Supplementary Information

Mannich-type allylic C−H functionalization of enol silyl ethers under photoredox-thiol hybrid catalysis

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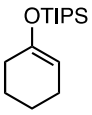
General Information

^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) and JEOL spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, and br = broad) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600II (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.16 ppm). The high-resolution mass spectra were measured on Thermo Fisher Scientific Exactive Plus (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was conducted on Silica gel 60 N (spherical, neutral, 40~50 μm; Kanto Chemical Co., Inc.). Preparative thin layer chromatography (PTLC) was performed on TLC plates (silica gel 70 F254; FUJIFILM Wako Pure Chemical Corporation).

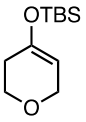
All air- and moisture-sensitive reactions were performed under an atmosphere of argon (Ar) in dried glassware. Acetonitrile (MeCN), 1,2-dichloroethane, and dichloromethane were supplied from Kanto Chemical Co., Inc. as “Dehydrated” and further purified by both A2 alumina and Q5 reactant using a GlassContour solvent dispensing system. The photocatalysts (**4a**-**4c**),[1,2] imines,[3] and enol silyl ethers[4] were synthesized according to the previously reported procedures. Other simple chemicals were purchased and used as such.

Characterization of Enol Silyl Ethers

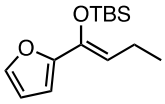


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90-4.86 (1H, m), 2.08-1.97 (4H, m), 1.70-1.62 (2H, m), 1.54 -1.47 (2H, m), 1.20-1.05 (3H, m), 1.08 (18H, d, J = 6.0 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8, 103.8, 30.1, 24.0, 23.4, 22.5, 18.2, 12.8.

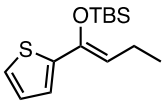
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64-4.60 (1H, m), 2.29-2.21 (4H, m), 1.90-1.80 (2H, m), 0.92 (9H, s), 0.15 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 102.6, 33.6, 28.8, 25.8, 21.5, 18.3, −4.4.



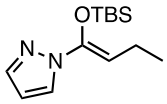
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84-4.81 (1H, m), 4.14 (2H, dd, J = 5.2, 2.8 Hz), 3.81 (2H, t, J = 5.8 Hz), 2.16-2.10 (2H, m), 0.93 (9H, s), 0.15 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 102.4, 64.9, 30.6, 25.8, −4.2.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, d, J = 1.6 Hz), 6.34 (1H, dd, J = 3.6, 1.6 Hz), 6.26 (1H, d, J = 3.6 Hz), 5.28 (1H, t, J = 7.6 Hz), 2.19 (2H, quin, J = 7.6 Hz), 1.02 (3H, t, J = 7.6 Hz), 1.00 (9H, s), 0.09 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9, 141.3, 140.3, 112.4, 111.0, 105.8, 26.0, 19.0, 18.5, 14.3, −4.0.

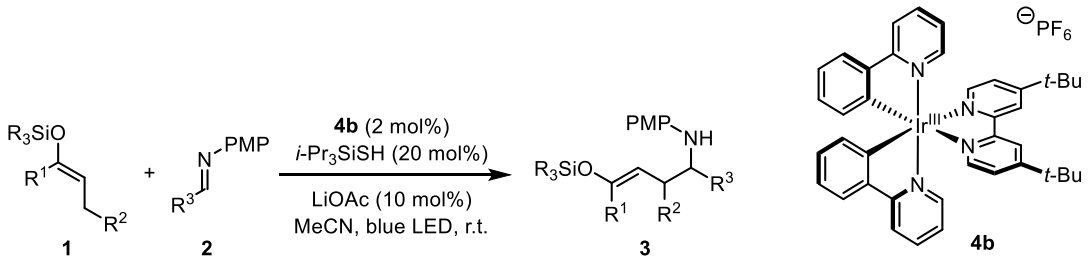


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (1H, dd, J = 5.2, 1.6 Hz), 7.02 (1H, dd, J = 3.6, 1.6 Hz), 6.92 (1H, dd, J = 5.2, 3.6 Hz), 5.14 (1H, t, J = 7.6 Hz), 2.18 (2H, quin, J = 7.6 Hz), 1.02 (3H, t, J = 7.6 Hz), 1.00 (9H, s), 0.06 (6H, s,); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 143.4, 126.9, 125.7, 123.7, 113.6, 26.0, 19.6, 18.5, 14.3, −3.8.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.58 (1H, m), 7.55 (1H, d, J = 2.2 Hz), 6.28 (1H, t, J = 2.2 Hz), 5.07 (1H, t, J = 7.6 Hz), 2.18 (1H, quin, J = 7.6 Hz), 1.05 (1H, t, J = 7.6 Hz), 0.98 (9H, s), 0.03 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 140.1, 127.9, 105.9, 102.4, 25.8, 18.8, 18.4, 14.4, −4.6.

General Experimental Procedures for Mannich-type C−H Alkylation of Enol Silyl Ethers



To a flame-dried test tube were added *N*-(4-methoxyphenyl) imine **2** (0.10 mmol, 1 equiv), $[Ir(ppy)_2(dtbbpy)]PF_6$ (**4b**) (1.83 mg, 0.002 mmol, 2 mol%), LiOAc (0.66 mg, 0.01 mmol, 10 mol%), and MeCN (1 mL, 0.1 M). The reaction tube was sealed with a rubber septum and then evacuated in *vacuo* and backfilled with Ar five times. Enol silyl ether **1** (0.15 mmol, 1.5 equiv) and *i*-Pr_3SiSH (4.3

μL, 0.02 mmol, 20 mol%) were successively introduced via syringe. The whole reaction mixture was stirred at 25 °C under the irradiation of blue LED (448 nm, 750 W/m^2) with a fan to keep the temperature. After appropriate reaction time (indicated with the characterization data for the reaction products), the mixture was directly evaporated. Purification of the resulting crude residue by column chromatography on silica gel (hexane 100% to hexane/Et_2O = 30:1 to 15:1) or preparative TLC (hexane/Et_2O = 10:1) afforded the corresponding aminoalkylated enol silyl ether **3**.

Measurement of Quantum Yield of Catalytic Reaction

Photon flux was measured by Shimadzu-QYM-01. Irradiation was carried out with Asahi Spectra-MAX 303 equipped with band pass filter. A 1 cm^2 quartz cuvette was charged with a solution of enol silyl ether **1a** (91.6 μL, 0.38 mmol), imine **2b** (52.8 mg, 0.25 mmol), photocatalyst **4b** (4.6 mg, 0.005 mmol), and LiOAc (1.6 mg, 0.025 mmol) in CH_3CN (2.5 mL). The solution was carefully evacuated in *vacuo* and backfilled with Ar five times (great care was taken to ensure that the solution was kept in the dark before light irradiation), and then *i*-Pr_3SiSH (10.7 μL, 0.05 mmol) was introduced via syringe. The reaction mixture was irradiated for 9 h or 12 h. After evaporation to remove solvent, the yield of the corresponding product **3b** was determined by ^{1}H NMR with styrene as an internal standard. Quantum yield (Φ) was calculated by the following formula.

$$\Phi = \frac{n_{\mathbf{3b}} \cdot N_A}{n_{ph}}$$

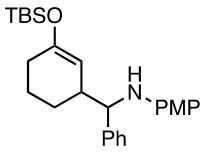
Φ: quantum yield
$n_{\mathbf{3b}}$: amount of product **3b** [mol]
N_A: Avogadro constant ($6.02 \cdot 10^{23}$ mol^{-1})
n_{ph}: number of absorbed photons

9 h: $n_{\mathbf{3b}} = 4.25 \cdot 10^{-5}$, $n_{ph} = 2.95 \cdot 10^{20}$: $\Phi = 0.087$

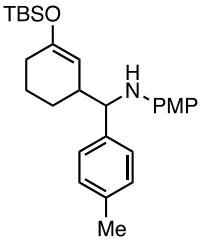
12 h: $n_{\mathbf{3b}} = 6.25 \cdot 10^{-5}$, $n_{ph} = 3.89 \cdot 10^{20}$: $\Phi = 0.097$

Average of quantum yield: $\Phi = 0.092$

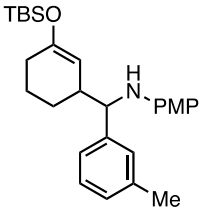
Characterization of Aminoalkylated Enol Silyl Ether



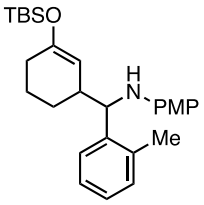
3b (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (8H, m), 7.24-7.18 (2H, m), 6.69-6.63 (4H, m), 6.44-6.37 (4H, m), 4.74 (1H, brs), 4.69 (1H, brs), 4.23 (1H, d, J = 4.0 Hz), 4.12 (1H, d, J = 5.6 Hz), 3.89 (2H, brs), 3.68 (6H, s), 2.70-2.60 (2H, m), 2.12-2.03 (2H, m), 2.01-1.92 (2H, m), 1.87-1.70 (3H, m), 1.52-1.30 (5H, m), 0.92 (9H, s), 0.91 (9H, s), 0.15 (3H, s), 0.11(4) (3H, s), 0.11(2) (3H, s), 0.10 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2, 153.8, 152.0, 151.6, 143.2, 142.7, 142.5, 142.1, 128.4, 127.2, 126.8(9), 126.8(5), 126.8, 115.0, 114.8(3), 114.7(7), 114.1, 106.7, 103.1, 63.3, 62.3, 56.0, 55.9, 43.2, 43.1, 30.2, 30.1, 27.6, 25.9, 25.8, 23.7, 22.3, 22.2, 18.2(4), 18.1(7), −4.0, −4.1, −4.2, −4.3, one peak was not found probably due to overlapping; HRMS (ESI): Calcd for $C_{26}H_{38}O_2NSi^+$ ($[M+H]^+$) 424.2666. Found 424.2673.



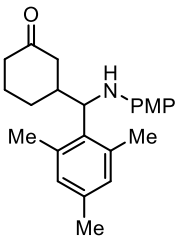
3c (mixture of diastereomers in the ratio of 1.2:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (2H, d, J = 8.4 Hz), 7.17 (2H, d, J = 8.4 Hz), 7.10(4) (2H, d, J = 8.4 Hz), 7.09(7) (2H, d, J = 8.4 Hz), 6.69-6.63 (4H, m), 6.44-6.37 (4H, m), 4.76 (1H, brs), 4.70 (1H, brs), 4.19 (1H, d, J = 4.4 Hz), 4.09 (1H, d, J = 5.2 Hz), 3.85 (2H, brs), 3.68 (6H, s), 2.66-2.58 (2H, m), 2.32 (3H, s), 2.31 (3H, s), 2.13-2.02 (2H, m), 2.00-1.91 (2H, m), 1.86-1.68 (3H, m), 1.65-1.25 (5H, m), 0.92 (9H, s), 0.91 (9H, s), 0.15 (3H, s), 0.12 (3H, s), 0.11 (3H, s), 0.10 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.1, 153.8, 151.9, 151.5, 142.6, 142.2, 140.2, 139.6, 136.3, 136.2, 129.1(3), 129.0(9), 127.0, 126.8, 115.0, 114.8(0), 114.7(6), 114.1, 106.8, 103.3, 63.0, 62.1, 56.0, 55.9, 43.2, 43.1, 30.2, 30.1, 27.6, 25.9, 25.8, 23.7, 22.3(3), 22.2(8), 21.2(2), 21.2(0), 18.2(3), 18.1(7), −4.0, −4.1, −4.2, −4.3; HRMS (ESI): Calcd for $C_{27}H_{40}O_2NSi^+$ ($[M+H]^+$) 438.2823. Found 438.2820.



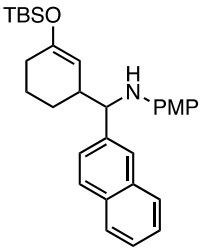
3d (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.06 (6H, m), 7.05-6.99 (2H, m), 6.70-6.64 (4H, m), 6.45-6.39 (4H, m), 4.76 (1H, brs), 4.68 (1H, brs), 4.19 (1H, d, J = 3.6 Hz), 4.07 (1H, d, J = 5.6 Hz), 3.87 (2H, brs), 3.69 (6H, s), 2.67-2.59 (2H, m), 2.33(2) (3H, s), 2.32(5) (3H, s), 2.15-2.03 (2H, m), 2.02-1.92 (2H, m), 1.88-1.70 (3H, m), 1.53-1.25 (5H, m), 0.92 (9H, s), 0.91 (9H, s), 0.16 (3H, s), 0.13 (3H, s), 0.12 (3H, s), 0.10 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2, 153.7, 151.9, 151.6, 143.3, 142.7, 142.6, 142.3, 137.8(9), 137.8(5), 128.3, 127.9, 127.6(3), 127.5(9), 124.2, 124.0, 115.0, 114.8(0), 114.7(7), 114.0, 106.7, 103.1, 63.4, 62.4, 56.0, 55.9, 43.2, 43.1, 30.2, 30.1, 27.7, 25.9, 25.8, 23.9, 22.4, 22.3, 21.7, 18.3, 18.2, −4.0, −4.1, −4.2, −4.4, three peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{27}H_{40}O_2NSi^+$ ($[M+H]^+$) 438.2823. Found 438.2820.



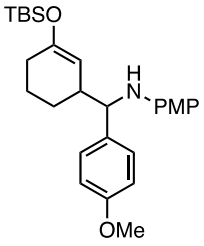
3e (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (1H, m), 7.30-7.25 (1H, m), 7.19-7.06 (6H, m), 6.68-6.62 (4H, m), 6.36-6.29 (4H, m), 4.76 (1H, brs), 4.65 (1H, brs), 4.43 (1H, d, J = 2.8 Hz), 4.35 (1H, d, J = 5.6 Hz), 3.90 (2H, brs), 3.67 (6H, s), 2.68-2.54 (2H, m), 2.43 (3H, s), 2.42 (3H, s), 2.19-2.05 (2H, m), 2.02-1.92 (2H, m), 1.91-1.74 (3H, m), 1.62-1.38 (5H, m), 0.94 (9H, s), 0.91 (9H, s), 0.20 (3H, s), 0.14 (3H, s), 0.12 (3H, s), 0.10 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 154.0, 152.0, 151.5, 142.6, 142.1, 140.8, 140.3, 134.9, 134.7, 130.8, 130.7, 127.1, 126.6, 126.1(2), 126.0(6), 126.0, 115.0, 114.8, 114.6, 113.8, 106.6, 102.4, 59.4, 58.3, 56.0, 55.9, 40.7, 40.5, 30.2, 30.1, 28.1, 25.9, 25.8, 23.9, 22.5, 22.3, 19.5, 19.3, 18.3, 18.2, −4.0, −4.0(5), −4.1(3), −4.3, one carbon atom was not found probably due to overlapping; HRMS (ESI): Calcd for $C_{27}H_{40}O_2NSi^+$ ($[M+H]^+$) 438.2823. Found 438.2818.



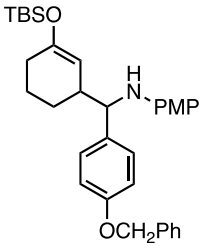
3f (purified and characterized after the conversion of enol silyl ether to the corresponding ketone. Mixture of diastereomers in the ratio of 1.2:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (2H, brs), 6.75 (2H, brs), 6.68 (2H, d, J = 8.4 Hz), 6.66 (2H, d, J = 8.4 Hz), 6.45 (2H, d, J = 8.4 Hz), 6.40 (2H, d, J = 8.4 Hz), 4.59 (1H, brs), 4.57 (1H, brs), 4.54 (2H, brs), 3.69 (3H, s), 3.68 (3H, s), 3.00-2.92 (1H, m), 2.41 (6H, s), 2.38 (6H, s), 2.35-2.23 (6H, m), 2.21 (3H, s), 2.20 (3H, s), 2.18-2.11 (2H, m), 2.10-1.96 (4H, m), 1.80-1.36 (5H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.3, 152.1, 152.0, 142.1, 142.0, 136.4, 136.3, 135.8, 134.7, 134.0, 132.0, 129.9, 115.0, 114.3, 114.2, 60.5, 60.2, 55.9, 47.1, 45.6, 44.6, 44.3, 41.6, 41.5, 30.1, 28.9, 25.6, 25.3, 21.7, 20.8(1), 20.7(7), five peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{23}H_{29}O_2NNa^+$ ($[M+Na]^+$) 374.2091. Found 374.2088.



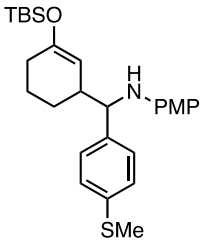
3g (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.73 (8H, m), 7.50-7.39 (6H, m), 6.68-6.61 (4H, m), 6.47-6.41 (4H, m), 4.80 (1H, brs), 4.74 (1H, brs), 4.38 (1H, d, J = 4.0 Hz), 4.29 (1H, d, J = 5.6 Hz), 3.99 (2H, brs), 3.66 (6H, s), 2.80-2.70 (2H, m), 2.15-2.03 (2H, m), 2.01-1.92 (2H, m), 1.88-1.72 (3H, m), 1.62-1.35 (5H, m), 0.92 (9H, s), 0.91 (9H, s), 0.15 (3H, s), 0.11(0) (3H, s), 0.10(6) (3H, s), 0.09 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 154.0, 152.0, 151.7, 142.5, 142.1, 140.8, 140.4, 133.5(9), 133.5(6), 132.9, 132.8, 128.2, 128.1, 128.0, 127.7(8), 127.7(6), 126.0(3), 125.9(8), 125.9, 125.6, 125.5, 125.4, 115.0(0), 114.9(4), 114.8, 114.2, 106.7, 103.1, 63.5, 62.7, 56.0, 55.9, 43.1, 30.2, 30.1, 27.7, 25.9, 25.8, 23.7, 22.3(4), 22.2(5), 18.2(4), 18.1(7), −4.0, −4.1, −4.2, −4.3, two peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{30}H_{40}O_2NSi^+$ ($[M+H]^+$) 474.2823. Found 474.2821.



