Iron-catalyzed boration of allylic alcohols with H_3BO_3 as an additive

Yuhan Zhou,* Huan Wang, Yang Liu, Yilong Zhao, Chunxia Zhang, Jingping Qu

State Key Laboratory of Fine Chemicals, School of Pharmaceutical Science and Technology, Dalian University of Technology, Dalian 116024, P.R. China.
E-mail: zhouyh@dl.cn

Supporting Information

Contents

Characterization of allylic boronates

2-(2-Phenylallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)[1]

Colourless liquid; yield 51%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.52-7.50 (m, 2H), 7.30-7.26 (m, 2H), 7.35-7.31 (m, 1H), 5.40 (d, J = 1.3 Hz, 1H), 5.14 (d, J = 1.3 Hz, 1H), 2.21 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 141.9, 128.1, 127.2, 125.9, 112.2, 83.4, 24.6.

2-(2-(4-Chlorophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)[1]

Pale yellow liquid; yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.38 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 5.32 (d, J = 1.0 Hz, 1H), 5.09 (d, J = 1.0 Hz, 1H), 2.12 (s, 2H), 1.15 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.3, 133.0, 128.1, 127.2, 112.8, 83.5, 24.6.

2-(2-(4-Bromophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)[1]

Colourless liquid; yield 32%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.40 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 5.33 (d, J = 1.1 Hz, 1H), 5.10 (d, J = 1.1 Hz, 1H), 2.11 (s, 2H), 1.15 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 140.7, 131.1, 127.5, 121.1, 112.8, 83.5, 24.6.

2-(2-(4-Fluorophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)[2]

Colourless liquid; yield 33%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.43 (m, 2H), 6.98 (m, 2H), 5.29 (s, 1H), 5.08 (s, 1H), 2.14 (s, 2H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 246.7 Hz), 143.3, 137.9 (d, J = 3.2 Hz), 127.5 (d, J = 7.9 Hz), 114.7 (d, J = 21.3 Hz), 112.1, 83.4, 24.5.

2-(2-(*p*-Tolyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)[1]

Colourless liquid; yield 31%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.37 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 5.34 (d, J = 1.2 Hz, 1H), 5.05 (d, J = 1.2 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 136.9, 128.7, 125.7, 111.4, 100.0, 83.4, 24.6, 21.1.

2-(2-(4-(*tert*-Butyl)phenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)[1]

Colourless liquid; yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.44 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 5.38 (d, J = 1.1 Hz, 1H), 5.09 (d, J = 1.1 Hz, 1H), 2.18 (s, 2H), 1.34 (s, 9H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 144.1, 139.0, 125.5, 124.9, 111.5, 83.4, 34.4, 31.3, 24.6.

2-(2-(3-(Trifluoromethyl)phenyl)allyl)-4,4,5,5-tetramethyl -1,3,2-dioxaborolane (3g)[1]

Colourless liquid; yield 32%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.73-7.41 (m, 4H), 5.43 (d, J = 0.9 Hz, 1H), 5.21 (d, J = 0.9 Hz, 1H), 2.19 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 142.6, 130.4 (q, J = 32.1 Hz), 129.1, 128.5, 124.3 (q, J = 272.3 Hz), 123.8 (q, J = 3.8 Hz), 122.7 (q, J = 3.8 Hz), 113.7, 83.6, 24.6.

2-(2-(3-Methoxyphenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)[1]

Pale yellow liquid; yield 44%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.21 (m, 1H), 7.05 (m, 2H), 6.79 (m, 1H), 5.37 (d, J = 1.3 Hz, 1H), 5.10 (d, J = 1.3 Hz, 1H), 3.80 (s, 3H), 2.15 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 144.3, 143.4, 129.0, 118.4, 112.9, 112.4, 111.5, 83.4, 55.1, 24.6.

2-(2-(Naphthalen-2-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)[1]

Pale yellow liquid; yield 48%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.85-7.65 (m, 5H), 7.42-7.39 (m, 2H), 5.54 (s, 1H), 5.21 (s, 1H), 2.28 (s, 2H), 1.15 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 138.8, 133.4, 132.8, 128.2, 127.6, 127.5, 126.0, 125.7, 124.5, 124.3, 112.8, 83.5, 24.6.

(*E/Z*)-2-(2-Phenylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67:33 mixture of regioisomers) (3j)[1]

Colourless liquid; yield 53%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.44 – 7.20 (m, 5H), 5.88 (q, J = 6.8 Hz, 1H × 0.67), 5.62 (q, J = 6.8 Hz, 1H × 0.33), 2.16 (s, 2H × 0.67), 2.09 (s, 2H × 0.33), , 1.84 (d, J = 6.8 Hz, 3H × 0.67), 1.64 (d, J = 6.8 Hz, 3H × 0.33), 1.22 (s, 12H × 0.67), 1.17 (s, 12H × 0.33); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.2, 137.6, 136.9, 128.4, 128.0, 127.8, 126.2, 125.9, 121.5, 121.4, 83.2, 83.1, 24.6, 15.0, 14.6.

(*E/Z*)-2-(2-(4-Methoxyphenyl)undec-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (60:40 mixture of regioisomers) (3k)[1]

Pale yellow liquid; yield 73%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.34-7.13 (m, 2H), 6.85-6.81 (br, 2H), 5.67 (m, 1H × 0.6), 5.43 (m, 1H × 0.4), 3.79 (s, 3H), 2.16 (s, 2H × 0.6), 2.04 (s, 2H × 0.4), 1.99 (m, 2H), 1.48-1.14 (m, 24H), 0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 158.0, 137.1, 135.9, 135.0, 134.9, 129.4, 127.5, 126.9, 126.5, 113.3, 113.1, 83.2, 83.1, 55.2, 55.1, 31.92, 31.89, 30.2, 29.7, 29.6, 29.54, 29.47, 29.34, 29.29, 29.2, 29.1, 24.64, 24.61, 24.5, 22.69, 22.67, 14.1.

2-(3-Methyl-2-phenylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)[1]

Pale yellow liquid; yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.37 – 7.27 (m, 2H), 7.24 – 7.07 (m, 3H), 2.04 (s, 2H), 1.84 (s, 3H), 1.63 (s, 3H), 1.19 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 130.8, 128.7, 127.8, 126.1, 125.6, 83.0, 24.7, 22.1, 20.8.

2-(3-Methyl-2-(p-tolyl)but-2-en-1-yl)- 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)

Colourless liquid; yield 52%; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.18 – 6.89 (m, 4H), 2.30 (s, 3H), 1.97 (s, 2H), 1.78 (s, 3H), 1.58 (s, 3H), 1.15 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 134.9, 130.6, 128.6, 128.5, 126.0, 83.0, 24.7, 22.2, 21.1, 20.9. HRMS(ESI): *m/z* calc. for $C_{18}H_{28}BO_2$ $[M+H]^+$: 287.2182, found: 287.2187.

Note: The carbon attached to boron is not observed, or just a broad and low intensity signal around 10 ppm in ^{13}C NMR spectra.[3]

References

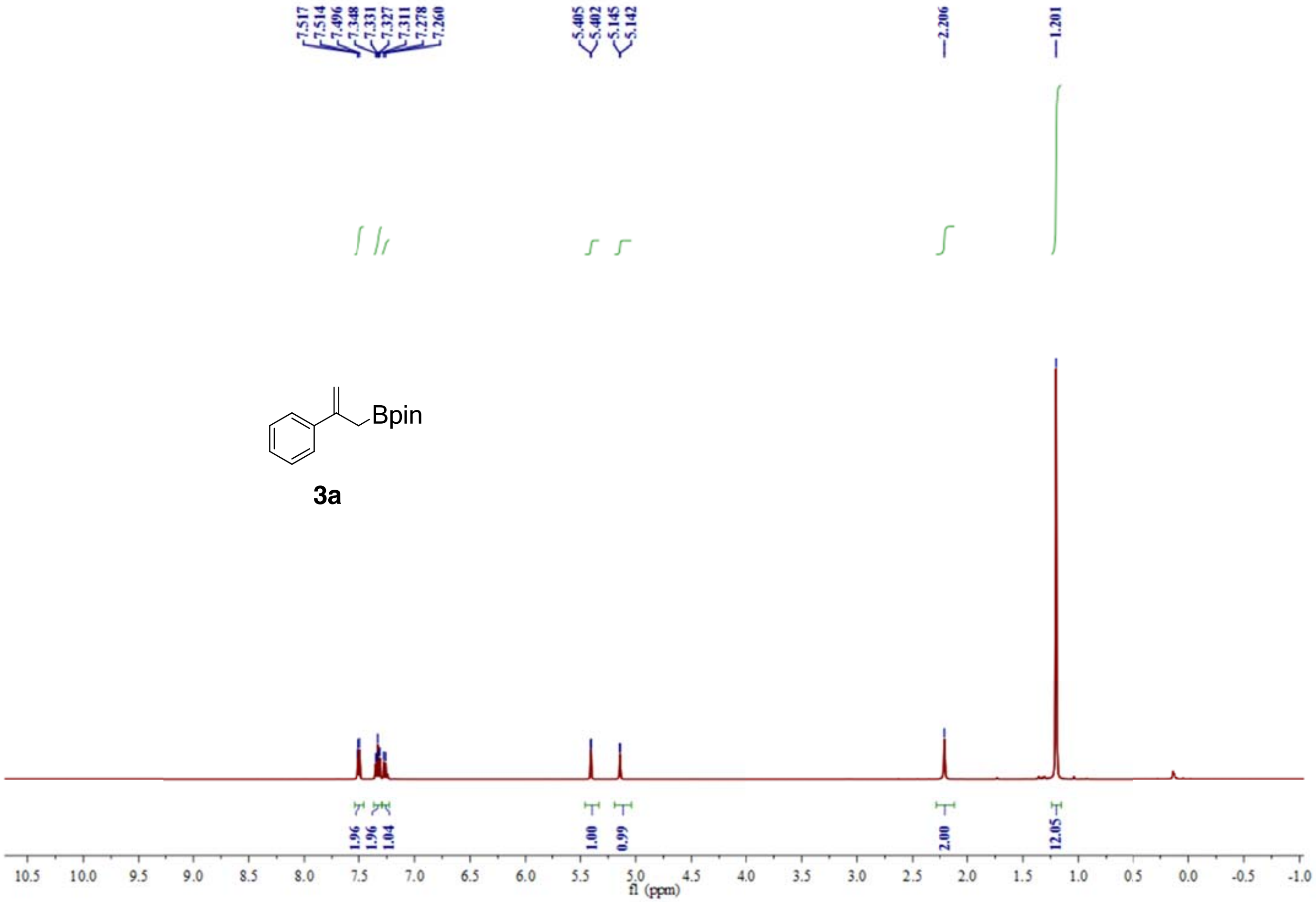
[1] Zhou, Y.; Wang, H.; Liu, Y.; Zhao, Y.; Zhang, C.; Qu, J. *Org. Chem. Front.* **2017**, *4*, 1580-1585.

[2] Corberan, R.; Mszar, N. W.; Hoveyda, A. H. *Angew. Chem, Int. Ed.*, **2011**, *50*, 7079-7082.

