Supporting Information for

Organocatalytic aminocarbonylation of α, β-unsaturated ketones with N, N-dimethyl carbamoylsilane

Shou-Shan Yang, Ying-Zheng Ren, Yu-Yu Guo, Guang-Fen Du*, Zhi-Hua Cai, Lin He*

Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan/School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang Uygur Autonomous Region, 832000, People's Republic of China.

E-mail: duguangfen@shzu.edu.cn; helin@shzu.edu.cn

Contents:

1. General methods and typical experimental procedures

1.1 General methods

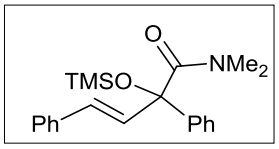
Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F_{254}. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) were recorded on a Bruker-DMX 400 spectrometer in $CDCl_3$, with tetramethylsilane as an internal standard and reported in ppm (δ). Chalcones (Table 2, **2a**-**o**, **2r**)[1], ynone (Table 2, **2u**)[2] and other enones (Table 2, **2p-q**, **2s**)[3] were prepared according to literature procedure. Carbamoylsilane **1a** was purchased from Shanghai Shenghong Co., Ltd. Phosphazene bases *t*-Bu-P_4, *t*-Bu-P_1 and *t*-Bu-P_2 were purchased from Sigma-Aldrich. All other chemicals were obtained from commercial supplies and used as received without any further purification. Anhydrous THF and toluene were distilled from sodium and benzophenone. Anhydrous DMF, DMSO and CH_3CN were obtained from commercial suppliers. Petroleum ether, where used, has a boiling point range of 60-90 ^{o}C.

1.2 General procedure for *t*-Bu-P_4-catalyzed aminocarbonylation reaction of ketones: To a solution of *t*-Bu-P_4 in hexane (0.80 M, 13 μL, 10 mol%) was added to a stirred solution of carbamoylsilane **1a** (24 μL,

0.15 mmol, 1.5 equiv.) and ketone **2** (0.1 mmol) in dry DMF (1 mL) under nitrogen. The resulting mixture was stirred at room temperature until full consumption of **2** that was indicated by TLC (24h). Then, the mixture was diluted with 15.0 mL EtOAc and washed with water (2.0 mL × 3). The organic layer was separated, dried over anhyd. Na_2SO_4 and filtered. The solvent was then removed under reduced pressure and the crude material was purified by flash column chromatography (silica gel, PE/EtOAc (v : v) = 20:1~5:1) to give the desired product **3**.

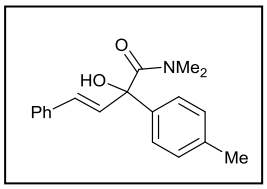
2. Spectroscopic data for all products

(E)-N,N-dimethyl-2,4-diphenyl-2-((trimethylsilyl)oxy)but-3-enamide



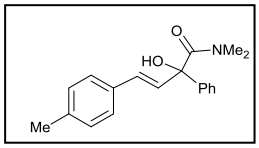
(3a)[4]: 25.0 mg, 73% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.38 – 7.13 (m,9H), 5.90 (d, J = 16.2 Hz, 1H), 2.94 (s, 3H), 2.76 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 142.2, 136.8, 134.1, 131.7, 128.4, 128.1, 127.6, 127.2, 126.6, 125.3, 81.8, 37.7, 37.1, 1.85.

(E)-2-hydroxy-N,N-dimethyl-4-phenyl-2-(*p*-tolyl)but-3-enamide (3b):



23.5 mg, 80% yield; pale yellow solid; m.p. 182.5-182.7 ℃ ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.33 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 7.10 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 15.6 Hz, 1H), 6.70 (d, J = 15.6 Hz, 1H), 5.63 (s, 1H), 3.00 (s, 3H), 2.66 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 139.6, 138.0, 136.6, 132.6, 129.7, 128.6, 128.0, 127.5, 126.8, 126.3, 77.7, 38.6, 37.7, 21.1; IR (KBr): v = 3658, 2916, 1718, 1631, 1458, 1103, 1043, 962, 819 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_2$ $[M+Na]^+$ 318.1465, found 318.1464.

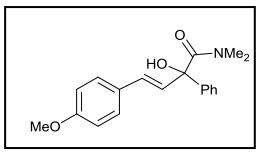
(E)-N,N-dimethyl-2-hydroxy-2-phenyl-4-(*p*-tolyl)but-3-enamide (3c):



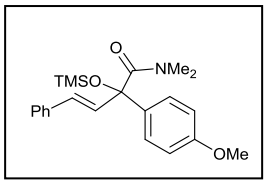
22 mg, 75% yield; white solid; m.p. 191.2-192.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 7H), 7.16 (d, J = 7.6 Hz, 2H), 7.05 (d, J = 15.6 Hz, 1H), 6.73 (d, J = 15.6 Hz,

1H), 5.75 (s, 1H), 3.08 (s, 3H), 2.71 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 142.6, 138.0, 133.7, 132.6, 129.4, 129.0, 128.2, 126.7, 126.4, 126.2, 77.8, 38.5, 37.7, 21.3; IR (KBr): v = 3624, 2922, 1640, 1550, 1446, 1104, 1078, 967, 795 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_2$ $[M+Na]^+$ 318.1465, found 318.1468.

(E)-N,N-dimethyl-2-hydroxy-4-(4-methoxyphenyl)-2-phenylbut-3-enamide (3d): 24 mg, 79% yield; pale yellow solid; m.p. 187.3-188.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 7H), 7.01 (d, J = 15.6 Hz, 1H), 6.93 – 6.83 (m, 2H), 6.64 (d, J = 15.6 Hz, 1H), 5.72 (s, 1H), 3.83 (s, 3H), 3.08 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 159.6, 142.7, 132.1, 129.3, 129.0, 128.1, 128.1 , 126.4, 125.0, 114.1, 77.8, 55.3, 38.5, 37.7; IR (KBr): v = 3534, 3012, 1636, 1511, 1364, 1249, 1031, 846 , 789; HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_3$ $[M+Na]^+$ 334.1411, found 334.1408.

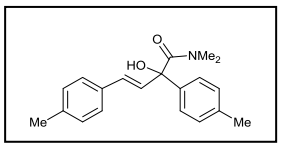


(E)-2-(4-methoxyphenyl)-N,N-dimethyl-4-phenyl-2-((trimethylsilyl)oxy)but-3-enamide (3e): 30 mg, 78% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 7.25 – 7.09 (m, 3H), 6.89 (d, J = 8.80 Hz, 2H), 5.90 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 2.94 (s, 3H), 2.80 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 158.2, 136.3, 133.8, 133.7, 131.0, 127.9, 127.0, 126.2, 126.9, 112.9, 81.2, 54.8, 37.3, 36.6, 1.40; IR



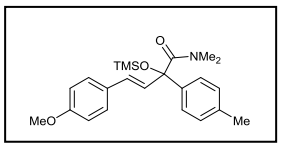
(KBr): v = 2925, 1643, 1601, 1447, 1252, 1097, 896, 842 cm^{-1} ; HRMS (APCI) *m/z* calcd for $C_{22}H_{29}NO_3Si$ $[M+H]^+$ 384.1990, found 384.1981.

(E)-2-hydroxy-N,N-dimethyl-2,4-di-p-tolylbut-3-enamide (3f):



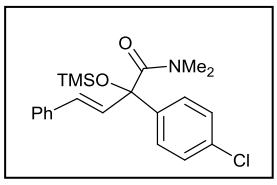
24mg,79% yield; white solid; m.p. 176.4-177.1 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.18 – 7.15 (m, 4H), 7.03 (d, J = 15.6 Hz, 1H), 6.72 (d, J = 15.6 Hz, 1H), 5.71 (s, 1H), 3.07 (s, 3H), 2.73 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 139.7, 137.9, 137.9, 133.8, 132.4, 129.7, 129.4, 126.7, 126.4, 126.3, 77.6, 38.6, 37.7, 21.3, 21.2; IR (KBr): v = 3609, 2923, 1654, 1502, 1455, 1254, 1095, 896, 824 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_2$ $[M+Na]^+$ 332.1621, found 332.1622.

(E)-4-(4-methoxyphenyl)-N,N-dimethyl-2-(*p*-tolyl)-2-((trimethylsilyl)oxy)but-3-enamide （3g）: 30 mg, 75% yield; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.01 (d, J = 16.2 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 5.83 (d, J = 16.4 Hz, 1H), 3.78 (s, 3H), 2.94 (s, 3H), 2.78 (s, 3H), 2.36 (s, 3H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 159.1, 139.3, 136.6, 132.1, 131.1, 129.7, 128.7, 127.8, 125.4, 113.8, 81.9, 55.2, 37.8, 37.1, 21.1, 1.9; IR



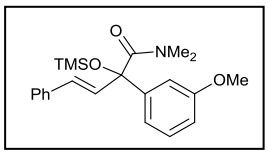
(KBr): v = 2920, 1641, 1511, 1390, 1250, 1063, 896, 841 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{31}NO_3Si$ $[M+Na]^+$ 420.1966, found 420.1959.

(E)-2-(4-chlorophenyl)-N,N-dimethyl-4-phenyl-2-((trimethylsilyl)oxy) but-3-enamide (3h): 25 mg, 65% yield; pale yellow oil; ^1H NMR (400



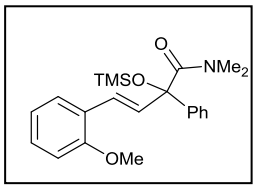
MHz, $CDCl_3$) δ 7.53 – 7.19 (m, 9H), 7.15 (d, J = 16.4 Hz, 1H), 5.87 (d, J = 16.0 Hz, 1H), 2.94 (s, 3H), 2.78 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 140.9, 136.5, 133.7, 133.0, 132.0, 128.5, 128.3, 127.7, 126.9 , 126.6, 81.5, 37.7, 37.1, 1.81; IR (KBr): v = 2923, 1644, 1488, 1398, 1253, 1089, 894, 841 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{26}ClNO_2Si$ $[M+Na]^+$ 410.1314, found 410.1311.

(E)-2-(3-methoxyphenyl)-N,N-dimethyl-4-phenyl-2-((trimethylsilyl)ox y)but-3-enamide (3i): 29mg, 78% yield; pale yellow

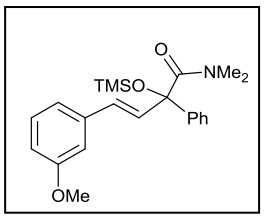


oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.40 – 7.31 (m, 2H), 7.33 – 7.25 (m, 1H), 7.22 – 7.12 (m, 2H), 6.93 – 6.81 (m, 2H), 6.75 (dd, J = 7.8, 2.2 Hz, 1H), 5.87 (d, J = 16.2 Hz, 1H), 3.78 (s, 3H), 2.95 (s, 3H), 2.77 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.6, 142.2, 138.2, 134.4, 131.6, 129.3, 128.1, 127.2, 125.3, 119.4, 113.5, 111.5, 81.8, 55.2, 37.7, 37.1, 1.9; IR (KBr): v = 3083, 1645, 1558, 1489, 1254, 1055, 893, 842 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{29}NO_2Si$ $[M+Na]^+$ 406.1806, found 406.1811.

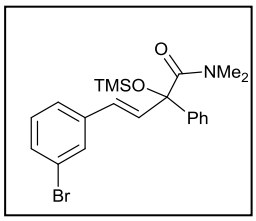
(E)-N,N-dimethyl-4-(2-methoxyphenyl)-2-phenyl-2-((trimethylsilyl)oxy)but-3-enamide (3j): 28 mg, 76% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 5H), 7.28 – 7.13 (m, 3H), 6.87 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 3.72 (s, 3H), 2.95 (s, 3H), 2.77 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 156.8, 142.7, 134.4, 128.5, 128.1, 127.2, 127.0, 126.3, 125.9, 125.3, 120.5, 110.8, 82.3, 55.4, 37.8, 37.1, 1.8; IR (KBr): v = 2955, 1644, 1489, 1464, 1246, 1026, 897, 843 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{29}NO_2Si$ $[M+Na]^+$ 406.1806, found 406.1815.



(E)-N,N-dimethyl-4-(3-methoxyphenyl)-2-phenyl-2-((trimethylsilyl)oxy)but-3-enamide (3k): 29 mg, 76% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 (m, 1H), 7.22 – 7.12 (m, 2H), 6.90 (d, J = 7.6 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.77 – 6.72 (m, 1H), 5.87 (d, J = 16.4 Hz, 1H), 3.78 (s, 3H), 2.95 (s, 3H), 2.77 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 159.7, 142.3, 138.3, 134.4, 131.7, 129.4, 128.1, 127.2, 125.3, 119.4, 113.6, 111.6, 81.9, 55.2, 37.7, 37.1, 1.9; IR (KBr): v = 2943, 1729, 1636, 1446, 1248, 1023, 891, 823 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{29}NO_3Si$ $[M+Na]^+$ 406.1809, found 406.1801.

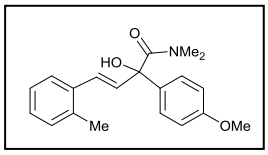


(E)-N,N-dimethyl-4-(3-bromophenyl)-2-phenyl-2-((trimethylsilyl)oxy) but-3-enamide (3l): 27 mg, 64% yield; pale yellow oil; ^{1}H NMR (400

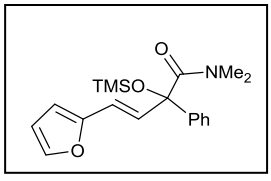


MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 7H), 7.25 – 7.07 (m, 3H), 5.82 (d, J = 16.4 Hz, 1H), 2.95 (s, 3H), 2.75 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 142.0, 139.0, 135.8, 130.4, 130.1, 129.9, 129.6, 128.2, 127.3, 125.2, 125.0, 122.6, 81.7, 37.6, 37.0, 1.8; IR (KBr): v = 2928, 1730, 1635, 1476, 1251, 1065, 871, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{26}BrNO_2Si$ $[M+Na]^+$ 454.0808, found 454.0811.

(E)-2-hydroxy-N,N-dimethyl-2-(4-methoxyphenyl)-4-(o-tolyl)but-3-en amide (3m): 25mg, 77% yield; white solid; m.p. 181.3-181.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 1H), 7.35 – 7.27 (m, 3H), 7.20 (m, 3H), 6.95 – 6.85 (m, 2H), 6.63 (d, J = 15.2 Hz, 1H), 5.72 (s, 1H), 3.81 (s, 3H), 3.08 (s, 3H), 2.75 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 159.3, 136.1, 135.8, 134.9, 130.5, 130.5, 128.9, 127.9, 127.7, 126.1, 125.8, 114.3, 77.6, 55.3, 38.6, 37.8, 19.9; IR (KBr): v = 3629, 2925, 1632, 1511, 1366, 1249, 1034, 835, 748 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_3$ $[M+Na]^+$ 348.1570, found 348.1566.

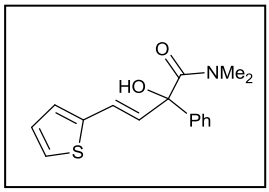


(E)-4-(furan-2-yl)-N,N-dimethyl-2-phenyl-2-((trimethylsilyl)oxy)but-3-enamide (3n)[4]: 24 mg, 72% yield; pale yellow oil; ^{1}H NMR (400



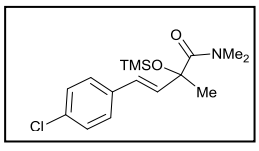
MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 7.05 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 4.8, 1.6 Hz, 1H), 6.12 (d, *J* = 3.6 Hz, 1H), 5.66 (d, *J* = 16.4 Hz, 1H), 2.94 (s, 3H), 2.75 (s, 3H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 152.5, 142.1, 141.7, 132.8, 128.1, 127.3, 125.5, 120.1, 111.1, 108.3, 81.9, 37.7, 37.0, 1.80.

(E)-2-hydroxy-N,N-dimethyl-2-phenyl-4-(thiophen-2-yl)but-3-enamide (3o): 20 mg,71% yield; white solid; m.p. 171.5-172.1 ℃; ^{1}H NMR (400



MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 7.25 – 7.17 (m, 2H), 7.11 – 6.94 (m, 2H), 6.61 (d, *J* = 15.6 Hz, 1H), 5.76 (s, 1H), 3.08 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 142.3, 141.5, 129.1, 128.3, 127.7, 126.9, 126.5, 126.4, 126.1, 124.7, 77.7, 38.5, 37.8; IR (KBr): *v* = 3729, 2921, 1636, 1493, 1367, 1257, 1108, 889, 771 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NO_2S$ $[M+Na]^+$ 310.0872, found 310.0871.

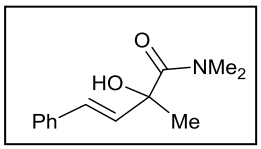
(E)-4-(4-chlorophenyl)-N,N,2-trimethyl-2-((trimethylsilyl)oxy)but-3-enamide (3p): 18 mg, 56% yield; pale yellow oil; ^{1}H



NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.2 Hz, 4H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.10 (s, 3H), 2.93 (s, 3H), 1.63 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 135.0, 134.3, 133.2, 128.7, 127.6, 126.3, 79.3, 38.2, 37.2, 28.6, 1.60; IR (KBr): *v* = 2981, 1664, 1550, 1476, 1243, 1091, 713, 665

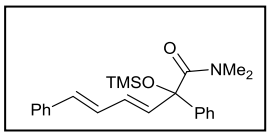
cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{24}ClNO_2Si$ $[M+Na]^+$ 348.1157, found 348.1160.

(E)-2-hydroxy-N,N,2-trimethyl-4-phenylbut-3-enamide (3q): 16 mg,



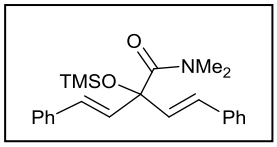
75% yield; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.33 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 6.69 (d, *J* = 16.4 Hz, 1H), 6.36 (d, *J* = 16.4 Hz, 1H), 5.15 (s, 1H), 3.08 (s, 6H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 136.3, 131.0, 130.6, 128.6, 128.0, 126.6, 72.9, 48.9, 44.4, 24.7; IR (KBr): *v* = 3713, 2923, 1625, 1491, 1360, 1255, 1163, 971, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NO_2$ $[M+Na]^+$ 242.1151, found 242.1151.

(3E,5E)-N,N-dimethyl-2,6-diphenyl-2-((trimethylsilyl)oxy)hexa-3,5-di enamide (3r)[4]: 28mg, 74% yield; white solid; m.p. 113.8-114.4 ℃; ^1H



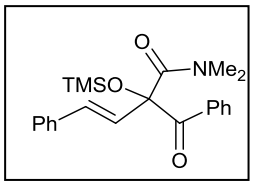
NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 9H), 7.23 – 7.13 (m, 1H), 6.87 – 6.71 (m, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 5.69 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.94 (s, 3H), 2.74 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 142.1, 138.1, 137.2, 133.0, 132.2, 128.6, 128.5, 128.1, 127.5, 127.2, 126.3, 125.2, 81.8, 37.7, 37.1, 1.84.

(E)-N,N-dimethyl-4-phenyl-2-((E)-styryl)-2-((trimethylsilyl)oxy)but-3 -enamide (3s)[4]: 31 mg, 82% yield; white solid;

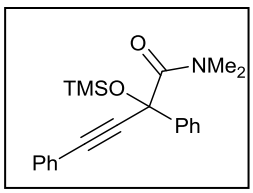


115.8-116.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 4H), 7.36 – 7.30 (m, 4H), 7.27 (t, J = 1.2 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.66 (q, J = 16.4 Hz, 4H), 3.15 (s, 3H), 2.98 (s, 3H), 0.17 (s,9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 136.5, 130.9, 130.5, 128.6, 127.7, 126.7, 80.8, 38.1, 37.4, 1.92.

