Supplementary Information

Trans selective cyclization of alpha-bromocarboxamides and *E*/*Z*-mixed internal olefin catalyzed by a Fe salt

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Table of Contents

1. General information

All reactions were carried out under nitrogen (99.95%) atmosphere. For TLC analyses precoated Kieselgel 60 F254 plates (Merck, 0.25 mm thick) were used; for column chromatography Silica *Flash*® P60 (SiliCycle, 40-63 µm) was used. Visualization was accomplished by UV light (254 nm), ^{1}H and ^{13}C NMR spectra were obtained using a JEOL 500 MHz NMR spectrometer. Chemical shifts for ^{1}H NMR were described in parts per million (chloroform as an internal standard **δ** = 7.26) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (**δ** = 77.16), unless otherwise noted. High resolution mass analyses were obtained using an ACQUITY UPLC/ TOF-MS for EI. Anhydrous solvents were purchased from Kanto Chemical Co., Ltd. Other chemicals were purchased from TCI, Sigma and Wako and used after distillation or from the bottles (solid). Iron chloride was purchased from Sigma Co., Ltd.

Starting Materials

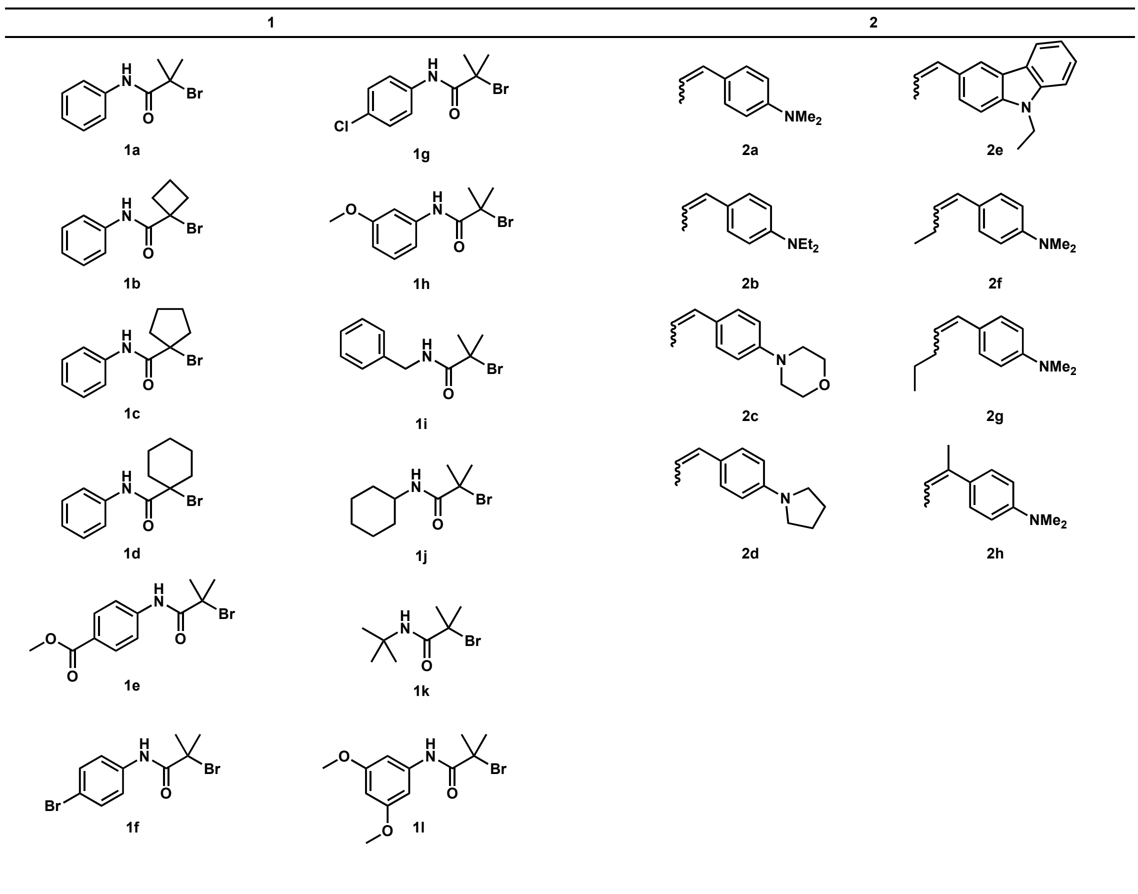


Figure S1. Starting materials.

Reported materials: **1a**, **1i**, **1k**, **1l**, **2a**, **2b**, **2c**, **2d**, **2e**, **2g**

1a, **2a**, **2b**, **2c**, **2d**, **2e**, **2g**: Nakashima, Y.; Matsumoto, J.; Nishikata, T. *ACS Catal*. **2021**, *11*, 11526-11531.

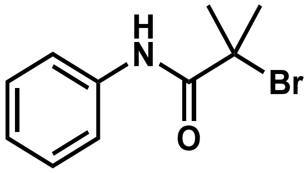
1i: Cavicchioni, G. *Tetrahedron Letters* **1987**, *28*, 2427-2430.

1k: Tomasik, C. A.; Mitra, A.; West, R. *Organometallics* **2009**, *28*, 378-381.

1l: Miwa, N.; Yamane,Y.; Nishikata, T. *Chem. Lett.* **2017**, *46*, 563-565.

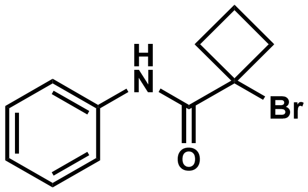
All 2-bromocarbonyls (**1**) were synthesized from reported procedures: Murata, Y.; Takeuchi, K.; Nishikata, T. *Tetrahedron* **2019**, *75*, 2726-2736.

2-bromo-2-methyl-N-phenylpropanamide (**1a**)



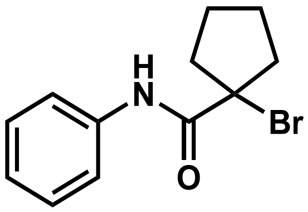
^{1}H NMR ($CDCl_3$) δ: 2.06 (s, 6H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 8.46 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 32.7, 63.3, 120.0, 125.0, 129.2, 137.5, 170.0

1-bromo-N-phenylcyclobutane-1-carboxamide (**1b**)



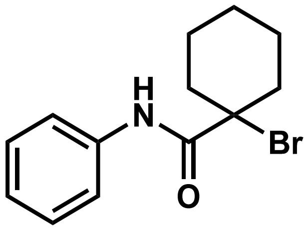
IR (neat) ν 3287, 2991, 1655, 1438, 1251, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.01-2.09 (m, 1H), 2.30-2.38 (m, 1H), 2.64-2.70 (m, 2H), 3.09-3.15 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.99 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 17.2, 38.0, 60.7, 119.9, 124.9, 129.1, 137.5, 169.0; HRMS (EI-MS) calcd. for $C_{11}H_{13}BrNO$ ($M+H^+$): 254.0181; found 254.0181

1-bromo-N-phenylcyclopentane-1-carboxamide (**1c**)