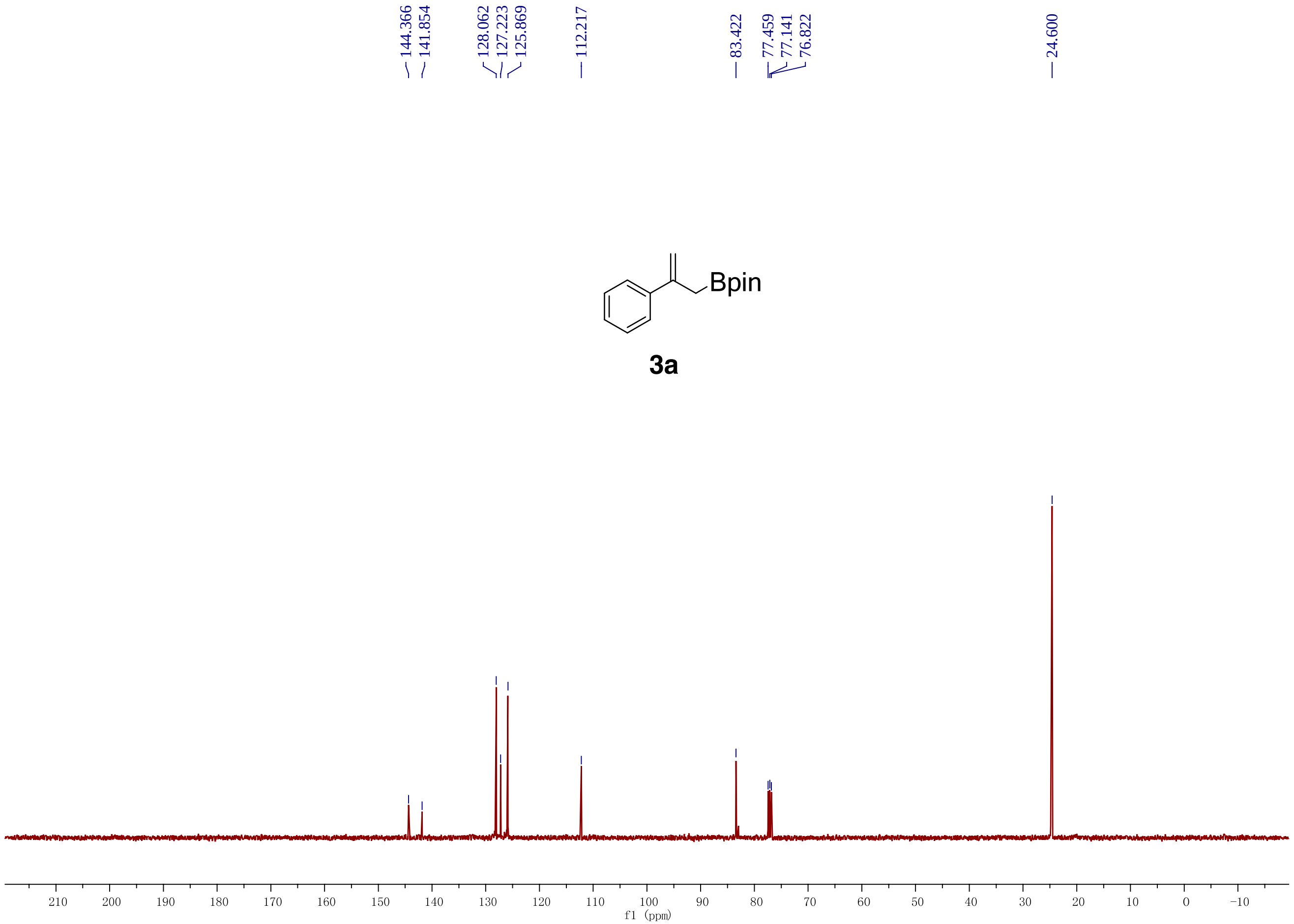
[3] (a) Unsworth, P. J.; Leonori, D.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 9846-9850; (b) Semba, K.; Nakao, Y. *J. Am. Chem. Soc*. **2014**, *136*, 7567-7570; (c) Yamamoto, E.; Izumi, K.; Horita, Y.; Ito, H. *J. Am. Chem. Soc*. **2012**, *134*, 19997-20000.