(E)-2-benzoyl-N,N-dimethyl-4-phenyl-2-((trimethylsilyl)oxy)but-3-en amide (3t): 26 mg, 70% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 16.0 Hz, 1H), 7.46 – 7.35 (m, 6H), 7.34 – 7.27 (m, 4H), 6.92 (d, J = 15.6 Hz, 1H), 3.03 (s, 3H), 2.83 (s, 3H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 171.0, 140.9, 138.9, 134.9, 130.0, 128.8, 128.6, 128.4, 128.4, 126.1, 123.1, 88.0, 38.3, 36.2, 2.15; IR (KBr): v = 2837, 1701, 1559, 1368, 1241, 1068, 931, 842 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{27}NO_3Si$ $[M+Na]^+$ 404.1652, found 404.1650.



N,N-dimethyl-2,4-diphenyl-2-((trimethylsilyl)oxy)but-3-ynamide (3u)[4]: 23 mg, 66% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.56 – 7.46 (m, 2H), 7.44 – 7.31 (m, 6H), 2.99 (d, J = 6.4 Hz, 6H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 141.8, 131.5, 128.7, 128.7, 128.3, 128.3, 128.0, 127.2, 125.9, 122.4, 88.9, 38.2, 37.7, 1.53.



(E)-2-hydroxy-N,N-dimethyl-2,4-diphenylbut-3-enamide (3v): 20.5 mg, 73% yield; pale yellow solid; m.p. 199.6-200.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 6.8 Hz, 2H), 7.40 – 7.26 (m, 8H), 7.09 (d, J = 15.6 Hz, 1H), 6.79 (d, J = 15.6 Hz, 1H), 5.74 (s, 1H), 3.08 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 142.5, 136.5, 132.7, 129.0, 128.7, 128.2, 128.0, 127.2, 126.8, 126.4, 77.9, 38.5, 37.7; IR (KBr): v = 3426, 2924, 1633, 1495, 1446, 1247, 1118, 893, 825 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}NO_2$ $[M+Na]^+$ 304.1308, found 304.1308.

3. Reference

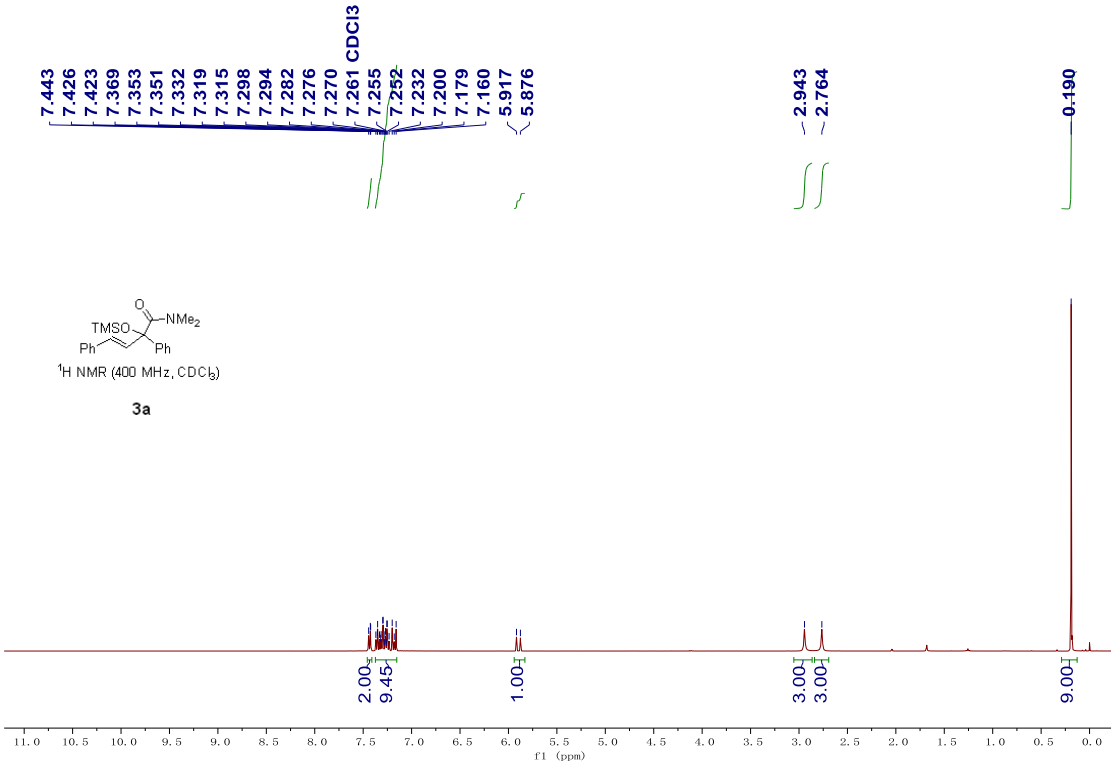
1 Y. J. Li, H. Xu, M. M. Xing, F. Huang, J. H. Jia and J. R. Gao, *Org. Lett.* 2015, **17**, 3690.

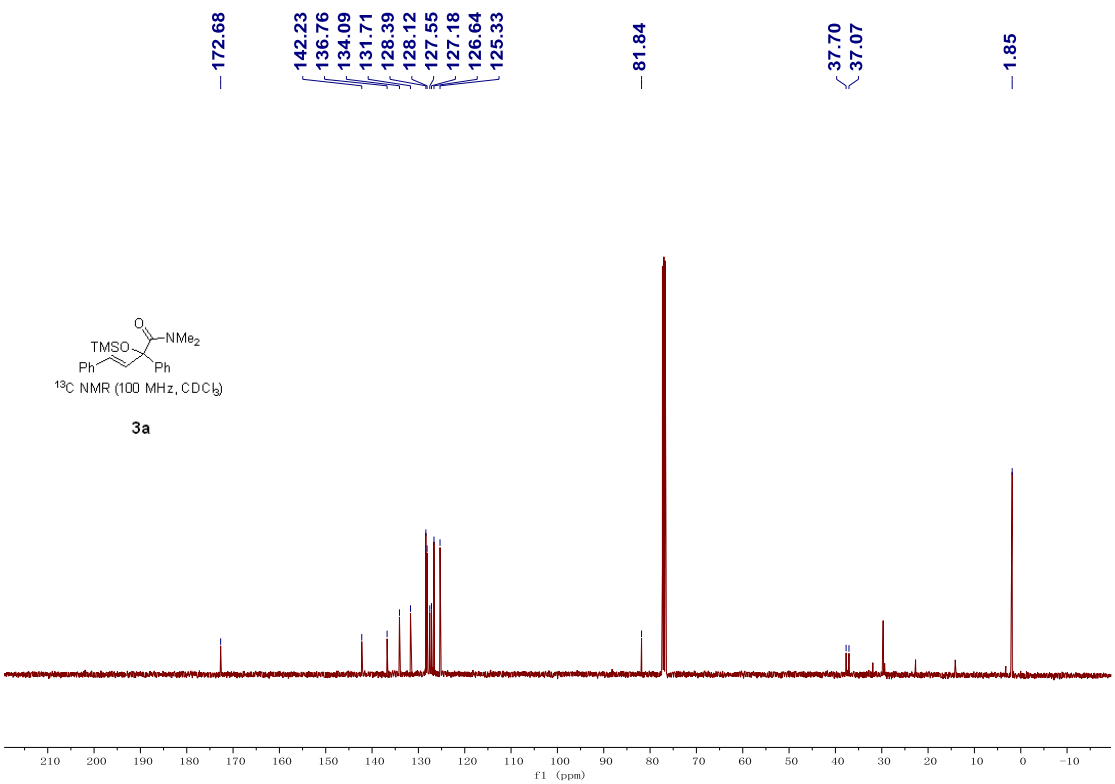
2 V. Le Fouler, Y. Chen, V. Gandon, V. Bizet, C. Salome, T. Fessard, F. Liu, K. N. Houk and N. Blanchard, *J. Am. Chem. Soc.* 2019, **141**, 15901.

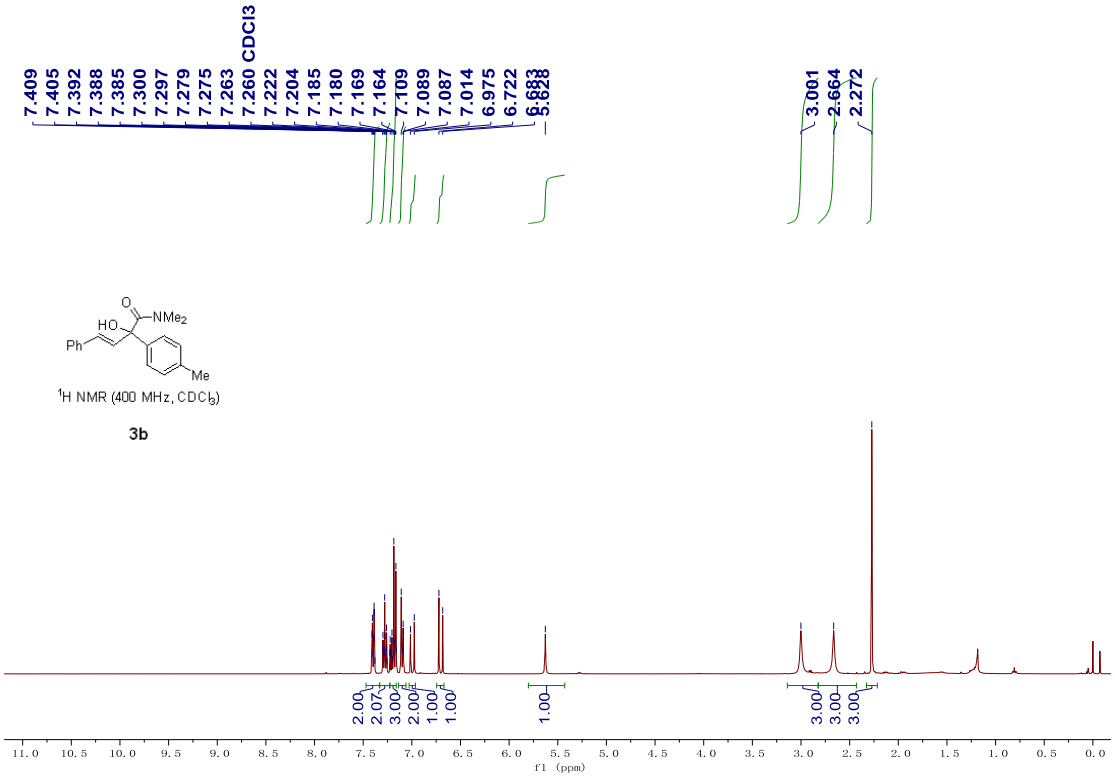
3 X. Liu, X. X. Xu, L. Pan, Q. Zhang and Q. Liu, *Org. Biomol. Chem.*, 2013, **11**, 6703.

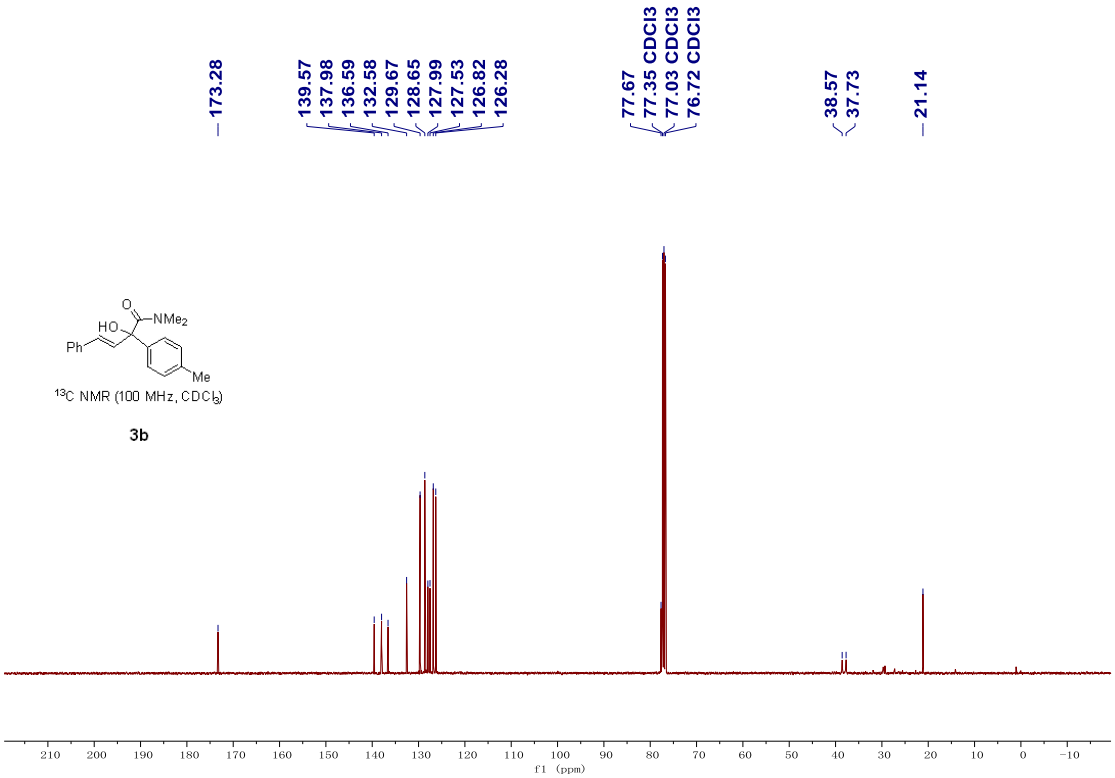
4 Y. Yao, W. D. Li and J. X. Chen, *Chin. J. of Org. Chem.*, 2014, **34**, 2124.

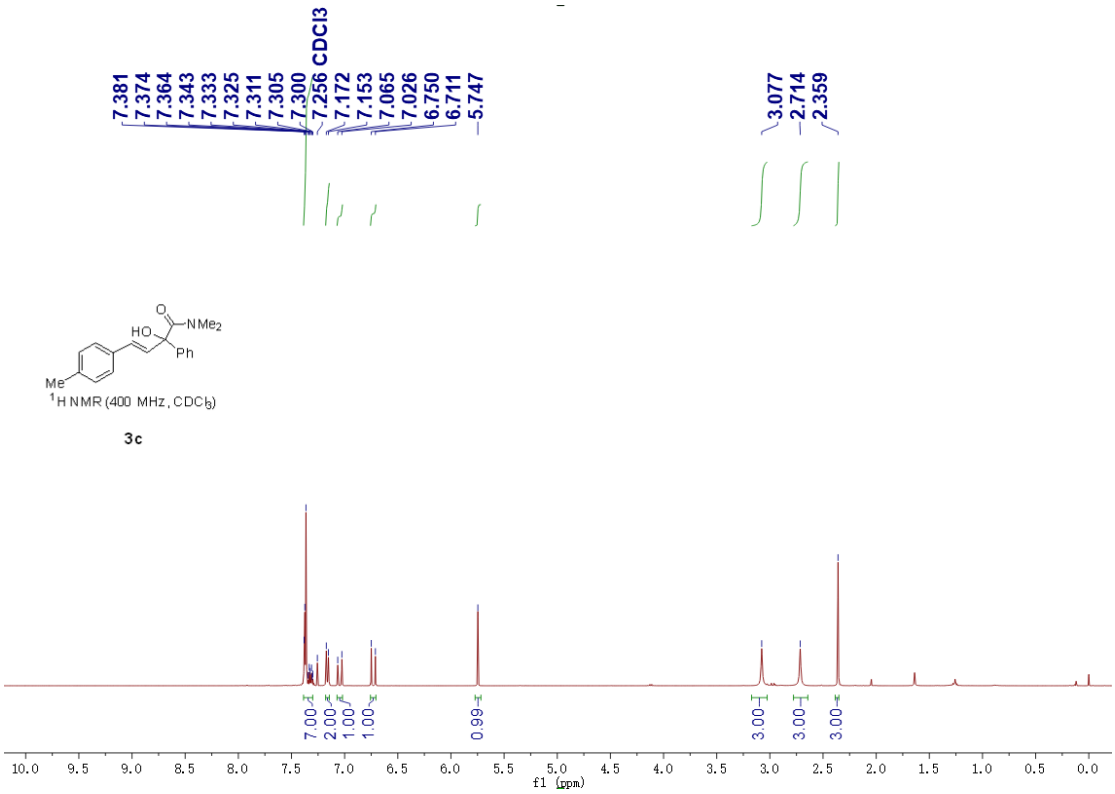
4. Copies of ^{1}H NMR and ^{13}C NMR Spectra

