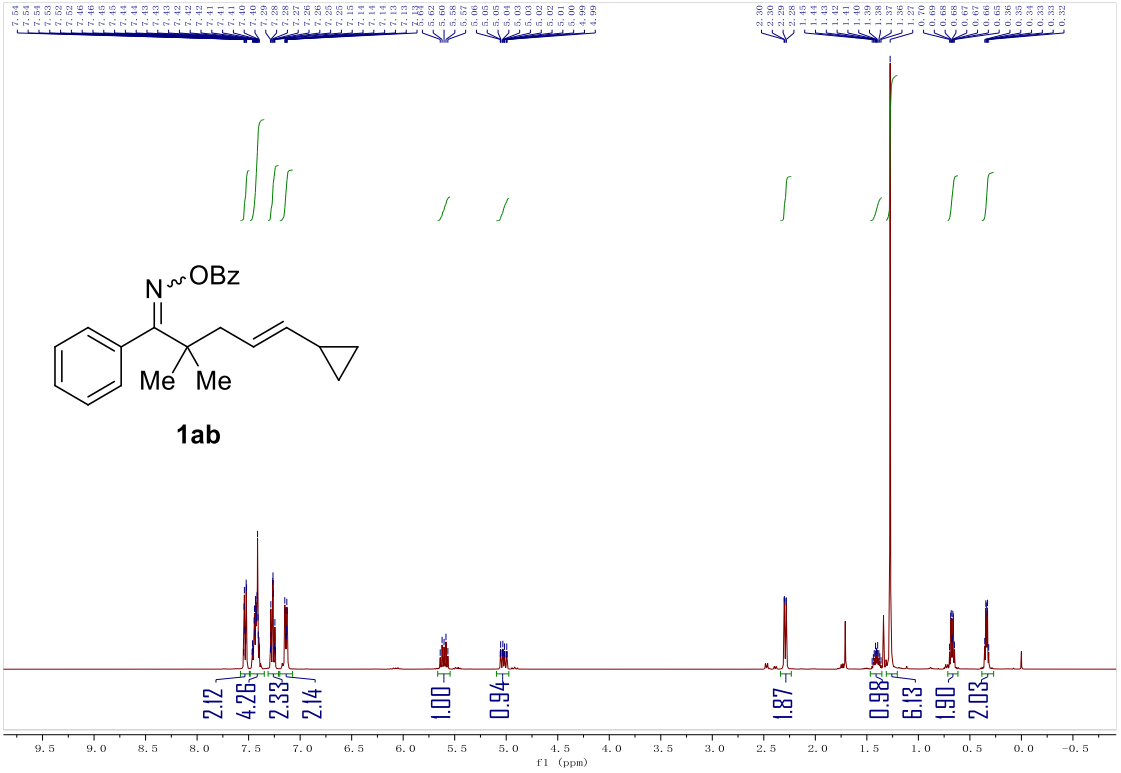
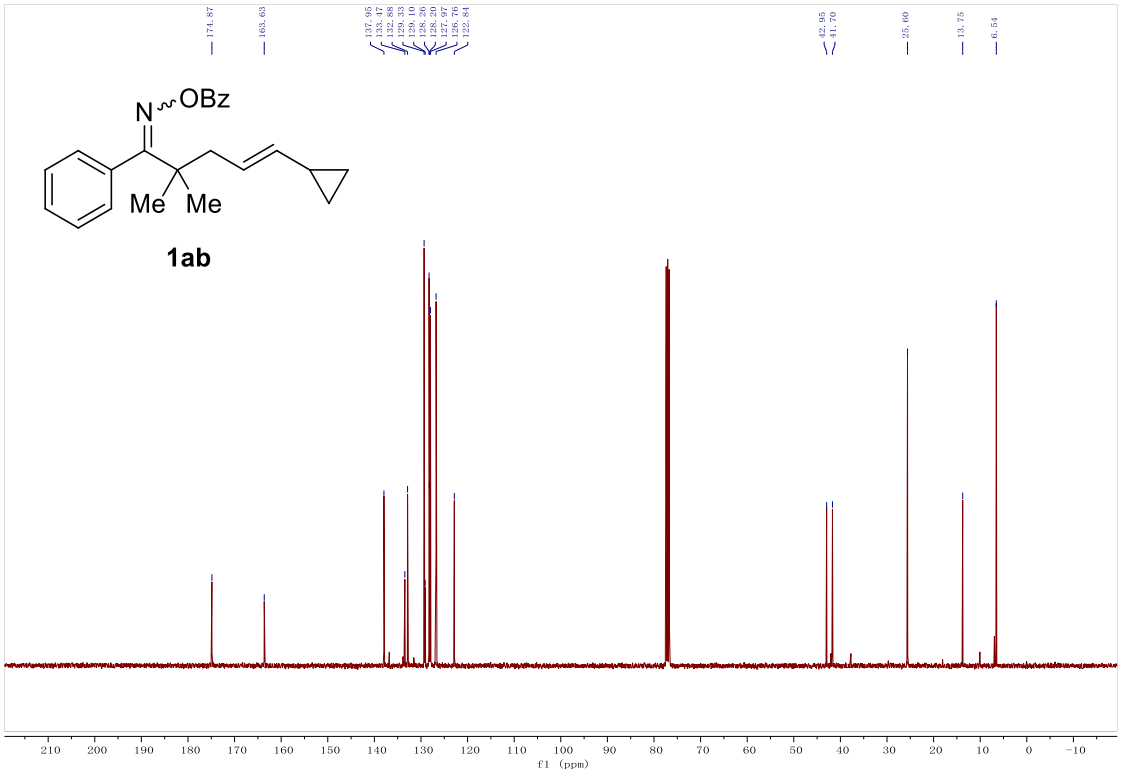
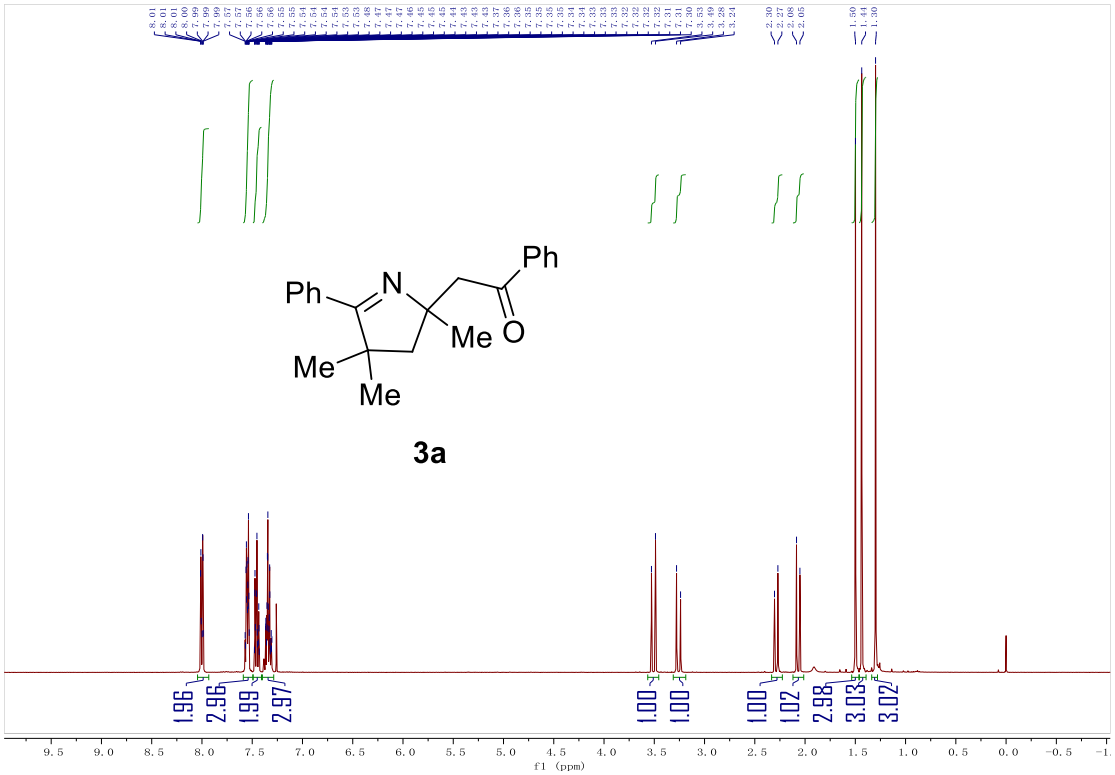
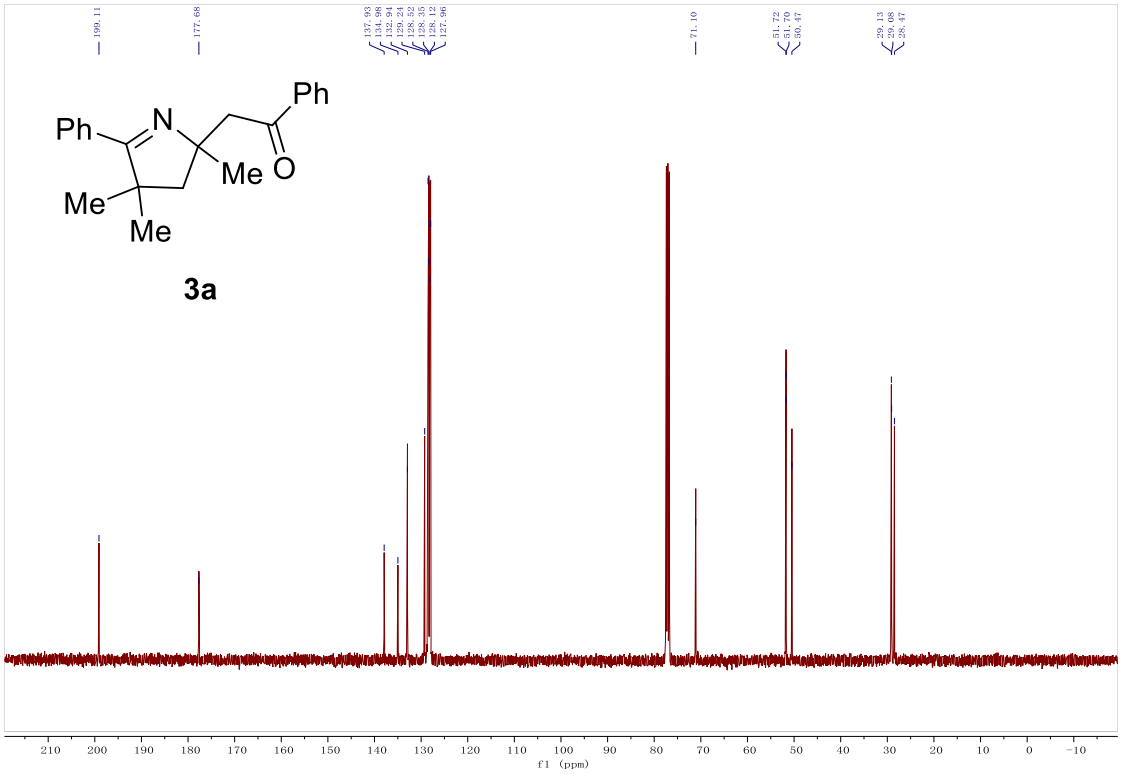
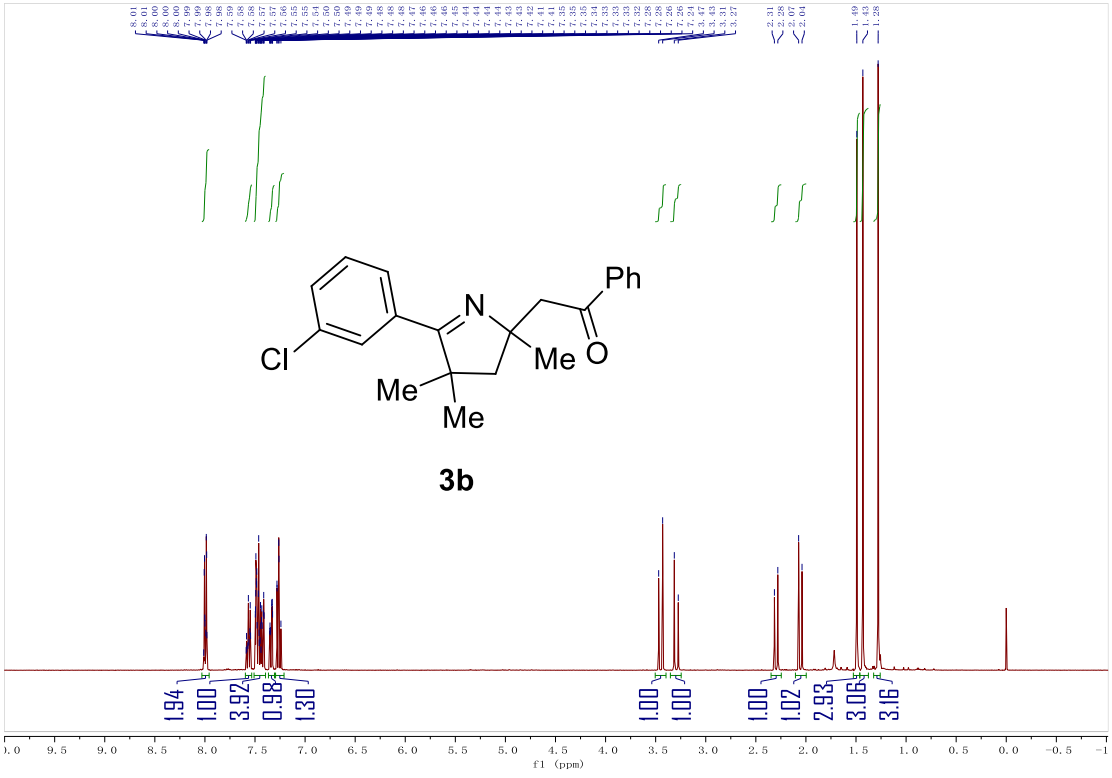
127.44
116.03
30.87
28.18
f1 (ppm)

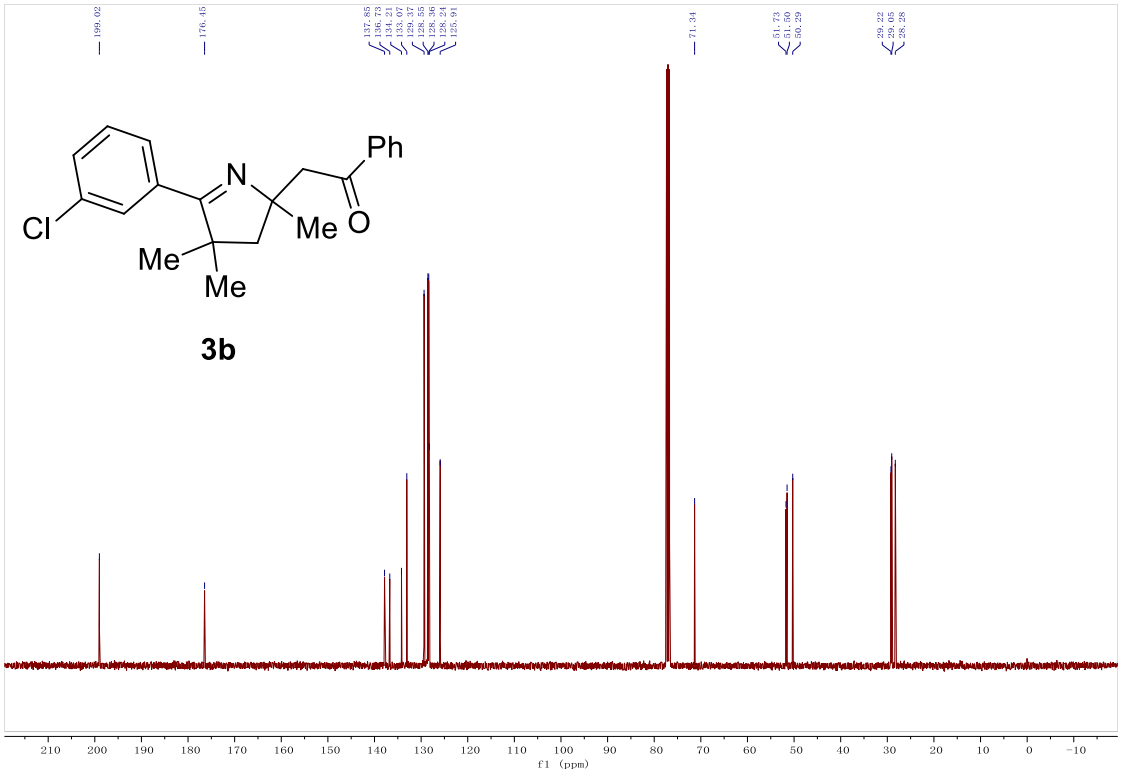

N
OBz
Me
Me
1ab
2.12
4.26
2.33
2.14
1.00
0.94
1.87
0.98
6.13
1.90
2.03
f1 (ppm)

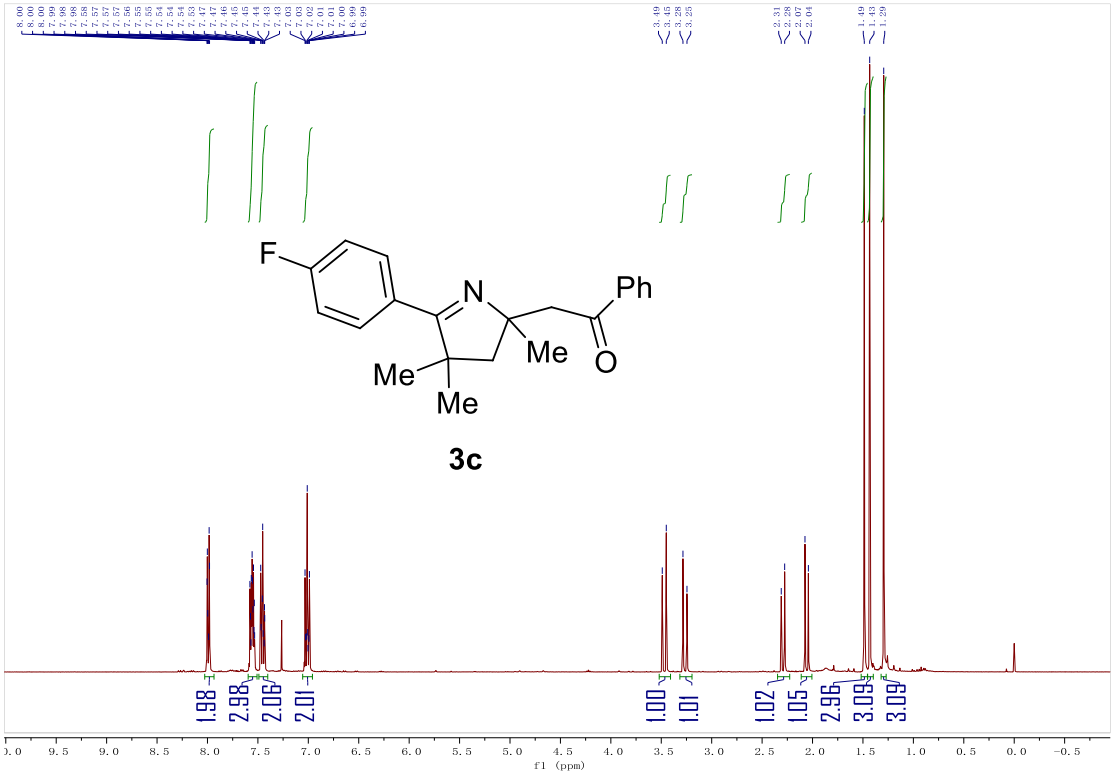

N
OBz
Me
Me
1ab
f1 (ppm)

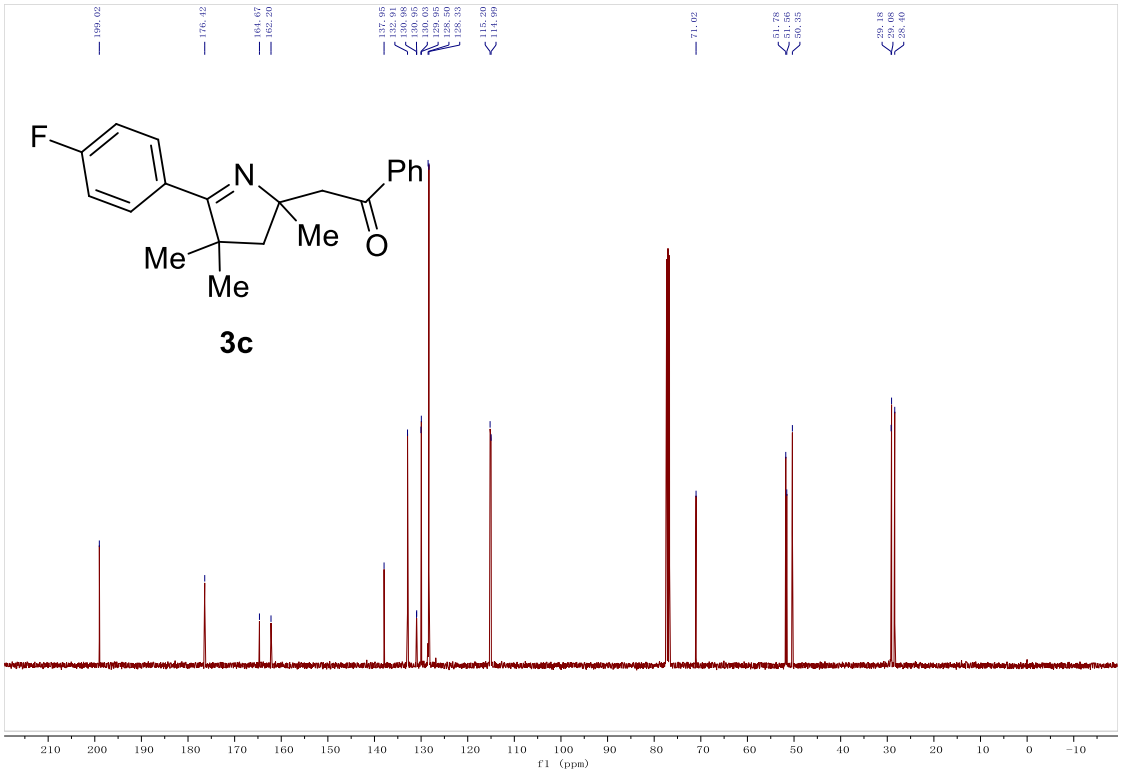

Ph
N
Ph
Me
O
Me
Me
3a
1.96
2.96
1.99
2.97
1.00
1.00
1.00
1.02
2.98
3.03
3.02
f1 (ppm)

