Supporting Information

Visible-Light-Promoted Oxidation/Condensation of Benzyl Alcohols with *N*,*N*-Dialkylacetamides to Access Cinnamides

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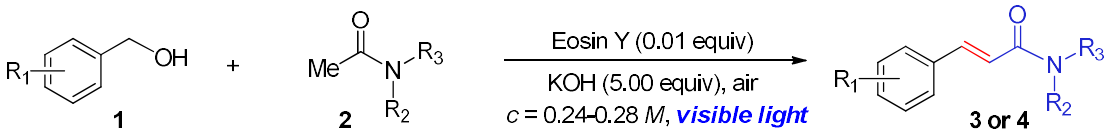
Materials and methods

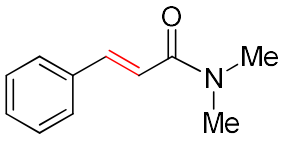
All the chemicals were purchased commercially, and used without further purification. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. ^{1}H NMR spectra were recorded on JEOL spectrometers (at 400 MHz) and were reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on JEOL Spectrometers (at 100 MHz). Data for ^{13}C NMR spectra were reported in terms of chemical shift. Mass spectrometric data were obtained using Bruker Apex IV RTMS. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

General procedure for cinnamides synthesis



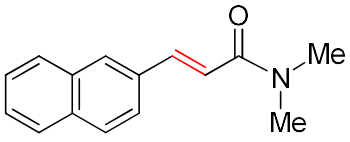
A flame-dried round bottom flask was equipped with magnetic stir bar and charged with benzyl alcohols **1** (0.246 mmol, 1.0 equiv), Eosin Y (0.00246 mmol, 0.01 equiv), KOH (1.228 mmol, 5.0 equiv), and *N,N*-dialkylacetamide (1.0 mL). Then the reaction mixture was irradiated by blue LEDs (18 *W*) under a balloon air atmosphere at room temperature until the starting material disappeared from the TLC. After that water (20 mL) was added and the aqueous layer was extracted with EtOAc (5 × 15 mL). The combined organic layers were washed with brine (2 × 30 mL), dried over Na_2SO_4, filtered and evaporated under the reduced pressure. The crude residue was purified by silica gel column chromatography using hexane/EtOAc (2/1 to EtOAc) to afford the desired pure product **3** or **4** in 29-87% yield.

^{1}H and ^{13}C spectra data of compounds 3a-3s, 4a-4h



3a

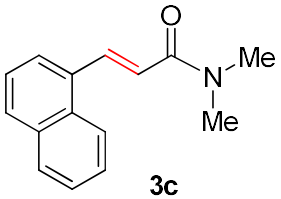
(*E*)-*N,N*-dimethylcinnamamide (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.55 (d, *J* = 15.6 Hz, 1H), 7.51-7.42 (m, 2H), 7.39-7.22 (m, 3H), 6.87-6.82 (d, *J* = 15.6 Hz, 1H), 3.11 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.4, 135.4, 129.6, 128.8, 127.8, 117.5, 37.5, 36.0; These data are consistent with literature values, see: S. W. Foo, S. Oishi and S. Saito, *Tetrahedron Lett.,* 2012, **53**, 5445. (White solid, 32.6 mg, 78% isolated yield)



3b

E/*Z* = 12.1

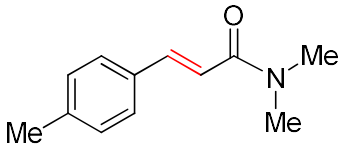
(*E*)-*N*,*N*-dimethyl-3-(naphthalen-2-yl)acrylamide (3b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85-7.72 (m, 4H), 7.68-7.66 (d, *J* = 8.4 Hz, 1H), 7.46-7.52 (m, 2H), 7.01-6.97 (d, *J* = 15.2 Hz, 1H), 3.19 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.5, 134.0, 133.5, 132.9, 129.3, 128.6, 128.5, 127.8, 126.9, 126.7, 123.7, 117.6, 37.6, 36.1; These data are consistent with literature values, see: S. W. Foo, S. Oishi and S. Saito, *Tetrahedron Lett.,* 2012, **53**, 5445. (White solid, 14.5 mg, 28% isolated yield)



3c

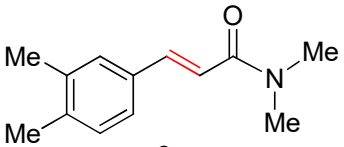
E/*Z* = 6.7

(*E*)-*N*,*N*-dimethyl-3-(naphthalen-1-yl)acrylamide (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51-8.46 (m, 1H), 8.22-8.20 (m, 1H), 7.86-7.84 (m, 2H), 7.72-7.69 (m, 1H), 7.54-7.43 (m, 3H), 6.95-6.91 (d, *J* = 15.2 Hz, 1H), 3.18 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 139.8, 133.7, 133.2, 131.6, 129.9, 128.7, 126.7, 126.2, 125.5, 124.6, 123.9, 120.6, 37.6, 36.1; These data are consistent with literature values, see: I. Sato, H. Suzuki, Y. Yamashita and S. Kobayashi, *Org. Chem. Front.,* 2016, **3**, 1241. (White solid, 39.3 mg, 76% isolated yield)



3d

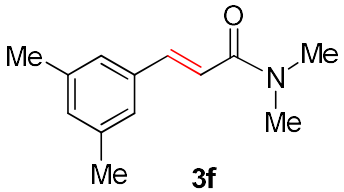
(*E*)-*N*,*N*-dimethyl-3-(*p*-tolyl)acrylamide (3d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.63 (d, *J* = 15.6 Hz, 1H), 7.43-7.41 (d, *J* = 8.0 Hz, 2H), 7.18-7.16 (d, *J* = 8.0 Hz, 2H), 6.86-6.82 (d, *J* = 15.2 Hz, 1H), 3.16 (s, 3H), 3.06 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 142.5, 139.9, 132.7, 129.6, 127.8, 116.3, 37.5, 36.0, 21.5; These data are consistent with literature values, see: S. W. Foo, S. Oishi and S. Saito, *Tetrahedron Lett.,* 2012, **53**, 5445. (White solid, 27.3 mg, 63% isolated yield)



3e

E/*Z* = 25.1

(*E*)-3-(3,4-dimethylphenyl)-*N*,*N*-dimethylacrylamide (3e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.58 (d, *J* = 15.6 Hz, 1H), 7.27-7.23 (m, 2H), 7.11-7.09 (d, *J* = 8.0 Hz, 1H), 6.83-6.79 (d, *J* = 15.6 Hz, 1H), 3.14 (m, 3H), 3.06 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 142.6, 138.6, 137.0, 133.1, 130.1, 129.0, 125.5, 116.2, 37.5, 36.0, 19.8; These data are consistent with literature values, see: P. Wang, P. Verma, G. Xia, J. Shi, J. X. Qiao, S. Tao, P. T. W. Cheng, M. A. Poss, M. E. Farmer, K. Yeung and J. Yu, *Nature*, **551**, 489. (White solid, 25.4 mg, 54% isolated yield)

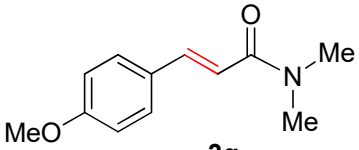


3f

E/*Z* = 6.7

(*E*)-3-(3,5-dimethylphenyl)-*N*,*N*-dimethylacrylamide (3f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (d, *J* = 14.8 Hz, 1H), 7.14 (s, 2H), 6.99 (s, 1H), 6.88-6.84 (d, *J* =

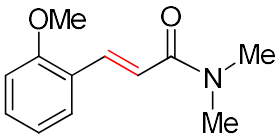
15.2 Hz, 1H), 3.18 (s, 3H), 3.07 (m, 3H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 142.9, 138.4, 135.3, 131.5, 125.7, 116.9, 37.5, 36.1, 21.4; HRMS calculated for $C_{13}H_{18}NO$ ($M + H^+$): 204.1388, found: 204.1385. (White solid, 31.9 mg, 68% isolated yield)



3g

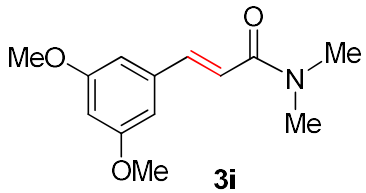
E/*Z* = 4.0

(*E*)-3-(4-methoxyphenyl)-*N*,*N*-dimethylacrylamide (3g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (d, *J* = 15.6 Hz, 1H), 7.49-7.47 (d, *J* = 8.8 Hz, 2H), 6.90-6.88 (d, *J* = 8.8 Hz, 2H), 6.84-6.74 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H), 3.15 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 160.8, 142.1, 129.8, 129.4, 115.0, 114.3, 55.4, 37.5, 36.0; These data are consistent with literature values, see: S. W. Foo, S. Oishi and S. Saito, *Tetrahedron Lett.,* 2012, **53**, 5445. (White solid, 36.2 mg, 76% isolated yield)



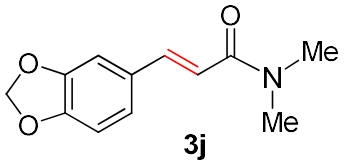
3h

(*E*)-3-(2-methoxyphenyl)-*N*,*N*-dimethylacrylamide (3h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.90 (d, *J* = 15.6 Hz, 1H), 7.50-7.48 (d, *J* = 7.6 Hz, 1H), 7.34-7.28 (m, 1H), 7.02-6.90 (m, 3H), 3.87 (s, 3H), 3.16 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 158.3, 138.0, 130.7, 129.1, 124.5, 120.7, 118.5, 111.2, 55.5, 37.5, 36.0; These data are consistent with literature values, see: S. W. Foo, S. Oishi and S. Saito, *Tetrahedron Lett.,* 2012, **53**, 5445. (Colorless oil, 37.5 mg, 74% isolated yield)



3i

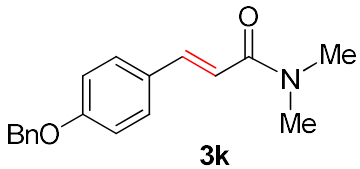
(*E*)-3-(3,5-dimethoxyphenyl)-*N*,*N*-dimethylacrylamide (3i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.57 (d, *J* = 15.6 Hz, 1H), 6.87-6.83 (d, *J* = 15.6 Hz, 1H), 6.67 (s, 2H), 6.44-6.41 (m, 1H), 3.78 (m, 6H), 3.14 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 161.0, 142.4, 137.4, 118.1, 105.9, 101.6, 55.5, 37.5, 36.0; HRMS calculated for $C_{13}H_{18}NO_3$ ($M + H^+$): 236.1287, found: 236.1263. (White solid, 44.2 mg, 81% isolated yield)



3j

E/*Z* = 3.3

(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-*N*,*N*-dimethylacrylamide (3j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (d, *J* = 15.6 Hz, 1H), 7.04-7.02 (m, 2H), 6.81-6.79 (d, *J* = 8.0 Hz, 1H), 6.74-6.70 (d, *J* = 15.6 Hz, 1H), 5.99 (s, 2H), 3.16 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 149.0, 148.3, 142.2, 129.9, 123.9, 115.4, 108.6, 106.4, 101.5, 37.5, 36.0; These data are consistent with literature values, see: R. U. Pathan, and S. L. Patil, *Orient. J. Chem.,* 2008, 3, 709. (White solid, 31.1 mg, 54% isolated yield)

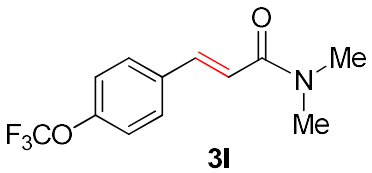


3k

E/*Z* = 5.3

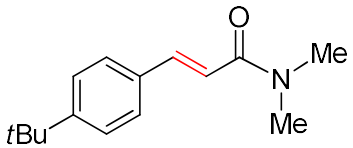
(*E*)-3-(4-(benzyloxy)phenyl)-*N*,*N*-dimethylacrylamide (3k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (d, *J* = 15.6 Hz, 1H), 7.48-7.46 (d, *J* = 8.8 Hz, 2H), 7.43-7.37 (m,

5H), 6.96-6.94 (d, *J* = 8.8 Hz, 2H), 6.77-6.73 (d, *J* = 15.6 Hz, 1H), 5.06 (s, 2H), 3.13 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 160.0, 142.1, 136.7, 129.5, 128.7, 128.4, 128.2, 127.6, 115.2, 115.1, 70.1, 37.5, 36.0; These data are consistent with literature values, see: M. Oberholzer, R. Gerber and C. M. Frech, *Adv. Synth. Catal.,* 2012, **354**, 627. (White solid, 56.8 mg, 87% isolated yield)



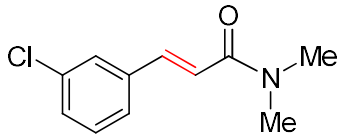
3l

(*E*)-*N*,*N*-dimethyl-3-(4-(trifluoromethoxy)phenyl)acrylamide (3l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.63 (d, *J* = 15.6 Hz, 1H), 7.56-7.54 (d, *J* = 8.4 Hz, 2H), 7.23-7.21 (d, *J* = 8.4 Hz, 2H), 6.89-6.85 (d, *J* = 15.6 Hz, 1H), 3.18 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 149.9, 140.8, 134.1, 129.2, 121.2, 118.4, 37.5, 36.1; HRMS calculated for $C_{12}H_{13}F_3NO_2$ ($M + H^+$): 260.0898, found: 260.0889. (Yellow oil, 44.4 mg, 73% isolated yield)



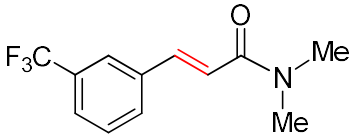
3m

(*E*)-3-(4-(tert-butyl)phenyl)-*N*,*N*-dimethylacrylamide (4c): 1H NMR (400 MHz, CDCl3) δ 7.68-7.64 (d, J = 15.6 Hz, 1H), 7.48-7.46 (d, J = 8.0 Hz, 2H), 7.40-7.38 (d, J = 8.0 Hz, 2H), 6.88-6.84 (d, J = 15.6 Hz, 1H), 3.17 (s, 3H), 3.06 (s, 3H), 1.32 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 167.0, 153.0, 142.3, 132.7, 127.7, 125.8, 116.6, 37.5, 36.0, 34.9, 31.3; HRMS calculated for $C_{15}H_{22}NO$ ($M + H^+$): 232.1701, found: 232.1712. (Colorless oil, 42.3 mg, 74% isolated yield)



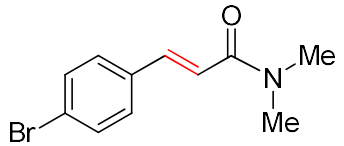
3n

(*E*)-3-(3-chlorophenyl)-*N*,*N*-dimethylacrylamide (3n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.58 (d, *J* = 15.6 Hz, 1H), 7.58 (s, 1H), 7.39-7.38 (m, 1H), 7.37-7.31 (m, 2H), 6.92-6.87 (d, *J* = 15.6 Hz, 1H), 3.18 (s, 3H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 140.9, 137.3, 134.8, 130.1, 129.5, 127.3, 126.4, 118.9, 37.5, 36.1; These data are consistent with literature values, see: X. Yang, W. Wei, H. Li, R. Song and J. Li, *Chem. Commun.,* 2014, **50**, 12867. (White solid, 36.6 mg, 71% isolated yield)



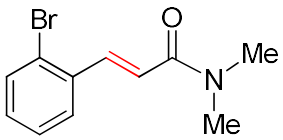
3o

(*E*)-*N*,*N*-dimethyl-3-(3-(trifluoromethyl)phenyl)acrylamide (3o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.70-7.66 (m, 2H), 7.60-7.58 (d, *J* = 8.0 Hz, 1H), 7.52-7.48 (m, 1H), 6.98-6.94 (d, *J* = 15.6 Hz, 1H), 3.18 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 140.8, 136.2, 131.3, 129.4, 126.0, 124.0, 121.2, 119.4, 37.6, 36.1; These data are consistent with literature values, see: C. E. Gregerson, K. N. Trentadue, E. J. T. Phipps, J. K. Kirsch, K. M. Reed, G. D. Dyke, J. H. Jansen, C. B. Otteman, J. L. Stachowski and J. B. Johnson, *Org. Biomol. Chem.,* 2017, **15**, 5944. (Pale yellow oil, 46.2 mg, 82% isolated yield)



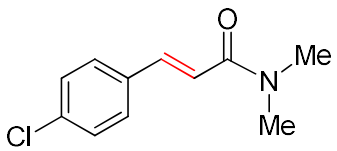
3p

(*E*)-3-(4-bromophenyl)-*N*,*N*-dimethylacrylamide (3p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (d, *J* = 15.6 Hz, 1H), 7.50-7.48 (d, *J* = 7.2 Hz, 2H), 7.39-7.37 (d, *J* = 7.2 Hz, 2H), 6.90-6.86 (d, *J* = 15.6 Hz, 1H), 3.16 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 141.1, 134.3, 132.0, 129.3, 123.7, 118.2, 37.5, 36.0; These data are consistent with literature values, see: I. Sato, H. Suzuki, Y. Yamashita and S. Kobayashi, *Org. Chem. Front.,* 2016, **3**, 1241. (White solid, 32.5 mg, 55% isolated yield)



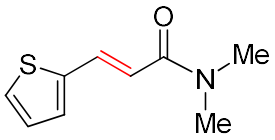
3q

(*E*)-3-(2-bromophenyl)-*N*,*N*-dimethylacrylamide (3q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.93 (d, *J* = 15.6 Hz, 1H), 7.61-7.56 (m, 2H), 7.31-7.28 (m, 1H), 7.21-7.17 (m, 1H), 6.84-6.80 (d, *J* = 15.6 Hz, 1H), 3.17 (s, 3H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 140.8, 135.7, 133.4, 130.5, 127.8, 127.6, 125.0, 120.9, 37.6, 36.0; These data are consistent with literature values, see: T. Weidlich, et al. *Monats. Chem.,* 2010, **141**, 205. (White solid, 45.4 mg, 68% isolated yield)



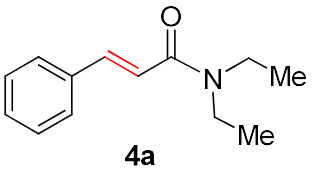
3r

(*E*)-3-(4-chlorophenyl)-*N*,*N*-dimethylacrylamide (3r): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (d, *J* = 15.6 Hz, 1H), 7.46-7.44 (m, 2H), 7.35-7.29 (m, 2H), 6.89-6.85 (d, *J* = 15.6 Hz, 1H), 3.17 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 141.0, 135.4, 133.9, 129.3, 129.1, 129.0, 118.0, 37.5, 36.0; These data are consistent with literature values, see: S. W. Foo, S. Oishi and S. Saito, *Tetrahedron Lett.,* 2012, **53**, 5445. (White solid, 34.1 mg, 70% isolated yield)



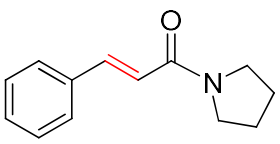
3s
E/*Z* = 6.3

(*E*)-*N*,*N*-dimethyl-3-(thiophen-2-yl)acrylamide (3s): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.77 (d, *J* = 15.6 Hz, 1H), 7.31-7.28 (m, 1H), 7.22-7.21 (m, 1H), 7.04-7.02 (m, 1H), 6.70-6.67 (d, *J* = 15.6 Hz, 1H), 3.15 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 140.5, 135.3, 130.3, 128.1, 127.2, 116.1, 37.5, 36.1; These data are consistent with literature values, see: M. Rodríguez-Fernández, X. Yan, J. F. Collados, P. B. White and S. R. Harutyunyan, *J. Am. Chem. Soc.,* 2017, **139**, 14224. (Pale yellow solid, 26.1 mg, 62% isolated yield)



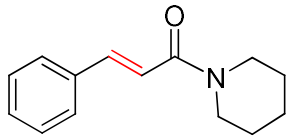
4a

(*E*)-*N*,*N*-diethylcinnamamide (4a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.69 (d, *J* = 15.6 Hz, 1H), 7.54-7.52 (m, 2H), 7.39-7.34 (m, 3H), 6.85-6.81 (d, *J* = 15.6 Hz, 1H), 3.53-3.45 (m, 4H), 1.28-1.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.4, 135.6, 129.5, 128.8, 127.8, 117.9, 42.4, 41.2, 15.2, 13.3; These data are consistent with literature values, see: D. Chen, B. Zhang, X. Liu, X. Li, X. Yang, L. Zhou, *Synlett., Bioorg. Med. Chem. Lett.*, 2018, **28**, 1149. (White solid, 35.9 mg, 64% isolated yield)



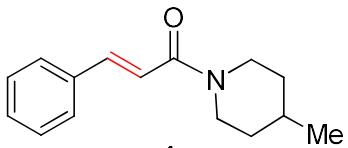
4c
E/*Z* = 9.1

(*E*)-3-phenyl-1-(pyrrolidin-1-yl)prop-2-en-1-one (4c): 7.72-7.69 (d, *J* = 15.6 Hz, 1H), 7.54-7.52 (m, 2H), 7.37-7.32 (m, 3H), 6.76-6.72 (d, *J* = 15.6 Hz, 1H), 3.65-3.58 (m, 4H), 3.04-1.98 (m, 2H), 1.94-1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 141.8, 135.4, 129.6, 128.8, 127.9, 118.9, 46.7, 46.2, 26.2, 24.4; These data are consistent with literature values, see: Y. Yamashita, et al., *Synlett.,* 2017, **28**, 1287. (White solid, 30.2 mg, 54% isolated yield)



4d

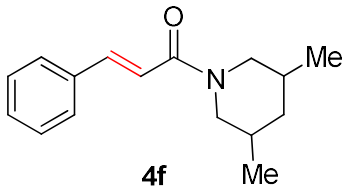
(*E*)-3-phenyl-1-(piperidin-1-yl)prop-2-en-1-one (4d): 7.67-7.63 (d, *J* = 15.6 Hz, 1H), 7.53-7.51 (m, 2H), 7.38-7.32 (m, 3H), 6.93-6.89 (d, *J* = 15.6 Hz, 1H), 3.67-3.59 (m, 4H), 1.69-1.61 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 142.2, 135.6, 129.5, 128.8, 127.8, 117.8, 47.1, 43.4, 26.8, 25.7, 24.7; These data are consistent with literature values, see: X. Yang, W. Wei, H. Li, R. Song and J. Li, *Chem. Commun.,* 2014, **50**, 12867. (White solid, 43.2 mg, 72% isolated yield)



4e

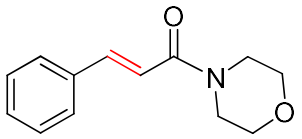
E/*Z* = 10.4

(*E*)-1-(4-methylpiperidin-1-yl)-3-phenylprop-2-en-1-one (4e): 7.67-7.62 (d, *J* = 15.6 Hz, 1H), 7.53-7.51 (m, 2H), 7.37-7.33 (m, 3H), 6.65-6.61 (d, *J* = 15.6 Hz, 1H), 4.70-4.58 (m, 1H), 4.09-4.06 (m, 1H), 3.12-3.06 (m, 1H), 2.73-2.64 (m, 1H), 1.74-1.63 (m, 3H), 1.21-1.12 (m, 2H), 0.97-0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 142.3, 135.6, 129.5, 128.8, 127.8, 117.8, 65.3, 46.4, 42.8, 35.0, 33.9, 31.3, 21.8; HRMS calculated for $C_{15}H_{20}NO$ ($M + H^+$): 230.1545, found: 230.1556. (White solid, 33.5 mg, 53% isolated yield)



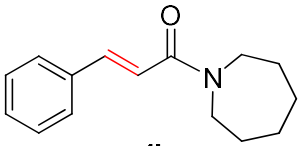
4f

(*E*)-1-(3,5-dimethylpiperidin-1-yl)-3-phenylprop-2-en-1-one (4f): 7.66-7.62 (d, *J* = 15.6 Hz, 1H), 7.54-7.52 (m, 2H), 7.38-7.36 (m, 3H), 6.93-6.89 (d, *J* = 15.6 Hz, 1H), 4.71-4.68 (m, 1H), 3.99-3.96 (m, 1H), 2.66-2.51 (m, 1H), 2.14-2.08 (m, 1H), 1.87-1.84 (m, 1H), 1.65-1.63 (m, 2H), 0.94-0.76 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 142.3, 135.6, 129.5, 128.8, 127.8, 117.9, 53.3, 49.5, 42.6, 32.4, 31.1, 19.2; HRMS calculated for $C_{16}H_{22}NO$ (M + H^+): 244.1701, found: 244.1795. (White solid, 26.6 mg, 39% isolated yield)