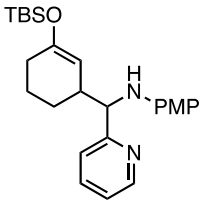
3h (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (2H, d, J = 8.8 Hz), 7.20 (2H, d, J = 9.2 Hz), 6.84(2) (2H, d, J = 9.2 Hz), 6.83(5) (2H, d, J = 8.8 Hz), 6.66 (2H, d, J = 9.2 Hz), 6.65 (2H, d, J = 9.2 Hz), 6.41 (2H, d, J = 8.8 Hz), 6.40 (2H, d, J = 8.8 Hz), 4.76 (1H, brs), 4.69 (1H, brs), 4.18 (1H, d, J = 4.4 Hz), 4.07 (1H, d, J = 5.2 Hz), 3.85 (2H, brs), 3.79 (3H, s), 3.78 (3H, s), 3.68 (6H, s), 2.65-2.56 (2H, m), 2.13-2.02 (2H, m), 2.01-1.91 (2H, m), 1.86-1.67 (3H, m), 1.62-1.25 (5H, m), 0.92 (9H, s), 0.91 (9H, s), 0.15 (3H, s), 0.12 (3H, s), 0.11 (3H, s), 0.10 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5(2), 158.4(6), 154.1, 153.7, 151.9, 151.6, 142.5, 142.2, 135.2, 134.7, 128.1, 127.8, 115.0, 114.9, 114.8, 114.1, 113.8(3), 113.8(1), 106.7, 103.3, 62.7, 61.8, 56.0, 55.9, 55.4, 43.3, 43.2, 30.2, 30.1, 27.6, 25.9, 25.8, 23.8, 22.3(3), 22.2(7), 18.2(4), 18.1(7), −3.9(8), −4.0(4), −4.2, −4.3, one peak was not found probably due to overlapping; HRMS (ESI): Calcd for $C_{27}H_{39}O_3NNaSi^+$ ([M+Na]$^+$) 476.2591. Found 476.2589.



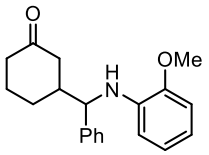
3i (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.28 (10H, m), 7.24 (2H, d, J = 9.0 Hz), 7.20 (2H, d, J = 9.0 Hz), 6.92 (2H, d, J = 8.8 Hz), 6.91 (2H, d, J = 8.8 Hz), 6.67 (2H, d, J = 8.8 Hz), 6.66 (2H, d, J = 8.8 Hz), 6.42 (2H, d, J = 9.0 Hz), 6.40 (2H, d, J = 9.0 Hz), 5.03 (2H, s), 5.02 (2H, s), 4.75 (1H, brs), 4.72 (1H, brs), 4.18 (1H, d, J = 4.0 Hz), 4.07 (1H, d, J = 5.6 Hz), 3.89-3.81 (2H, brm), 3.68 (6H, s), 2.65-2.56 (2H, m), 2.13-2.02 (2H, m), 2.01-1.91 (2H, m), 1.87-1.68 (3H, m), 1.61-1.21 (5H, m), 0.92 (9H, s), 0.91 (9H, s), 0.15 (3H, s), 0.12 (3H, s), 0.11 (3H, s), 0.10 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8(3), 157.7(7), 154.1, 153.7, 151.9, 151.6, 142.5, 142.2, 137.3(3), 137.2(9), 135.5, 135.0, 128.7, 128.1(3), 128.0(5), 127.9, 127.7, 115.0, 114.9, 114.8, 114.7, 114.1, 106.7, 103.2, 70.2, 62.7, 61.7, 56.0, 55.9, 43.3, 43.1, 30.2, 30.1, 27.5, 25.9, 25.8, 23.8, 22.3(3), 22.2(5), 18.2(4), 18.1(7), −3.9(8), −4.0(4), −4.2, −4.3, five peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{33}H_{43}O_3NNaSi^+$ ([M+Na]$^+$) 552.2904. Found 552.2911.



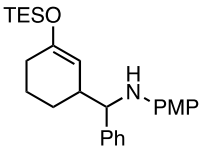
3j (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.17 (8H, m), 6.67 (2H, d, J = 8.8 Hz), 6.66 (2H, d, J = 8.8 Hz), 6.40 (2H, d, J = 8.8 Hz), 6.39 (2H, d, J = 8.8 Hz), 4.73 (1H, brs), 4.69 (1H, brs), 4.19 (1H, d, J = 4.0 Hz), 4.09 (1H, d, J = 5.2 Hz), 3.86 (2H, brs), 3.68 (6H, s), 2.66-2.58 (2H, m), 2.47 (3H, s), 2.46 (3H, s), 2.14-2.02 (2H, m), 2.01-1.92 (2H, m), 1.87-1.69 (3H, m), 1.52-1.24 (5H, m), 0.92 (9H, s), 0.91 (9H, s), 0.15 (3H, s), 0.12 (3H, s), 0.11(4) (3H, s), 0.10(6) (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 154.0, 152.0, 151.7, 142.3, 142.0, 140.4, 139.9, 136.3(9), 136.3(6), 127.7, 127.4, 126.9, 115.0, 114.9, 114.8, 114.1, 106.5, 103.0, 62.8, 61.9, 55.9(4), 55.8(5), 43.2, 43.0, 30.2, 30.1, 27.6, 25.9, 25.8, 23.6, 22.3, 22.2, 18.2(3), 18.1(7), 16.1(9), 16.1(6), −4.0, −4.1, −4.2, −4.3, one carbon atom was not found probably due to overlapping; HRMS (ESI): Calcd for $C_{27}H_{40}O_2NSSi^+$ ([M+H]$^+$) 470.2544. Found 470.2544.



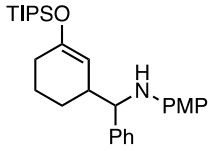
3k (mixture of diastereomers in the ratio of 1.2:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (2H, d, J = 4.4 Hz), 7.57 (2H, t, J = 7.6 Hz), 7.31 (1H, d, J = 7.6 Hz), 7.27 (1H, d, J = 7.6 Hz), 7.15-7.08 (2H, m), 6.69 (2H, d, J = 8.2 Hz), 6.67 (2H, d, J = 8.2 Hz), 6.44 (4H, d, J = 8.2 Hz), 4.69 (1H, brs), 4.64 (1H, brs), 4.34 (1H, d, J = 3.6 Hz), 4.24 (1H, d, J = 5.2 Hz), 4.13 (2H, brs), 3.69 (6H, s), 2.96-2.87 (2H, m), 2.14-2.02 (2H, m), 2.01-1.91 (2H, m), 1.86-1.70 (3H, m), 1.64-1.35 (5H, m), 0.92 (9H, s), 0.90 (9H, s), 0.14 (3H, s), 0.11 (3H, s), 0.08(4) (3H, s), 0.08(0) (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) 162.6, 162.2, 154.2, 153.6, 152.2, 151.8, 149.7, 149.6, 142.2, 142.0, 136.3(0), 136.2(6), 122.2, 121.9, 121.4, 115.0(1), 114.9(7), 114.8, 114.3, 106.4, 103.3, 64.5, 63.9, 55.9(4), 55.8(5), 41.4, 30.1(1), 30.0(9), 27.4, 25.9, 25.8, 23.9, 22.3, 22.1, 18.2(4), 18.1(7), −4.0, −4.1, −4.2, −4.3, two peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{25}H_{37}O_2N_2Si^+$ ([M+H]$^+$) 425.2619. Found 425.2623.



3l (purified and characterized after the conversion of enol silyl ether to the corresponding ketone. Mixture of diastereomers in the ratio of 1.2:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.19 (10H, m), 6.76 (1H, dd, J = 4.2, 1.4 Hz), 6.74 (1H, dd, J = 3.8, 1.4 Hz), 6.70-6.64 (2H, m), 6.63-6.56 (2H, m), 6.35 (1H, dd, J = 3.0, 1.8 Hz), 6.33 (1H, dd, J = 3.0, 1.4 Hz), 4.76 (2H, brs), 4.29 (1H, d, J = 4.0 Hz), 4.23 (1H, d, J = 4.0 Hz), 3.89 (3H, s), 3.88 (3H, s), 2.72-2.60 (1H, m), 2.40-2.31 (3H, m), 2.31-2.16 (6H, m), 2.13-2.01 (3H, m), 1.81-1.73 (1H, m), 1.68-1.38 (4H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.4, 211.3, 146.9, 141.5, 141.2, 137.1(2), 137.1(0), 128.6(4), 128.6(2), 127.4(3), 127.4(1), 127.3, 127.2, 121.3, 121.2, 116.7(4), 116.7(0), 111.0, 110.9, 109.5, 109.4, 62.6, 62.1, 55.6, 45.6, 45.4, 45.2, 41.4(8), 41.4(5), 28.5, 27.7, 25.2, 25.1, three carbon atoms were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{20}H_{24}O_2N^+$ ([M+H]$^+$) 310.1802. Found 310.1802.

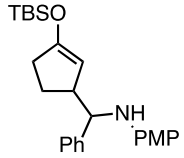


3m (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (8H, m), 7.24-7.17 (2H, m), 6.70-6.63 (4H, m), 6.43-6.36 (4H, m), 4.73 (1H, brs), 4.67 (1H, brs), 4.24 (1H, d, J = 3.6 Hz), 4.11 (1H, d, J = 5.6 Hz), 3.90 (2H, brs), 3.68 (6H, s), 2.70-2.60 (2H, m), 2.17-2.04 (2H, m), 2.03-1.93 (2H, m), 1.88-1.71 (3H, m), 1.62-1.24 (5H, m), 0.95(3) (9H, t, J = 8.0 Hz), 0.95(0) (9H, t, J = 8.0 Hz), 0.65 (6H, q, J = 8.0 Hz), 0.63 (6H, q, J = 8.0 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2, 153.8, 152.0, 151.6, 143.2, 142.8, 142.5, 142.1, 128.4, 127.2, 126.9, 126.8, 115.0, 114.7(8), 114.7(5), 114.0, 106.1, 102.4, 63.3, 62.2, 56.0, 55.9, 43.2, 43.1, 30.1, 30.0, 27.7, 23.8, 22.4, 22.3, 6.9, 5.2(2), 5.1(7), three peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{26}H_{38}O_2NSi^+$ ([M+H]$^+$) 424.2666. Found 424.2664.

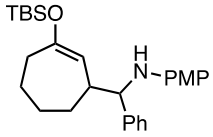


3n (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (8H, m), 7.23-7.16 (2H, m), 6.69-6.62 (4H, m), 6.42-6.35 (4H, m), 4.72 (1H, brs), 4.65 (1H, brs), 4.24 (1H, d, J = 4.0

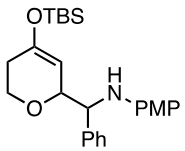
Hz), 4.10 (1H, d, J = 6.0 Hz), 3.88 (2H, brs), 3.67 (6H, s), 2.70-2.58 (2H, m), 2.21-2.09 (2H, m), 2.06-1.97 (2H, m), 1.89-1.71 (3H, m), 1.63-1.30 (5H, m), 1.18-1.02 (42H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 153.9, 151.9, 151.6, 143.3, 142.8, 142.5, 142.2, 128.4, 127.2, 126.9, 126.8(2), 126.7(6), 115.0, 114.8, 114.7, 114.0, 105.6, 101.9, 63.4, 62.3, 56.0, 55.9, 43.3, 43.2, 30.1, 30.0, 27.7, 23.9, 22.4, 22.3, 18.2, 18.1, 12.7(0), 12.6(7), one peak was not found probably due to overlapping; HRMS (ESI): Calcd for $C_{29}H_{44}O_2NSi^+$ ([M+H]$^+$) 466.3136. Found 466.3131.



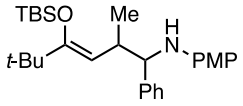
3o (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (8H, m), 7.24-7.16 (2H, m), 6.70-6.63 (4H, m), 6.46-6.39 (4H, m), 4.48 (1H, brs), 4.40 (1H, brs), 4.21 (1H, d, J = 3.6 Hz), 4.10 (1H, d, J = 6.4 Hz), 3.98 (2H, brs), 3.67 (6H, s), 3.17-3.02 (2H, m), 2.40-2.22 (4H, m), 2.12-1.99 (1H, m), 1.89-1.75 (3H, m), 0.94 (9H, s), 0.92 (9H, s), 0.19 (3H, s), 0.16 (6H, s), 0.14 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 157.6, 152.0, 151.6, 143.8, 143.3, 142.4, 142.1, 128.5, 128.4, 127.0, 126.8, 126.7, 115.0, 114.8, 114.2, 104.1, 101.6, 63.1, 62.3, 55.9(4), 55.8(9), 50.1, 33.8, 33.3, 25.8, 23.7, 18.3(2), 18.3(0), −4.3(6), −4.4(2), −4.5, six peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{25}H_{36}O_2NSi^+$ ([M+H]$^+$) 410.2510. Found 410.2519.



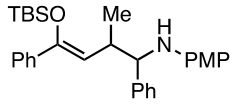
3p (mixture of diastereomers in the ratio of 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (8H, m), 7.23-7.17 (2H, m), 6.67 (4H, d, J = 8.4 Hz), 6.41 (4H, d, J = 8.4 Hz), 4.90 (1H, d, J = 4.8 Hz), 4.89 (1H, d, J = 4.8 Hz), 4.20 (1H, d, J = 4.4 Hz), 4.16 (1H, d, J = 5.6 Hz), 3.89 (2H, brs), 3.68(4) (3H, s), 3.68(0) (3H, s), 2.65-2.55 (2H, m), 2.40-2.24 (2H, m), 2.18-2.07 (2H, m), 2.00-1.62 (6H, m), 1.60-1.24 (6H, m), 0.88 (9H, s), 0.87 (9H, s), 0.05 (3H, s), 0.03 (6H, s), 0.00 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 156.4, 151.9, 151.8, 143.2, 142.4, 142.3, 142.2, 128.5, 128.4, 127.5, 127.2, 126.9, 114.9, 114.8, 114.5, 114.2, 111.0, 108.7, 64.3, 63.9, 55.9(3), 55.8(7), 44.3, 43.8, 35.2(2), 35.1(8), 32.6, 30.0, 29.8, 29.2, 25.9, 25.0, −4.2, −4.3(1), −4.3(4), −4.4, three peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{27}H_{40}O_2NSi^+$ ([M+H]$^+$) 438.2823. Found 438.2820.



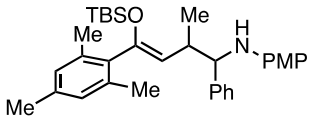
3q (mixture of diastereomers in the ratio of 1.2:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.20 (10H, m), 6.68-6.62 (4H, m), 6.48-6.39 (4H, m), 4.65 (1H, brs), 4.61 (1H, brs), 4.49 (2H, brs), 4.30-4.24 (1H, m), 4.12 (1H, d, J = 6.0 Hz), 4.12-3.99 (2H, m), 3.72-3.61 (2H, m), 3.67 (6H, s), 2.46-2.24 (2H, m), 2.05-1.95 (1H, m), 1.91-1.82 (1H, m), 0.91 (9H, s), 0.90 (9H, s), 0.12 (3H, s), 0.11 (3H, s), 0.10 (3H, s), 0.09 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.1, 152.0, 151.2, 150.5, 142.3, 142.0, 141.3, 140.0, 128.6, 128.5, 127.8, 127.6, 127.5, 127.3, 115.0, 114.8(4), 114.8(1), 114.7(6), 103.4, 101.3, 78.2, 77.9, 64.6, 63.8, 63.6, 62.5, 55.8(9), 55.8(7), 30.5, 30.4, 25.7(9), 25.7(7), 18.1(8), 18.1(7), −4.0, −4.1, −4.4, −4.5; HRMS (ESI): Calcd for $C_{25}H_{36}O_3NSi^+$ ([M+H]$^+$) 426.2459. Found 426.2454.



3r (*Z*/*E* > 20:1, dr of *Z*-isomer is 1.2:1): The reaction was performed with **1q** (0.2 mmol, 2 equiv), *i*-Pr_3SiSH (0.04 mmol, 40 mol%) and LiOAc (0.02 mmol, 20 mol%) for 48 hours. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 7.2 Hz), 7.31 (2H, t, J = 7.2 Hz), 7.28-7.17 (6H, m), 6.62 (4H, d, J = 9.2 Hz), 6.35 (2H, d, J = 9.2 Hz), 6.32 (2H, d, J = 9.2 Hz), 4.45 (1H, d, J = 10.8 Hz), 4.30 (2H, brs), 4.21 (1H, d, J = 2.4 Hz), 4.19 (1H, d, J = 3.2 Hz), 3.66 (3H, s), 3.65 (3H, s), 3.61 (1H, d, J = 9.6 Hz), 3.18-3.07 (1H, m), 2.80-2.68 (1H, m), 1.11 (9H, s), 1.08 (9H, s), 1.05 (9H, s), 1.02 (9H, s), 0.90 (3H, d, J = 6.8 Hz), 0.75 (3H, d, J = 6.8 Hz), 0.23 (3H, s), 0.22(4) (3H, s), 0.22(1) (3H, s), 0.20 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 159.3, 151.8, 151.2, 143.8, 143.2, 141.8, 140.8, 128.4, 128.3, 127.8(3), 127.8(0), 127.0, 126.9, 114.9, 114.8, 114.5, 113.8, 108.1, 105.5, 66.6, 63.5, 55.9, 37.5, 37.0, 36.9, 34.9, 29.2, 29.1, 26.7(2), 26.6(7), 19.4(2), 19.3(7), 18.5, 18.3, −2.5(9), −2.6(1), −2.7, −2.9, one peak was not found probably due to overlapping; HRMS (ESI): Calcd for $C_{28}H_{44}O_2NSi^+$ ([M+H]$^+$) 454.3136. Found 454.3140.