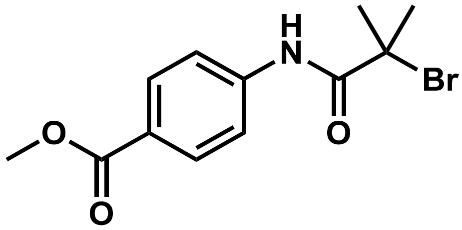
IR (neat) ν 3371, 2875, 1668, 1529, 1436, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.90-1.97 (m, 2H), 2.00-2.07 (m, 2H), 2.32-2.36 (m, 2H), 2.52-2.58 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 8.52 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 24.0, 42.7, 74.4, 120.0, 124.9, 129.1, 137.5, 169.1; HRMS (EI-MS) calcd. for $C_{12}H_{15}BrNO$ ($M+H^+$): 268.0337; found 268.0337

1-bromo-N-phenylcyclohexane-1-carboxamide (**1d**)



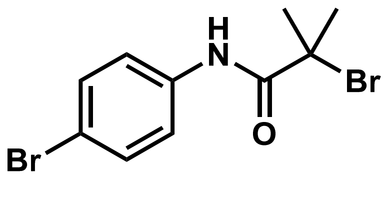
IR (neat) ν 3311, 2934, 1649, 1536, 1441, 1119, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.32-1.41 (m, 1H), 1.69-1.85 (m, 5H), 2.14-2.25 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 8.37 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 22.9, 24.8, 31.0, 38.2, 120.1, 124.9, 129.2, 137.6, 169.8; HRMS (EI-MS) calcd. for $C_{13}H_{17}BrNO$ ($M+H^+$): 282.0494; found 282.0494

methyl 4-(2-bromo-2-methylpropanamido)benzoate (**1e**)



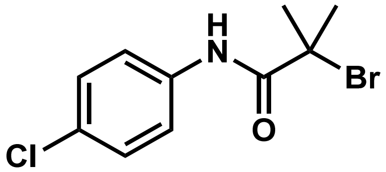
IR (neat) ν 3341, 2948, 1684, 1524, 1170, 1100, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.06 (s, 6H), 3.91 (s, 3H), 7.64 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 8.59 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 32.6, 52.2, 62.9, 119.1, 126.3, 130.9, 141.6, 166.6, 170.3; HRMS (EI-MS) calcd. for $C_{12}H_{15}BrNO_3$ ($M+H^+$): 300.0235; found 300.0236

4-bromophenyl-2-bromo-2-methylpropanamide (**1f**)



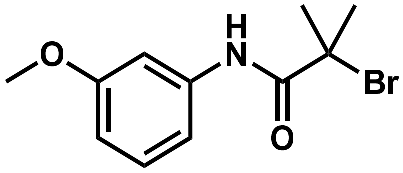
IR (neat) ν 3310, 2983, 1659, 1485, 1109, 819 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.04 (s, 6H), 7.43-7.48 (m, 4H), 8.44 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 32.6, 63.1, 117.7, 121.6, 132.1, 136.6, 170.1; HRMS (EI-MS) calcd. for $C_{10}H_{12}Br_2NO$ ($M+H^+$): 319.9286; found 319.9287

4-chlorophenyl-2-bromo-2-methylpropanamide (**1g**)



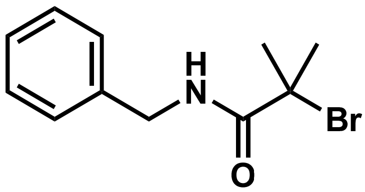
IR (neat) ν 3328, 2930, 1637, 1527, 1106, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.04 (s, 6H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 8.45 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 32.6, 63.1, 121.3, 129.2, 130.0, 136.0, 170.1; HRMS (EI-MS) calcd. for $C_{10}H_{12}BrClNO$ ($M+H^+$): 275.9791; found 275.9792

2-bromo-N-(3-methoxyphenyl)-2-methylpropanamide (**1h**)



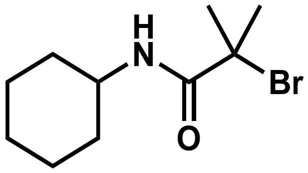
IR (neat) ν 3290, 2931, 1655, 1447, 1276, 1032, 788 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.05 (s, 6H), 3.82 (s, 3H), 6.70 (dd, *J* = 2.5 and 8.4 Hz, 1H), 7.00 (dd, *J* = 2.0, and 8.0 Hz, 1H), 7.24 (t, *J* = 8.2, 1H), 7.32 (t, *J* = 2.3 Hz, 1H), 8.44 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 32.6, 55.4, 63.2, 105.4, 111.0, 112.0, 129.8, 138.7, 160.3, 170.1; HRMS (EI-MS) calcd. for $C_{11}H_{15}BrNO_2$ ($M+H^+$): 272.0286; found 272.0286

N-benzyl-2-bromo-2-methylpropanamide (**1i**)



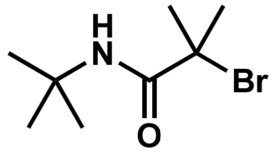
^1H NMR ($CDCl_3$) δ: 2.00 (s, 6H), 4.46 (d, *J* = 5.7 Hz, 2H), 7.00 (s, 1H), 7.27-7.32 (m, 3H), 7.34-7.38 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 32.7, 44.5, 63.1, 127.6, 127.7, 128.9, 137.8, 172.0

2-bromo-N-cyclohexyl-2-methylpropanamide (**1j**)



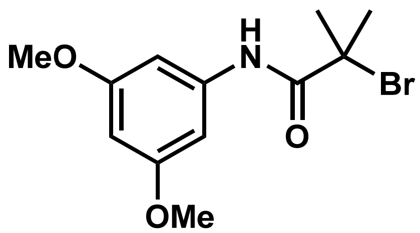
IR (neat) ν 3329, 2930, 2850, 1636, 1528, 1105, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.17-1.24 (m, 3H), 1.34-1.42 (m, 2H), 1.58-1.64 (m, 1H), 1.69-1.74 (m, 2H), 1.89-1.93 (m, 2H), 1.94 (s, 6H), 3.66-3.74 (m, 1H), 6.60 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 24.7, 25.6, 32.7, 32.7, 49.1, 63.9, 171.1; HRMS (EI-MS) calcd. for $C_{10}H_{19}BrNO$ ($M+H^+$): 248.0650; found 248.0652

2-bromo-N-(tert-butyl)-2-methylpropanamide (**1k**)



[1]H NMR ($CDCl_3$) δ: 1.37 (s, 9H), 1.92 (s, 6H), 6.57 (s, 1H). [13]C NMR ($CDCl_3$) δ: 28.4, 32.6, 51.7, 64.0, 171.3

2-bromo-N-(3,5-dimethoxyphenyl)-2-methylpropanamide (**1l**)

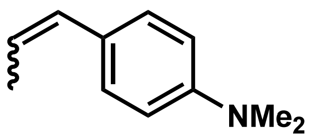


[1]H NMR ($CDCl_3$) δ: 2.04 (s, 6H), 3.79 (s, 6H), 6.27 (t, J = 2.2 Hz, 1H), 6.78 (d, J = 2.2 Hz, 2H), 8.40 (s, 1H). [13]C NMR ($CDCl_3$) δ: 32.6, 55.5, 3.2, 97.6, 98.1, 139.2, 161.2, 170.1

Styrene derivatives (**2**) were synthesized by Wittig reactions.