4g

(*E*)-1-morpholino-3-phenylprop-2-en-1-one (4g): 7.72-7.68 (d, *J* = 15.6 Hz, 1H), 7.53-7.51 (m, 2H), 7.38-7.34 (m, 3H), 6.89-6.83 (d, *J* = 15.6 Hz, 1H), 3.73-3.67 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 143.4, 135.2, 129.9, 128.9, 127.8, 116.6, 66.9, 46.3, 42.6; These data are consistent with literature values, see: X. Yang, W. Wei, H. Li, R. Song and J. Li, *Chem. Commun.,* 2014, **50**, 12867. (White solid, 24.4 mg, 40% isolated yield)

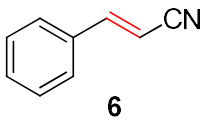


4h

E/*Z* = 10.3

(*E*)-1-(azepan-1-yl)-3-phenylprop-2-en-1-one (4h): 7.72-7.69 (d, *J* = 15.6 Hz, 1H), 7.54-7.52 (m, 2H), 7.42-7.31 (m, 3H), 6.89-6.85 (d, *J* = 15.6 Hz, 1H), 3.66-3.59 (m,

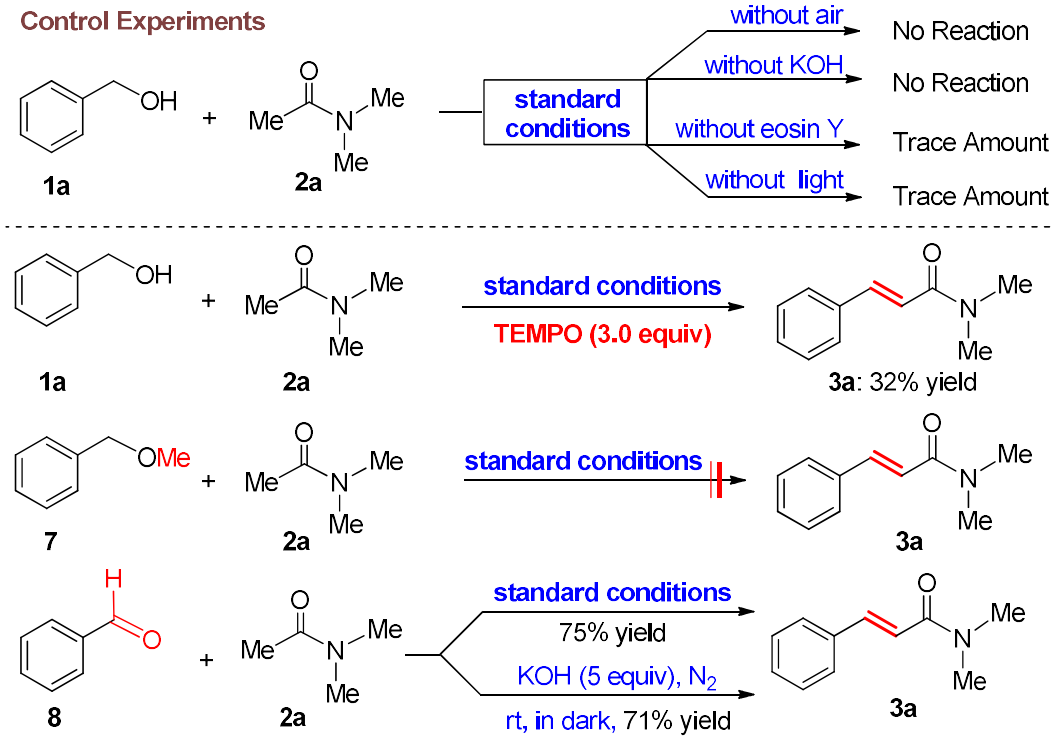
4H), 1.89-1.71 (m, 4H), 1.68-1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 142.3, 135.6, 129.5, 128.8, 128.5, 127.8, 117.9, 48.1, 46.6, 29.5, 27.7, 27.1, 26.7; These data are consistent with literature values, see: Y. Shao, X. Wu, S. Tian, *Eur. J. Org. Chem.,* 2012, **2012**, 1590. (White solid, 41.3 mg, 62% isolated yield)



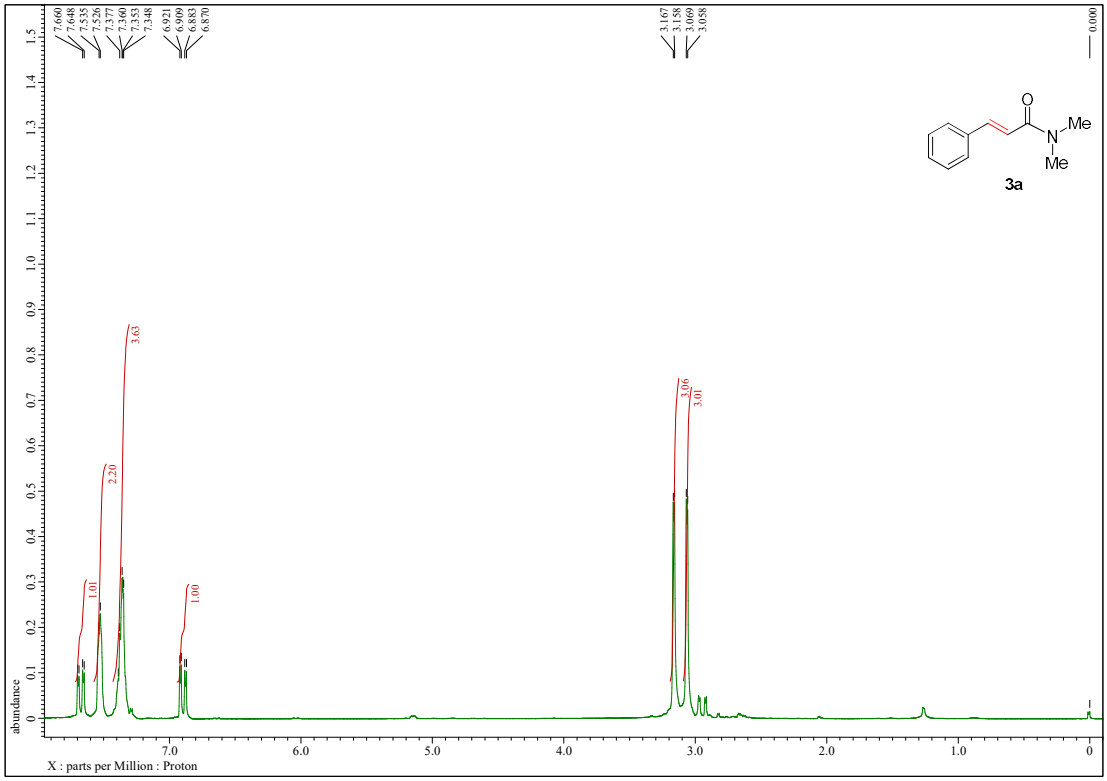
6

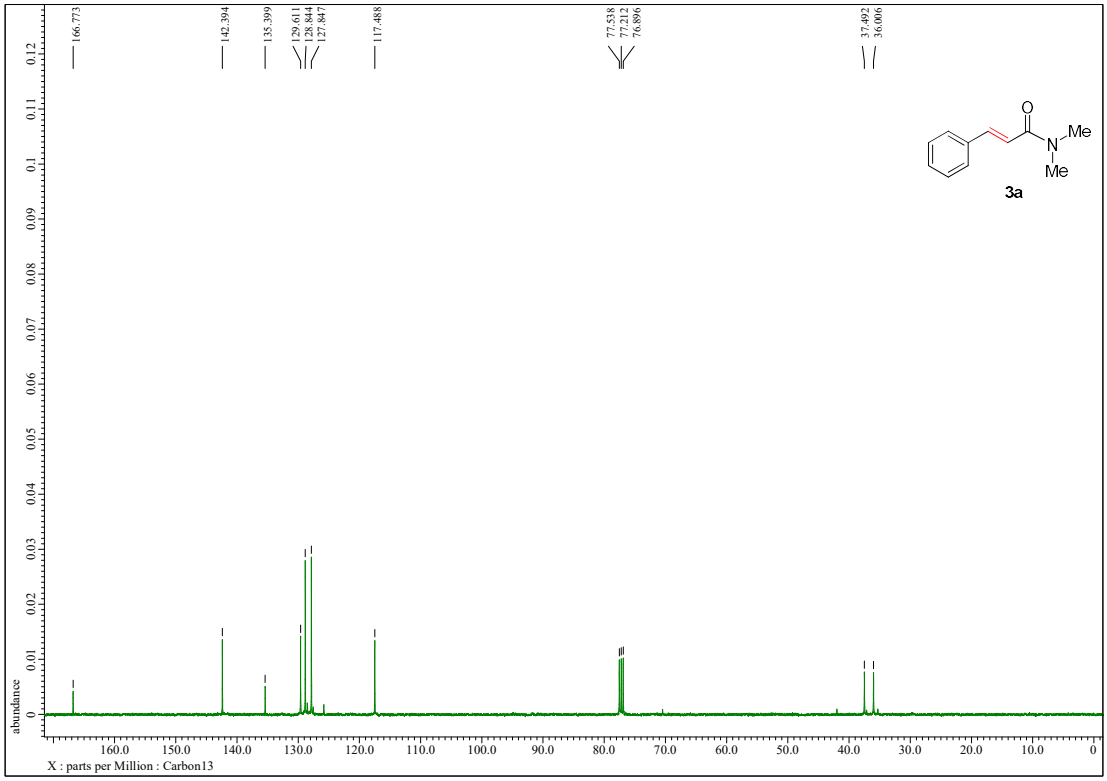
(*E*)-cinnamonitrile (6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.28 (m, 6H), 5.91-5.87 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 133.6, 131.3, 129.2, 127.5, 118.3, 94.4. (Pale yellow oil, 25.0 mg, 52% isolated yield)

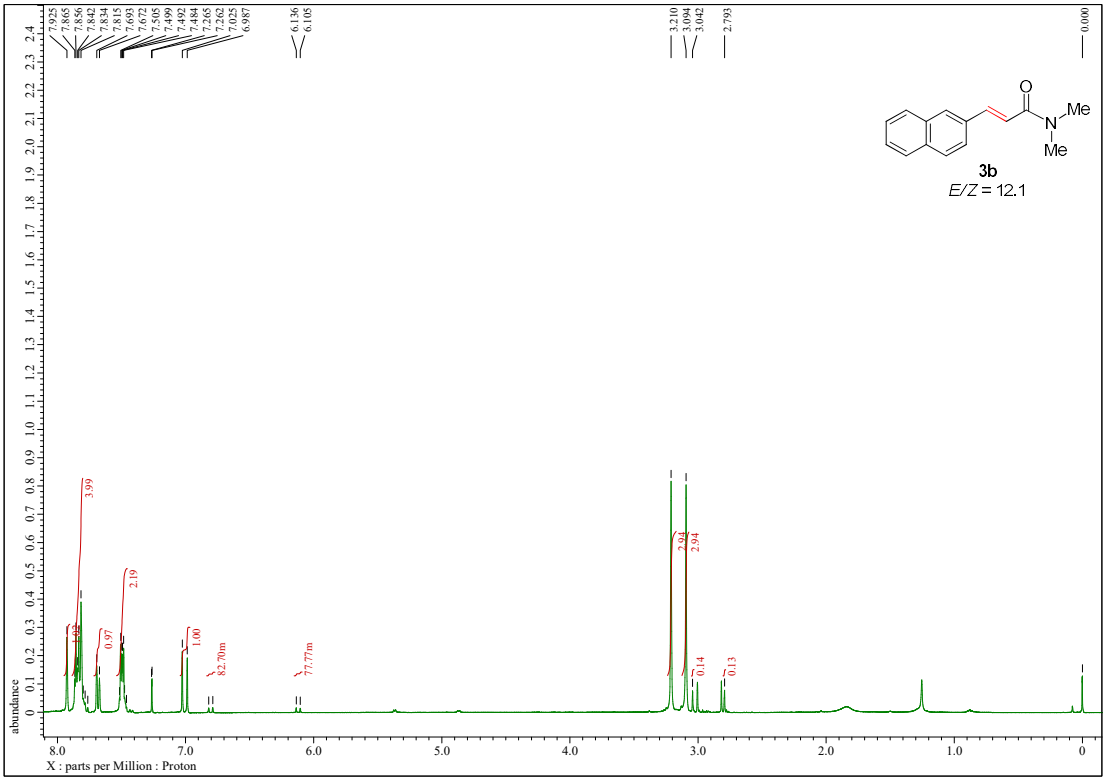
Control experiments on reaction parameters

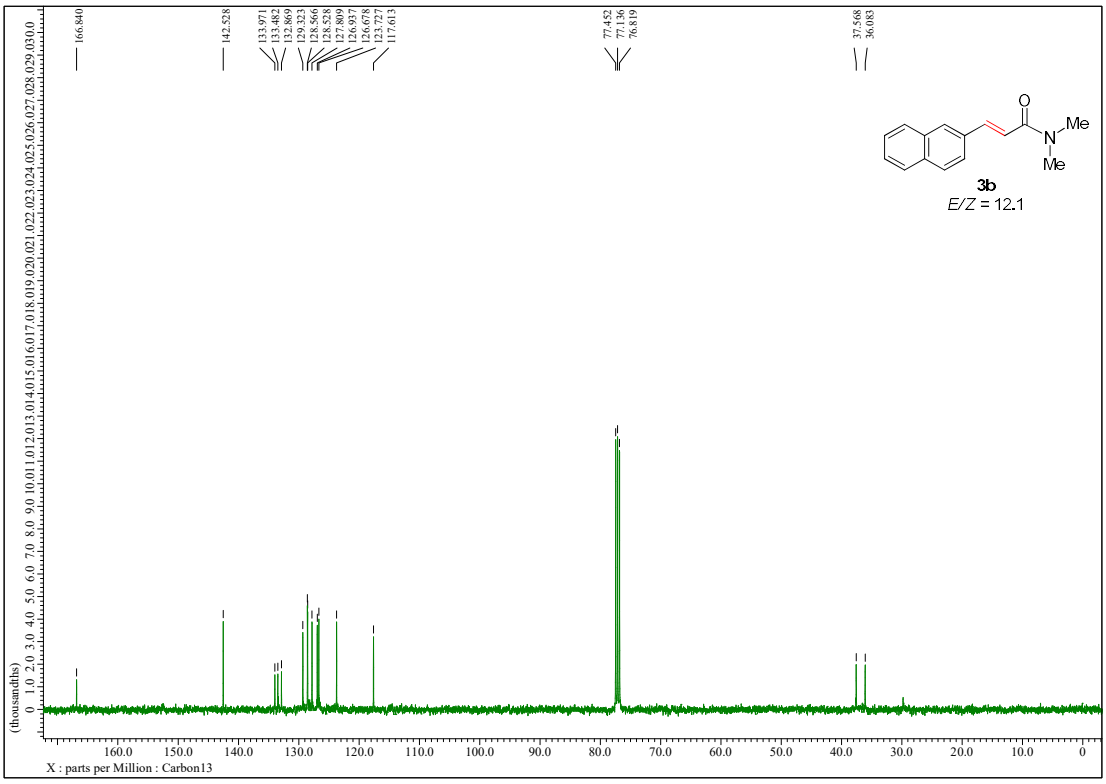


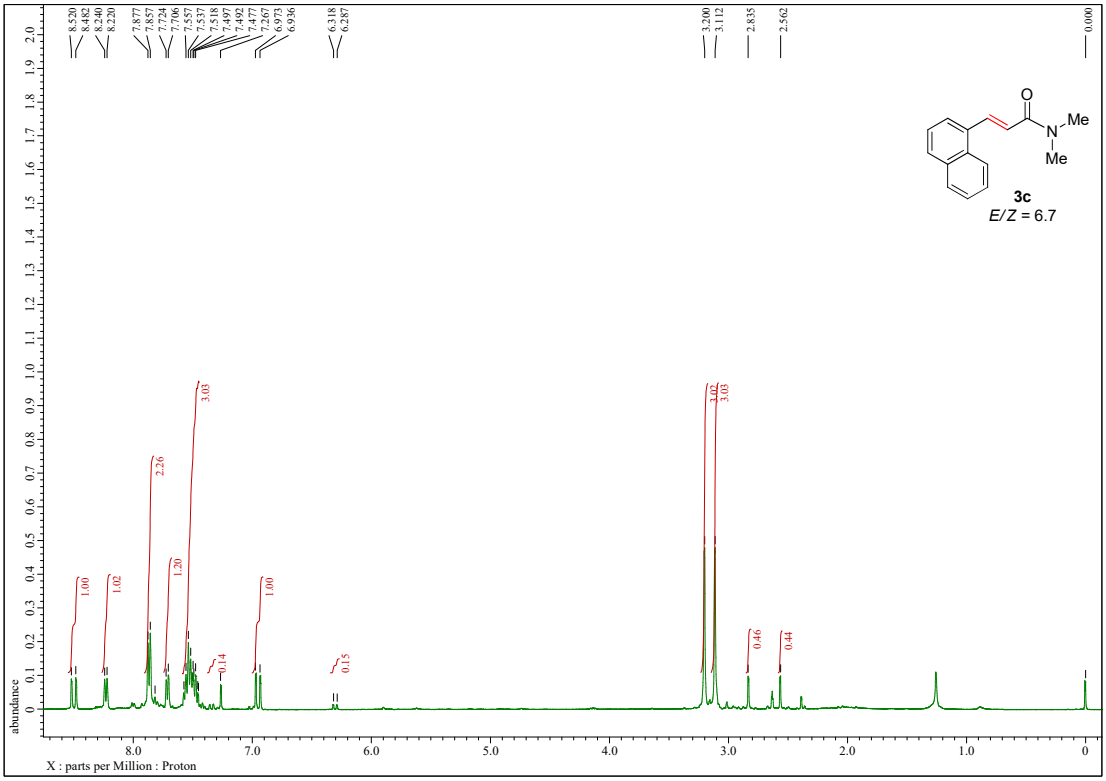
Copies of ^{1}H NMR and ^{13}C NMR spectra

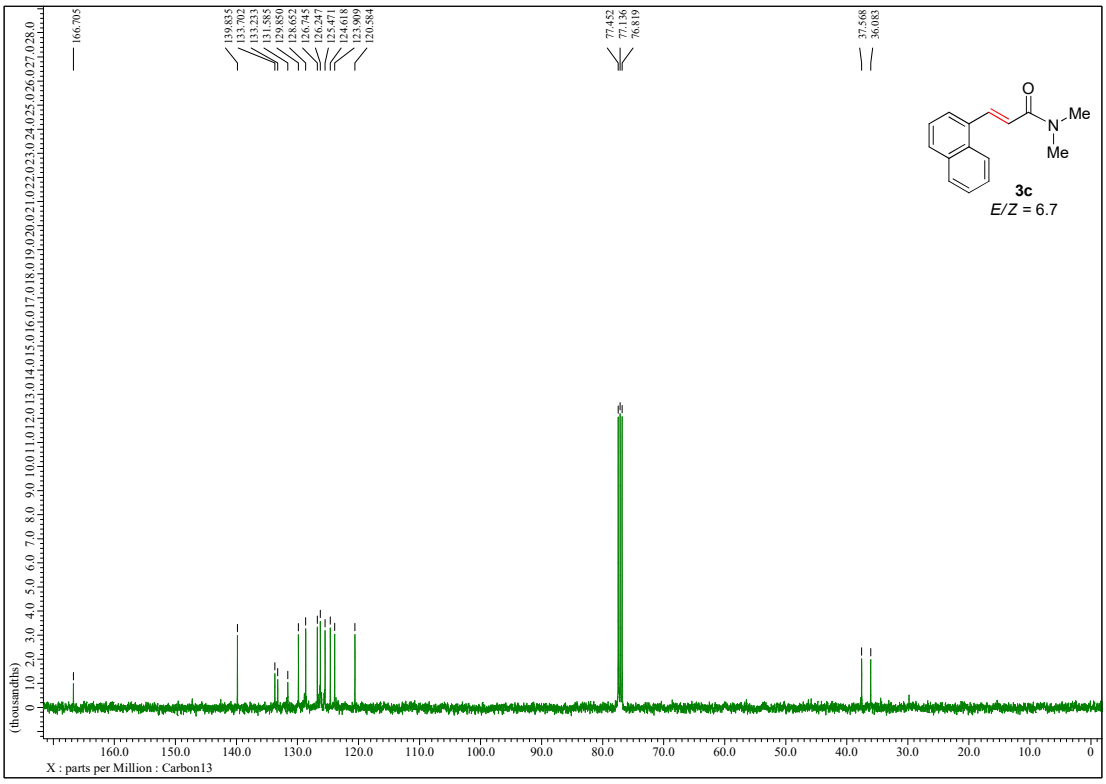


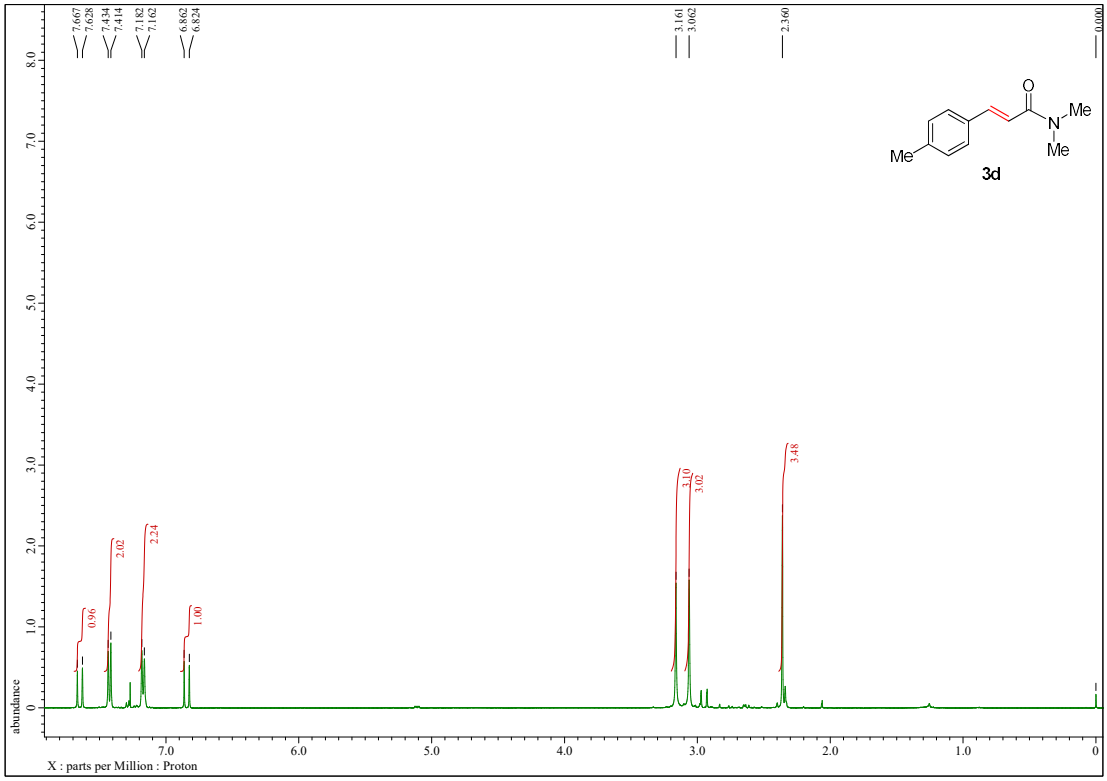


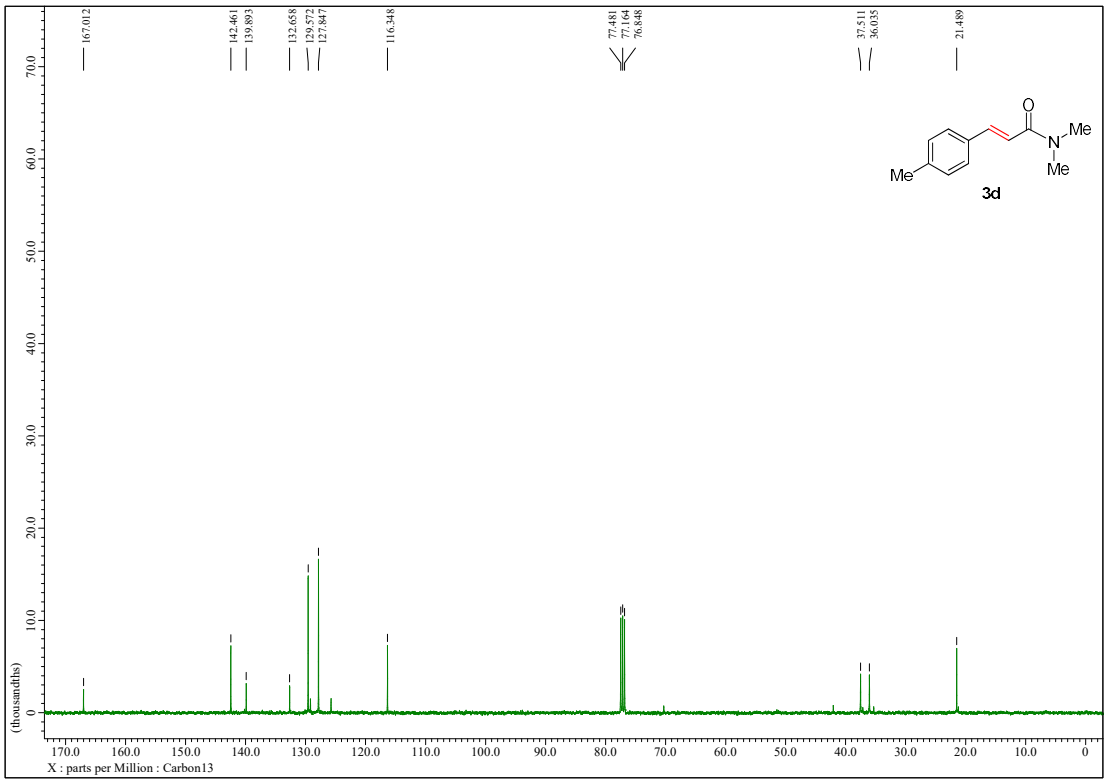

7.925
7.865
7.856
7.842
7.834
7.815
7.693
7.672
7.505
7.499
7.492
7.484
7.265
7.025
6.987
6.136
6.105
3.210
3.094
3.042
2.793
0.000
O
N
Me
Me
3b
E/Z = 12.1
3.99
2.19
1.03
0.97
1.00
2.92
2.94
0.14
0.13
82.70m
77.77m
abundance
X : parts per Million : Proton