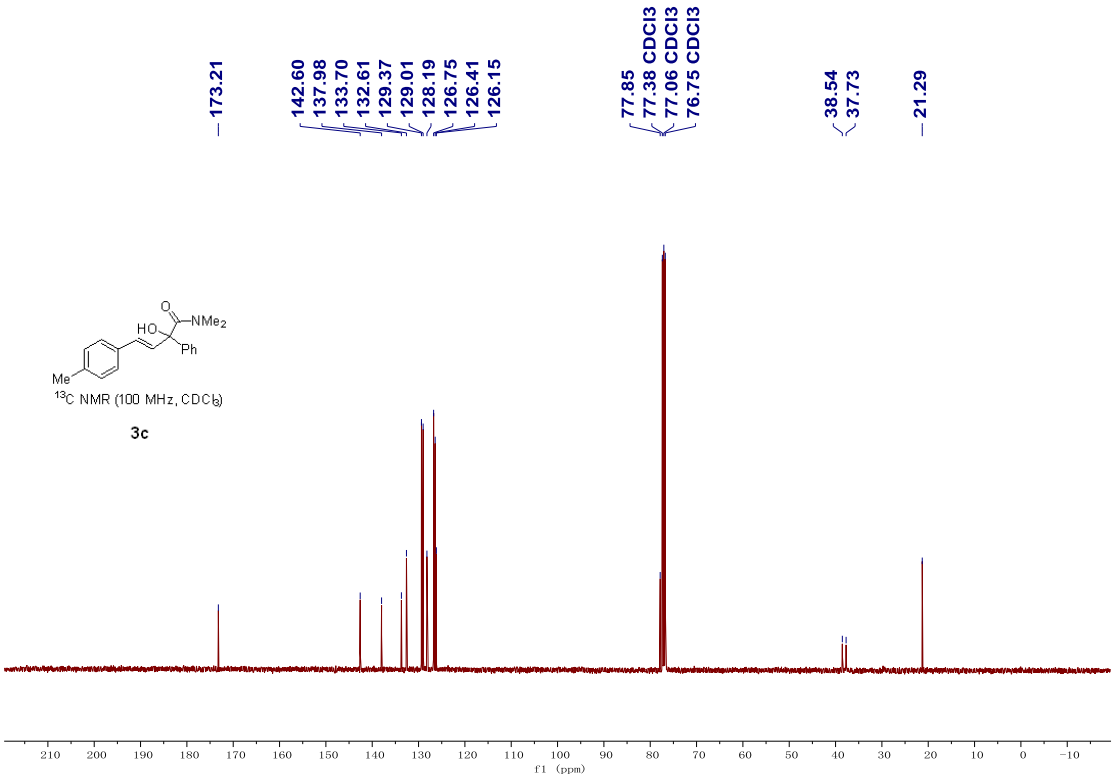


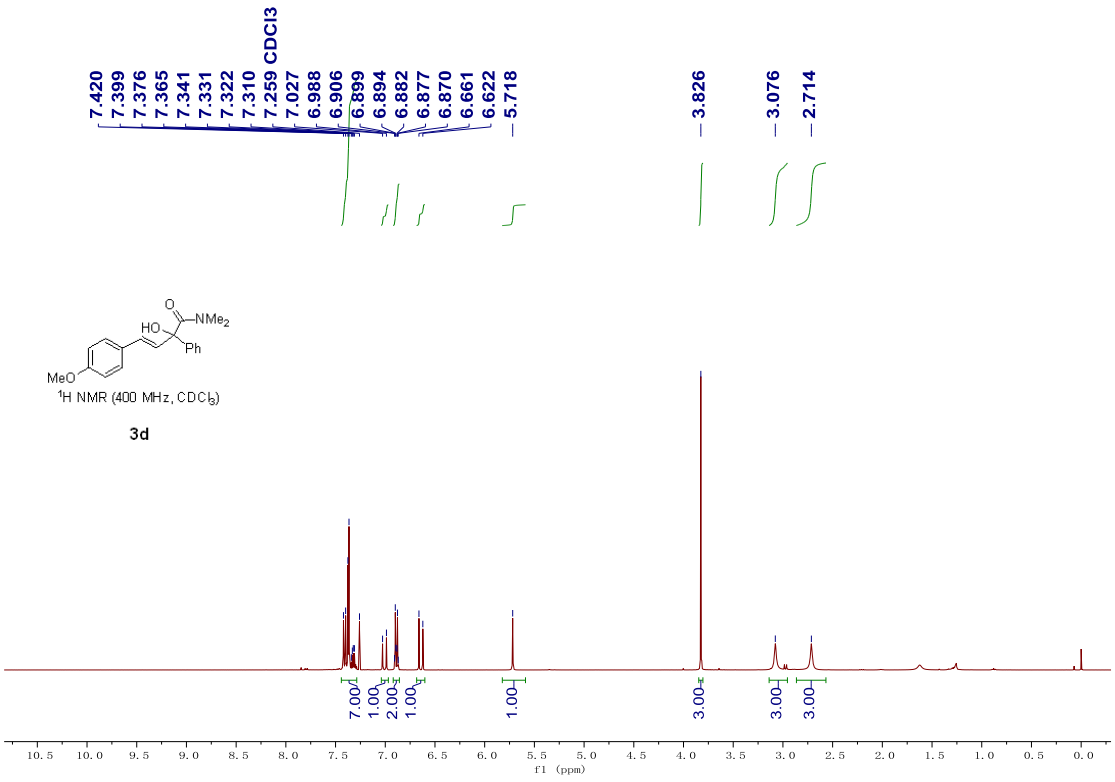


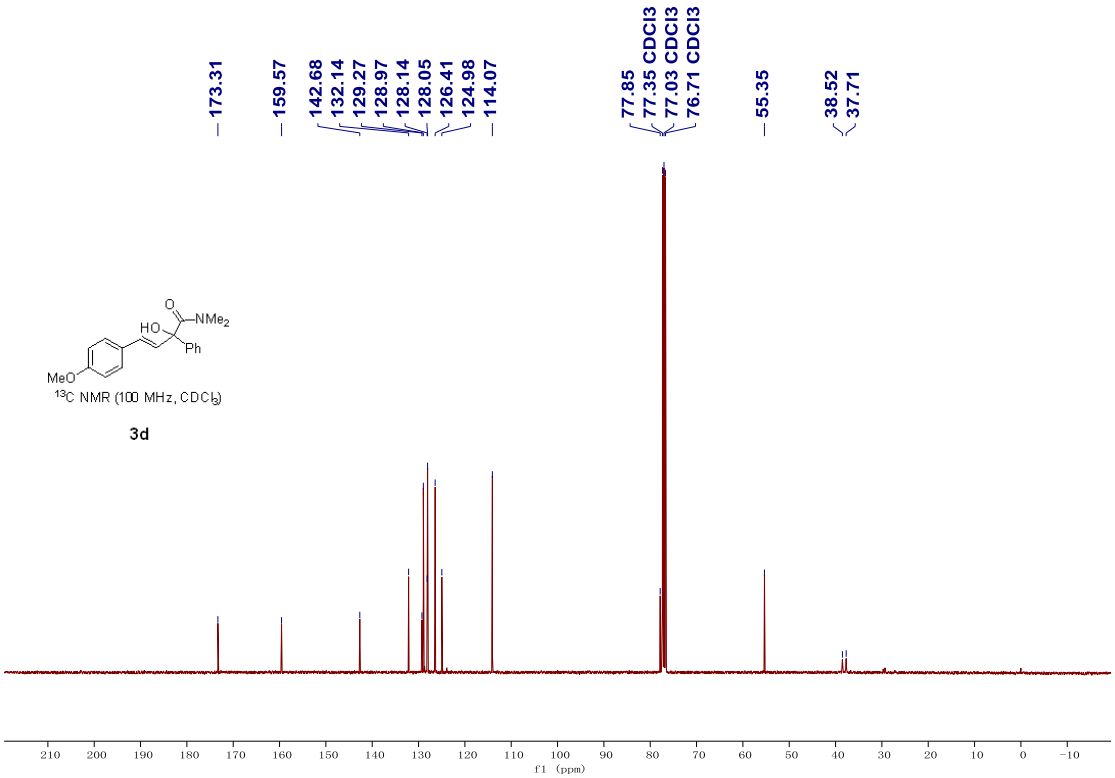

7.409
7.405
7.392
7.388
7.385
7.300
7.297
7.279
7.275
7.263
7.260 CDCl3
7.222
7.204
7.185
7.180
7.169
7.164
7.109
7.089
7.087
7.014
6.975
6.722
6.683
6.628
5.928
3.001
2.664
2.272
O
NMe2
HO
Ph
Me
1H NMR (400 MHz, CDCl3)
3b
2.00
2.07
3.00
2.00
1.00
1.00
1.00
3.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

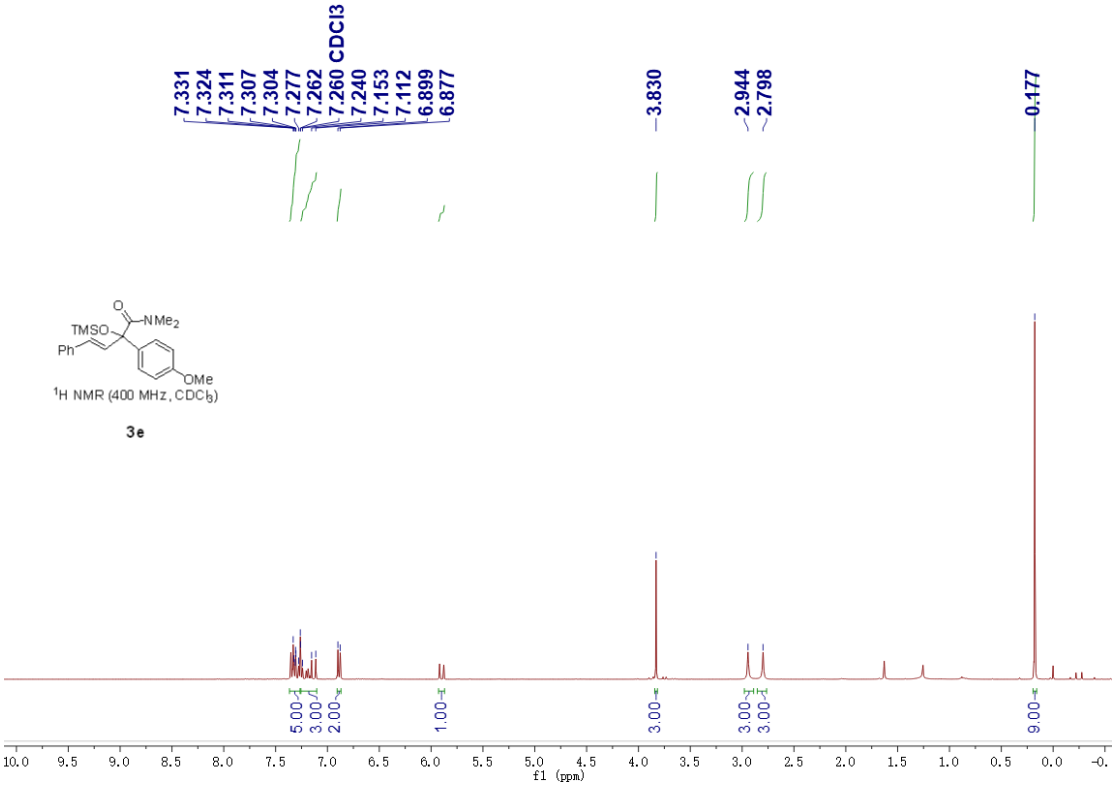

173.28
139.57
137.98
136.59
132.58
129.67
128.65
127.99
127.53
126.82
126.28
77.67
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
38.57
37.73
21.14
O
NMe2
HO
Ph
Me
13C NMR (100 MHz, CDCl3)
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

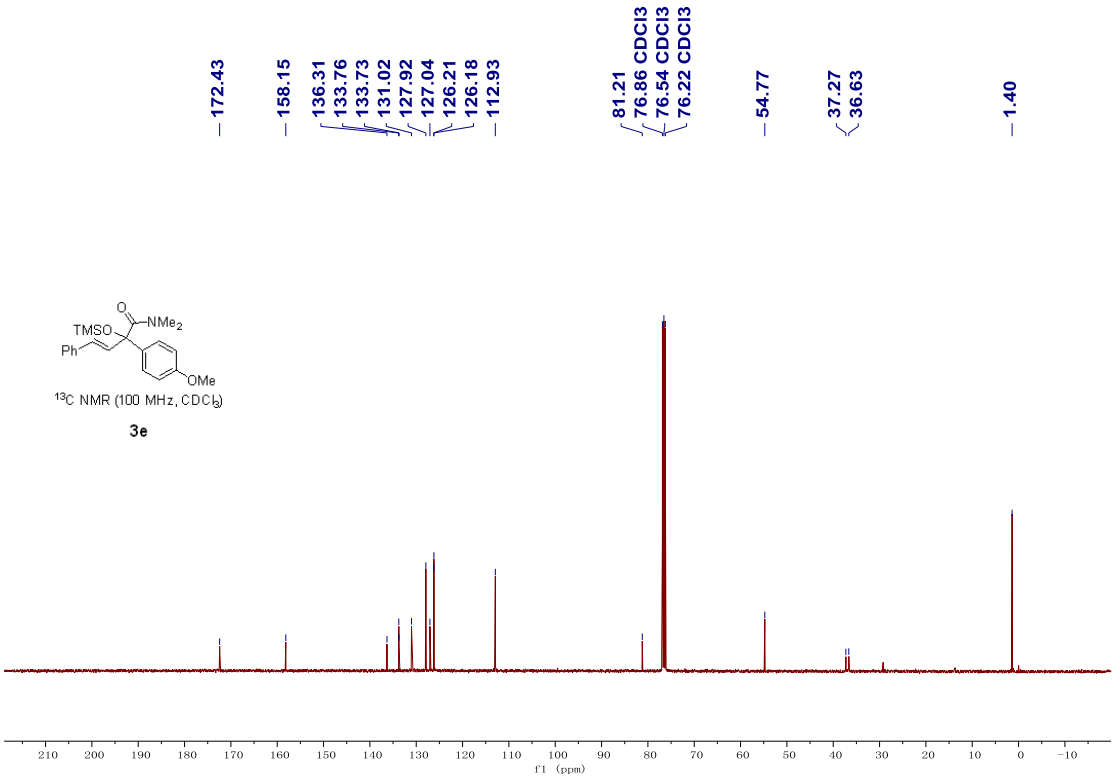

7.381
7.374
7.364
7.343
7.333
7.325
7.311
7.305
7.300
7.256 CDCl3
7.172
7.153
7.065
7.026
6.750
6.711
5.747
3.077
2.714
2.359
HO
NMe2
O
Ph
Me
1H NMR (400 MHz, CDCl3)
3c
7.00
2.00
1.00
1.00
0.99
3.00
3.00
3.00
f1 (ppm)

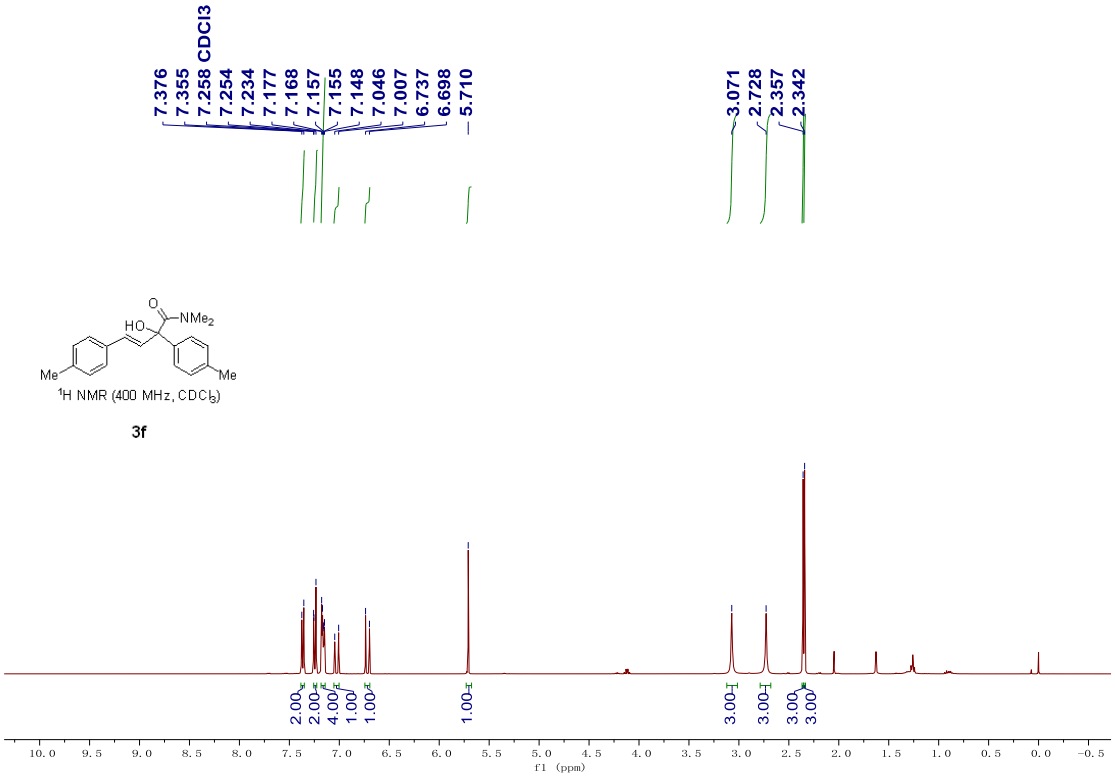

173.21
142.60
137.98
133.70
132.61
129.37
129.01
128.19
126.75
126.41
126.15
77.85
77.38 CDCl3
77.06 CDCl3
76.75 CDCl3
38.54
37.73
21.29
HO
NMe2
O
Ph
Me
13C NMR (100 MHz, CDCl3)
3c
f1 (ppm)

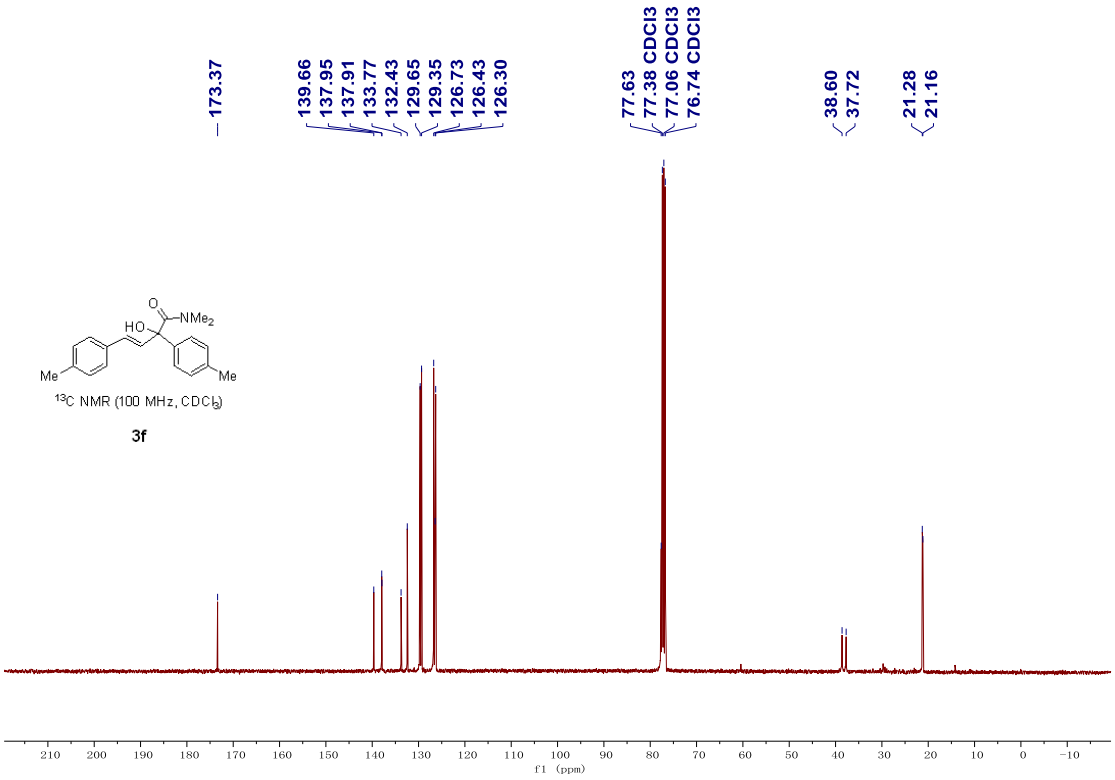

7.420
7.399
7.376
7.365
7.341
7.331
7.322
7.310
7.259 CDCl3
7.027
6.988
6.906
6.899
6.894
6.882
6.877
6.870
6.661
6.622
5.718
3.826
3.076
2.714
O
NMe2
HO
Ph
MeO
1H NMR (400 MHz, CDCl3)
3d
7.00
1.00
2.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

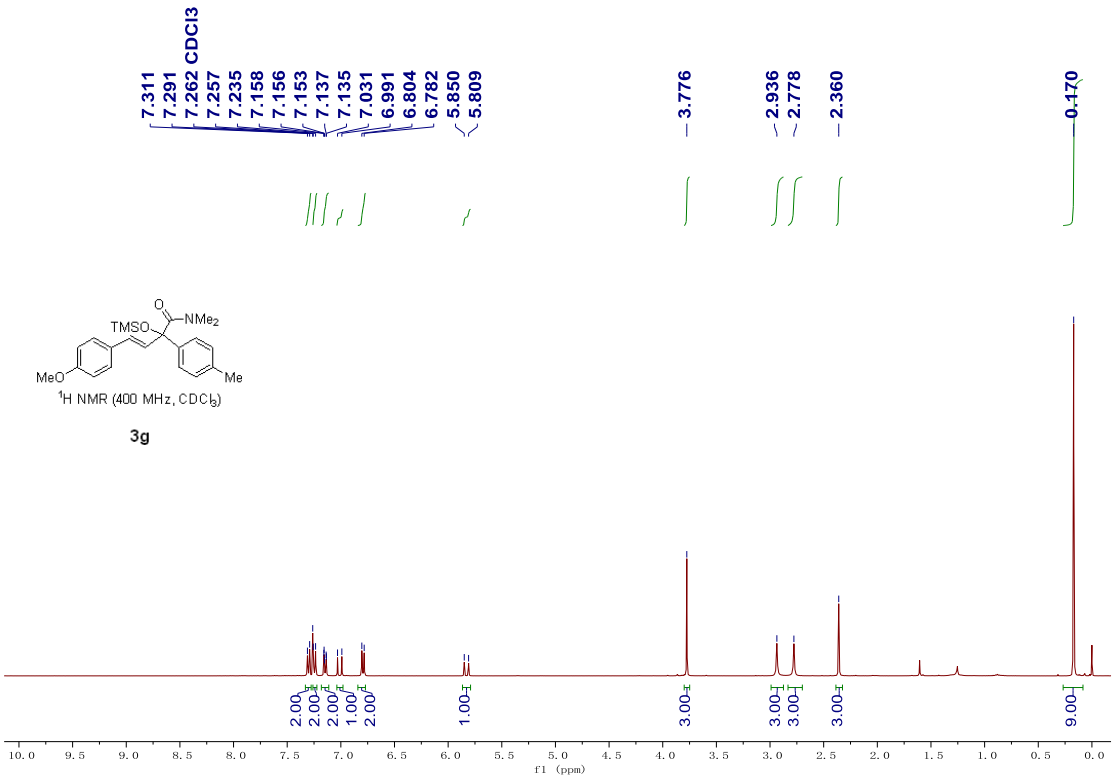

173.31
159.57
142.68
132.14
129.27
128.97
128.14
128.05
126.41
124.98
114.07
77.85
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
55.35
38.52
37.71
O
NMe2
HO
Ph
MeO
13C NMR (100 MHz, CDCl3)
3d
f1 (ppm)