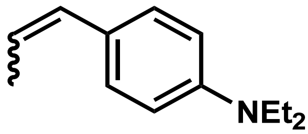
^{t}BuOK (2 equiv) was added to THF solution of ethyltriphenylphosphonium bromide (2 equiv) at 0 ºC and the resulting solution was stirred for several hours. After stirring, aldehyde (1 equiv) was added to the mixture. The resulting mixture vigorously stirred overnight at room temperature. After this time, the contents of the flask were washed with brine, and extracted with EtOAc. The combined organic layer was dried over $MgSO_4$ and evaporated. The crude residue was purified by flash chromatography, eluting hexane-EtOAc to afford the product **2**.

N,N-dimethyl-4-(prop-1-en-1-yl)aniline (*E* : *Z* = 23 : 77) (**2a**)



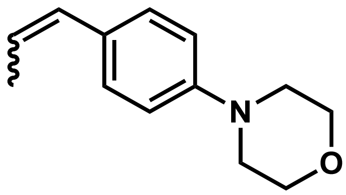
[1]H NMR ($CDCl_3$) δ: 1.85 (dd, J = 1.6 and 6.7 Hz, 0.6H), 1.92 (dd, J = 1.7 and 7.1 Hz, 2.4H), 2.94 (s, 1.2H), 2.96 (s, 4.8H), 5.62 (dq, J = 7.1 and 11.4 Hz, 0.8H), 6.03 (dq, J = 6.6 and 15.6 Hz, 0.2H), 6.30-6.36 (m, 1H), 6.67 (d, J = 8.9 Hz, 0.4H), 6.72 (d, J = 9.0 Hz, 1.6H), 7.21-7.25 (m, 2H). [13]C NMR ($CDCl_3$) δ: 14.8, 18.5, 40.5, 40.5, 112.1, 112.6, 121.2, 123.3, 126.2, 126.7, 126.7, 129.7, 129.8, 130.8, 149.1, 149.6

N,N-diethyl-4-(prop-1-en-1-yl)aniline (*E* : *Z* = 22 : 78) (**2b**)



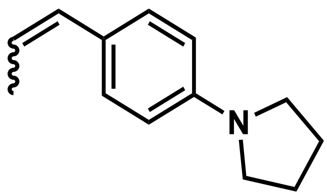
[1]H NMR ($CDCl_3$) δ: 1.17 (t, *J* = 7.0 Hz, 6H), 1.84 (dd, *J* = 1.8 and 6.6 Hz, 0.7H), 1.92 (d, *J* = 1.7 and 7.1 Hz, 2.3H), 3.36 (q, *J* = 7.0 Hz, 4H), 5.58 (dq, *J* = 7.2 and 11.6 Hz, 0.8H), 5.99 (dq, *J* = 6.6 and 15.6 Hz, 0.2H), 6.29-6.33 (m, 1H), 6.61 (d, *J* = 8.0 Hz, 0.5H), 6.66 (d, *J* = 8.5 Hz, 1.5H), 7.19-7.22 (m, 2H). [13]C NMR ($CDCl_3$) δ: 12.7, 14.8, 18.5, 44.4, 111.4, 111.9, 120.7, 122.8, 125.2, 125.7, 126.9, 129.7, 130.1, 130.8, 146.3, 146.8

4-(4-(prop-1-en-1-yl)phenyl)morpholine (*E* : *Z* = 21 : 79) (**2c**)



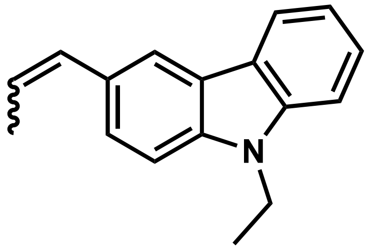
[1]H NMR ($CDCl_3$) δ: 1.85 (dd, *J* = 1.6 and 6.5 Hz, 0.6H), 1.90 (dd, *J* = 1.8 and 7.0 Hz, 2.4H), 3.15 (t, *J* = 4.8 Hz, 1H), 3.16 (t, *J* = 4.9 Hz, 3H), 3.84-3.87 (m, 4H), 5.67 (dq, *J* = 7.2 and 11.6 Hz, 0.7H), 6.09 (dq, *J* = 6.6 and 15.7Hz, 0.2H), 6.31-6.35 (m, 1H), 6.84 (d, *J* = 8.7 Hz, 0.4H), 6.88 (d, *J* = 8.8 Hz, 1.6H), 7.24 (d, *J* = 8.6 Hz, 2H). [13]C NMR ($CDCl_3$) δ: 14.8, 18.5, 49.3, 49.4, 67.0, 115.2, 115.7, 123.2, 124.9, 126.7, 129.4, 129.6, 129.9, 130.1, 130.5, 149.7, 150.2

1-(4-(prop-1-en-1-yl)phenyl)pyrrolidine (*E* : *Z* = 17 : 83) (**2d**)



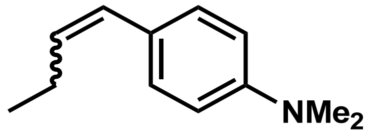
[1]H NMR ($CDCl_3$) δ: 1.84 (dd, *J* = 1.5 and 6.5 Hz, 0.5H), 1.91 (dd, J = 1.8 and 7.1 Hz, 2.4H), 1.99-2.04 (m, 4H), 3.27-3.34 (m, 4H), 5.58 (dq, *J* = 7.2 and 11.6 Hz, 0.8H), 6.01 (dq, *J* = 6.6 and 15.6 Hz, 0.2H), 6.29-6.37 (m, 1H), 6.50 (d, *J* = 8.0 Hz, 0.4H), 6.54 (d, J = 8.5 Hz, 1.6H), 7.21-7.23 (m, 2H). [13]C NMR ($CDCl_3$) δ: 14.8, 18.5, 25.5, 47.7, 111.3, 111.7, 120.6, 122.8, 125.2, 126.8, 130.0, 131.0, 146.6

9-ethyl-3-(prop-1-en-1-yl)-9H-carbazole (*E* : *Z* = 30 : 70) (**2e**)



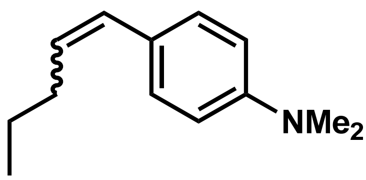
^{1}H NMR ($CDCl_3$) δ: 1.45 (t, *J* = 7.3 Hz, 3H), 1.94 (dd, *J* = 1.7 and 6.6 Hz, 0.9H), 2.02 (dd, *J* = 1.8 and 7.1 Hz, 2H), 4.33-4.40 (m, 2H), 5.79 (dq, *J* = 7.1 and 11.5 Hz, 0.7H), 6.26 (dq, *J* = 6.6 and 15.6 Hz, 0.3H), 6.59-6.66 (m, 1H), 7.21-7.25 (m, 1H), 7.32-7.51 (m, 4H), 8.06 (s, 1H), 8.09-8.12 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 13.7, 14.8, 18.6, 21.0, 37.4, 60.3, 108.0, 108.4, 108.5, 117.8, 118.7, 118.8, 120.4, 120.6, 122.7, 122.8, 123.0, 123.1, 123.8, 124.5, 125.6, 125.6, 127.0, 128.6, 129.2, 130.6, 131.7, 138.6, 139.2, 140.2