NMR Spectra of products

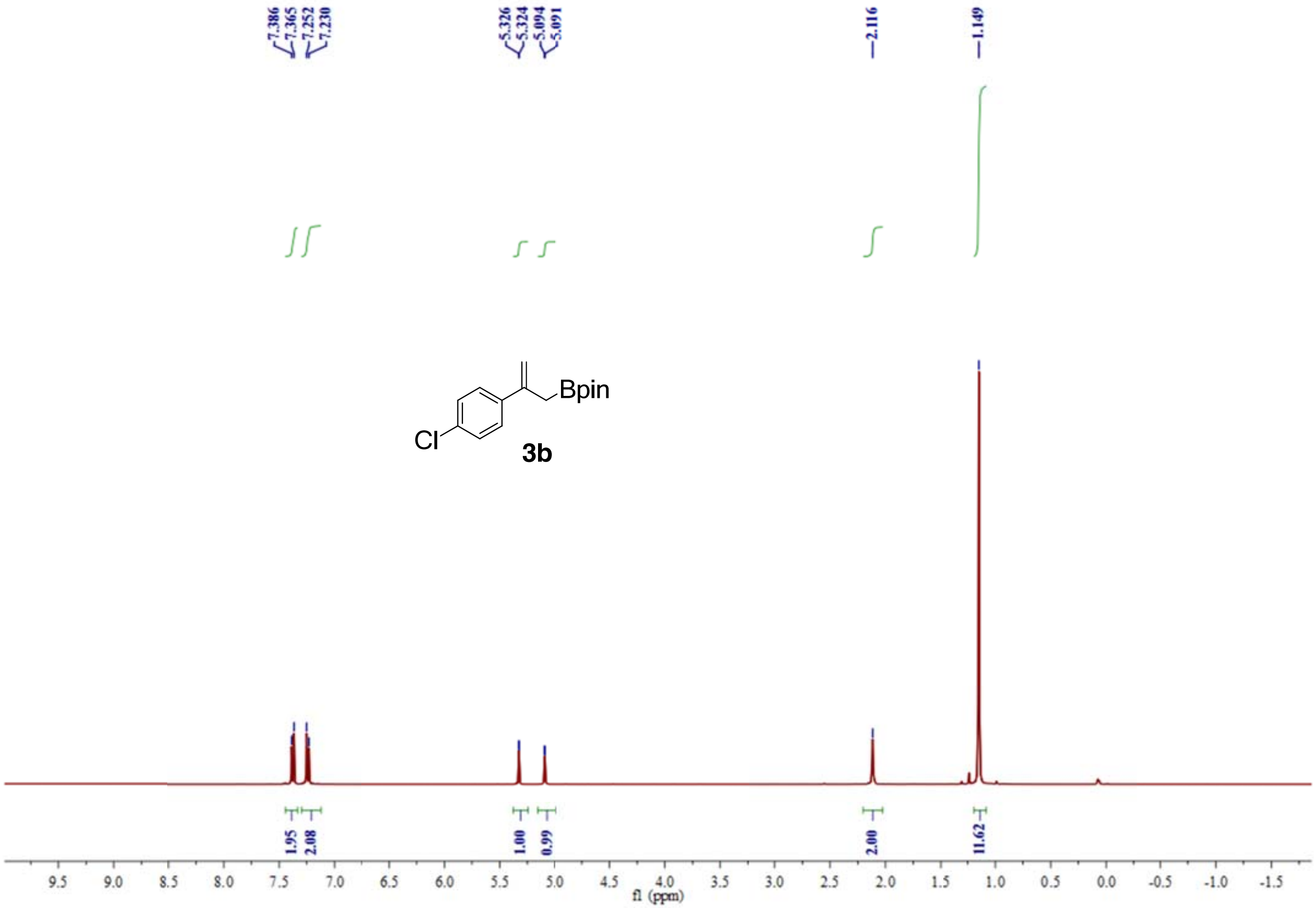
^{1}H NMR (400 MHz, $CDCl_3$) **(3a)**



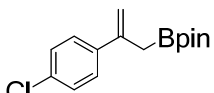
^{13}C NMR (101 MHz, $CDCl_3$) **(3a)**



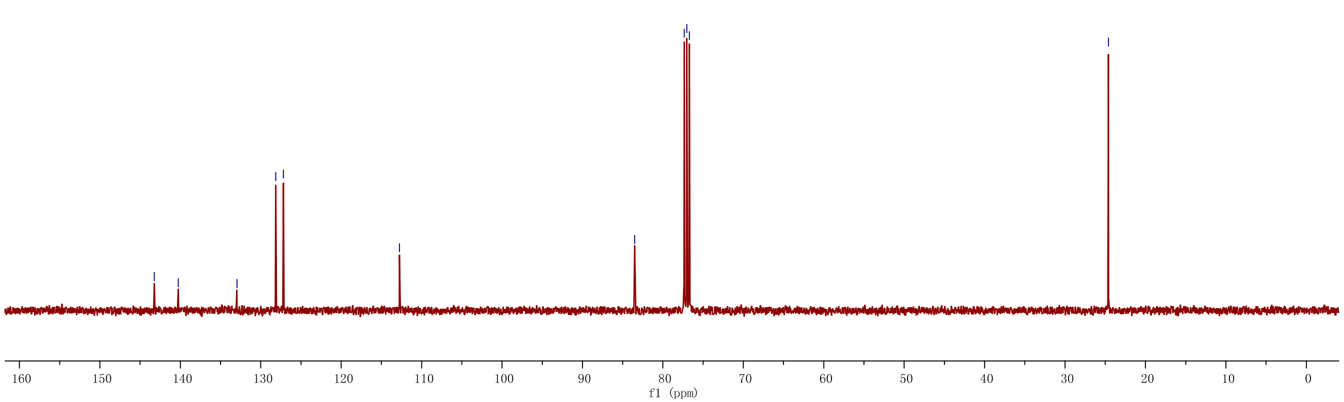
^{1}H NMR (400 MHz, $CDCl_3$) **(3b)**



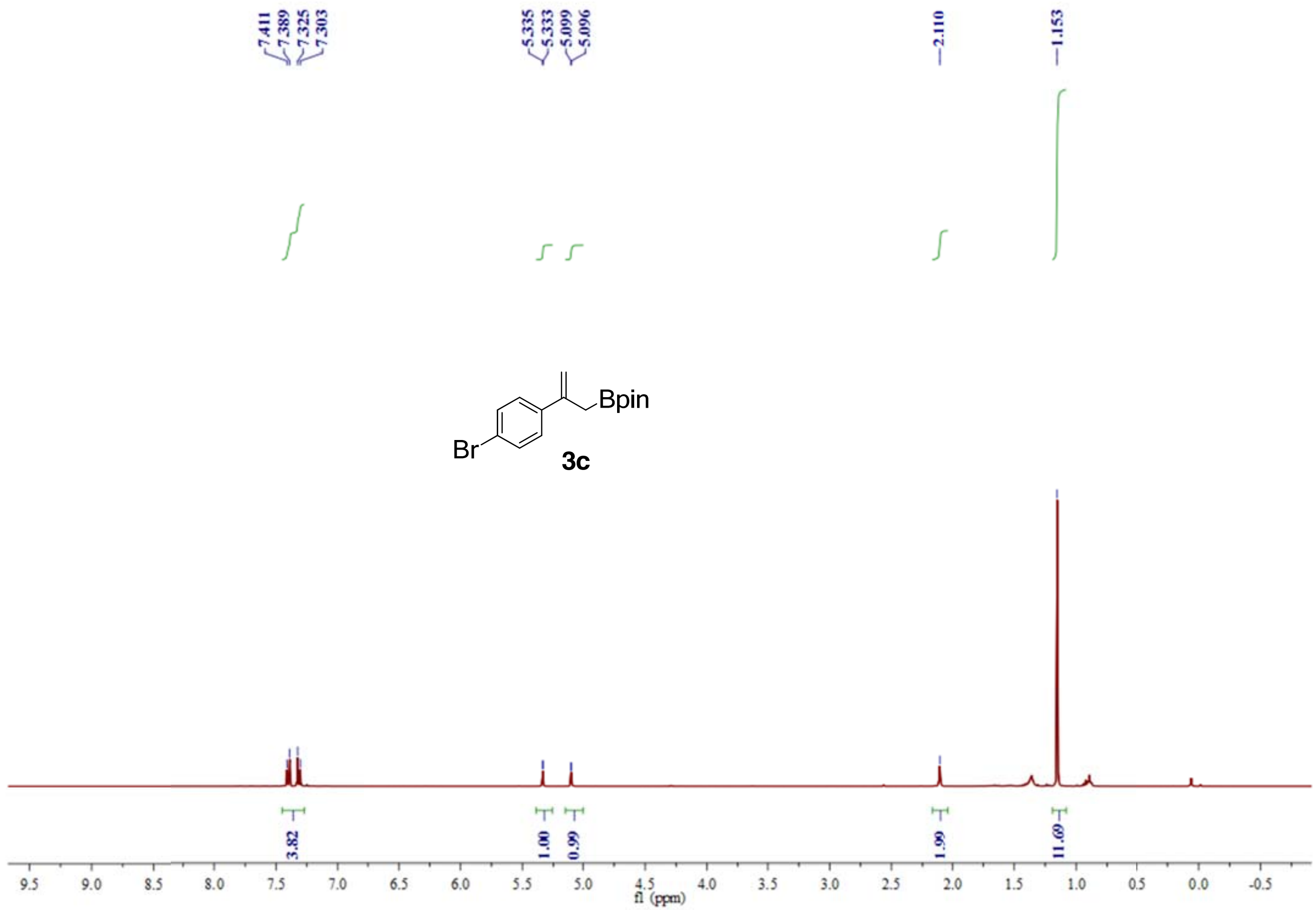
^{13}C NMR (101 MHz, $CDCl_3$) **(3b)**