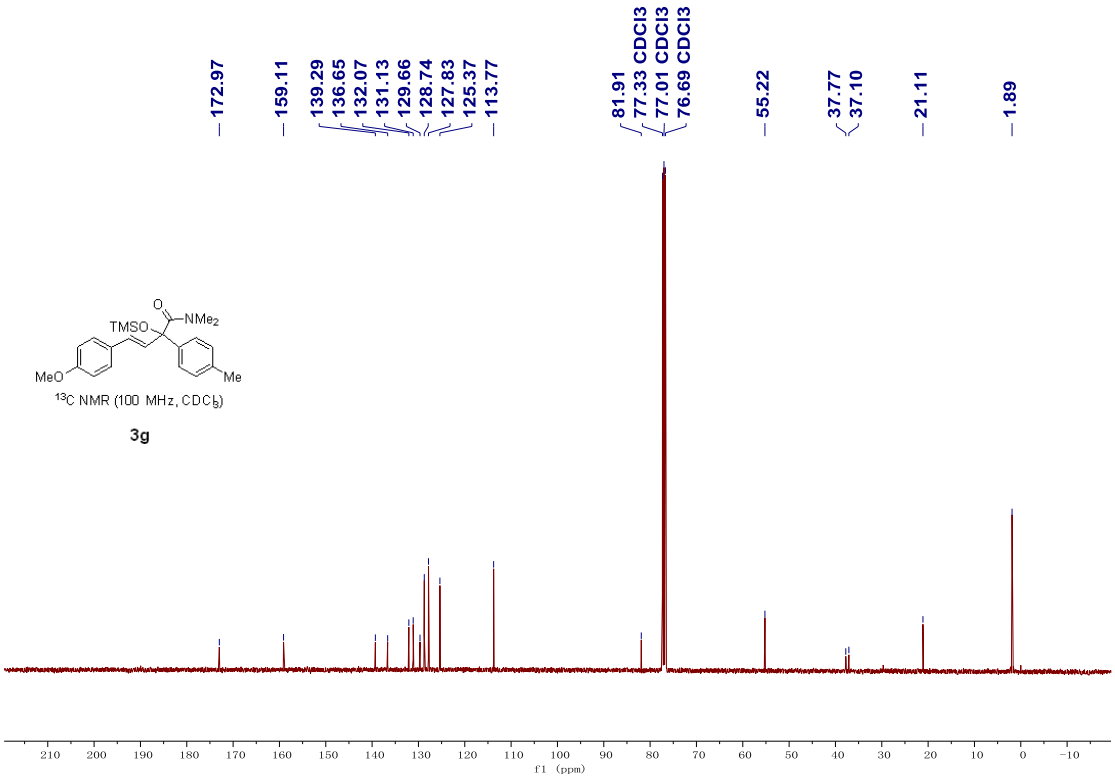

7.331
7.324
7.311
7.307
7.304
7.277
7.262
7.260 CDCl3
7.240
7.153
7.112
6.899
6.877
3.830
2.944
2.798
0.477
TMSO
NMe2
Ph
OMe
1H NMR (400 MHz, CDCl3)
3e
5.00
3.00
2.00
1.00
3.00
3.00
3.00
9.00
f1 (ppm)

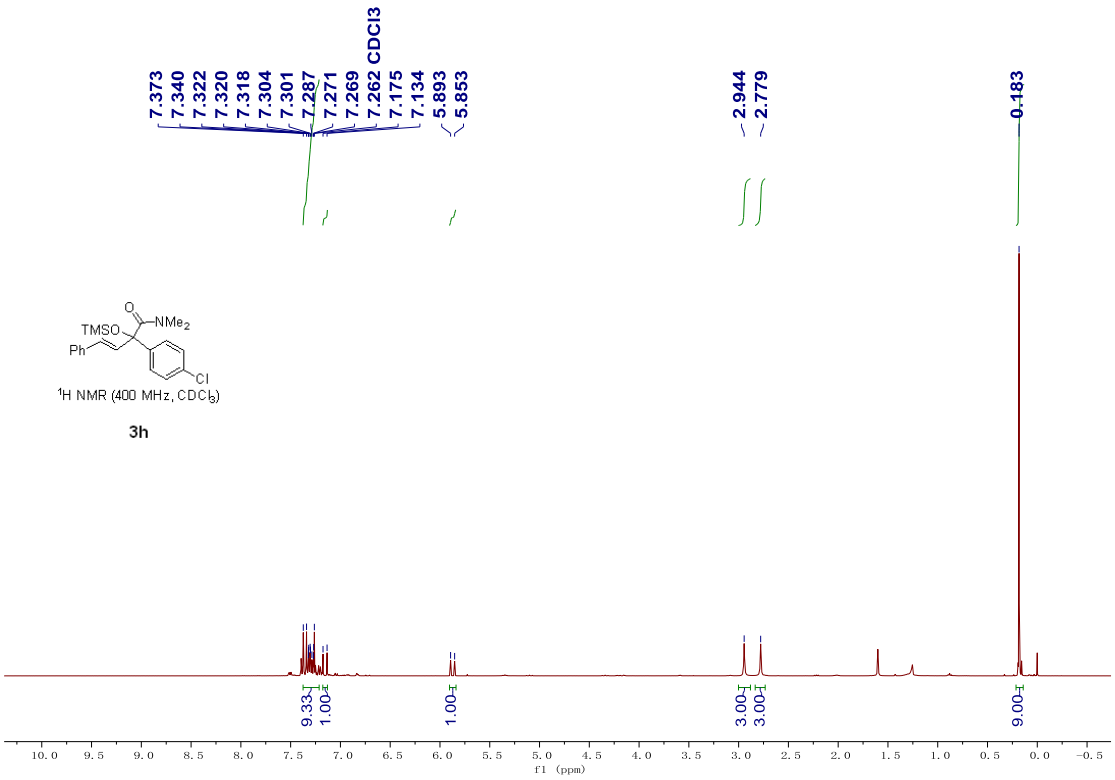

172.43
158.15
136.31
133.76
133.73
131.02
127.92
127.04
126.21
126.18
112.93
81.21
76.86 CDCl3
76.54 CDCl3
76.22 CDCl3
54.77
37.27
36.63
1.40
TMSO
NMe2
Ph
OMe
13C NMR (100 MHz, CDCl3)
3e
f1 (ppm)

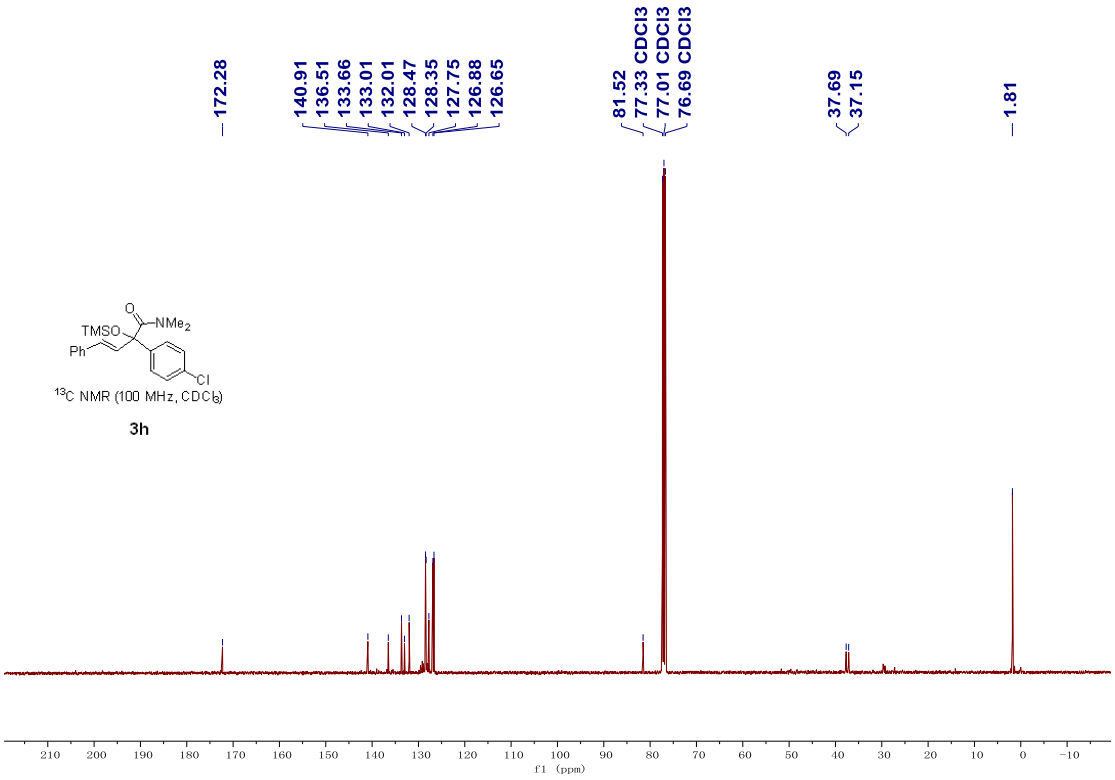

7.376
7.355
7.258 CDCl3
7.254
7.234
7.177
7.168
7.157
7.155
7.148
7.046
7.007
6.737
6.698
5.710
3.071
2.728
2.357
2.342
HO
O
NMe2
Me
Me
1H NMR (400 MHz, CDCl3)
3f
2.00
2.00
4.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)

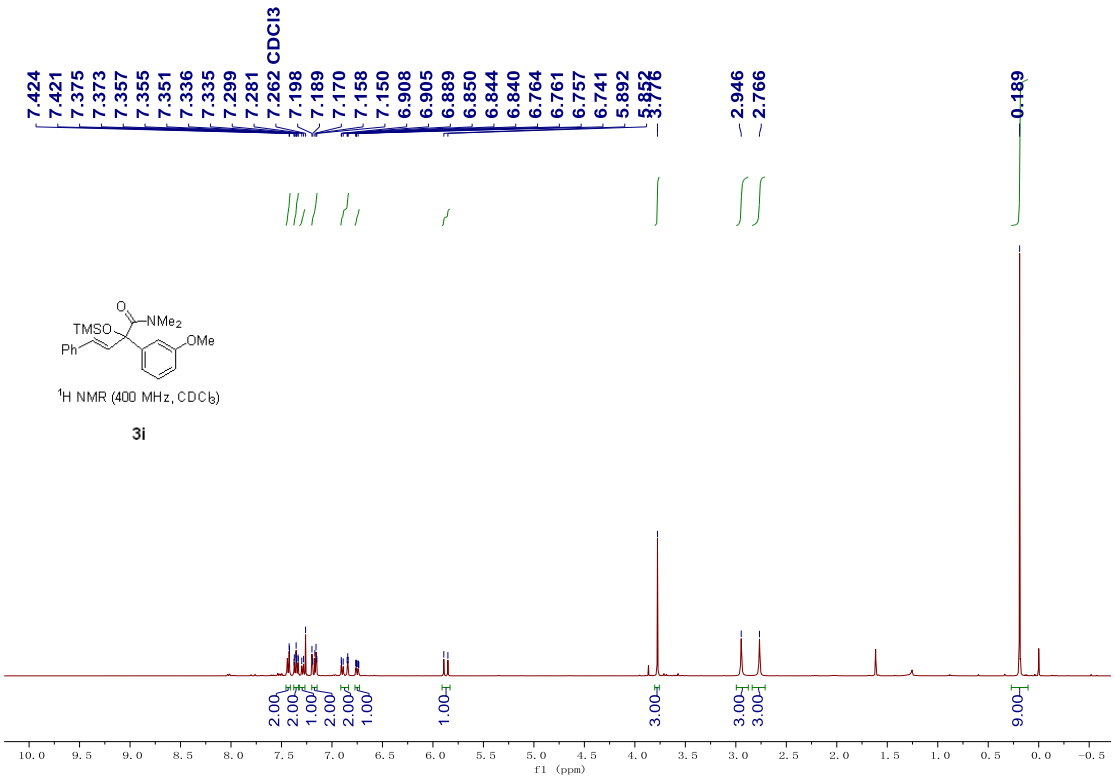

173.37
139.66
137.95
137.91
133.77
132.43
129.65
129.35
126.73
126.43
126.30
77.63
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
38.60
37.72
21.28
21.16
HO
O
NMe2
Me
Me
13C NMR (100 MHz, CDCl3)
3f
f1 (ppm)

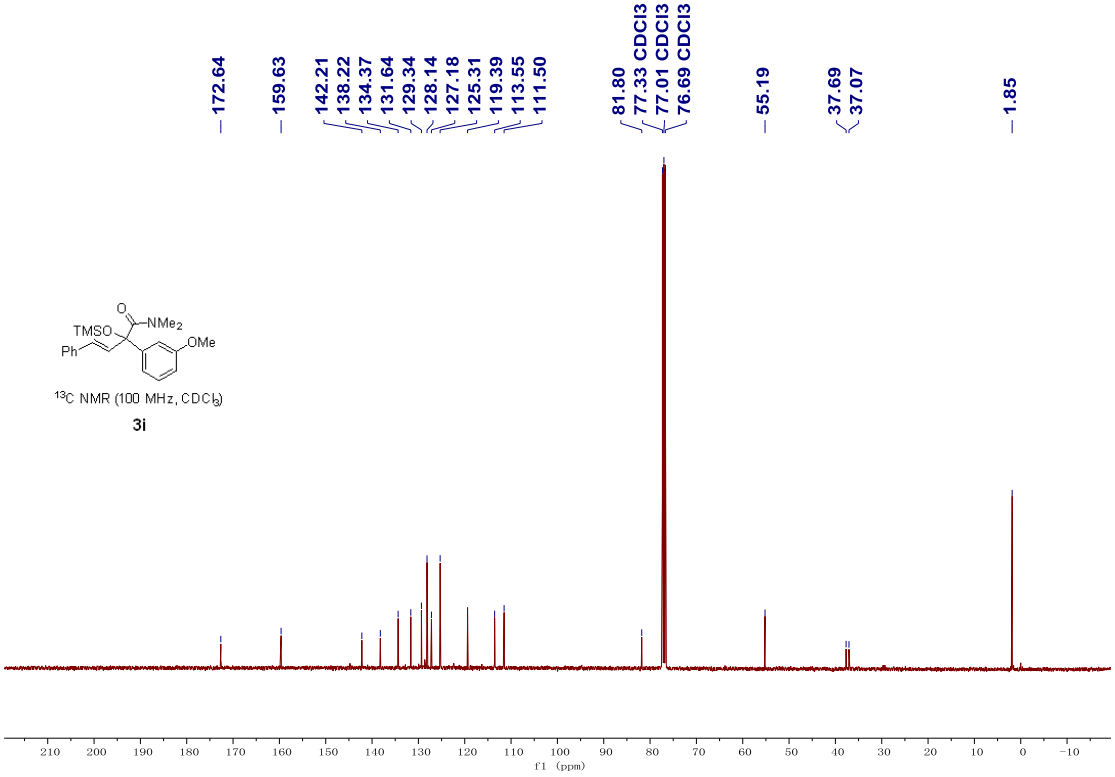

7.311
7.291
7.262 CDCl3
7.257
7.235
7.158
7.156
7.153
7.137
7.135
7.031
6.991
6.804
6.782
5.850
5.809
3.776
2.936
2.778
2.360
0.170
TMSO
NMe2
MeO
Me
1H NMR (400 MHz, CDCl3)
3g
2.00
2.00
2.00
1.00
2.00
1.00
3.00
3.00
3.00
3.00
9.00
f1 (ppm)

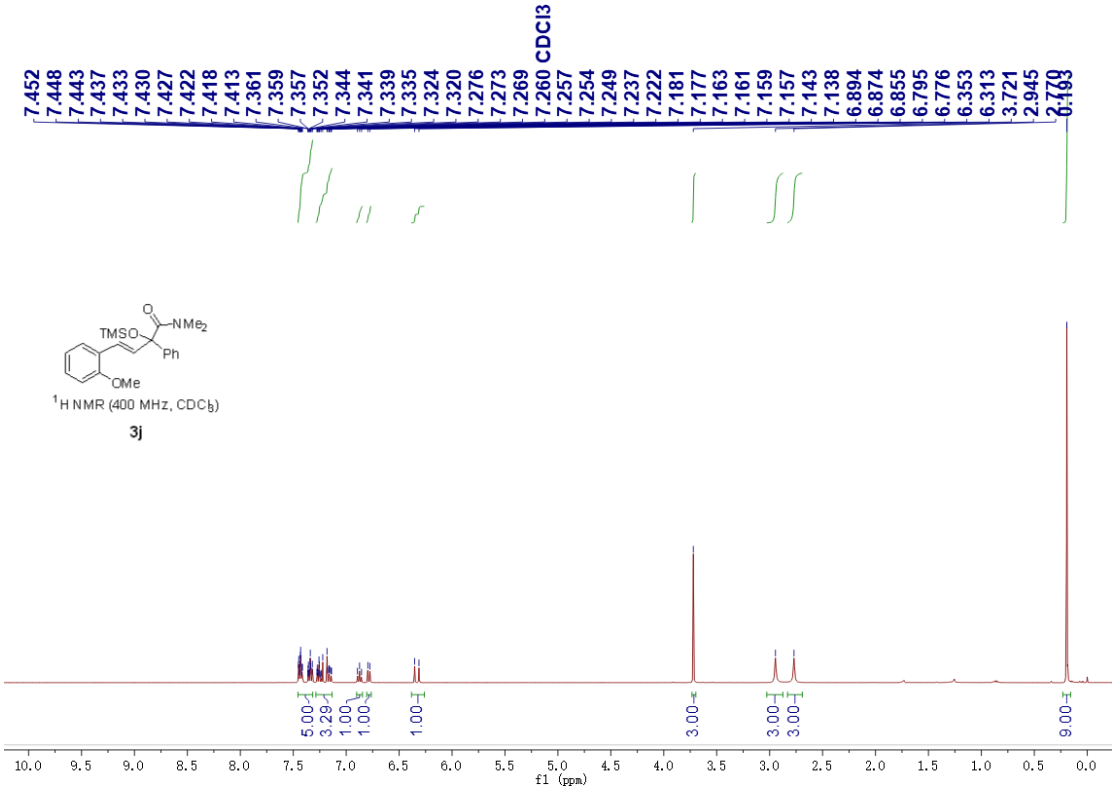

172.97
159.11
139.29
136.65
132.07
131.13
129.66
128.74
127.83
125.37
113.77
81.91
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
55.22
37.77
37.10
21.11
1.89
TMSO
NMe2
MeO
Me
13C NMR (100 MHz, CDCl3)
3g
f1 (ppm)