N,N-dimethyl-4-(but-1-en-1-yl)aniline (*E* : *Z* = 13 : 87) (**2f**)



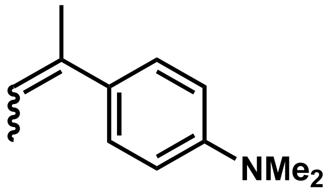
IR (neat) ν 2959, 2871, 1608, 1518, 1347, 1161, 946, 824 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.08-1.12 (m, 3H), 2.23 (dquin, *J* = 1.6 and 7.4 Hz, 0.2H), 2.40 (dquin, *J* = 1.9 and 7.4 Hz, 1.8H), 2.96 (s, 0.7H), 2.98 (s, 5.3H), 5.50 (dt, *J* = 7.2 and 11.4 Hz, 0.9H), 6.09 (dt, *J* = 6.5 and 15.7 Hz, 0.1H), 6.30-6.34 (m, 1H), 6.70-6.75 (m, 2H), 7.23-7.28 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 14.0, 14.7, 22.1, 26.1, 40.4, 40.5, 112.1, 112.6, 126.3, 126.7, 128.2, 128.7, 129.7, 131.3, 149.1, 149.6; HRMS (EI-MS) calcd. for $C_{12}H_{18}N$ (M+H$^+$): 176.1439; found 176.1440

N,N-dimethyl-4-(pent-1-en-1-yl)aniline (*E* : *Z* = 12 : 88) (**2g**)



^{1}H NMR ($CDCl_3$) δ: 0.97 (t, *J* = 7.4 Hz, 3H), 1.49 (sext, *J* = 7.3 Hz, 2H), 2.15-2.19 (m, 0.2H), 2.33-2.38 (m, 1.8H), 2.95 (s, 2H), 2.97 (s, 6H), 5.50 (dt, *J* = 7.2 and 11.6 Hz, 0.9 H), 6.04 (dt, *J* = 6.6 and 15.6 Hz, 0.1 H), 6.29-6.34 (m, 1H), 6.69-6.73 (m, 2H), 7.22-7.26 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 13.8, 14.0, 22.9, 23.4, 31.0, 35.3, 40.7, 40.8, 112.3, 112.8, 126.6, 126.8, 126.0, 126.8, 127.0, 128.8, 129.9, 130.0, 148.2, 148.7

4-(but-2-en-2-yl)-*N,N*-dimethylaniline (*E* : *Z* = 15 : 85) (**2h**)



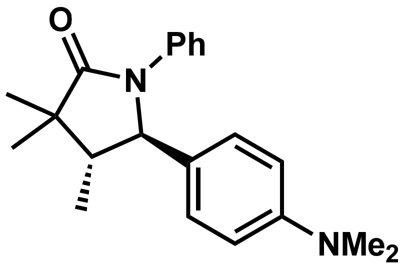
IR (neat) ν 2961, 2796, 1609, 1519, 1345, 1165, 946, 823 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.65 (d, J = 6.8 Hz, 2.5H), 1.78 (d, J = 6.8 Hz, 0.5H), 2.00-2.02 (m, 3H), 2.94 (s, 1H), 2.96 (s, 5H), 5.48 (dq, J = 1.3 and 6.8 Hz, 0.8H), 5.76 (dq, J = 1.3 and 6.7 Hz, 0.1H), 6.71 (d, J = 8.9 Hz, 0.4H), 6.72 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.6 Hz, 1.6H), 7.29 (d, J = 8.8 Hz, 0.3H). ^{13}C NMR ($CDCl_3$) δ:14.3, 15.1, 15.4, 25.4, 40.6, 40.7, 112.1, 112.5, 119.2, 120.3, 123.2, 128.9, 129.9, 136.4, 149.2; HRMS (EI-MS) calcd. for $C_{12}H_{18}N$ ($M+H^+$): 176.1439; found 176.1439

2. General procedure

General procedure for the synthesis of 3.

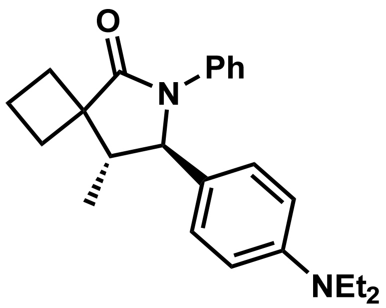
Substrate **1** (0.50 mmol), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv) and L13 (16.8 mg, 0.025 mmol, 0.05 equiv) were sequentially added under air to a drum vial equipped with a stir bar and a screw cap. After flashing nitrogen gas (purity 99.95%), dried 1,4-dioxane (1.0 mL), $^{i}Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv) and substrate **2** (1.00 mmol, 2.0 equiv) were added by syringe and the resulting mixture was vigorously stirred under nitrogen atmosphere for 24 h at 110 °C. After this time, the contents of the flask were filtered through the plug of silica gel, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting hexane/EtOAc to afford the product **3**.

5-(4-(dimethylamino)phenyl)-3,3,4-trimethyl-1-phenylpyrrolidin-2-one (**3a**)



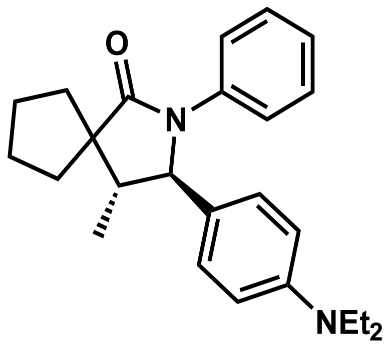
Following the general procedure above, using **1a** (121.4 mg, 0.50 mmol), styrene **2a** (0.17 mL, 1.00 mmol, 2.0 equiv, $E : Z = 23 : 77$), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), $^{i}Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3a** (132.2 mg, 82%); IR (neat) ν 3316, 2968, 2871, 1780, 1686, 1617, 1521, 1354, 1175, 948, 804, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.00 (d, J = 6.8 Hz, 3H), 1.10 (s, 3H), 1.29 (s, 3H), 1.93-1.99 (m, 1H), 2.88 (s, 6H), 4.53 (d, J = 9.4 Hz, 1H), 6.59 (d, J = 8.6 Hz, 2H), 7.00 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.6 Hz, 2H), 7.19 (t, J = 8.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.3, 19.0, 23.9, 40.5, 44.0, 49.2, 67.3, 112.4, 123.4, 124.7, 126.6, 128.1, 128.3, 138.3, 150.0, 179.9; HRMS (EI-MS) calcd. for $C_{21}H_{27}N_2O$ ($M+H^+$): 323.2123; found 323.2124

7-(4-(diethylamino)phenyl)-8-methyl-6-phenyl-6-azaspiro[3.4]octan-5-one (**3b**)