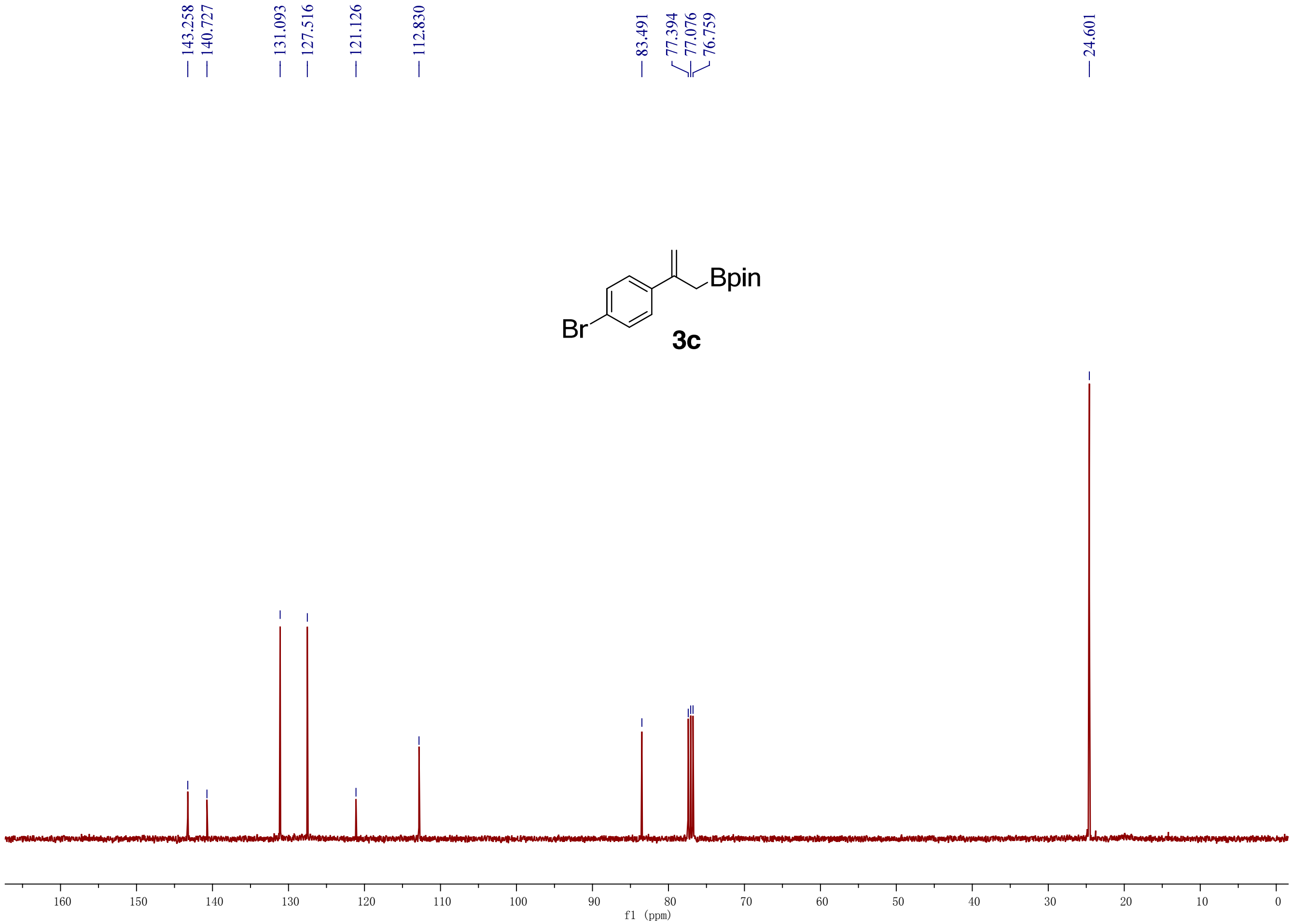
3b



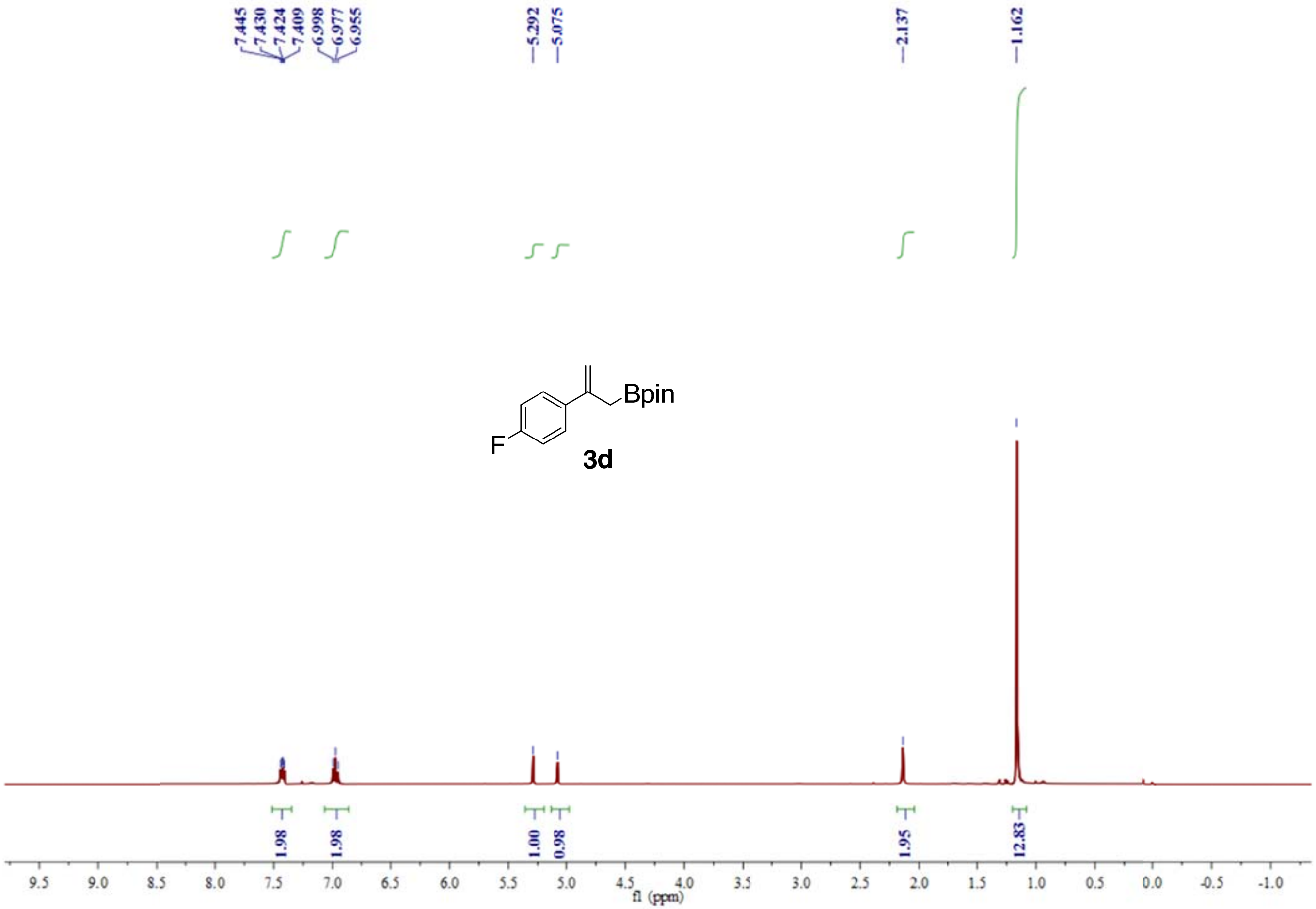
^{1}H NMR (400 MHz, $CDCl_3$) **(3c)**



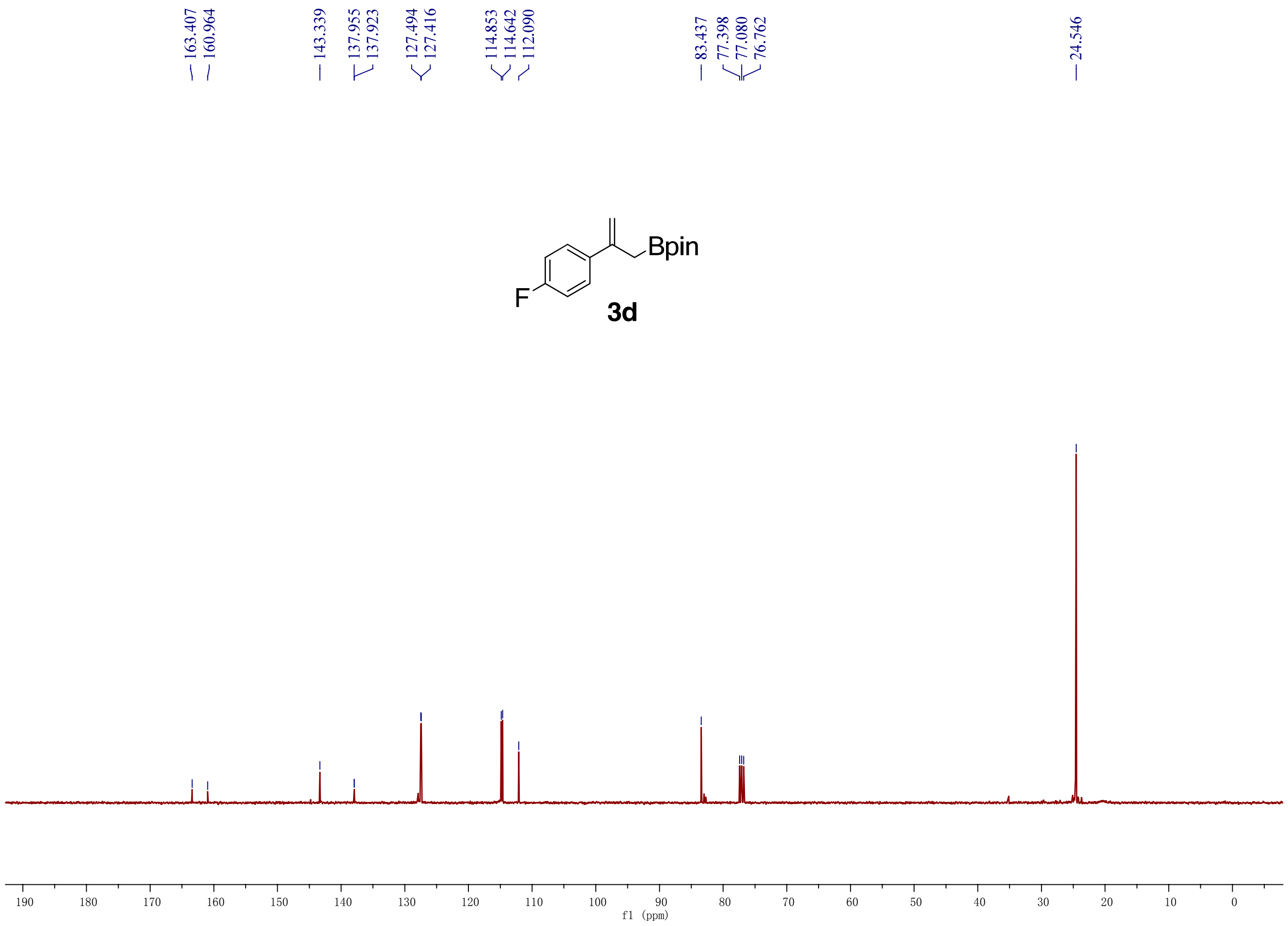
^{13}C NMR (101 MHz, $CDCl_3$) **(3c)**



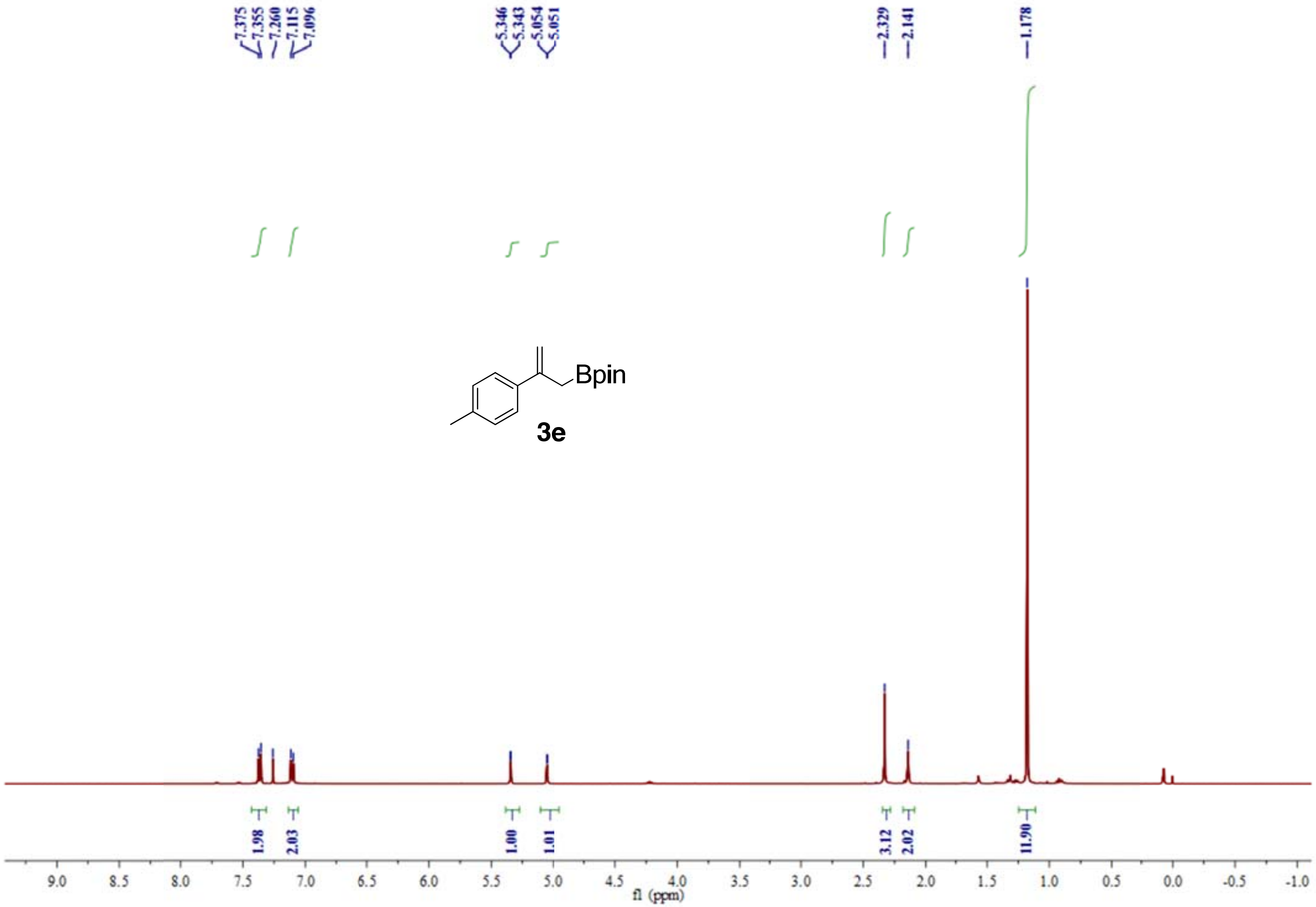
^{1}H NMR (400 MHz, $CDCl_3$) **(3d)**



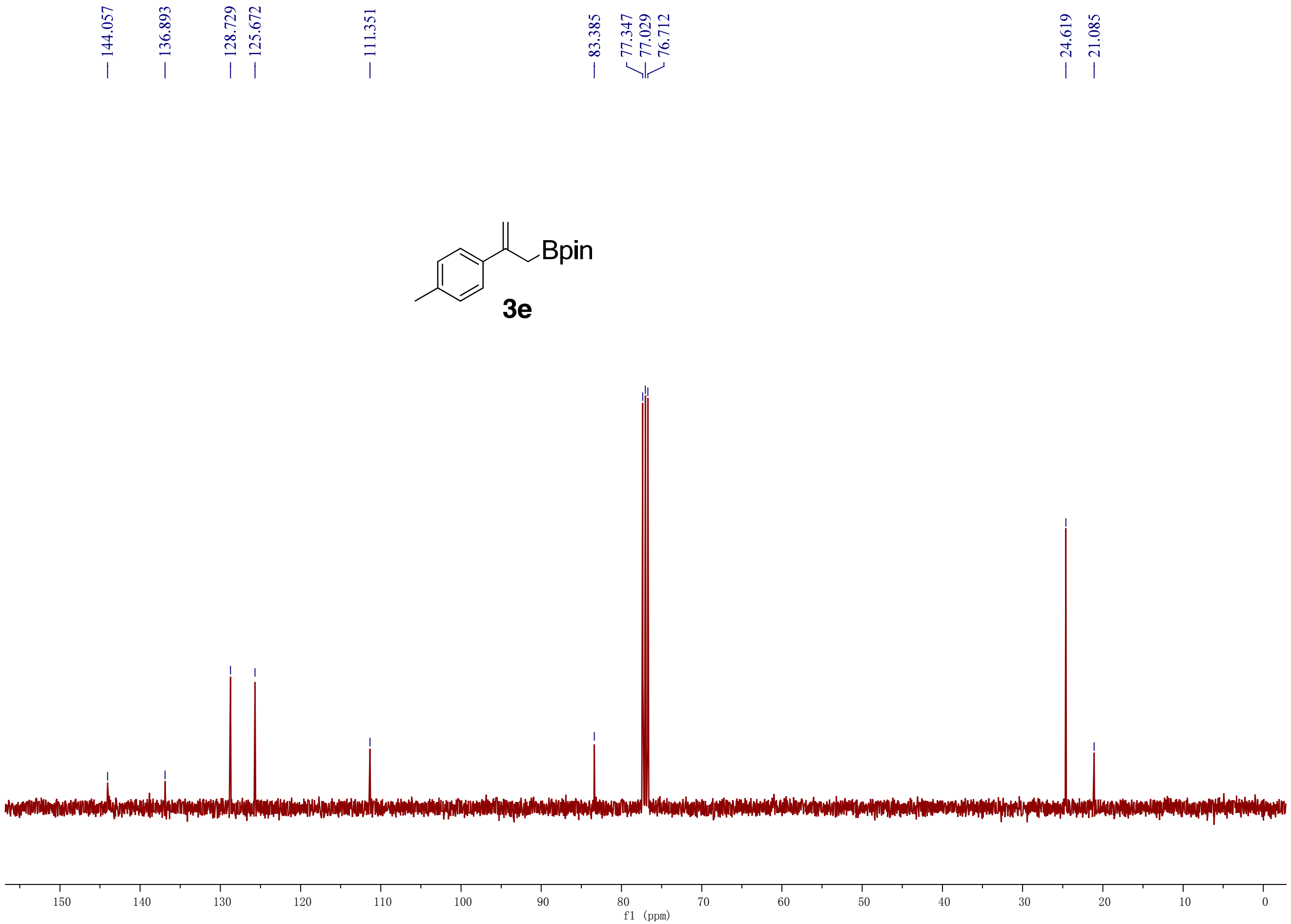
^{13}C NMR (101 MHz, $CDCl_3$) **(3d)**