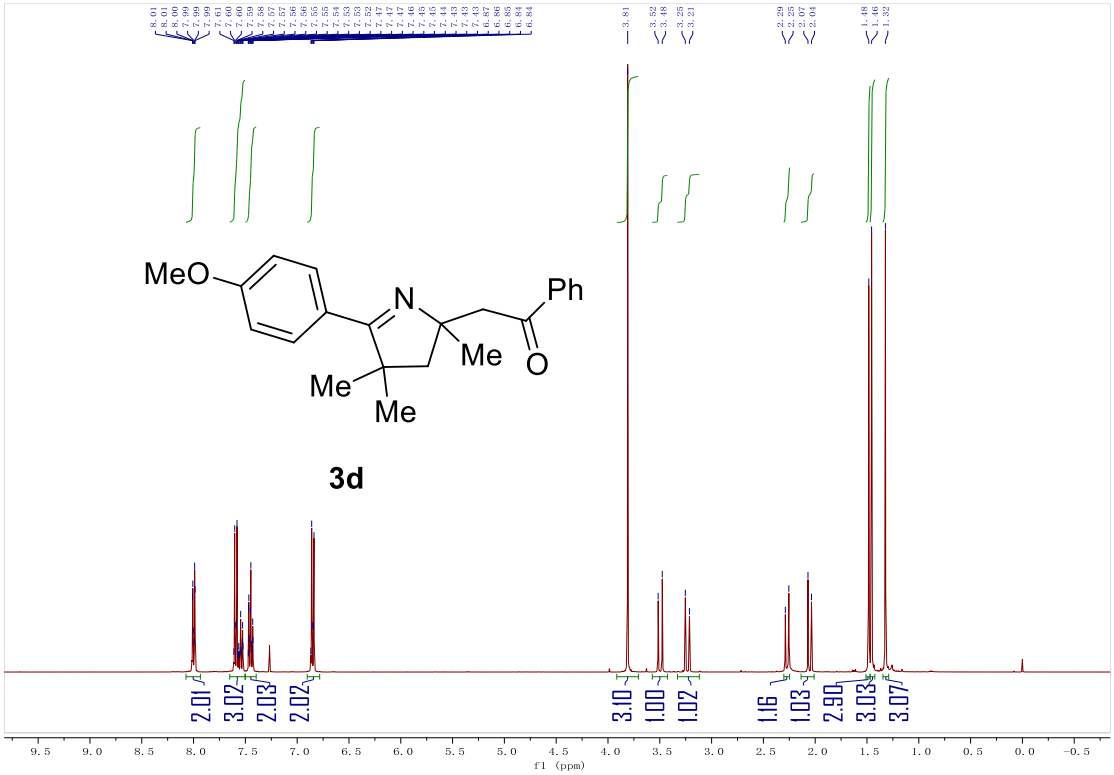

199.11
177.68
137.93
134.98
132.94
129.24
128.52
128.35
126.12
127.96
71.10
51.72
51.70
46.47
29.13
29.08
28.47
Ph
N
Ph
Me
O
Me
Me
3a
f1 (ppm)

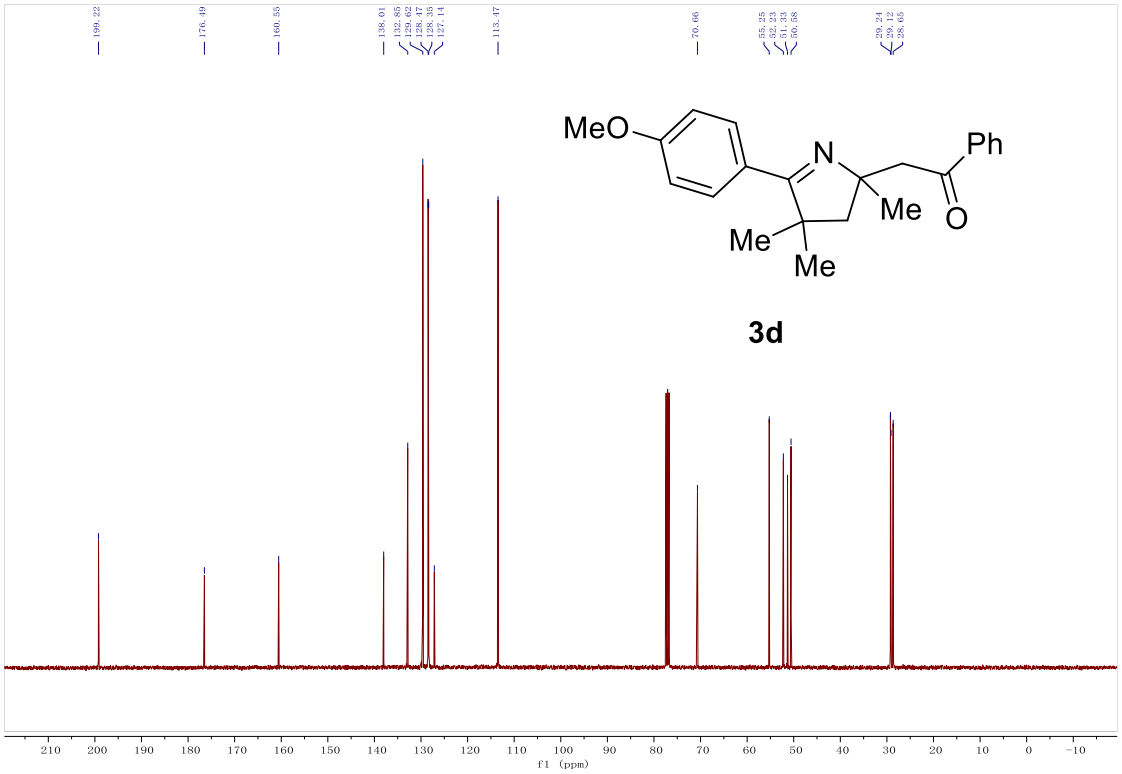

Cl
N
Ph
Me
O
Me
Me
3b
1.94
1.00
3.92
0.98
1.30
1.00
1.00
1.00
1.02
2.93
3.06
3.16
f1 (ppm)

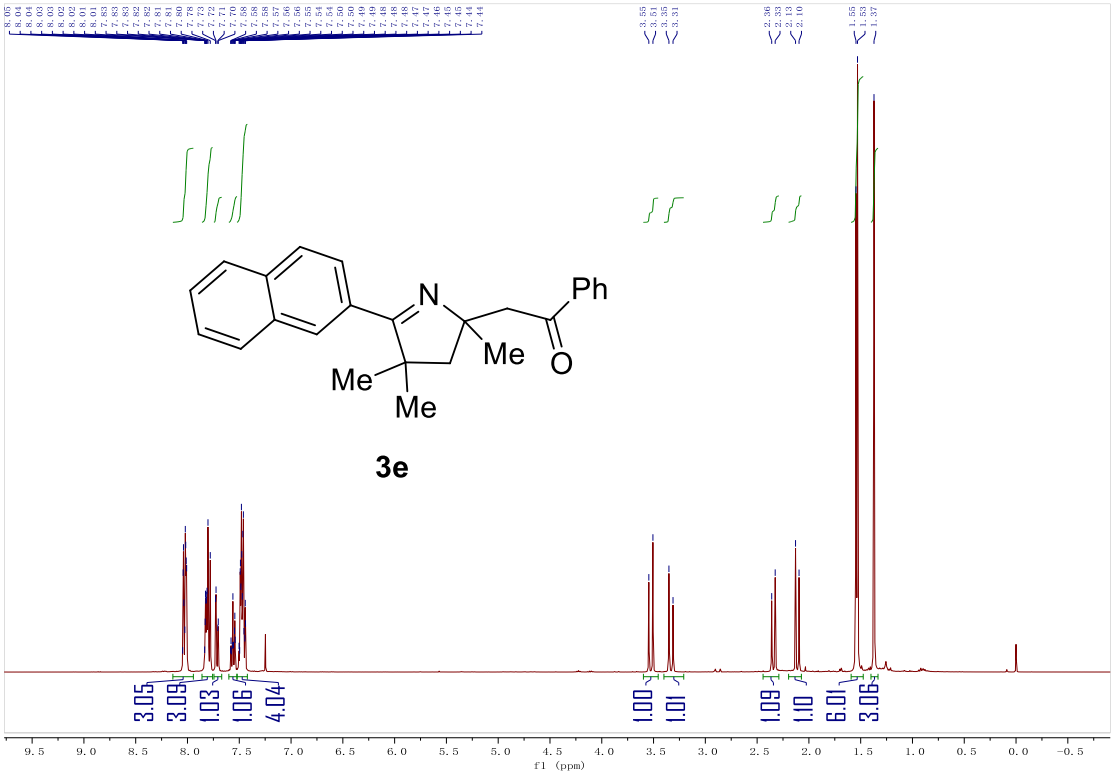

199.02
176.45
137.65
136.73
134.21
133.07
129.37
128.55
128.36
128.24
125.91
71.34
61.73
61.59
30.29
29.22
29.05
28.28
Cl
N
Ph
O
Me
Me
Me
3b
f1 (ppm)

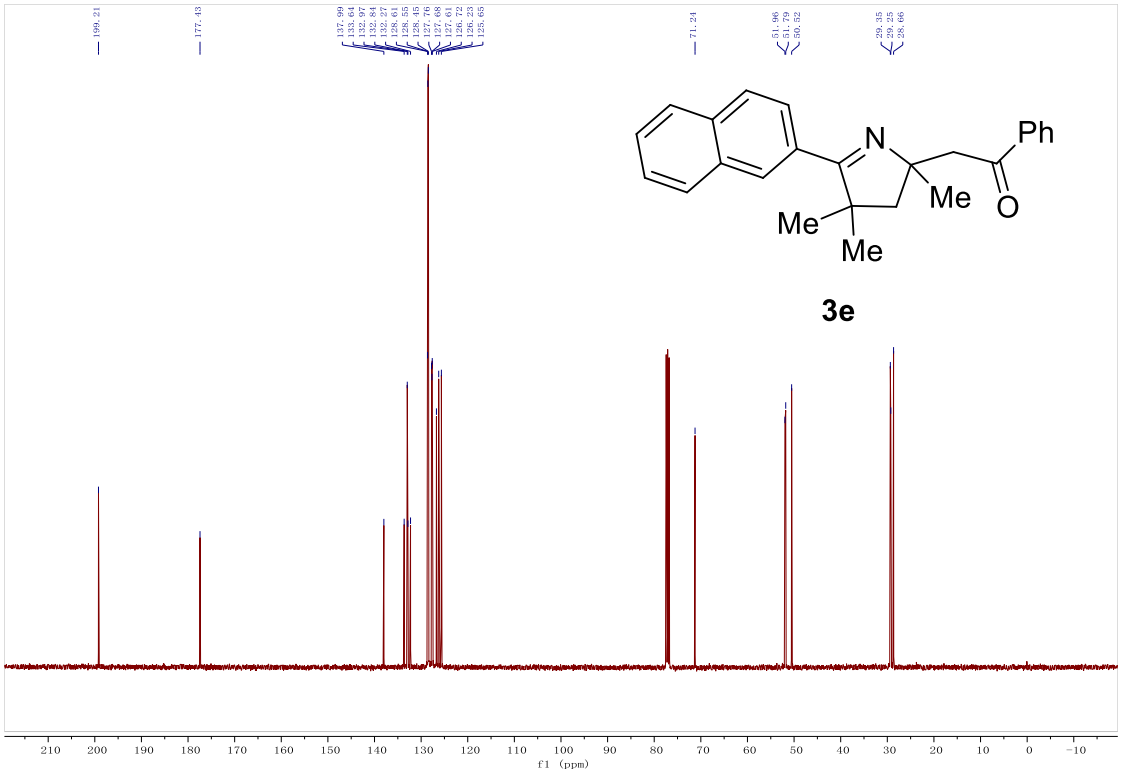

F
N
Ph
O
Me
Me
Me
3c
1.98
2.98
2.08
2.01
1.00
1.01
1.02
1.05
2.96
3.09
3.09
f1 (ppm)

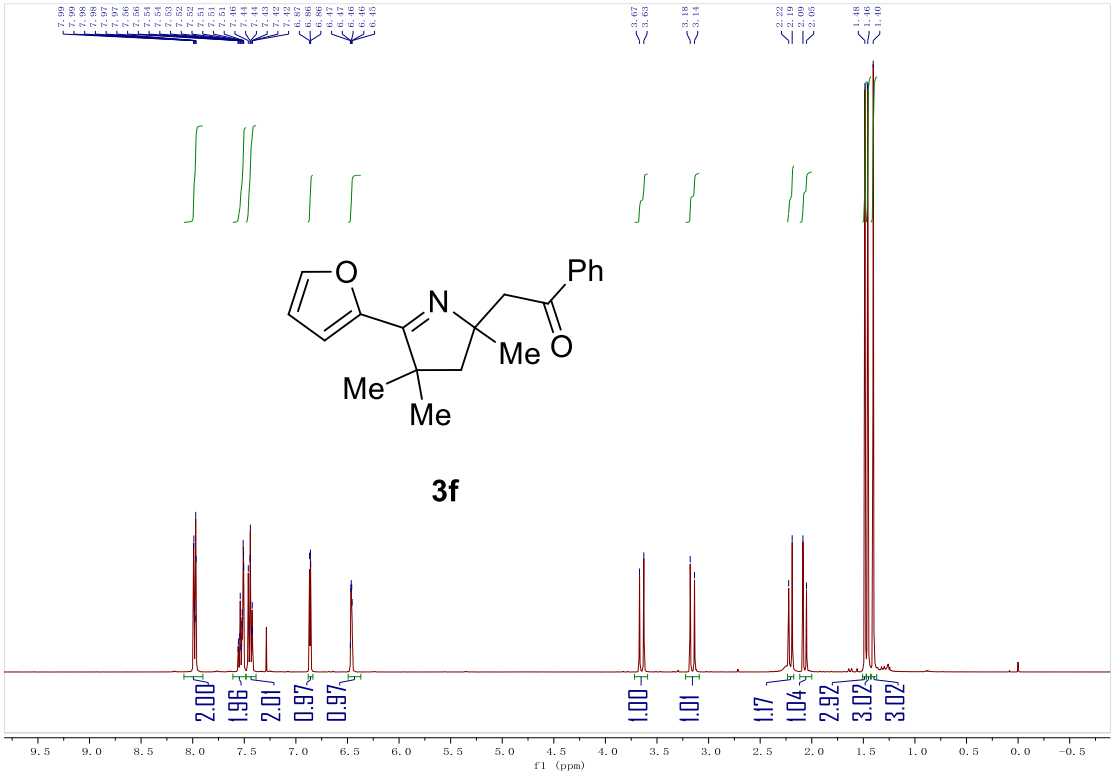

F
N
Ph
Me
O
Me
Me
3c
f1 (ppm)

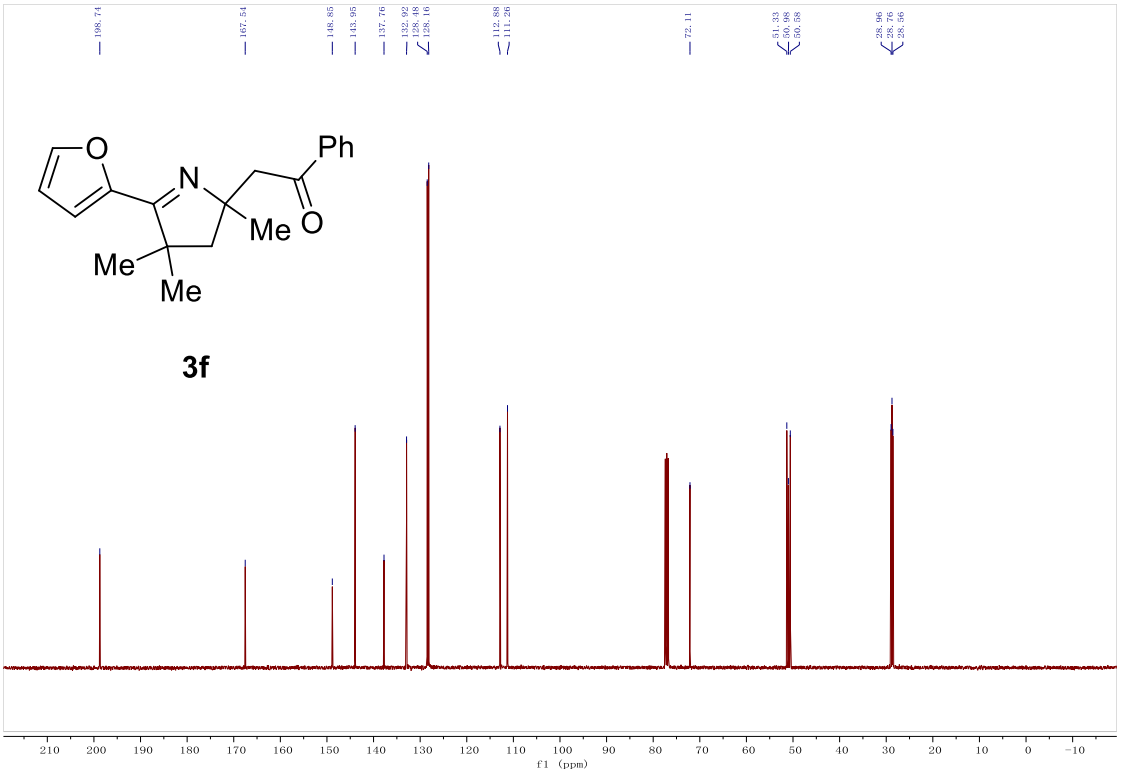

MeO
N
Ph
Me
O
Me
Me
3d
2.01
3.02
2.03
2.02
3.10
1.00
1.02
1.16
1.03
2.90
3.03
3.07
f1 (ppm)

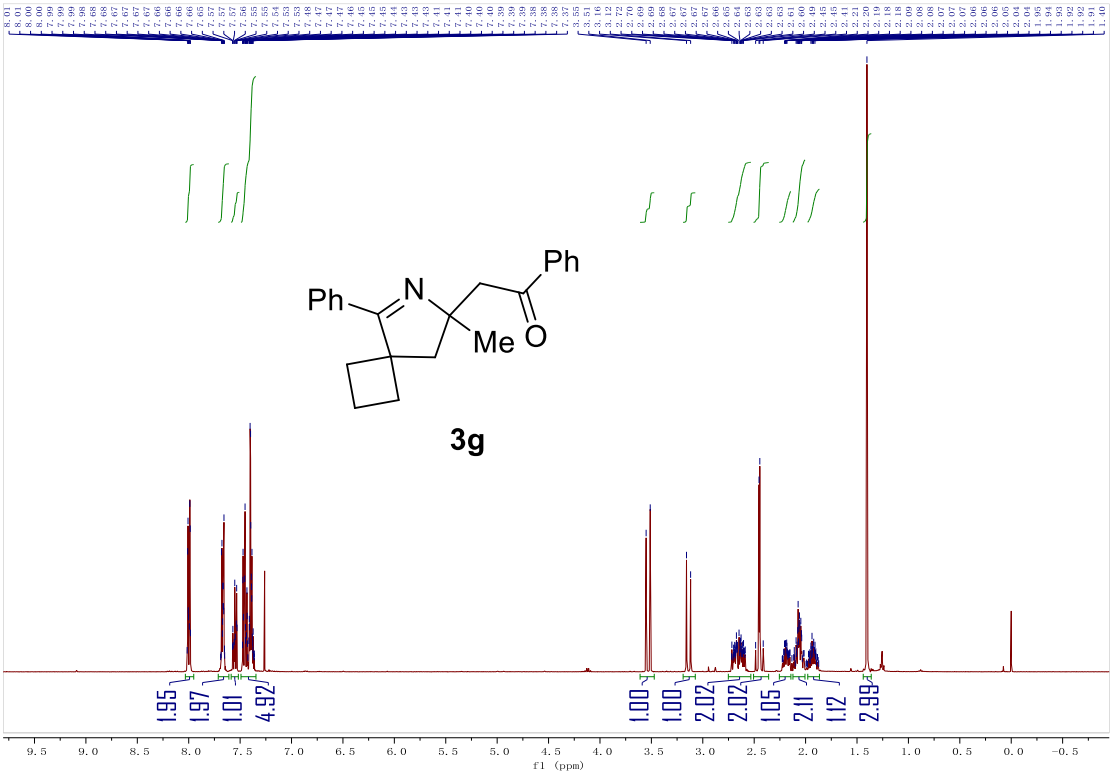

199.22
176.49
160.55
138.01
132.85
129.62
128.47
128.35
127.14
113.47
70.66
55.25
52.33
51.38
50.58
29.24
29.12
28.65
MeO
N
Ph
Me
O
Me
Me
3d
f1 (ppm)

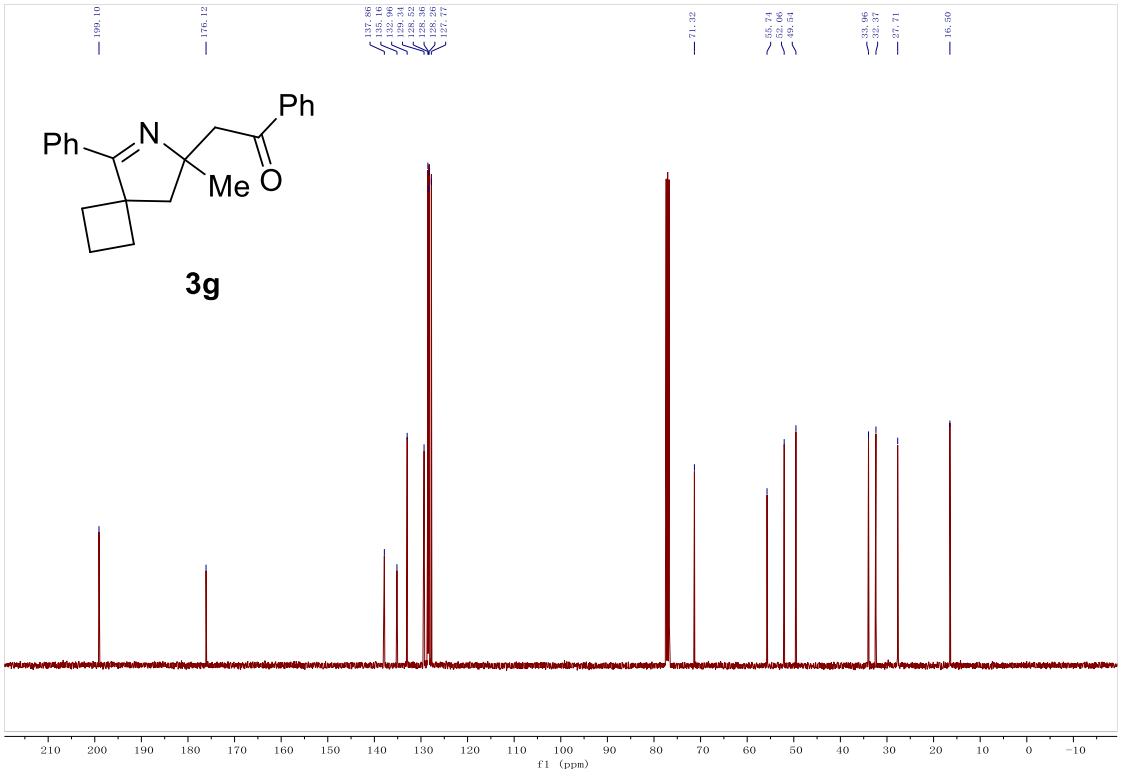

N
Ph
Me
O
Me
Me
3e
3.05
3.09
1.03
1.06
4.04
1.00
1.01
1.09
1.10
6.01
3.06
f1 (ppm)