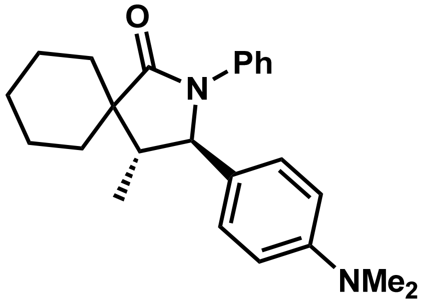
Following the general procedure above, using **2b** (127.1 mg, 0.50 mmol), styrene **2b** (0.20 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 22 : 78), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), $^{i}Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3b** (144.7 mg, 80%); IR (neat) ν 2968, 2109, 1686, 1518, 1352, 1265, 1187, 1154, 1079, 801 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.10 (t, *J* = 7.1 Hz, 6H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.82-1.91 (m, 2H), 2.05-2.28 (m, 4H), 2.58-2.66 (m, 1H), 3.26 (q, *J* = 6.9 Hz, 4H), 4.47 (d, *J* = 6.9 Hz, 1H), 6.52 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 12.7, 13.0, 16.6, 24.9, 29.4, 44.2, 47.2, 50.1, 67.9, 111.6, 122.7, 124.4, 126.0, 127.8, 128.4, 138.7, 147.3, 178.8; HRMS (EI-MS) calcd. for $C_{24}H_{31}N_2O$ (M+H$^+$): 363.2436; found 363.2436

3-(4-(diethylamino)phenyl)-4-methyl-2-phenyl-2-azaspiro[4.4]nonan-1-one (**3c**)



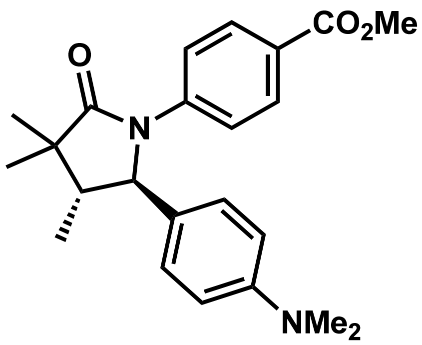
Following the general procedure above, using **1c** (134.1 mg, 0.50 mmol), styrene **2b** (0.20 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 22 : 78), $FeCl_2$ (3.1 mg, 0.025 mmol, 0.05 equiv), L13 (16.8 mg, 0.025 mmol, 0.05 equiv), $^{i}Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3c** (87.3 mg, 46%); IR (neat) ν 2963, 2086, 1685, 1518, 1352, 1188, 1071, 800, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.02 (d, *J* = 6.8 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 6H), 1.48-1.54 (m, 1H), 1.63-1.73 (m, 2H), 1.82-1.96 (m, 4H), 2.04-2.10 (m, 1H), 2.32-2.37 (m, 1H), 3.26 (q, *J* = 7.0 Hz, 4H), 4.50 (d, *J* = 8.8 Hz, 1H), 6.52 (d, *J* = 8.7 Hz, 2H), 6.98-7.01 (m, 3H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.6, 12.6, 26.3, 26.5, 30.6, 35.6, 44.2, 48.5, 54.5, 68.0, 111.5, 123.1, 124.4, 125.5, 128.1, 128.3, 138.5, 147.3, 180.7; HRMS (EI-MS) calcd. for $C_{25}H_{33}N_2O$ (M+H$^+$): 377.2593; found 377.2593

3-(4-(dimethylamino)phenyl)-4-methyl-2-phenyl-2-azaspiro[4.5]decan-1-one (**3d**)



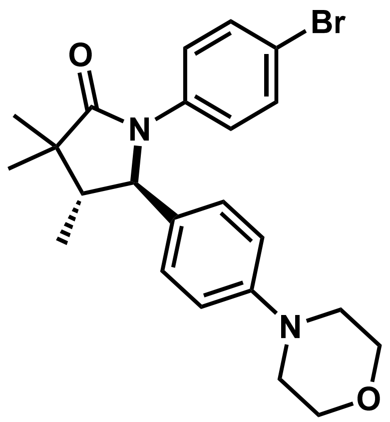
Following the general procedure above, using **1d** (128.1 mg, 0.50 mmol), styrene **2a** (0.20 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 23 : 77), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), $^iPr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3d** (71.4 mg, 39%); IR (neat) ν 2926, 2364, 1688, 1356, 1201, 1081, 800, 742, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.03 (d, *J* = 6.9 Hz, 3H), 1.25-1.32 (m, 1H), 1.44-1.56 (m, 4H), 1.67-1.76 (m, 3H), 1.84-1.96 (m, 2H), 2.26-2.33 (m, 1H), 2.88 (s, 6H), 4.57 (d, *J* = 8.8 Hz, 1H), 6.58 (d, *J* = 8.9 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.6, 21.7, 22.1, 25.9, 28.1, 33.8, 40.5, 45.9, 49.4, 67.0, 112.4, 123.2, 124.5, 127.3, 127.9, 128.3, 138.4, 149.9, 179.3; HRMS (EI-MS) calcd. for $C_{24}H_{31}N_2O$ ($M+H^+$): 363.2436; found 363.2436

methyl 4-(5-(4-(dimethylamino)phenyl)-3,3,4-trimethyl-2-oxopyrrolidin-1-yl)benzoate (**3e**)



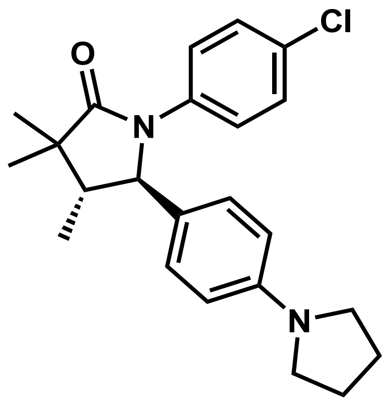
Following the general procedure above, using **1e** (150.4 mg, 0.50 mmol), styrene **2a** (0.17 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 23 : 77), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.8 mg, 0.025 mmol, 0.05 equiv), $^iPr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3e** (149.9 mg, 79%); IR (neat) ν 3303, 2956, 2110, 1697, 1603, 1523, 1351, 1275, 1176, 1108, 794, 762, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.00 (d, *J* = 6.8 Hz, 3H), 1.09 (s, 3H), 1.29 (s, 3H), 1.93-1.99 (m, 1H), 2.87 (s, 6H), 3.81 (s, 3H), 4.56 (d, *J* = 9.4 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.3, 19.0, 23.8, 40.4, 44.2, 49.1, 52.0, 67.1, 112.4, 122.4, 125.6, 126.0, 127.9, 129.9, 142.5, 150.1, 166.8, 180.1; HRMS (EI-MS) calcd. for $C_{23}H_{29}N_2O_3$ ($M+H^+$): 381.2178; found 381.2179

1-(4-bromophenyl)-3,3,4-trimethyl-5-(4-morpholinophenyl)pyrrolidin-2-one (**3f**)