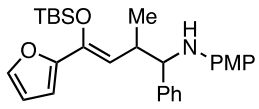


3s (*Z*/*E* = 8.7:1, dr of *Z* isomer is 1.3:1): The reaction was performed with **1r** (0.2 mmol, 2 equiv) for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) (for *Z* isomer) δ 7.46-7.38 (8H, m), 7.37-7.16 (12H, m), 6.66-6.59 (4H, m), 6.42-6.35 (4H, m), 5.00 (1H, d, J = 10.0 Hz), 4.78 (1H, d, J = 10.0 Hz), 4.67 (2H, br), 4.31 (1H, d, J = 4.4 Hz), 3.78 (1H, d, J = 9.2 Hz), 3.66 (3H, s), 3.64 (3H, s), 3.38-3.26 (1H, m), 3.02-2.90 (1H, m), 1.07 (9H, s), 1.02(0) (9H, s), 1.01(6) (3H, d, J = 7.6 Hz), 0.86 (3H, d, J = 6.8 Hz), 0.03 (3H, s), 0.02 (3H, s), −0.08 (3H, s), −0.12 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) (for *Z* isomer) δ 151.7, 151.4, 151.2, 150.6, 144.0, 143.0, 142.1, 141.1, 139.4, 139.3, 128.5, 128.1(4), 128.1(0), 128.0(9), 128.0(7), 128.0(0), 127.9(7), 127.7, 127.1, 126.9, 126.6, 126.5, 115.6, 114.9(0), 114.8(9), 114.3, 113.9, 113.1, 66.3, 64.1, 56.0, 55.9, 38.3, 36.3, 26.1, 18.4, 18.2, 17.8, −3.4(7), −3.5(4), −4.1, −4.2, two peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{31}H_{40}O_2NSi^+$ ([M+H]$^+$) 474.2823. Found 474.2826.

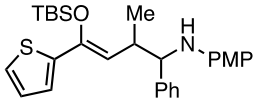


3t (isolated as a mixture of geometrical isomers (*Z*/*E* = 3.0:1), both of which consist of two diastereomers (dr = 1:1)): The reaction was performed with **1s** (0.2 mmol, 2 equiv), *i*-Pr_3SiSH (0.04 mmol, 40 mol%) and LiOAc (0.02 mmol, 20 mol%) for 48 h. ^{1}H NMR (400 MHz, $CDCl_3$) (for *Z* isomer) δ 7.42 (2H, d, J = 7.2 Hz), 7.34-7.13 (8H, m), 6.84 (2H, brs), 6.81 (2H, brs), 6.67-6.58 (4H, m), 6.42-6.36 (4H, m), 4.50 (1H, d, J = 9.6 Hz), 4.27 (1H, d, J = 4.8 Hz), 4.23 (1H, d, J = 10.0 Hz), 3.80 (1H, d, J = 9.2 Hz), 3.67 (3H, s), 3.66 (3H, s), 3.50-3.37 (1H, m), 3.14-3.02 (1H, m), 2.33(3) (3H, s), 2.32(5) (3H, s), 2.30 (3H, s), 2.26 (6H, s), 2.23 (3H, s), 1.04 (3H, d, J = 9.6 Hz), 1.00 (9H, s), 0.97 (9H, s), 0.90 (3H, d, J = 6.8 Hz), −0.11 (3H, s), −0.12 (3H, s), −0.25 (3H, s), −0.27 (3H, s) , (for *E* isomer) δ 7.34-7.13 (10H, m), 6.94 (2H, brs), 6.90 (2H, brs), 6.67-6.58 (4H, m), 6.33 (2H, d, J = 9.2 Hz), 6.25 (2H, d, J = 8.8 Hz), 4.80 (1H, d, J = 10.0 Hz), 4.64 (1H, d, J = 10.8 Hz), 4.02 (1H, d, J = 3.6 Hz), 3.84 (1H, d, J = 8.0 Hz), 3.67 (3H, s), 3.65 (3H, s), 3.50-3.37 (1H, m), 3.14-3.02 (1H, m), 2.40 (12 H, s), 2.25 (3H, s), 2.24 (3H, s), 0.93 (3H, d, J = 7.2 Hz), 0.87 (9H, s), 0.85 (9H, s), 0.81 (3H, d, J = 6.8 Hz), 0.09 (3H, s), 0.07 (3H, s), 0.05 (3H, s), 0.02 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) (for *Z* isomer) δ 151.5, 151.3, 148.1, 147.4, 144.1, 142.6, 142.2,

141.1, 137.5(4), 137.4(7), 137.0, 136.7, 136.0, 135.9, 135.7, 135.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 127.0, 126.8, 114.9, 114.8, 114.1, 113.8, 65.3, 64.1, 56.0, 55.9, 38.0, 35.9, 25.9, 21.2, 20.8, 20.5, 20.4, 18.5, 18.4, −4.2, −4.2(7), −4.3(4), −4.4, three carbon atoms were not found probably due to overlapping, (for *E* isomer) *δ* 151.8, 149.8, 149.2, 142.8, 142.1, 141.3, 137.4, 137.3, 136.5, 135.9, 135.8, 134.1, 133.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.0, 126.9, 116.4, 114.8, 114.5, 114.4, 112.5, 110.6, 64.8, 64.1, 55.9(0), 55.8(7), 39.3, 38.6, 25.8, 21.3, 20.2, 20.1, 20.0, 18.3, 17.9, −4.4, eight carbon atoms were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{33}H_{46}O_2NSi^+$ ([M+H]$^+$) 516.3292. Found 516.3304.

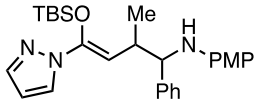


3u (isolated as a mixture of geometrical isomers (*Z*/*E* = 1.2:1), both of which consist of two diastereomers (dr = 1.2:1)): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) (for *Z* isomers) *δ* 7.42-7.38 (2H, m), 7.36-7.18 (10H, m), 6.66-6.59 (4H, m), 6.51-6.47 (2H, m), 6.44-6.30 (6H, m), 5.22 (1H, d, *J* = 10.4 Hz), 5.00 (1H, d, *J* = 10.8 Hz), 3.85 (1H, d, *J* = 9.2 Hz), 3.80 (1H, d, *J* = 9.6 Hz), 3.66 (6H, s), 3.32-3.22 (1H, m), 3.00-2.87 (1H, m), 1.08 (9H, s), 0.96 (9H, s), 0.91 (3H, d, *J* = 6.8 Hz), 0.85 (3H, d, *J* = 6.8 Hz), 0.15 (3H, s), 0.12 (9H, s), (for *E* isomer) *δ* 7.44 (2H, d, *J* = 1.2 Hz), 7.42-7.38 (2H, m), 7.36-7.18 (8H, m), 6.66-6.59 (4H, m), 6.44-6.30 (8H, m), 4.86 (1H, d, *J* = 10.4 Hz), 4.71 (1H, d, *J* = 10.8 Hz), 4.31 (2H, d, *J* = 4.4 Hz), 3.70-3.56 (1H, m), 3.66 (3H, s), 3.64 (3H, s), 3.32-3.22 (1H, m), 1.04 (9H, s), 1.02 (3H, d, *J* = 7.2 Hz), 1.00 (3H, d, *J* = 7.2 Hz), 0.94 (9H, s), 0.12 (3H, s), 0.11 (3H, s), 0.08 (3H, s), 0.07 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) (for all isomers) *δ* 152.1(3), 152,0(8), 151.9, 151.8(2), 151.7(8), 151.7, 151.4, 143.7, 143.4, 142.7, 142.3, 142.1(9), 142.1(5), 142.1(2), 142.0, 141.9, 141.7(9), 141.7(6), 141.7, 141.6, 141.2, 141.0, 140.9, 128.5, 128.4, 128.1(1), 128.0(9), 128.0, 127.8, 127.7, 127.2, 127.1, 127.0(2), 126.9(5), 115.2, 115.0, 114.9, 114.8, 114.7, 114.6, 114.5, 114.3, 114.0, 113.8, 112.7, 111.6, 111.1(3), 111.0(8), 111.0(2), 110.9(9), 109.8, 109.7, 107.0, 106.9, 66.0, 65.4, 63.8, 63.6, 55.9(4), 55.9(1), 55.8(6), 38.7, 37.7, 36.6, 35.6, 26.1, 25.9, 19.2, 19.0, 18.7, 18.5, 18.3, 18.1, 17.7, −3.6, −3.7, −4.1(2), −4.1(3), −4.3(5), −4.4(2), −4.6, nine peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{28}H_{38}O_3NSi^+$ ([M+H]$^+$) 464.2615. Found 464.2614.



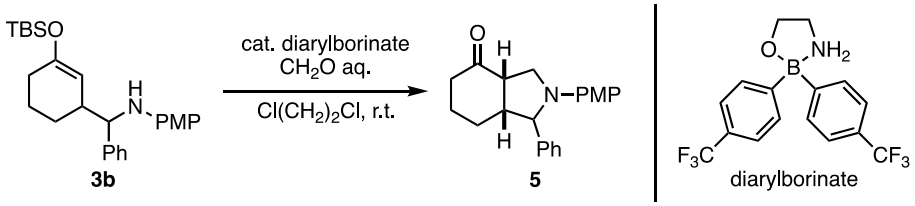
3v (isolated as a mixture of geometrical isomers (*Z*/*E* = 1.5:1), both of which consist of two diastereomers (dr = 1.1:1)): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) (for *Z* isomer) *δ* 7.39 (2H, t, *J* = 8.0 Hz), 7.35-7.20 (10H, m), 7.17-7.13 (1H, m), 7.07 (1H, dd, *J* = 3.6, 0.8 Hz), 7.03-6.98 (1H, m), 6.94 (1H, t, *J* = 4.4 Hz), 6.66-6.59 (4H, m), 6.44-6.35 (4H, m), 5.08 (1H, d, *J* = 9.6 Hz), 4.90 (1H, d, *J* = 10.8 Hz), 3.88 (1H, d, *J* = 8.8 Hz), 3.79 (1H, d, *J* = 9.2 Hz), 3.66 (6H, s), 3.03-2.85 (2H, m), 1.08 (9H, s), 0.97 (9H, s), 0.95 (3H, d, *J* = 6.8 Hz), 0.85 (3H, d, *J* = 6.8 Hz), 0.13(2) (3H, s), 0.12(6) (3H, s), 0.07 (3H, s), 0.04 (3H, s), (for *E* isomer) *δ* 7.39 (2H, t, *J* = 8.0 Hz), 7.35-7.20 (10H, m), 7.18 (1H, d, *J* = 3.6 Hz), 7.04 (1H, dd, *J* = 3.6, 0.8 Hz), 7.03-6.98 (1H, m), 6.94 (1H, t, *J* = 4.4 Hz), 6.66-6.59 (4H, m), 6.44-6.35 (4H, m), 4.86 (1H, d, *J* = 10.8 Hz), 4.81 (1H, d, *J* = 10.8 Hz), 4.31 (1H, d, *J* = 8.4 Hz), 4.30 (1H, d, *J* = 7.2 Hz), 3.65 (6H, s), 3.35-3.20 (2H, m), 1.04(3) (3H, d, *J* = 7.2 Hz), 1.03(8) (9H, s), 1.00 (3H, d, *J* = 7.2 Hz), 0.94

(9H, s), 0.11 (6H, s), 0.09 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) (for *Z* isomer) δ 152.0, 151.8, 145.4, 145.3, 143.1, 142.9, 142.1, 141.6, 140.6, 128.5, 128.2, 128.1, 127.8, 127.7, 127.3, 127.1, 127.0(1), 126.9(8), 126.9, 126.3, 125.7, 124.6, 124.5, 115.3, 114.9, 114.7, 114.4, 114.0, 112.1, 66.2, 65.4, 56.0, 55.9, 40.1, 38.2, 25.9, 18.8, 18.6, 18.0, −3.4, −4.0, −4.2, −4.4, two peaks were not found probably due to overlapping, (for *E* isomer) δ 152.6, 151.4, 144.9, 144.7, 143.7, 142.6, 141.9, 141.3, 140.8(4), 140.8(0), 128.0(4), 127.9(9), 127.0, 126.8, 126.4, 125.6, 124.5(4), 124.4(7), 114.9(1), 114.8(5), 114.5, 114.4, 112.9, 64.0, 63.2, 55.9(3), 55.8(9), 38.1, 36.2, 26.1, 18.5, 18.4, 17.7, −3.5, −3.9, −4.3, −4.4, seven peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{28}H_{38}O_2NSSi^+$ ($[M+H]^+$) 480.2387. Found 480.2382.



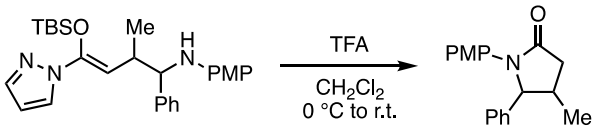
3w (*Z*/*E* > 20:1, dr of *Z*-isomer is 1.1:1): The reaction was performed for 18 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, d, *J* = 2.0 Hz), 7.58 (1H, d, *J* = 2.0 Hz), 7.56 (1H, d, *J* = 2.0 Hz), 7.53 (1H, d, *J* = 2.0 Hz), 7.39 (2H, d, *J* = 7.2 Hz), 7.35-7.17 (8H, m), 6.68-6.60 (4H, m), 6.45-6.38 (4H, m), 6.30 (1H, t, *J* = 2.0 Hz), 6.29 (1H, t, *J* = 2.0 Hz), 4.99 (1H, d, *J* = 10.4 Hz), 4.80 (1H, d, *J* = 10.4 Hz), 4.33 (1H, d, *J* =4.4 Hz), 3.89 (1H, d, *J* = 9.2 Hz), 3.67 (3H, s), 3.66 (3H, s), 3.21-3.10 (1H, m), 2.92-2.80 (1H, m), 1.07 (3H, d, *J* = 7.6 Hz), 1.04 (9H ,s), 1.01 (9H, s), 0.94 (3H, d, *J* = 6.8 Hz), 0.09 (3H, s), 0.07 (3H, s), 0.02 (3H, s), −0.02 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 151.7, 144.1, 143.4(1), 143.3(5), 142.4, 141.8, 141.0, 140.5, 140.4, 128.6, 128.5, 128.4, 128.2, 127.9, 127.6, 127.2, 127.0, 114.9, 114.8, 114.6, 114.3, 106.4, 106.2, 104.0, 102.4, 65.5, 63.6, 55.9(2), 55.9(0), 37.9, 36.4, 25.9, 18.4, 18.3, 17.7, −4.4, −4.6, −4.7(0), −4.7(2), two peaks were not found probably due to overlapping; HRMS (ESI): the peak pattern corresponding to **3w** was not observed probably due to the loss of pyrazole group under the measurement condition.

Derivatization of Alkylated Enol Silyl Ethers



To a flame-dried test tube were added **3b** (21.2 mg, 0.05 mmol), diarylborinate (1.8 mg, 0.005 mmol, 10 mol%) and 1,2-dichloroethane (1 mL, 0.05 M). The reaction tube was sealed with rubber septum and then evacuated in *vacuo* and backfilled with Ar five times. A 37% aqueous solution of formaldehyde (14.9 μL, 0.15 mmol, 3 equiv) was introduced via syringe. After stirring overnight, the reaction mixture was concentrated. The resulting crude material was purified by column chromatography on silica gel (hexane/EtOAc = 15: to 5:1 as eluent) to afford **5** in 92% yield (14.8 mg, 0.046 mmol, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.15 (10H, m), 6.74 (2H, d, *J* = 9.0 Hz), 6.72 (2H, d, *J* = 9.0 Hz), 6.42 (2H, d, *J* = 9.0 Hz), 6.41 (2H, d, *J* = 9.0 Hz), 4.70 (1H, d, *J* = 7.2 Hz), 4.43 (1H, d, *J* = 3.2 Hz), 4.24 (1H, dd, *J* = 9.0, 6.4 Hz), 3.80 (2H, d, *J* = 8.0 Hz), 3.70 (3H, s), 3.69 (3H, s), 3.51 (1H, t, *J* = 9.0 Hz), 3.17 (1H, q, *J* = 8.0 Hz), 3.12-2.99 (2H, m), 2.63-2.46 (1H, m), 2.44-2.35 (1H, m), 2.30 (2H, t, *J* = 6.6

Hz), 2.13-1.98 (2H, m), 1.86-1.67 (2H, m), 1.65-1.44 (3H, m), 1.44-1.34 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.0, 210.5, 151.5, 151.4, 143.2, 142.0, 141.5, 140.2, 128.9, 128.6, 127.2, 125.9, 114.9, 114.6(9), 114.6(7), 113.4, 68.9, 67.3, 56.0, 55.9, 52.1, 51.3, 51.0, 50.1, 49.9, 46.9, 39.3(4), 39.2(8), 26.5, 24.2, 23.7, 23.6, two peaks were not found probably due to overlapping; HRMS (ESI): Calcd for $C_{21}H_{23}O_2NNa^+$ ([M+Na]$^+$) 344.1621. Found 344.1611.