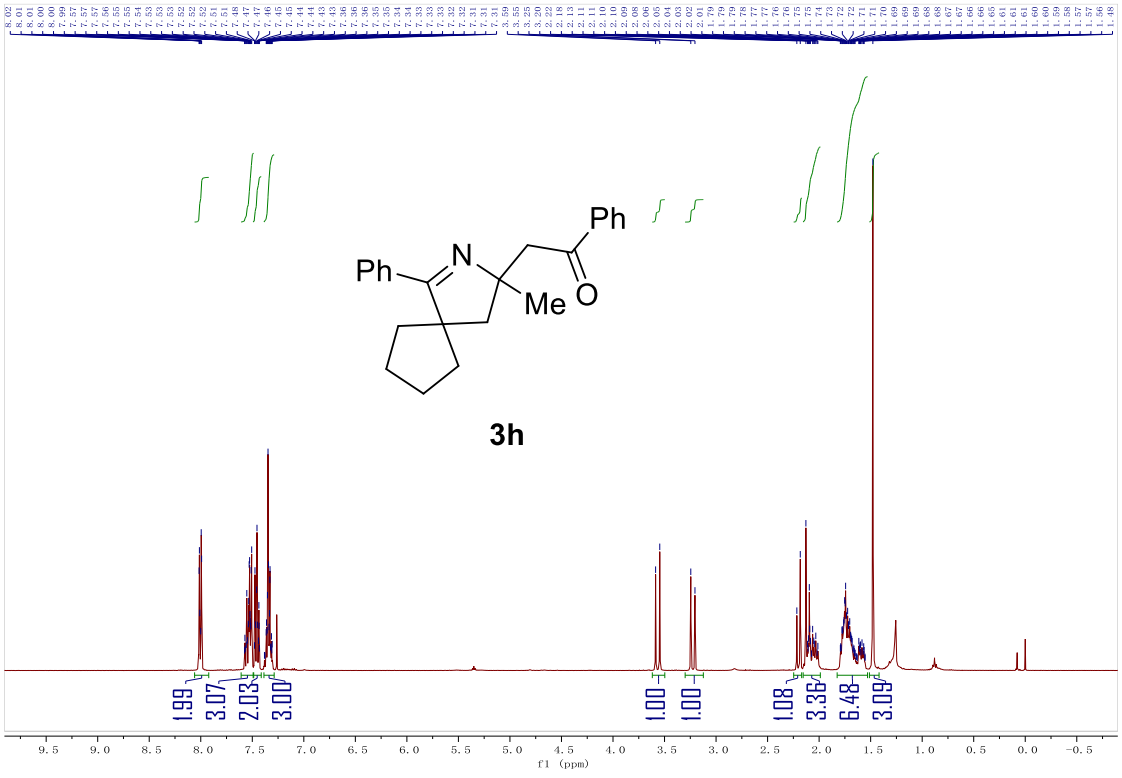

199.21
177.43
137.99
133.64
132.97
132.84
132.27
128.61
128.55
128.45
127.76
127.68
127.61
126.72
126.23
125.65
71.24
51.96
51.79
50.52
29.35
29.25
28.66
N
Ph
Me
O
Me
Me
3e
f1 (ppm)

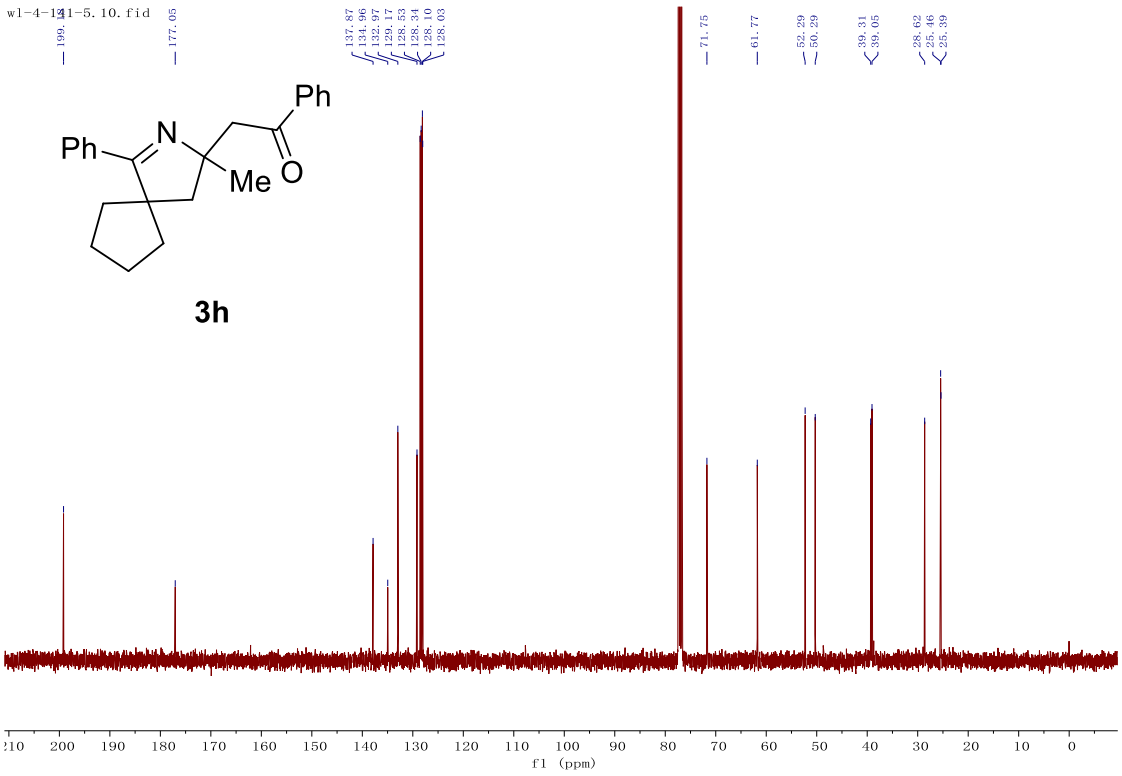

7.99
7.99
7.98
7.98
7.97
7.97
7.96
7.56
7.54
7.54
7.53
7.52
7.51
7.51
7.51
7.46
7.44
7.44
7.43
7.42
6.87
6.86
6.47
6.46
6.46
6.45
3.67
3.63
3.18
3.14
2.22
2.19
2.09
2.05
1.48
1.46
1.40
O
N
Ph
Me
O
Me
Me
3f
2.00
1.96
2.01
0.97
0.97
1.00
1.01
1.17
1.04
2.92
3.02
3.02
f1 (ppm)

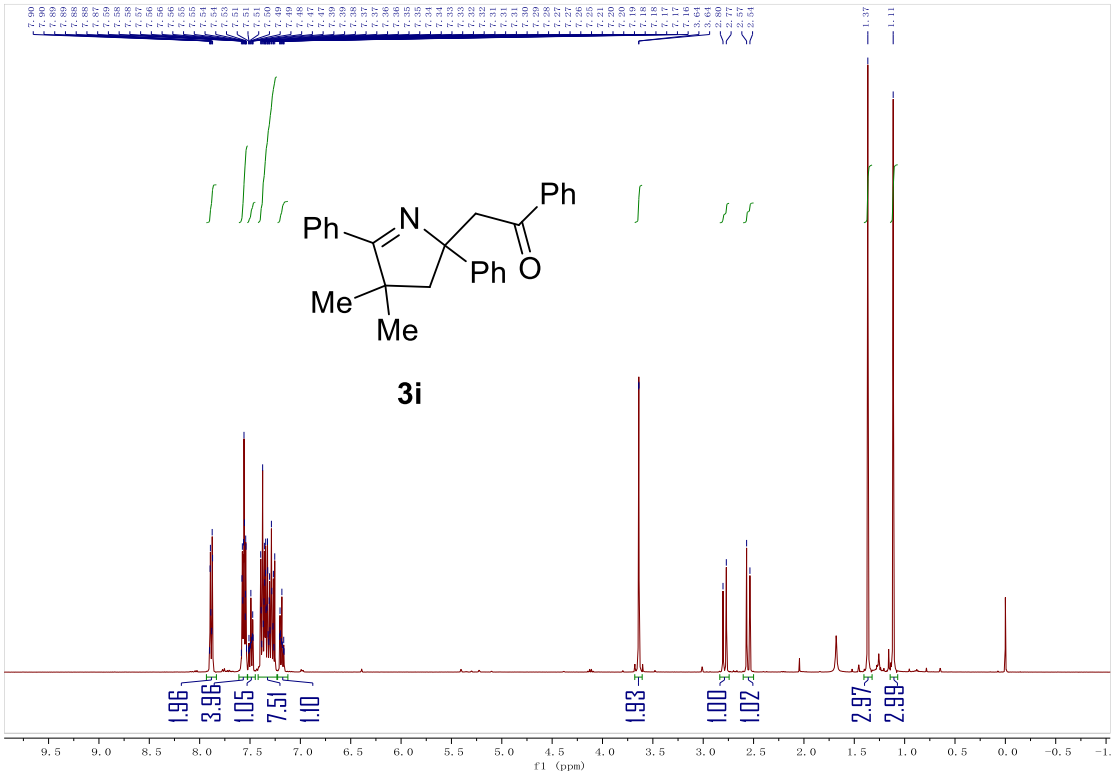

198.74
167.54
148.85
143.95
137.76
132.92
128.48
128.16
112.88
111.26
72.11
51.33
50.98
50.58
28.96
28.76
28.56
O
N
Ph
O
Me
Me
Me
3f
f1 (ppm)

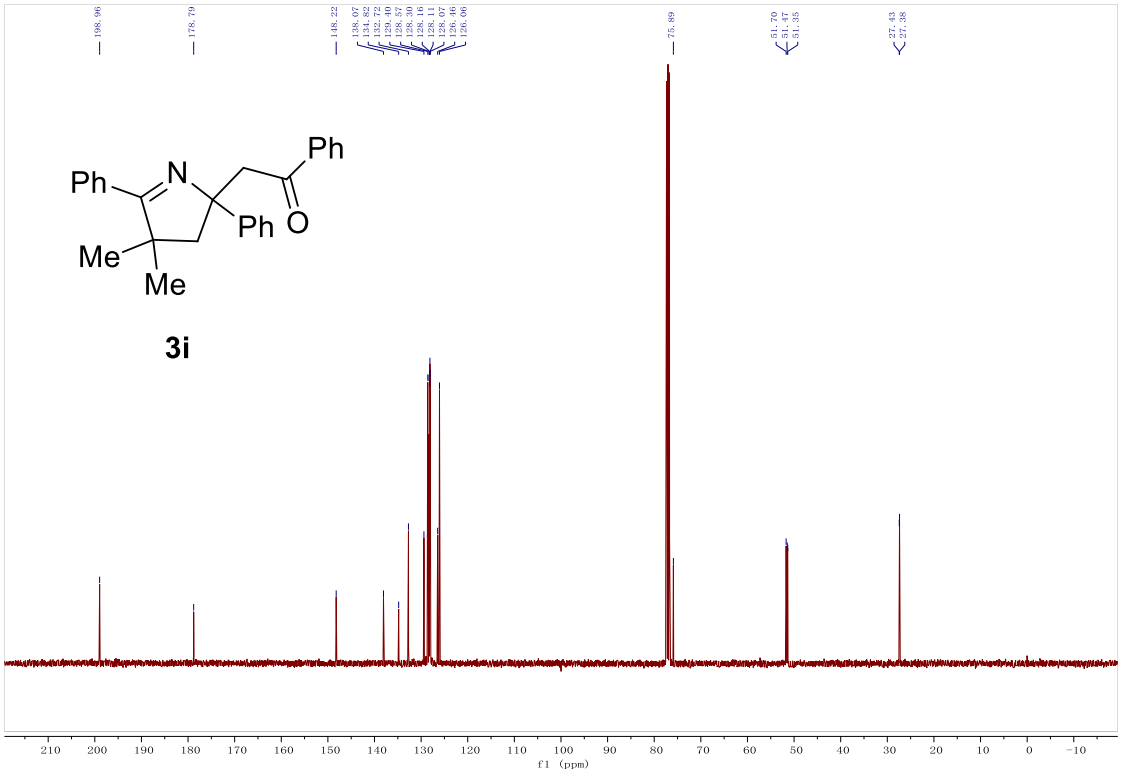

Ph
N
Ph
Me
O
3g
1.95
1.97
1.01
4.92
1.00
1.00
2.02
2.02
1.05
2.11
1.12
2.99
f1 (ppm)

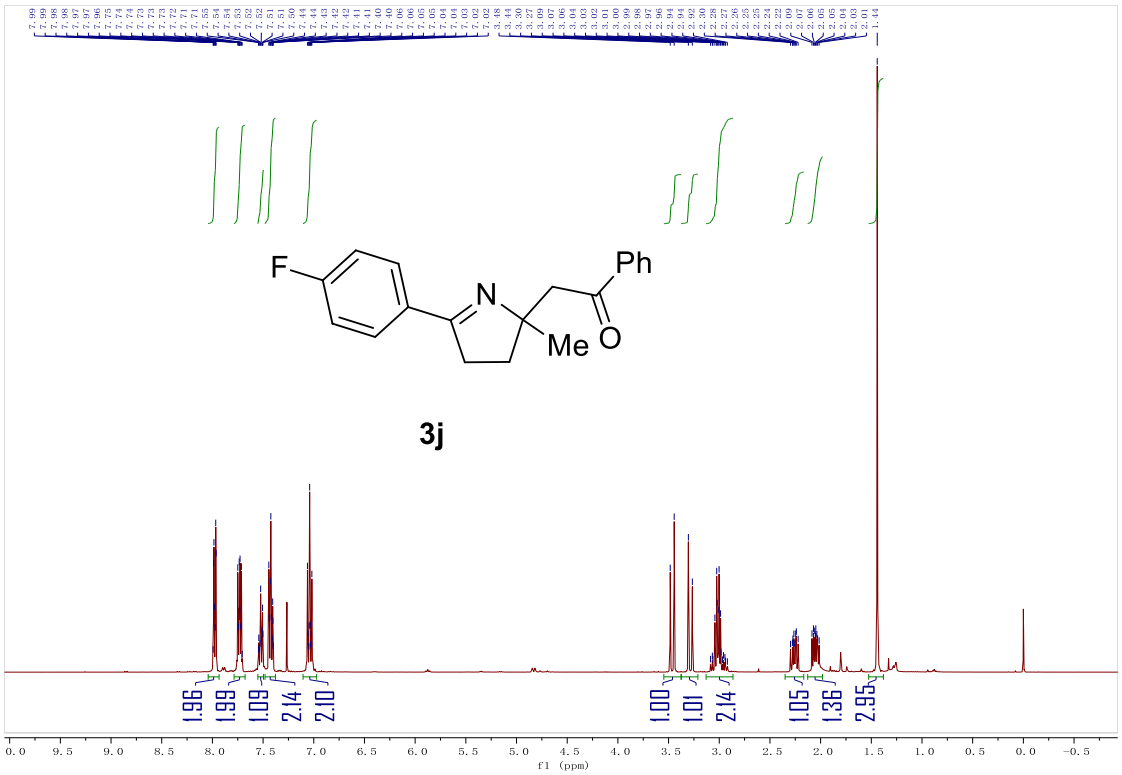

199.10
176.12
137.86
135.14
132.96
129.34
128.52
128.36
128.26
127.77
71.32
55.74
52.06
49.54
33.96
32.37
27.71
16.50
Ph
N
Ph
Me
O
3g
f1 (ppm)

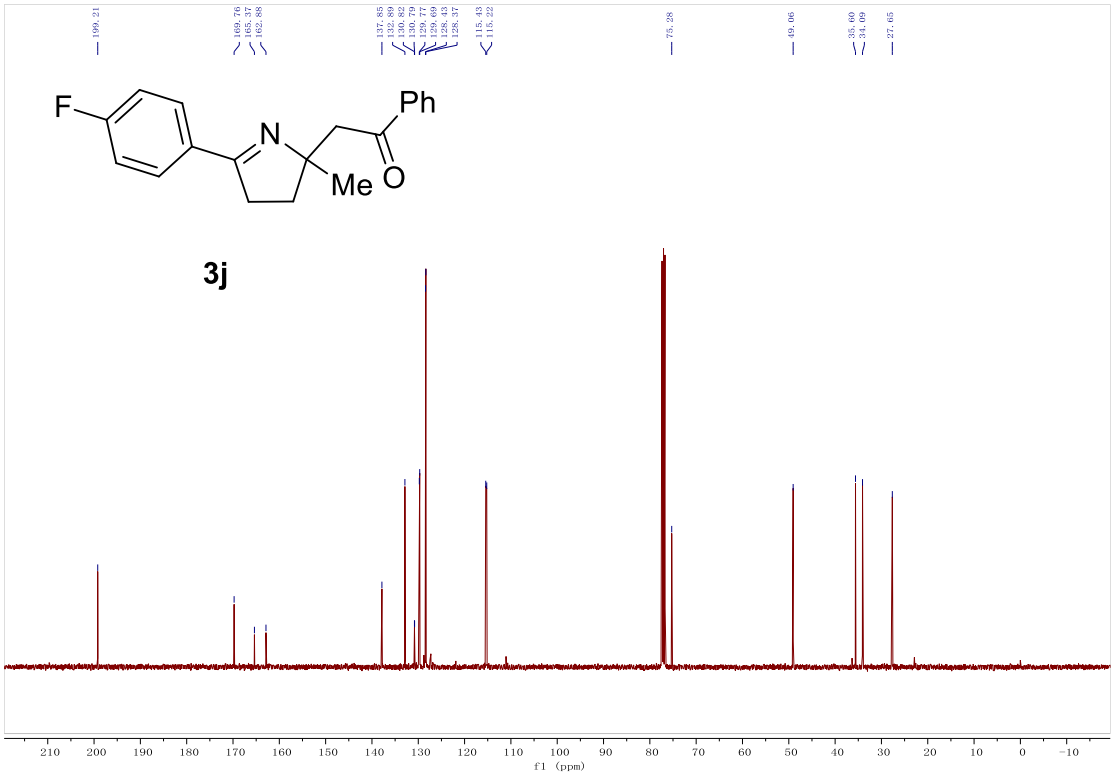

Ph
N
Ph
Me
O
3h
1.99
3.07
2.08
3.00
1.00
1.00
1.08
3.36
6.48
3.09
f1 (ppm)

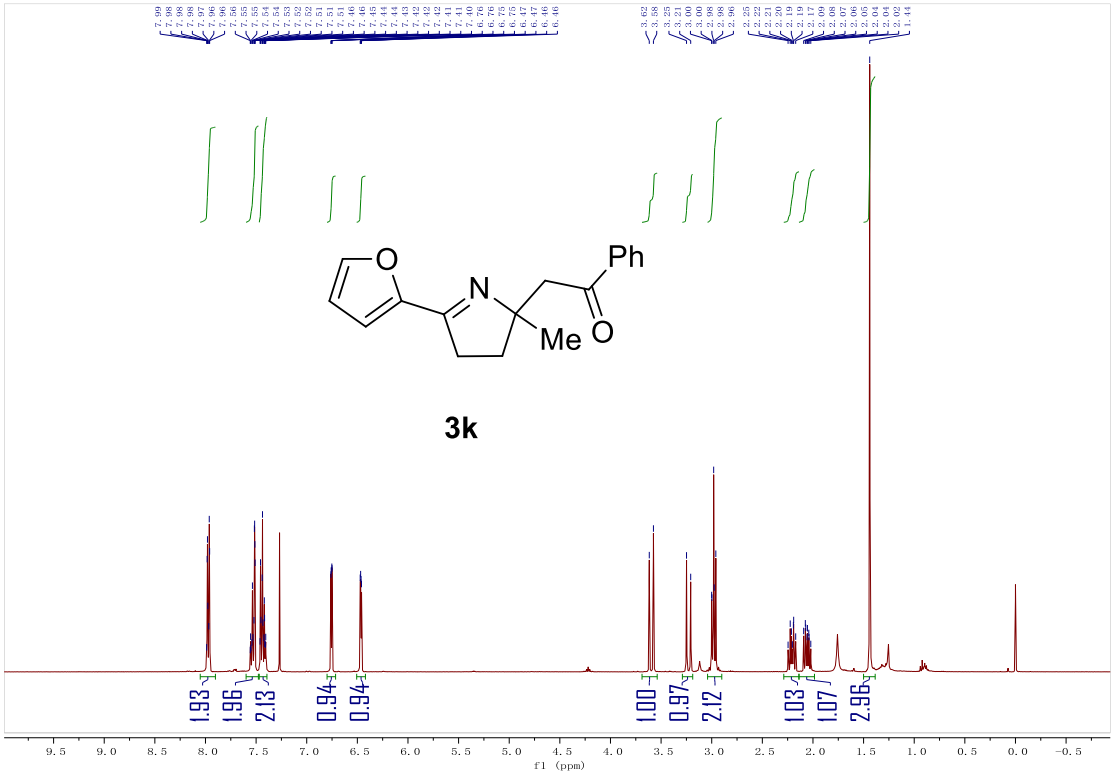

wl-4-121-5.10.fid
199.41
177.05
137.87
134.96
132.97
129.17
128.53
128.34
128.10
128.03
71.75
61.77
52.29
50.29
39.31
39.05
28.62
25.46
25.39
Ph
N
Ph
Me
O
Ph
3h
f1 (ppm)

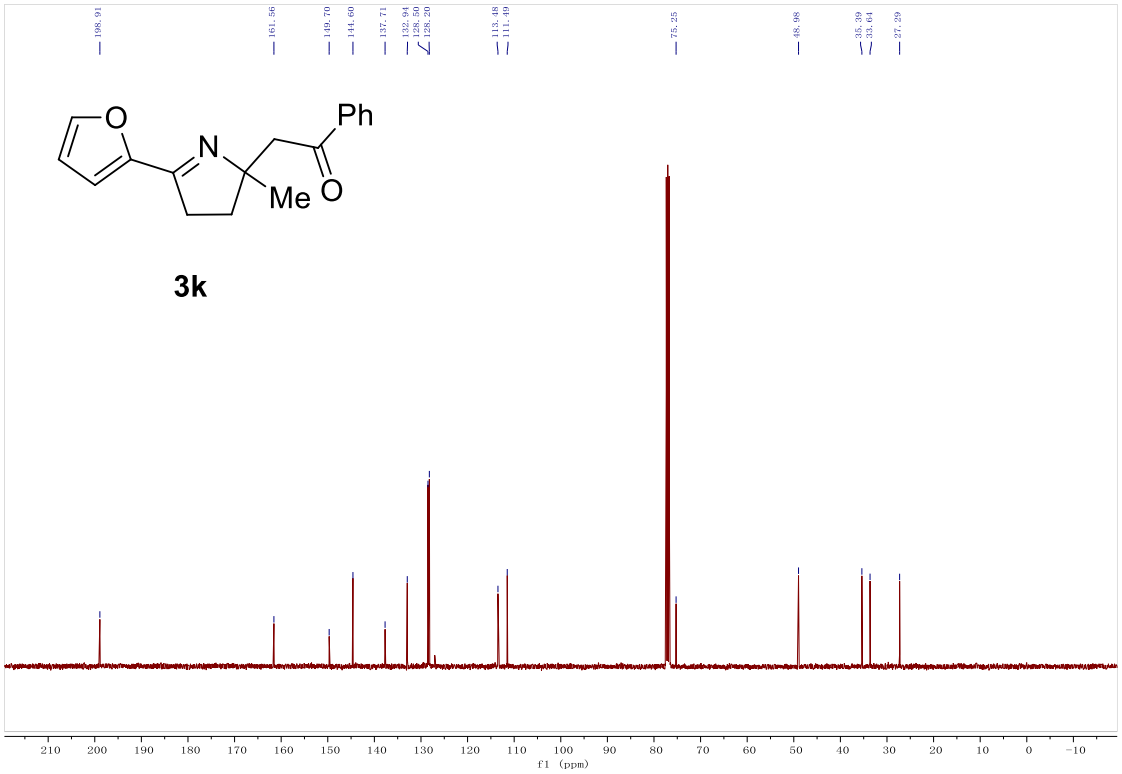

1.37
1.11
Ph
N
Ph
Ph
O
Me
Me
3i
1.96
3.96
1.05
7.51
1.10
1.93
1.00
1.02
2.97
2.98
f1 (ppm)