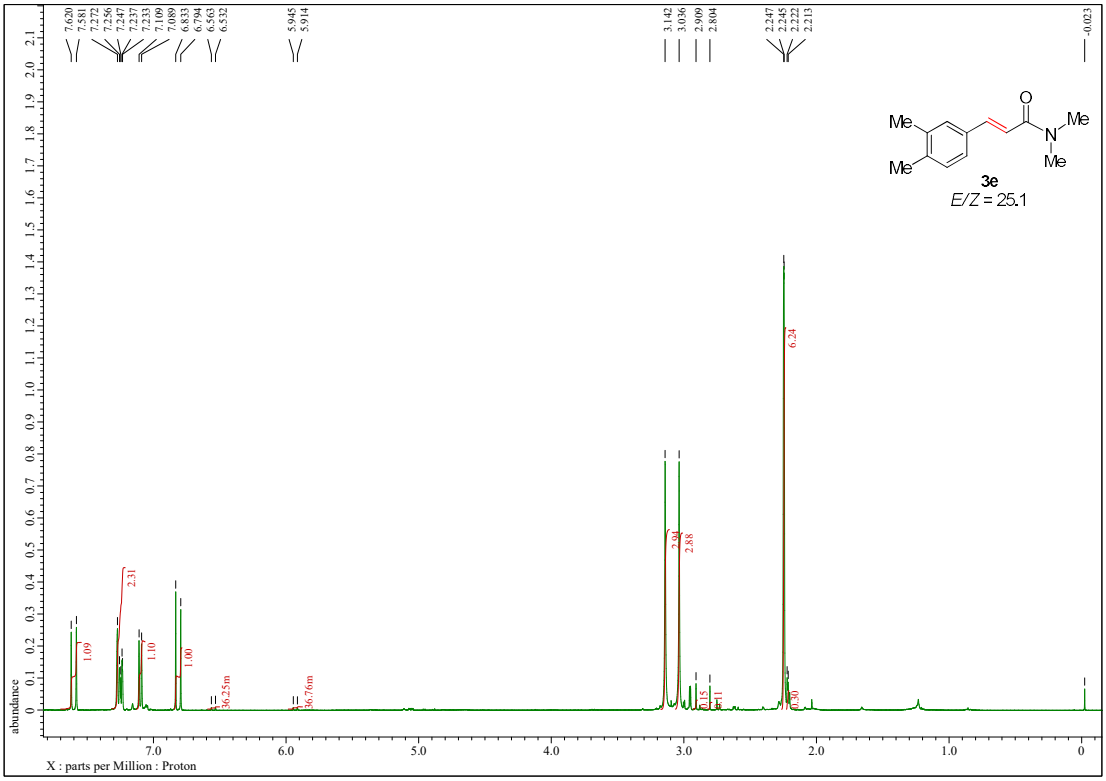

166.840
142.528
133.971
133.483
132.869
129.323
128.566
128.528
127.809
126.937
126.678
123.727
117.613
77.452
77.136
76.819
37.568
36.083
O
N
Me
Me
3b
E/Z = 12.1
(thousandths)
X : parts per Million : Carbon13

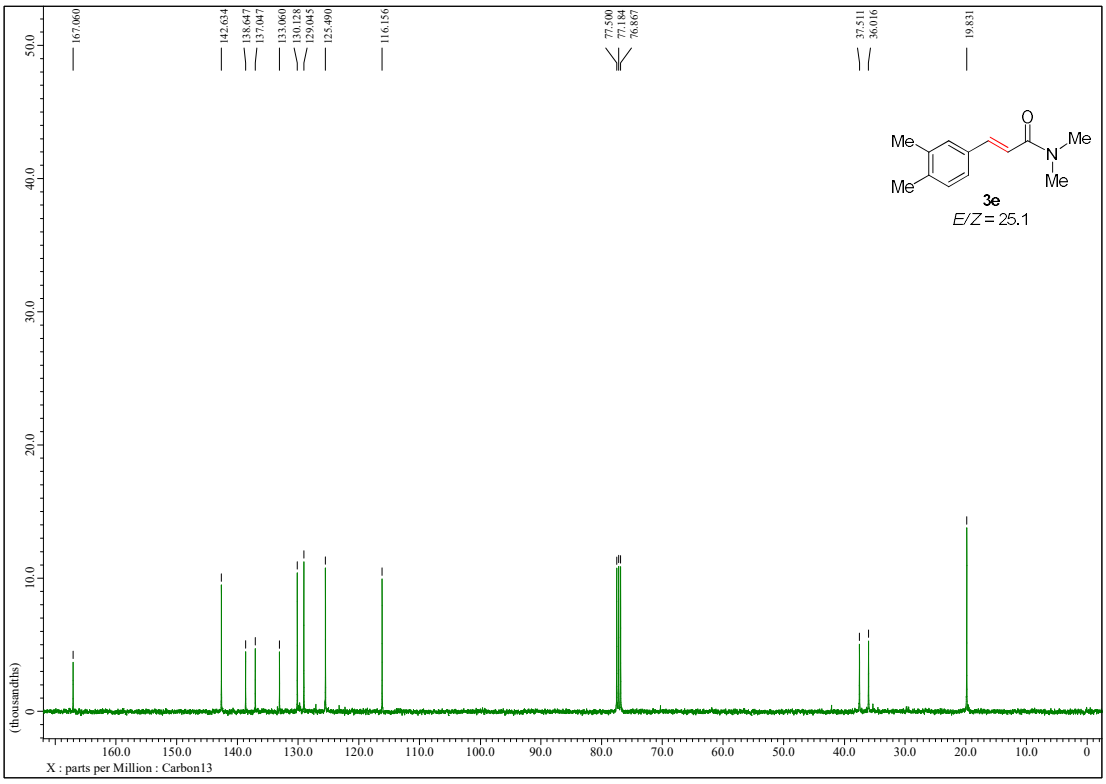

8.520
8.482
8.240
8.220
7.877
7.857
7.724
7.706
7.557
7.537
7.518
7.497
7.492
7.477
7.267
6.973
6.936
6.318
6.287
3.200
3.112
2.835
2.562
0.000
1.00
1.02
2.26
1.20
3.03
0.14
1.00
0.15
3.02
3.03
0.46
0.44
abundance
X : parts per Million : Proton
O
N
Me
Me
3c
E/Z = 6.7

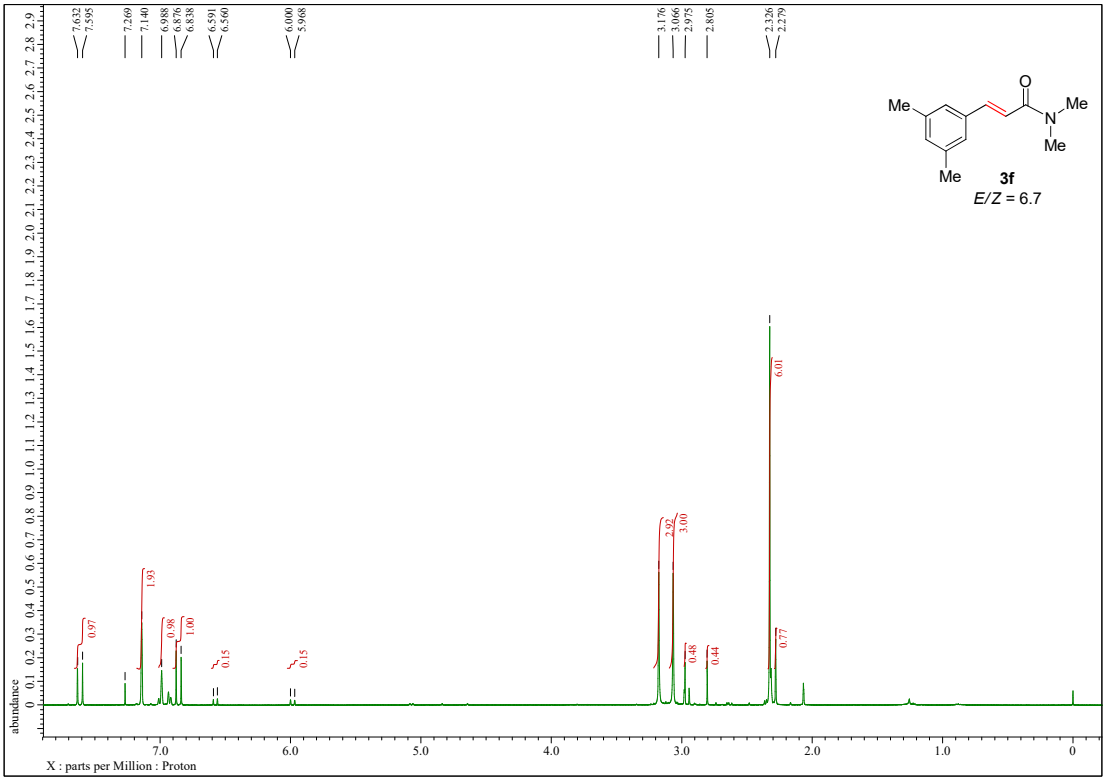

166.705
139.835
133.702
133.233
131.585
129.850
128.652
126.745
126.247
125.471
124.618
123.909
120.584
77.452
77.136
76.819
37.568
36.083
(thousandths)
X : parts per Million : Carbon13
O
N
Me
Me
3c
E/Z = 6.7

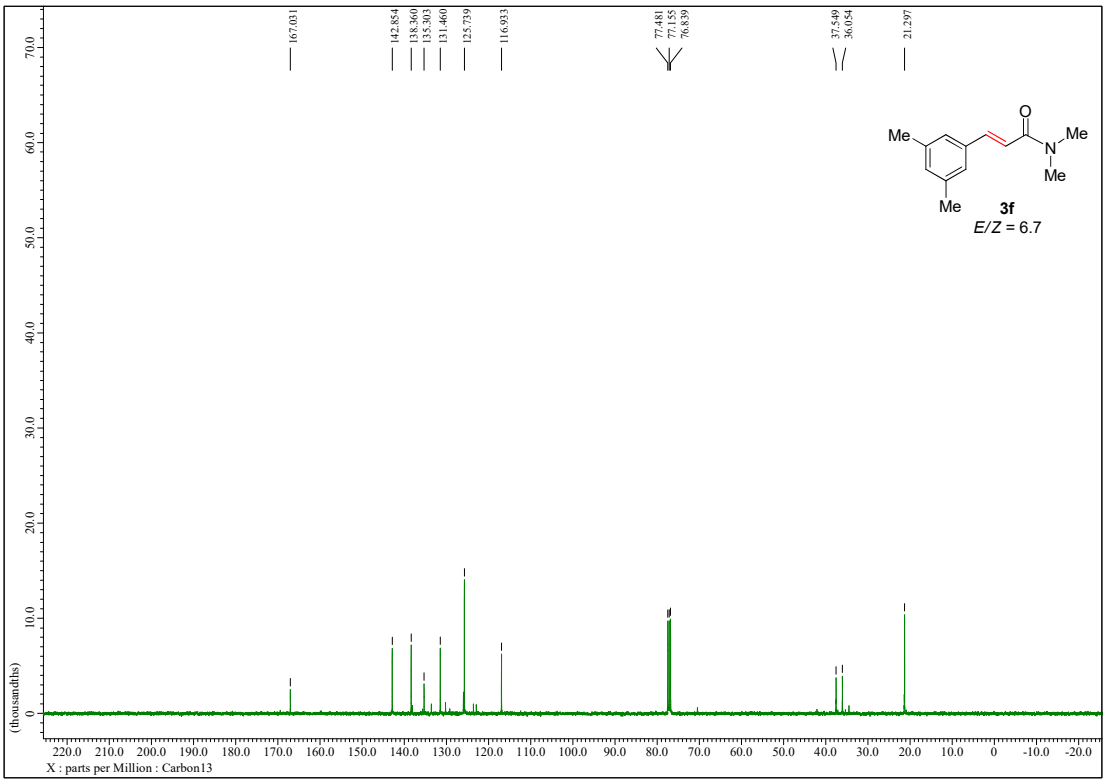

7.667
7.628
7.434
7.414
7.182
7.162
6.862
6.824
3.161
3.062
2.360
0.000
3.448
3.110
3.02
2.02
2.24
0.96
1.00
abundance
X : parts per Million : Proton
Me
O
N
Me
Me
3d

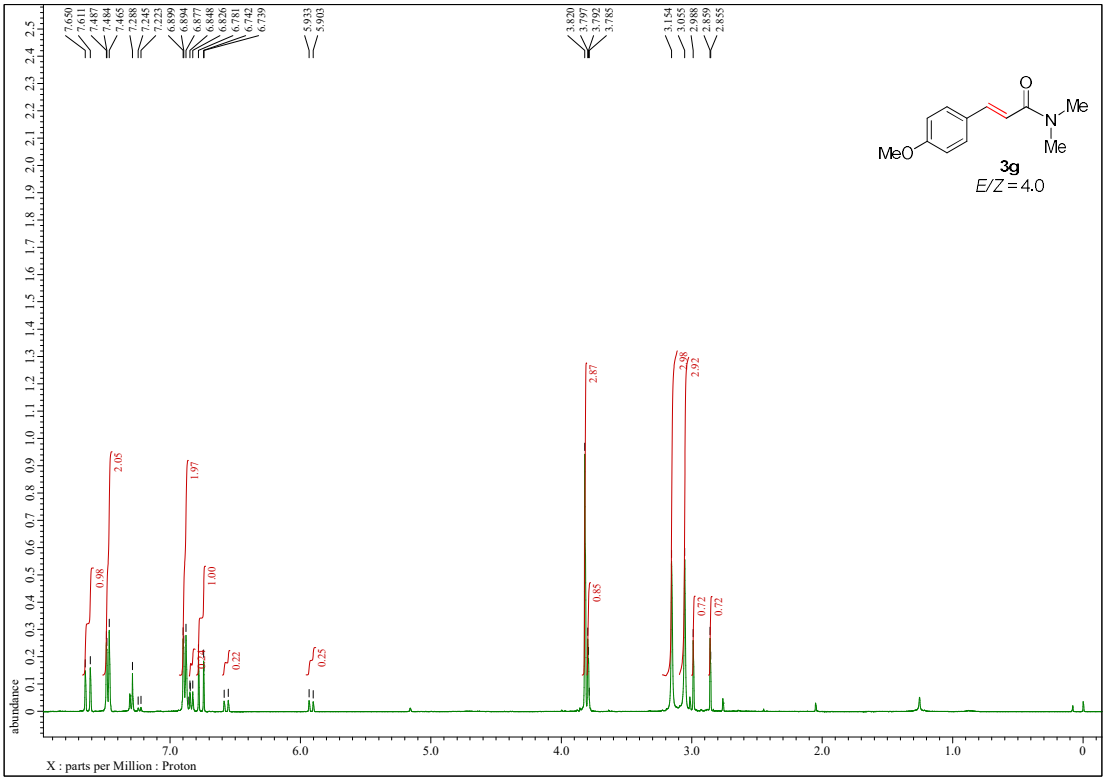

167.012
142.461
139.893
132.658
129.572
127.847
116.348
77.481
77.164
76.848
37.511
36.035
21.489
(thousandths)
X : parts per Million : Carbon13
Me
O
N
Me
Me
3d


7.620
7.581
7.272
7.256
7.247
7.237
7.233
7.109
7.089
6.833
6.794
6.563
6.532
5.945
5.914
3.142
3.056
2.999
2.804
2.247
2.245
2.222
2.213
-0.023
Me
Me
O
N
Me
Me
3e
E/Z = 25.1
1.09
2.31
1.10
1.00
36.25m
36.76m
2.90
2.88
0.15
0.11
6.24
0.30
abundance
X : parts per Million : Proton


167.060
142.634
138.647
137.047
133.060
130.128
129.045
125.490
116.156
77.500
77.184
76.867
37.511
36.016
19.831
Me
Me
O
N
Me
Me
3e
E/Z = 25.1
(thousandths)
X : parts per Million : Carbon13


7.632
7.595
7.269
7.140
6.988
6.976
6.838
6.591
6.560
6.000
5.968
3.176
3.066
2.975
2.805
2.326
2.279
Me
O
N
Me
Me
Me
3f
E/Z = 6.7
6.01
2.92
3.00
1.93
0.97
0.98
1.00
0.15
0.15
0.48
0.44
0.77
abundance
X : parts per Million : Proton


167.031
142.854
138.360
135.303
131.460
125.739
116.933
77.481
77.155
76.839
37.549
36.054
21.297
Me
O
N
Me
Me
Me
3f
E/Z = 6.7
(thousandths)
X : parts per Million : Carbon13