3w **6**

To a solution of **3w** (32.7 mg, 0.071 mmol, 1 equiv) in CH_2Cl_2 (1.4 mL, 0.05 M) was added trifluoroacetic acid (TFA) (27.2 μL, 0.36 mmol, 5 equiv) dropwise at 0 °C, and the resulting mixture was allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was diluted with water and the extractive work-up was conducted with CH_2Cl_2. The combined organic layers were washed with saturated aqueous solution of $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated. The resulting crude material was purified by column chromatography on silica gel (hexane/EtOAc = 3:1 to 1:1 as eluent) to give **6** in 87% yield (17.5 mg, 0.062 mmol, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.13 (10H, m), 6.80-6.73 (4H, m), 5.09 (1H, d, J = 8.0 Hz), 4.65 (1H, d, J = 5.6 Hz), 3.72 (3H, s), 3.71 (3H, s), 2.98-2.83 (1H, m), 2.88 (1H, dd, J = 19.2, 9.2 Hz), 2.69 (1H, dd, J = 17.0, 9.8 Hz), 2.42 (1H, dd, J = 17.0, 9.8 Hz), 2.37-2.27 (1H, m), 2.30 (1H, dd, J = 19.2, 9.2 Hz), 1.25 (3H, d, J = 6.4 Hz), 0.71 (3H, d, J = 6.8 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 174.4, 157.0, 156.8, 140.3, 137.5, 131.9, 131.3, 128.9, 128.8, 128.1, 128.0, 127.2, 126.7, 124.6, 123.7, 114.0(9), 114.0(5), 72.1, 68.8, 55.4(8), 55.4(5), 39.5, 38.8, 37.7, 32.7, 18.9, 16.1; HRMS (ESI): Calcd for $C_{18}H_{19}O_2NNa^+$ ([M+Na]$^+$) 304.1308. Found 304.1308.

Supplementary References

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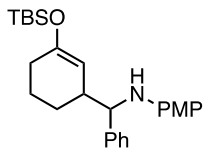
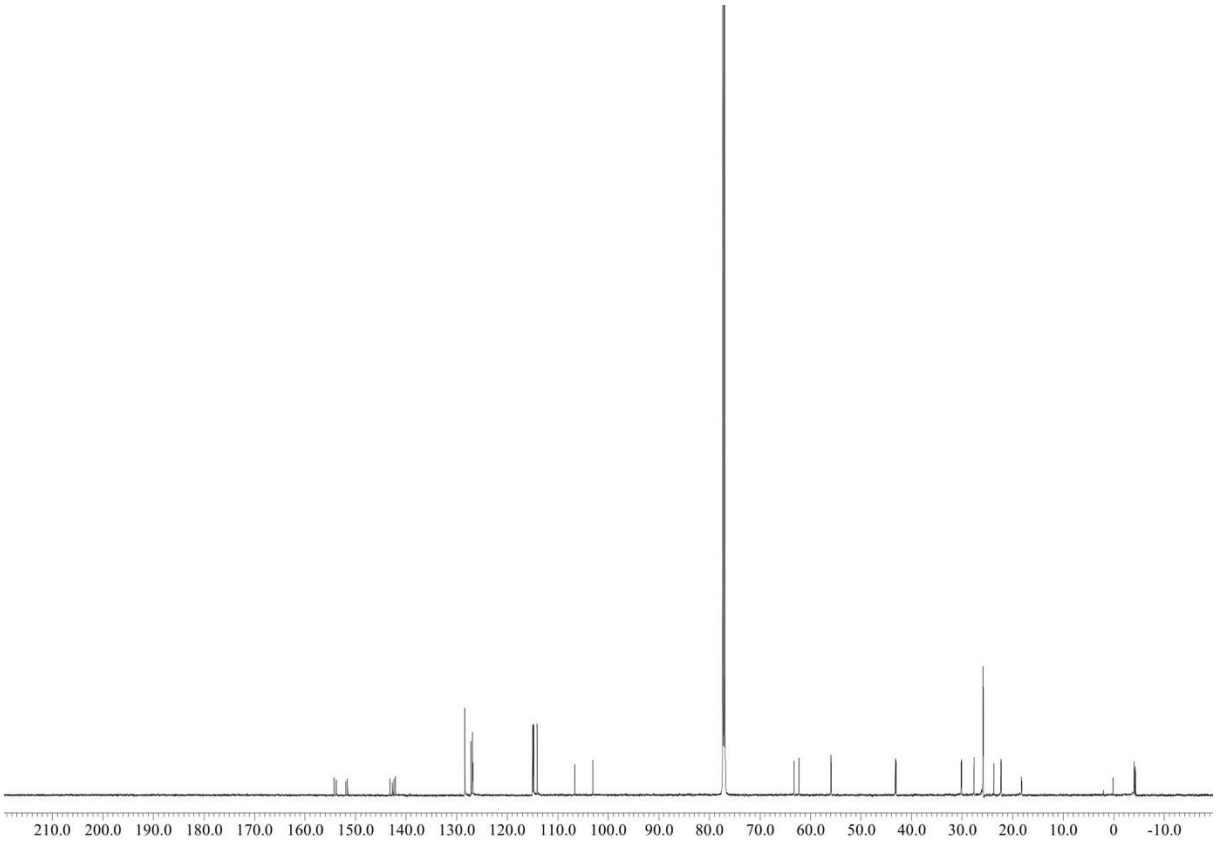
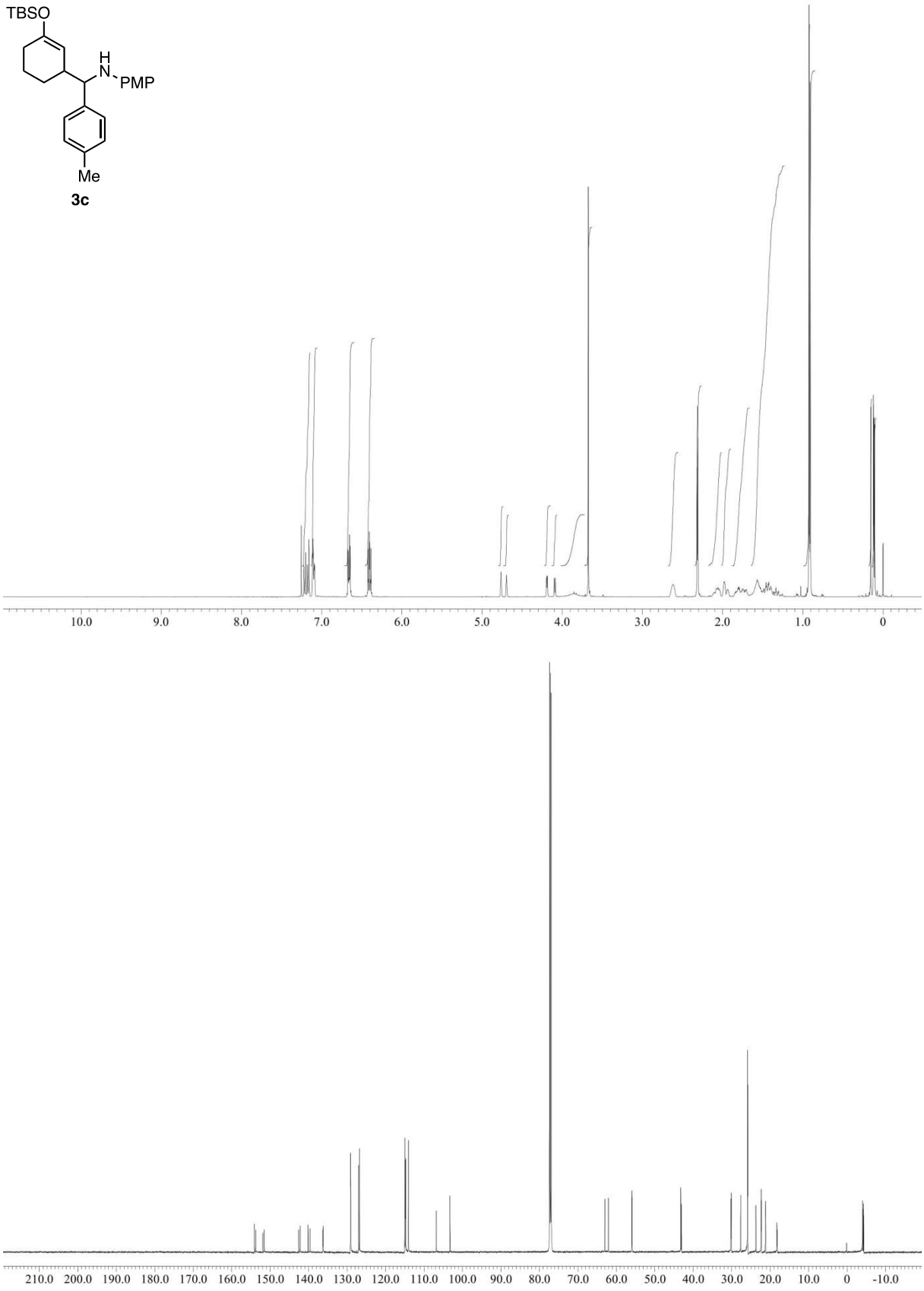
2. M. S. Lowry, W. R. Hudson, R. A. Jr. Pascal, S. Bernhard, *J. Am. Chem. Soc.* 2004, **126**, 14129-14135.
3. J. Jia, R. Kancherla, M. Rueping, L. Huang, *Chem. Sci.* 2020, **11**, 4954-4959.
4. K. Ohmatsu, T. Nakashima, M. Sato, T. Ooi, *Nat. Commun.* 2019, **10**, 2706.