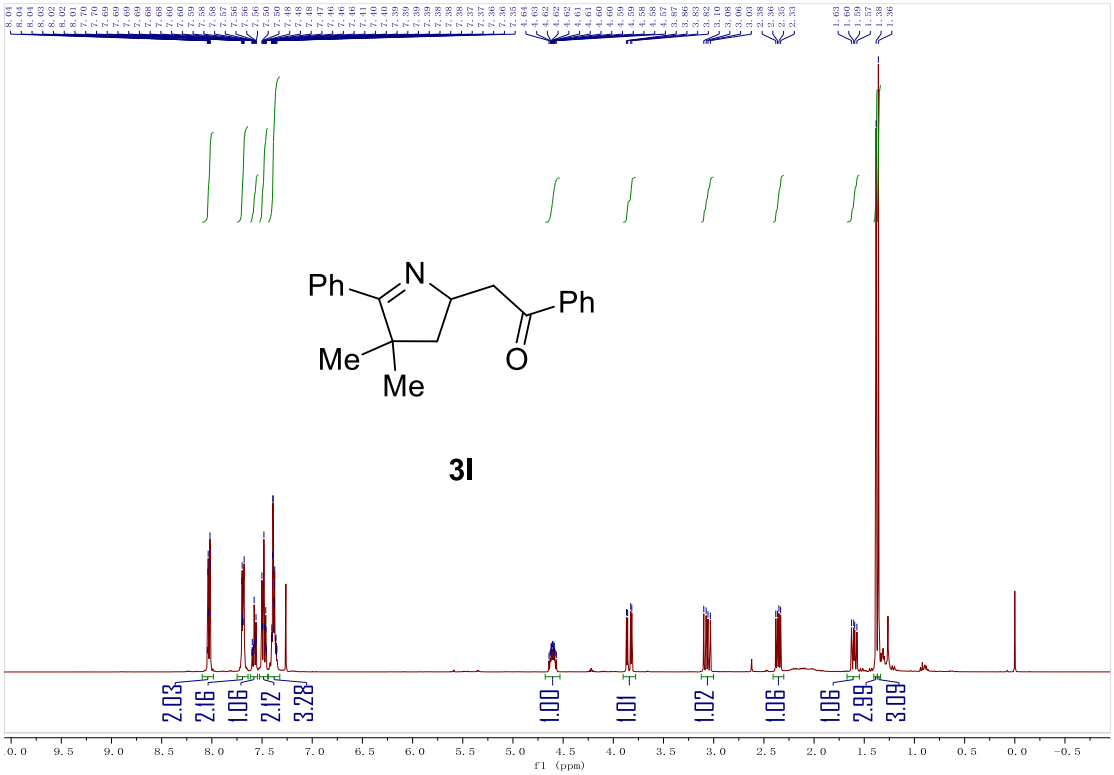

Ph
N
Ph
Ph
O
Me
Me
3i
f1 (ppm)

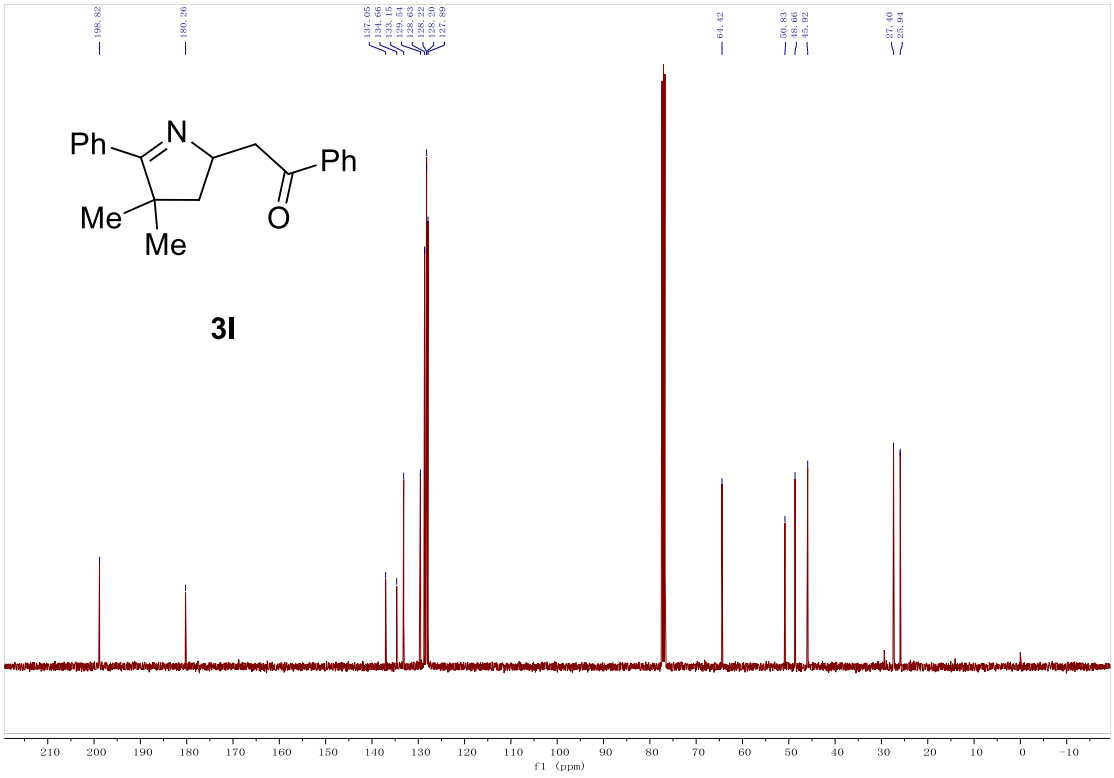

F
N
Ph
Me
O
3j
1.96
1.99
1.09
2.14
2.10
1.00
1.01
2.14
1.05
1.38
2.95
f1 (ppm)

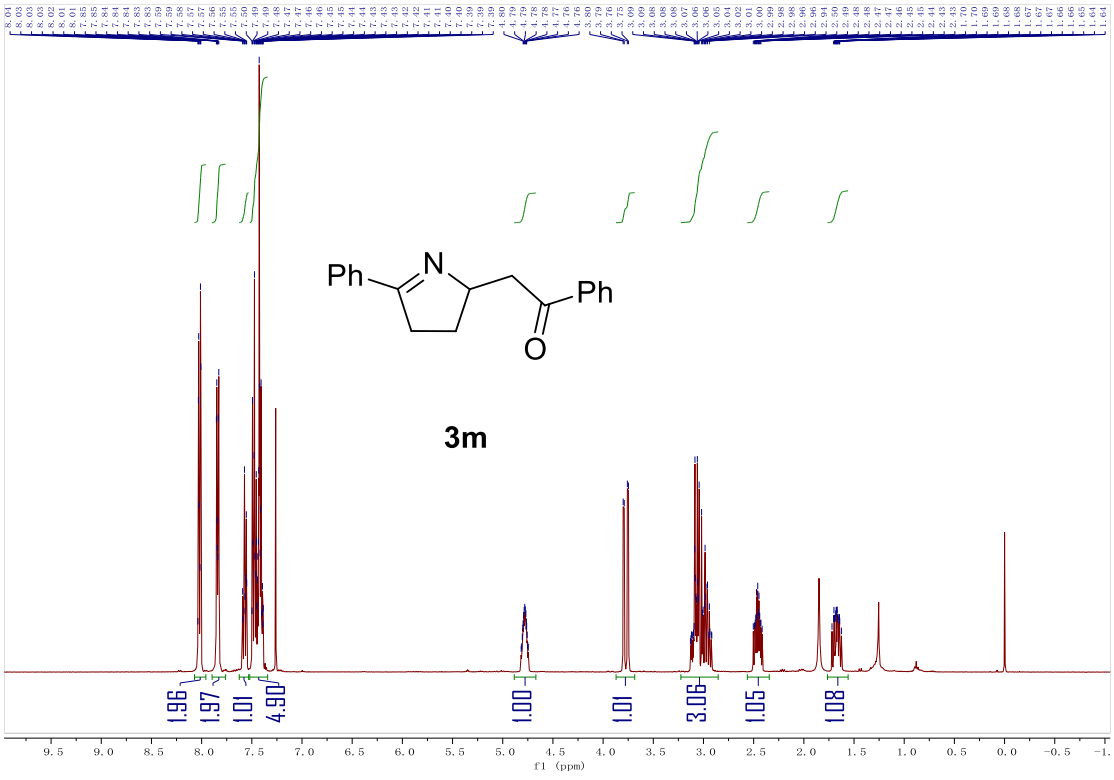

F
N
Ph
O
Me
3j
f1 (ppm)

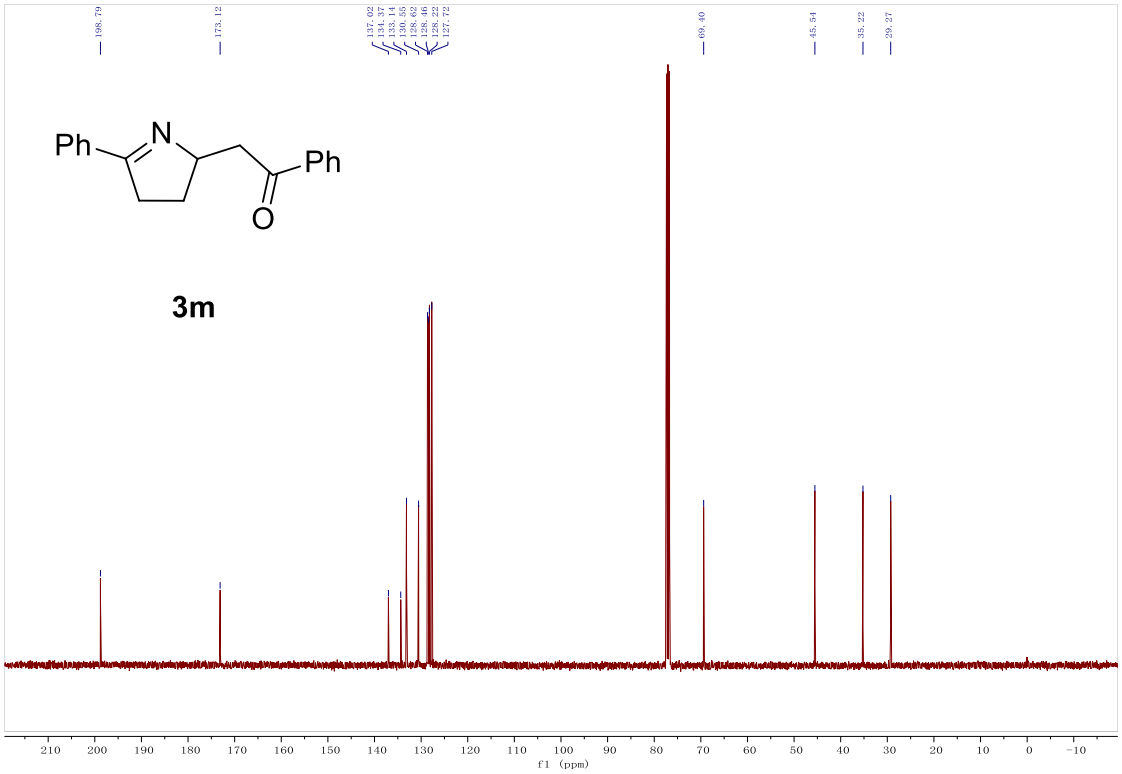

O
N
Ph
O
Me
3k
1.93
1.96
2.13
0.94
0.94
1.00
0.97
2.12
1.03
1.07
2.96
f1 (ppm)

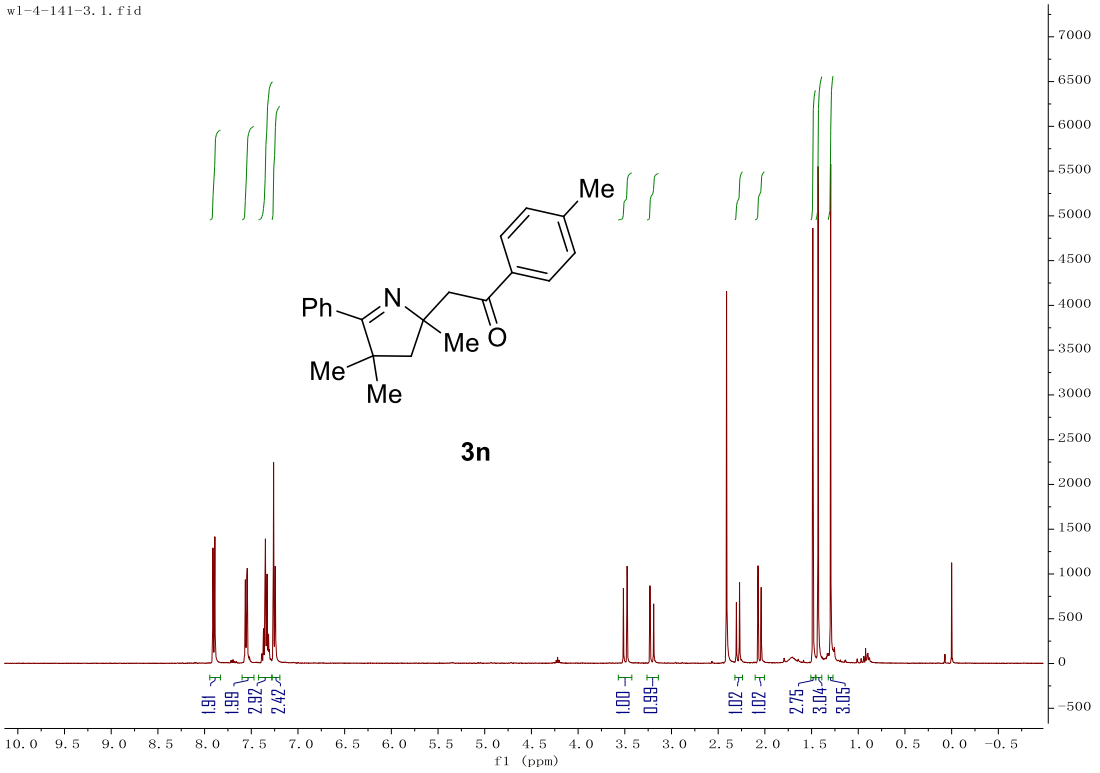

198.91
161.56
149.70
144.60
137.71
132.94
128.50
128.20
118.48
111.49
75.25
48.98
35.39
33.64
27.29
O
N
Ph
Me
O
3k
f1 (ppm)

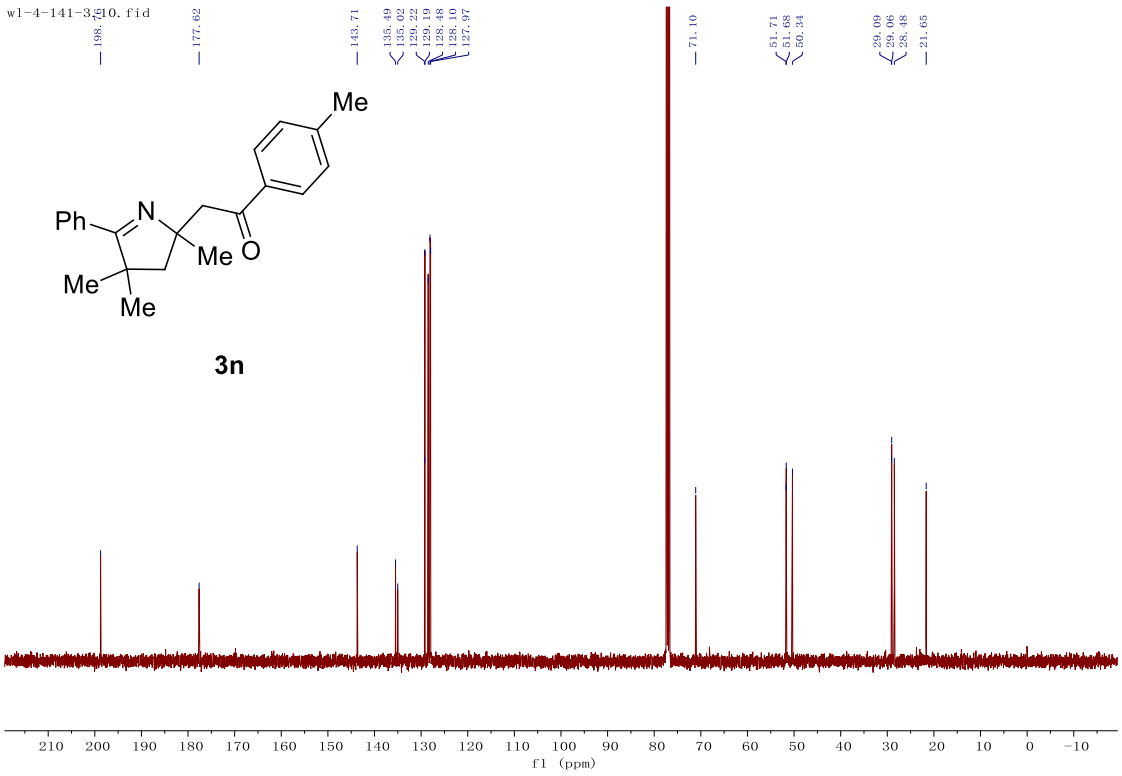

Ph
N
Ph
Me
Me
O
3l
2.03
2.16
1.06
2.12
3.28
1.00
1.01
1.02
1.06
1.06
2.99
3.09
f1 (ppm)

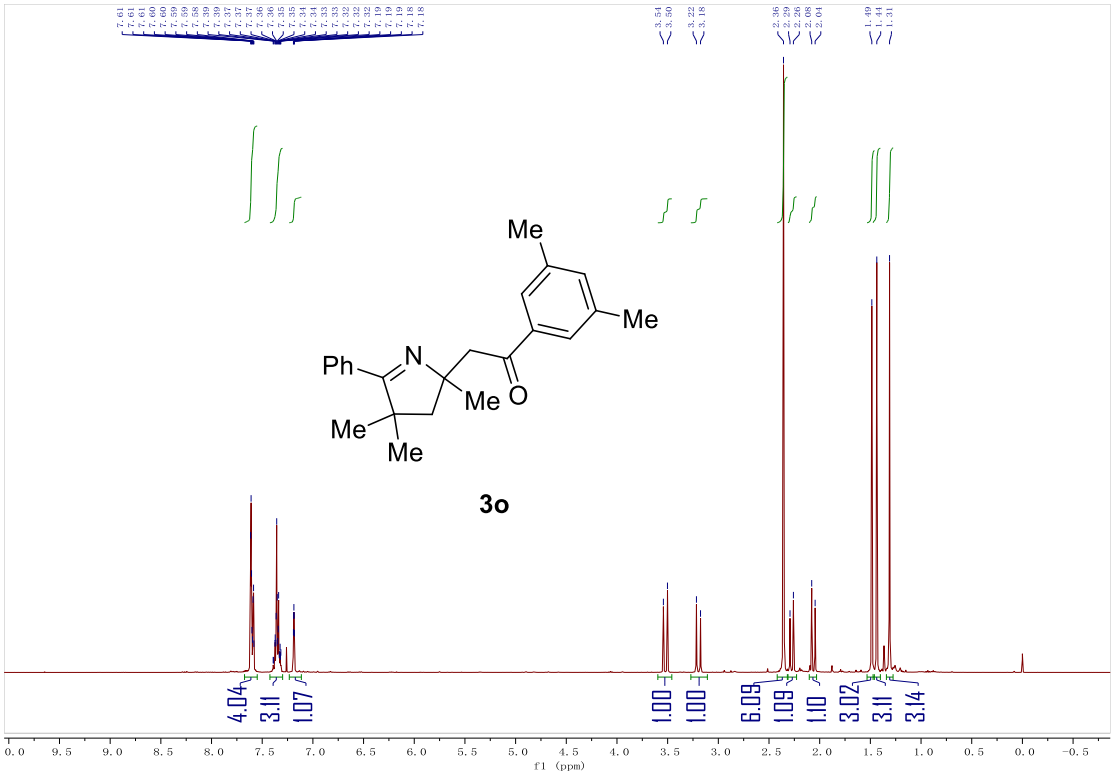

198.82
180.26
137.05
134.66
133.15
129.54
128.63
128.27
128.20
127.89
64.42
50.83
48.66
45.92
27.49
25.94
Ph
N
Ph
Me
Me
O
3l
f1 (ppm)

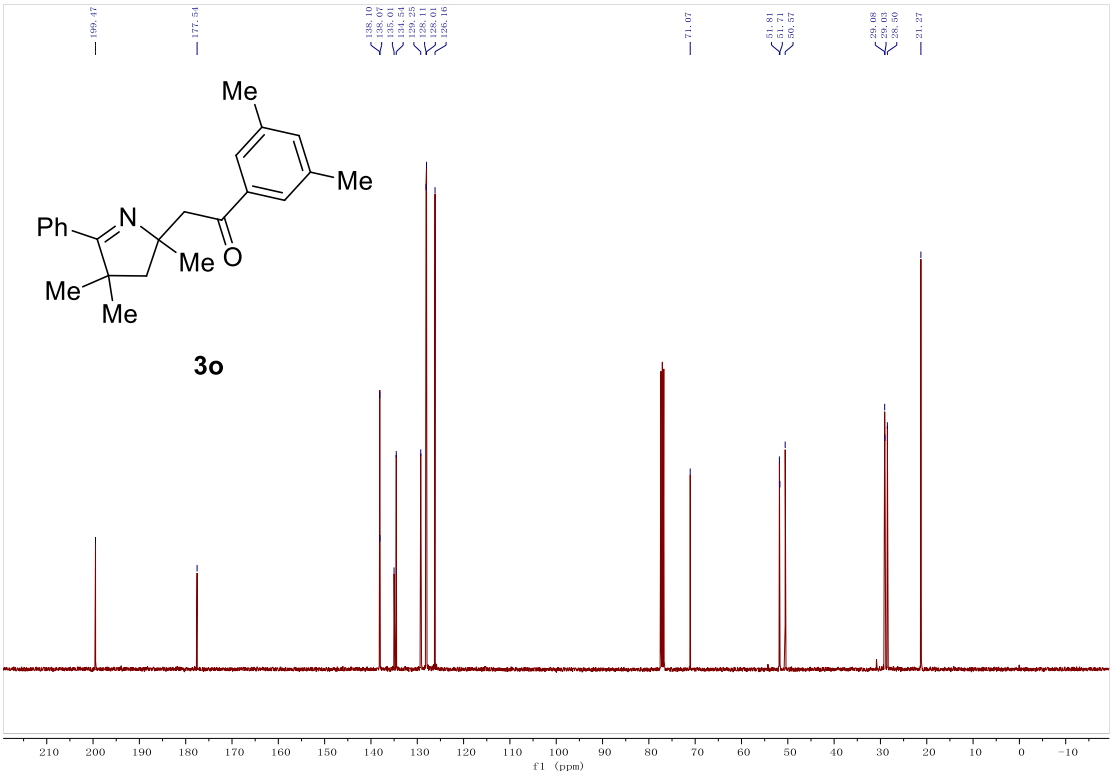

Ph
N
Ph
O
3m
1.96
1.97
1.01
4.90
1.00
1.01
3.06
1.05
1.08
f1 (ppm)