7.650
7.611
7.487
7.484
7.465
7.288
7.245
7.223
6.899
6.894
6.877
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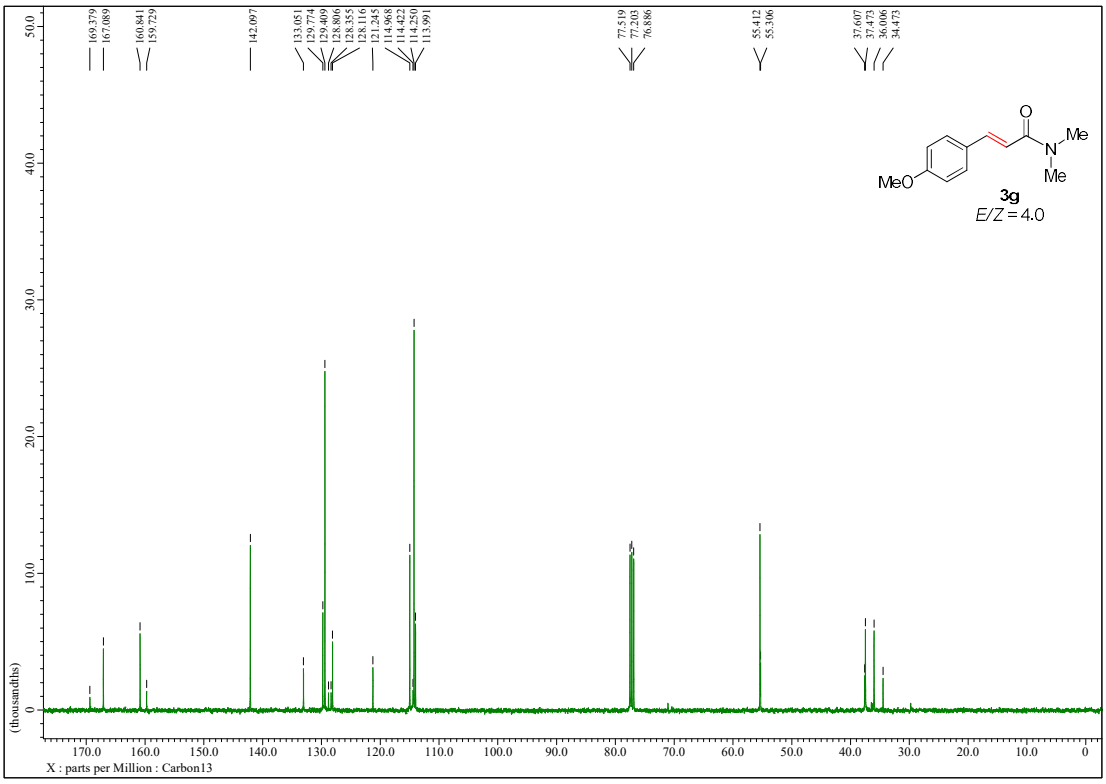
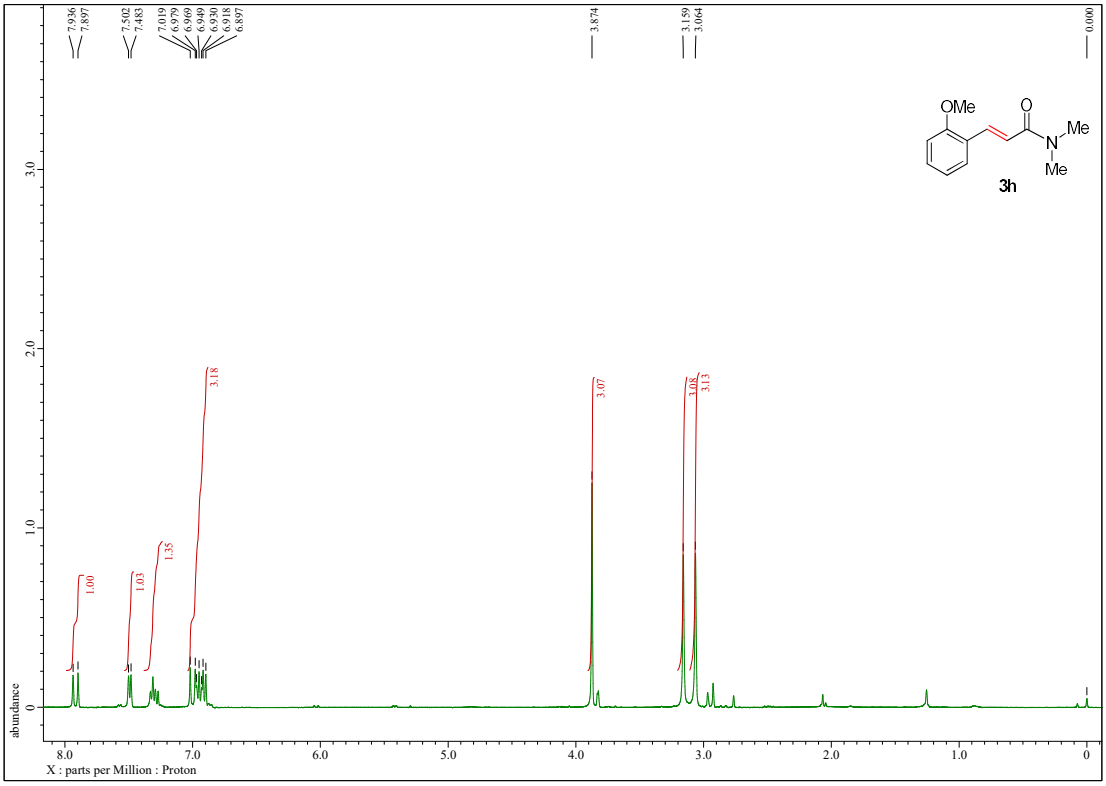
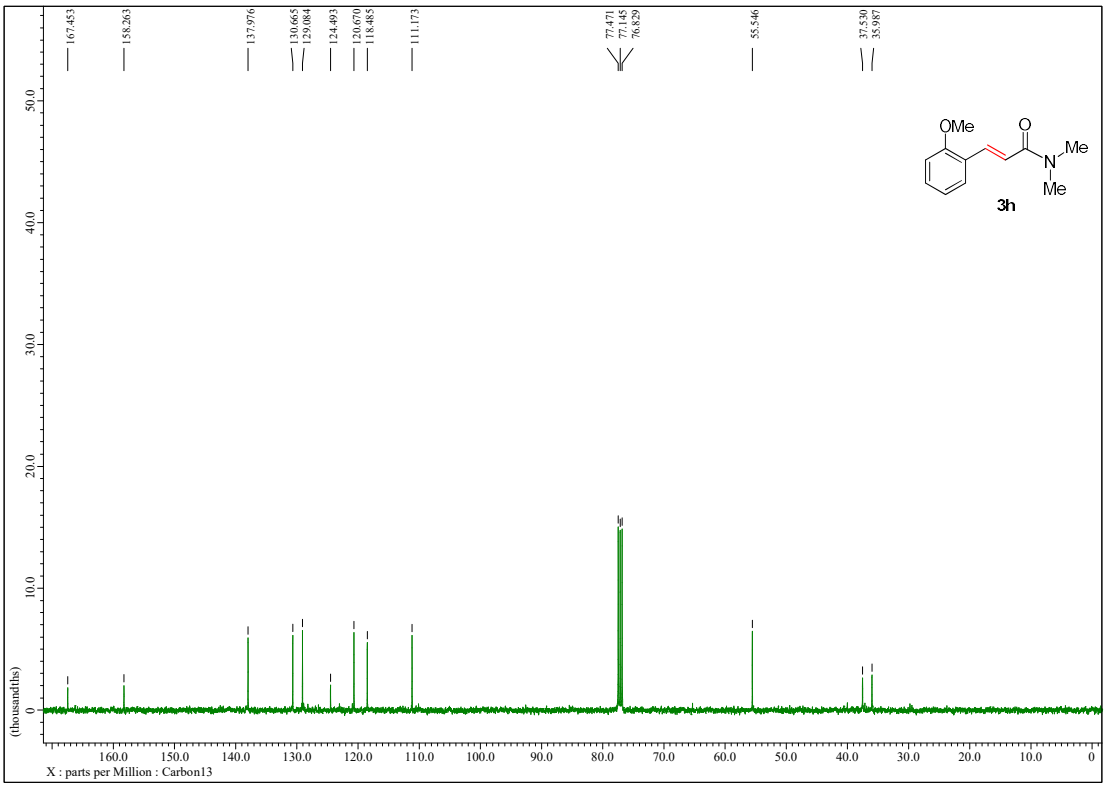
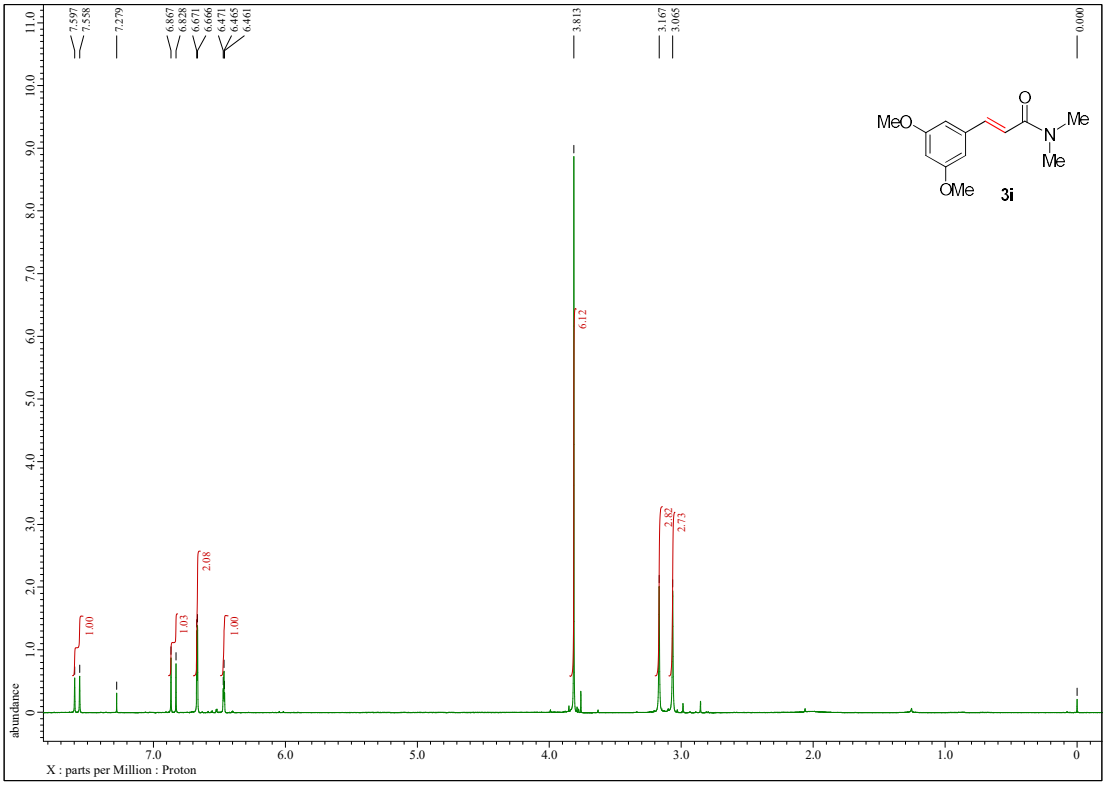
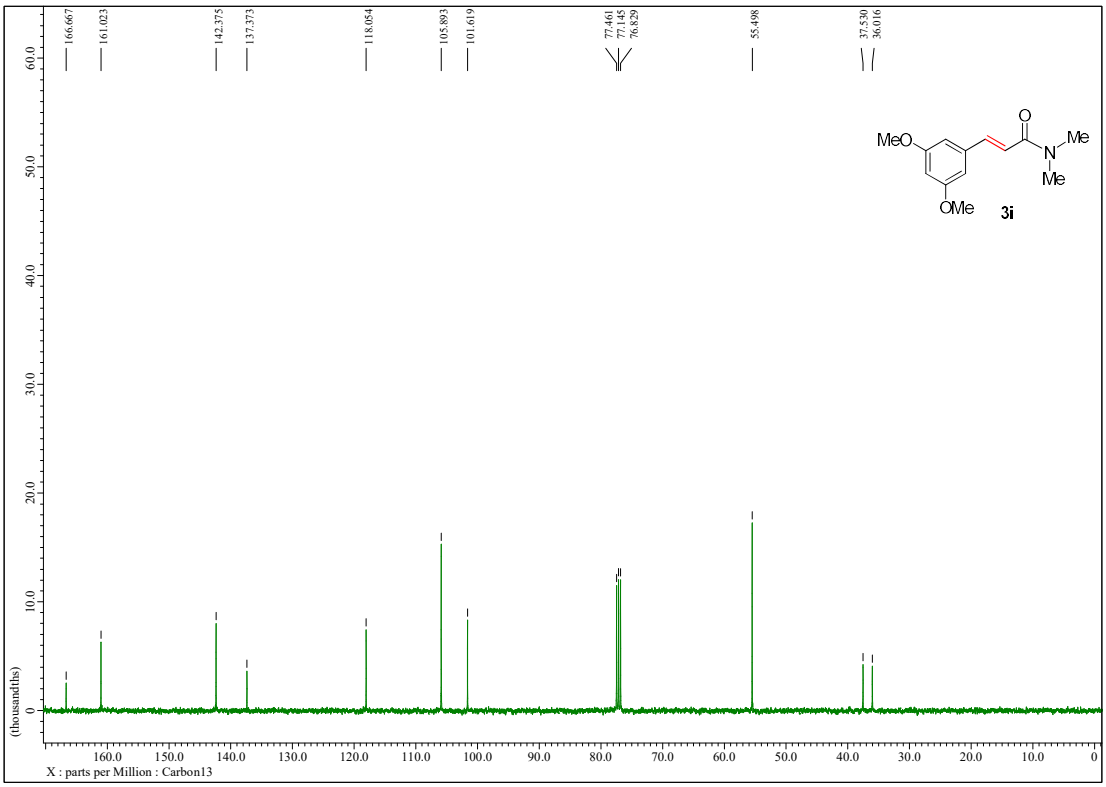
6.826
6.781
6.742
6.739
5.933
5.903
3.830
3.797
3.792
3.785
3.154
3.055
2.988
2.859
2.855
2.87
2.98
2.92
2.05
1.97
1.00
0.98
0.85
0.72
0.72
0.25
0.22
abundance
X : parts per Million : Proton
MeO
N
Me
Me
O
3g
E/Z = 4.0

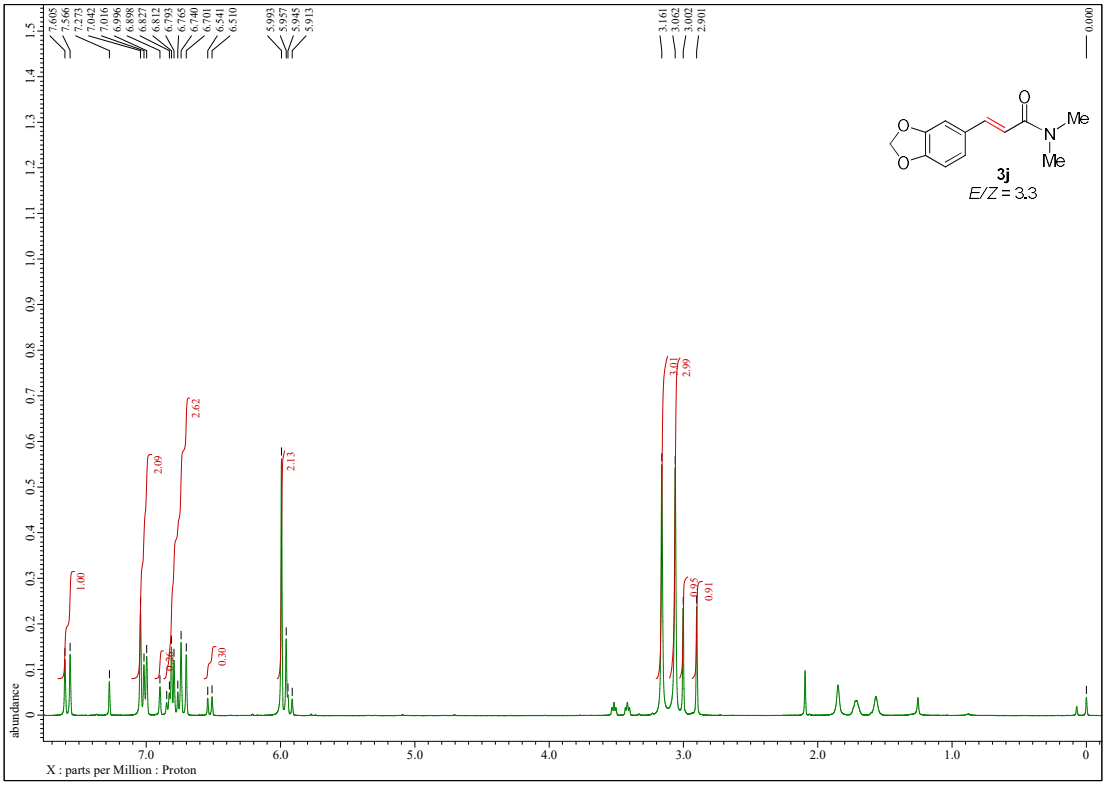

169.379
167.089
160.841
159.729
142.097
133.051
129.774
129.409
128.806
128.355
128.116
121.345
114.968
114.427
114.250
113.991
77.519
77.203
76.886
55.412
55.306
37.607
37.473
36.006
34.473
(thousandths)
X : parts per Million : Carbon13
MeO
N
Me
Me
O
3g
E/Z = 4.0

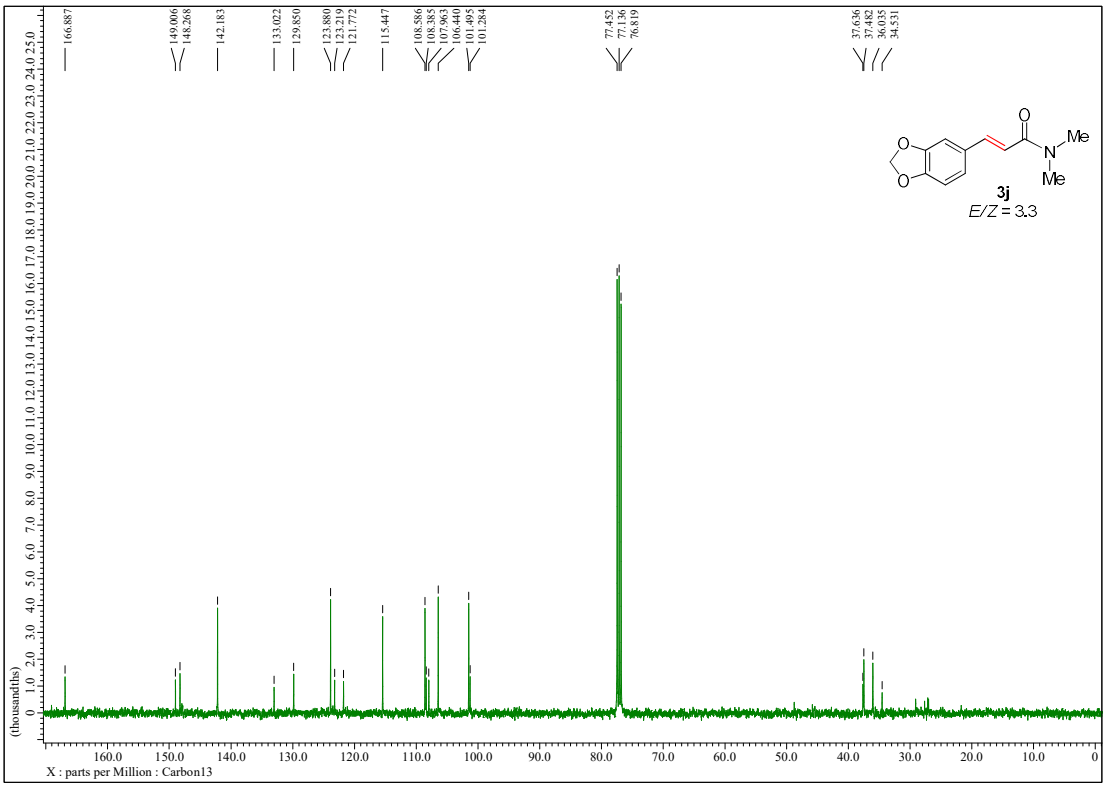

7.936
7.897
7.502
7.483
7.019
6.979
6.969
6.949
6.930
6.918
6.897
3.874
3.159
3.064
0.000
OMe
O
Me
N
Me
3h
3.18
3.07
3.08
3.13
1.00
1.03
1.35
abundance
X : parts per Million : Proton

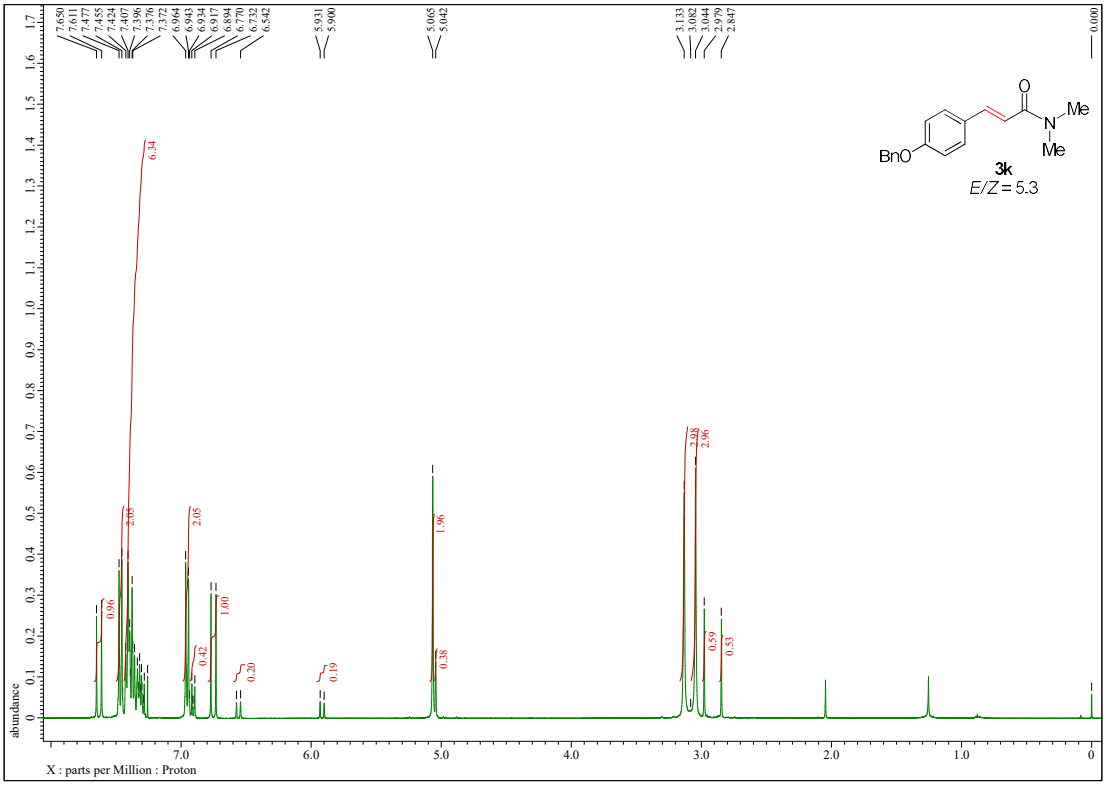

167.453
158.263
137.976
130.665
129.084
124.493
120.670
118.485
111.173
77.471
77.145
76.829
55.546
37.530
35.987
OMe
O
Me
N
Me
3h
(thousandths)
X : parts per Million : Carbon13

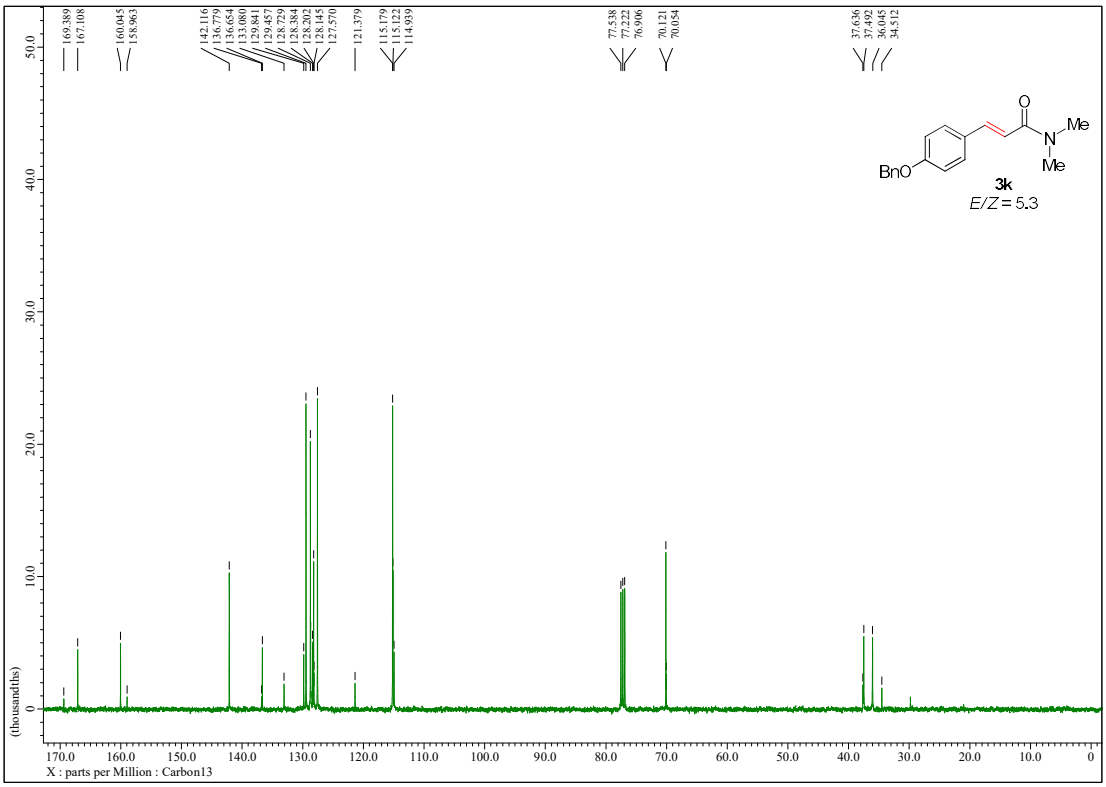

7.597
7.558
7.279
6.867
6.828
6.671
6.666
6.471
6.465
6.461
3.813
3.167
3.065
0.000
MeO
O
N
Me
Me
OMe
3i
6.12
2.08
2.03
2.02
2.73
1.00
1.03
1.00
abundance
X : parts per Million : Proton

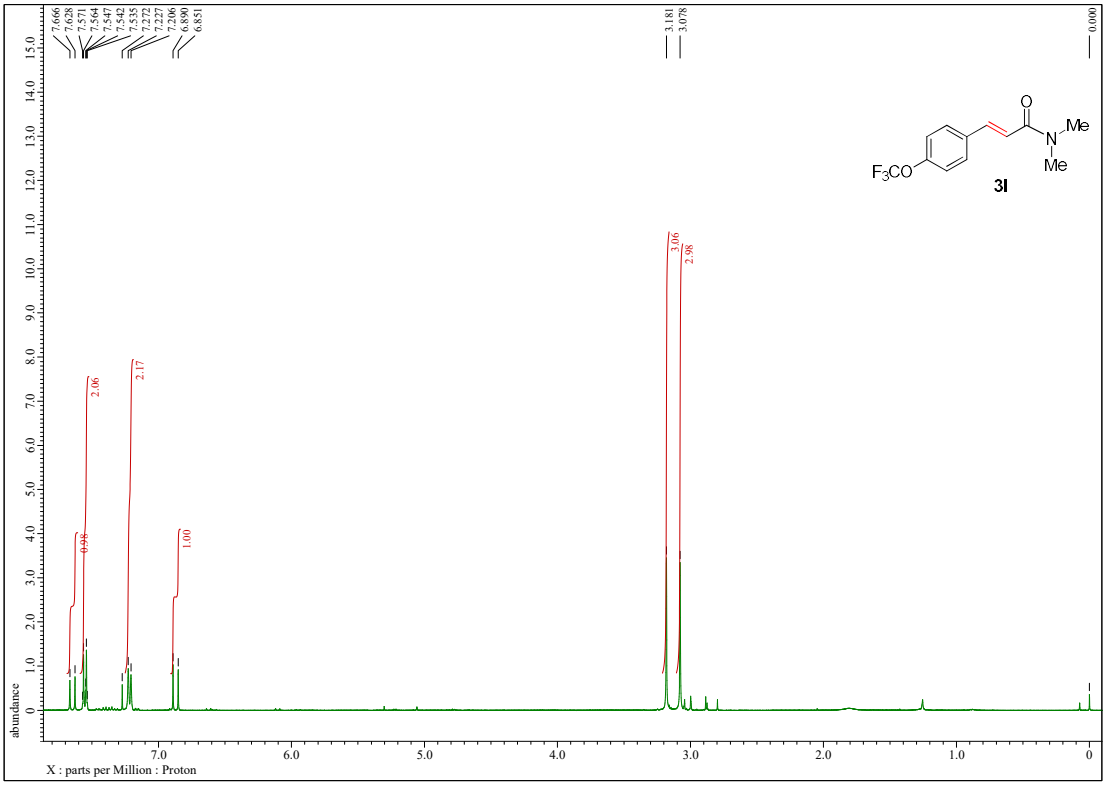

166.667
161.023
142.375
137.373
118.054
105.893
101.619
77.461
77.145
76.829
55.498
37.530
36.016
MeO
O
N
Me
Me
OMe
3i
(thousandths)
X : parts per Million : Carbon13