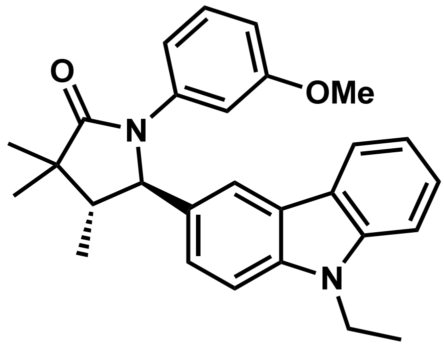
Following the general procedure above, using **1f** (160.5 mg, 0.50 mmol), styrene **2e** (0.19 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 21 : 79), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), $^i Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3f** (188.5 mg, 85%); IR (neat) ν 2961, 2855, 1693, 1488, 1348, 1222, 1113, 924, 822, 726 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.98 (d, J = 6.8 Hz, 3H), 1.08 (s, 3H), 1.27 (s, 3H), 1.93 (dq, J = 6.8 and 9.4 Hz, 1H), 3.10-3.11 (m, 4H), 3.80-3.82 (m, 4H), 4.51 (d, J = 9.4 Hz, 1H), 6.78 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.2, 18.9, 23.7, 44.0, 49.0, 49.1, 66.8, 67.0, 115.6, 117.7, 124.7, 128.0, 131.4, 131.9, 137.1, 150.6, 179.8; HRMS (EI-MS) calcd. for $C_{23}H_{28}N_2O_2$ ($M+H^+$): 443.1334; found 443.1333

1-(4-chlorophenyl)-3,3,4-trimethyl-5-(4-(pyrrolidin-1-yl)phenyl)pyrrolidin-2-one (**3g**)



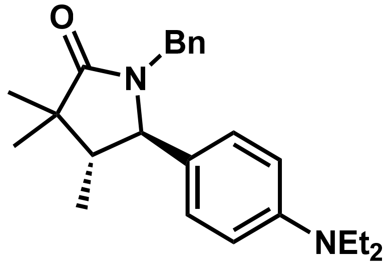
Following the general procedure above, using **1g** (138.4 mg, 0.50 mmol), styrene **2d** (0.18 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 17 : 83), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), $^i Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3g** (138.6 mg, 72%); IR (neat) ν 2961, 2094, 1686, 1524, 1491, 1366, 1185, 1079, 833, 792 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.98 (d, J = 6.8 Hz, 3H), 1.08 (s, 3H), 1.28 (s, 3H), 1.91-1.98 (m, 5H), 3.21 (t, J = 6.5 Hz, 4H), 4.47 (d, J = 9.4 Hz, 1H), 6.42 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.2, 18.9, 23.8, 25.5, 44.0, 47.5, 49.2, 67.4, 111.6, 124.5, 124.8, 128.2, 128.4, 129.8, 136.8, 147.5, 179.9; HRMS (EI-MS) calcd. for $C_{23}H_{28}ClN_2O$ (M+H$^+$): 383.1890; found 383.1890

5-(9-ethyl-9H-carbazol-3-yl)-1-(3-methoxyphenyl)-3,3,4-trimethylpyrrolidin-2-one (**3h**)



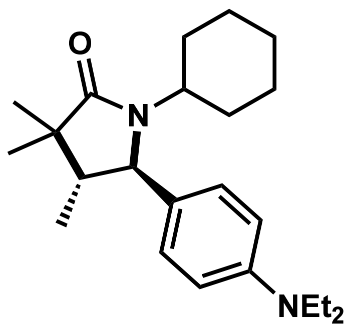
Following the general procedure above, using **1h** (136.2 mg, 0.50 mmol), styrene **2e** (0.20 mL, 1.00 mmol, 2.0 equiv, E : Z = 30 : 70), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.8 mg, 0.025 mmol, 0.05 equiv), ^{i}Pr$_2$NEt (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3h** (157.9 mg, 74%); IR (neat) ν 3555, 2959, 1707, 1688, 1604, 1491, 1345, 1231, 1050, 774, 755, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.04 (d, J = 6.5 Hz, 3H), 1.15 (s, 3H), 1.34 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H), 2.06-2.12 (m, 1H), 3.67 (s, 3H), 4.28 (q, J = 7.2 Hz, 2H), 4.79 (d, J = 9.1 Hz, 1H), 6.49 (d, J = 8.1 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 7.01 (t, J = 8.1 Hz, 1H), 7.10 (s, 1H), 7.21 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 6.8 Hz, 2H), 7.36 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.93 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 10.3, 13.9, 19.1, 23.9, 37.7, 44.2, 49.6, 55.2, 68.2, 108.6, 108.8, 109.2, 110.7, 115.4, 118.9, 119.4, 120.4, 122.5, 122.9, 124.4, 125.9, 128.9, 129.8, 139.4, 139.6, 140.3, 159.5, 180.1; HRMS (EI-MS) calcd. for $C_{28}H_{31}N_2O_2$ (M+H$^+$): 427.2386; found 427.2387

1-benzyl-5-(4-(diethylamino)phenyl)-3,3,4-trimethylpyrrolidin-2-one (**3i**)



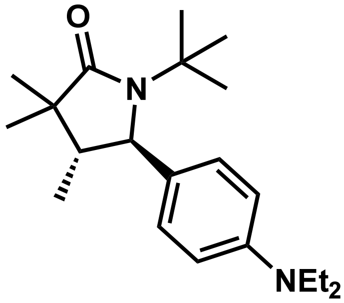
Following the general procedure above, using **1i** (128.1 mg, 0.50 mmol), styrene **2b** (0.20 mL, 1.00 mmol, 2.0 equiv, E : Z = 22 : 78), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), ^{i}Pr$_2$NEt (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3i** (139.8 mg, 77%); IR (neat) ν 3358, 2966, 1682, 1518, 1399, 1357, 1263, 1195, 1075, 803, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.81 (d, *J* = 6.9 Hz, 3H), 0.94 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 6H), 1.23 (s, 3H), 1.85-1.91 (m, 1H), 3.37 (q, *J* = 7.0 Hz, 4H), 3.45 (d, *J* = 14.3 Hz, 1H), 3.60 (d, *J* = 9.4 Hz, 1H), 5.03 (d, *J* = 14.3 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.00 (dd, *J* = 2.4 and 7.6 Hz, 2H), 7.21-7.25 (m, 3H). ^{13}C NMR (CDCl$_3$) δ: 10.3, 12.7, 18.6, 23.5, 43.3, 44.1, 44.4, 48.7, 65.3, 111.7, 124.4, 127.3, 128.4, 128.7, 129.0, 137.1, 147.8, 180.5; HRMS (EI-MS) calcd. for $C_{24}H_{33}N_2O$ (M+H$^+$): 365.2593; found 365.2593

1-cyclohexyl-5-(4-(diethylamino)phenyl)-3,3,4-trimethylpyrrolidin-2-one (**3j**)