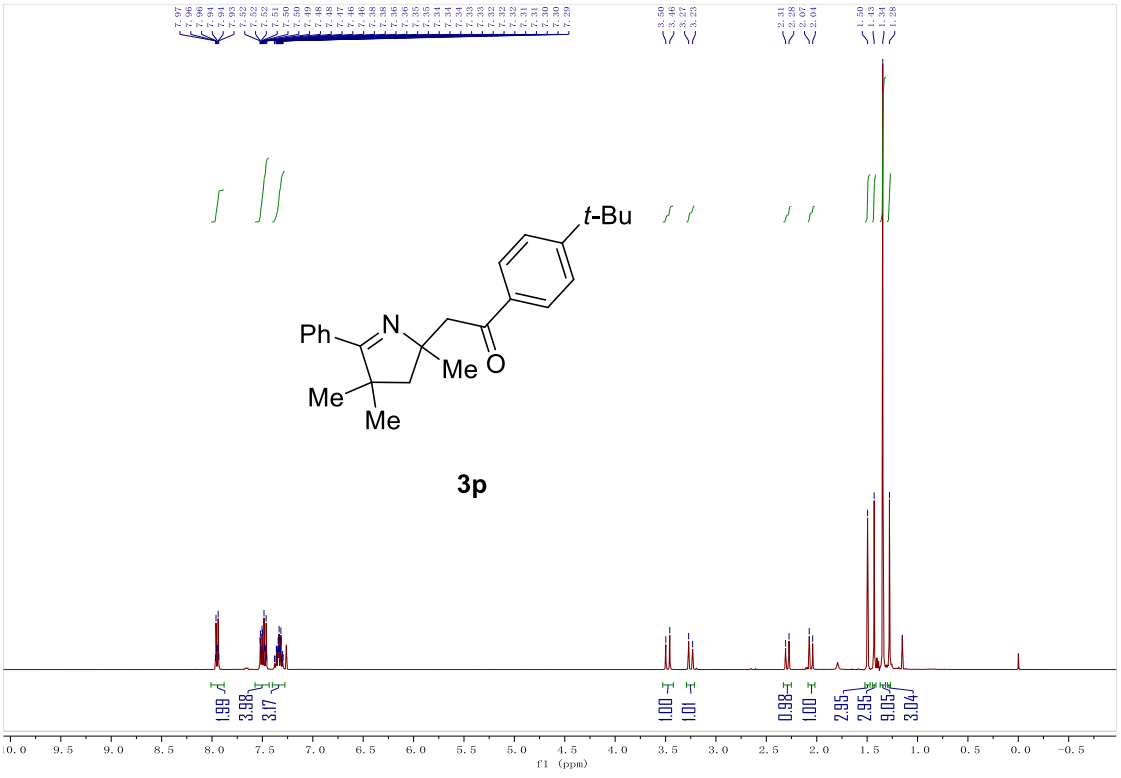

198.79
173.12
137.02
134.37
133.14
130.55
128.62
128.46
128.22
127.72
69.40
45.54
35.22
29.27
Ph
N
Ph
O
3m
f1 (ppm)

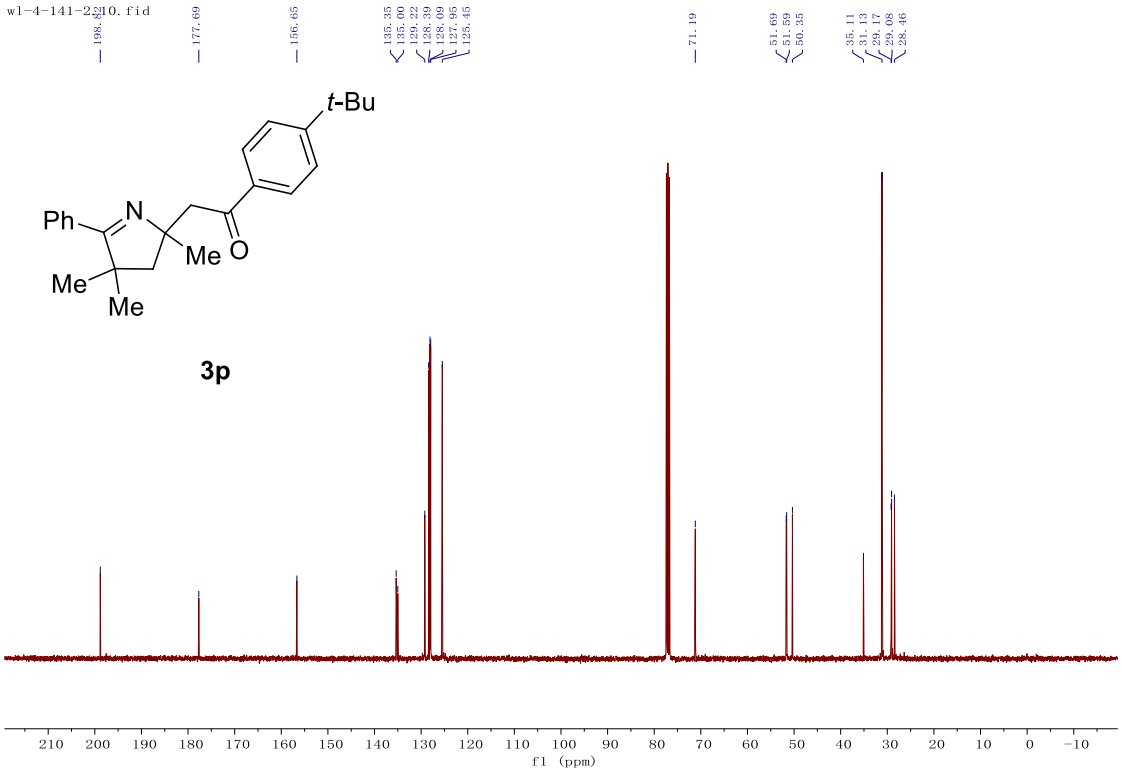

w1-4-141-3.1.fid
Me
Ph
N
Me
O
Me
Me
3n
1.91
1.99
2.92
2.42
1.00
0.99
1.02
1.02
2.75
3.04
3.05
f1 (ppm)

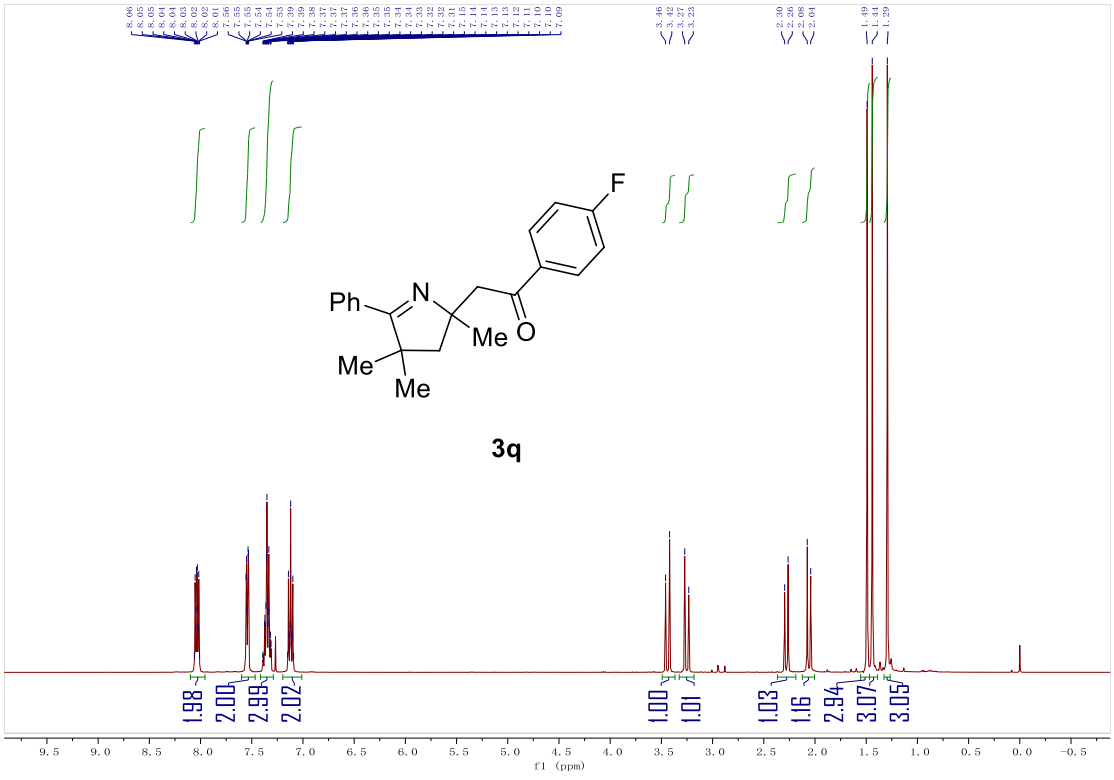

wl-4-141-3-10.fid
198.74
177.62
143.71
135.49
135.02
129.22
129.19
128.48
128.10
127.97
71.10
51.71
51.68
50.34
29.09
29.06
28.48
21.65
Me
Ph
N
Me
O
Me
Me
Me
3n
f1 (ppm)

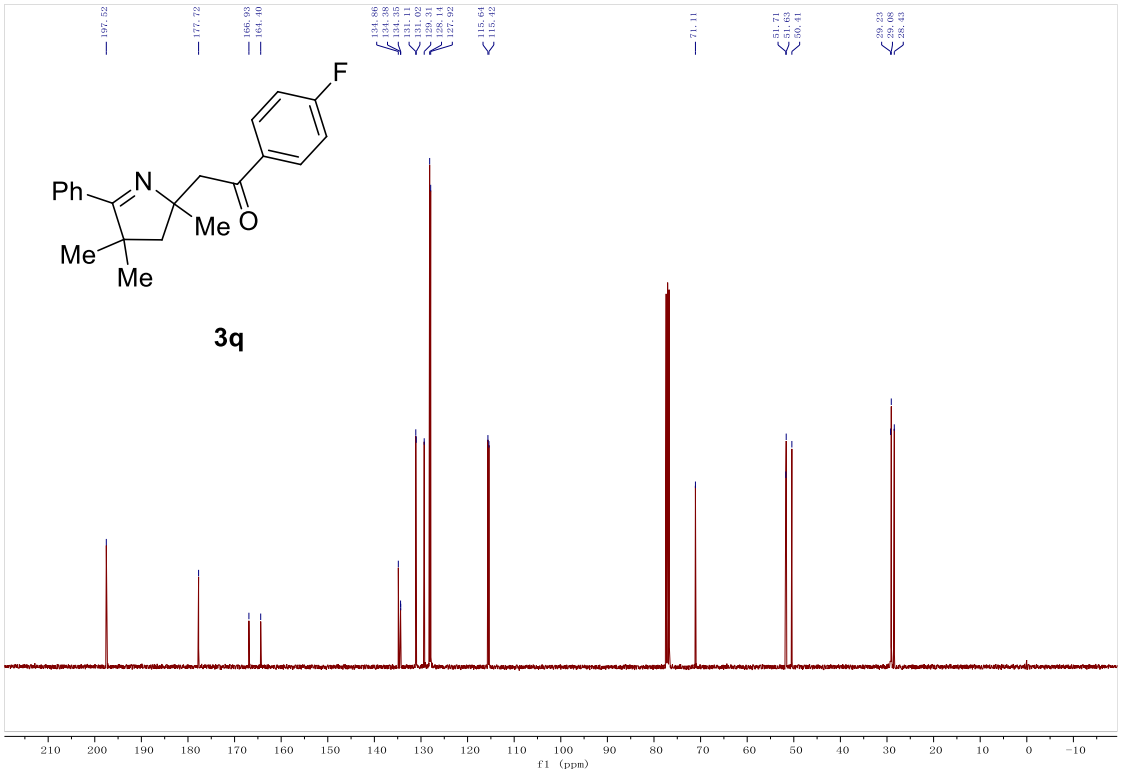

7.61
7.61
7.61
7.60
7.59
7.59
7.58
7.39
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.19
7.19
7.18
7.18
3.54
3.50
3.22
3.18
2.36
2.29
2.26
2.08
2.04
1.49
1.44
1.31
Me
Me
Ph
N
Me
O
Me
Me
3o
4.04
3.11
1.07
1.00
1.00
6.09
1.09
1.10
3.02
3.11
3.14
f1 (ppm)

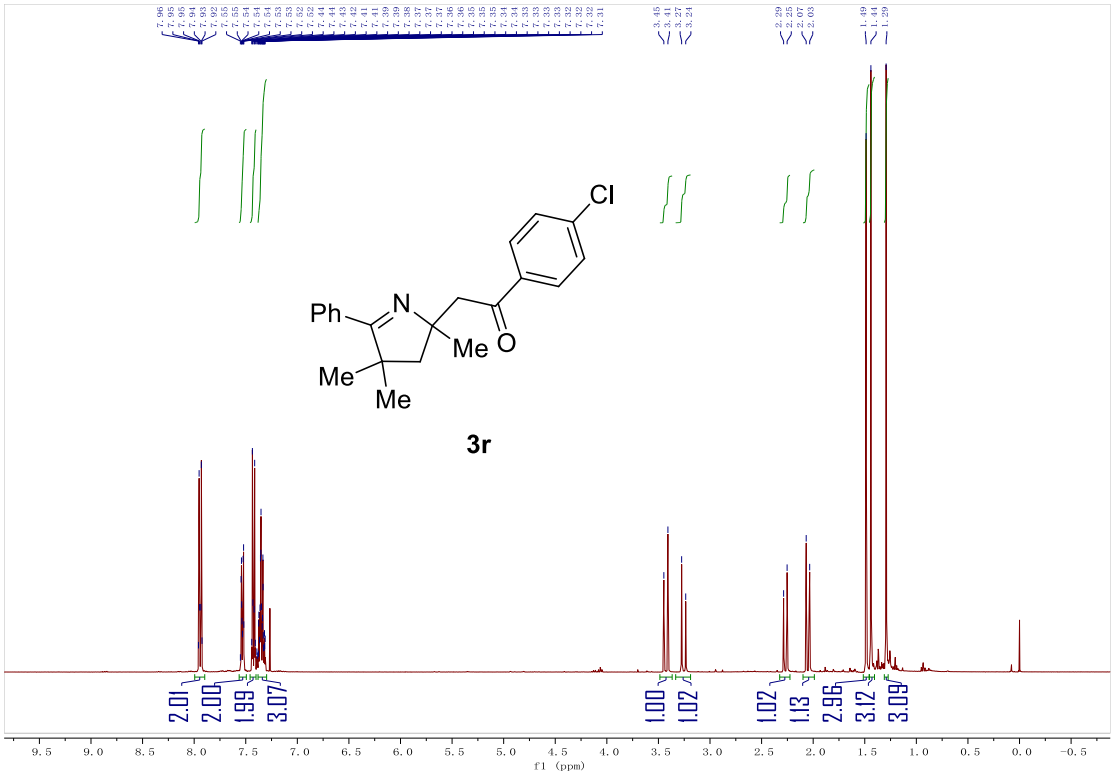

Me
Me
Ph
N
Me
O
Me
Me
3o
f1 (ppm)


t-Bu
Ph
N
Me
O
Me
Me
3p
f1 (ppm)


wl-4-141-2-10.fid
198.55
177.69
156.65
135.35
135.00
129.22
128.39
128.09
127.95
125.45
71.19
51.69
51.59
50.35
35.11
31.13
29.17
29.08
28.46
t-Bu
Ph
N
Me
O
Me
Me
3p
f1 (ppm)


F
Ph
N
Me
O
Me
Me
3q
1.98
2.00
2.99
2.02
1.00
1.01
1.03
1.16
2.94
3.07
3.05
f1 (ppm)


197.52
177.72
166.93
164.40
134.86
134.38
134.35
131.11
131.02
129.31
128.14
127.92
115.64
115.42
71.11
61.71
61.63
60.41
29.23
29.08
28.43
F
Ph
N
Me
O
Me
Me
3q
f1 (ppm)


7.96
7.95
7.95
7.94
7.93
7.92
7.92
7.55
7.54
7.54
7.54
7.53
7.53
7.52
7.52
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7.41
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7.36
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7.34
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7.33
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7.33
7.32
7.32
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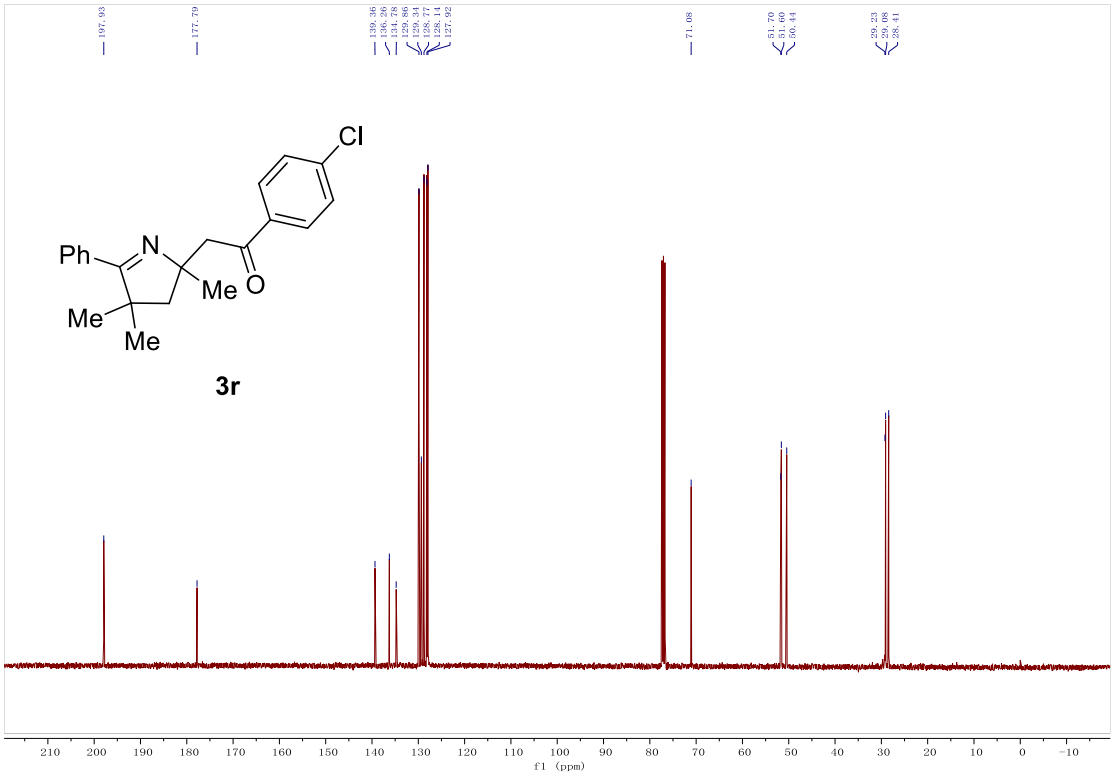
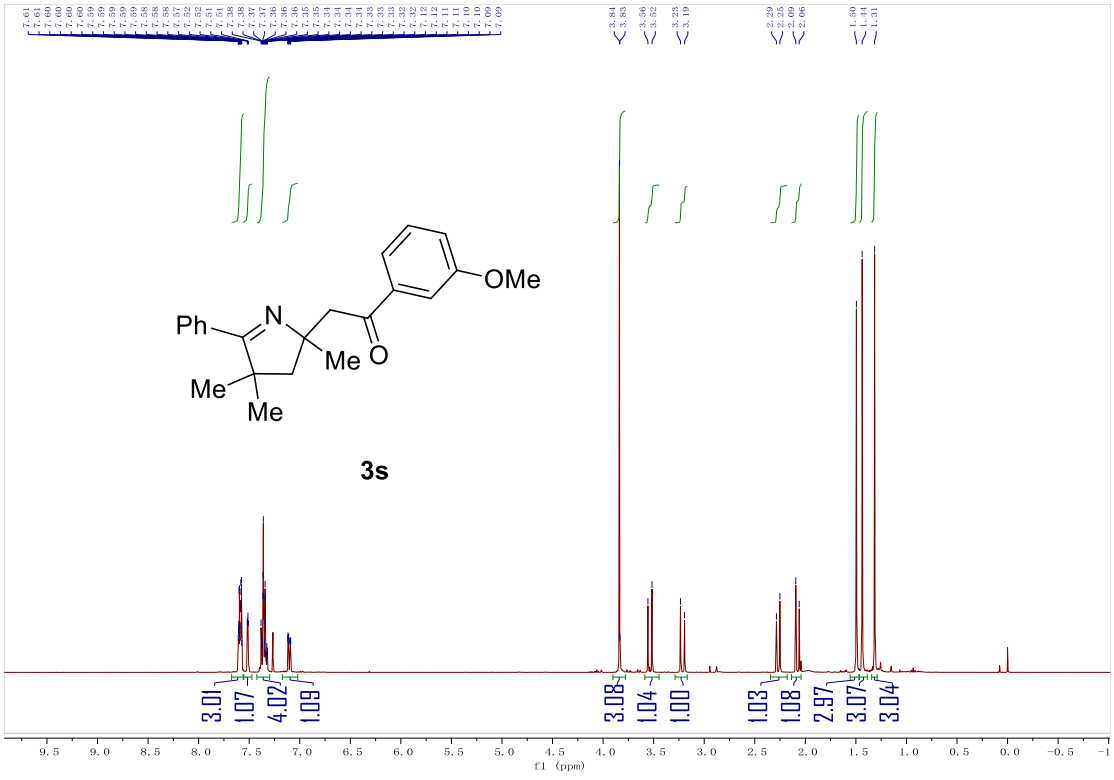
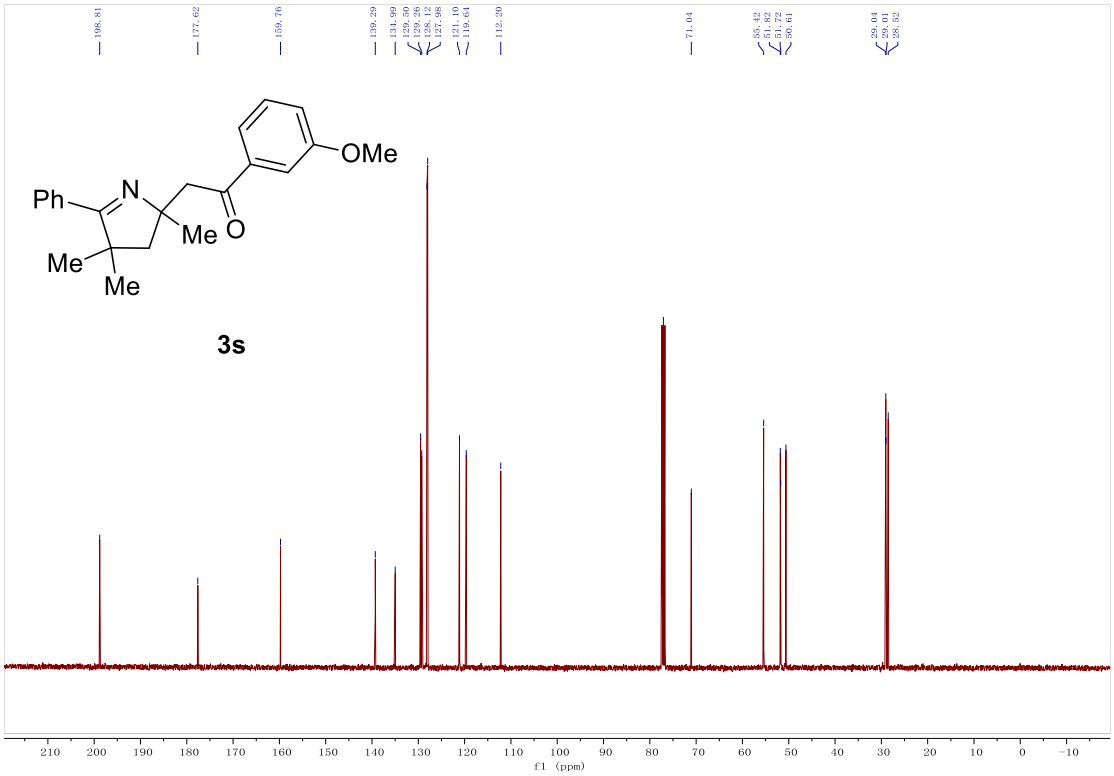
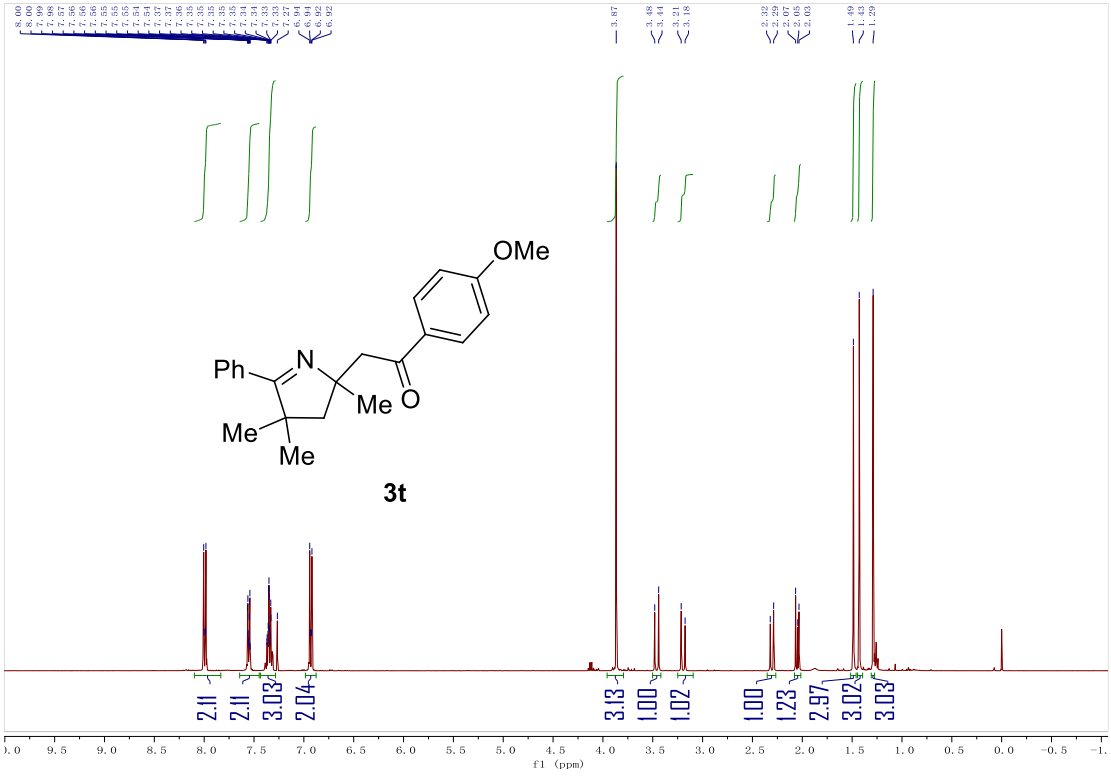
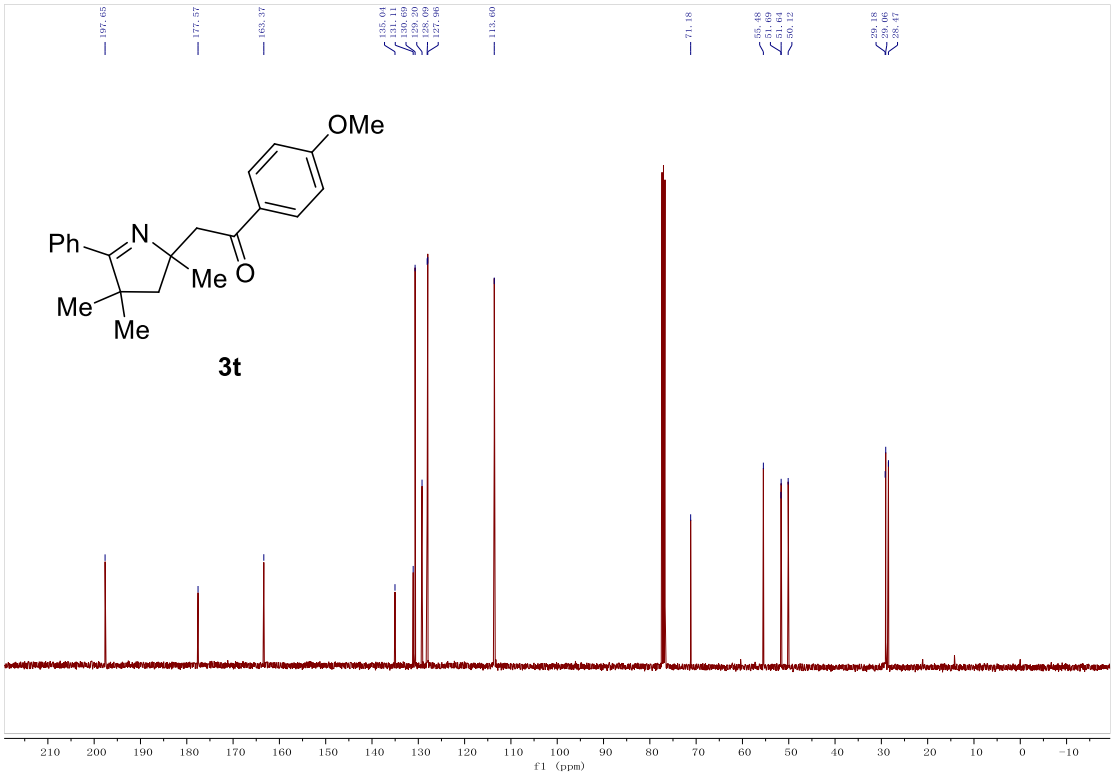
7.32
7.31
3.45
3.41
3.27
3.24
2.29
2.25
2.07
2.03
1.49
1.44
1.29
Cl
Ph
N
Me
O
Me
Me
3r
2.01
2.00
1.99
3.07
1.00
1.02
1.02
1.13
2.96
3.12
3.09
f1 (ppm)