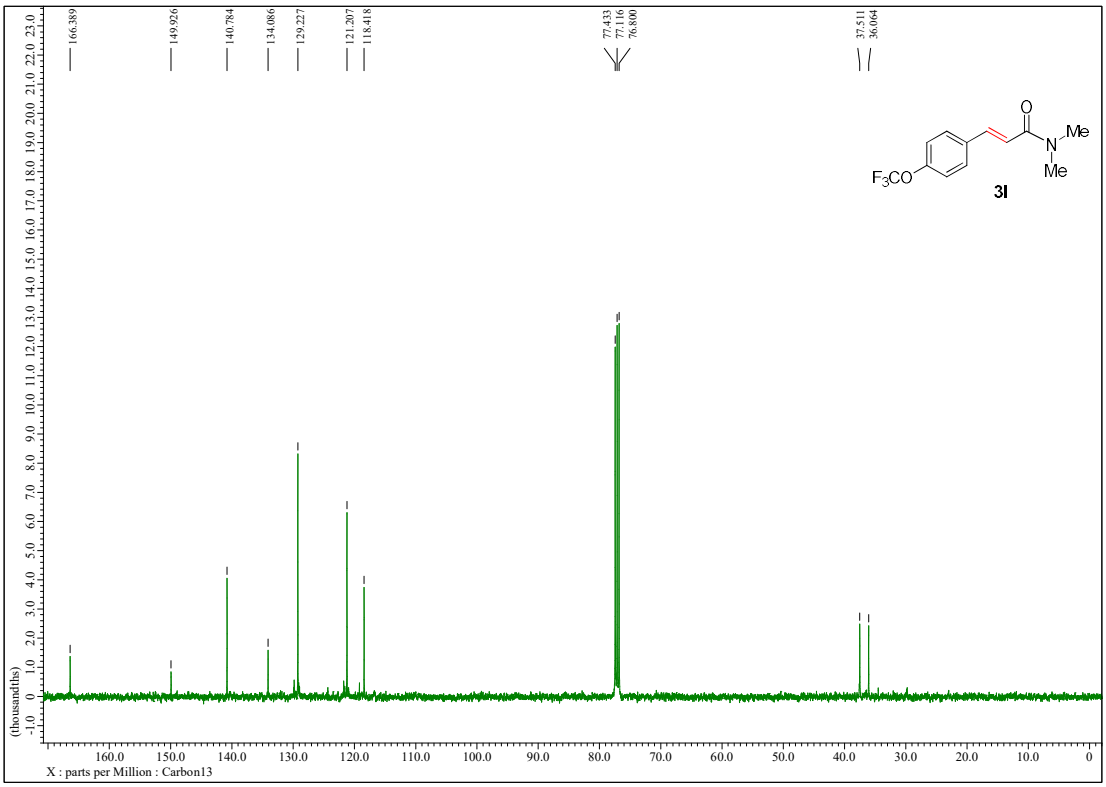

7.605
7.566
7.273
7.042
7.016
6.996
6.898
6.827
6.812
6.793
6.765
6.740
6.701
6.541
6.510
5.993
5.957
5.945
5.913
3.161
3.062
3.002
2.901
0.000
1.00
2.09
2.62
2.13
3.01
2.99
0.35
0.91
0.30
abundance
X : parts per Million : Proton
Me
N
Me
O
O
O
3j
E/Z = 3.3

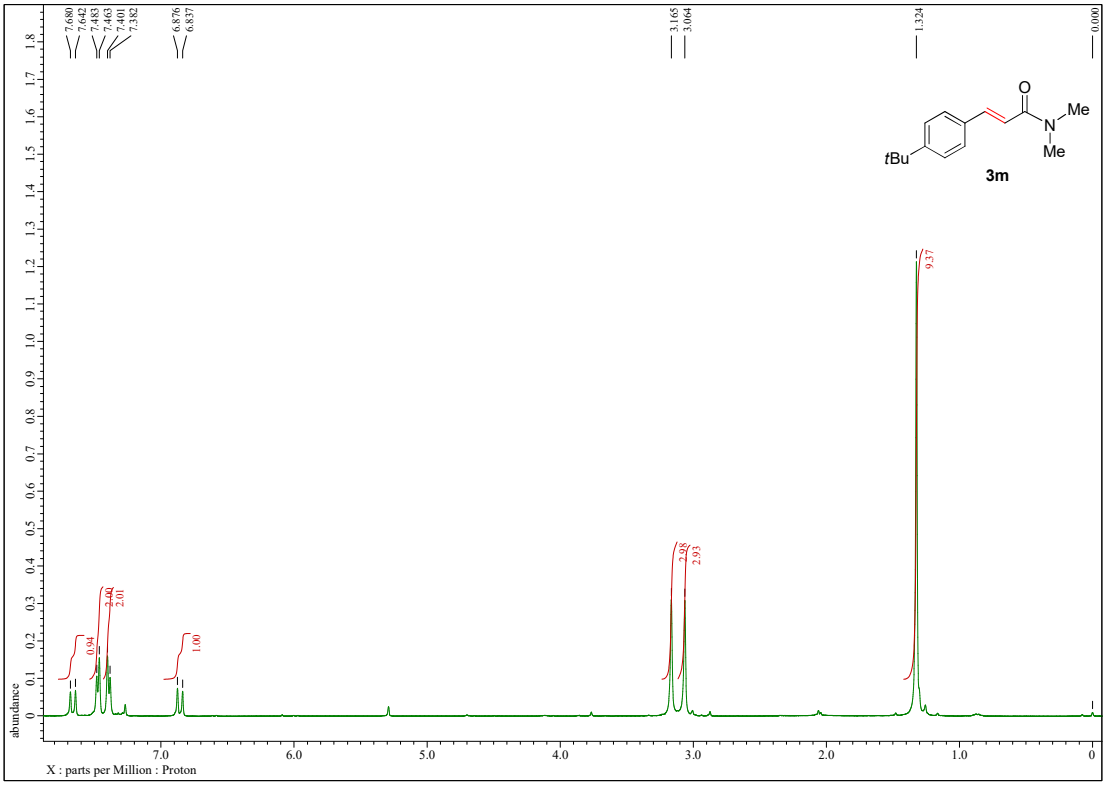

166.887
149.006
148.268
142.183
133.022
129.850
123.880
123.219
121.772
115.447
108.586
108.385
107.964
106.440
101.495
101.284
77.452
77.136
76.819
37.636
37.482
36.035
34.531
(thousandths)
X : parts per Million : Carbon13
Me
N
Me
O
O
O
3j
E/Z = 3.3

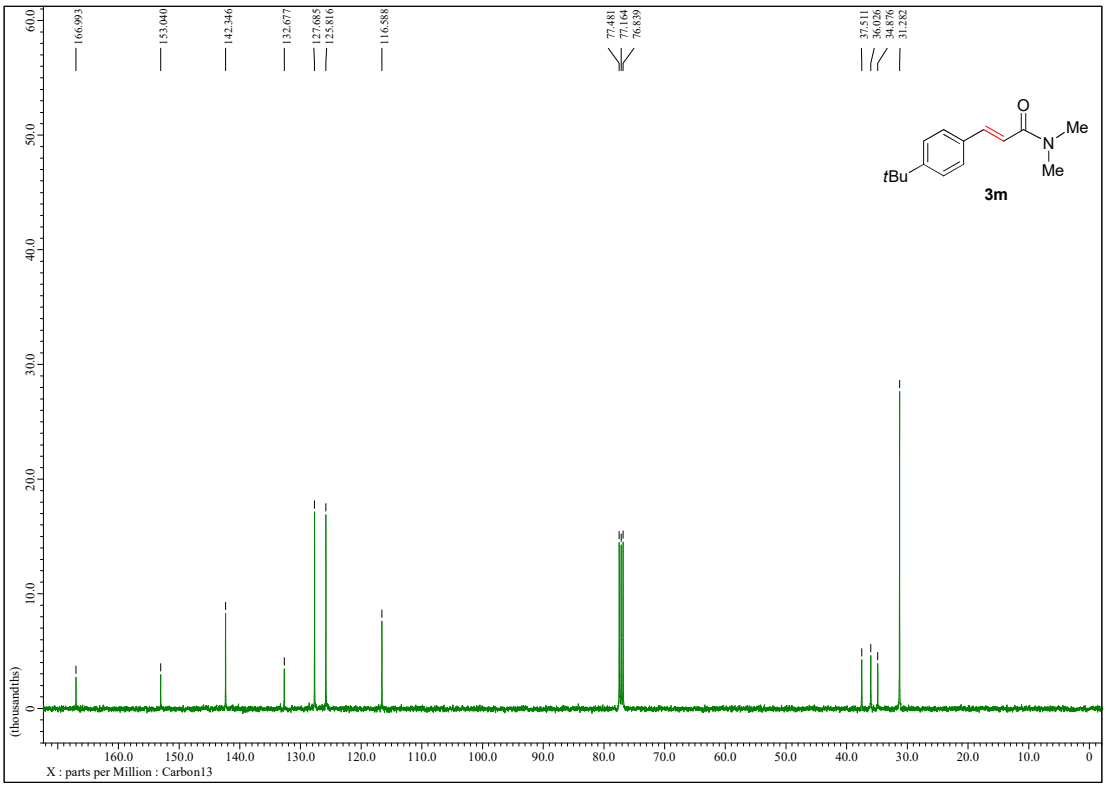

7.650
7.611
7.477
7.455
7.424
7.407
7.396
7.376
7.372
6.964
6.943
6.934
6.917
6.894
6.770
6.732
6.542
5.931
5.900
5.065
5.042
3.133
3.082
3.044
2.979
2.847
0.000
6.34
2.65
2.05
1.96
1.00
0.96
0.42
0.20
0.19
0.38
2.98
2.96
0.59
0.53
abundance
X : parts per Million : Proton
BnO
O
N
Me
Me
3k
E/Z = 5.3

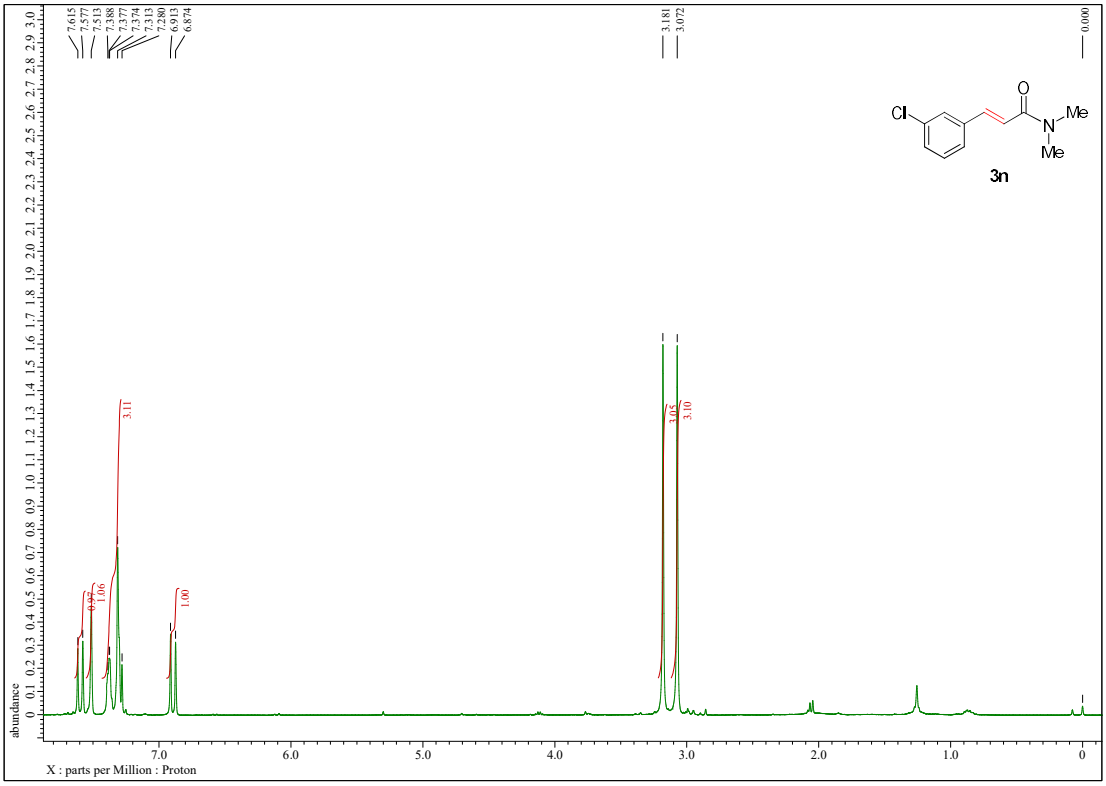

169.389
167.108
160.045
158.963
142.116
136.779
136.654
133.080
129.841
129.457
128.729
128.384
128.202
128.145
127.570
121.379
115.179
115.122
114.939
77.538
77.222
76.906
70.121
70.054
37.636
37.492
36.045
34.512
(thousandths)
X : parts per Million : Carbon13
BnO
O
N
Me
Me
3k
E/Z = 5.3

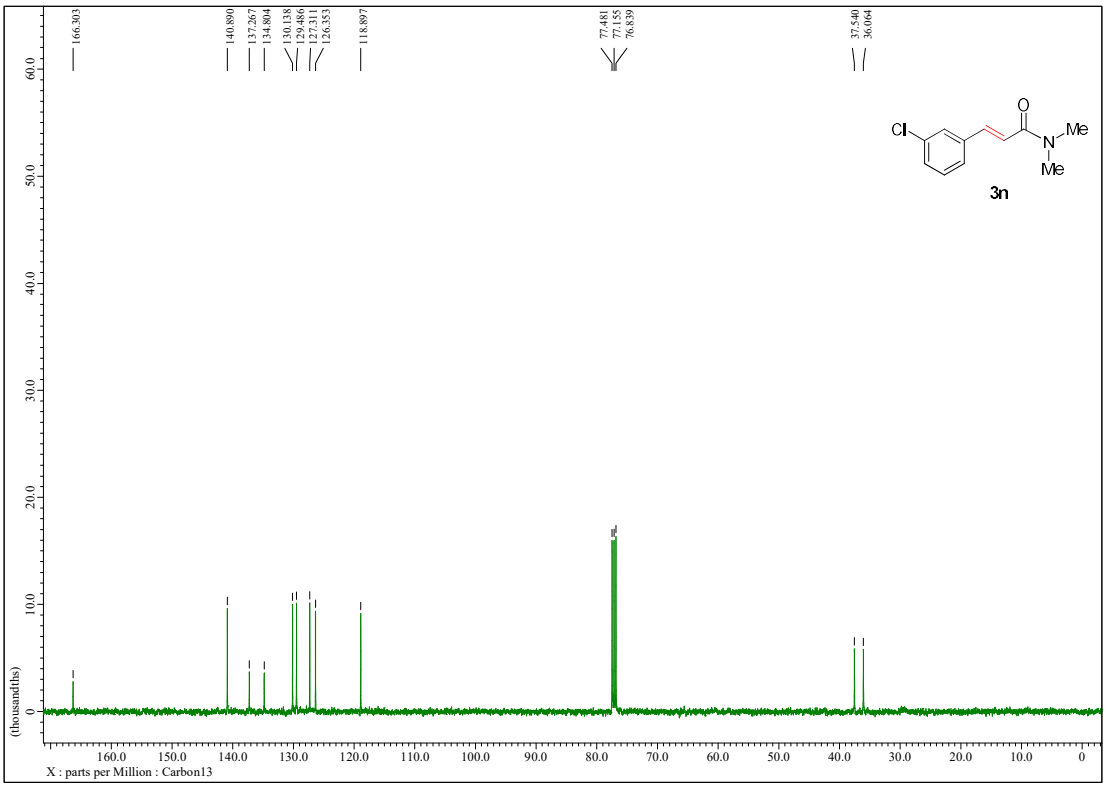

7.666
7.628
7.571
7.564
7.547
7.542
7.535
7.272
7.227
7.206
6.890
6.851
3.181
3.078
0.000
2.06
2.17
0.98
1.00
3.06
2.98
abundance
X : parts per Million : Proton
F3CO
Me
N
Me
O
3l

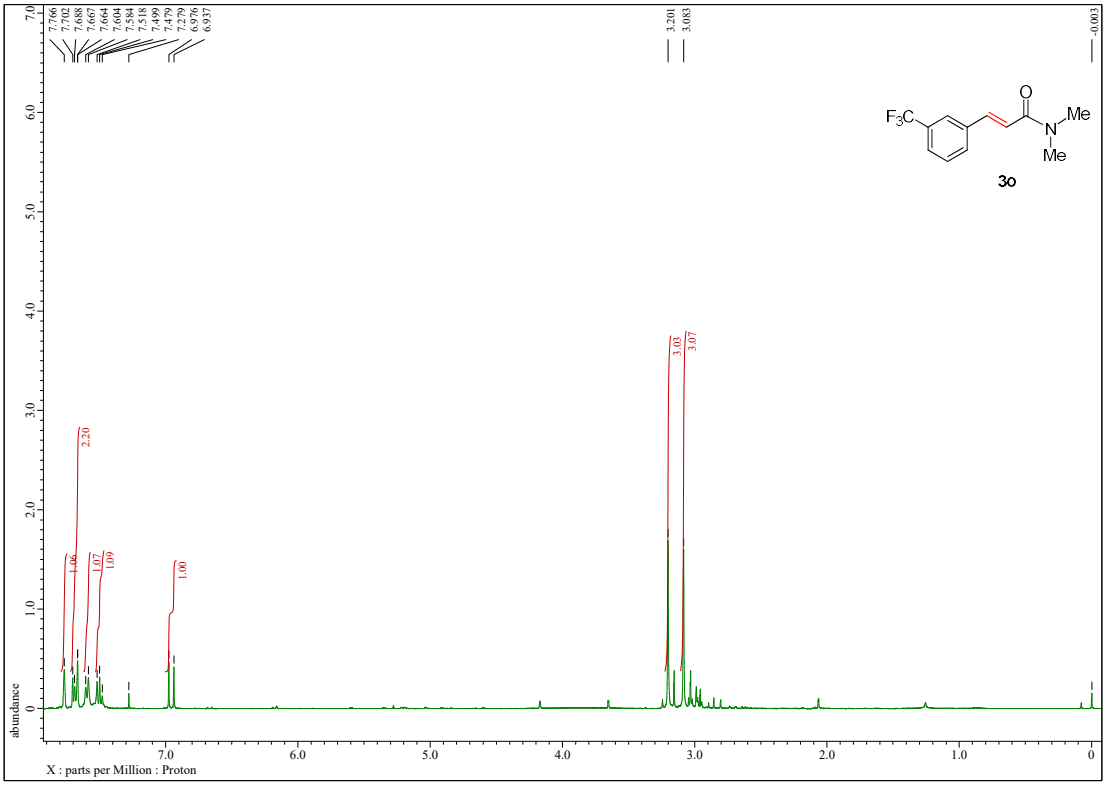

166.389
149.926
140.784
134.086
129.227
121.207
118.418
77.433
77.116
76.800
37.511
36.064
(thousandths)
X : parts per Million : Carbon13
F3CO
Me
N
Me
O
3l

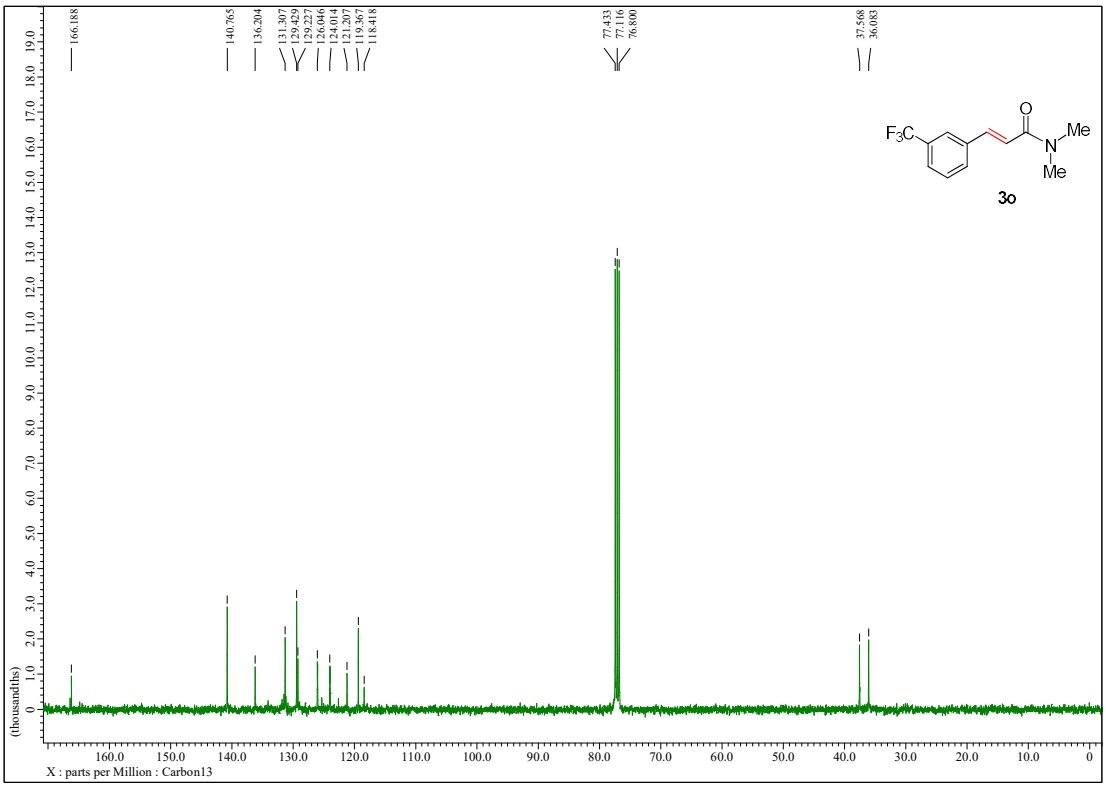

7.680
7.642
7.483
7.465
7.401
7.382
6.876
6.837
3.165
3.064
1.324
0.000
9.37
2.98
2.93
3.40
2.01
0.94
1.00
abundance
X : parts per Million : Proton
tBu
N
Me
Me
O
3m

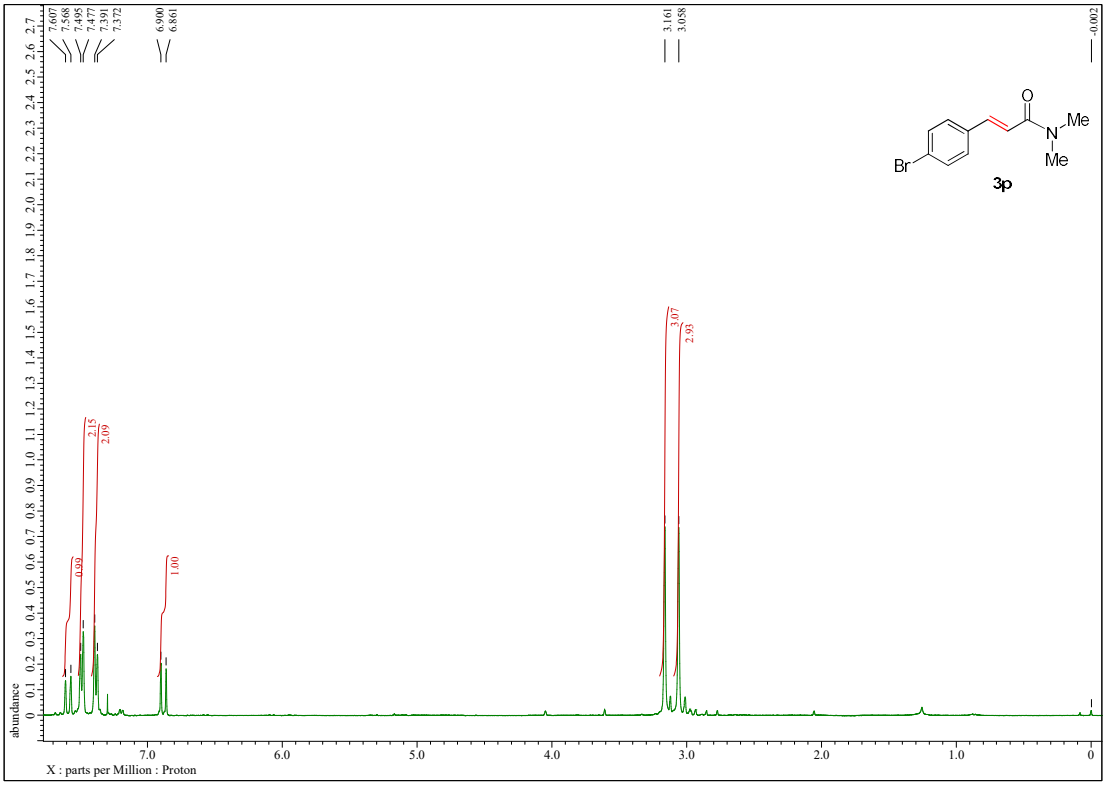

166.993
153.040
142.346
132.677
127.685
125.816
116.588
77.481
77.164
76.839
37.511
36.026
34.876
31.282
(thousandths)
X : parts per Million : Carbon13
tBu
N
Me
Me
O
3m