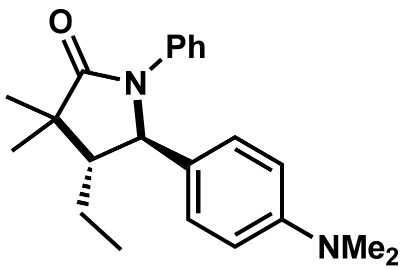
Following the general procedure above, using **1j** (124.1 mg, 0.50 mmol), styrene **2b** (0.20 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 22 : 78), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.8 mg, 0.025 mmol, 0.05 equiv), ^{i}Pr$_2$NEt (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3j** (105.6 mg, 59%); IR (neat) ν 2962, 2856, 1678, 1518, 1356, 1265, 1075, 798 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.83 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 3H), 0.95-1.01 (m, 1H), 1.05-1.13 (m, 2H), 1.16 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 6H), 1.36 (dq, *J* = 3.5 and 12.4 Hz, 1H), 1.48 (t, *J* = 12.7 Hz, 2H), 1.59-1.67 (m, 3H), 1.80 (dq, *J* = 6.9 and 9.3 Hz, 1H), 1.97 (dq, *J* = 3.2 and 12.0 Hz, 1H), 3.23 (t, *J* = 12.0 Hz, 1H), 3.35 (q, *J* = 7.0 Hz, 4H), 3.86 (d, *J* = 9.3 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H)2, 7.05 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ: 10.4, 12.7, 18.8, 23.7, 25.5, 26.0, 26.3, 29.8, 30.1, 43.3, 44.4, 48.9, 54.3, 66.8, 111.6, 126.8, 128.9, 147.7, 181.2; HRMS (EI-MS) calcd. for $C_{23}H_{37}N_2O$ (M+H$^+$): 357.2906; found 357.2904

1-(tert-butyl)-5-(4-(dimethylamino)phenyl)-3,3,4-trimethylpyrrolidin-2-one (**3k**)



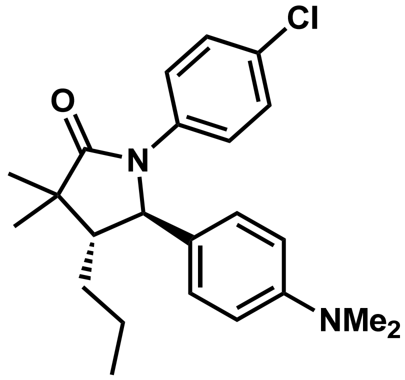
Following the general procedure above, using **1k** (111.2 mg, 0.50 mmol), styrene **2b** (0.20 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 23 : 77), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (17.0 mg, 0.025 mmol, 0.05 equiv), $^iPr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3k** (65.3 mg, 40%); IR (neat) ν 2958, 1672, 1613, 1519, 1387, 1348, 1195, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.87 (d, *J* = 6.9 Hz, 3H), 0.94 (s, 3H), 1.11 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 6H), 1.25 (s, 9H), 1.68-1.74 (m, 1H), 3.34 (q, *J* = 7.0 Hz, 4H), 4.00 (d, *J* = 8.1 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.0, 12.7, 19.6, 23.8, 28.7, 43.6, 44.4, 49.3, 55.7, 67.4, 111.7, 127.6, 131.8, 147.2, 182.3; HRMS (EI-MS) calcd. for $C_{21}H_{35}N_2O$ ($M+H^+$): 331.2749; found 331.2749

5-(4-(dimethylamino)phenyl)-4-ethyl-3,3-dimethyl-1-phenylpyrrolidin-2-one (**3l**)



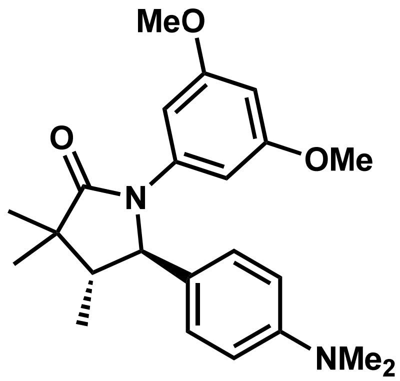
Following the general procedure above, using **1a** (121.1 mg, 0.50 mmol), styrene **2f** (0.18 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 13 : 87), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), $^iPr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3m** (109.1 mg, 65%); IR (neat) ν 2965, 2929, 1876, 1696, 1524, 1348, 1171, 1114, 813, 791, 754, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.85 (t, *J* = 7.5 Hz, 3H), 1.15 (s, 3H), 1.39 (s, 3H), 1.52-1.59 (m, 2H), 1.86-1.90 (m, 1H), 2.88 (s, 6H), 4.53 (d, *J* = 9.1 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 13.2, 19.0, 20.7, 25.7, 40.5, 44.1, 55.5, 66.6, 112.3, 123.7, 124.8, 127.2, 128.3, 128.5, 138.2, 149.9, 179.8; HRMS (EI-MS) calcd. for $C_{22}H_{29}N_2O$ ($M+H^+$): 337.2280; found 337.2280

1-(4-chlorophenyl)-5-(4-(dimethylamino)phenyl)-3,3-dimethyl-4-propylpyrrolidin-2-one (**3m**)



Following the general procedure above, using **1g** (138.4 mg, 0.50 mmol), styrene **2g** (0.18 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 12 : 88), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), $^{i}Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3m** (114.9 mg, 60%); IR (neat) ν 2965, 2931, 2868, 1684, 1528, 1359, 1172, 1083, 1013, 817, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.80 (t, *J* = 7.3 Hz, 3H), 1.10-1.17 (m, 1H), 1.13 (s, 3H), 1.24-1.30 (m, 1H), 1.36 (s, 3H), 1.41-1.53 (m, 2H), 1.94-1.98 (m, 1H), 2.90 (s, 6H), 4.48 (d, *J* = 9.2 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 14.6, 19.0, 21.5, 25.4, 30.1, 40.4, 44.2, 53.5, 66.7, 112.3, 124.8, 126.5, 128.4, 128.5, 129.9, 136.7, 150.0, 179.8; HRMS (EI-MS) calcd. for $C_{23}H_{30}ClN_2O$ ($M+H^+$): 385.2047; found 385.2047

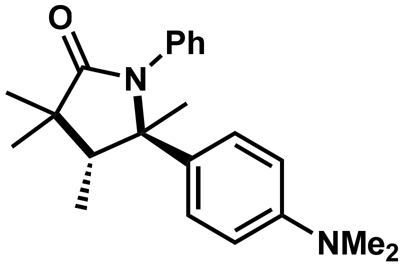
1-(3,5-dimethoxyphenyl)-5-(4-(dimethylamino)phenyl)-3,3,4-trimethylpyrrolidin-2-one (**3n**)



Following the general procedure above, using **1l** (136.2 mg, 0.50 mmol), styrene **2a** (0.17 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 23 : 77), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), ligand (16.8 mg, 0.025 mmol, 0.05 equiv), $^{i}Pr_2NEt$ (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3n** (160.6 mg, 84%); IR (neat) ν 3466, 2960, 1666, 1593, 1470, 1203, 1151, 1051, 831, 806, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.98 (d, *J* = 6.8 Hz, 3H), 1.08 (s, 3H), 1.28 (s, 3H), 1.93 (dq, *J* = 6.8, and 9.3 Hz, 1H), 2.89 (s, 6H), 3.67 (s, 6H), 4.47 (d, *J* = 9.3 Hz, 1H), 6.13 (t, *J*

= 2.2 Hz, 1H), 6.54 (d, *J* = 2.2 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.3, 19.0, 23.8, 40.5, 44.2, 49.0, 55.4, 67.5, 97.6, 101.7, 112.6, 127.0, 127.9, 140.0, 150.1, 160.3, 180.1; HRMS (EI-MS) calcd. for $C_{23}H_{31}N_2O_3$ (M+H$^+$): 383.2335; found 383.2335