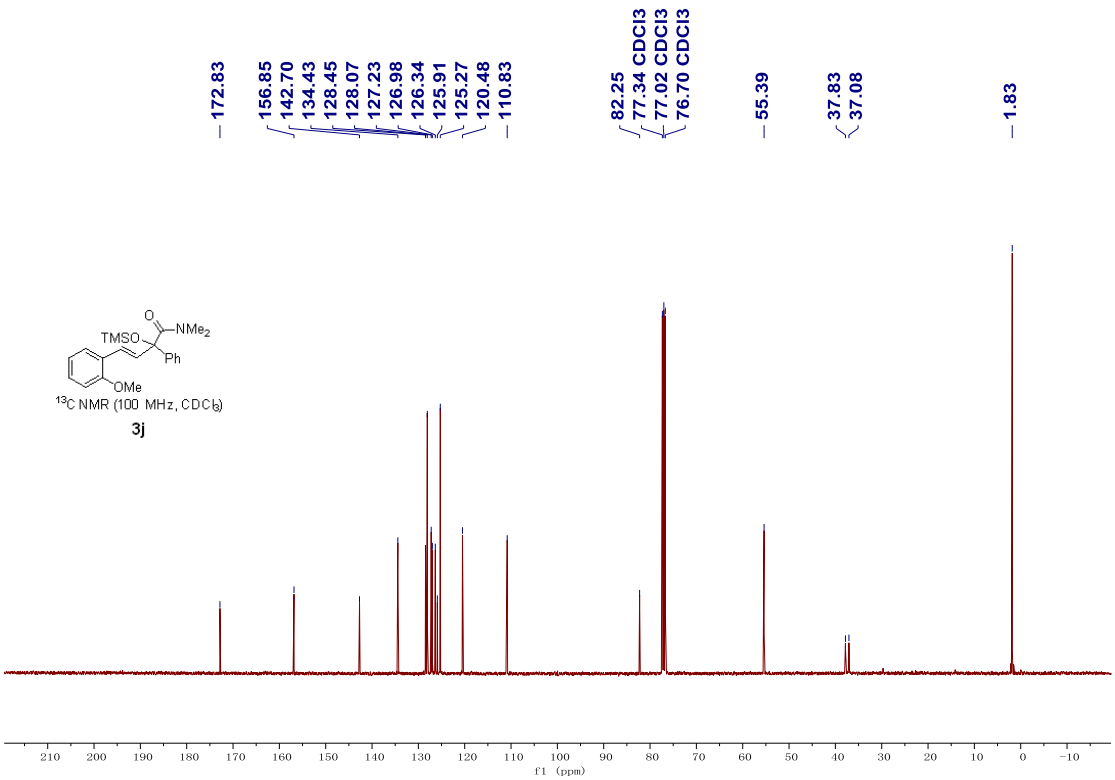

7.373
7.340
7.322
7.320
7.318
7.304
7.301
7.287
7.271
7.269
7.262 CDCl3
7.175
7.134
5.893
5.853
2.944
2.779
0.183
TMSO
NMe2
Ph
Cl
1H NMR (400 MHz, CDCl3)
3h
9.33
1.00
1.00
3.00
3.00
9.00
f1 (ppm)

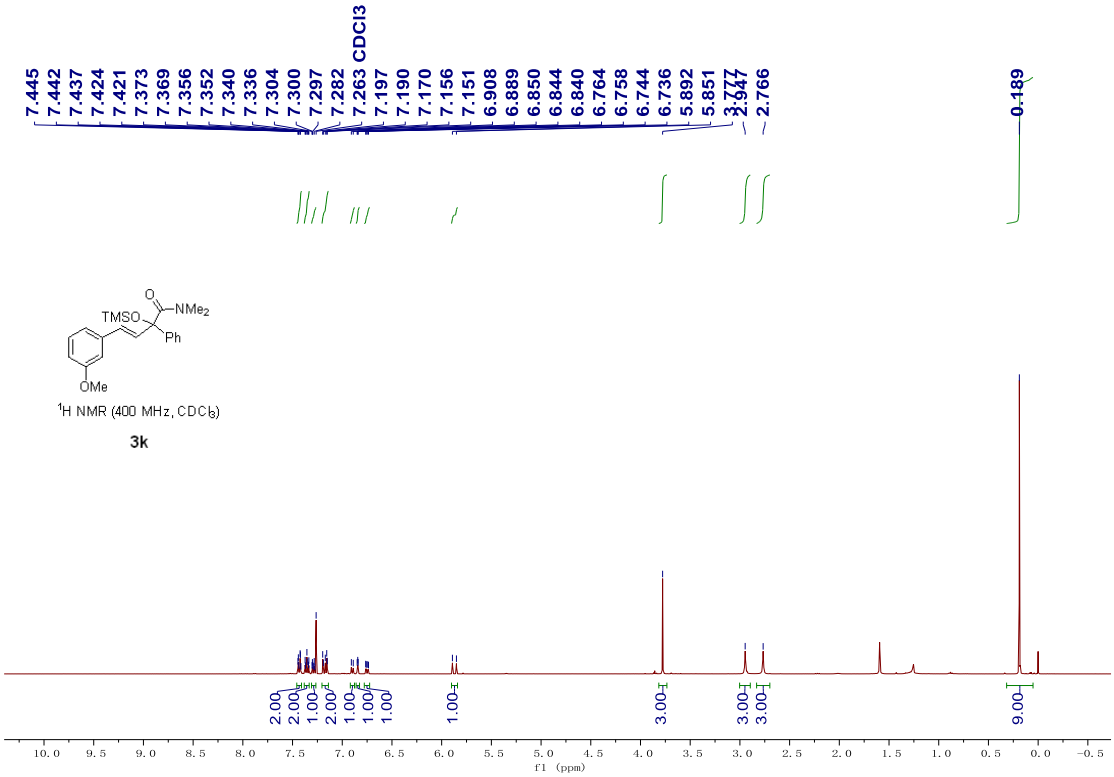

172.28
140.91
136.51
133.66
133.01
132.01
128.47
128.35
127.75
126.88
126.65
81.52
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
37.69
37.15
1.81
TMSO
NMe2
Ph
Cl
13C NMR (100 MHz, CDCl3)
3h
f1 (ppm)

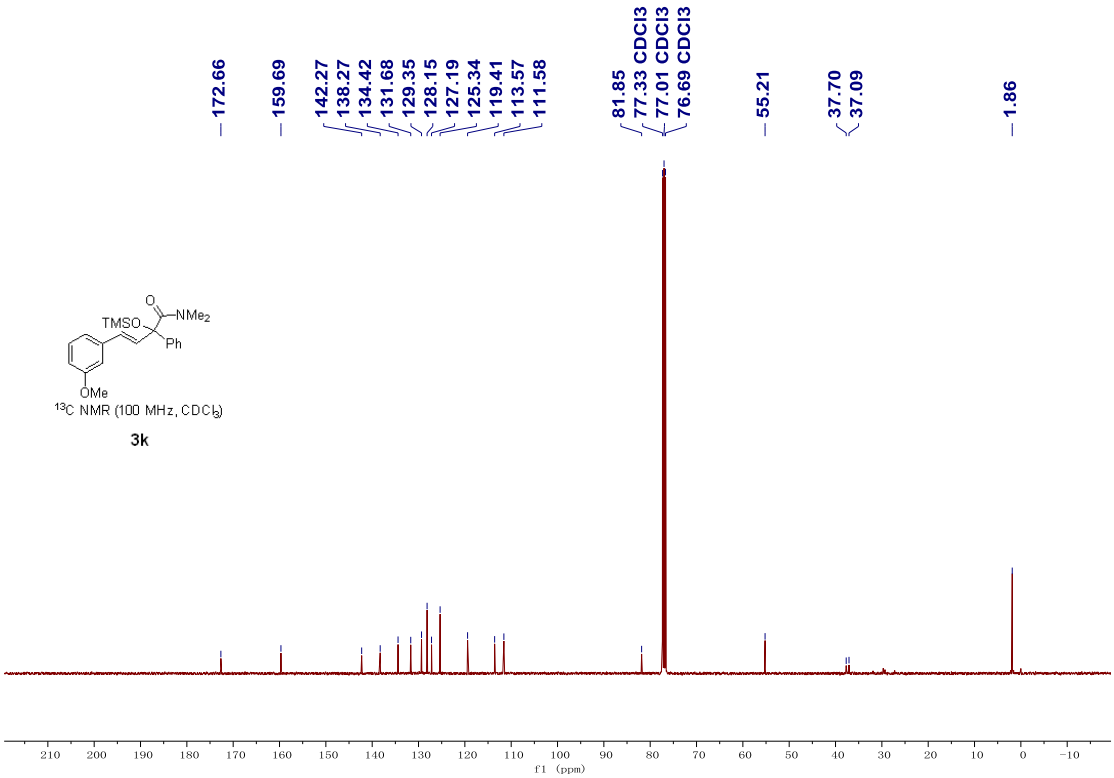

7.424
7.421
7.375
7.373
7.357
7.355
7.351
7.336
7.335
7.299
7.281
7.262 CDCl3
7.198
7.189
7.170
7.158
7.150
6.908
6.905
6.889
6.850
6.844
6.840
6.764
6.761
6.757
6.741
5.892
5.852
3.776
2.946
2.766
0.189
TMSO
NMe2
O
Ph
OMe
1H NMR (400 MHz, CDCl3)
3i
2.00
2.00
1.00
2.00
2.00
1.00
1.00
3.00
3.00
3.00
9.00
f1 (ppm)

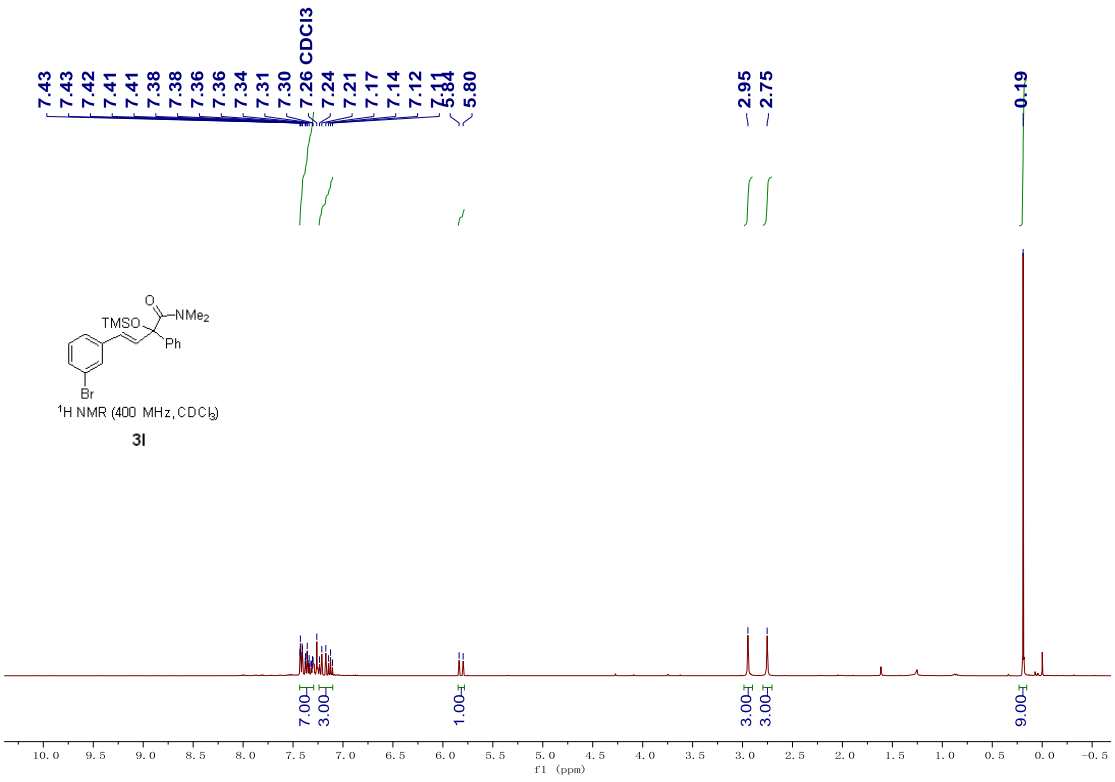

172.64
159.63
142.21
138.22
134.37
131.64
129.34
128.14
127.18
125.31
119.39
113.55
111.50
81.80
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
55.19
37.69
37.07
1.85
TMSO
NMe2
O
Ph
OMe
13C NMR (100 MHz, CDCl3)
3i
f1 (ppm)

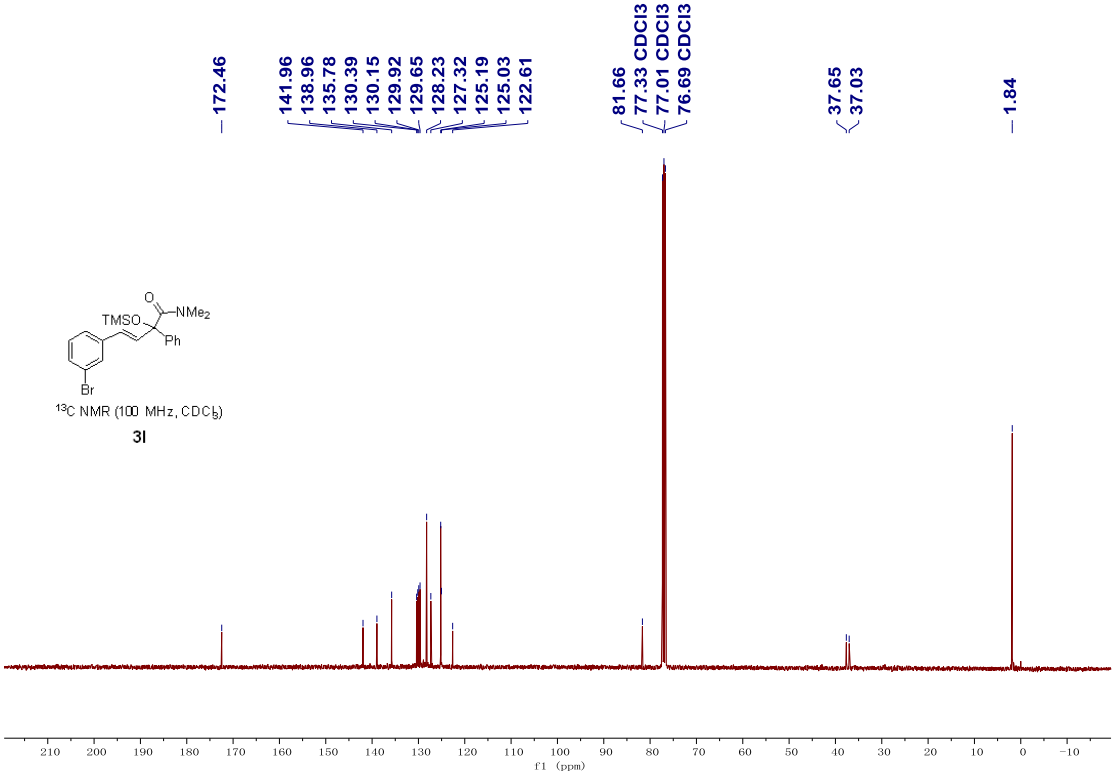

7.452
7.448
7.443
7.437
7.433
7.430
7.427
7.422
7.418
7.413
7.361
7.359
7.357
7.352
7.344
7.341
7.339
7.335
7.324
7.320
7.276
7.273
7.269
7.260 CDCl3
7.257
7.254
7.249
7.237
7.222
7.181
7.177
7.163
7.161
7.159
7.157
7.143
7.138
6.894
6.874
6.855
6.795
6.776
6.353
6.313
3.721
2.945
2.770
2.760
0.193
TMSO
NMe2
Ph
OMe
1H NMR (400 MHz, CDCl3)
3j
5.00
3.29
1.00
1.00
1.00
3.00
3.00
3.00
9.00
f1 (ppm)

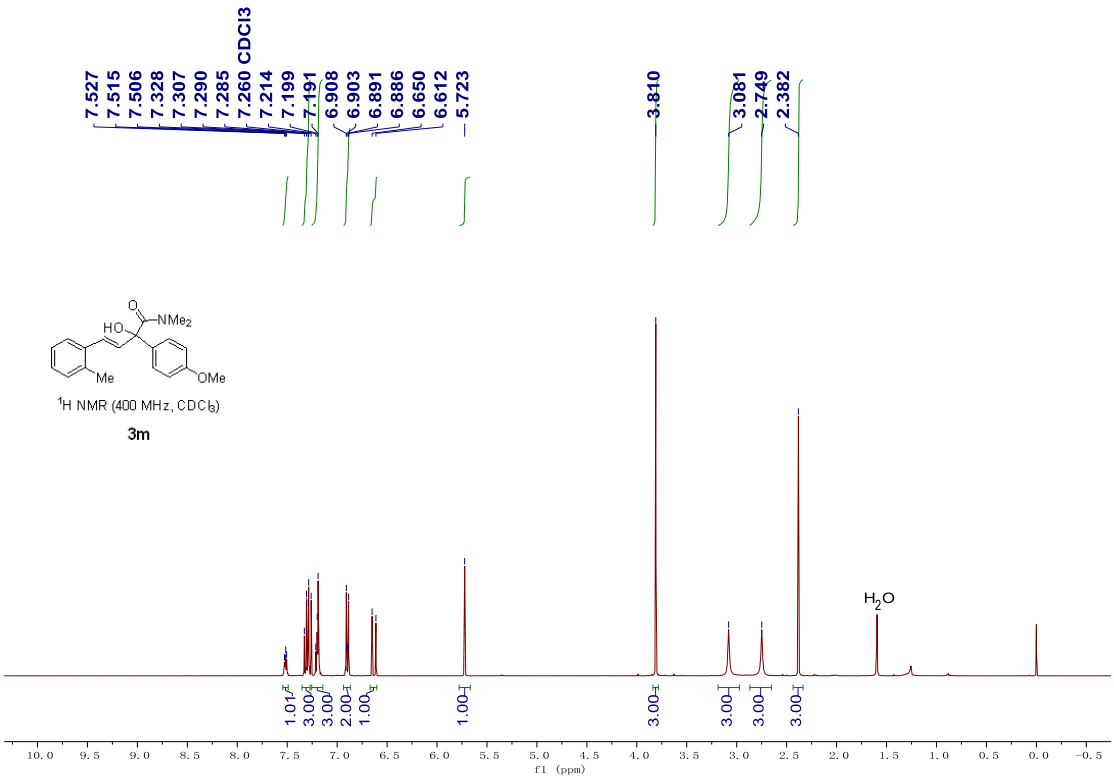

172.83
156.85
142.70
134.43
128.45
128.07
127.23
126.98
126.34
125.91
125.27
120.48
110.83
82.25
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
55.39
37.83
37.08
1.83
TMSO
NMe2
Ph
OMe
13C NMR (100 MHz, CDCl3)
3j
f1 (ppm)