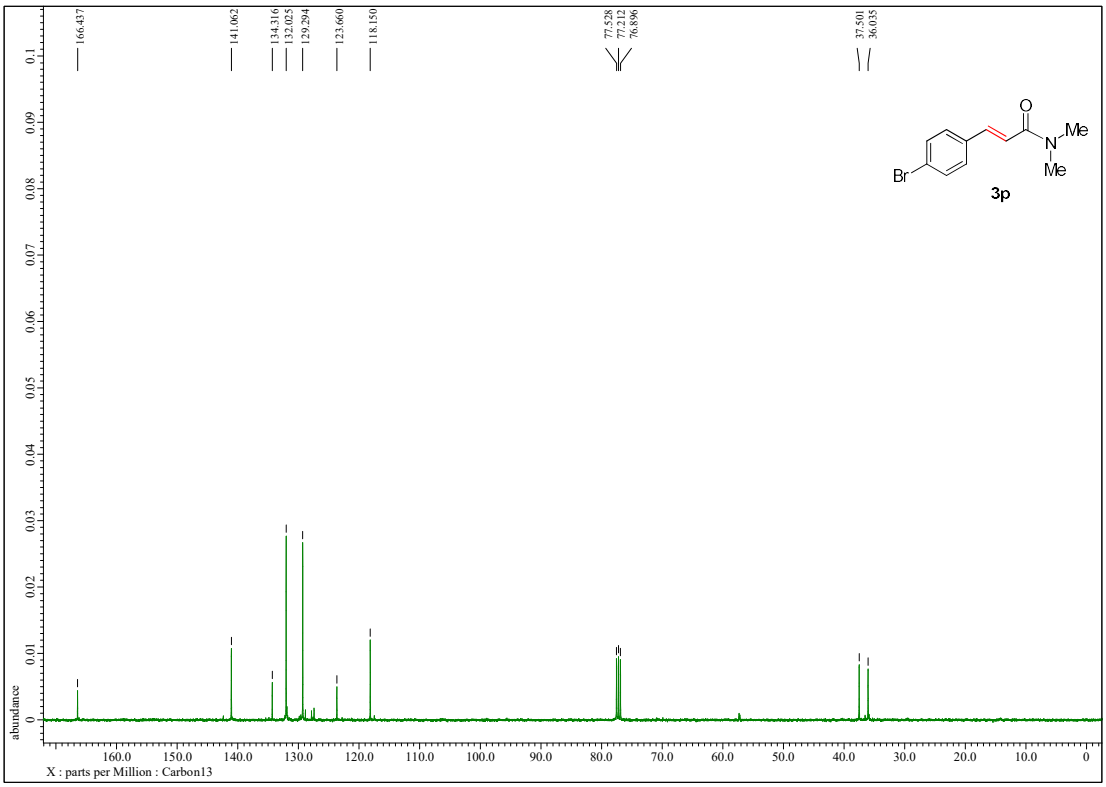

7.615
7.577
7.513
7.388
7.377
7.374
7.313
7.280
6.913
6.874
3.181
3.072
0.000
3.11
1.06
1.00
3.05
3.10
abundance
X : parts per Million : Proton
Cl
O
N
Me
Me
3n

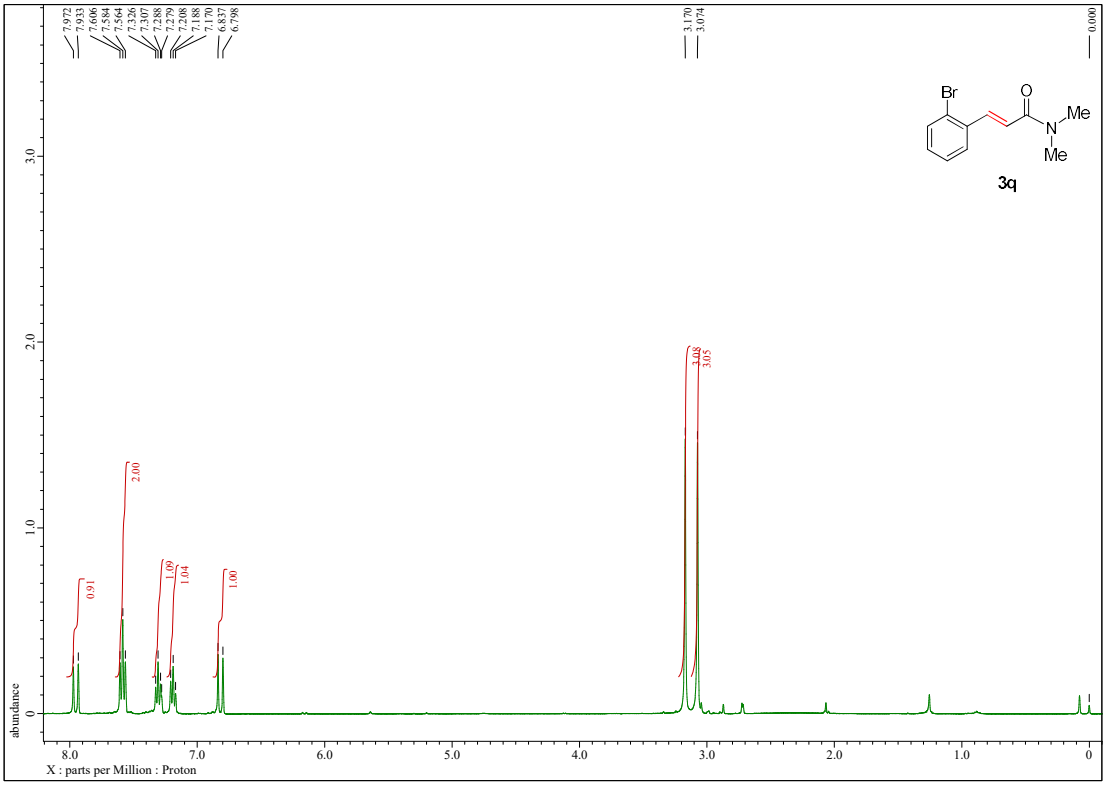

166.303
140.890
137.267
134.804
130.138
129.486
127.311
126.353
118.897
77.481
77.155
76.839
37.540
36.064
(thousandths)
X : parts per Million : Carbon13
Cl
O
N
Me
Me
3n

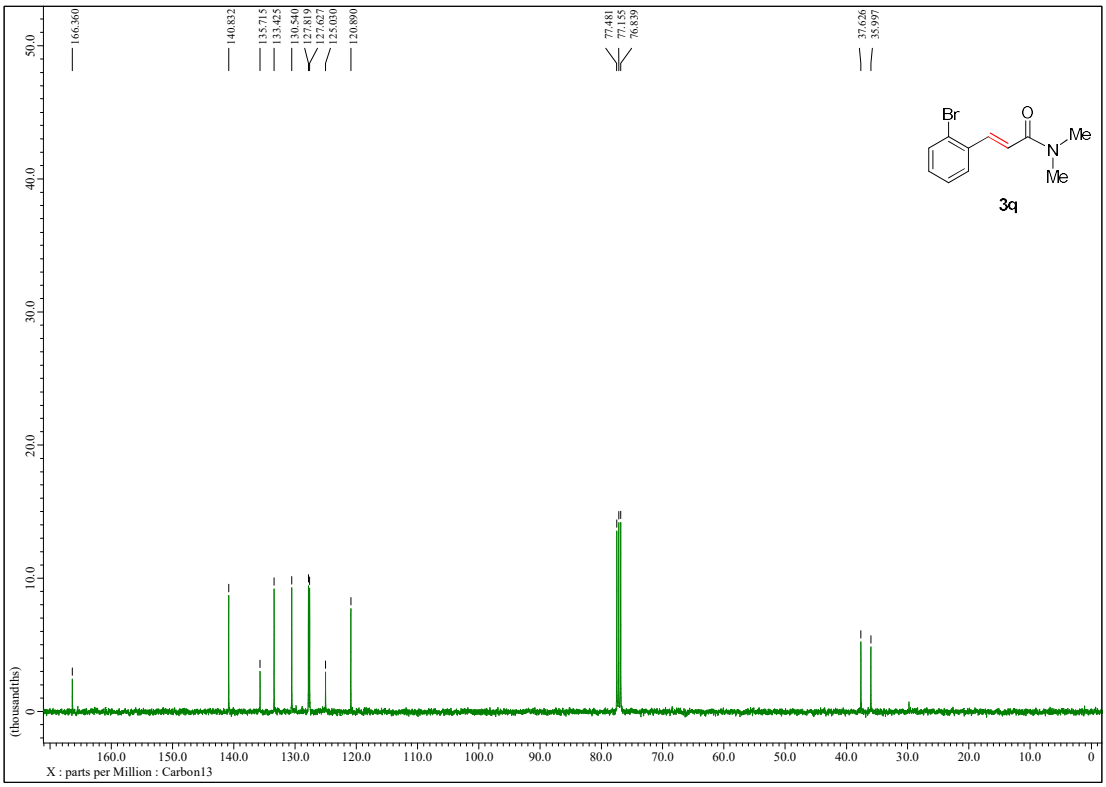

7.766
7.703
7.688
7.667
7.664
7.604
7.584
7.518
7.499
7.479
7.279
6.976
6.937
3.201
3.083
-0.003
3.03
3.07
2.20
1.06
1.07
1.09
1.00
abundance
X : parts per Million : Proton
F3C
O
N
Me
Me
3o

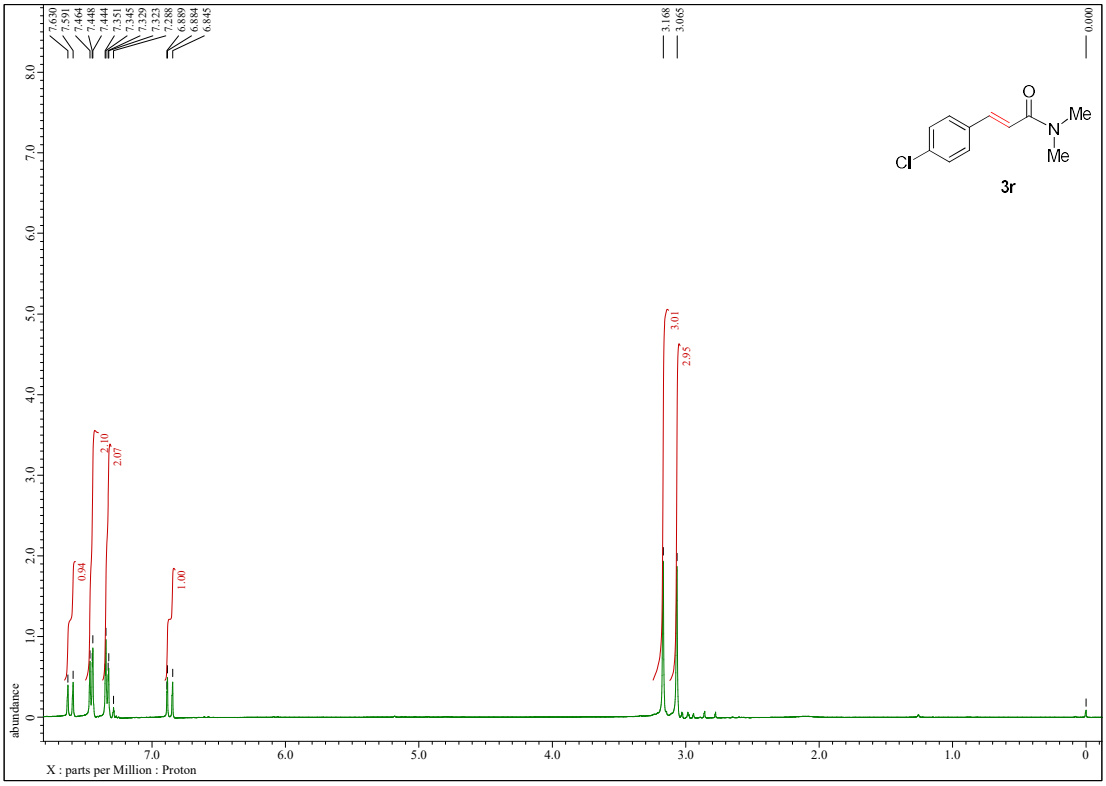

166.188
140.765
136.204
131.307
129.429
129.227
126.046
124.014
121.207
119.367
118.418
77.433
77.116
76.800
37.568
36.083
(thousandths)
X : parts per Million : Carbon13
F3C
O
N
Me
Me
3o

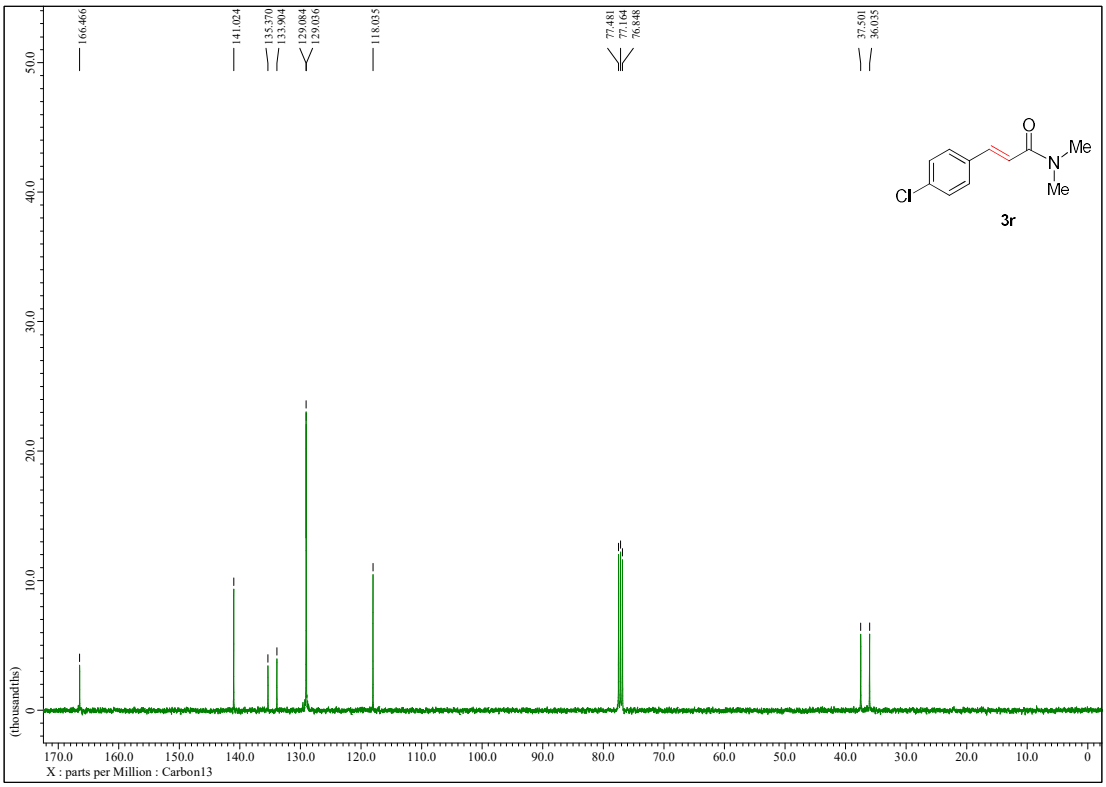

7.667
7.568
7.498
7.477
7.391
7.372
6.900
6.861
3.161
3.058
-0.002
2.15
2.09
0.99
1.00
3.07
2.93
abundance
X : parts per Million : Proton
Br
O
N
Me
Me
3p

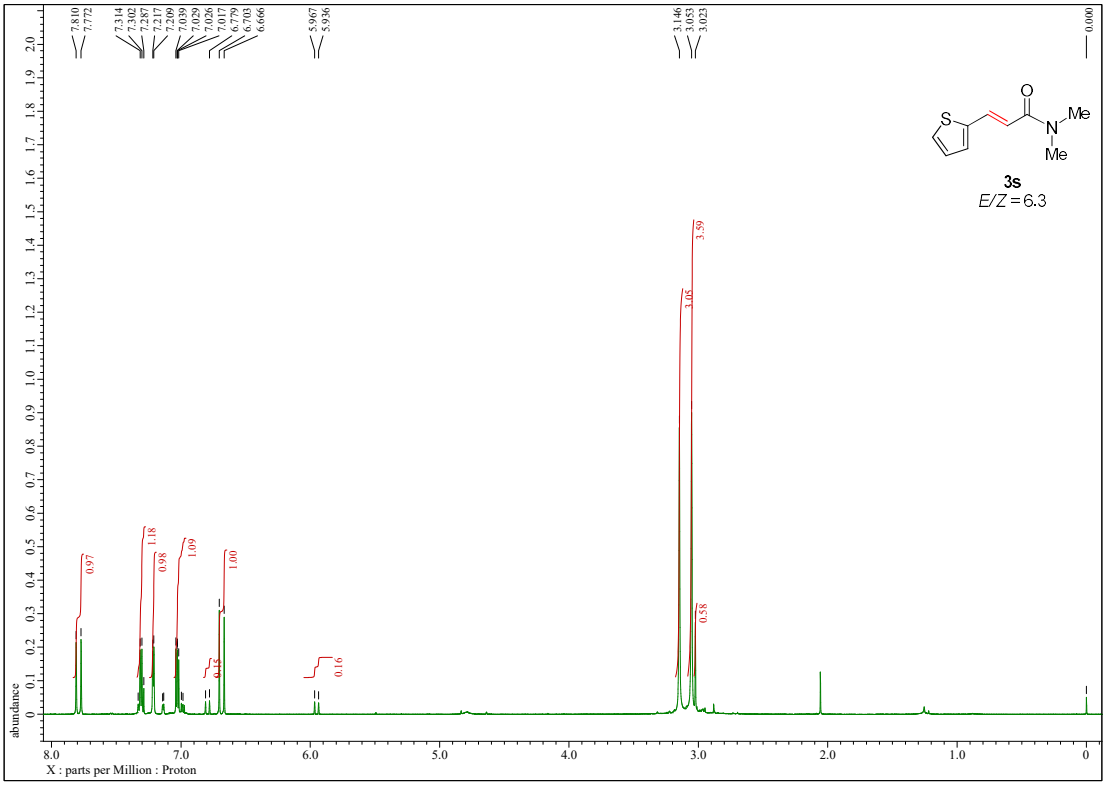

166.437
141.062
134.316
132.025
129.294
123.660
118.150
77.528
77.212
76.896
37.501
36.035
abundance
X : parts per Million : Carbon13
Br
O
N
Me
Me
3p

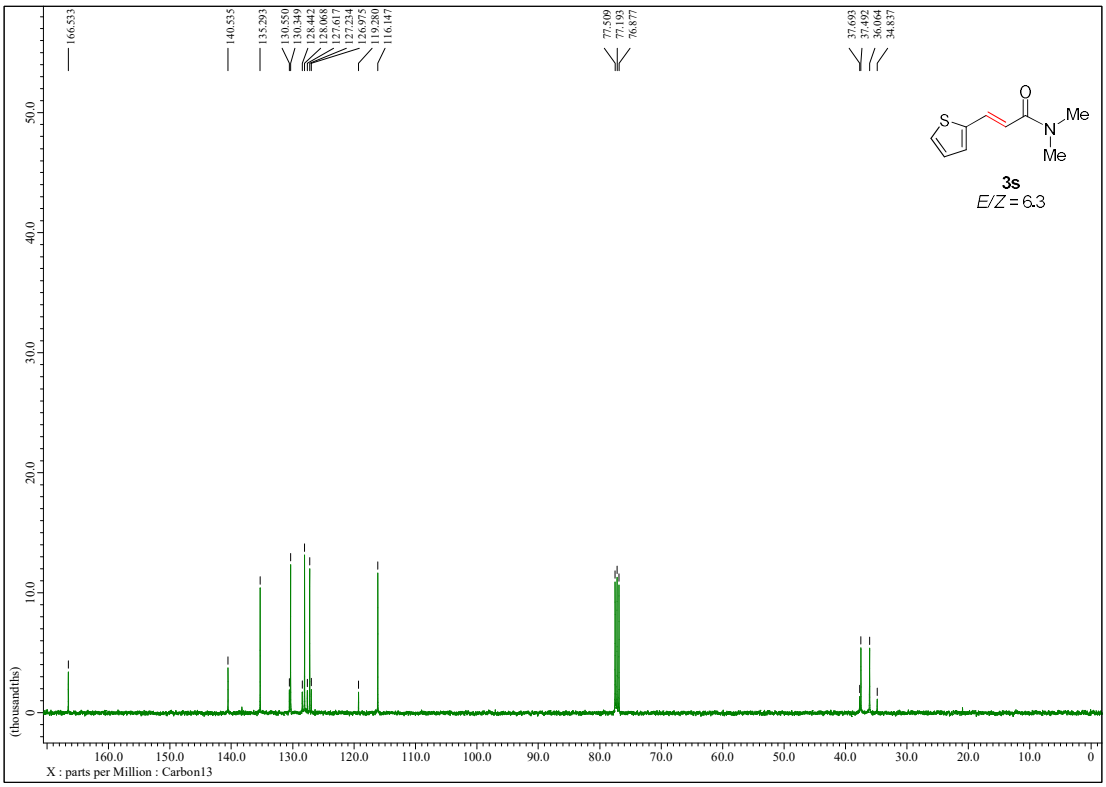

7.972
7.933
7.606
7.584
7.564
7.326
7.307
7.288
7.279
7.208
7.188
7.170
6.837
6.798
3.170
3.074
0.000
Br
O
N
Me
Me
3q
3.08
3.05
2.00
1.09
1.04
0.91
1.00
abundance
X : parts per Million : Proton