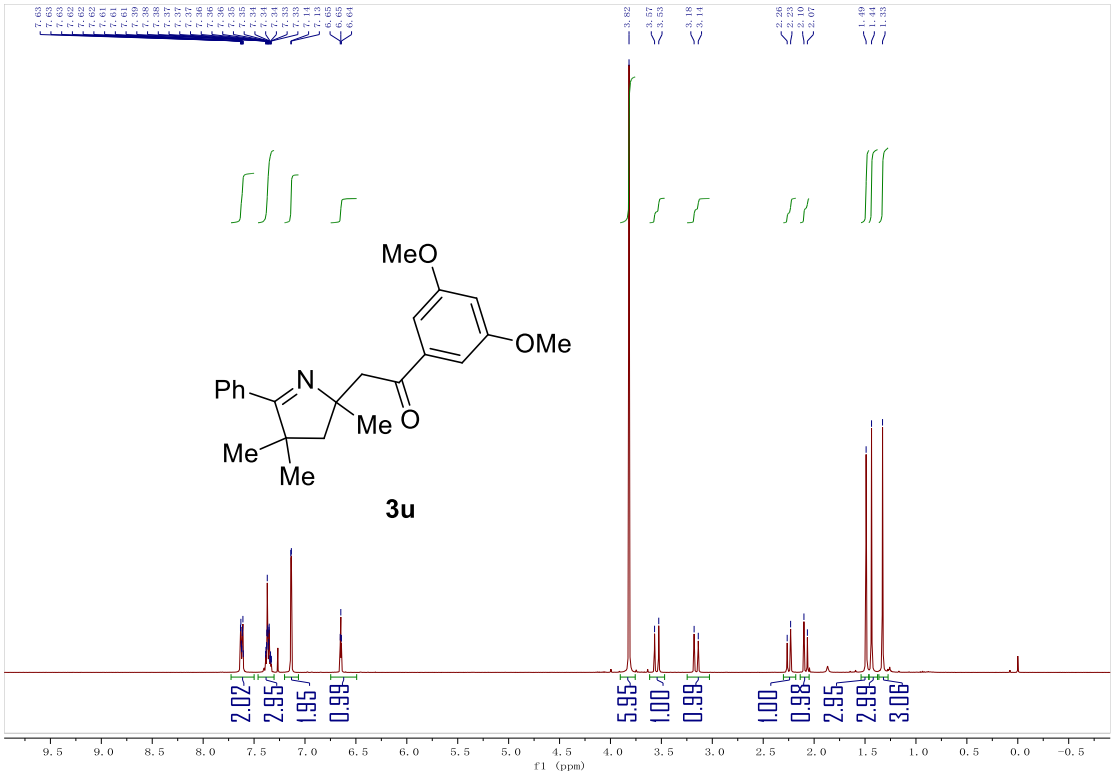

Cl
Ph
N
Me
O
Me
Me
3r
f1 (ppm)

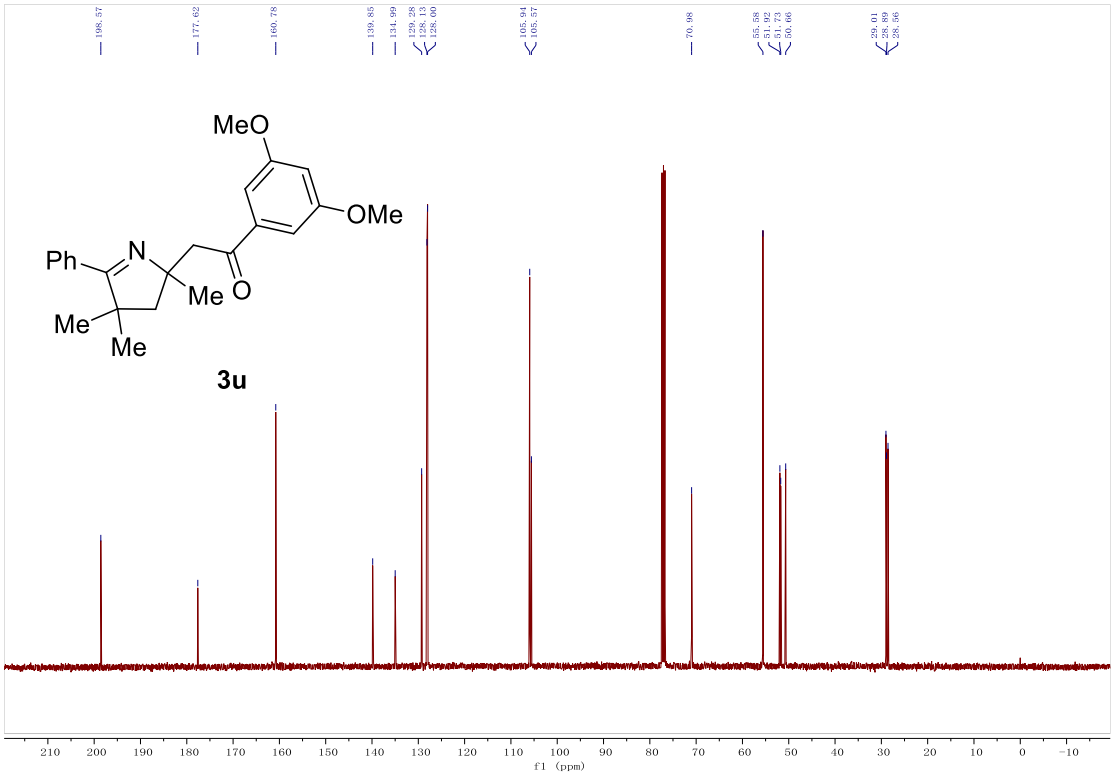

OMe
Ph
N
Me
O
Me
Me
3s
3.01
1.07
4.02
1.09
3.08
1.04
1.00
1.03
1.08
2.97
3.07
3.04
f1 (ppm)

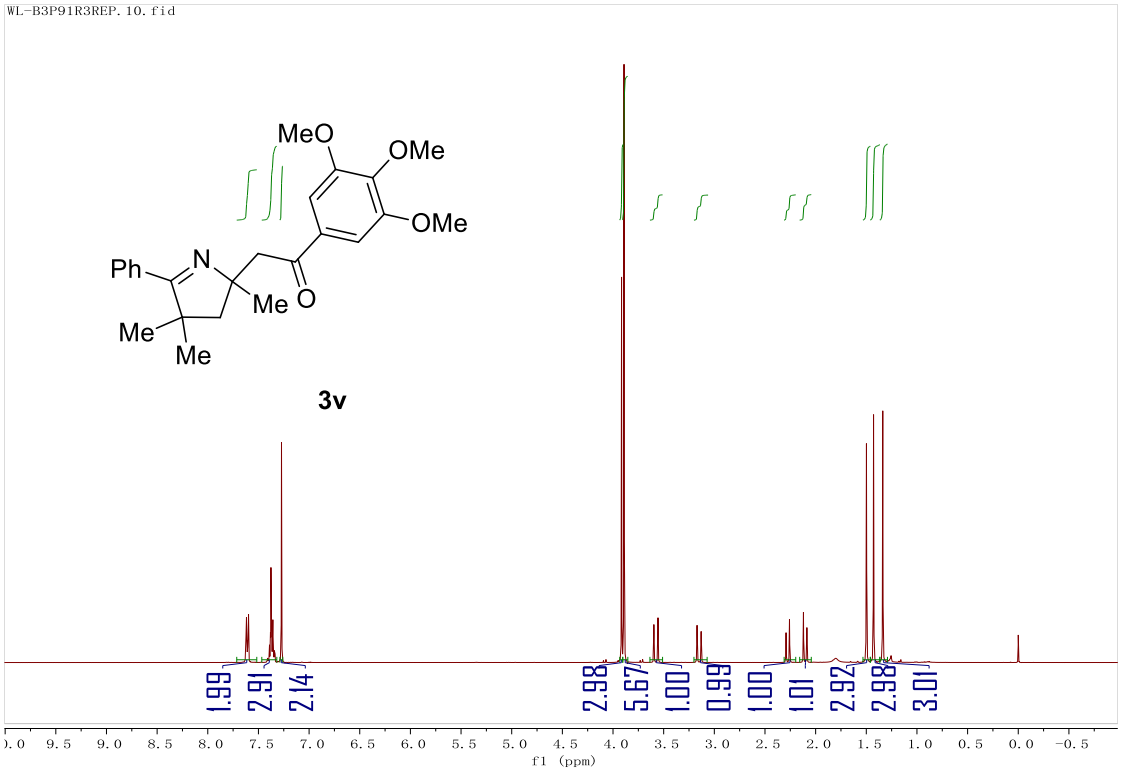

198.81
177.62
159.76
139.29
134.99
129.50
129.36
128.12
127.98
121.10
119.64
112.20
71.04
55.42
51.82
51.72
50.61
29.04
28.01
26.52
OMe
Ph
N
Me
O
Me
Me
3s
f1 (ppm)

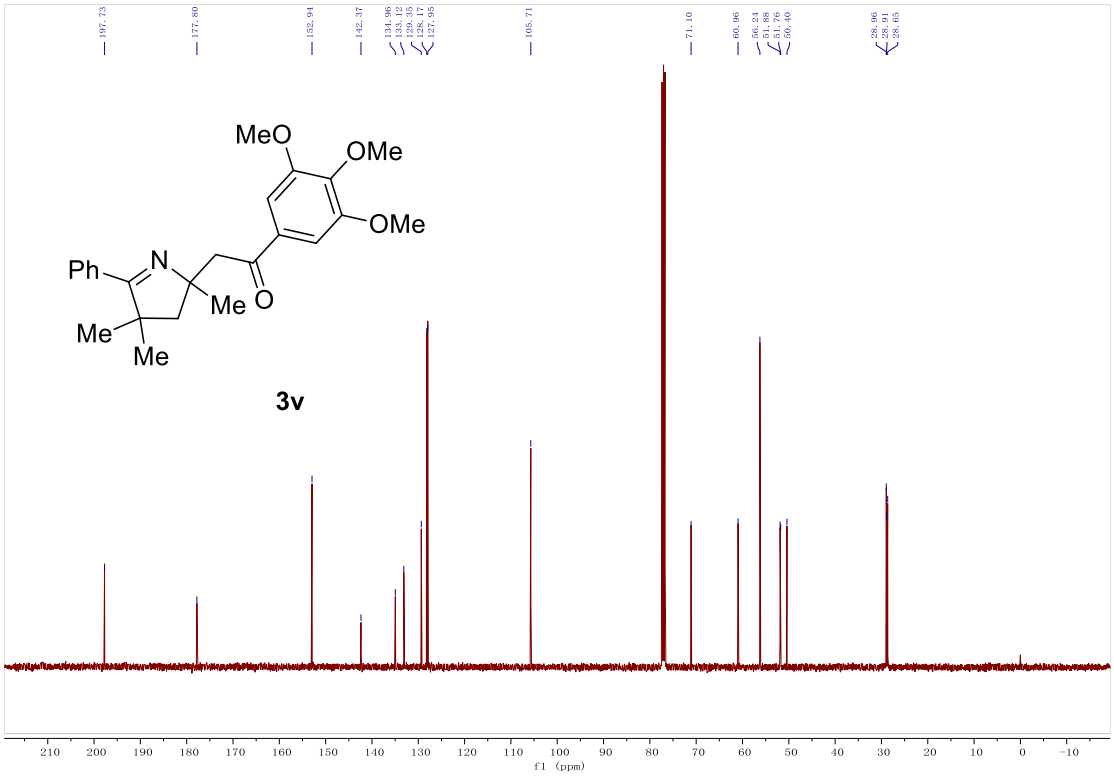

3.87
3.48
3.44
3.21
3.18
2.32
2.29
2.07
2.05
2.03
1.49
1.43
1.29
OMe
Ph
N
Me
O
Me
Me
3t
2.11
2.11
3.03
2.04
3.13
1.00
1.02
1.00
1.23
2.97
3.02
3.03
f1 (ppm)

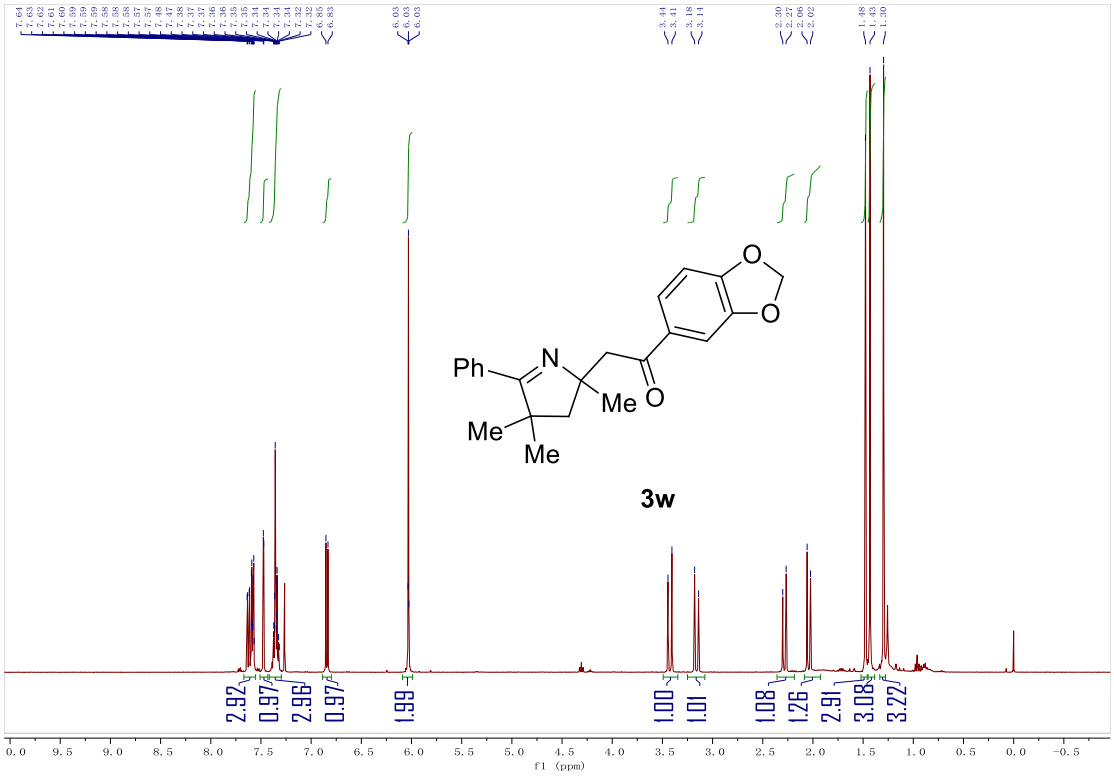

OMe
Ph
N
Me
O
Me
Me
3t
f1 (ppm)

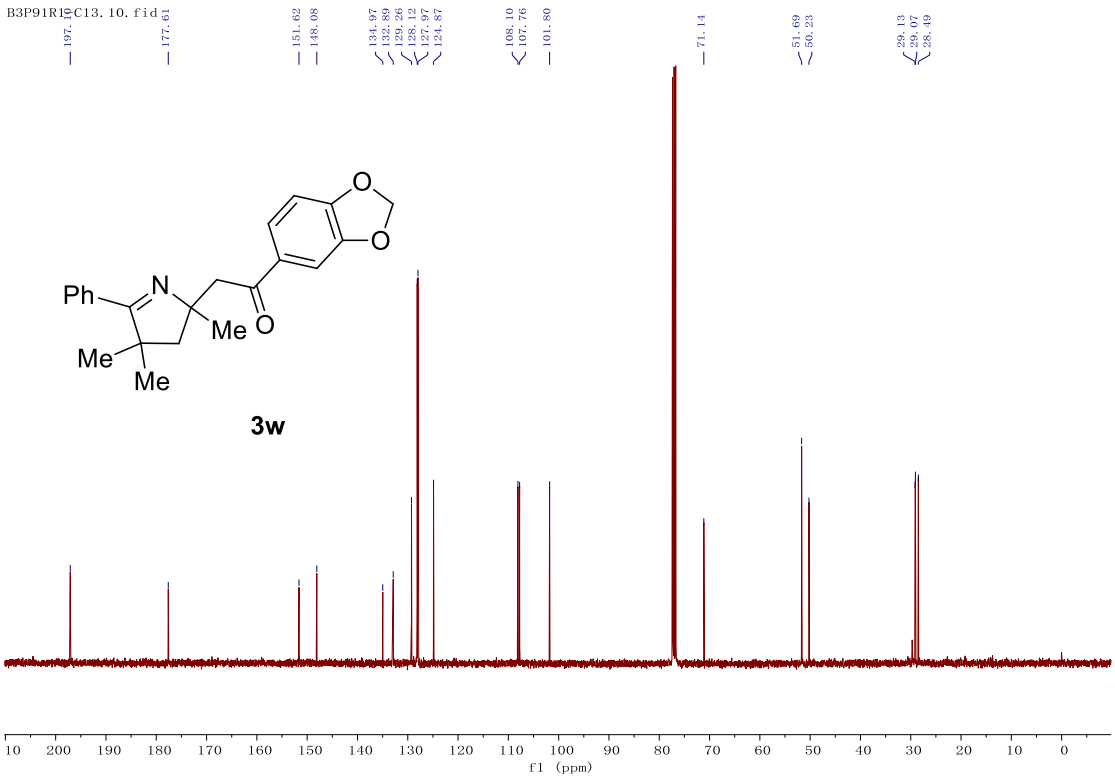

MeO
OMe
Ph
N
Me
O
Me
Me
3u
2.02
2.99
1.95
0.99
5.95
1.00
0.99
1.00
0.98
2.95
2.99
3.09
f1 (ppm)