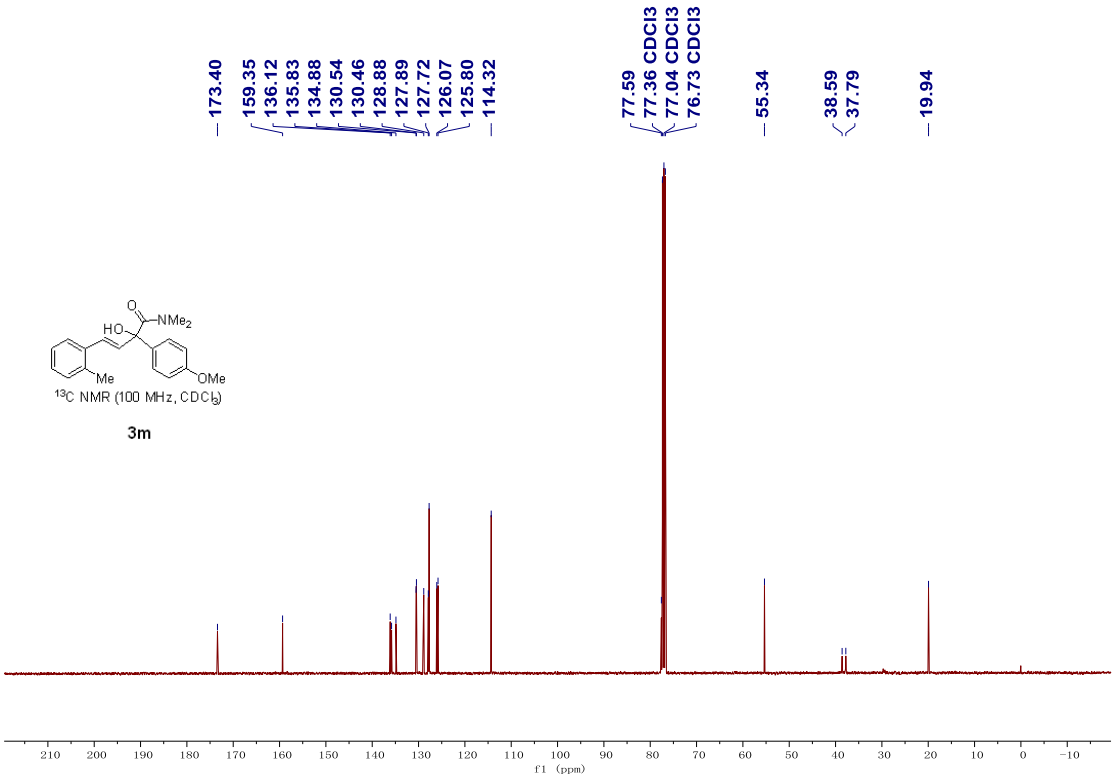

7.445
7.442
7.437
7.424
7.421
7.373
7.369
7.356
7.352
7.340
7.336
7.304
7.300
7.297
7.282
7.263 CDCl3
7.197
7.190
7.170
7.156
7.151
6.908
6.889
6.850
6.844
6.840
6.764
6.758
6.744
6.736
5.892
5.851
3.777
3.047
2.766
0.189
TMSO
NMe2
Ph
OMe
1H NMR (400 MHz, CDCl3)
3k
2.00
2.00
1.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
9.00
f1 (ppm)

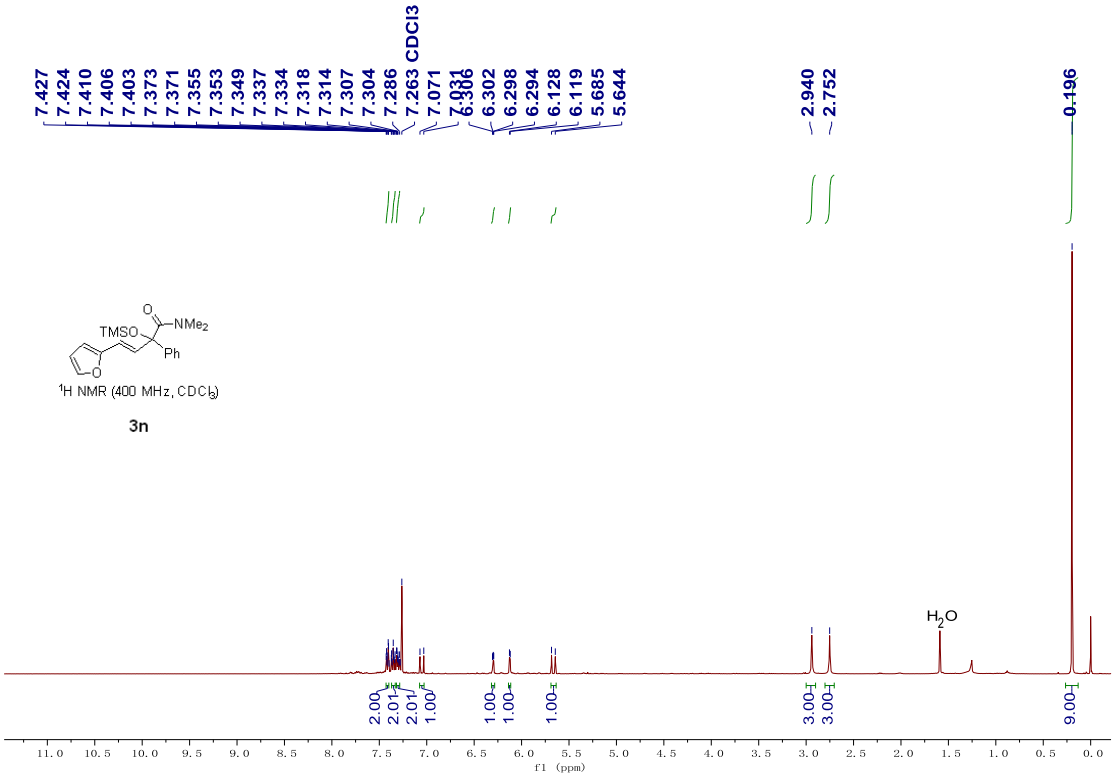

172.66
159.69
142.27
138.27
134.42
131.68
129.35
128.15
127.19
125.34
119.41
113.57
111.58
81.85
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
55.21
37.70
37.09
1.86
TMSO
NMe2
Ph
OMe
13C NMR (100 MHz, CDCl3)
3k
f1 (ppm)

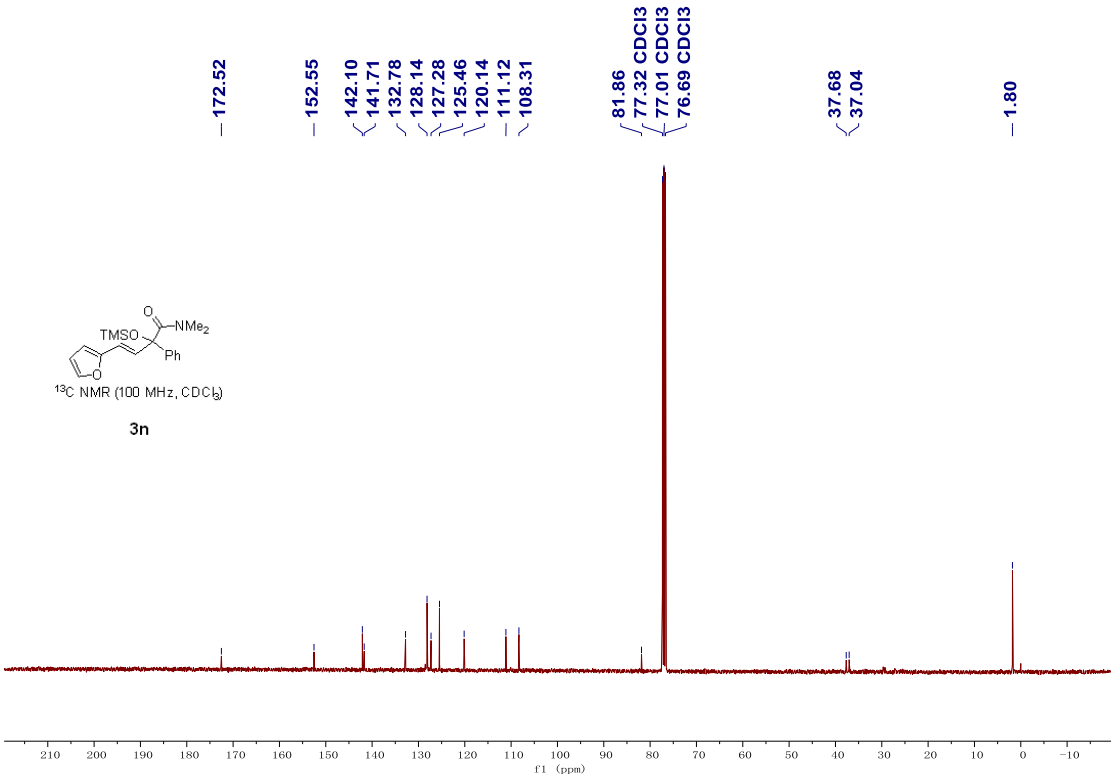

7.43
7.43
7.42
7.41
7.41
7.38
7.38
7.36
7.36
7.34
7.31
7.30
7.26 CDCl3
7.24
7.21
7.17
7.14
7.12
7.11
5.84
5.80
2.95
2.75
0.19
TMSO
O
NMe2
Ph
Br
1H NMR (400 MHz, CDCl3)
3l
7.00
3.00
1.00
3.00
3.00
9.00
f1 (ppm)

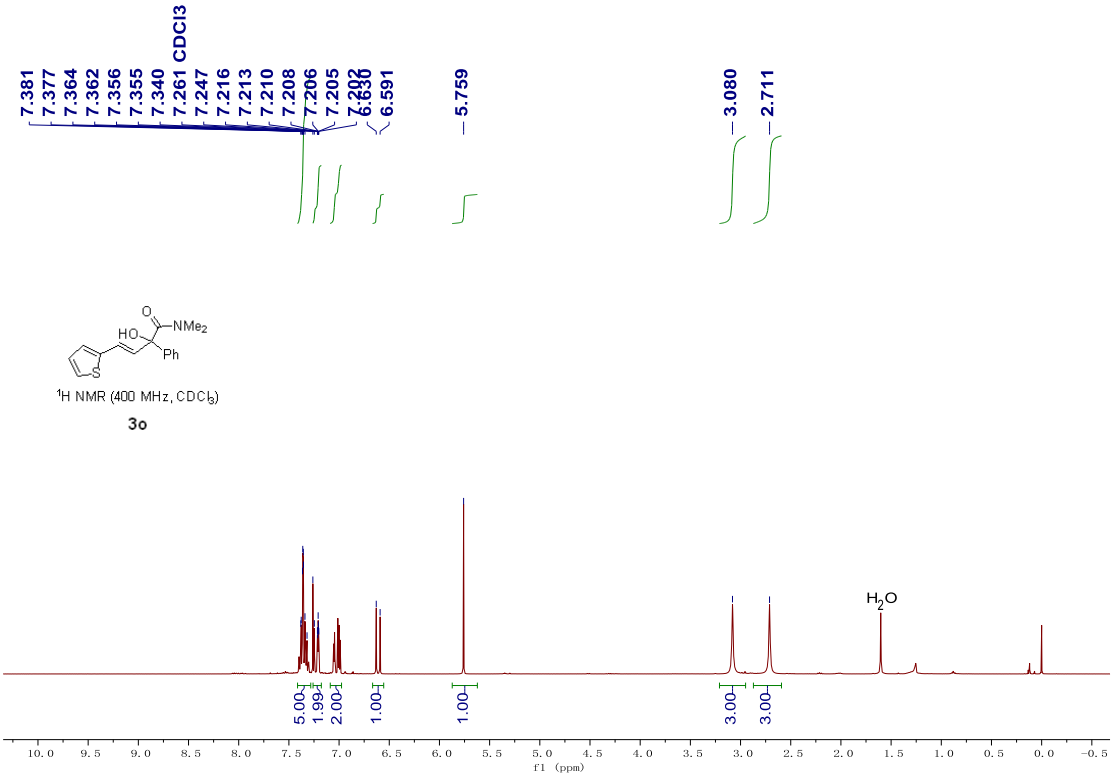

172.46
141.96
138.96
135.78
130.39
130.15
129.92
129.65
128.23
127.32
125.19
125.03
122.61
81.66
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
37.65
37.03
1.84
TMSO
O
NMe2
Ph
Br
13C NMR (100 MHz, CDCl3)
3l
f1 (ppm)

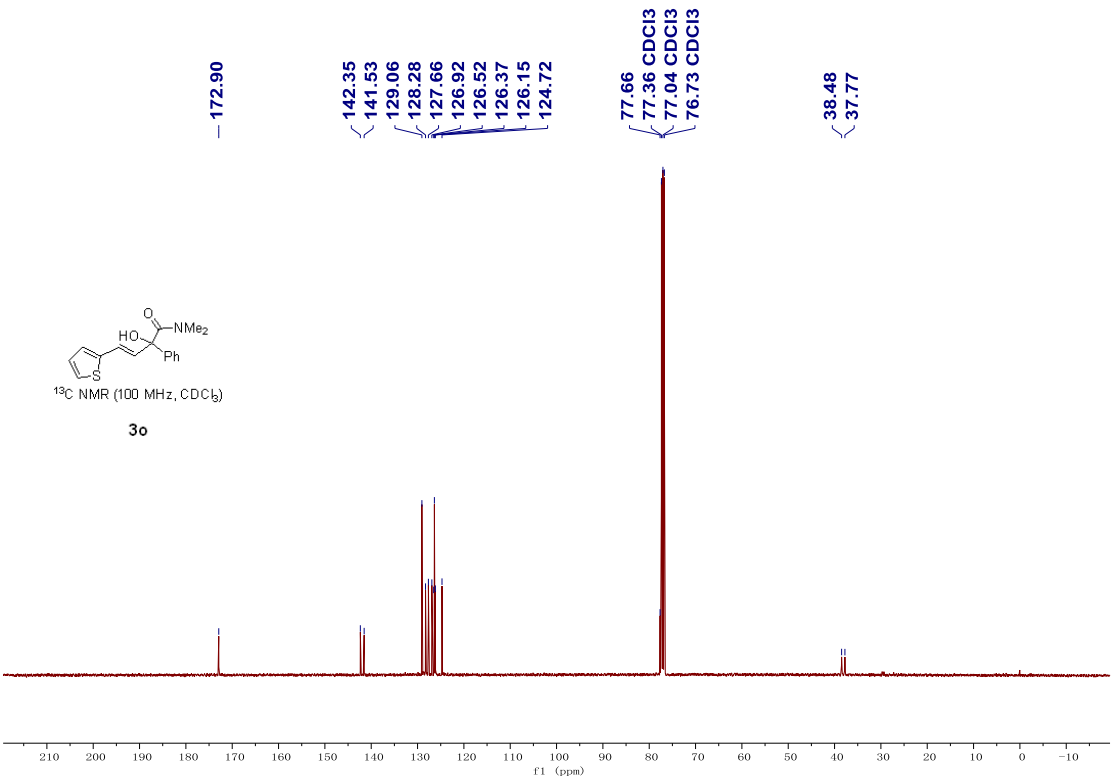

7.527
7.515
7.506
7.328
7.307
7.290
7.285
7.260 CDCl3
7.214
7.199
7.191
6.908
6.903
6.891
6.886
6.650
6.612
5.723
3.810
3.081
2.749
2.382
HO
NMe2
Me
OMe
1H NMR (400 MHz, CDCl3)
3m
H2O
1.01
3.00
3.00
2.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)

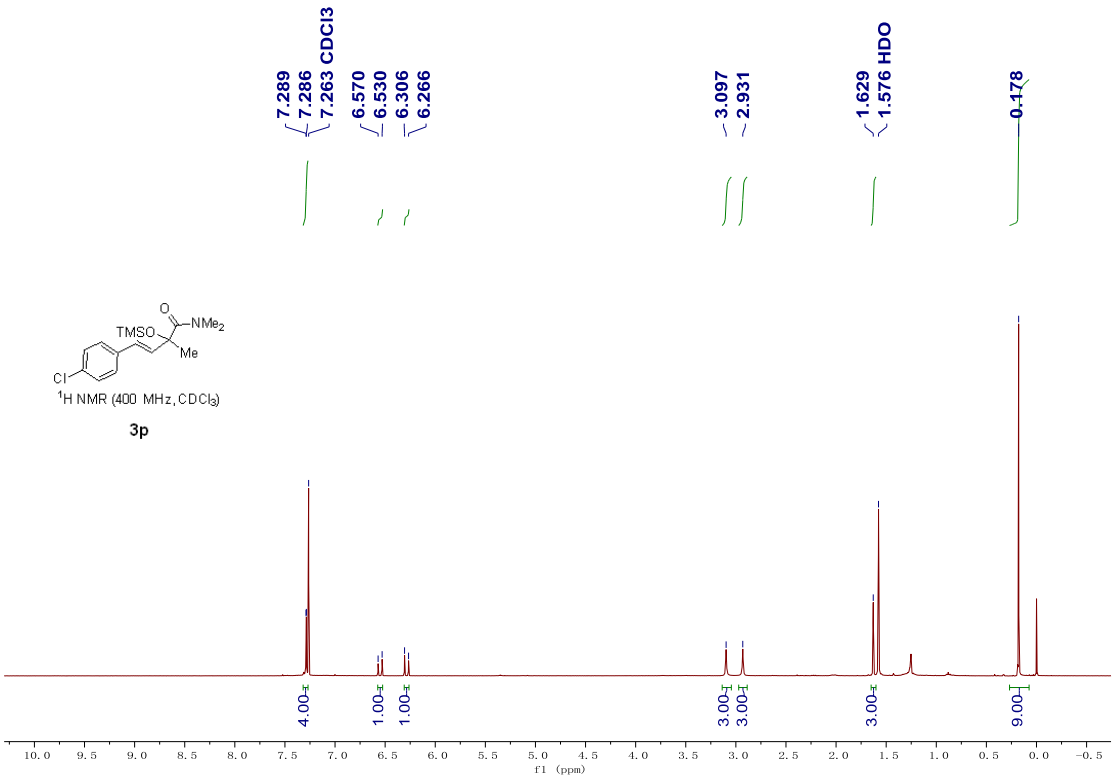

173.40
159.35
136.12
135.83
134.88
130.54
130.46
128.88
127.89
127.72
126.07
125.80
114.32
77.59
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
55.34
38.59
37.79
19.94
HO
NMe2
Me
OMe
13C NMR (100 MHz, CDCl3)
3m
f1 (ppm)

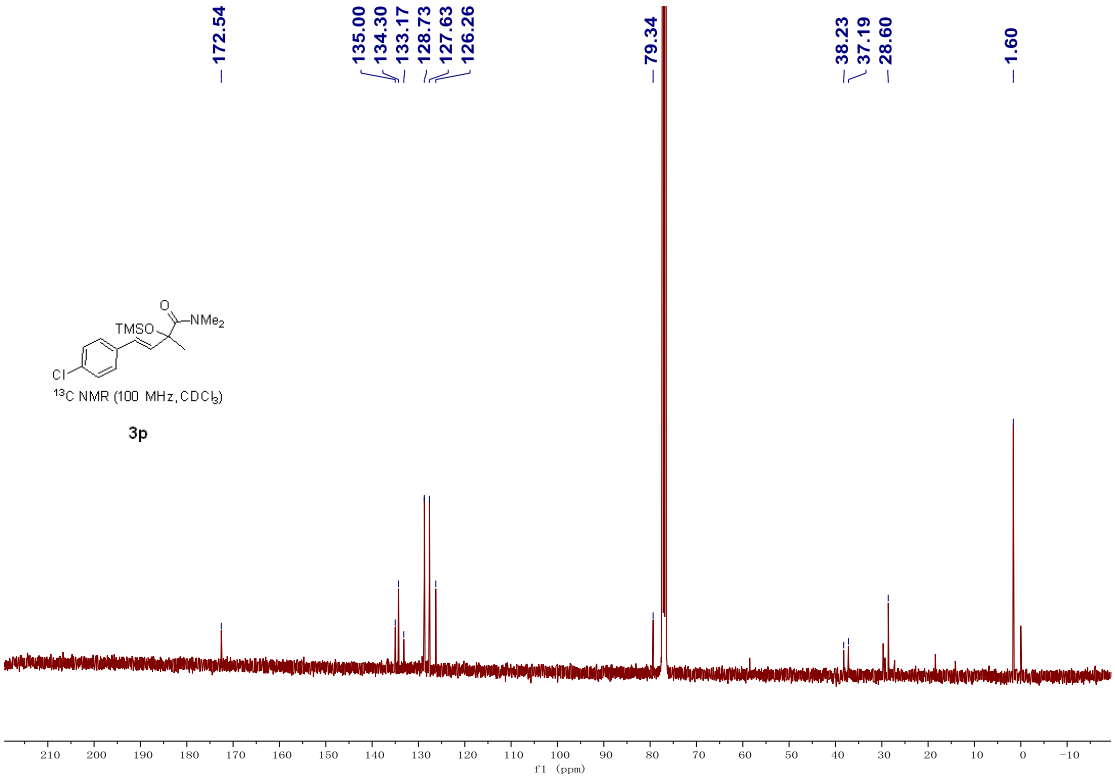

7.427
7.424
7.410
7.406
7.403
7.373
7.371
7.355
7.353
7.349
7.337
7.334
7.318
7.314
7.307
7.304
7.286
CDCl3
7.263
7.071
6.306
6.302
6.298
6.294
6.128
6.119
5.685
5.644
2.940
2.752
0.196
TMSO
NMe2
Ph
O
1H NMR (400 MHz, CDCl3)
3n
H2O
2.00
2.01
2.01
1.00
1.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)