^{1}H and ^{13}C NMR Spectra of Products



3b

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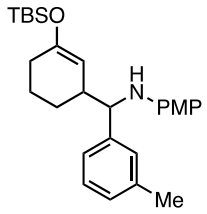
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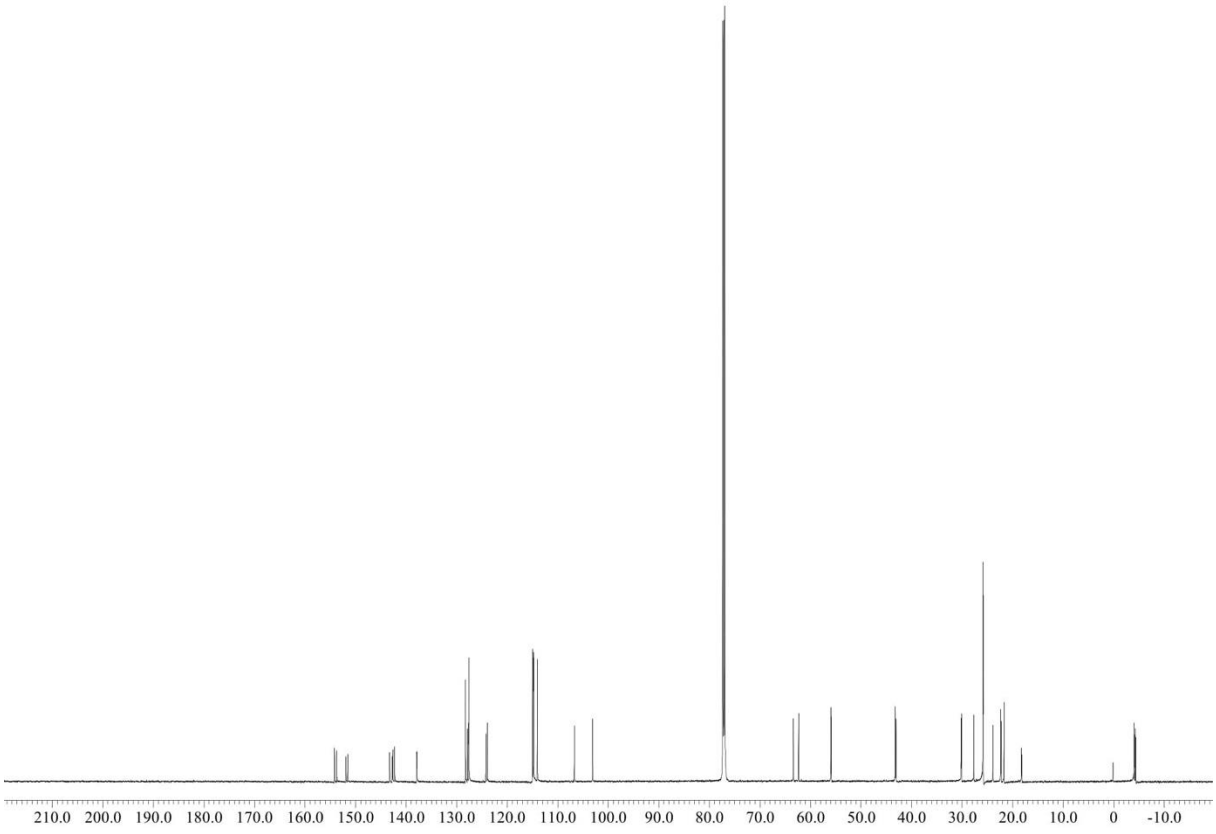
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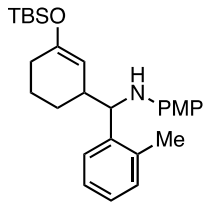
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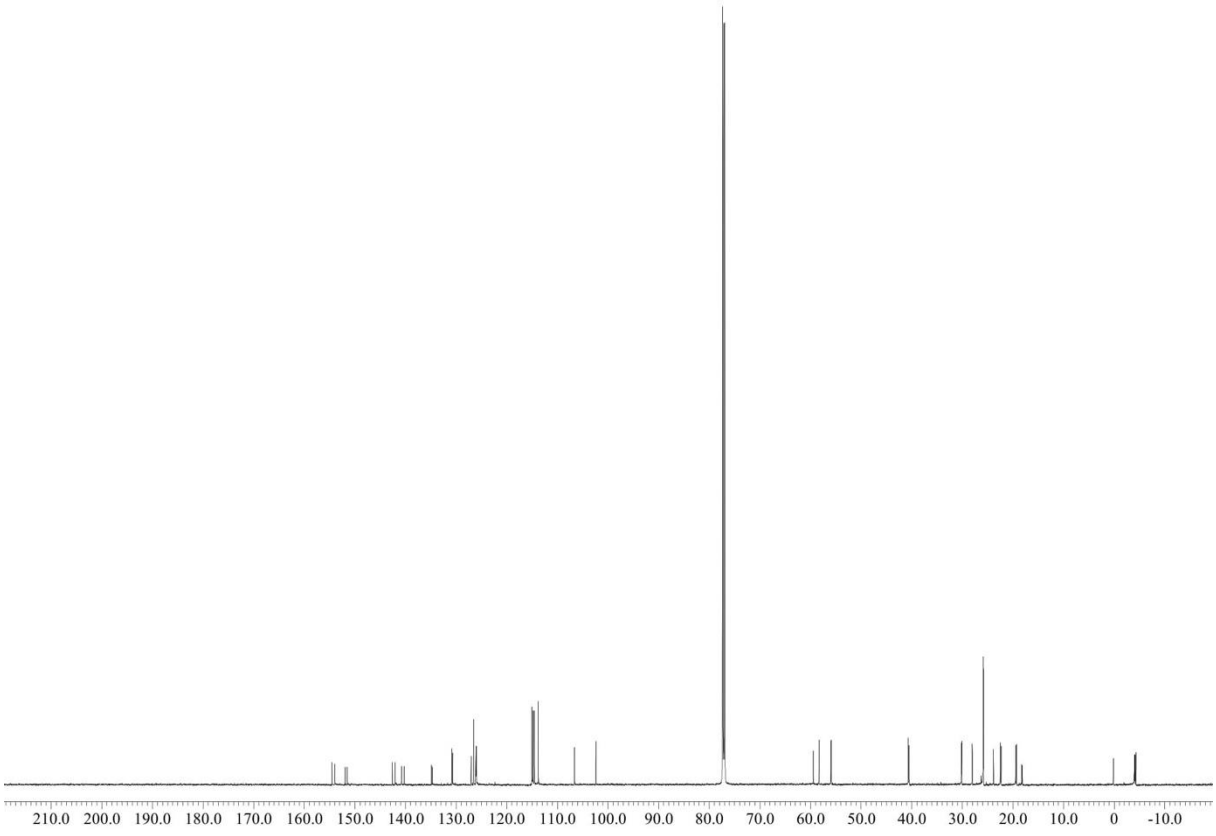
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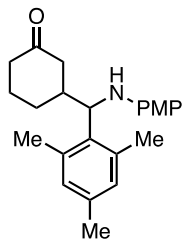
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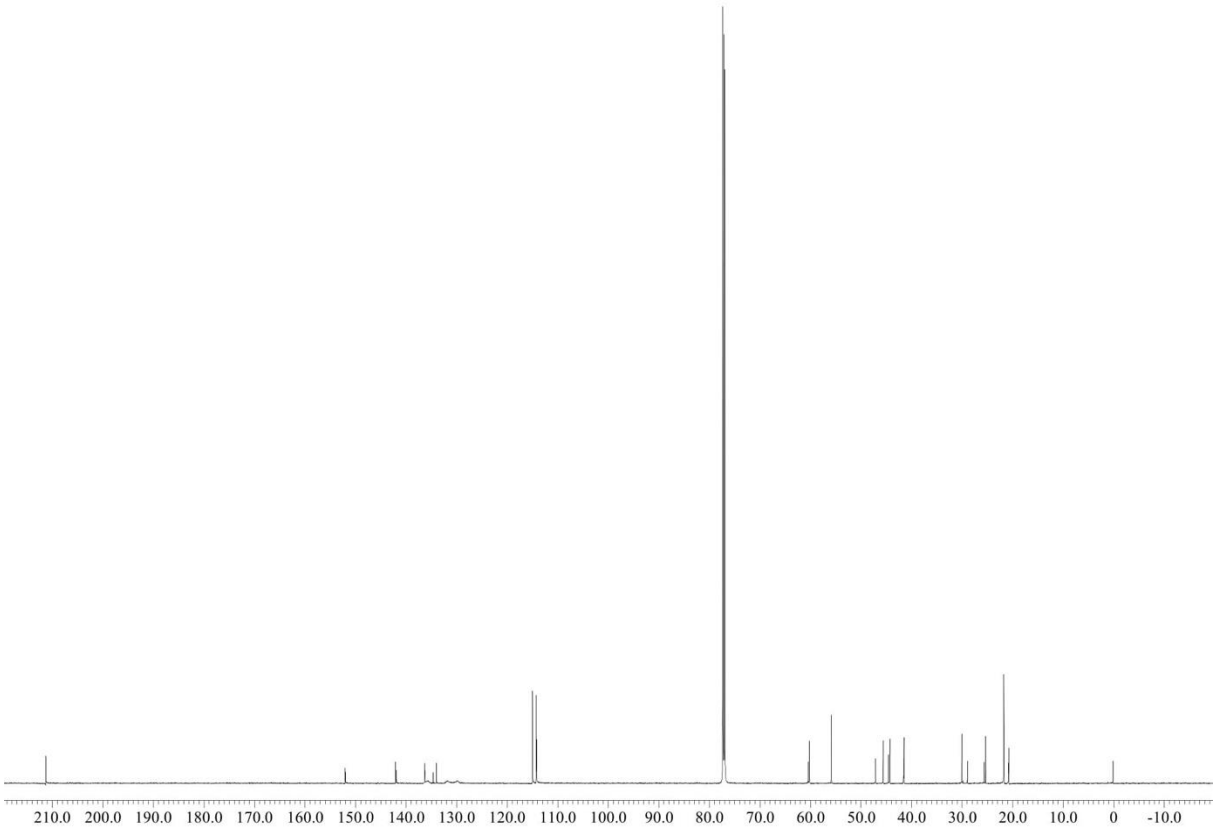
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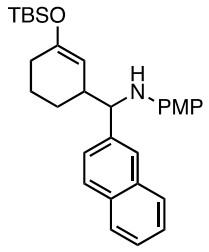
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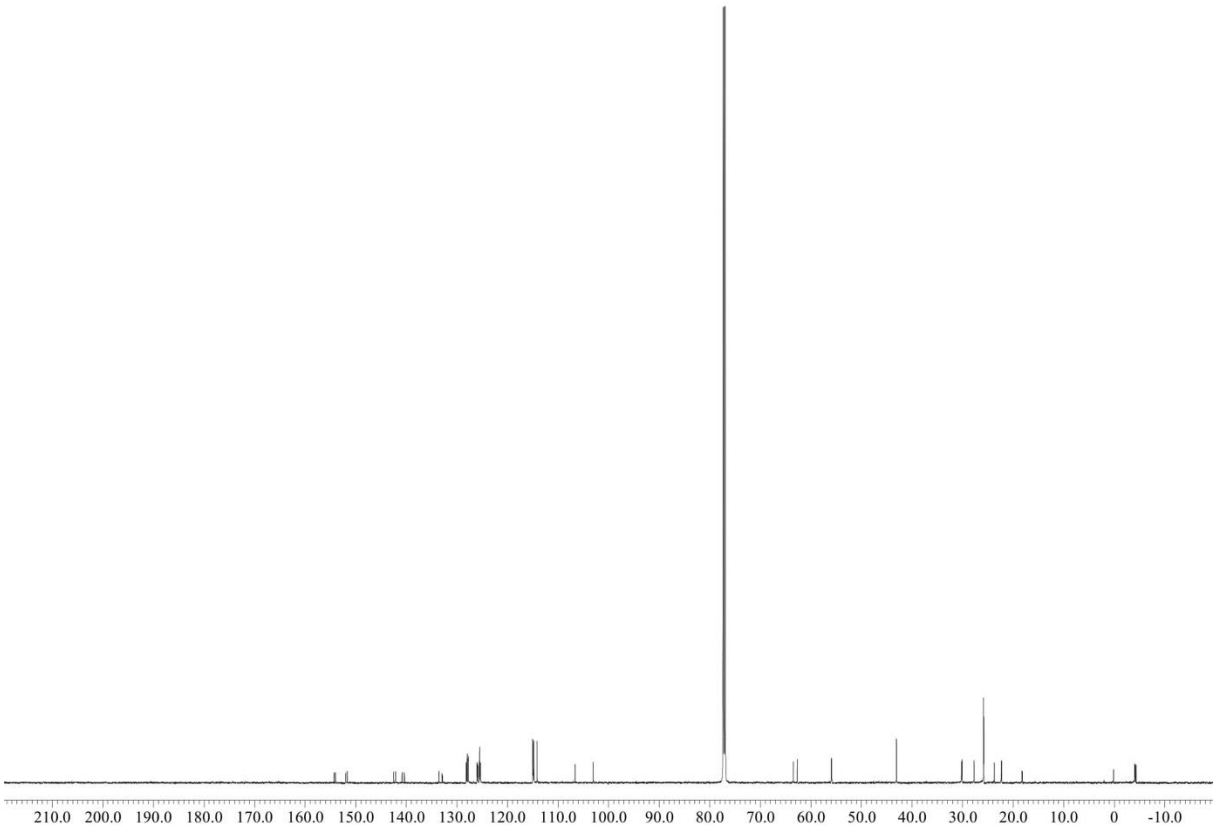
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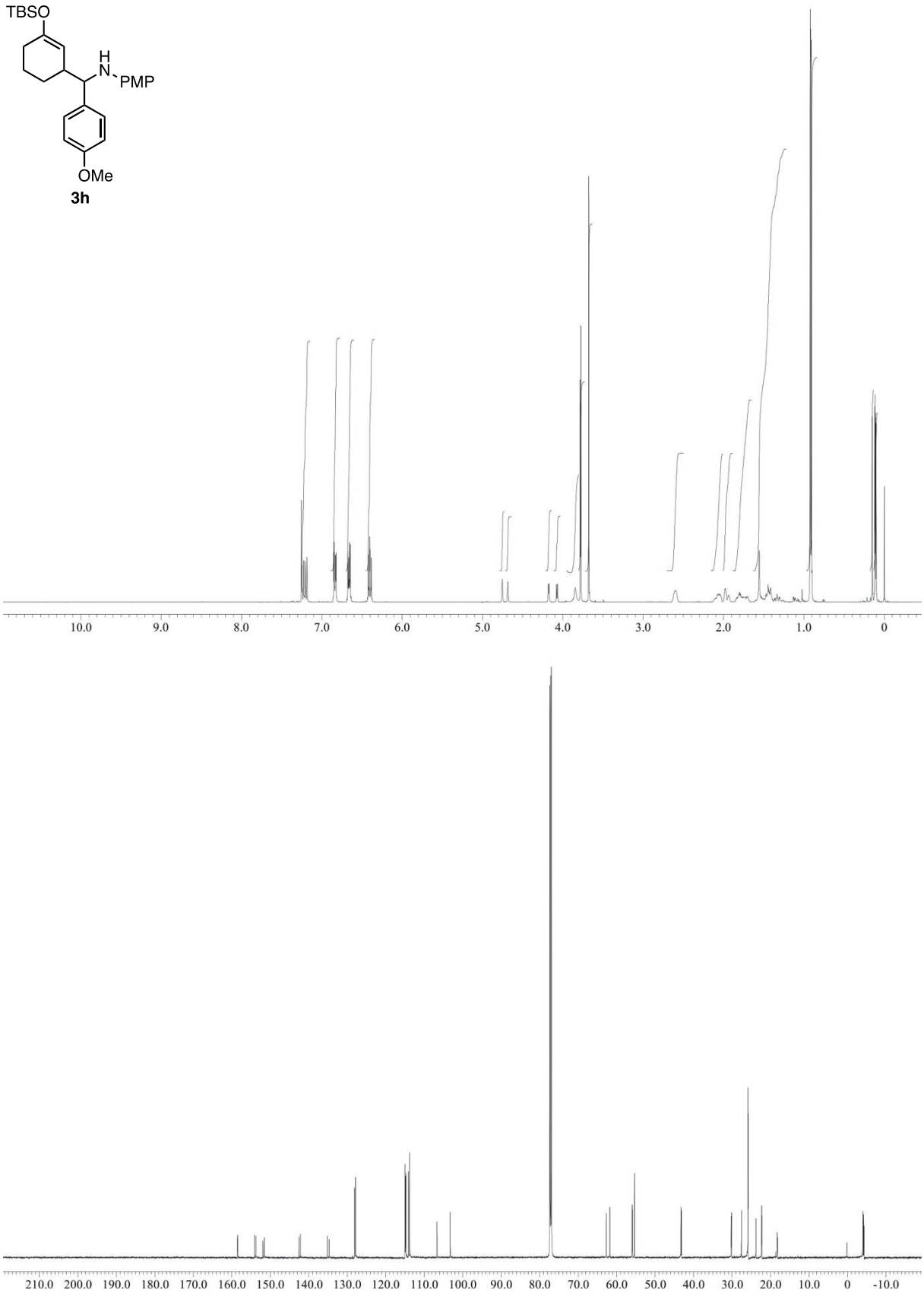