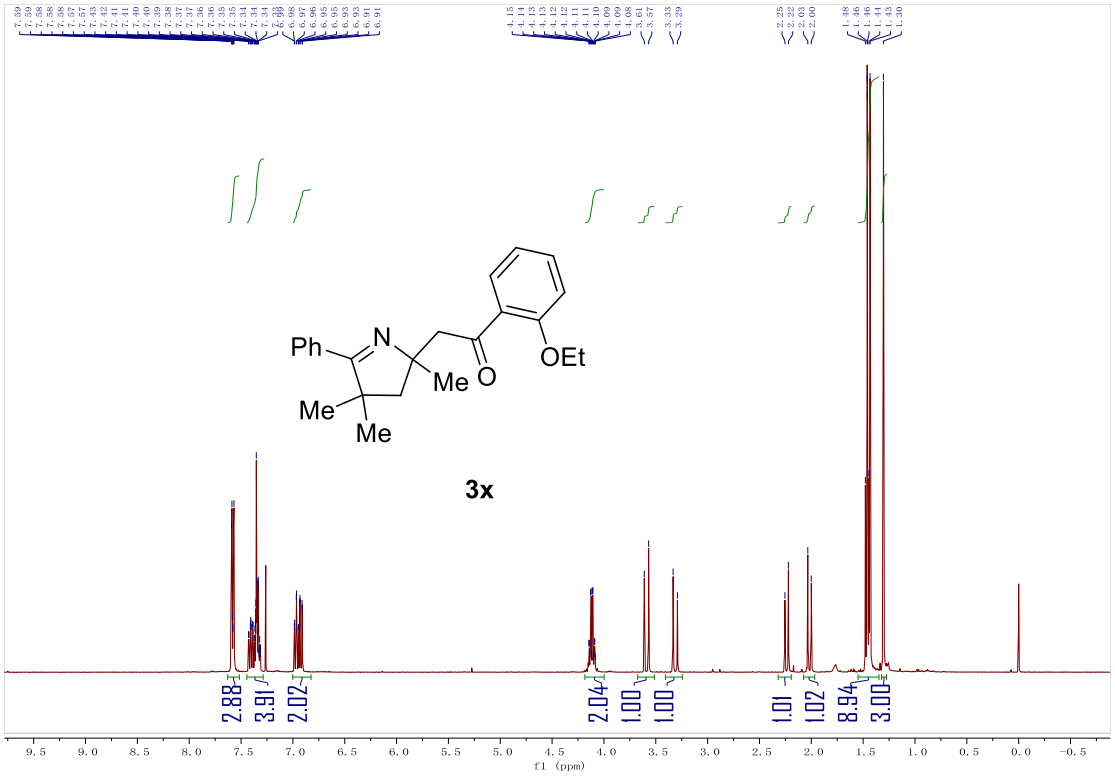

198.57
177.62
160.78
139.85
134.99
129.28
128.13
126.00
105.94
105.57
70.98
55.58
51.92
51.73
50.66
29.01
28.89
26.66
MeO
OMe
Ph
N
Me
O
Me
Me
3u
f1 (ppm)

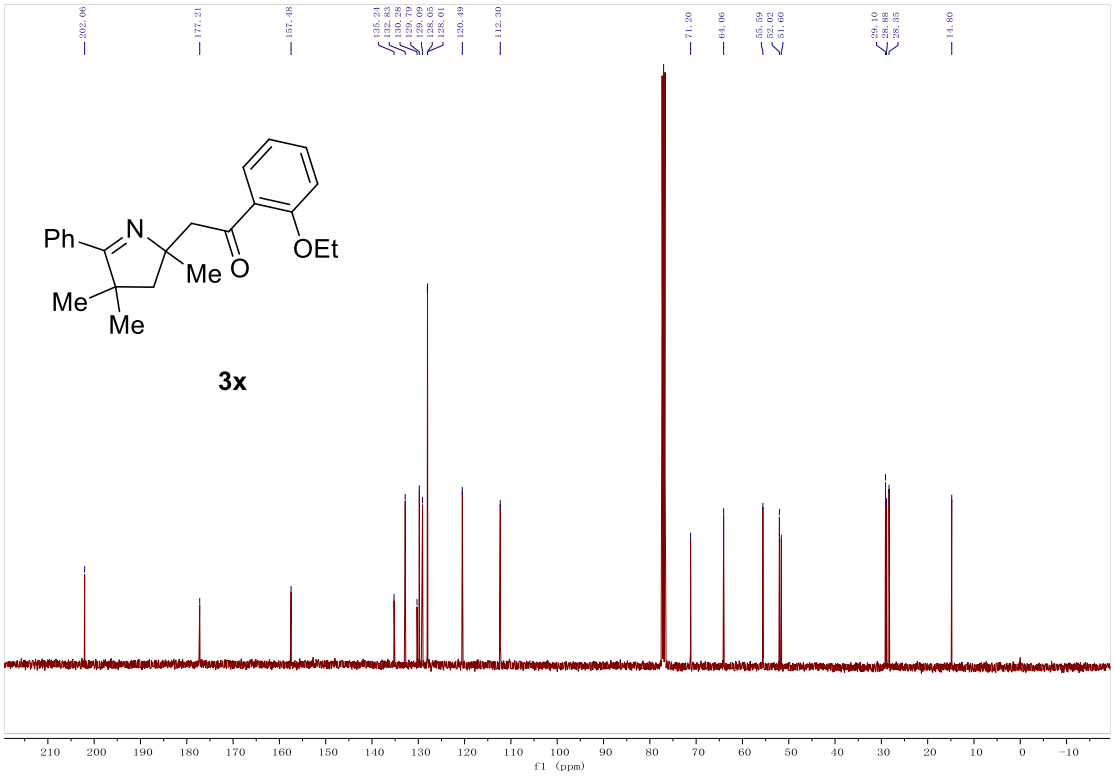

WL-B3P91R3REP.10.fid
MeO
OMe
OMe
Ph
N
Me
O
Me
Me
3v
1.99
2.91
2.14
2.98
5.67
1.00
0.99
1.00
1.01
2.92
2.98
3.01
f1 (ppm)


MeO
OMe
OMe
Ph
N
Me
O
Me
Me
3v
f1 (ppm)

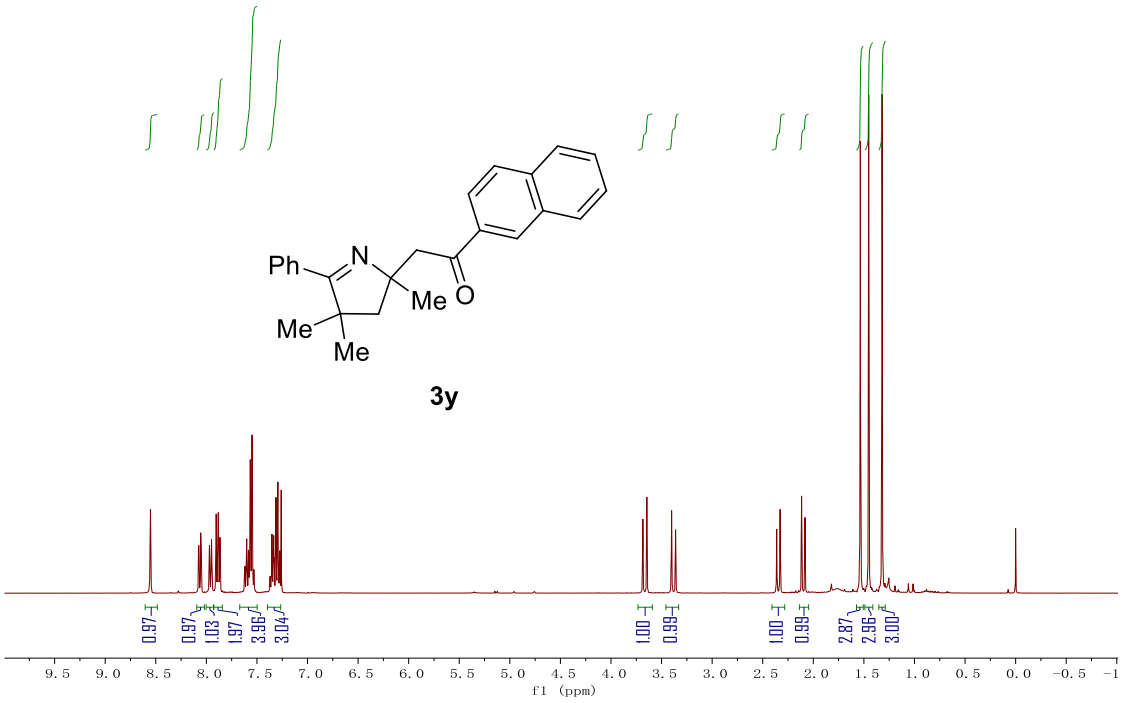

O
O
Ph
N
Me
O
Me
Me
3w
f1 (ppm)

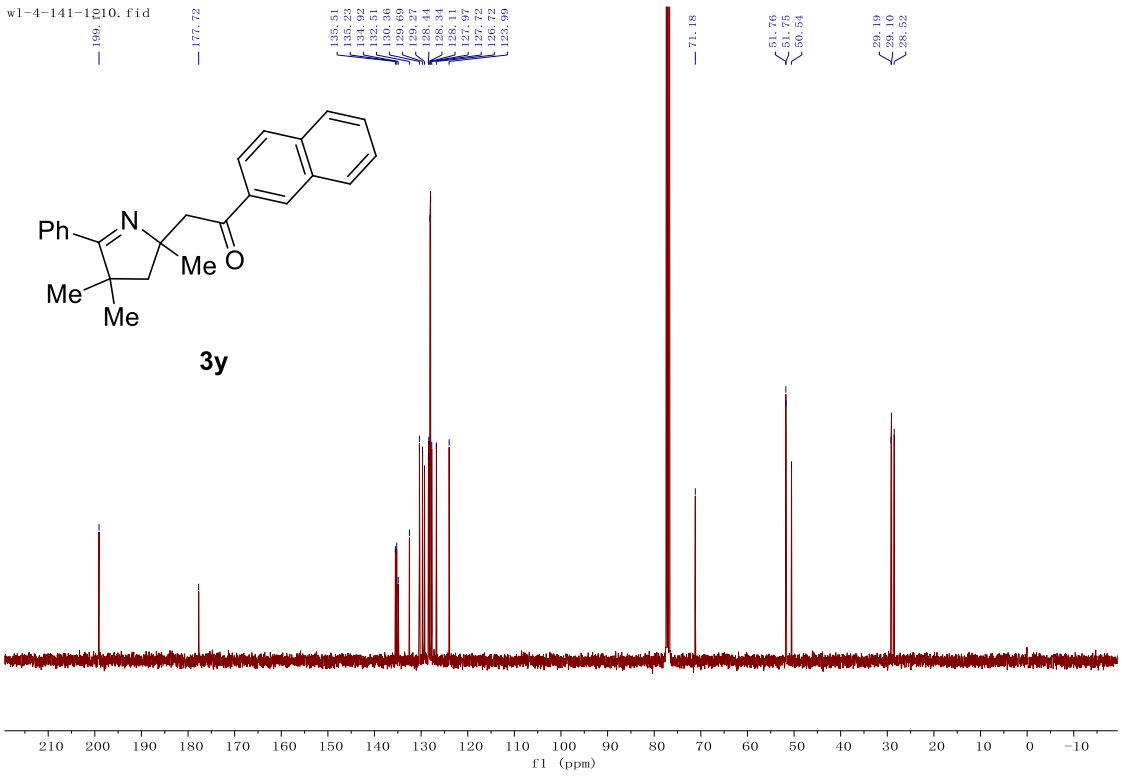

B3P91R1-C13.10.fid
197.10
177.61
151.62
148.08
134.97
132.89
129.26
128.12
127.97
124.87
108.10
107.76
101.80
71.14
51.69
50.23
29.13
29.07
28.49
O
O
Ph
N
Me
O
Me
Me
3w
f1 (ppm)

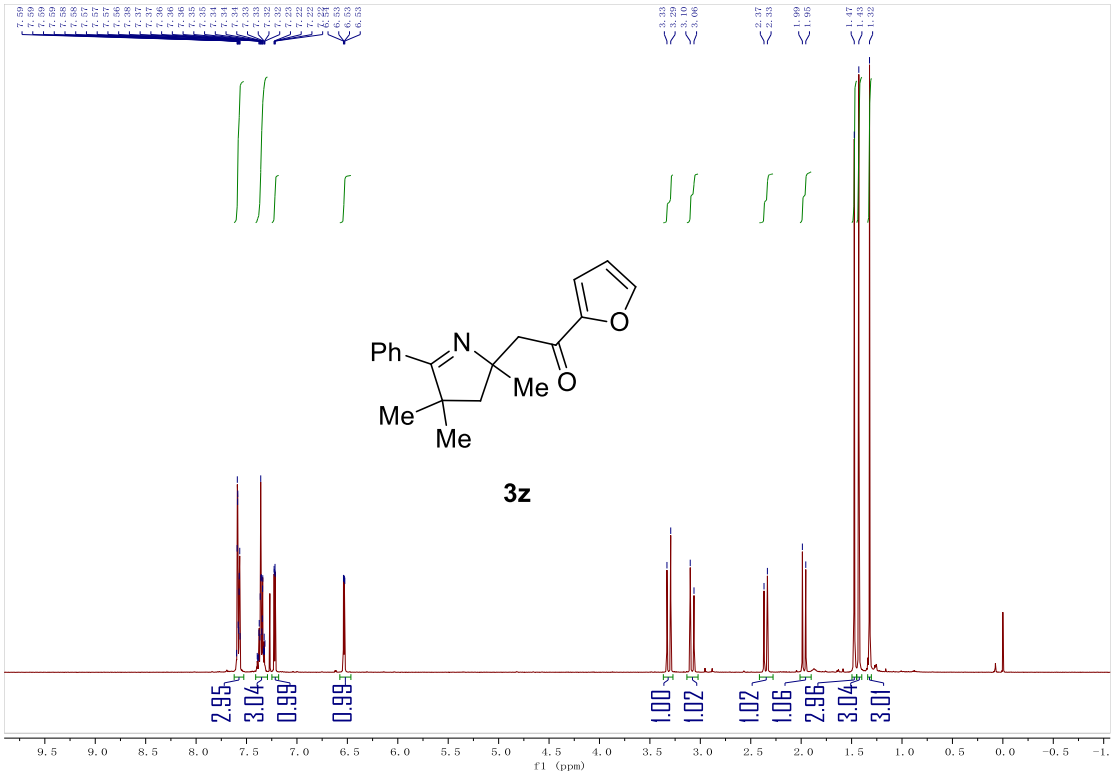

Ph
N
Me
O
OEt
Me
Me
3x
2.88
3.91
2.02
2.04
1.00
1.00
1.01
1.02
8.94
3.00
f1 (ppm)

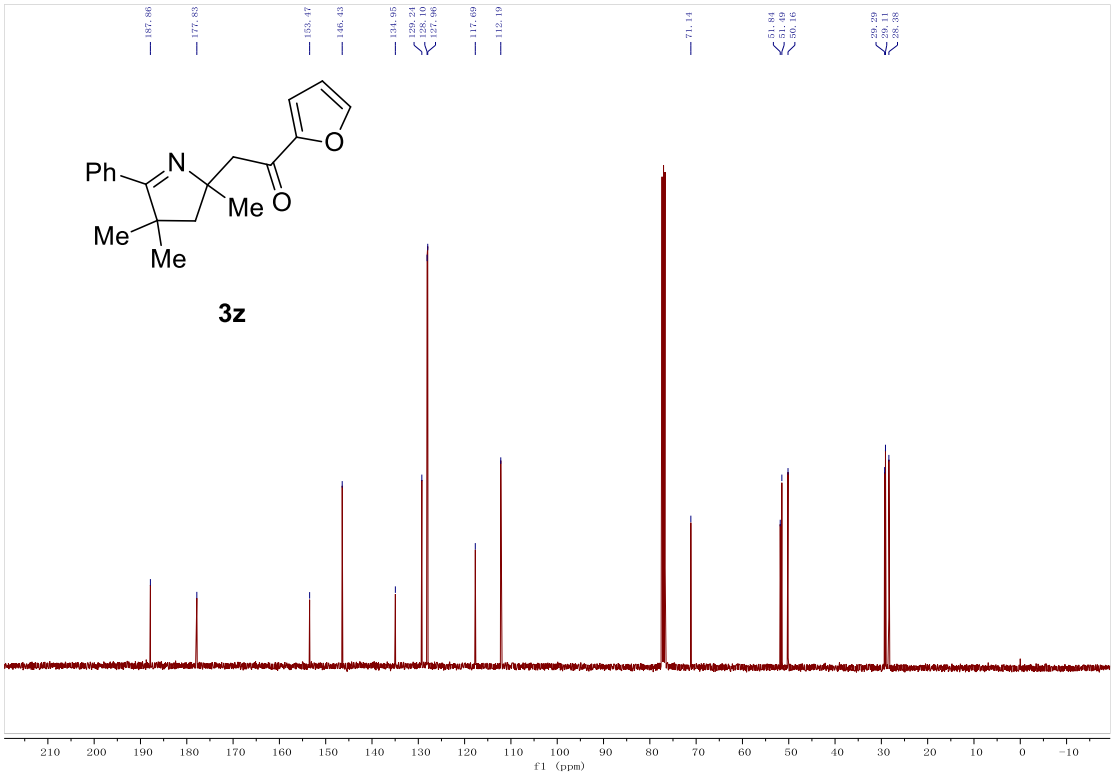


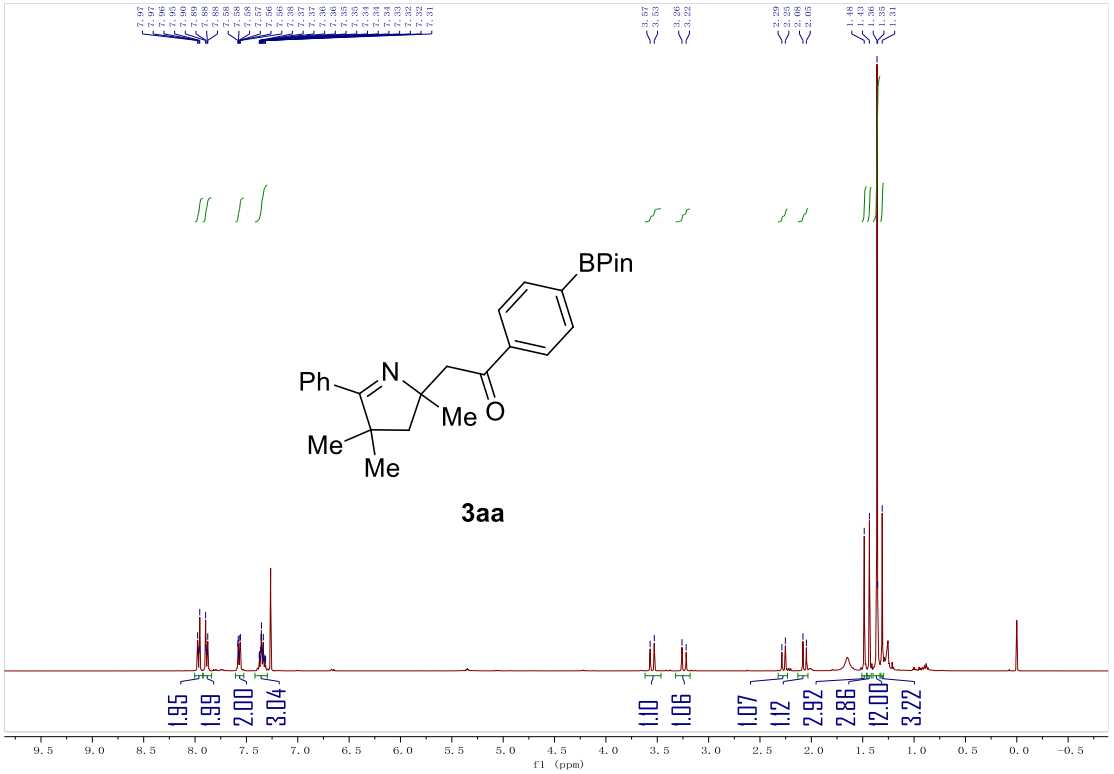
wl-4-141-1.11.fid

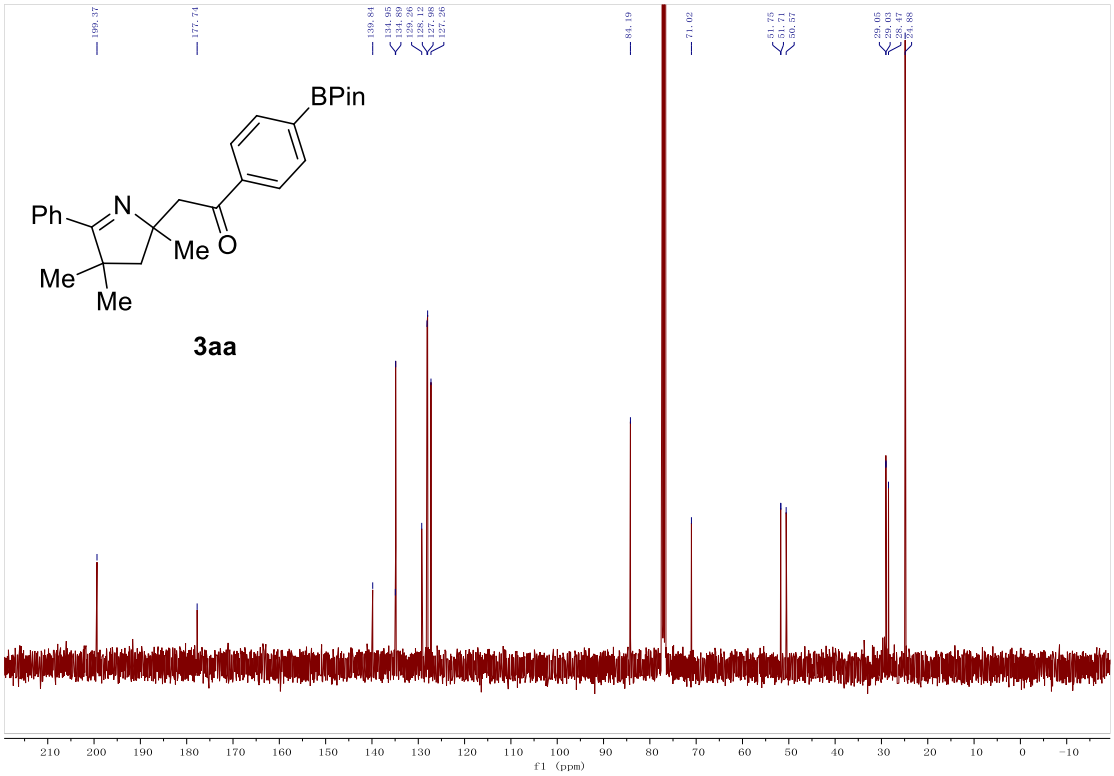


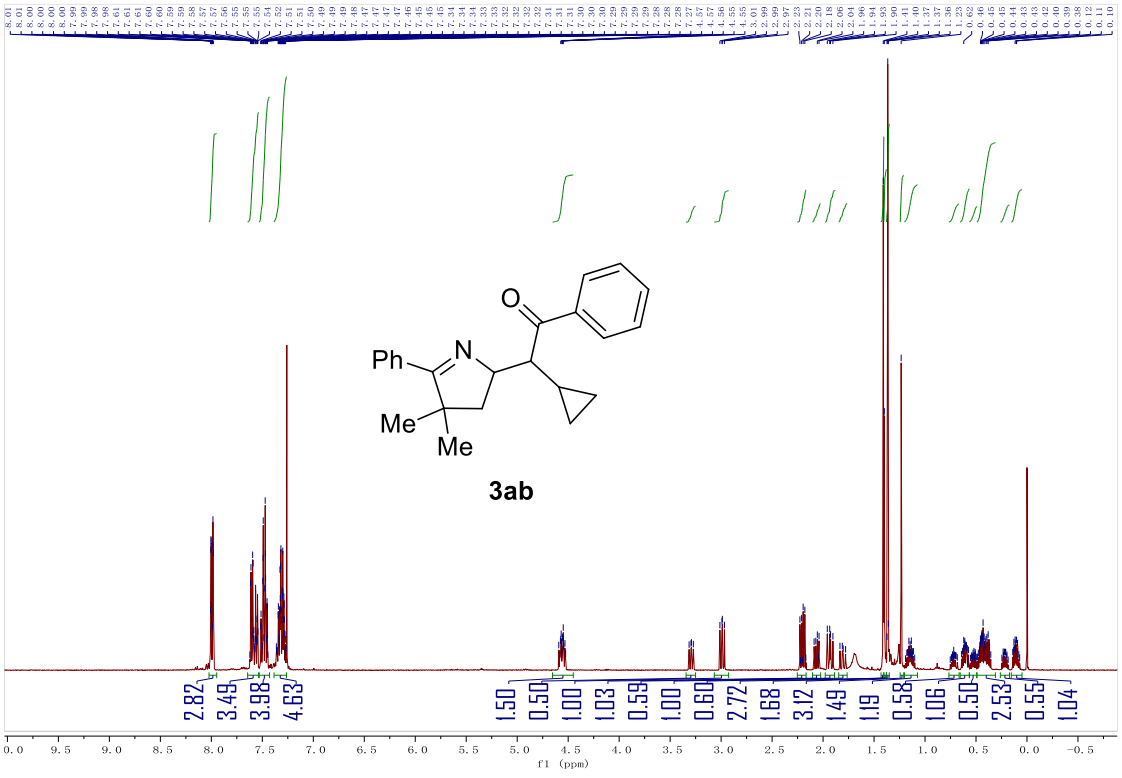

wl-4-141-1C10.fid
199.10
177.72
135.51
135.23
134.92
132.51
130.36
129.69
129.27
128.44
128.34
128.11
127.97
127.72
126.72
123.99
71.18
51.76
51.75
50.54
29.19
29.10
28.52
Ph
N
Me
O
Me
Me
3y
f1 (ppm)