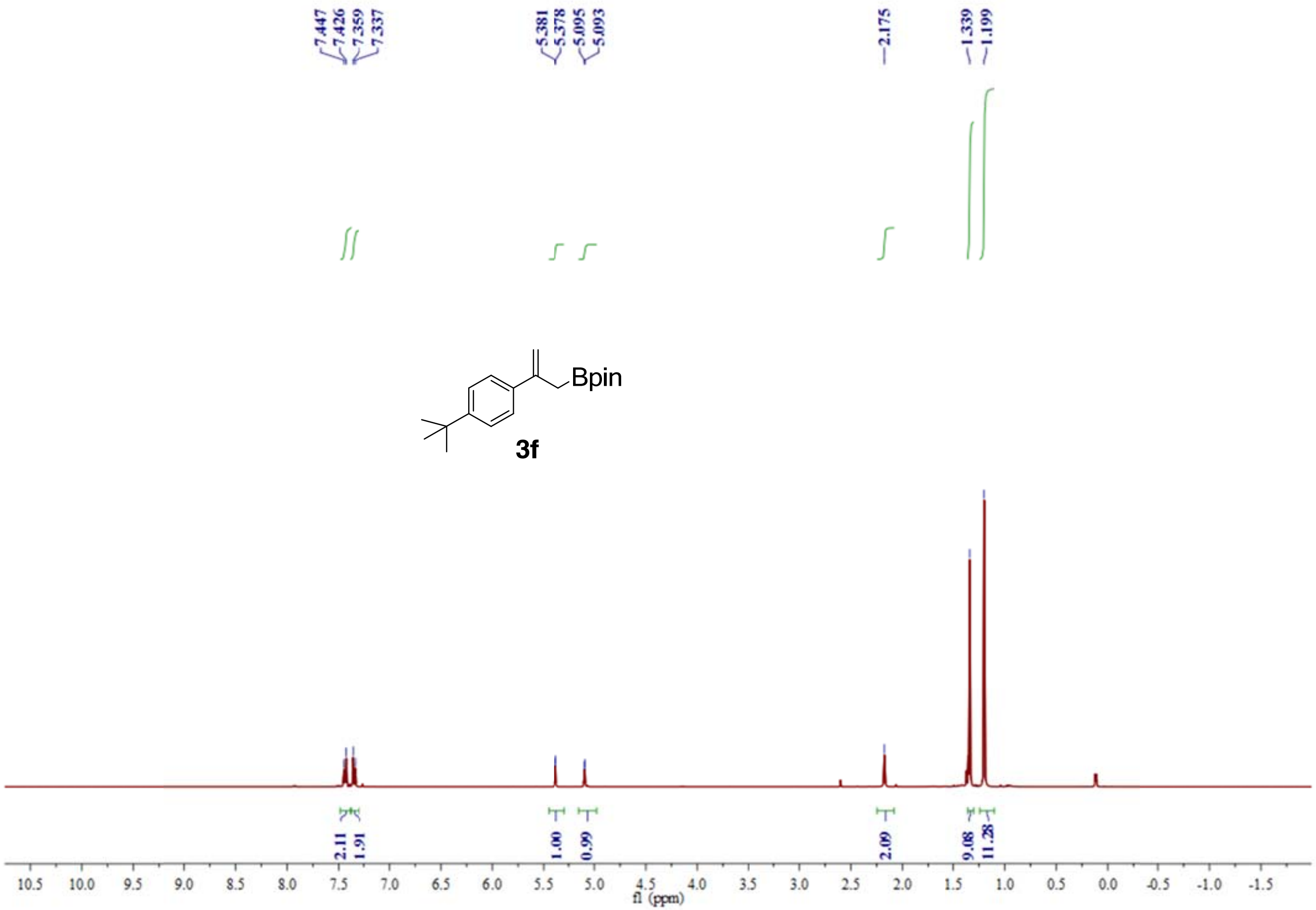
^{1}H NMR (400 MHz, $CDCl_3$) **(3e)**



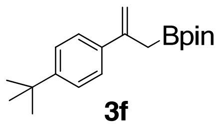
^{13}C NMR (101 MHz, $CDCl_3$) **(3e)**



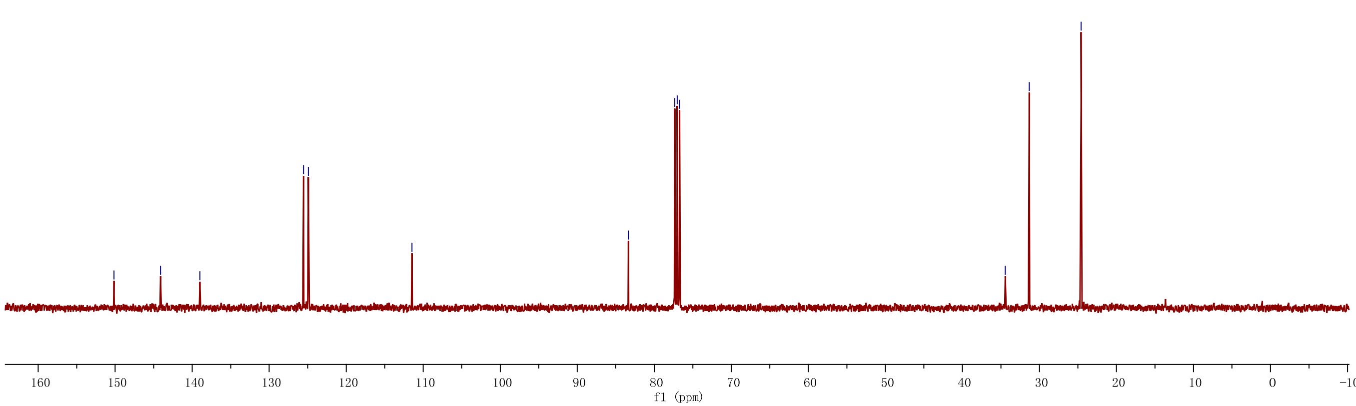
[1]H NMR (400 MHz, $CDCl_3$) **(3f)**



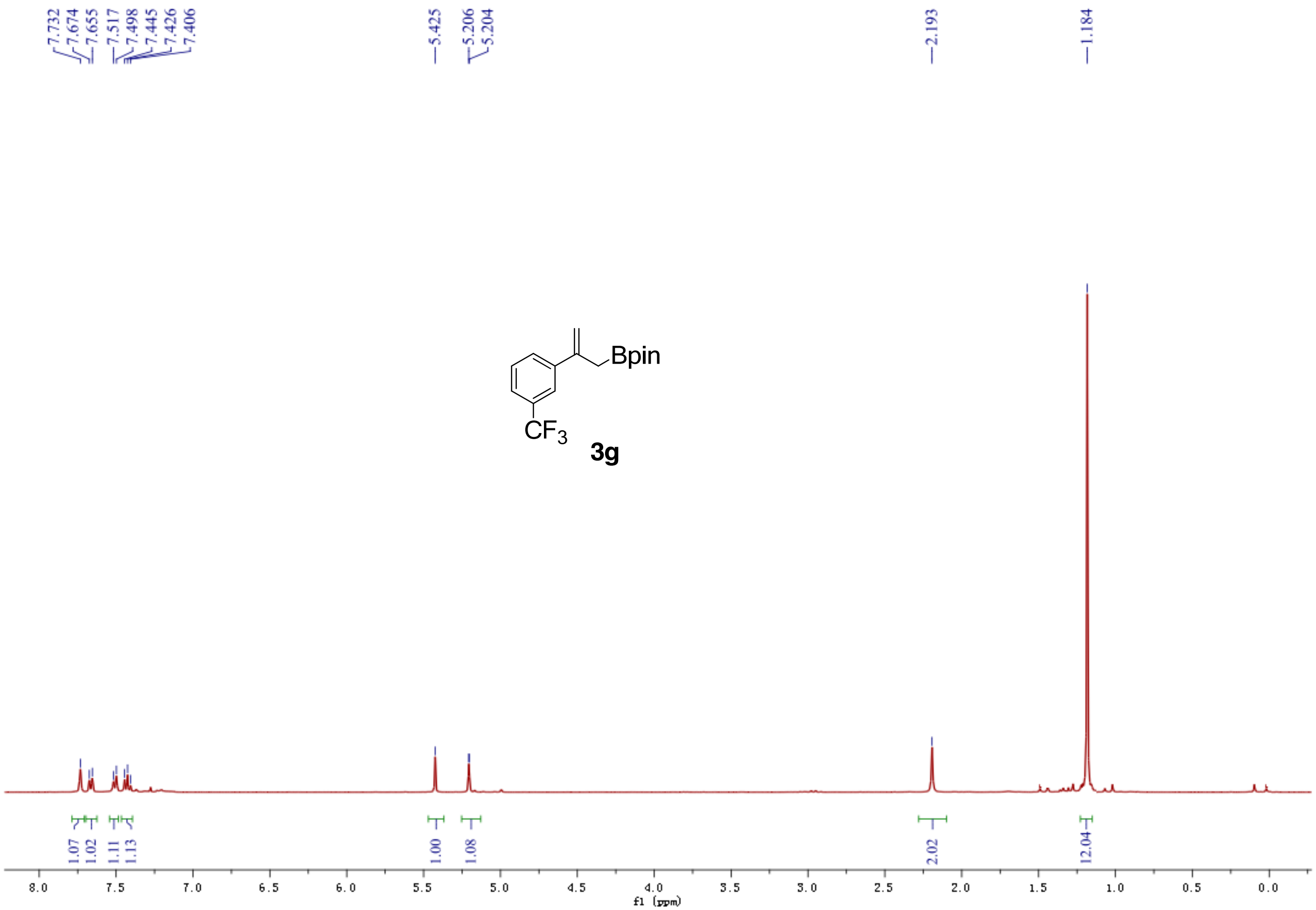
^{13}C NMR (101 MHz, $CDCl_3$) **(3f)**



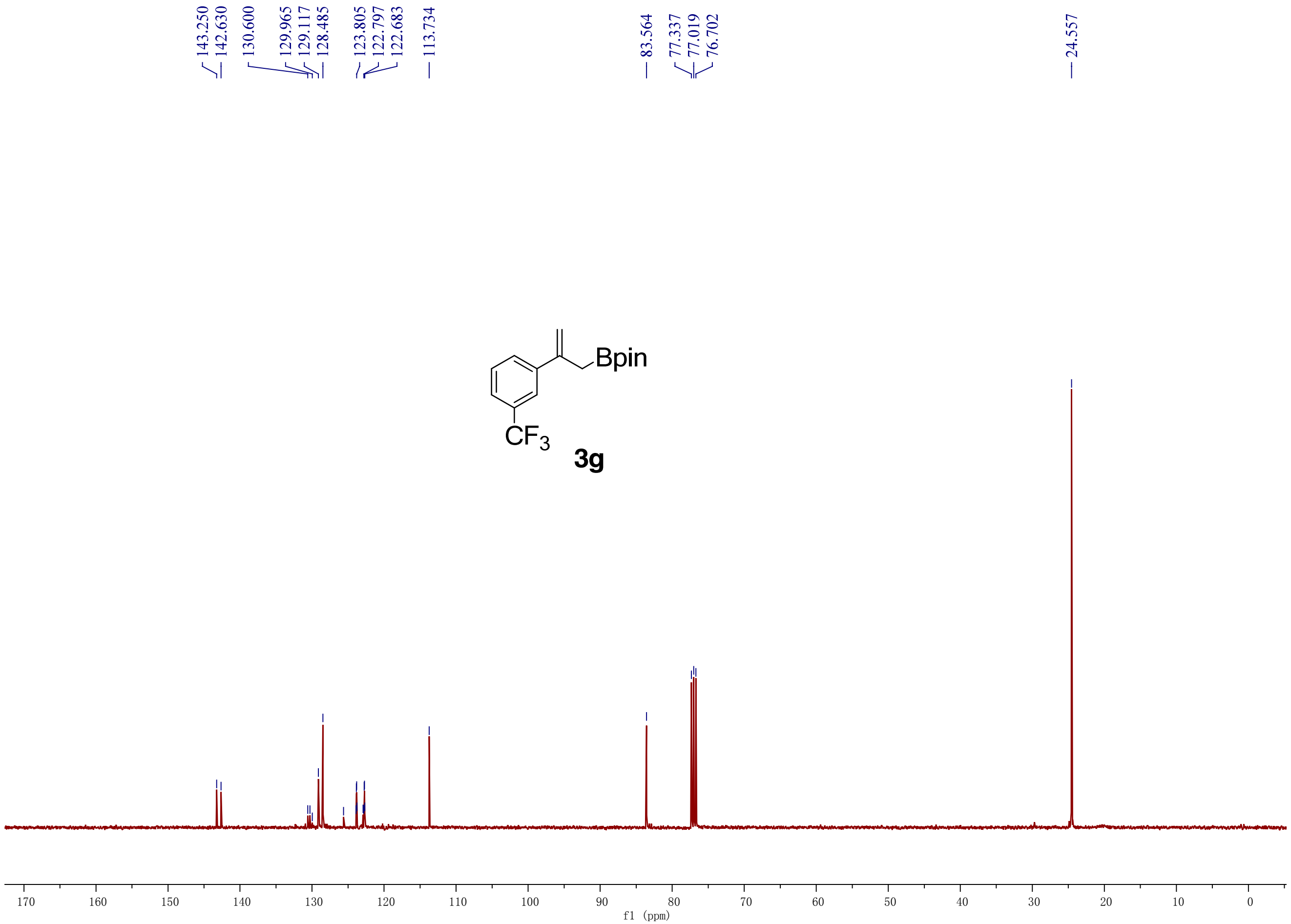
3f