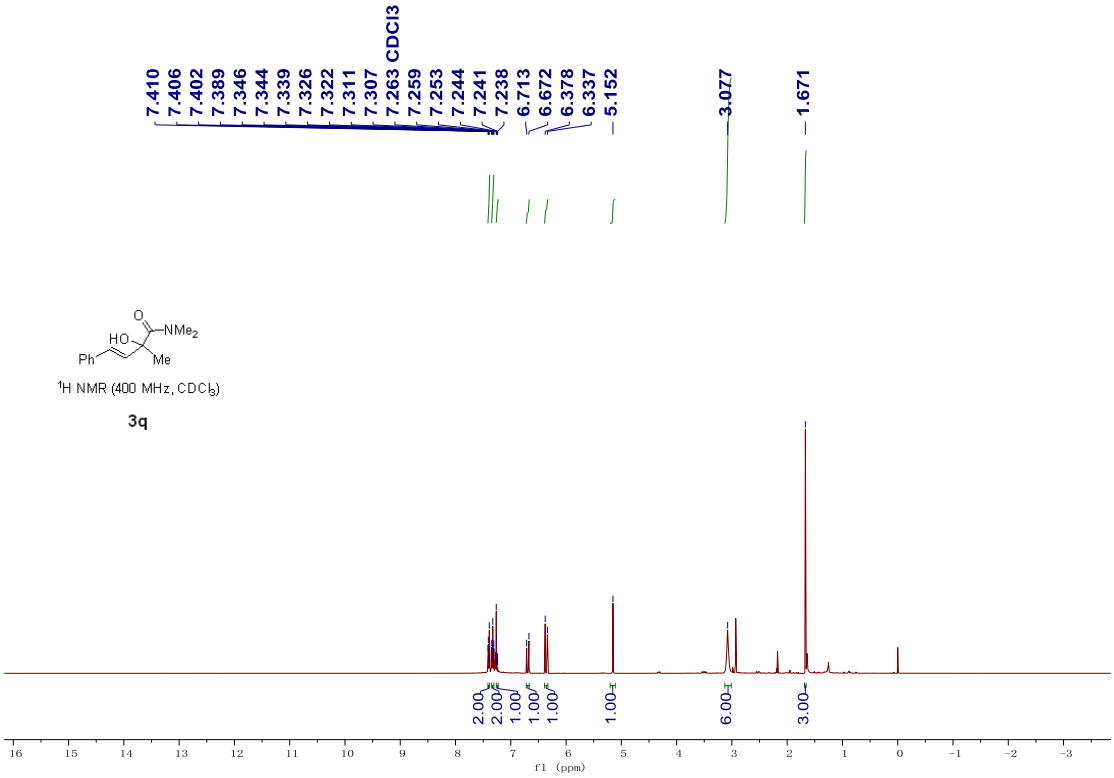

172.52
152.55
142.10
141.71
132.78
128.14
127.28
125.46
120.14
111.12
108.31
81.86
77.32 CDCl3
77.01 CDCl3
76.69 CDCl3
37.68
37.04
1.80
TMSO
NMe2
Ph
O
13C NMR (100 MHz, CDCl3)
3n
f1 (ppm)

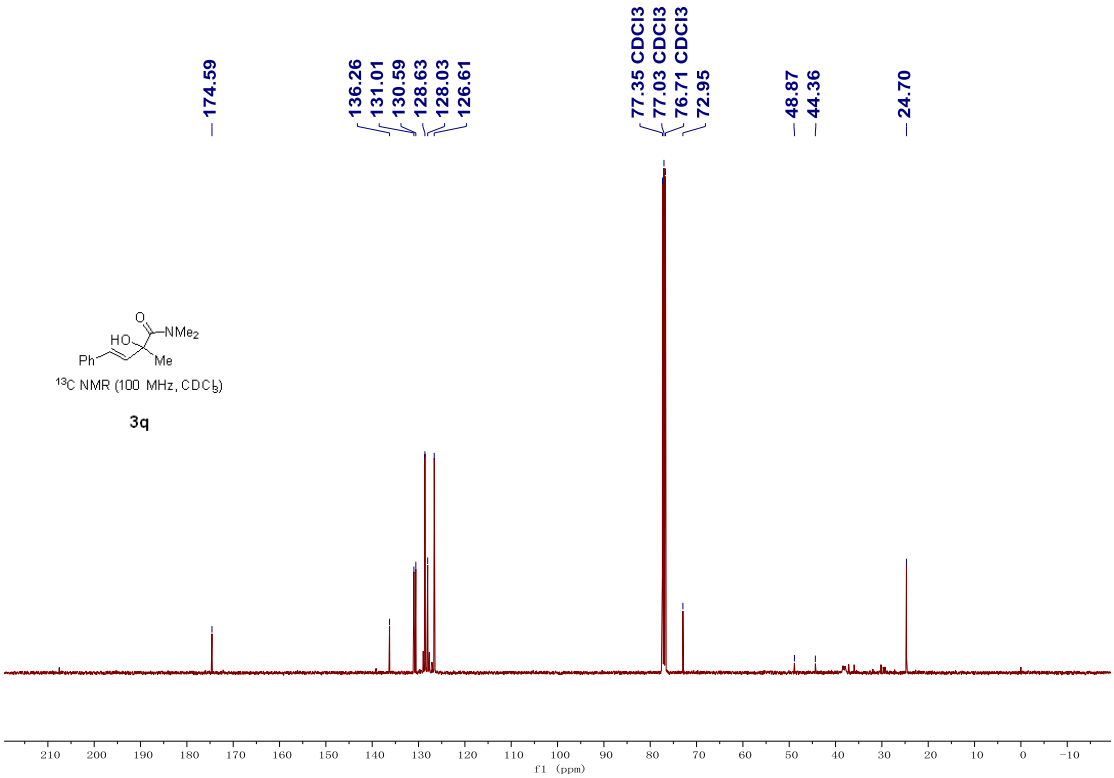

7.381
7.377
7.364
7.362
7.356
7.355
7.340
7.261 CDCl3
7.247
7.216
7.213
7.210
7.208
7.206
7.205
6.630
6.591
5.759
3.080
2.711
NMe2
HO
Ph
S
1H NMR (400 MHz, CDCl3)
3o
H2O
5.00
1.99
2.00
1.00
1.00
3.00
3.00
f1 (ppm)

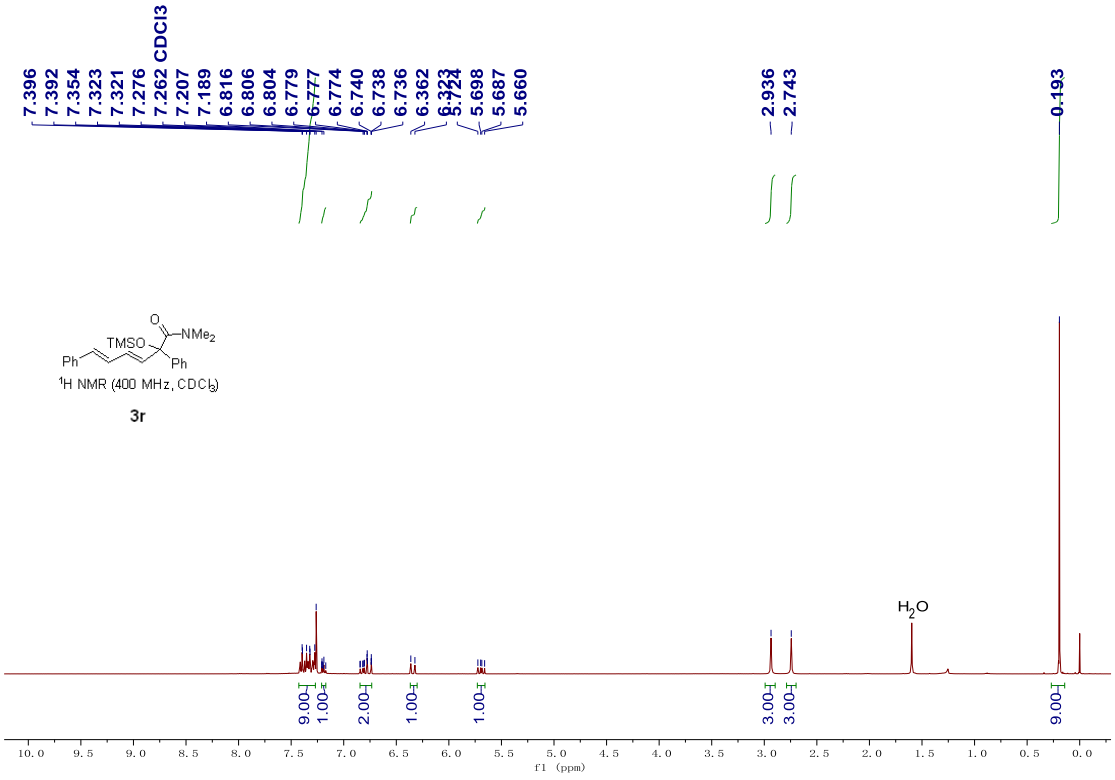

172.90
142.35
141.53
129.06
128.28
127.66
126.92
126.52
126.37
126.15
124.72
77.66
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
38.48
37.77
NMe2
HO
Ph
S
13C NMR (100 MHz, CDCl3)
3o
f1 (ppm)

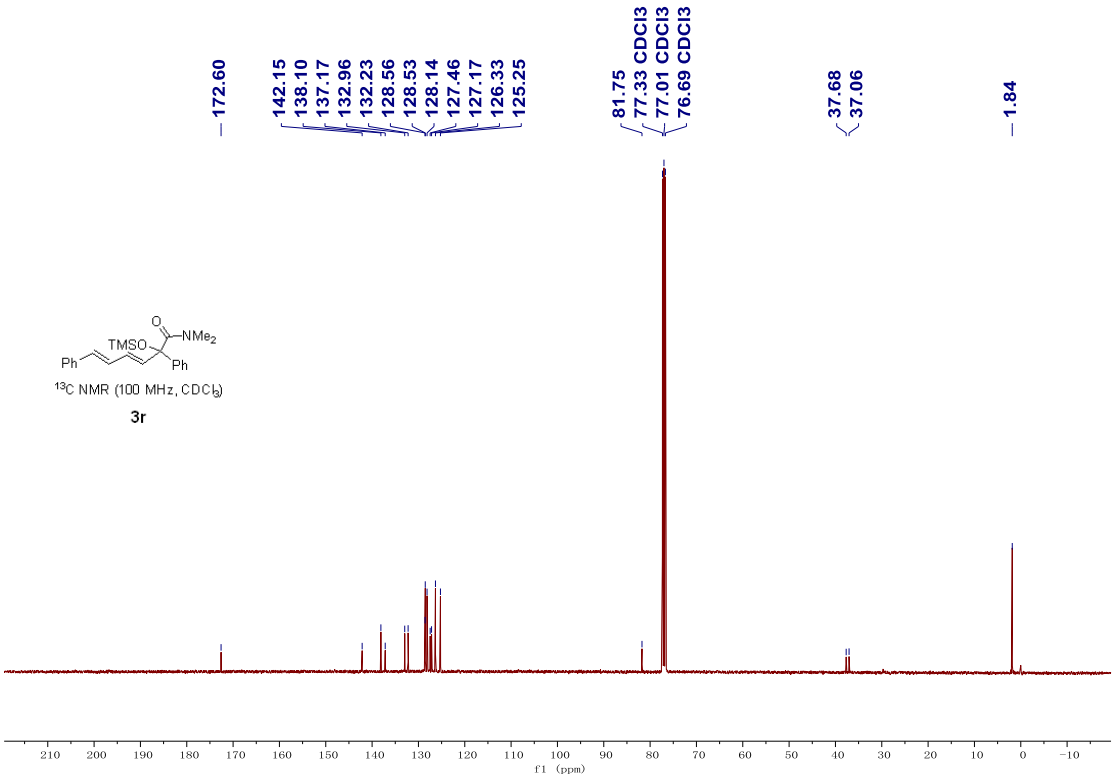

7.289
7.286
7.263 CDCl3
6.570
6.530
6.306
6.266
3.097
2.931
1.629
1.576 HDO
0.178
TMSO
NMe2
Me
Cl
1H NMR (400 MHz, CDCl3)
3p
4.00
1.00
1.00
3.00
3.00
3.00
9.00
f1 (ppm)

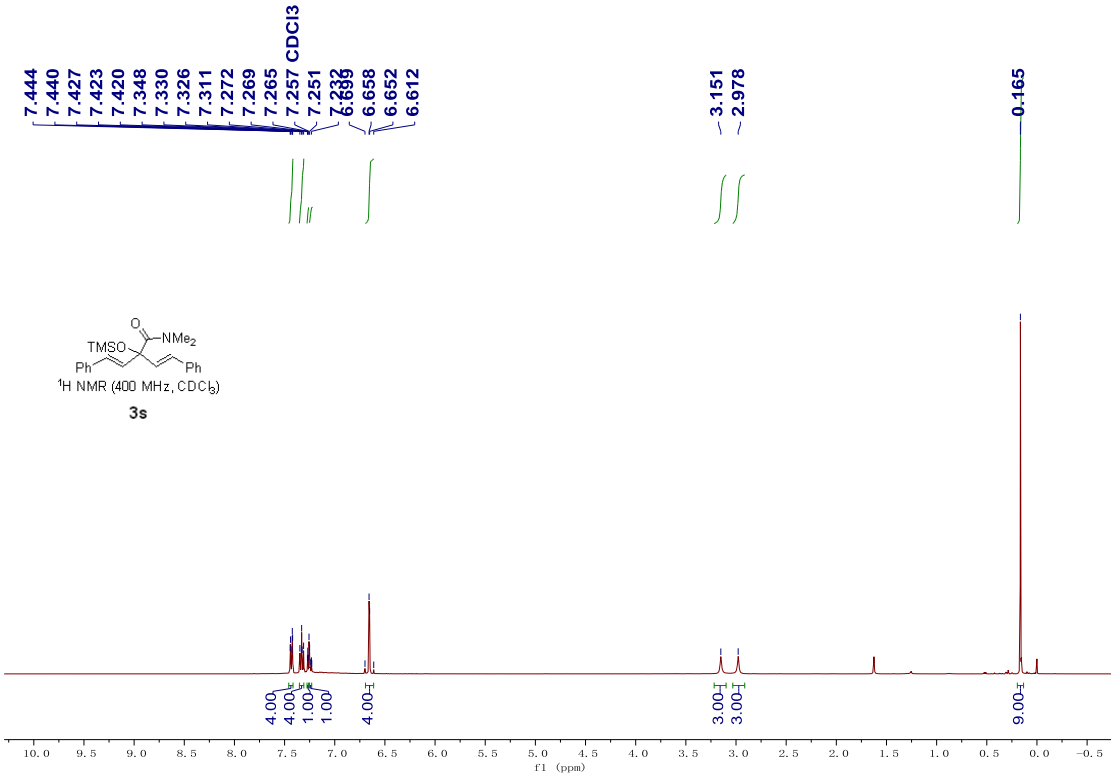

172.54
135.00
134.30
133.17
128.73
127.63
126.26
79.34
38.23
37.19
28.60
1.60
TMSO
NMe2
Cl
13C NMR (100 MHz, CDCl3)
3p
f1 (ppm)

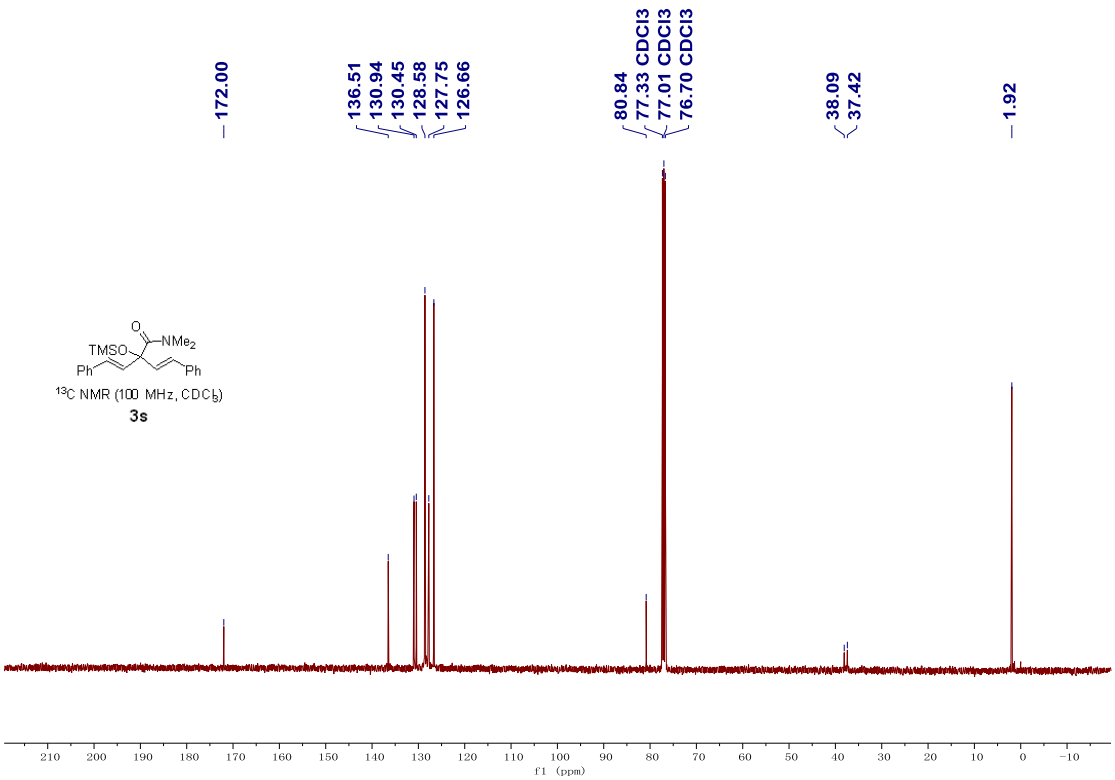

7.410
7.406
7.402
7.389
7.346
7.344
7.339
7.326
7.322
7.311
7.307
7.263 CDCl3
7.259
7.253
7.244
7.241
7.238
6.713
6.672
6.378
6.337
5.152
3.077
1.671
O
NMe2
HO
Ph
Me
1H NMR (400 MHz, CDCl3)
3q
2.00
2.00
1.00
1.00
1.00
1.00
6.00
3.00
f1 (ppm)