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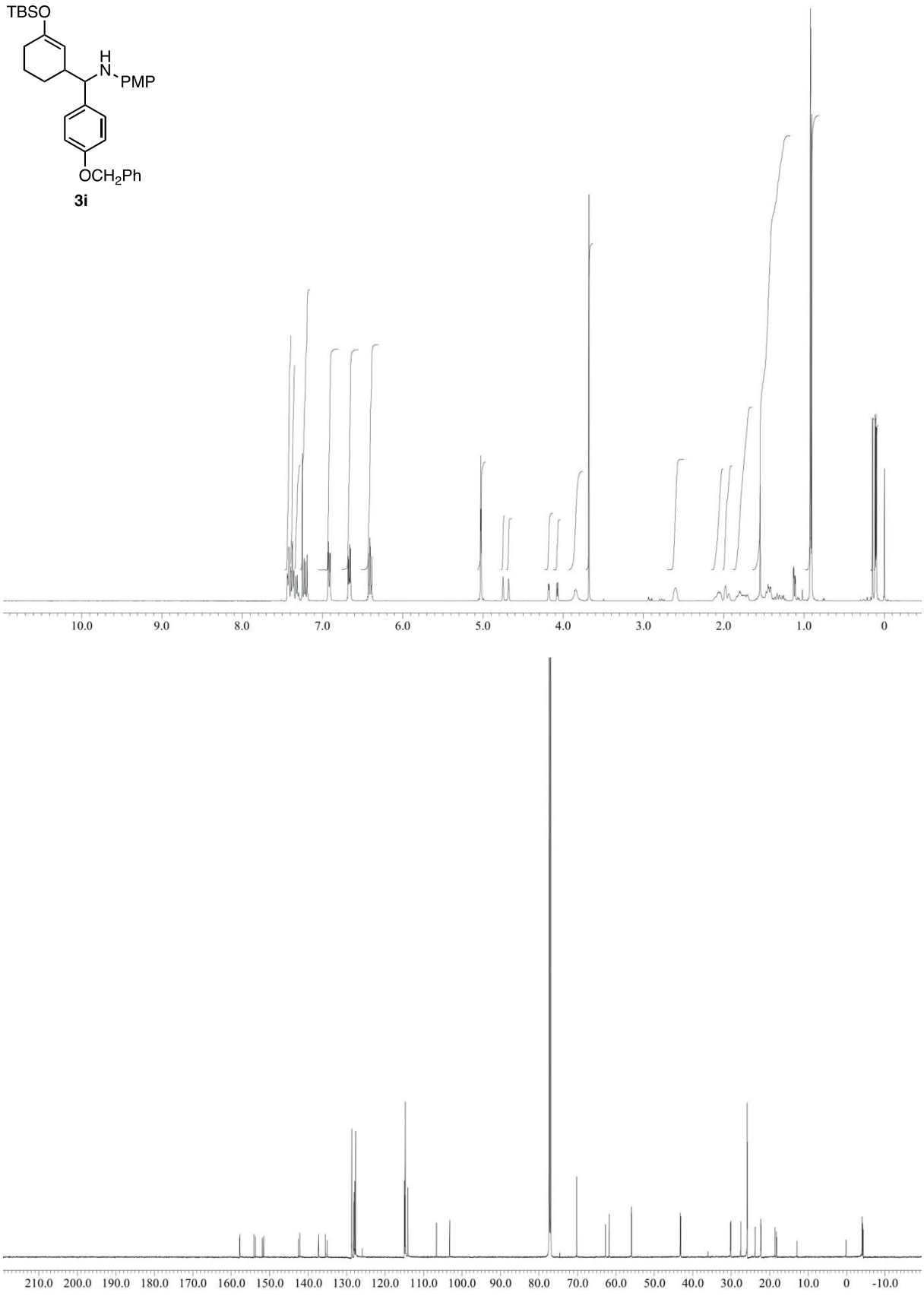
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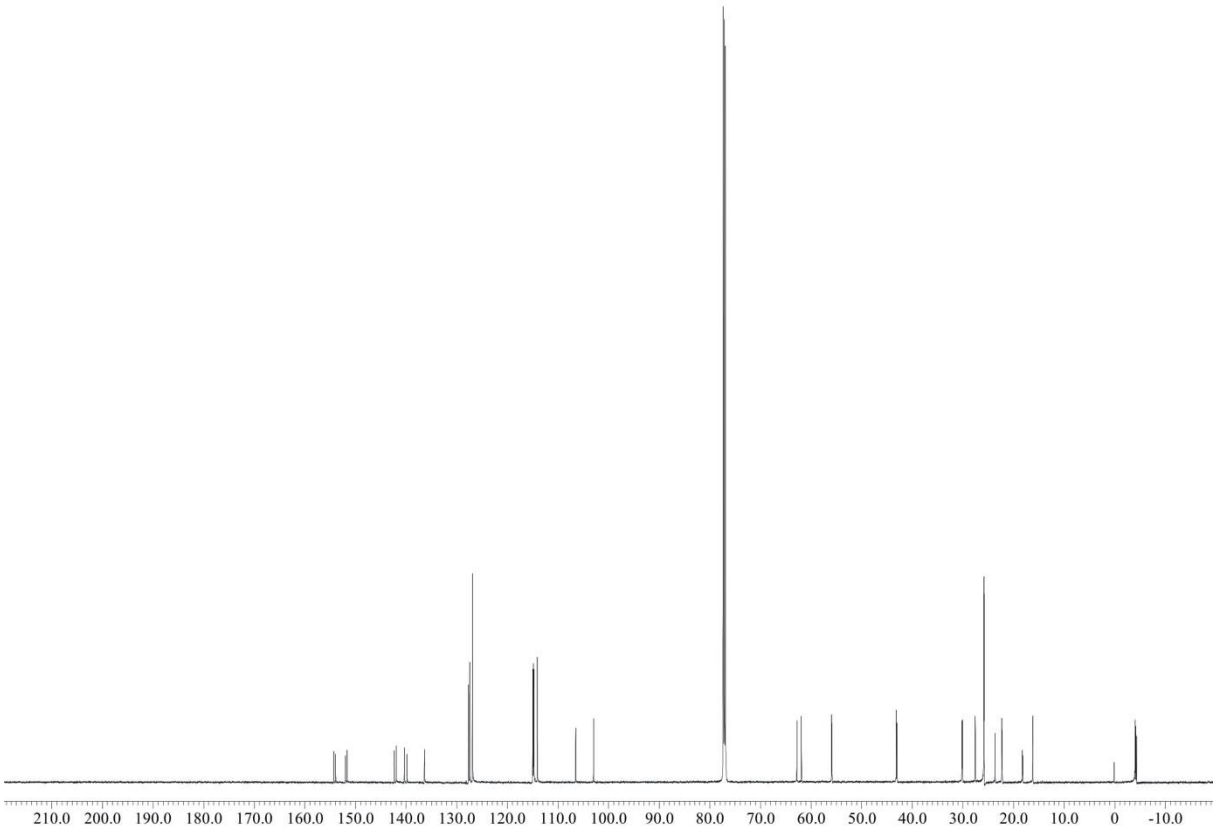
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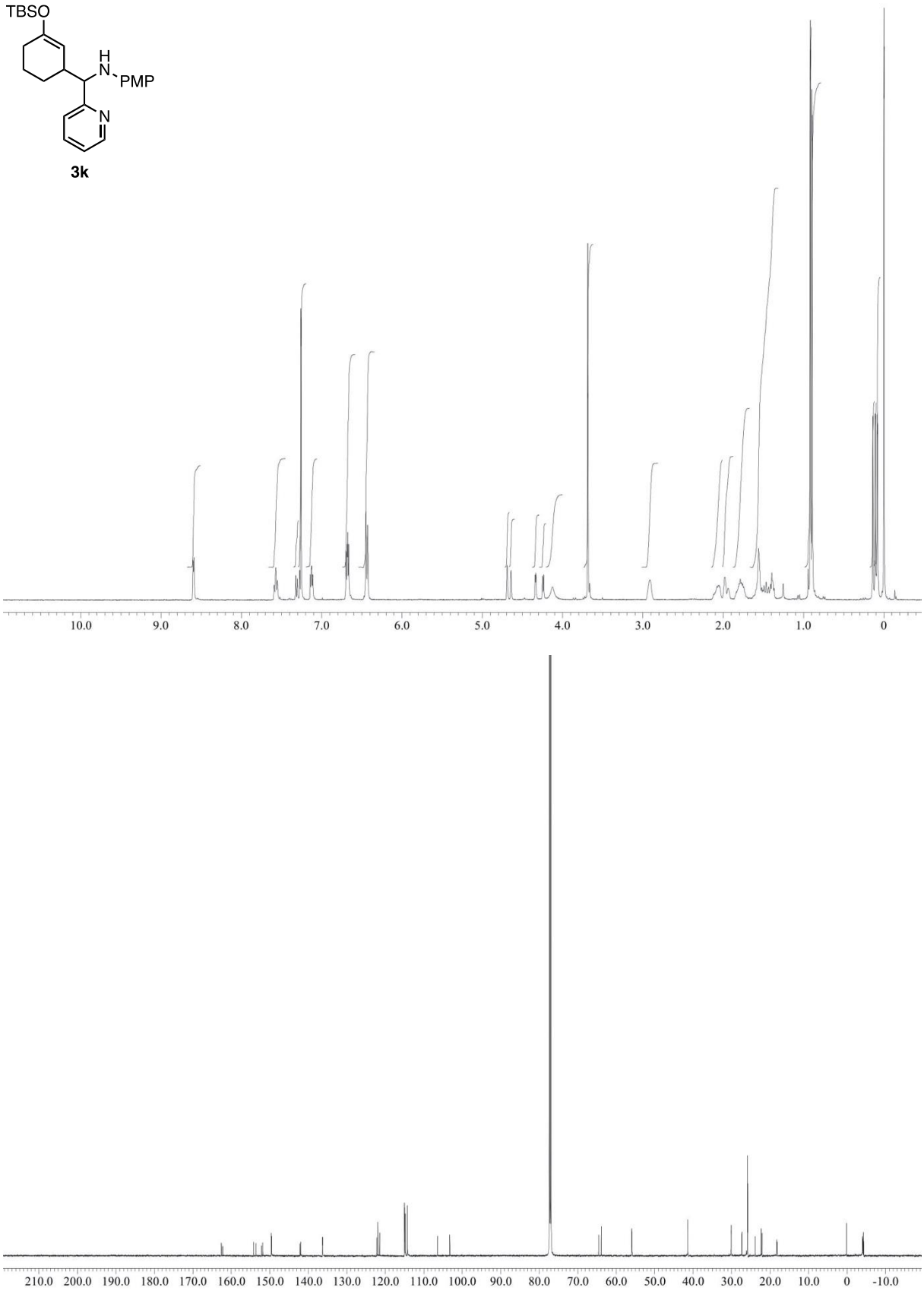
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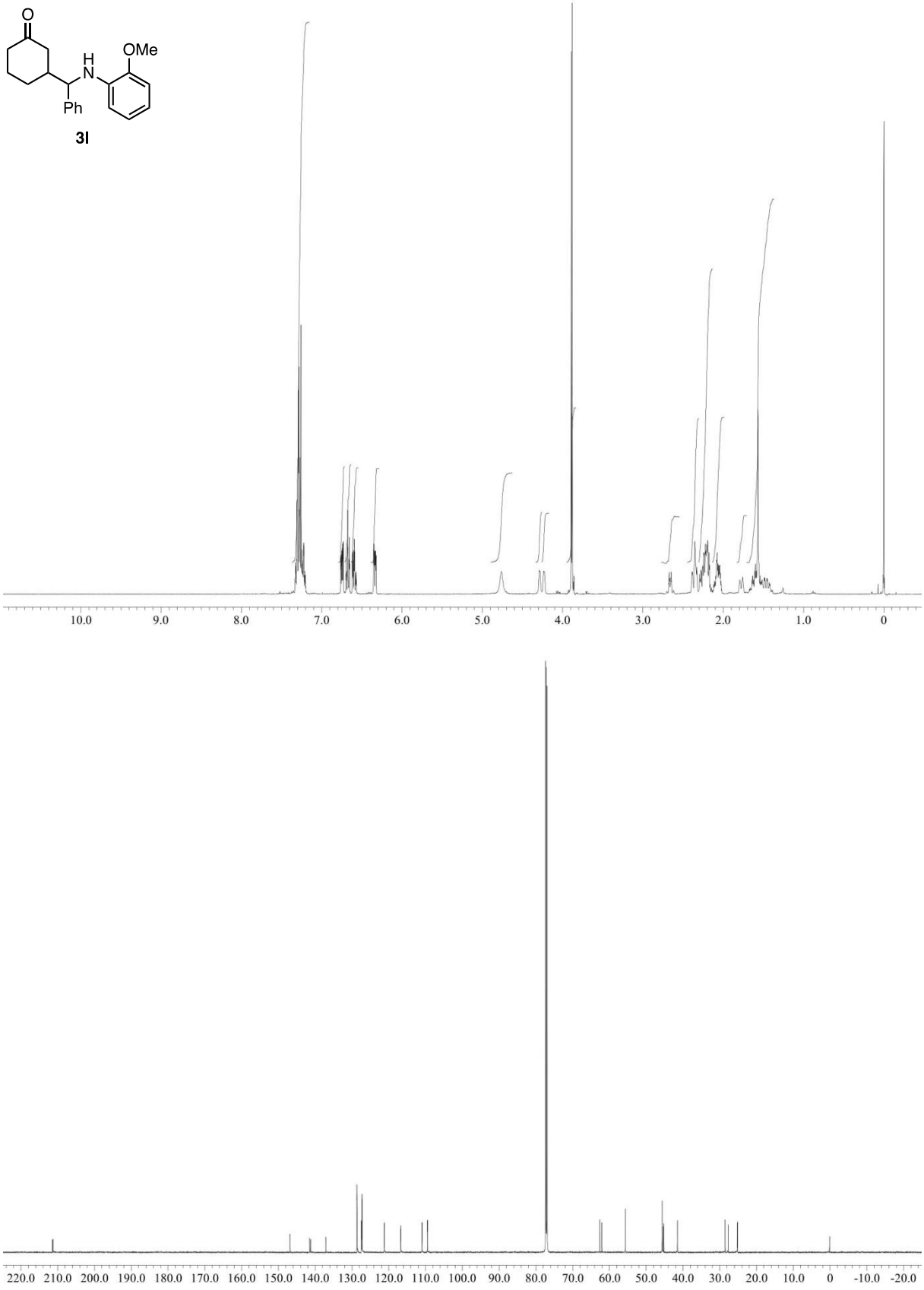
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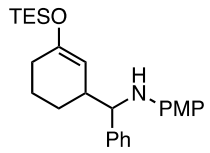
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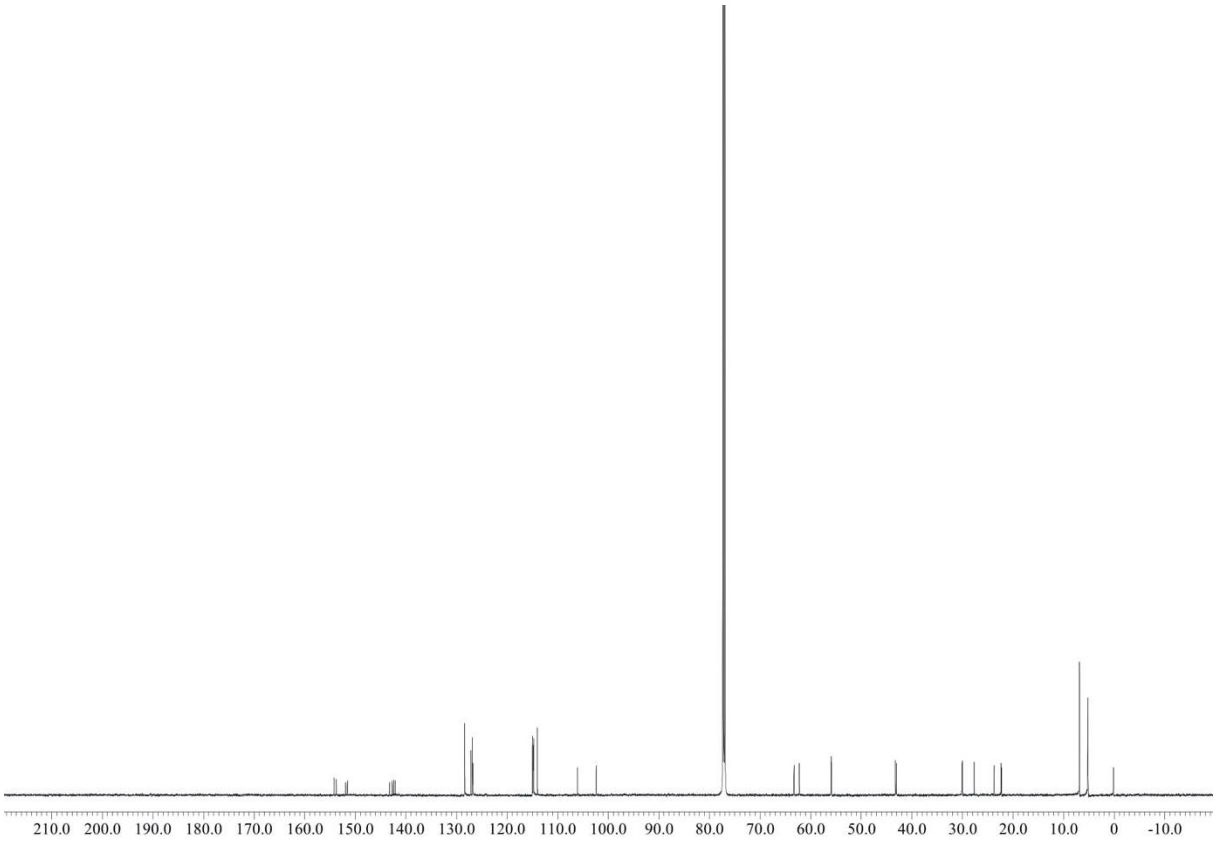
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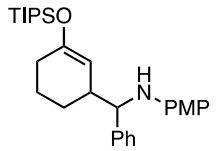
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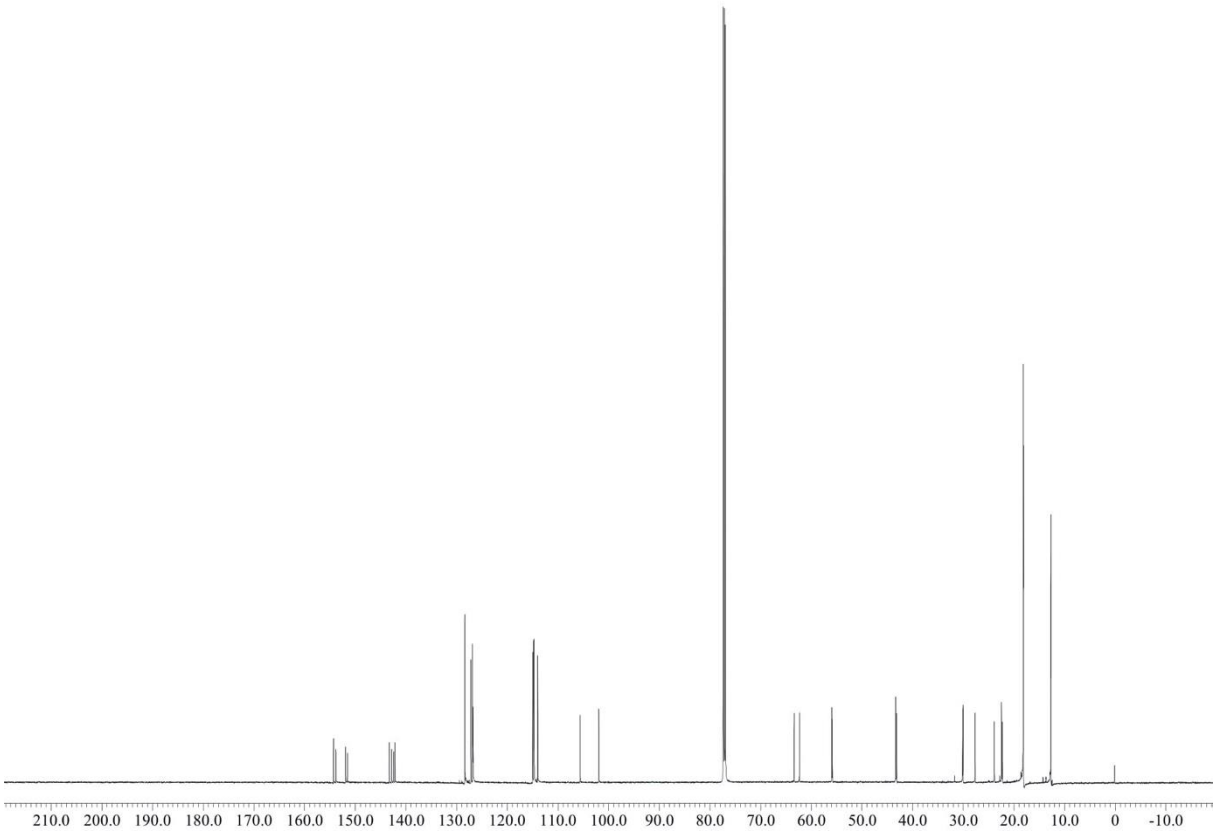
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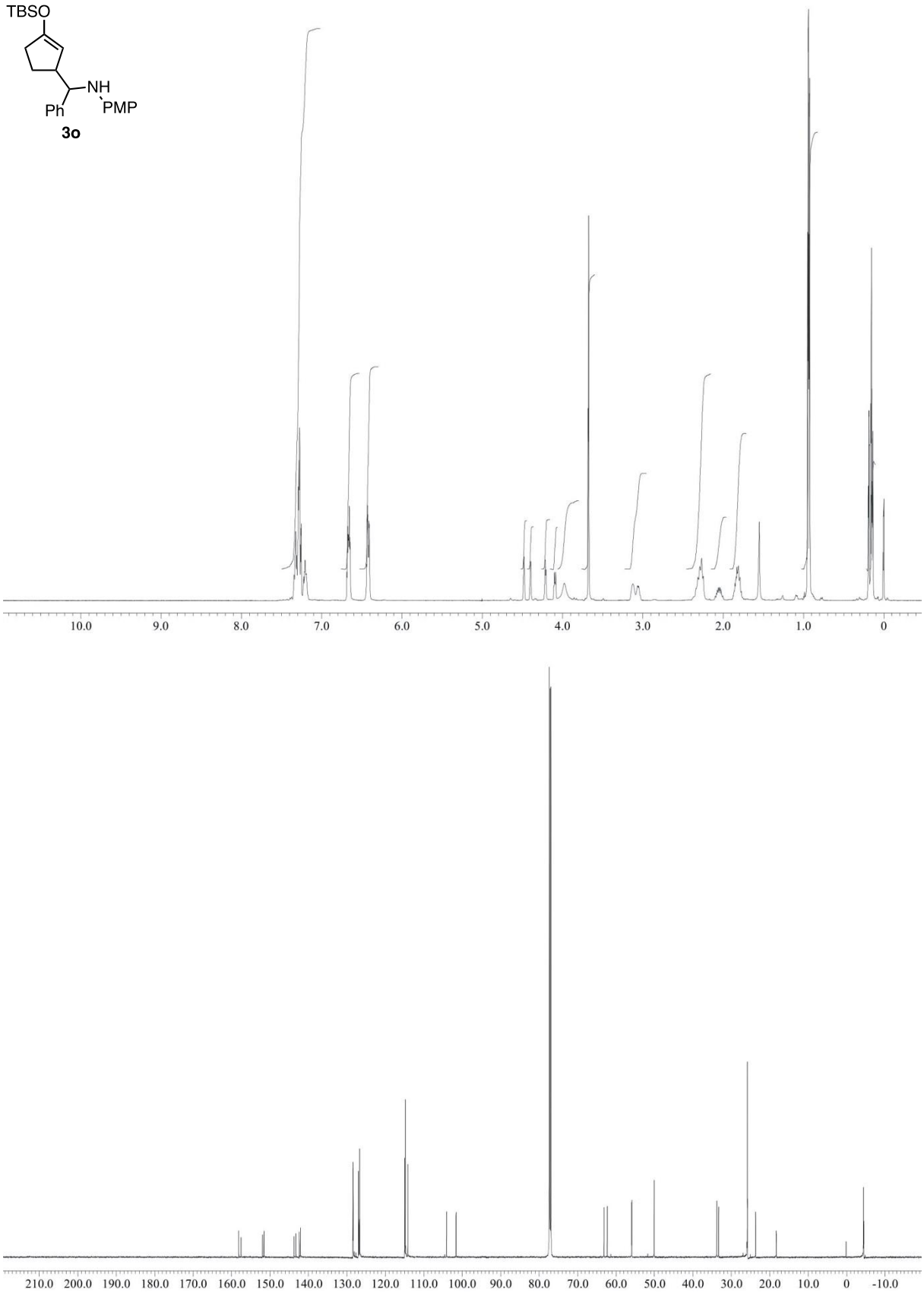