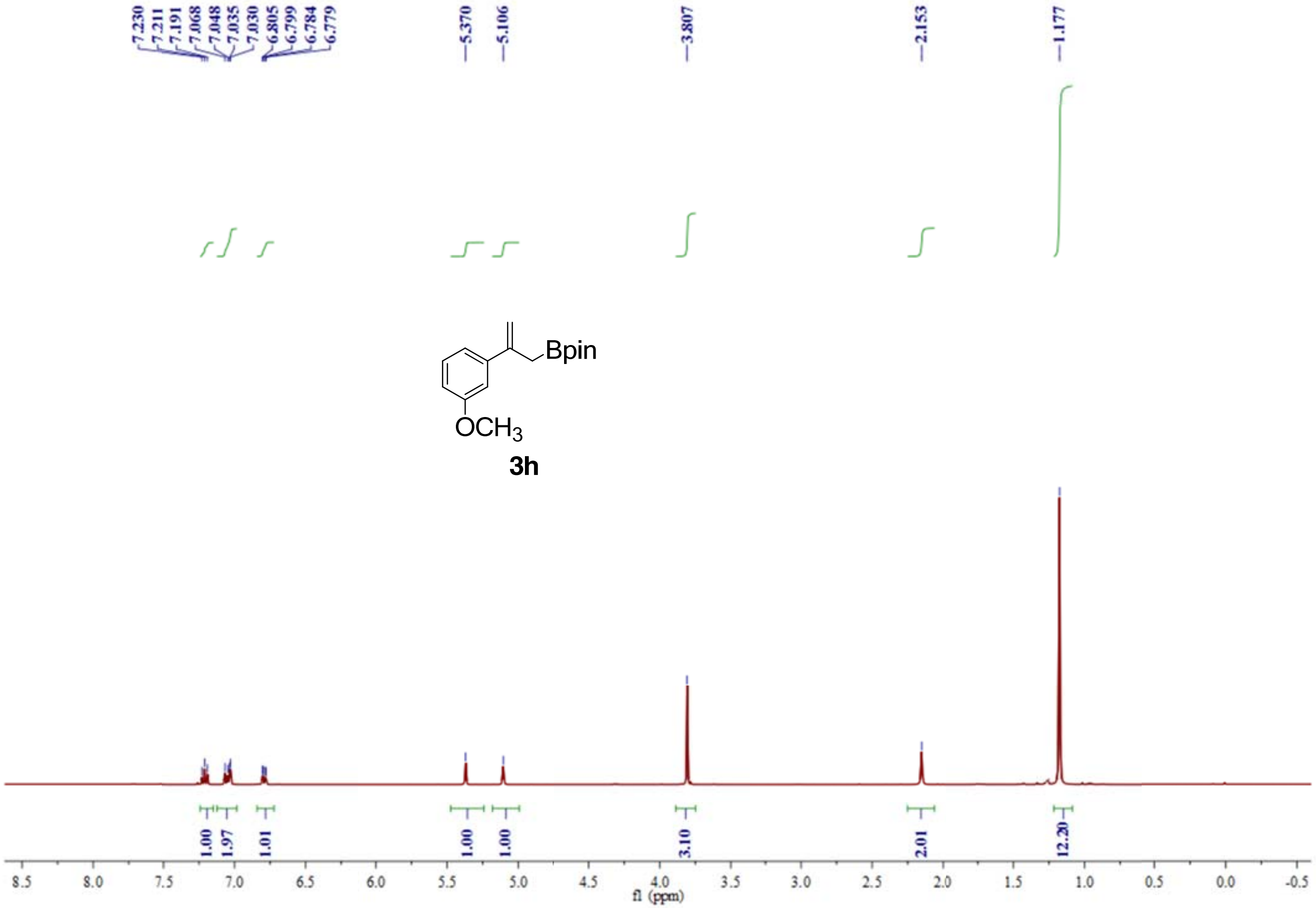
^{1}H NMR (400 MHz, $CDCl_3$) **(3g)**



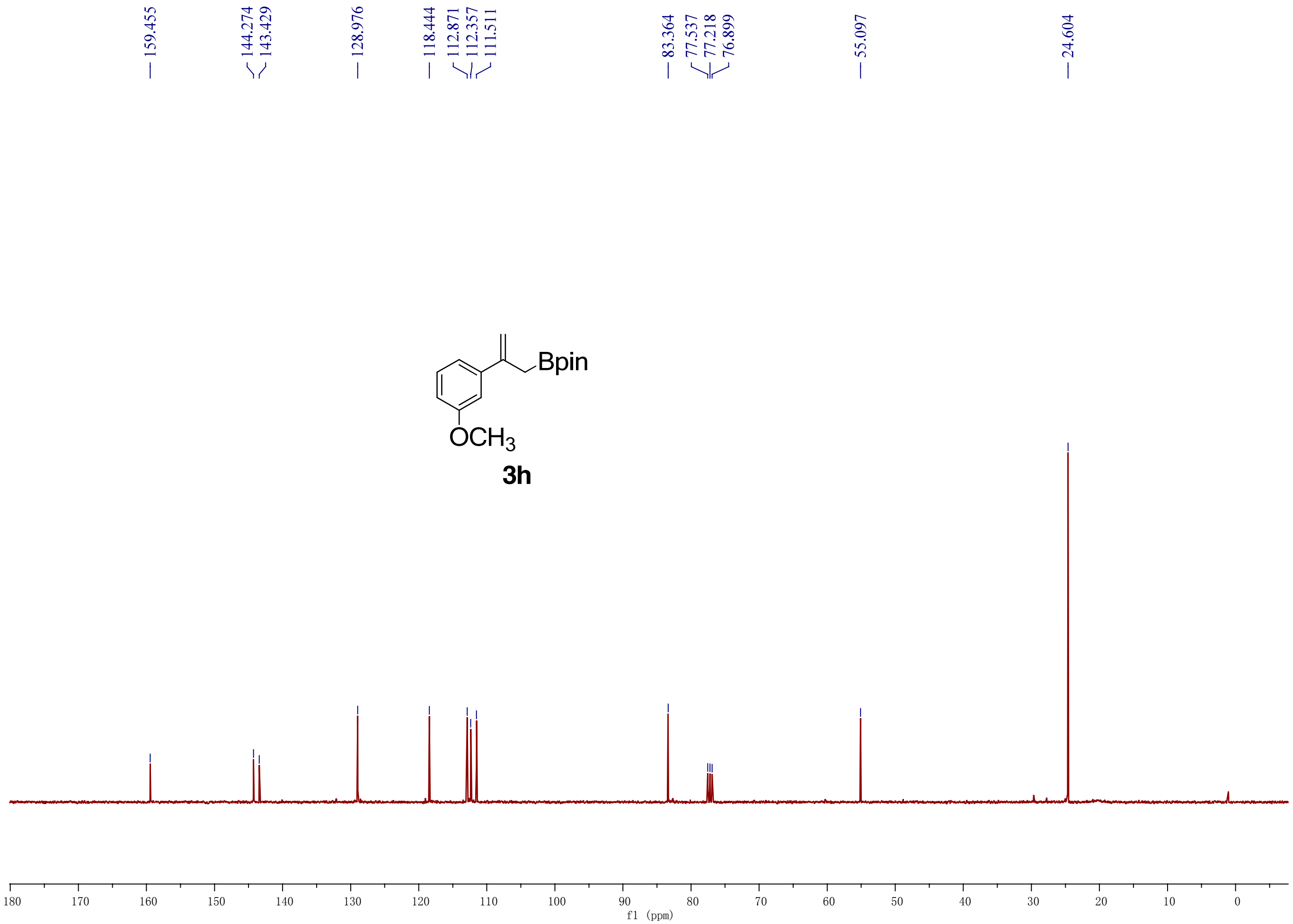
^{13}C NMR (101 MHz, $CDCl_3$) **(3g)**



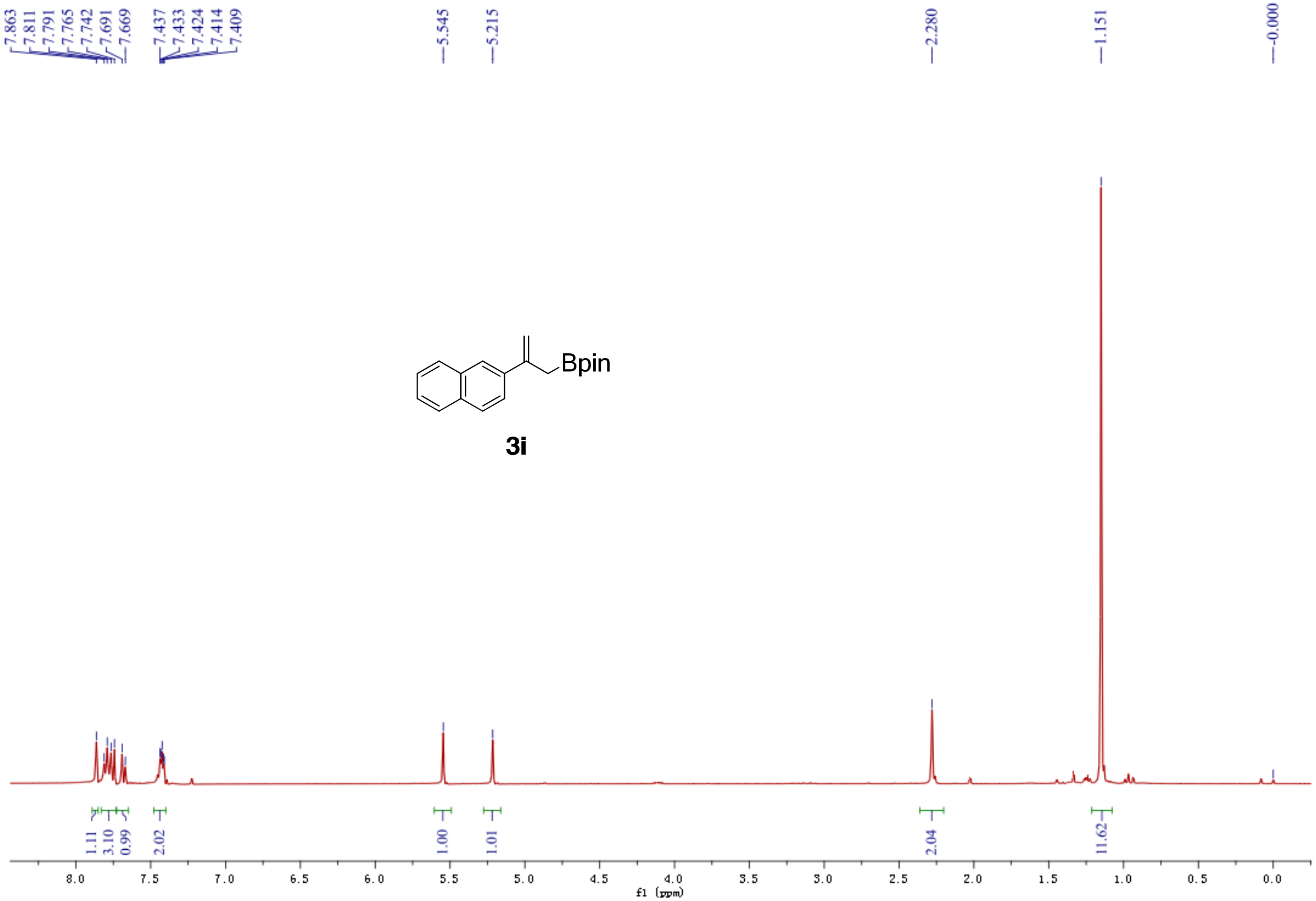
[1]H NMR (400 MHz, $CDCl_3$) **(3h)**



^{13}C NMR (101 MHz, $CDCl_3$) **(3h)**

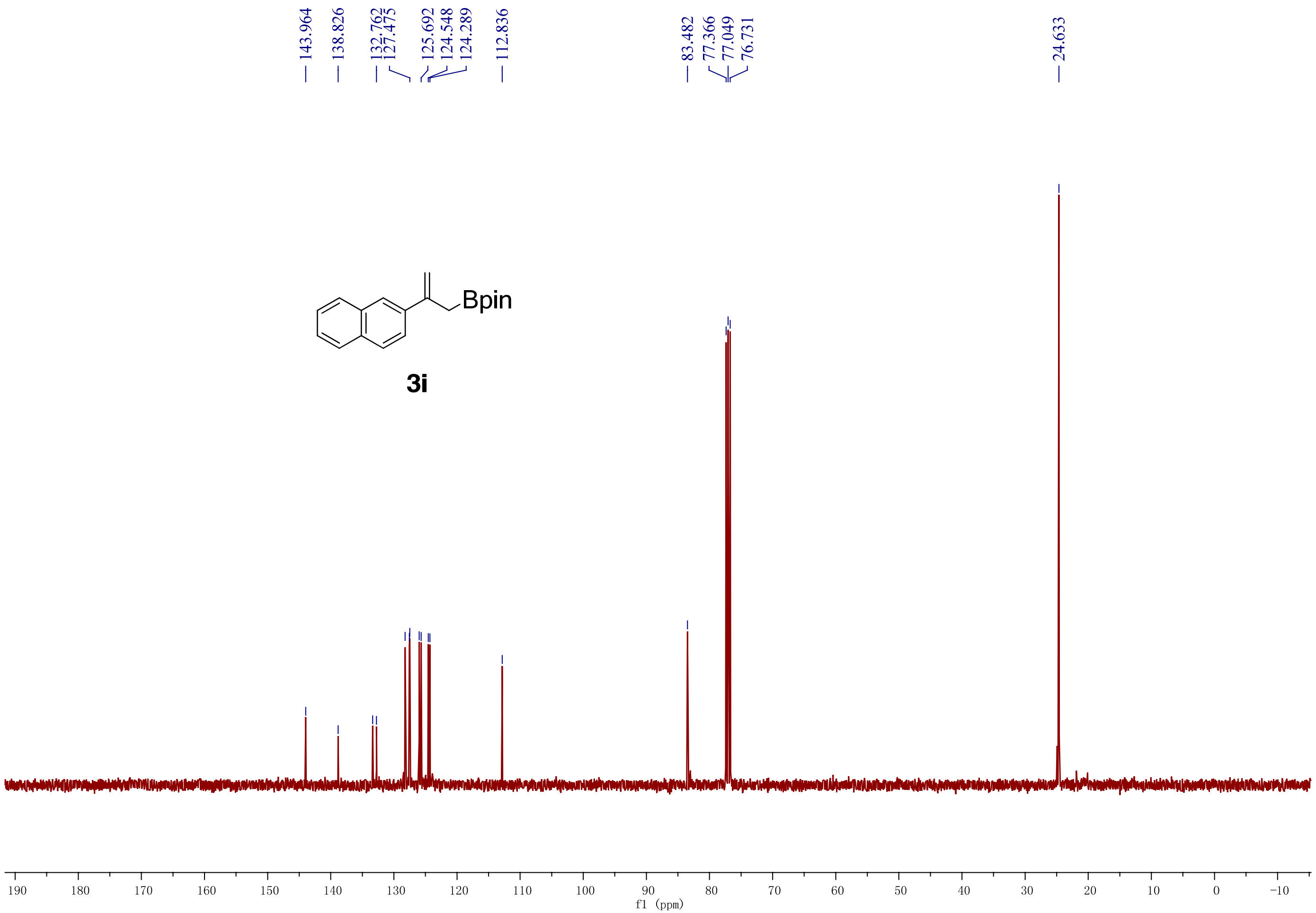


[1]H NMR (400 MHz, $CDCl_3$) **(3i)**

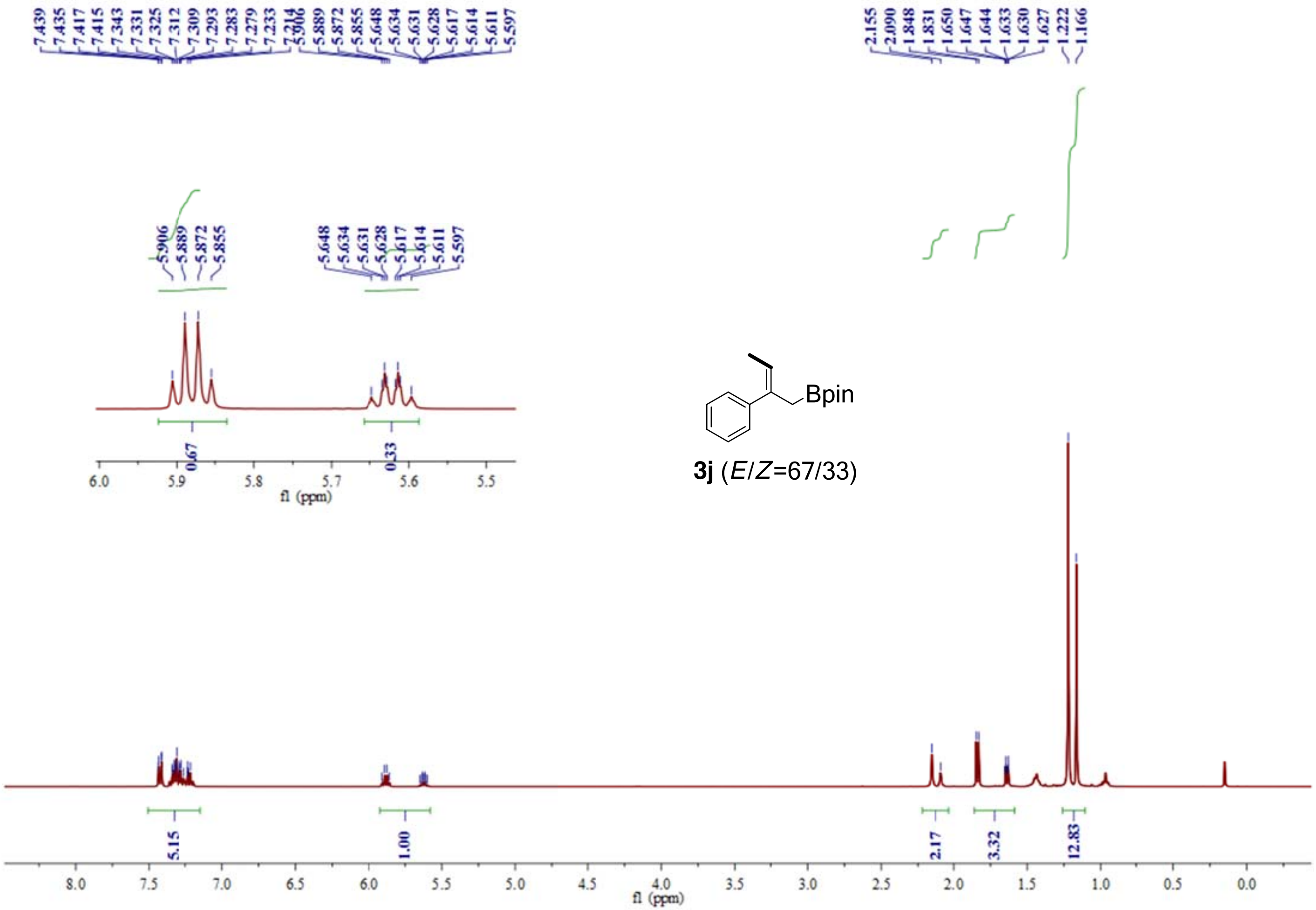