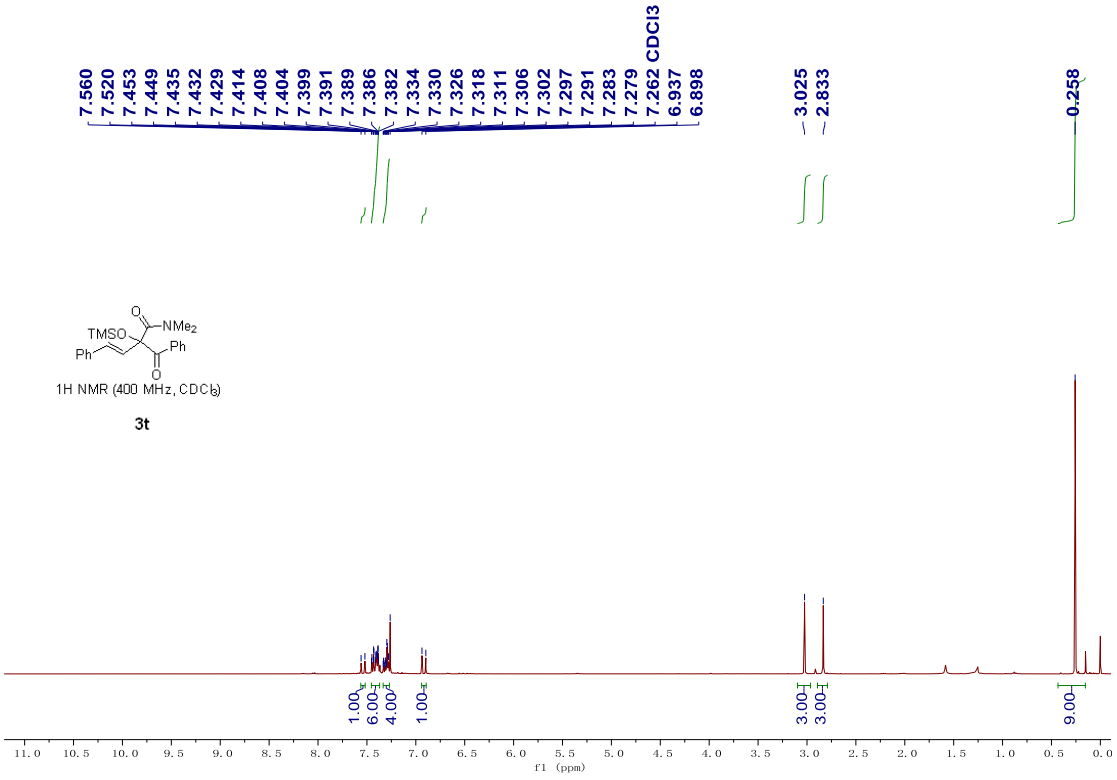

174.59
136.26
131.01
130.59
128.63
128.03
126.61
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
72.95
48.87
44.36
24.70
O
NMe2
HO
Ph
Me
13C NMR (100 MHz, CDCl3)
3q
f1 (ppm)

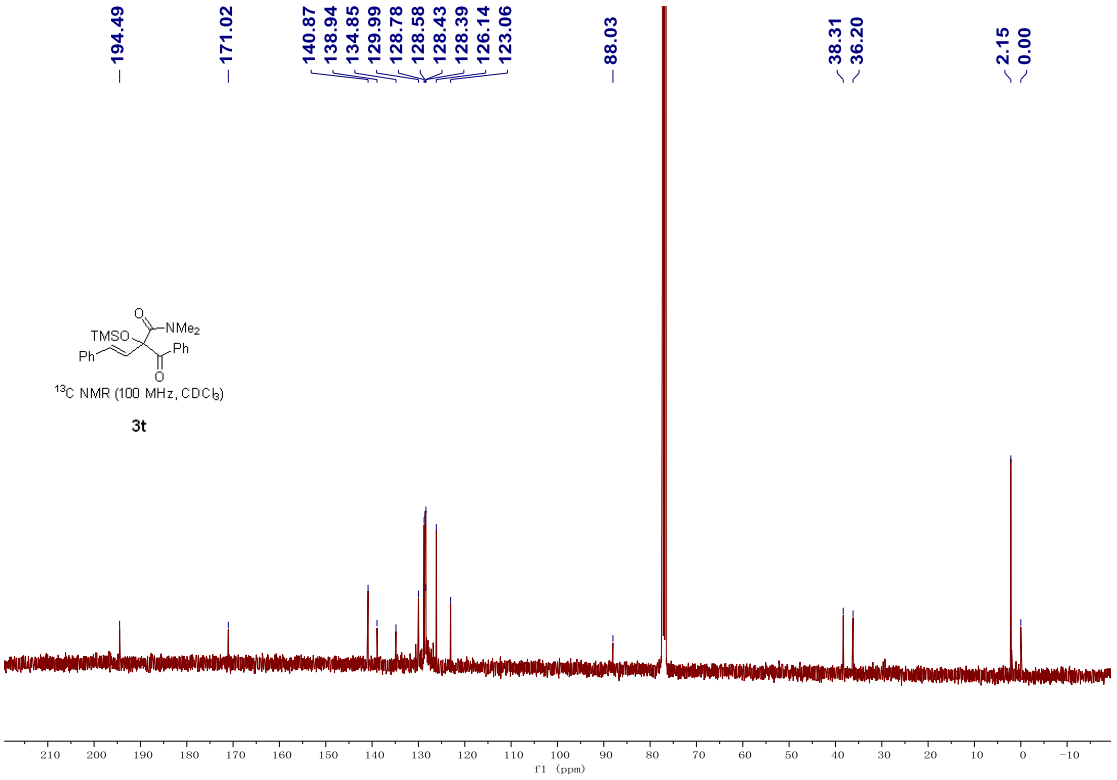

7.396
7.392
7.354
7.323
7.321
7.276
7.262 CDCl3
7.207
7.189
6.816
6.806
6.804
6.779
6.777
6.774
6.740
6.738
6.736
6.362
6.323
5.724
5.698
5.687
5.660
2.936
2.743
0.193
TMSO
NMe2
Ph
Ph
1H NMR (400 MHz, CDCl3)
3r
H2O
9.00
1.08
2.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)

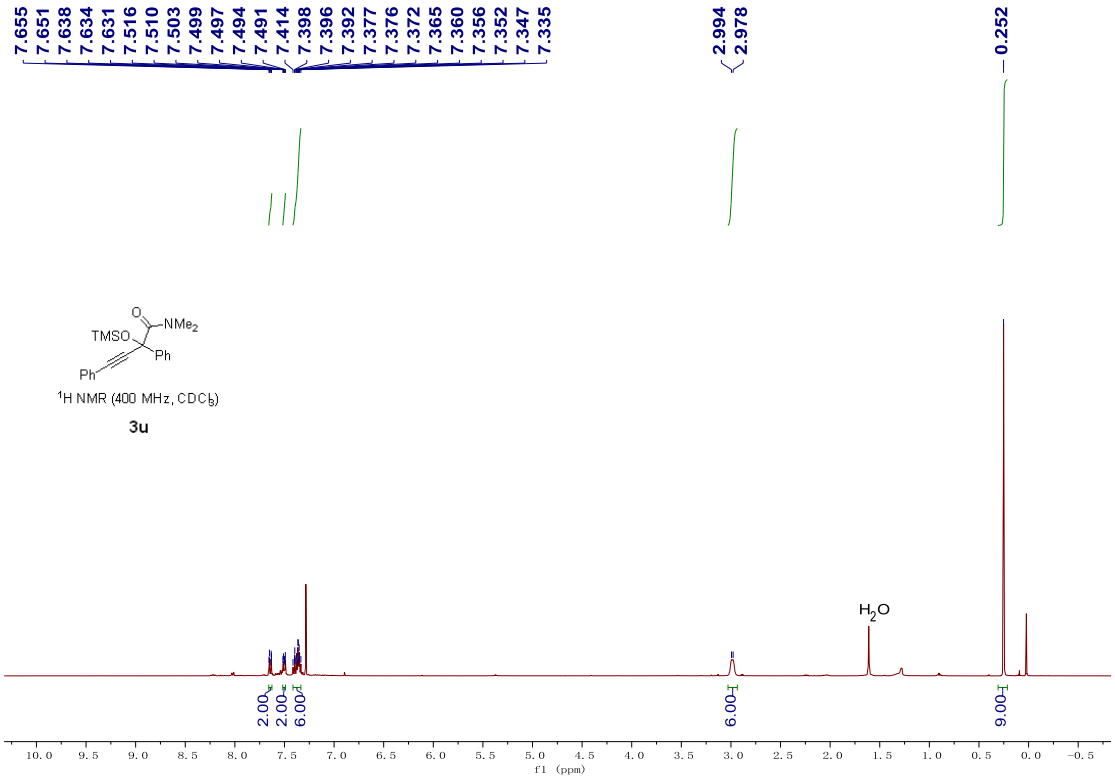

172.60
142.15
138.10
137.17
132.96
132.23
128.56
128.53
128.14
127.46
127.17
126.33
125.25
81.75
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
37.68
37.06
1.84
TMSO
NMe2
Ph
Ph
13C NMR (100 MHz, CDCl3)
3r
f1 (ppm)

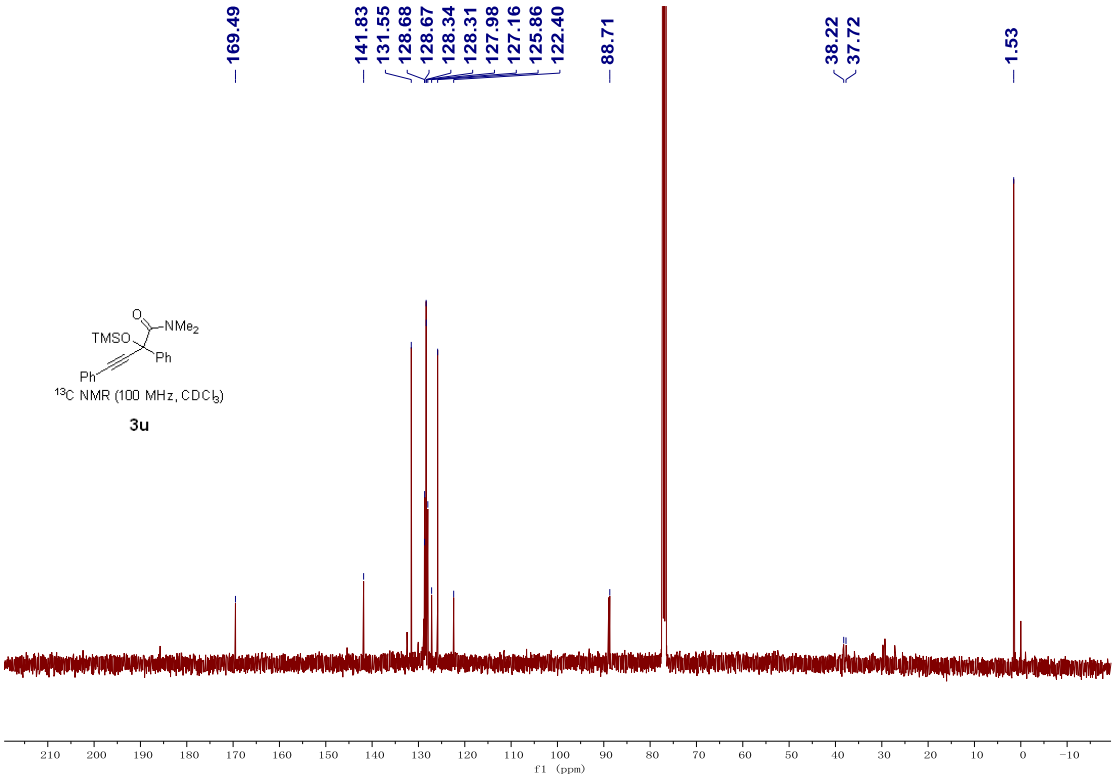

7.444
7.440
7.427
7.423
7.420
7.348
7.330
7.326
7.311
7.272
7.269
7.265
7.257 CDCl3
7.251
6.658
6.652
6.612
3.151
2.978
0.165
TMSO
NMe2
Ph
Ph
1H NMR (400 MHz, CDCl3)
3s
4.00
4.00
1.00
1.00
4.00
3.00
3.00
9.00
f1 (ppm)

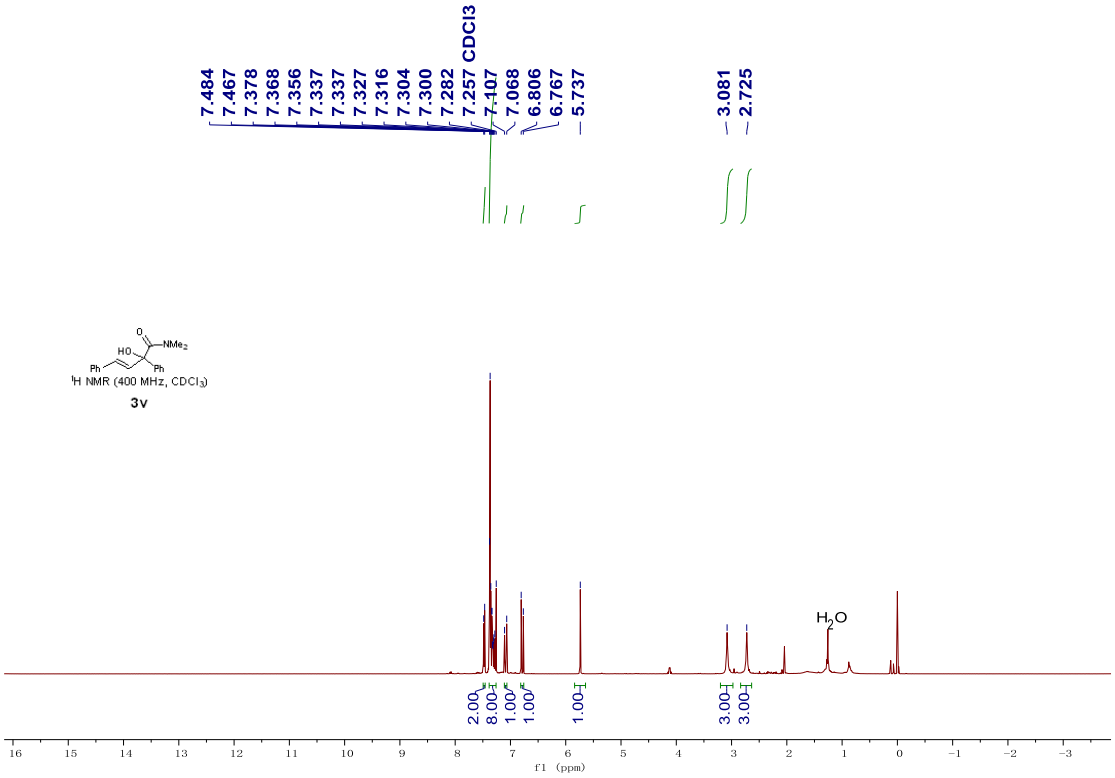

172.00
136.51
130.94
130.45
128.58
127.75
126.66
80.84
77.33 CDCl3
77.01 CDCl3
76.70 CDCl3
38.09
37.42
1.92
TMSO
NMe2
Ph
Ph
13C NMR (100 MHz, CDCl3)
3s
f1 (ppm)

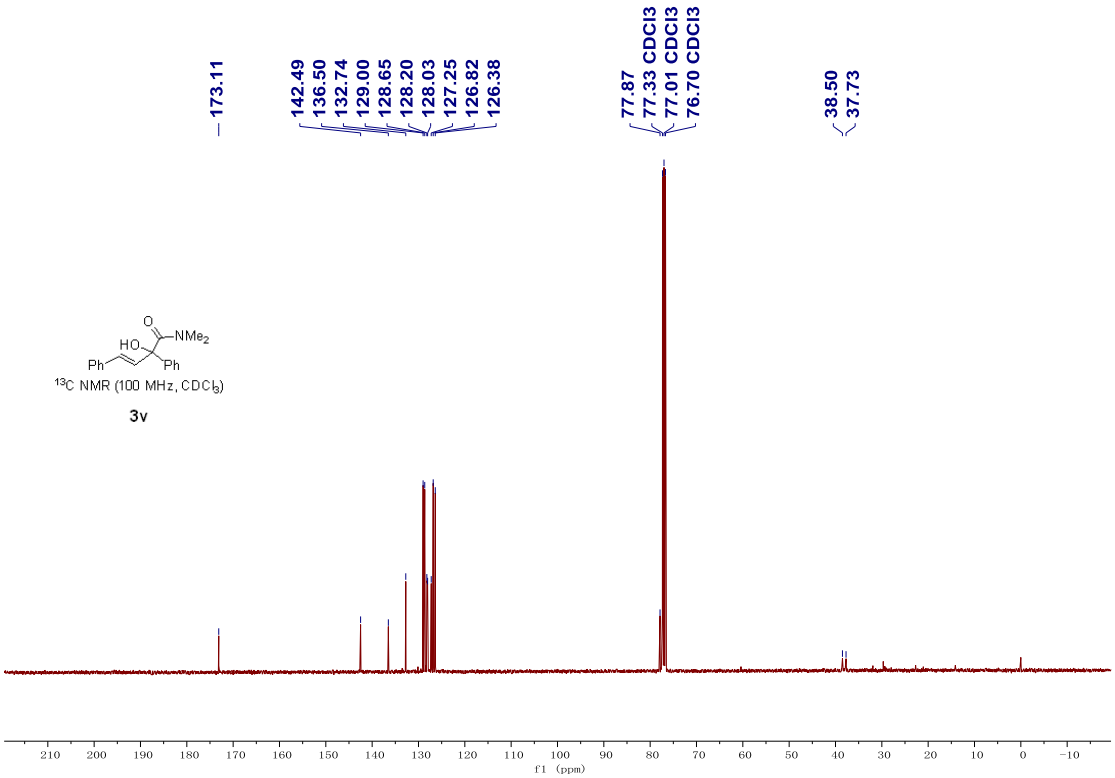

7.560
7.520
7.453
7.449
7.435
7.432
7.429
7.414
7.408
7.404
7.399
7.391
7.389
7.386
7.382
7.334
7.330
7.326
7.318
7.311
7.306
7.302
7.297
7.291
7.283
7.279
7.262 CDCl3
6.937
6.898
3.025
2.833
0.258
TMSO
NMe2
Ph
Ph
O
O
1H NMR (400 MHz, CDCl3)
3t
1.00
6.00
4.00
1.00
3.00
3.00
9.00
f1 (ppm)


194.49
171.02
140.87
138.94
134.85
129.99
128.78
128.58
128.43
128.39
126.14
123.06
88.03
38.31
36.20
2.15
0.00
TMSO
NMe2
Ph
Ph
O
O
13C NMR (100 MHz, CDCl3)
3t
f1 (ppm)


7.655
7.651
7.638
7.634
7.631
7.516
7.510
7.503
7.499
7.497
7.494
7.491
7.414
7.398
7.396
7.392
7.377
7.376
7.372
7.365
7.360
7.356
7.352
7.347
7.335
2.994
2.978
0.252
TMSO
NMe2
Ph
Ph
1H NMR (400 MHz, CDCl3)
3u
H2O
2.00
2.00
6.00
6.00
9.00
f1 (ppm)


169.49
141.83
131.55
128.68
128.67
128.34
128.31
127.98
127.16
125.86
122.40
88.71
38.22
37.72
1.53
TMSO
NMe2
Ph
Ph
13C NMR (100 MHz, CDCl3)
3u
f1 (ppm)


7.484
7.467
7.378
7.368
7.356
7.337
7.337
7.327
7.316
7.304
7.300
7.282
7.257 CDCl3
7.107
7.068
6.806
6.767
5.737
3.081
2.725
NMe2
HO
Ph
Ph
1H NMR (400 MHz, CDCl3)
3v
H2O
2.00
8.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


173.11
142.49
136.50
132.74
129.00
128.65
128.20
128.03
127.25
126.82
126.38
77.87
77.33 CDCl3
77.01 CDCl3
76.70 CDCl3
38.50
37.73
NMe2
HO
Ph
Ph
13C NMR (100 MHz, CDCl3)
3v
f1 (ppm)