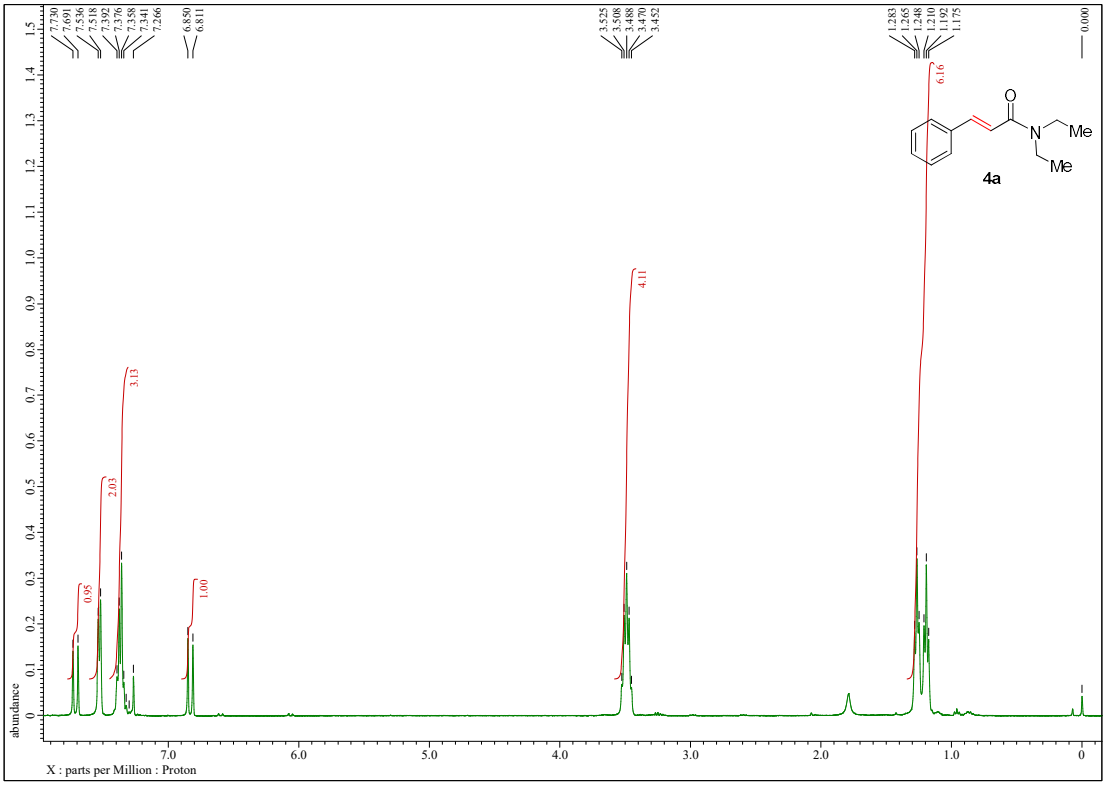

166.360
140.832
135.715
133.425
130.540
127.819
127.627
125.030
120.890
77.481
77.155
76.839
37.626
35.997
Br
O
N
Me
Me
3q
(thousandths)
X : parts per Million : Carbon13

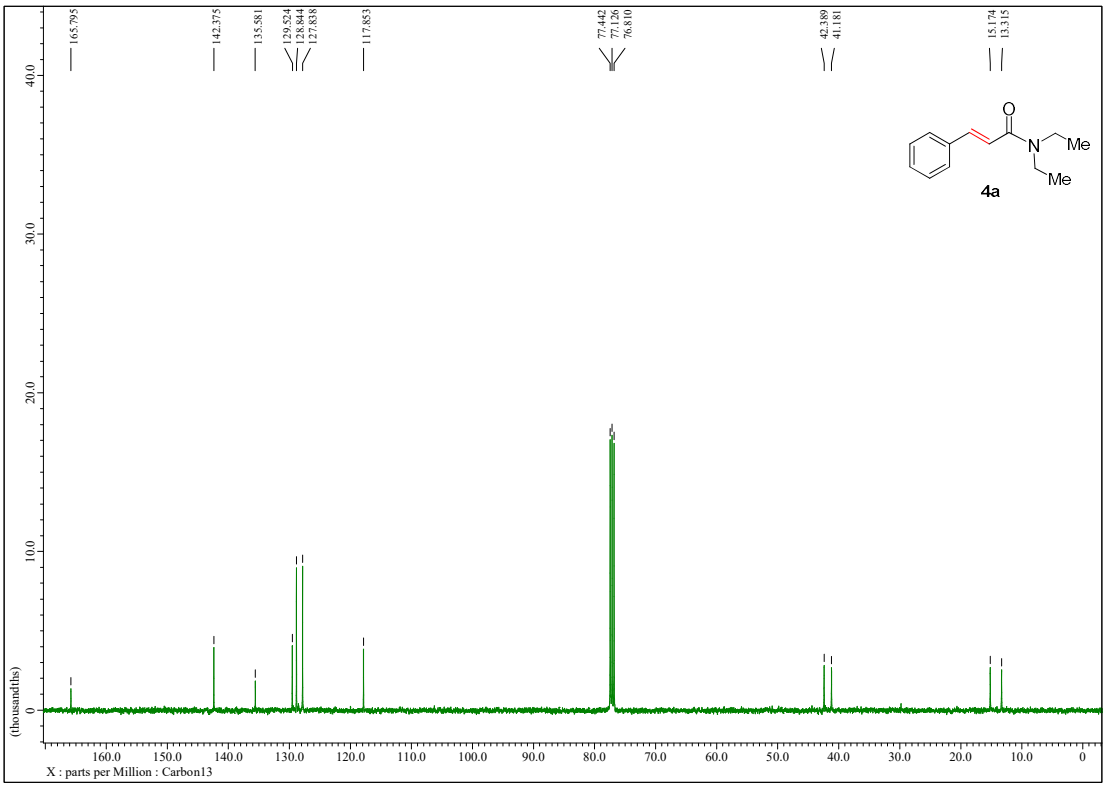

7.630
7.591
7.464
7.448
7.444
7.351
7.345
7.329
7.323
7.288
6.889
6.884
6.845
3.168
3.065
0.000
3.01
2.95
2.10
2.07
0.94
1.00
abundance
X : parts per Million : Proton
O
Me
N
Me
Cl
3r

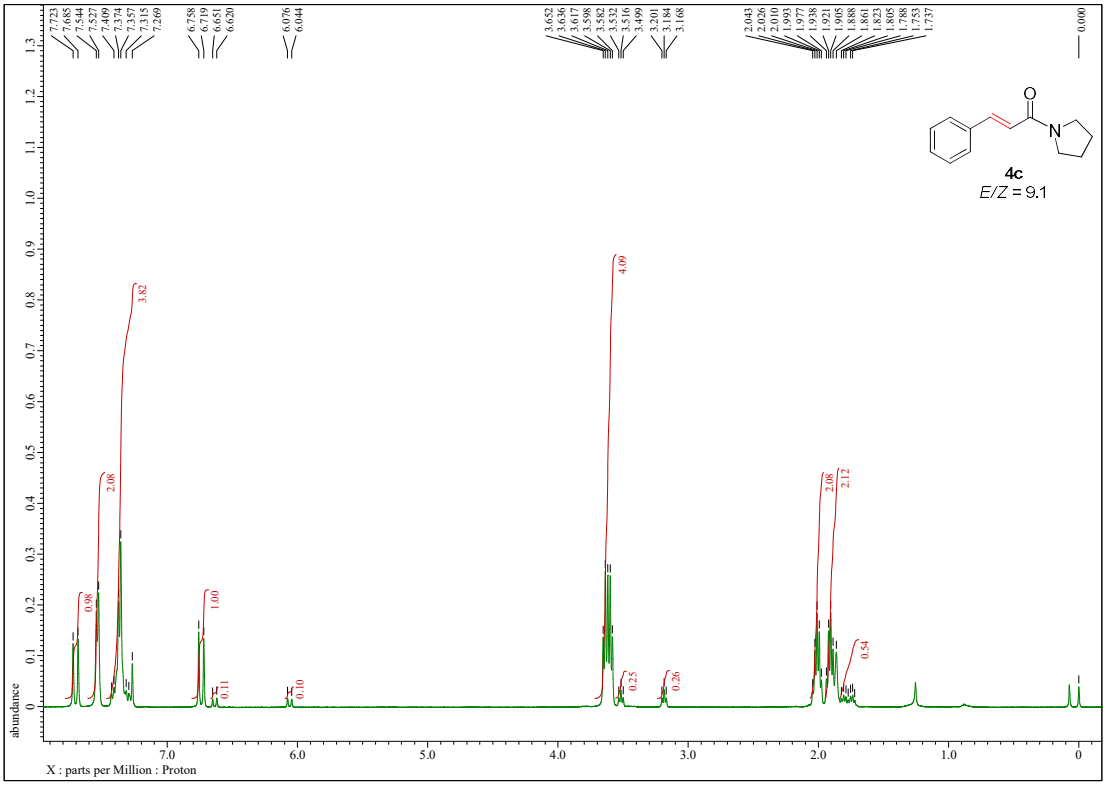

166.466
141.024
135.370
133.904
129.084
129.036
118.035
77.481
77.164
76.848
37.501
36.035
(thousandths)
X : parts per Million : Carbon13
O
Me
N
Me
Cl
3r

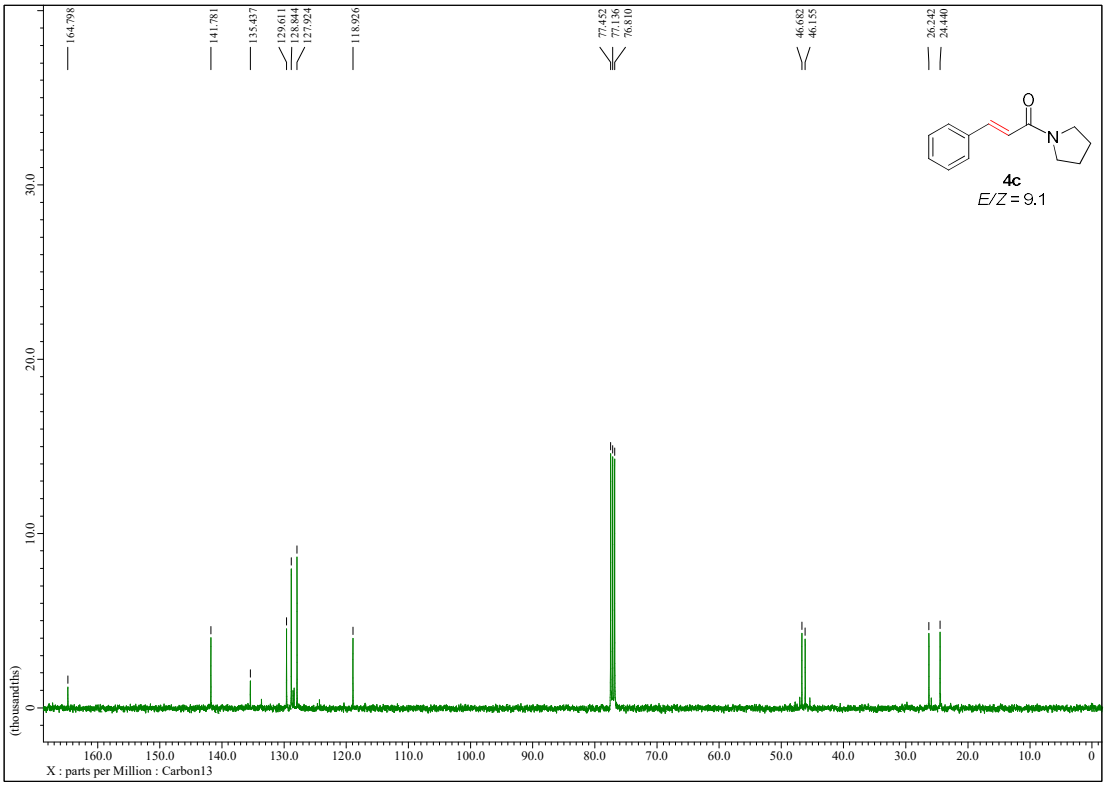

7.810
7.772
7.314
7.302
7.287
7.217
7.209
7.039
7.029
7.026
7.017
6.709
6.705
6.666
5.967
5.936
3.146
3.053
3.023
0.000
3s
E/Z = 6.3
0.97
1.18
0.98
1.09
1.00
0.16
3.06
3.59
0.58
abundance
X : parts per Million : Proton

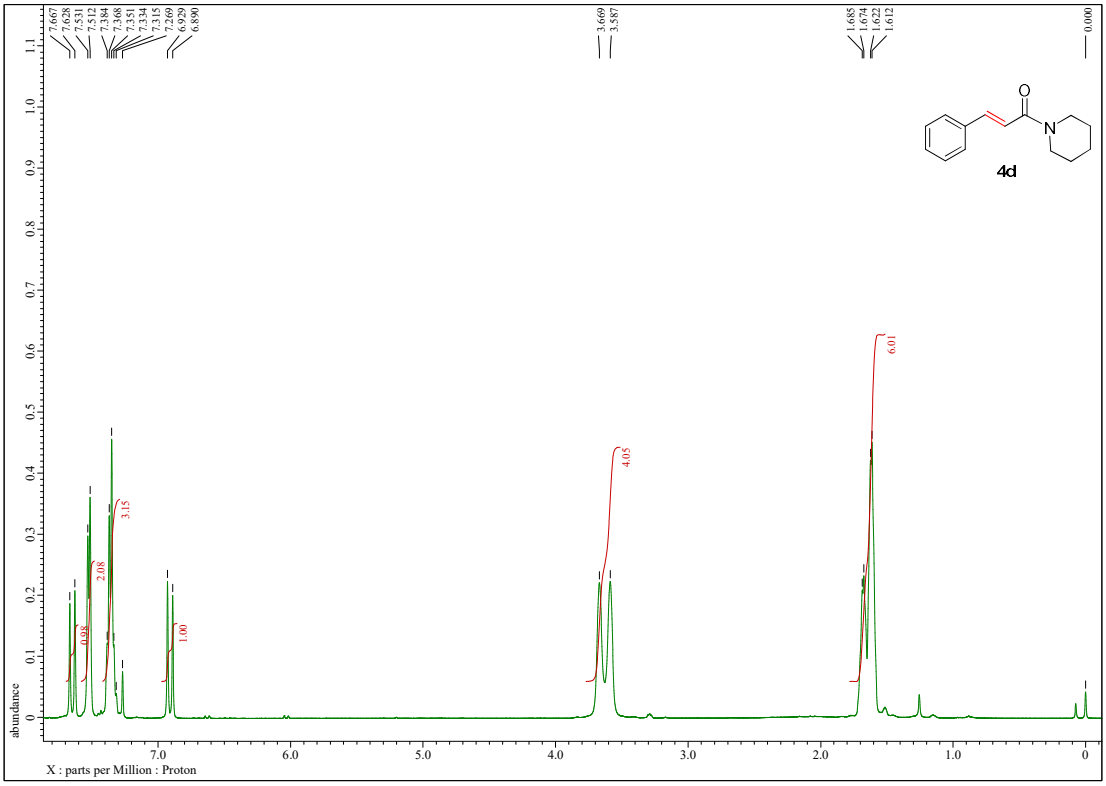

166.533
140.535
135.293
130.550
130.349
128.442
128.068
127.617
127.234
126.975
119.280
116.147
77.509
77.193
76.877
37.693
37.492
36.064
34.837
3s
E/Z = 6.3
(thousandths)
X : parts per Million : Carbon13

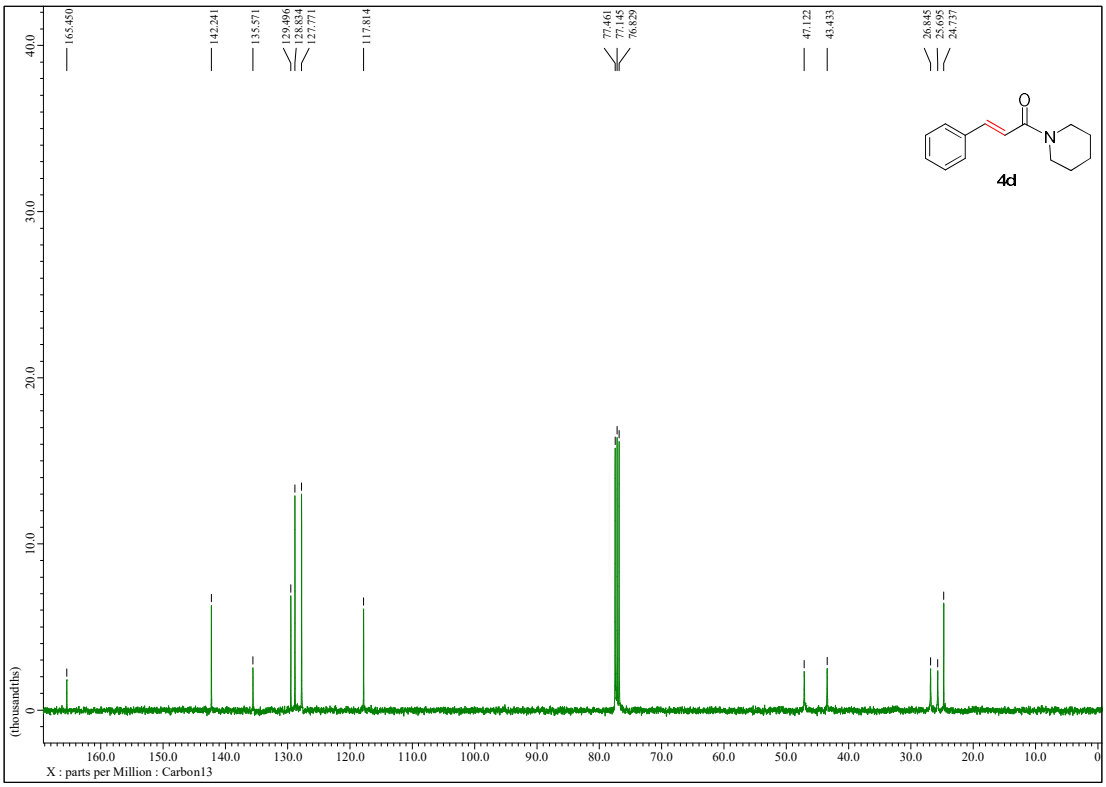

7.730
7.691
7.556
7.518
7.392
7.376
7.358
7.341
7.266
6.850
6.811
3.525
3.508
3.488
3.470
3.452
1.283
1.265
1.248
1.210
1.192
1.175
0.000
6.16
4.11
3.13
2.03
0.95
1.00
O
N
Me
Me
4a
abundance
X : parts per Million : Proton

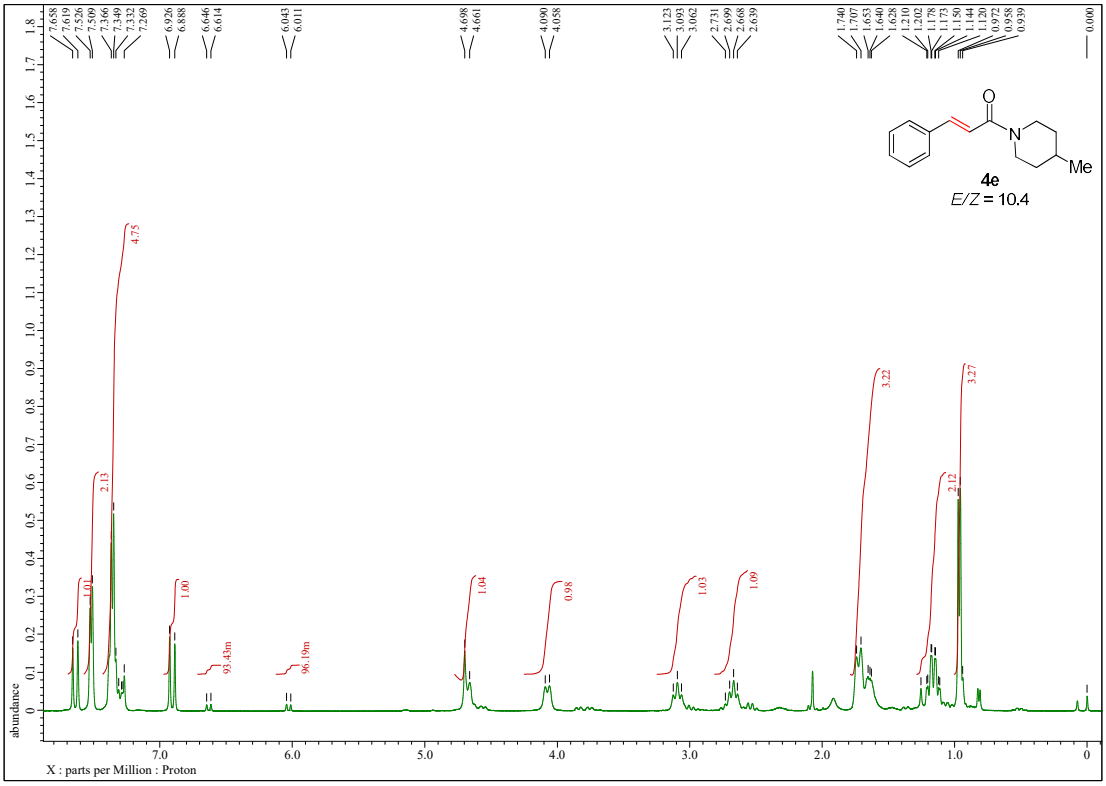

165.795
142.375
135.581
129.524
128.844
127.838
117.853
77.442
77.126
76.810
42.389
41.181
15.174
13.315
O
N
Me
Me
4a
(thousandths)
X : parts per Million : Carbon13