3i

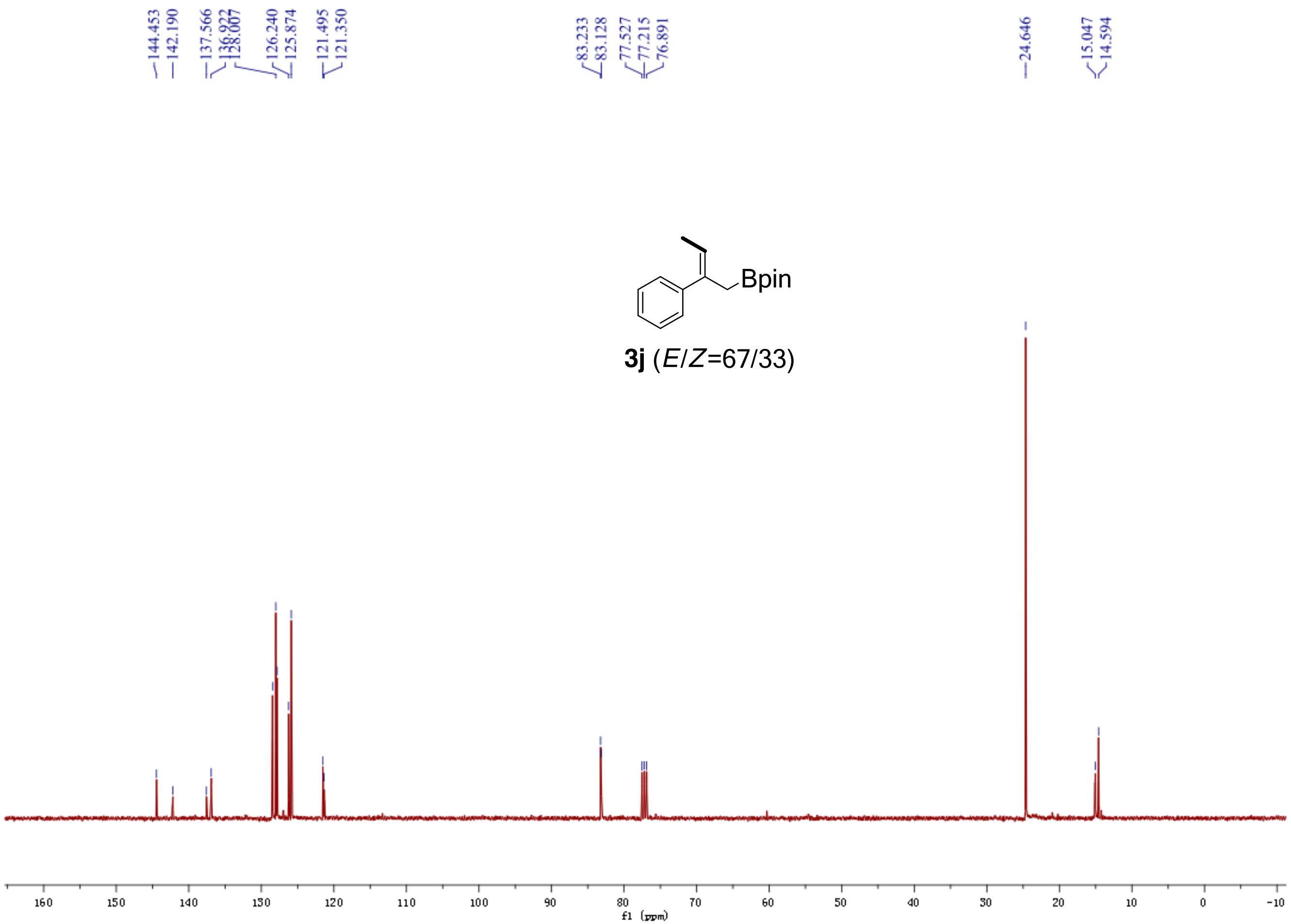
[13]C NMR (101 MHz, $CDCl_3$) **(3i)**



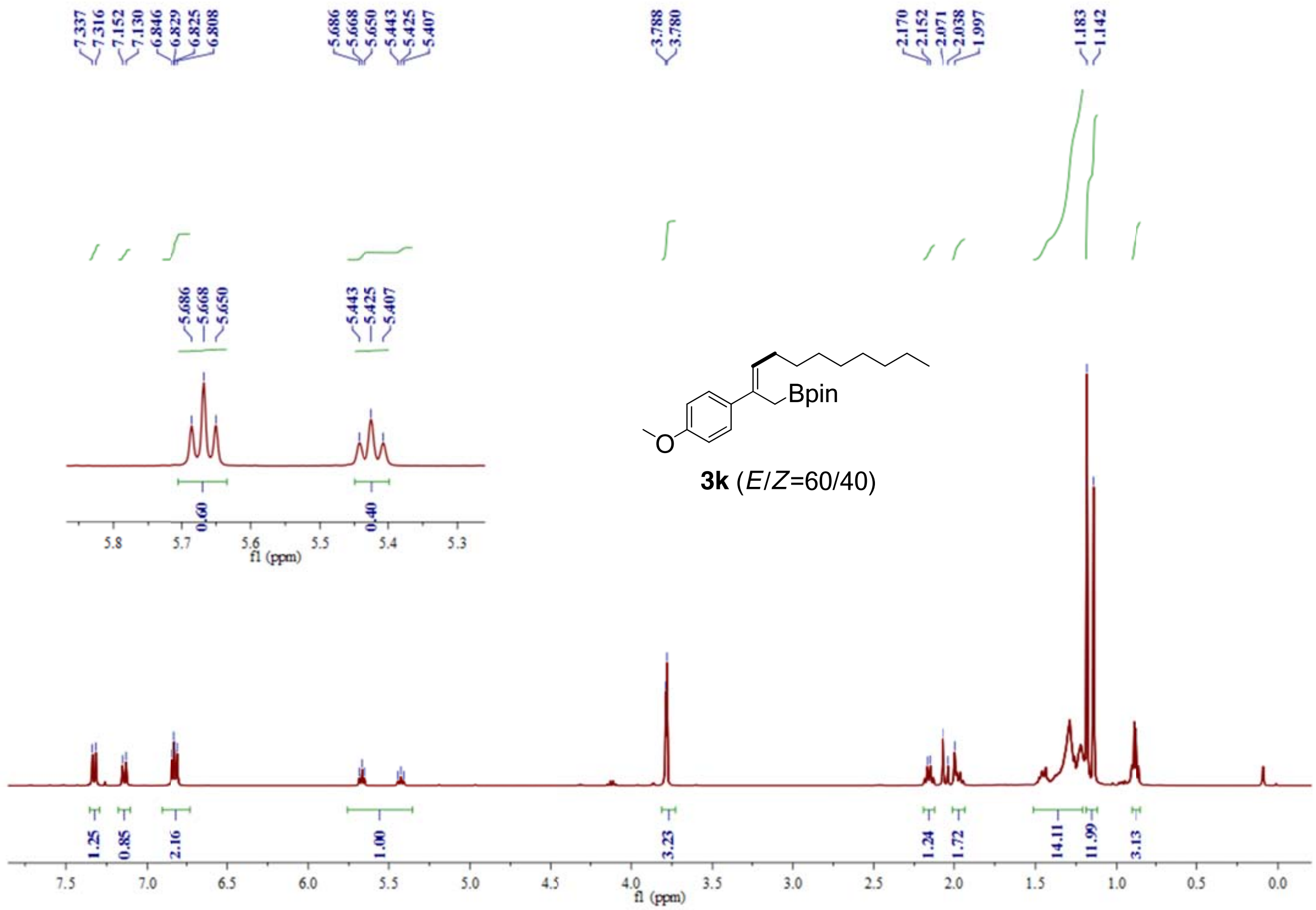
^{1}H NMR (400 MHz, $CDCl_3$) **(3j)**



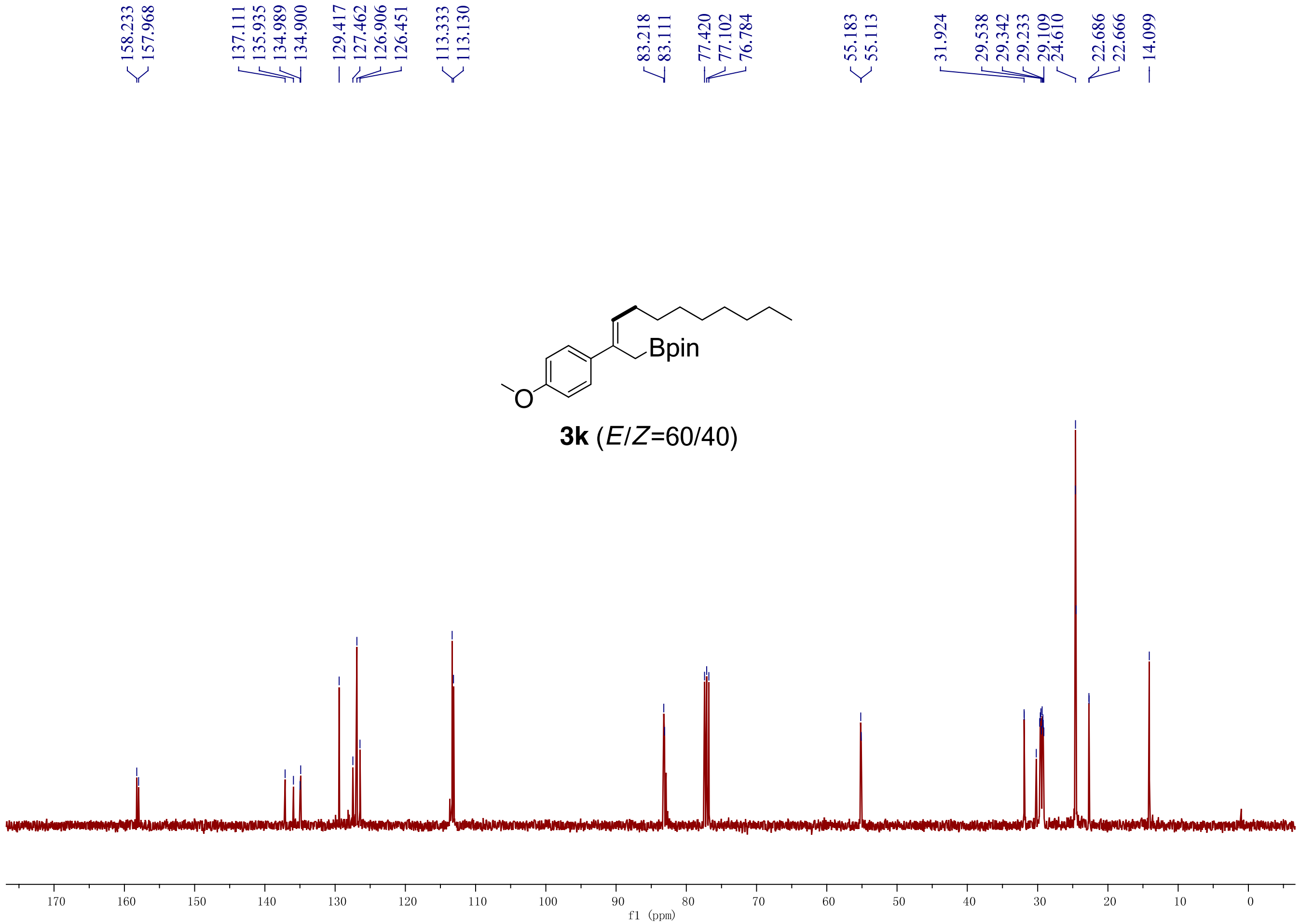
^{13}C NMR (101 MHz, $CDCl_3$) **(3j)**



^{1}H NMR (400 MHz, $CDCl_3$) **(3k)**

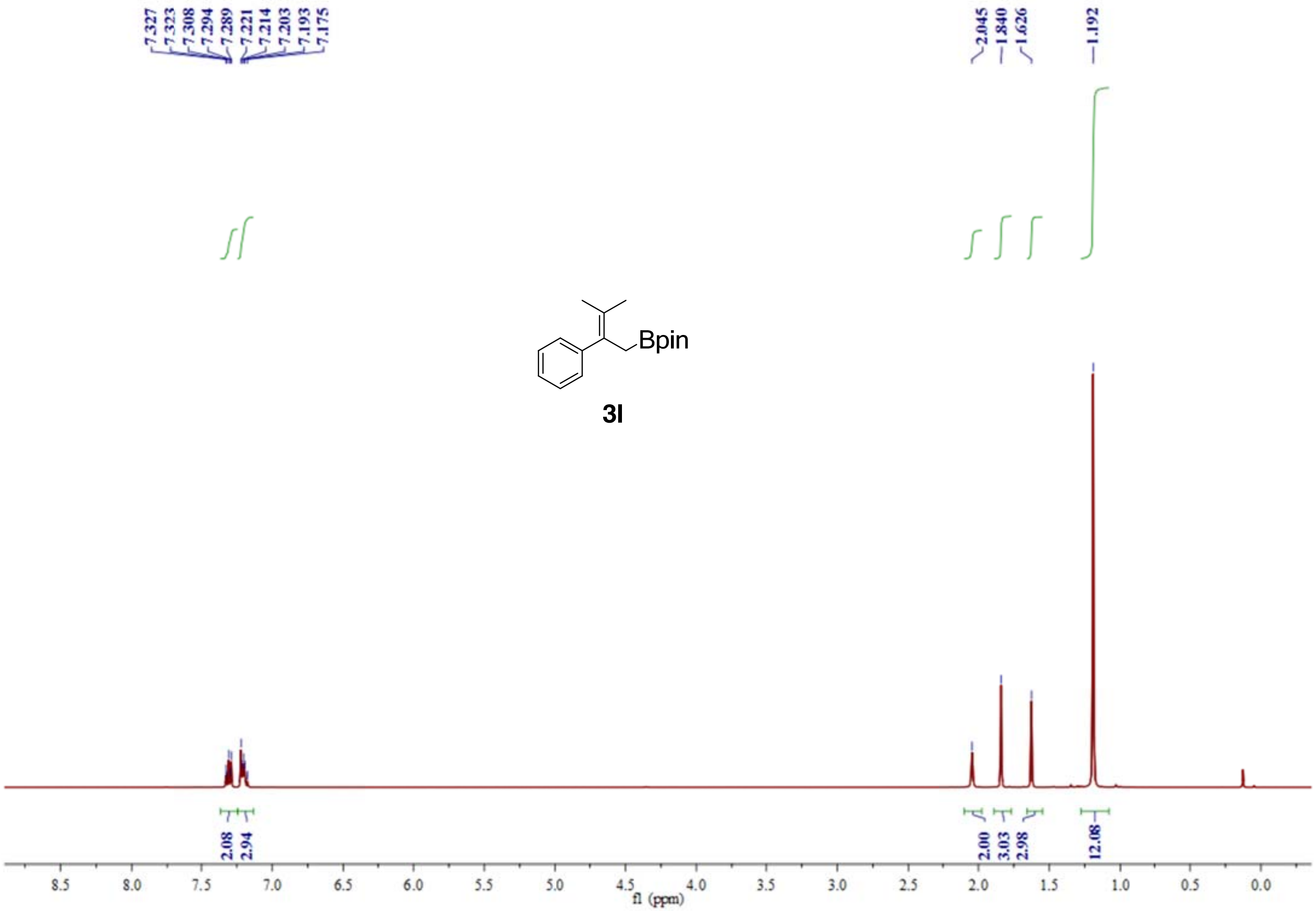


^{13}C NMR (101 MHz, $CDCl_3$) **(3k)**