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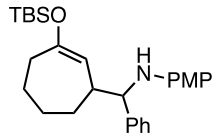
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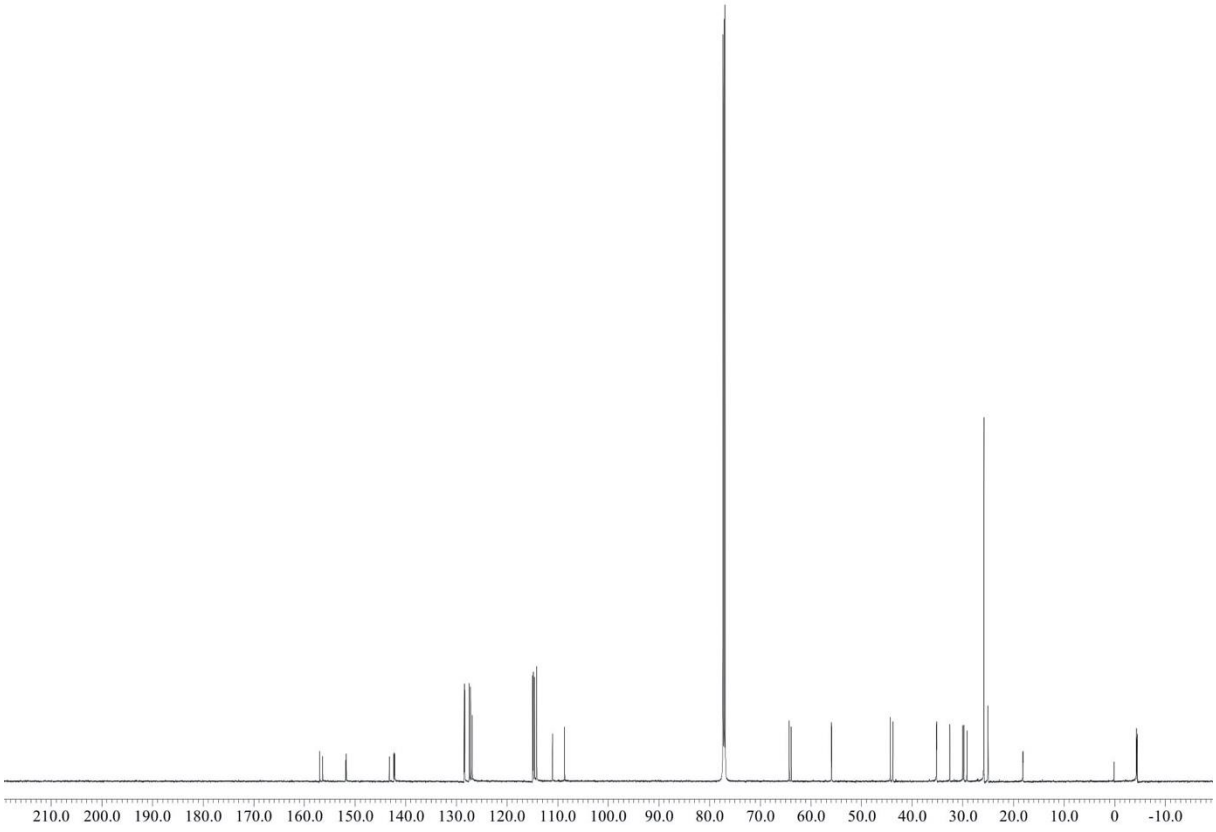
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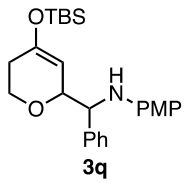
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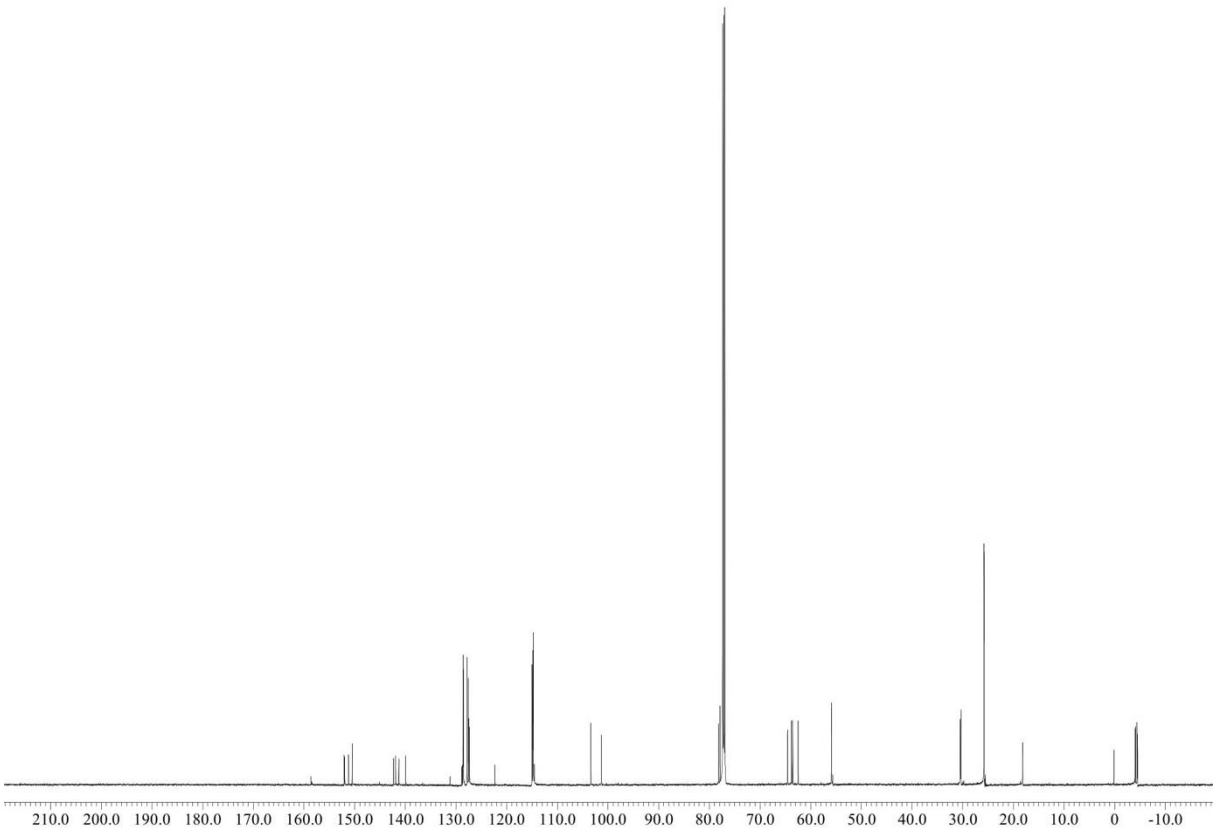
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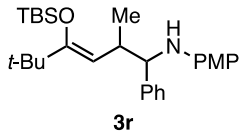
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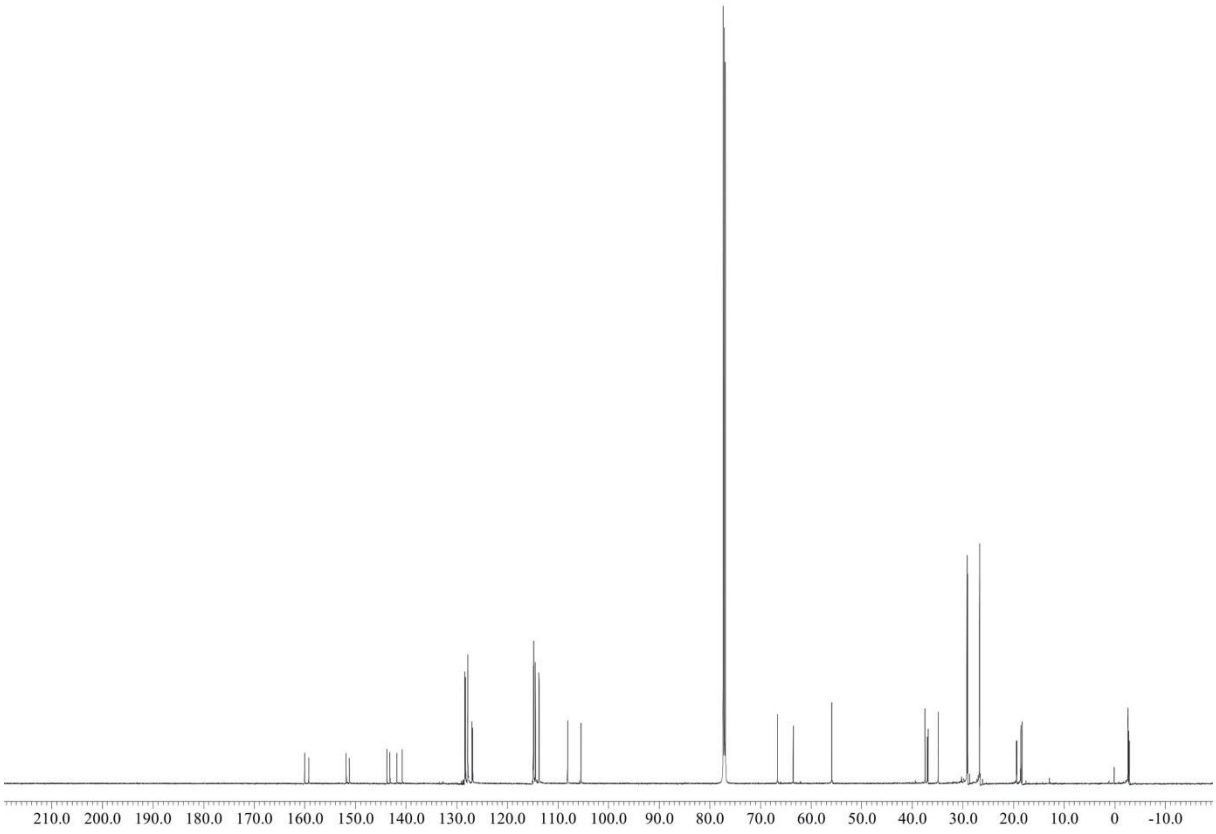
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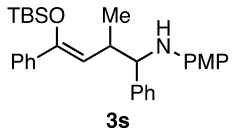
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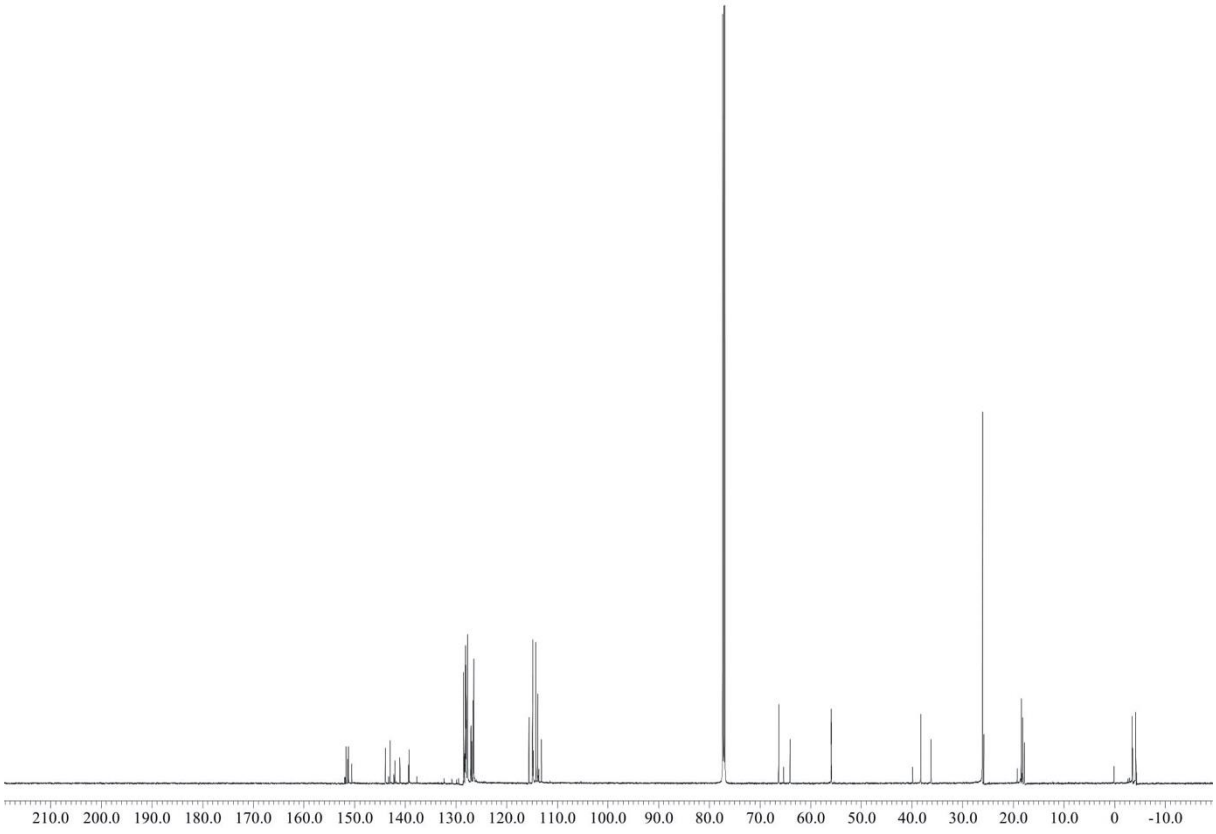
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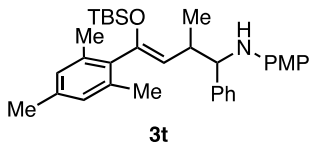