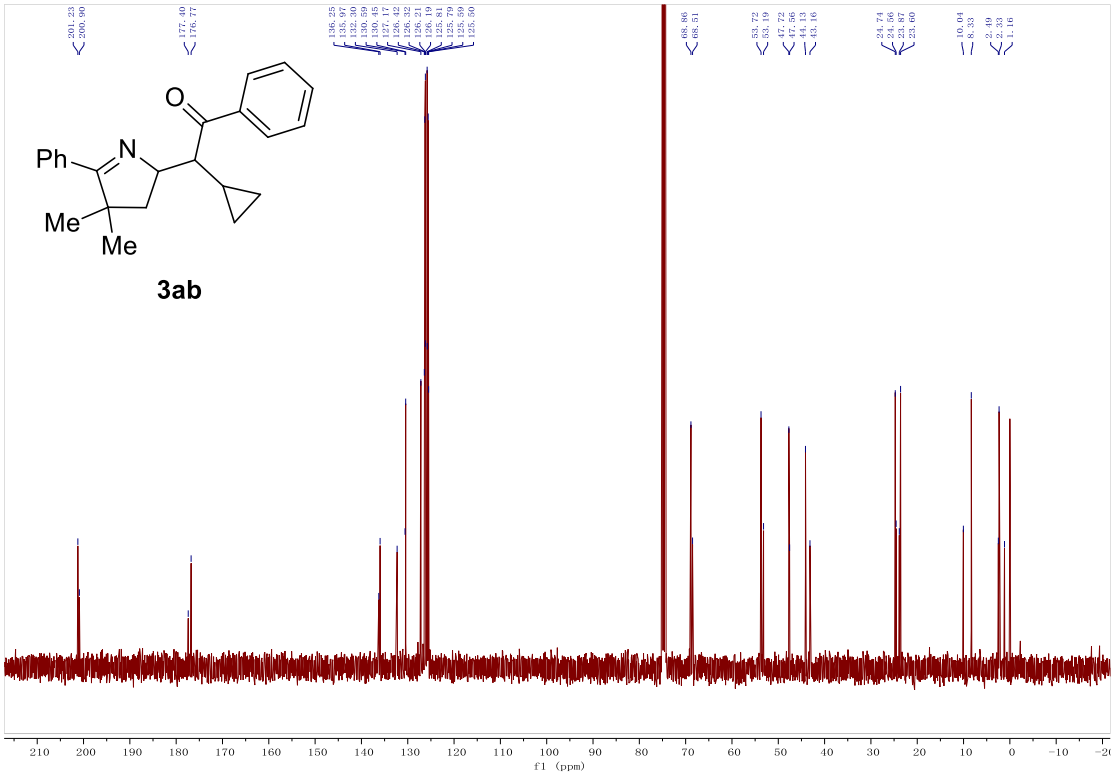

7.59
7.59
7.59
7.59
7.58
7.58
7.57
7.57
7.57
7.57
7.56
7.56
7.38
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.23
7.22
7.22
6.54
6.53
6.53
3.33
3.29
3.10
3.06
2.37
2.33
1.99
1.95
1.47
1.43
1.32
Ph
N
Me
O
O
Me
Me
3z
2.95
3.04
0.99
0.99
1.00
1.02
1.02
1.06
2.96
3.04
3.01
f1 (ppm)

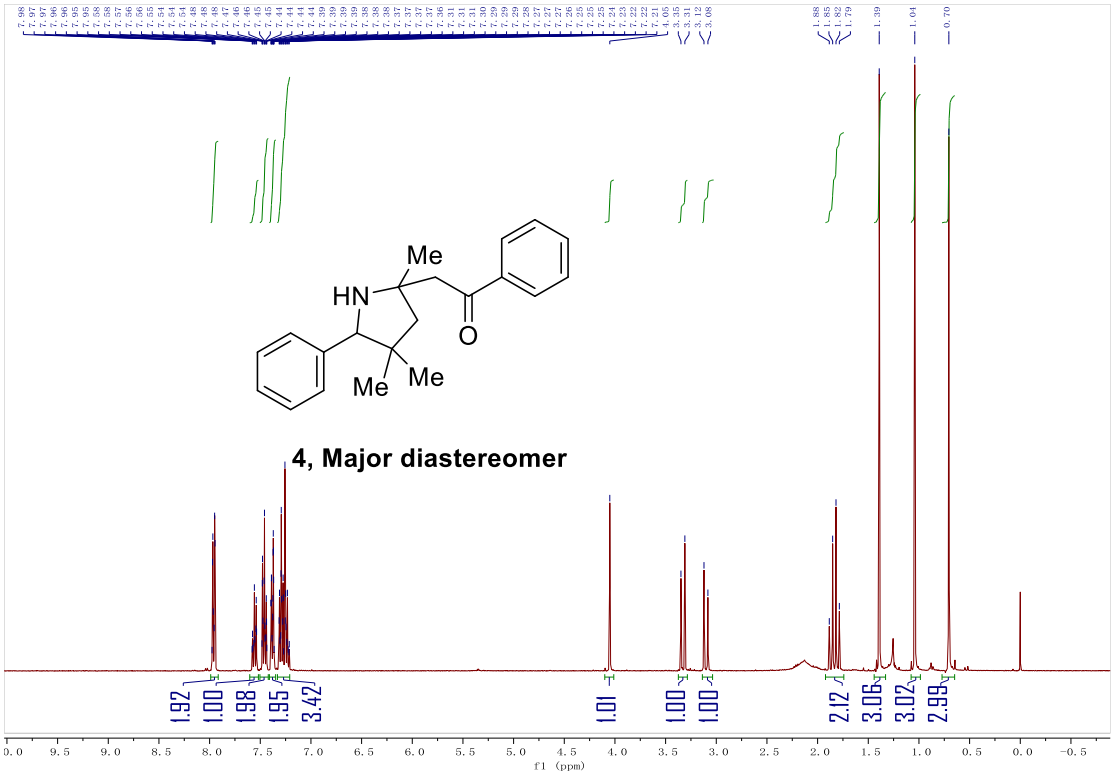

187.86
177.83
153.47
146.43
134.95
129.24
128.10
124.96
117.69
112.19
71.14
51.84
51.49
50.16
29.29
29.11
28.38
Ph
N
O
Me
O
Me
Me
3z
f1 (ppm)

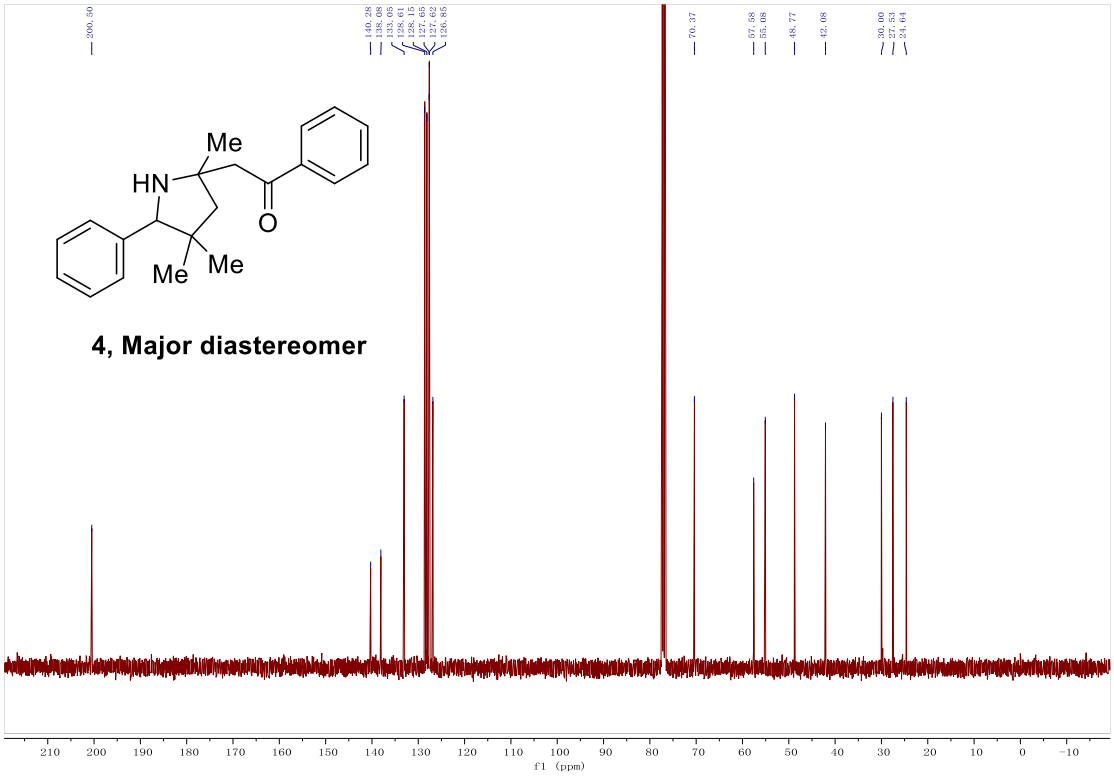

BPin
Ph
N
Me
O
Me
Me
3aa
1.95
1.99
2.00
3.04
1.10
1.06
1.07
1.12
2.92
2.86
12.00
3.22
f1 (ppm)

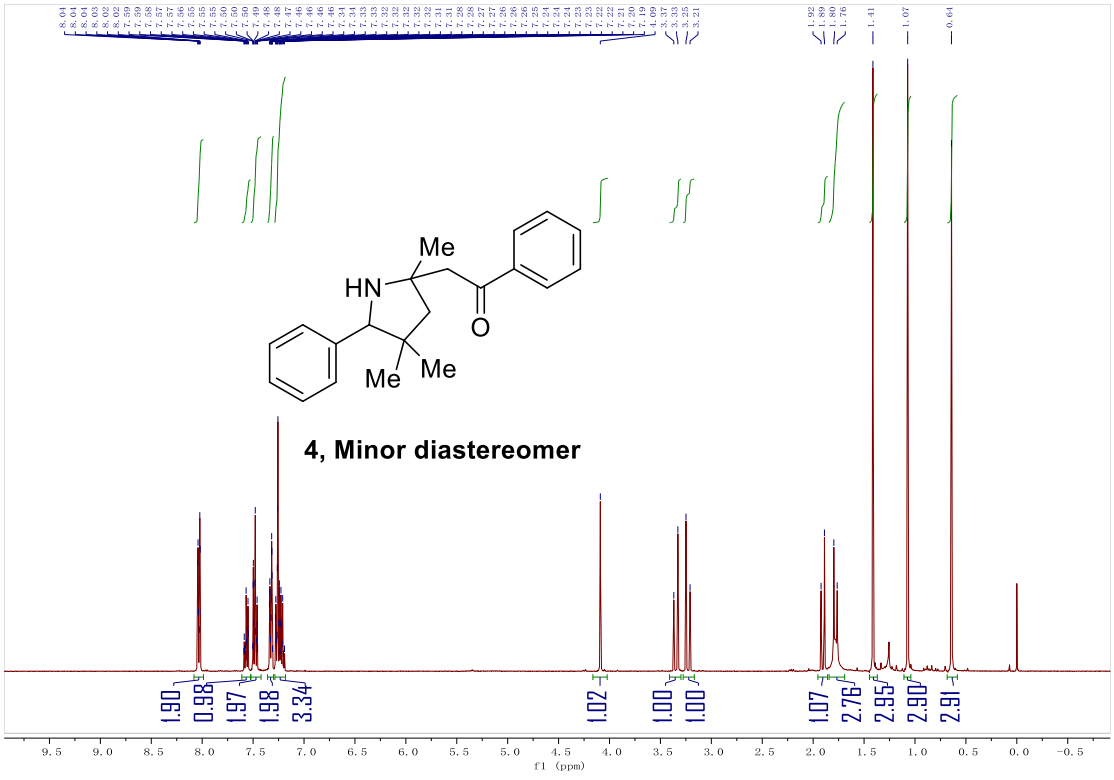

BPin
Ph
N
Me
O
Me
Me
3aa
f1 (ppm)

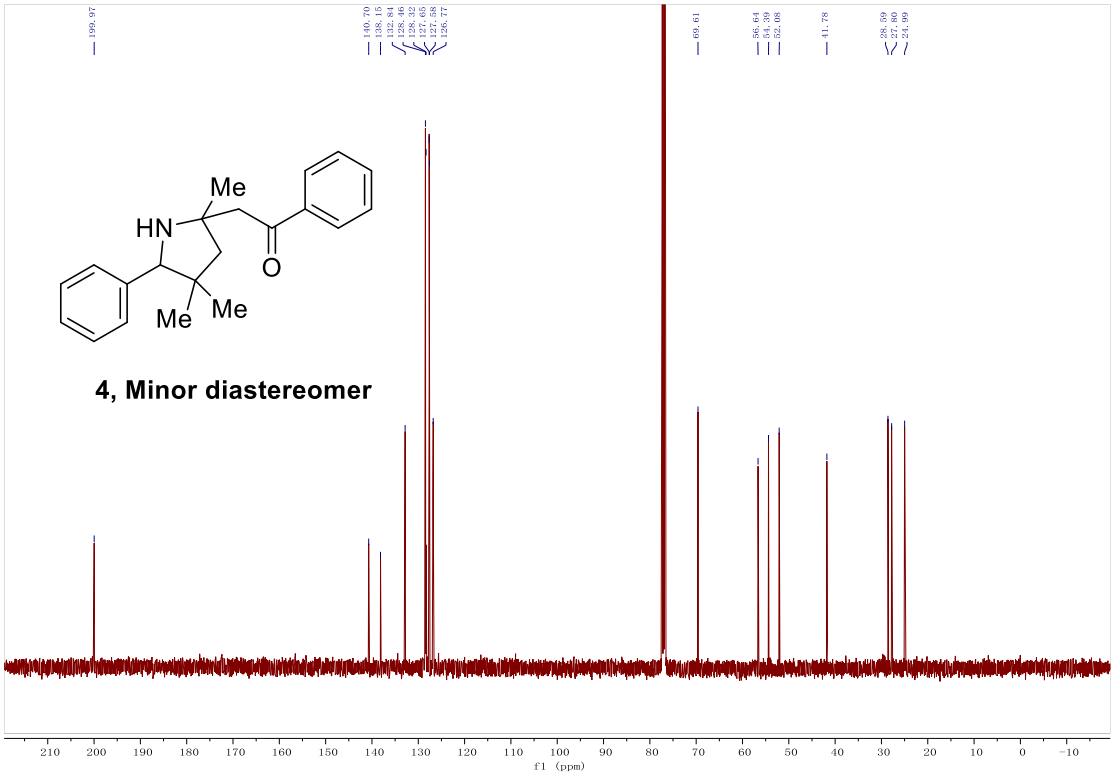

O
Ph
N
Me
Me
3ab
f1 (ppm)

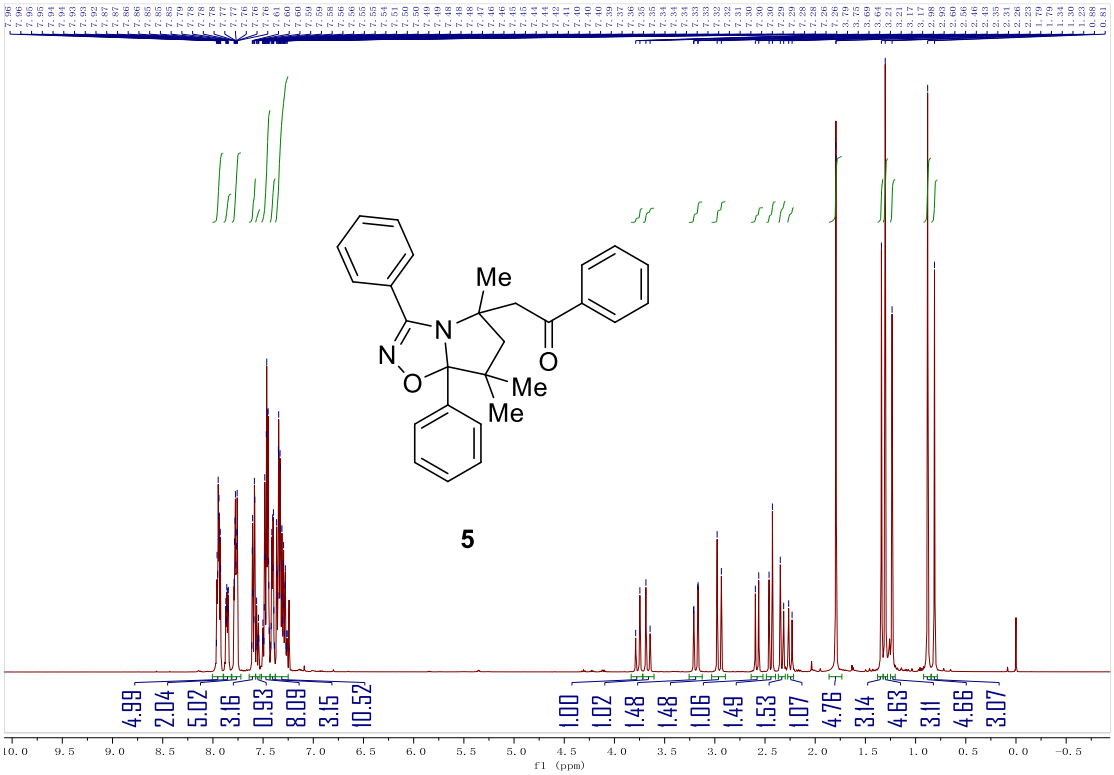

Ph
N
O
Me
Me
3ab
f1 (ppm)

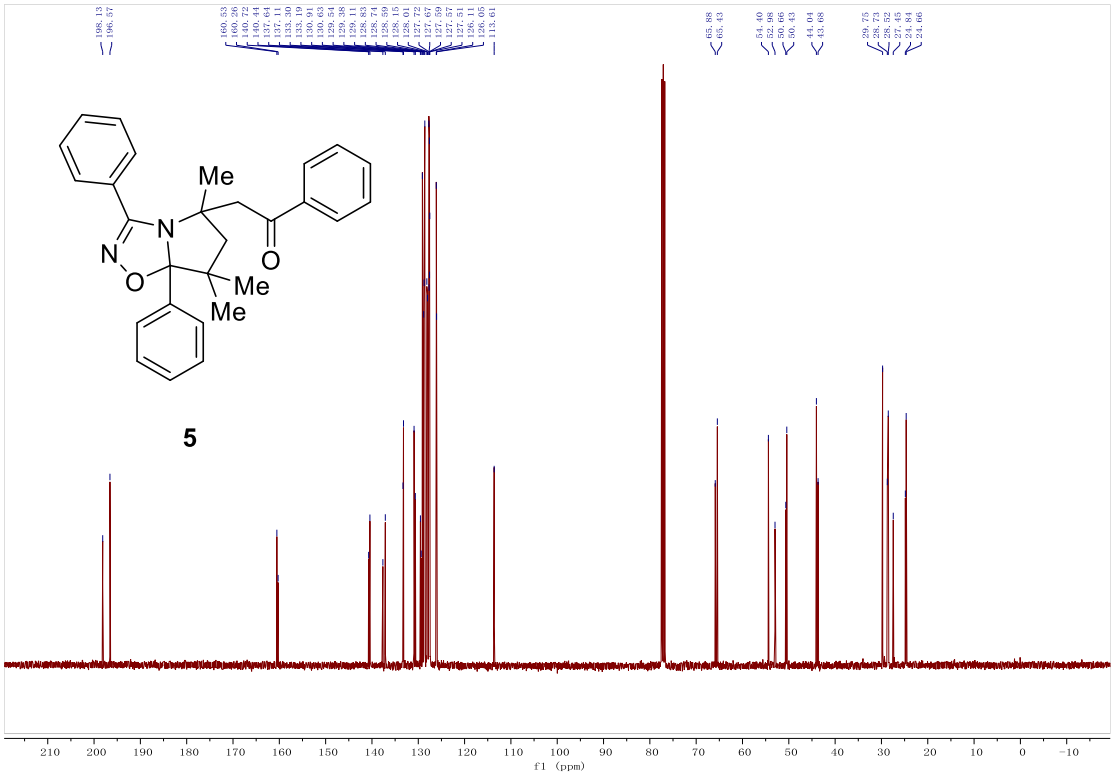

Me
HN
O
Me
Me
4, Major diastereomer
1.92
1.00
1.98
1.95
3.42
1.01
1.00
1.00
2.12
3.06
3.02
2.99
f1 (ppm)


Me
HN
O
Me
Me
4, Major diastereomer
f1 (ppm)


Me
HN
O
Me
Me
4, Minor diastereomer
1.90
0.98
1.97
1.98
3.34
1.02
1.00
1.00
1.07
2.76
2.95
2.90
2.91
f1 (ppm)


199.97
140.70
139.15
132.84
128.46
128.32
127.65
127.58
126.77
69.61
56.64
54.39
52.08
41.78
28.59
27.80
24.99
Me
HN
O
Me
Me
4, Minor diastereomer
f1 (ppm)


Me
N
N
O
O
Me
Me
5
4.99
2.04
5.02
3.16
0.93
8.09
3.15
10.52
1.00
1.02
1.48
1.48
1.06
1.49
1.53
1.07
4.76
3.14
4.63
3.11
4.66
3.07
f1 (ppm)


198.13
196.57
160.53
160.26
140.72
140.44
137.64
137.11
133.30
133.19
130.91
130.63
129.54
129.38
128.11
128.83
128.74
128.59
128.15
128.01
127.72
127.67
127.59
127.57
127.51
126.11
126.05
115.61
65.88
65.43
54.49
52.98
50.66
50.43
44.04
43.68
29.75
28.73
28.52
27.45
24.84
24.66
Me
N
N
O
O
Me
Me
5
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)