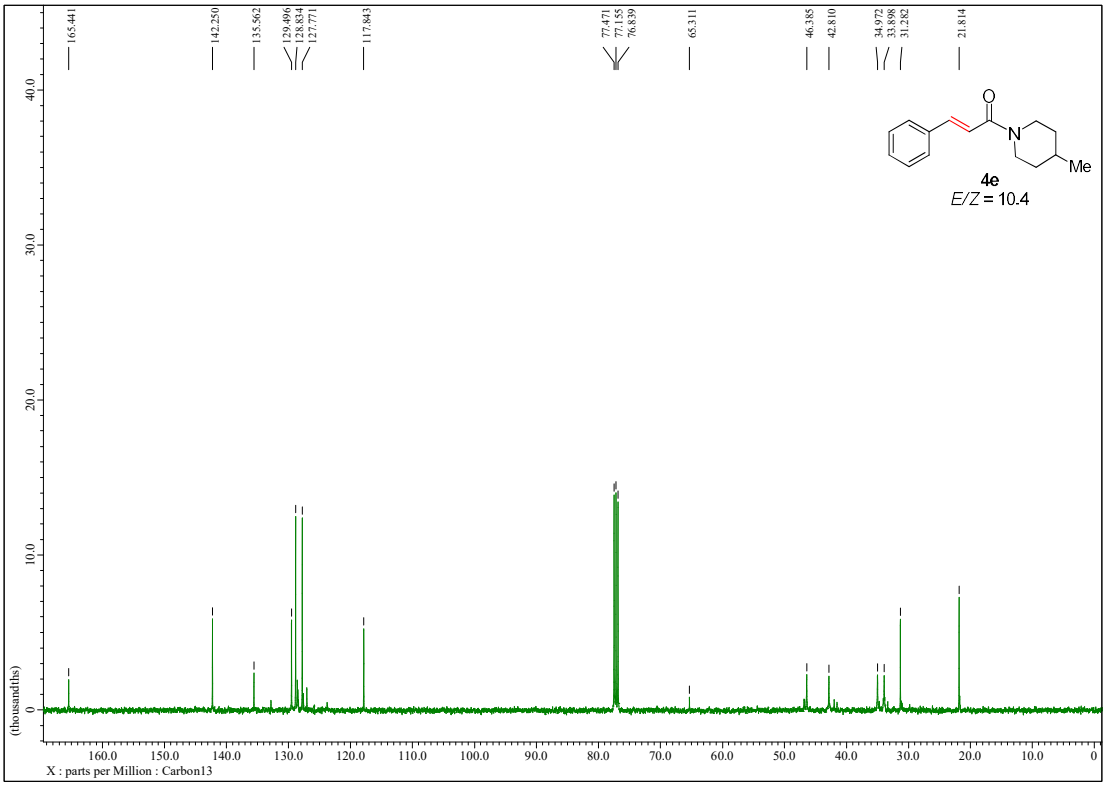

4c
E/Z = 9.1
abundance
X : parts per Million : Proton

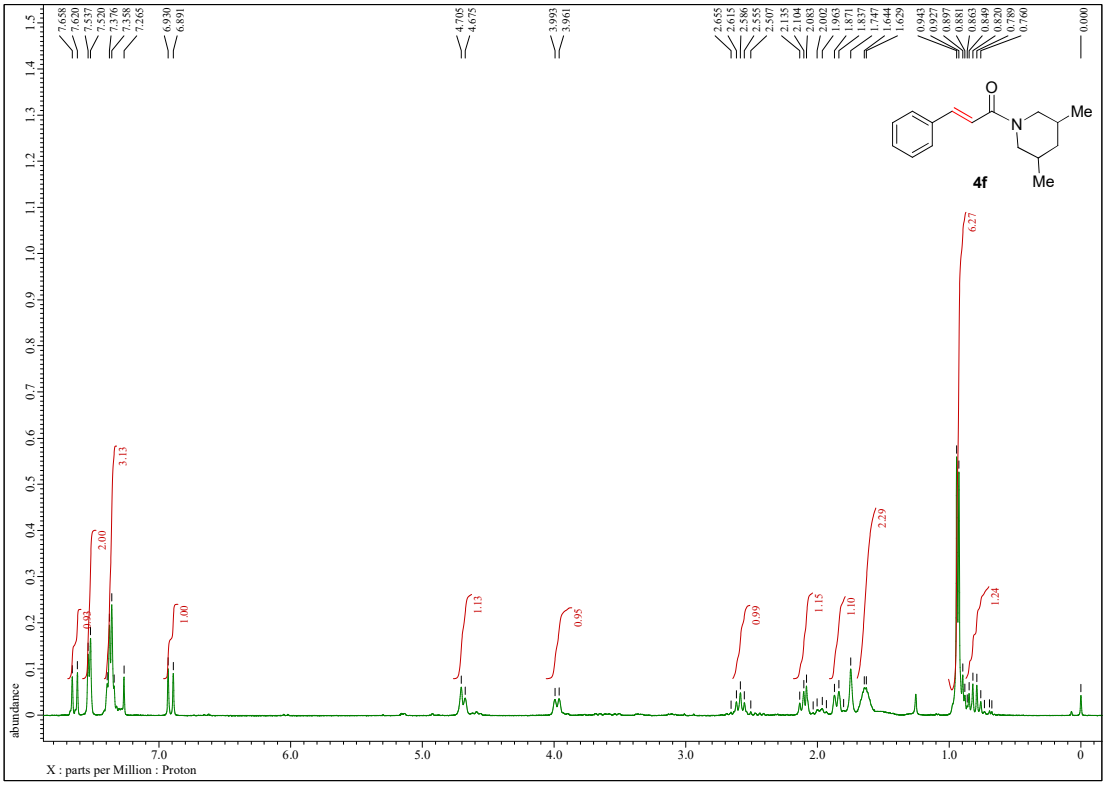

4c
E/Z = 9.1
(thousandths)
X : parts per Million : Carbon13

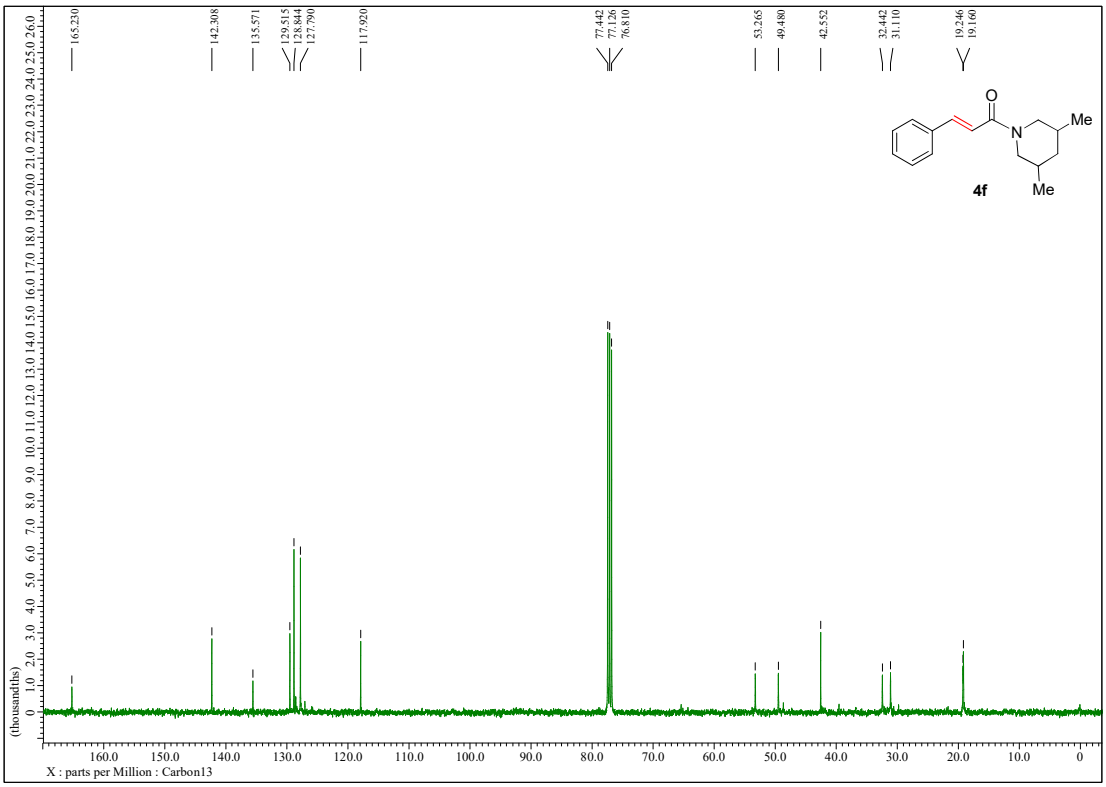

7.667
7.638
7.531
7.512
7.384
7.368
7.351
7.334
7.315
7.269
6.929
6.890
3.669
3.587
1.685
1.654
1.622
1.612
0.000
4d
6.01
4.05
3.15
2.08
0.98
1.00
abundance
X : parts per Million : Proton

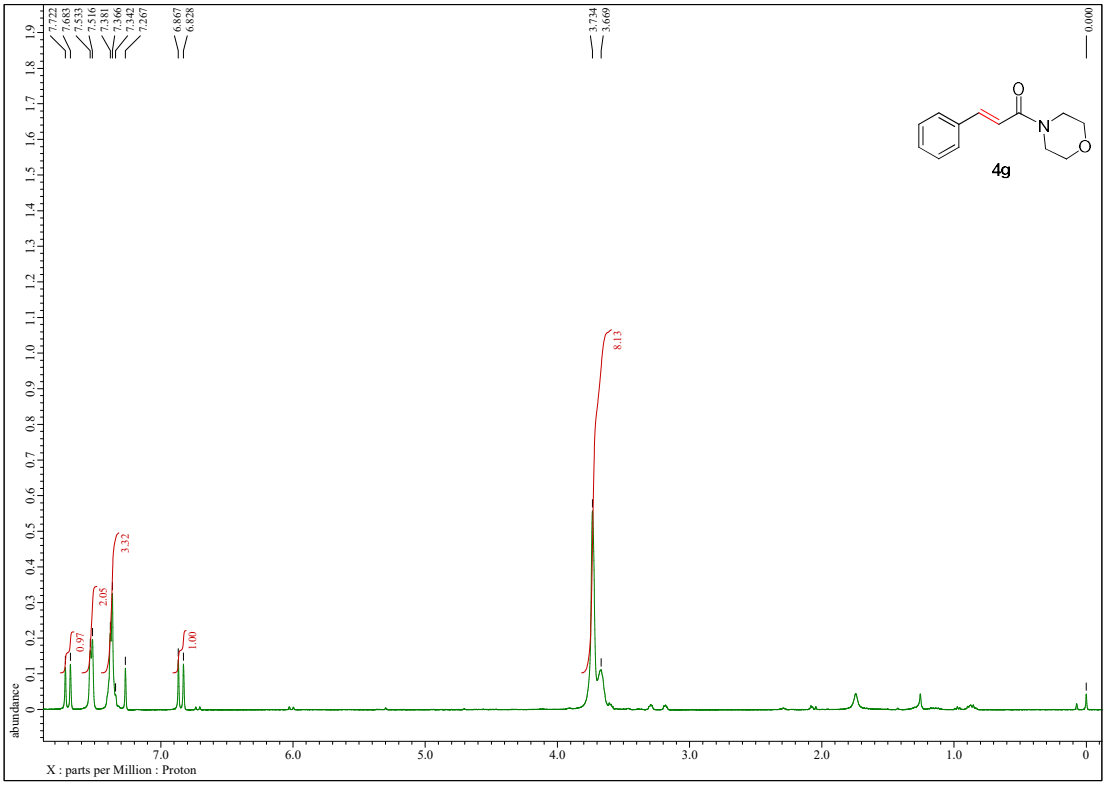

165.450
142.241
135.571
129.496
128.834
127.771
117.814
77.461
77.145
76.829
47.122
43.433
26.845
25.695
24.737
4d
(thousandths)
X : parts per Million : Carbon13

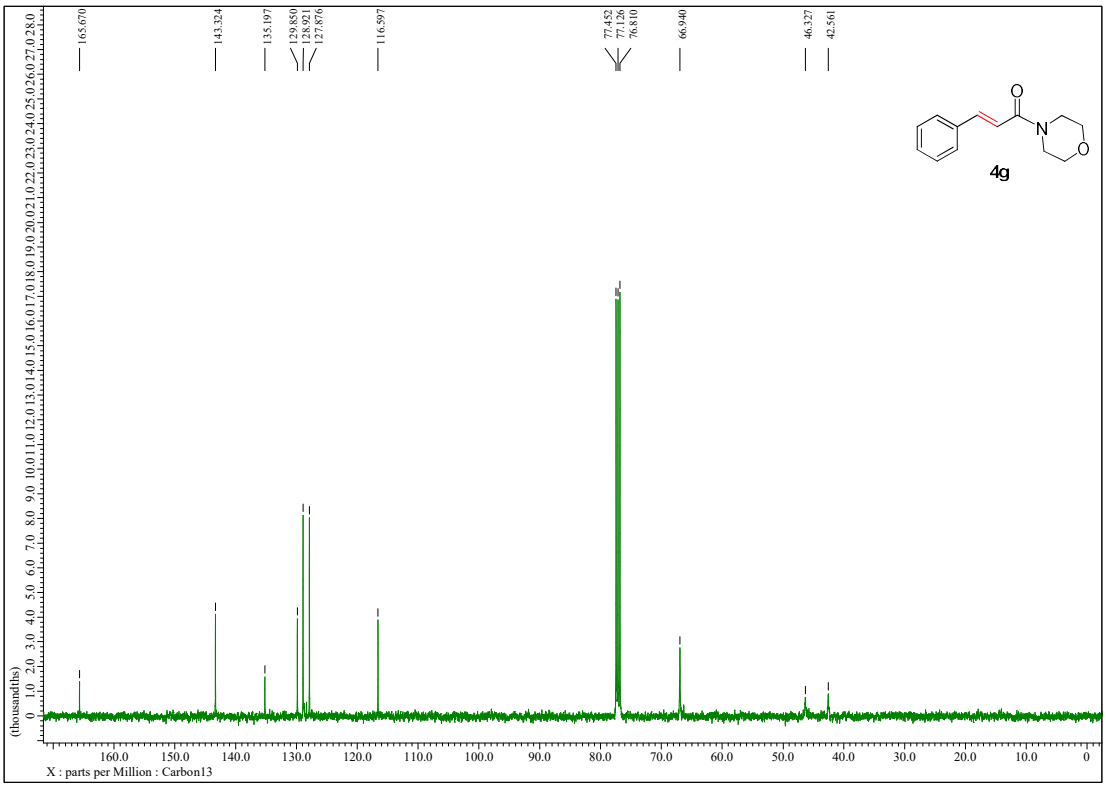

4e
E/Z = 10.4
abundance
X : parts per Million : Proton

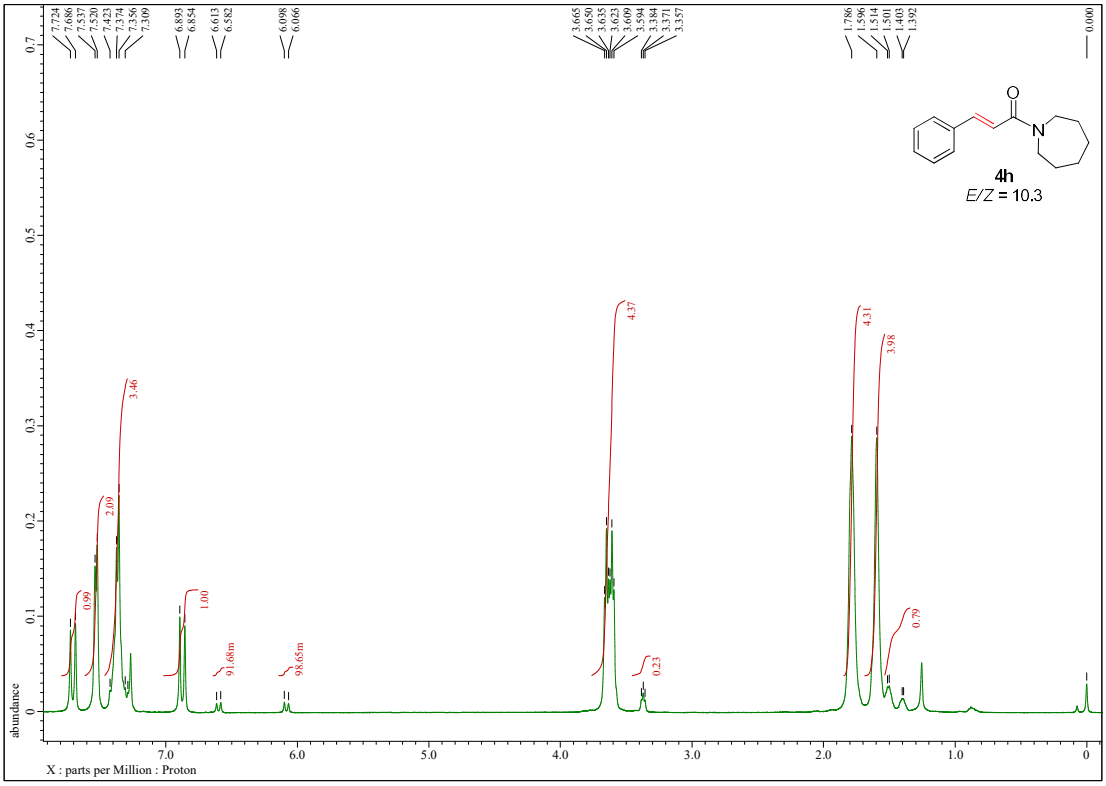

4e
E/Z = 10.4
(thousandths)
X : parts per Million : Carbon13

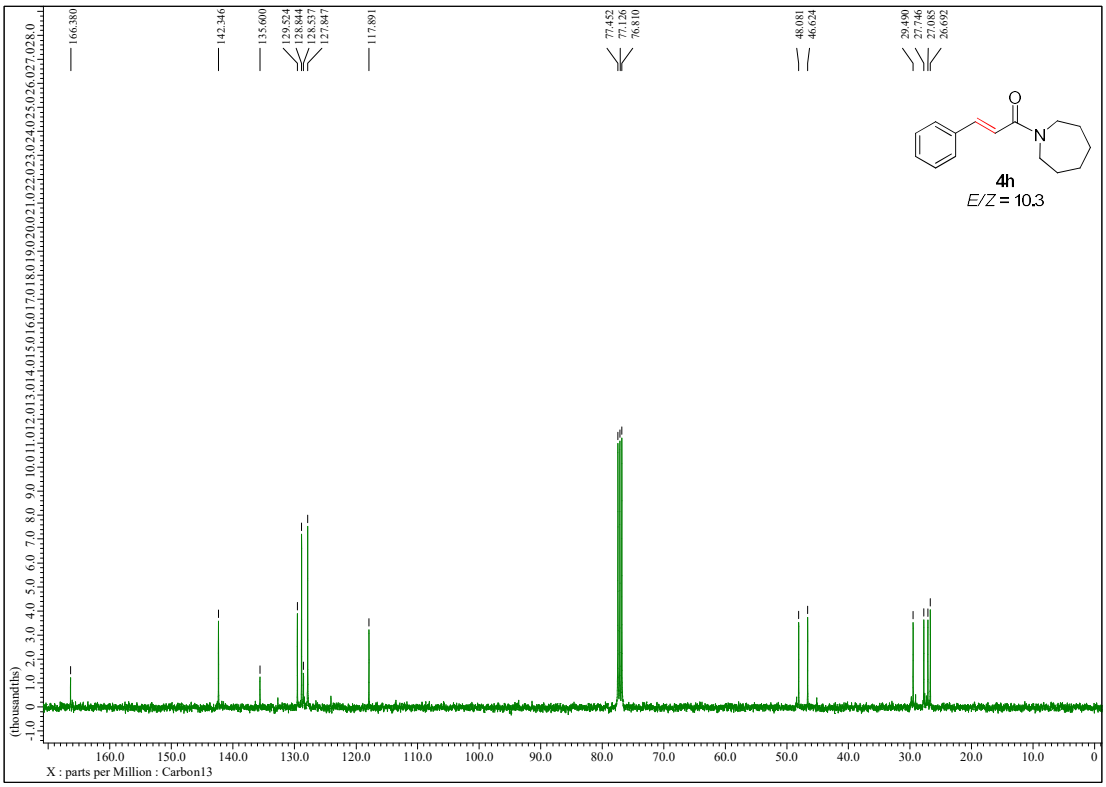

7.658
7.620
7.537
7.520
7.376
7.358
7.265
6.930
6.891
4.705
4.675
3.993
3.961
2.655
2.615
2.586
2.555
2.507
2.135
2.104
2.083
2.002
1.965
1.871
1.837
1.747
1.644
1.629
0.943
0.927
0.897
0.881
0.863
0.849
0.820
0.789
0.760
0.000
O
N
Me
Me
4f
6.27
3.13
2.00
2.00
1.00
1.13
0.95
0.99
1.15
1.10
2.29
1.24
abundance
X : parts per Million : Proton

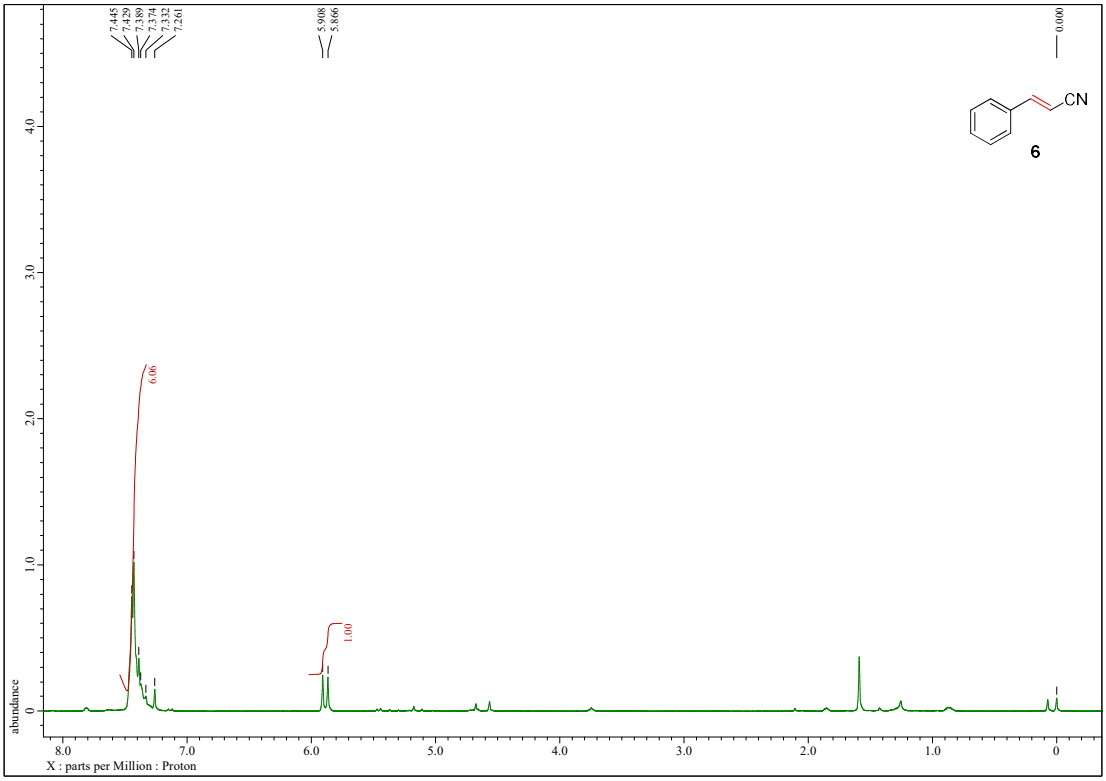

165.230
142.308
135.571
129.515
128.844
127.790
117.920
77.442
77.126
76.810
53.265
49.480
42.552
32.442
31.110
19.246
19.160
O
N
Me
Me
4f
(thousandths)
X : parts per Million : Carbon13

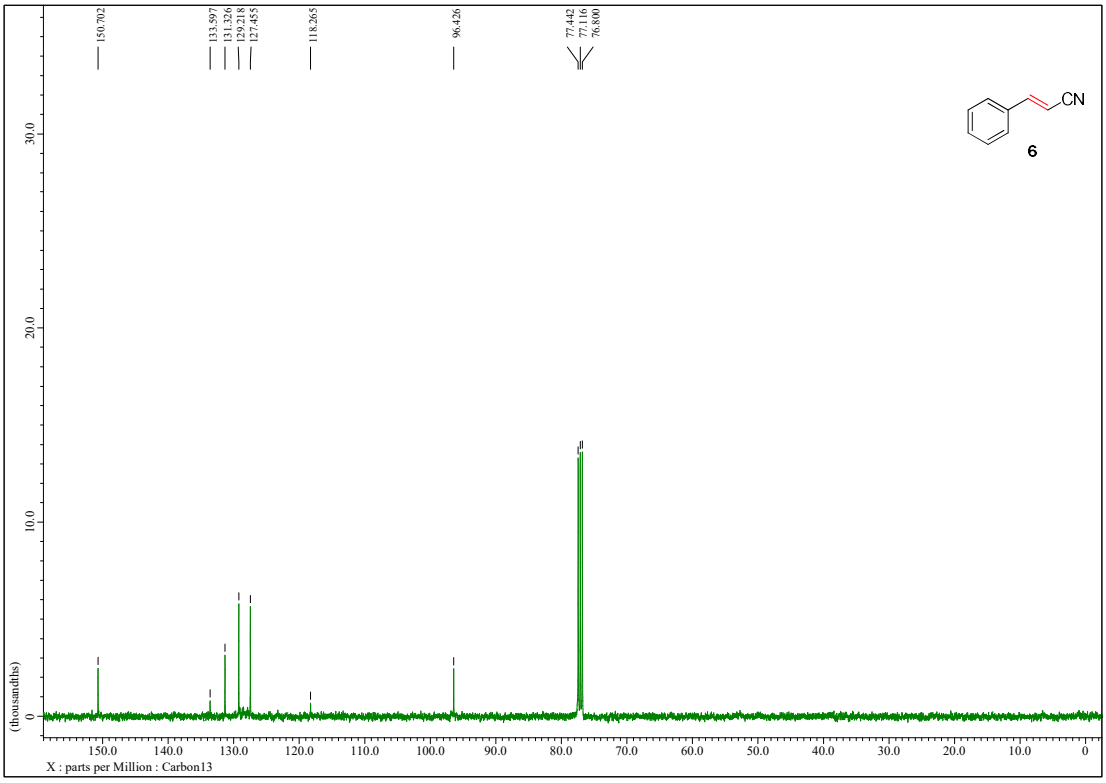

7.722
7.683
7.533
7.516
7.381
7.366
7.342
7.267
6.867
6.828
3.734
3.669
0.000
8.13
3.32
2.05
0.97
1.00
4g
abundance
X : parts per Million : Proton


165.670
143.324
135.197
129.850
128.921
127.876
116.597
77.452
77.126
76.810
66.940
46.327
42.561
4g
(thousandths)
X : parts per Million : Carbon13


7.724
7.686
7.537
7.530
7.423
7.374
7.356
7.309
6.893
6.854
6.613
6.582
6.098
6.066
3.665
3.650
3.635
3.623
3.609
3.594
3.384
3.371
3.357
1.786
1.596
1.514
1.501
1.403
1.392
0.000
4h
E/Z = 10.3
0.99
2.09
3.46
1.00
91.68m
98.65m
4.37
0.23
4.31
3.98
0.79
abundance
X : parts per Million : Proton


166.380
142.346
135.600
129.524
128.844
128.537
127.847
117.891
77.452
77.126
76.810
48.081
46.624
29.490
27.746
27.085
26.692
4h
E/Z = 10.3
(thousandths)
X : parts per Million : Carbon13


7.445
7.429
7.389
7.374
7.332
7.261
5.908
5.866
0.000
CN
6
6.06
1.00
abundance
X : parts per Million : Proton


150.702
133.597
131.326
129.218
127.455
118.265
96.426
77.442
77.116
76.800
CN
6
(thousandths)
X : parts per Million : Carbon13