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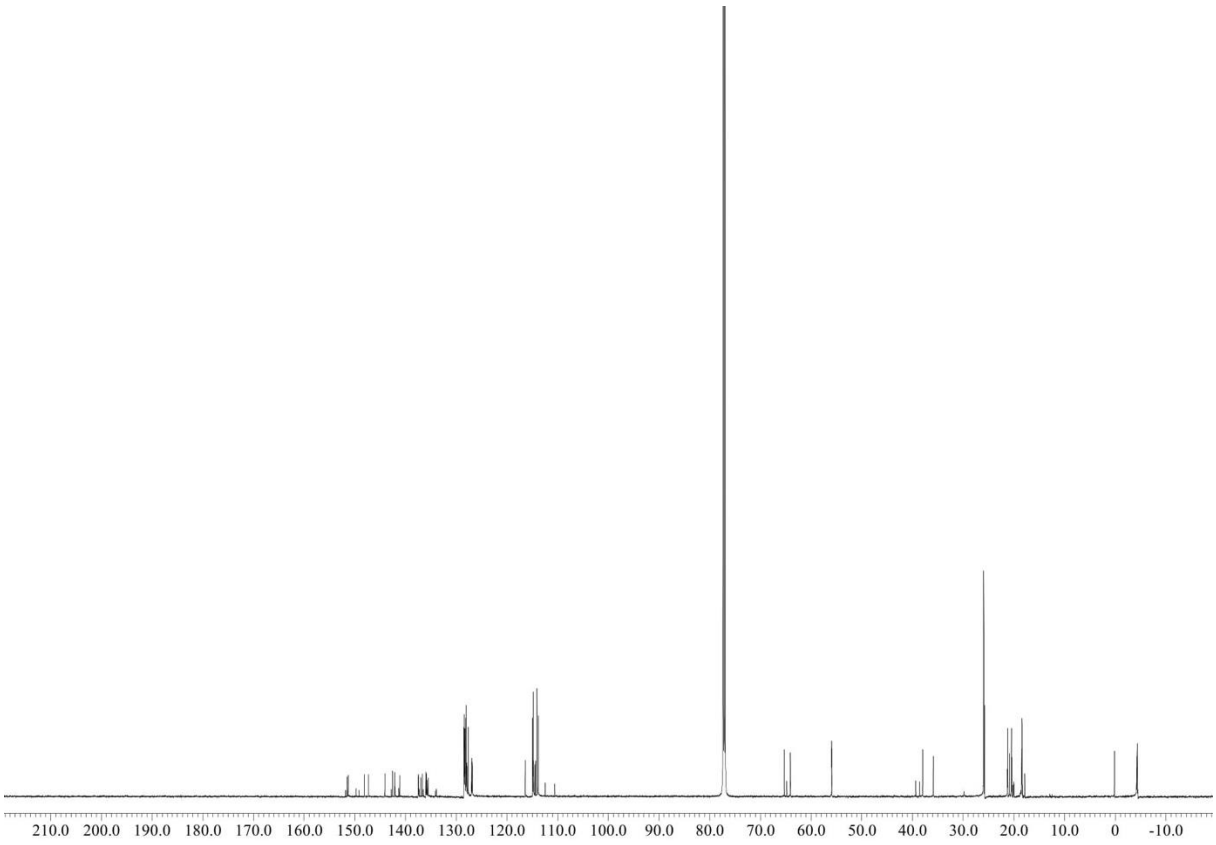
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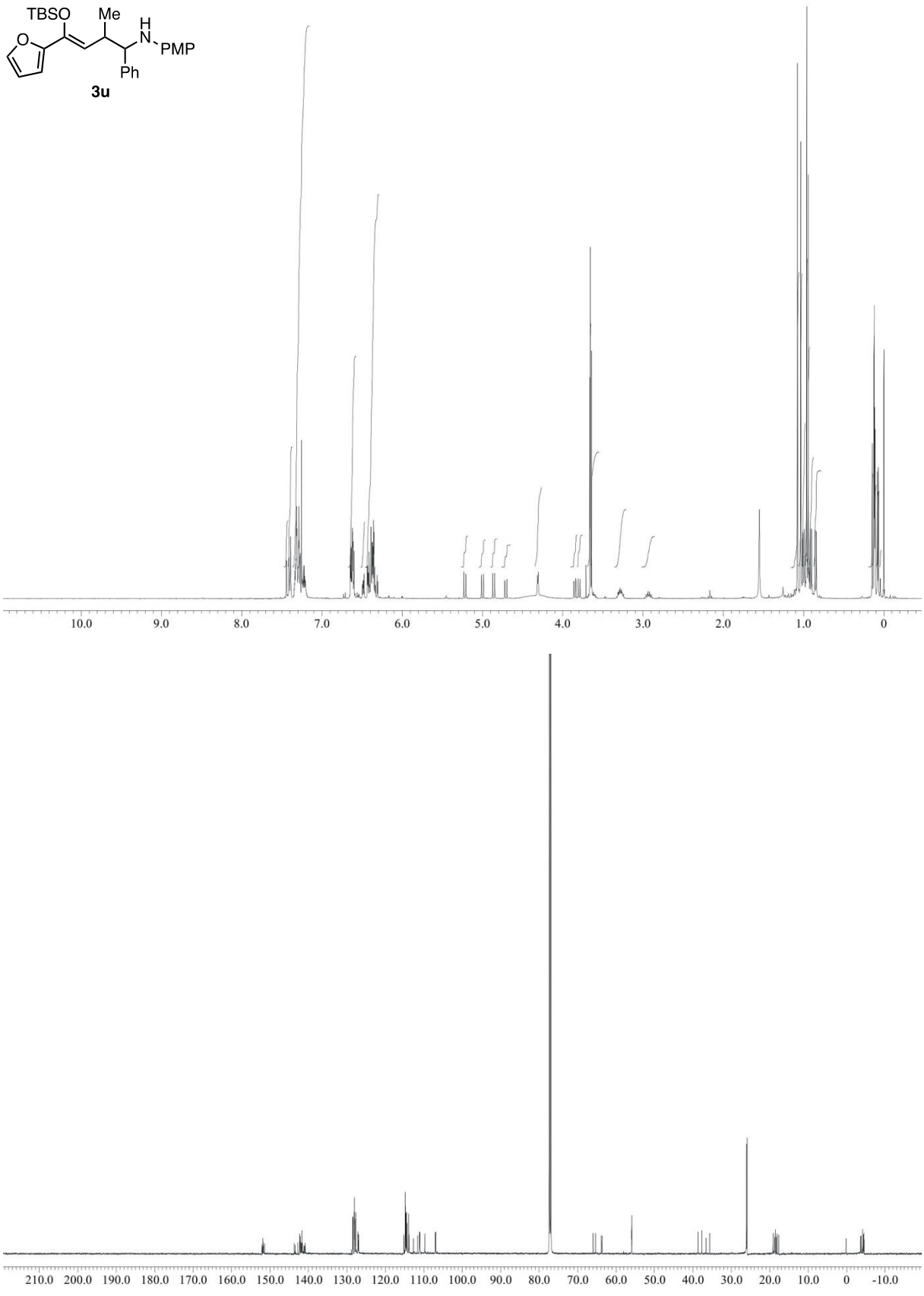
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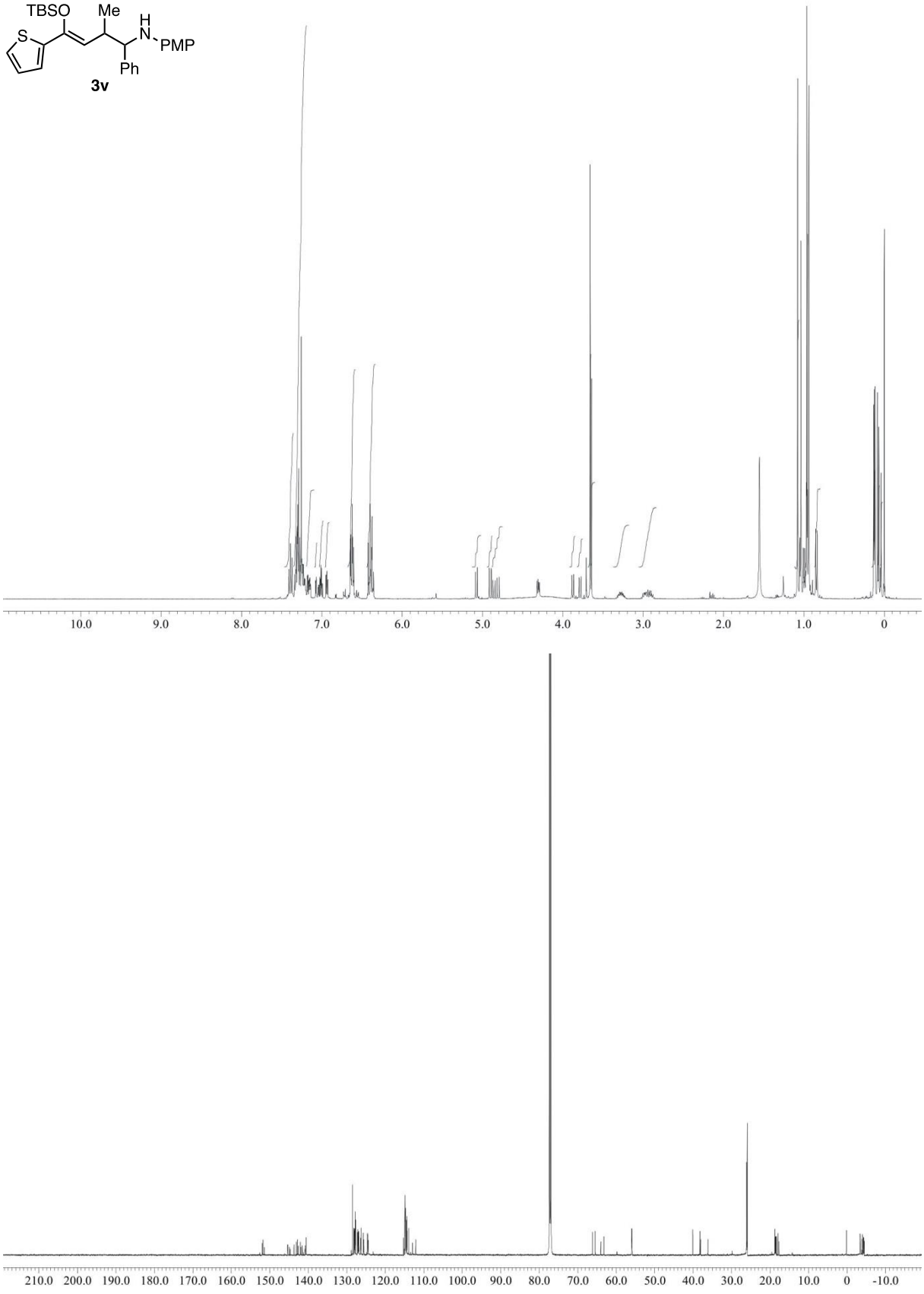
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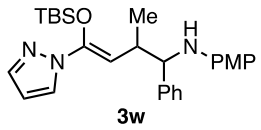
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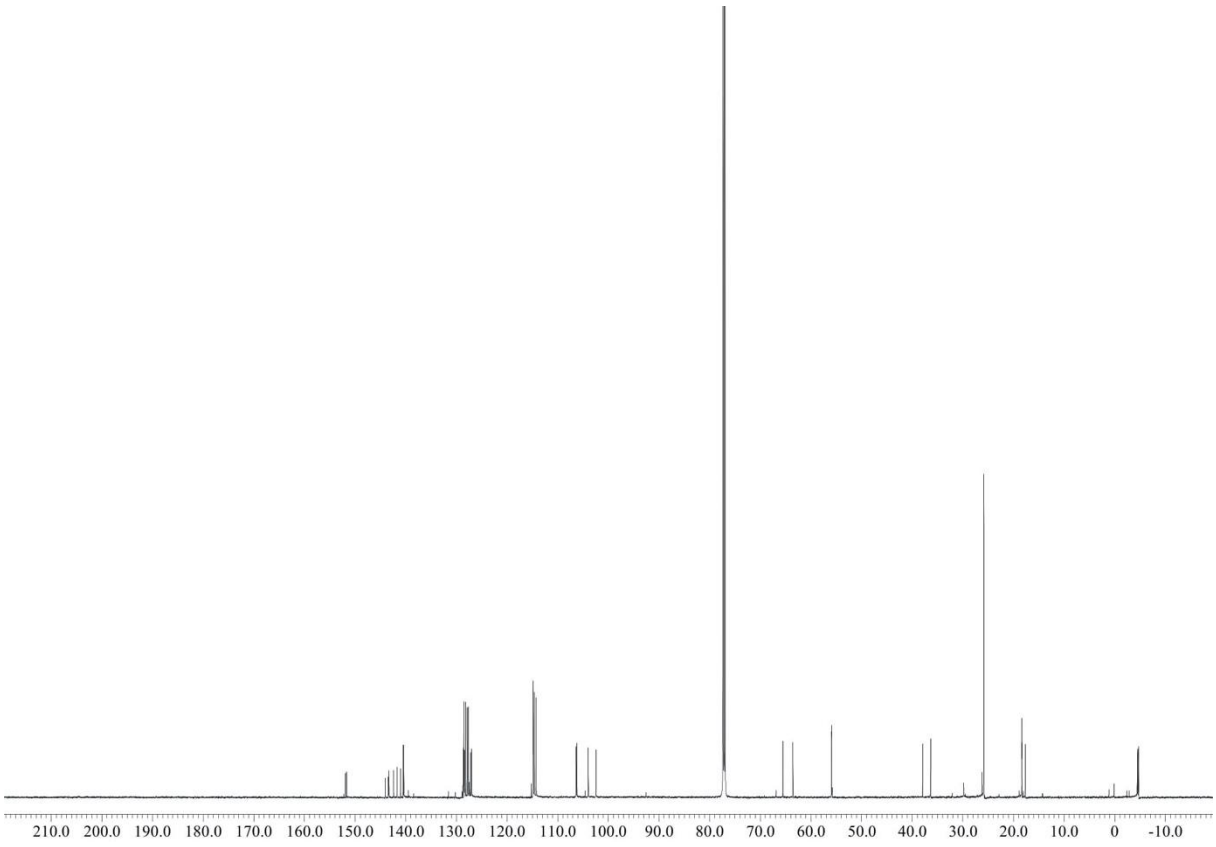
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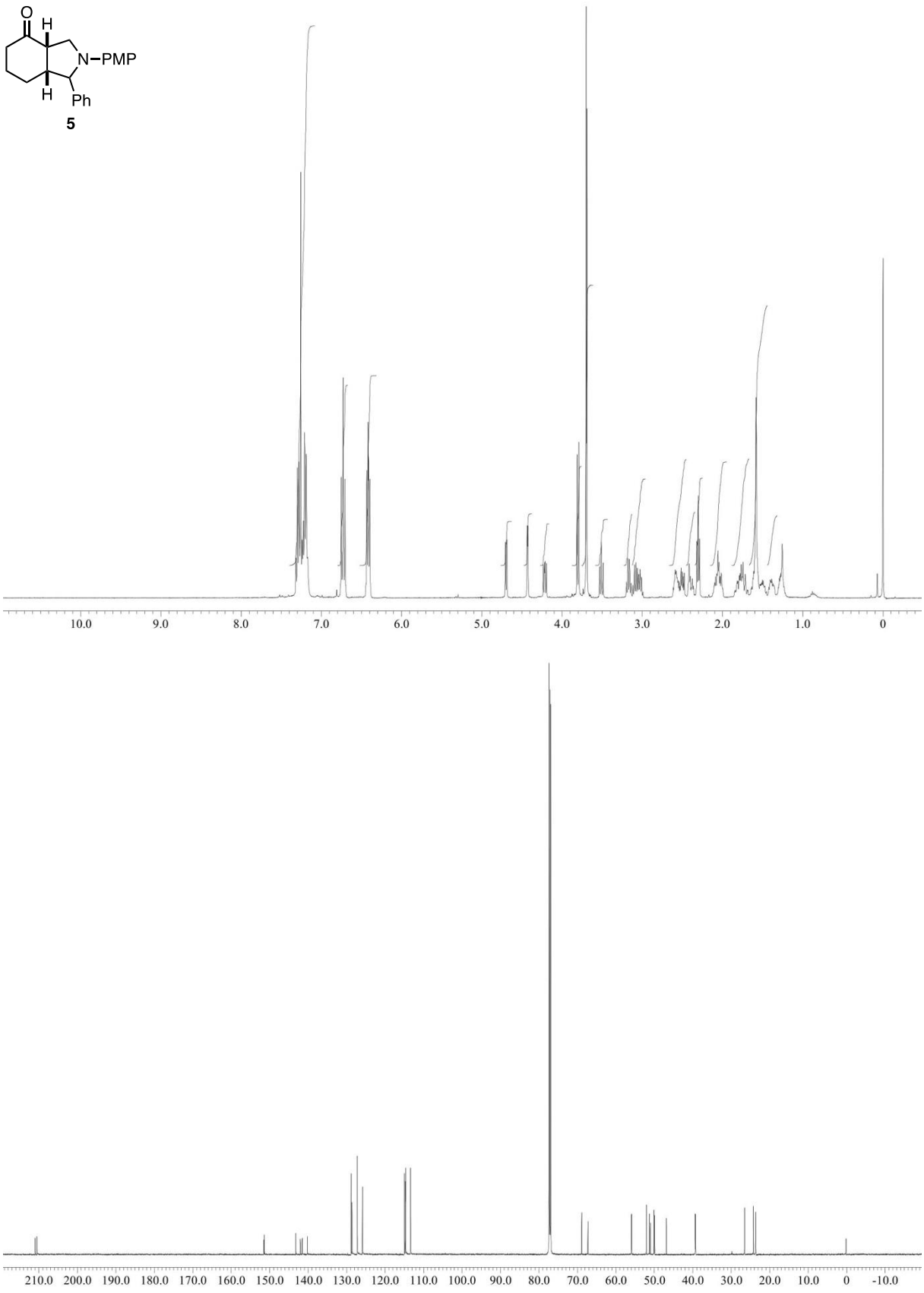
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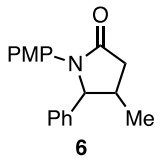
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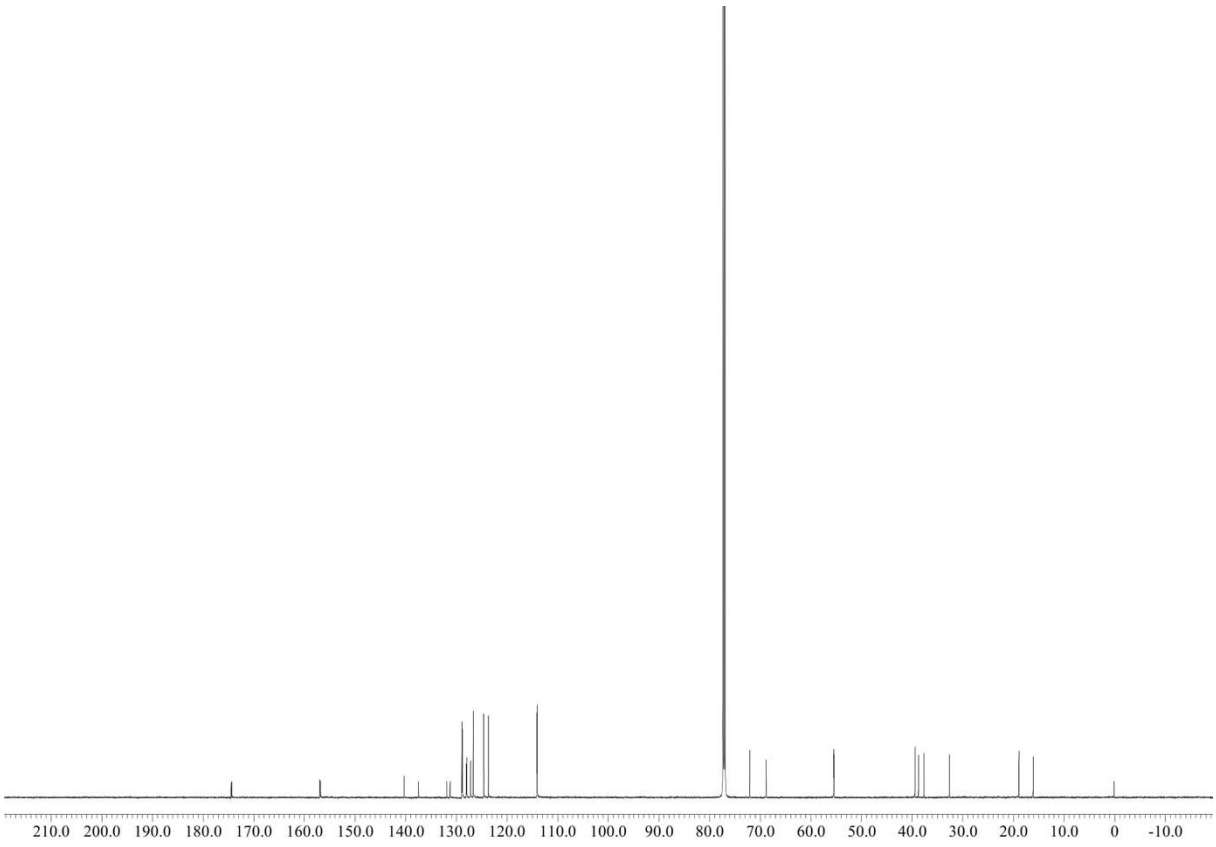
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