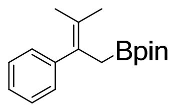


3k (*E*/*Z*=60/40)

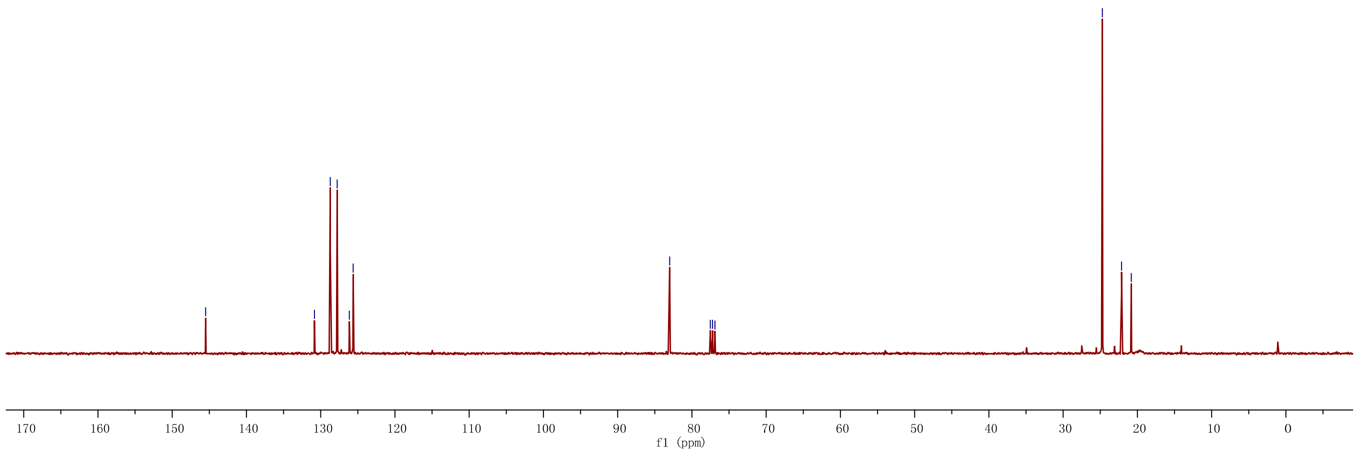
[1]H NMR (400 MHz, $CDCl_3$) **(3l)**



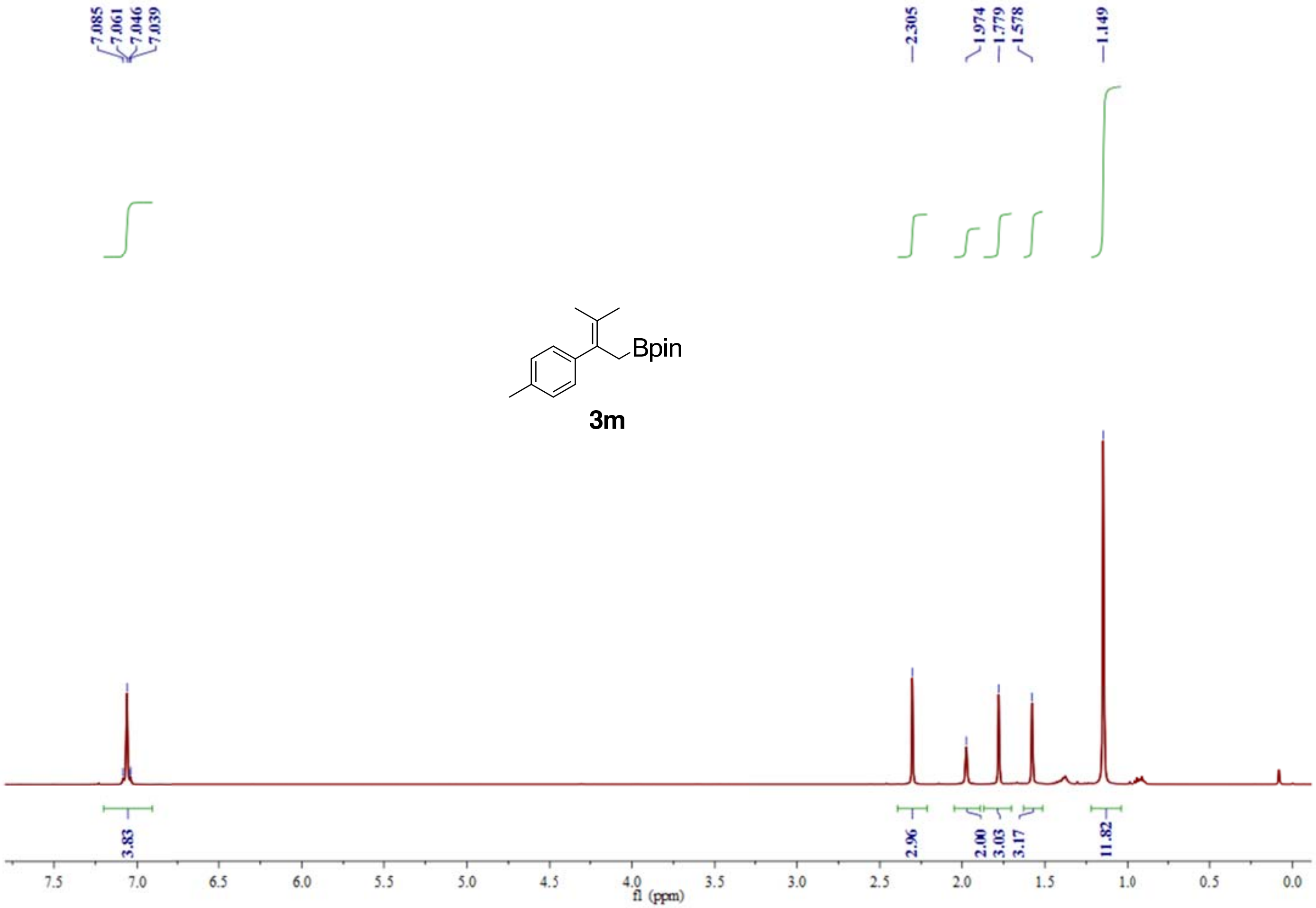
^{13}C NMR (101 MHz, $CDCl_3$) **(3l)**



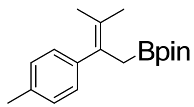
3l



^{1}H NMR (400 MHz, $CDCl_3$) **(3m)**



^{13}C NMR (101 MHz, $CDCl_3$) **(3m)**



3m