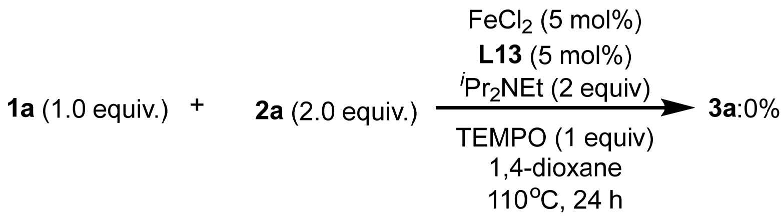
5-(4-(dimethylamino)phenyl)-3,3,4,5-tetramethyl-1-phenylpyrrolidin-2-one (**3o**)



Following the general procedure above, using **1a** (121.1 mg, 0.50 mmol), styrene **2h** (0.19 mL, 1.00 mmol, 2.0 equiv, *E* : *Z* = 15 : 85), $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv), L13 (16.9 mg, 0.025 mmol, 0.05 equiv), ^{i}Pr$_2$NEt (0.17 mL, 1.00 mmol, 2.0 equiv), and dried 1,4-dioxane (1.00 mL) at 110 °C, yielded the product **3o** (48.4 mg, 29%); IR (neat) ν 3351, 2969, 1685, 1520, 1351, 1198, 1130, 798, 754, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.93 (d, *J* = 7.2 Hz, 3H), 1.26 (s, 3H), 1.33 (s, 3H), 1.57 (s, 3H), 2.48 (q, *J* = 7.5 Hz, 1H), 2.95 (s, 6H), 6.65 (d, *J* = 8.9 Hz, 2H), 6.96-6.97 (m, 2H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.16-7.19 (m, 2H), 7.23 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 8.8, 19.8, 21.5, 26.7, 40.5, 42.8, 52.1, 68.4, 111.8, 126.7, 127.8, 128.1, 128.5, 132.8, 137.8, 149.5, 180.7; HRMS (EI-MS) calcd. for $C_{22}H_{29}N_2O$ (M+H$^+$): 337.2280; found 337.2280

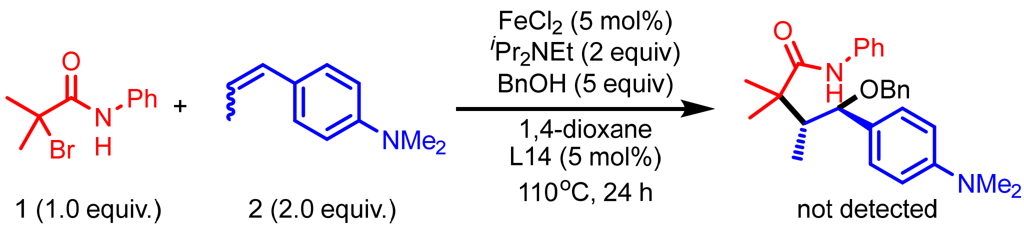
3. Control experiments

#1: Radical inhibitor test



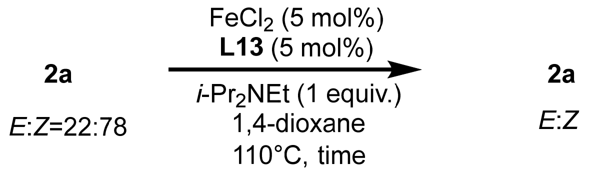
Substrate **1a** (0.50 mmol), substrate **2a** (1.00 mmol, 2.0 equiv), radical inhibitor (TEMPO : 78.1 mg, 0.5 mmol, 1.0 equiv, BHT : 110.2 mg, 0.5 mmol, 1.0 equiv) and $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv) were sequentially added under air to a drum vial equipped with a stir bar and a screw cap. After flashing nitrogen gas (purity 99.95%), dried 1,4-dioxane (1.0 mL) and ^{i}Pr$_2$NEt (0.17 mL, 1.00 mmol, 2.0 equiv) were added by syringe and the resulting mixture was vigorously stirred under nitrogen atmosphere for 24 h at 110 °C. After this time, the contents of the flask were checked by GC-MS.

#2: Cation trapping test



Substrate **1a** (0.50 mmol), substrate **2a** (1.00 mmol, 2.0 equiv), BnOH (0.26 mL, 2.5 mmol, 5 equiv) and $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv) were sequentially added under air to a drum vial equipped with a stir bar and a screw cap. After flashing nitrogen gas (purity 99.95%), dried 1,4-dioxane (1.0 mL) and ^{i}Pr$_2$NEt (0.17 mL, 1.00 mmol, 2.0 equiv) were added by syringe and the resulting mixture was vigorously stirred under nitrogen atmosphere for 24 h at 110 °C. After this time, the contents of the flask were filtered through the plug of silica gel. But desired product **3a-Nu** was not obtained.

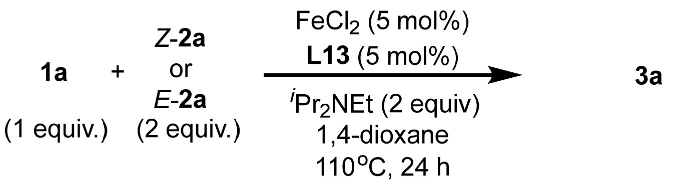
#3: *E*-*Z* isomerization test for **2a**

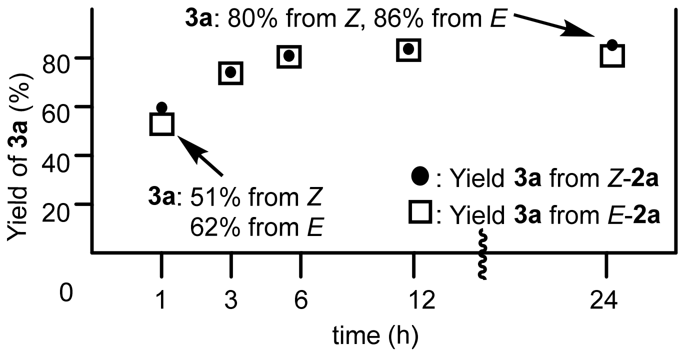


time (h)	yield (%)	*E*:*Z*	time (h)	yield (%)	*E*:*Z*
0	-	22:78	6	>99	21:79
1	>99	21:79	12	>99	21:79
3	>99	21:79	24	>99	21:79

Substrate **2a** (161.2 mg, 1.0 mmol) and $FeCl_2$ (3.2 mg, 0.05 mmol, 0.05 equiv) were sequentially added under air to a drum vial equipped with a stir bar and a screw cap. After flashing nitrogen gas (purity 99.95%), dried 1,4-dioxane (1.0 mL) and ${}^{i}Pr_2NEt$ (0.17 mL, 1.0 mmol, 1.0 equiv) were added by syringe and the resulting mixture was vigorously stirred under nitrogen atmosphere for 1-24 h at 110 °C. After this time, the contents of the flask were filtered through the plug of silica gel, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting hexane/EtOAc to afford the product **2a**. *E*/*Z* ratios were determined by ^{1}H NMR analysis.

#4: Reactivities of *Z*- and *E*-**2a**





From *E*-**2a**

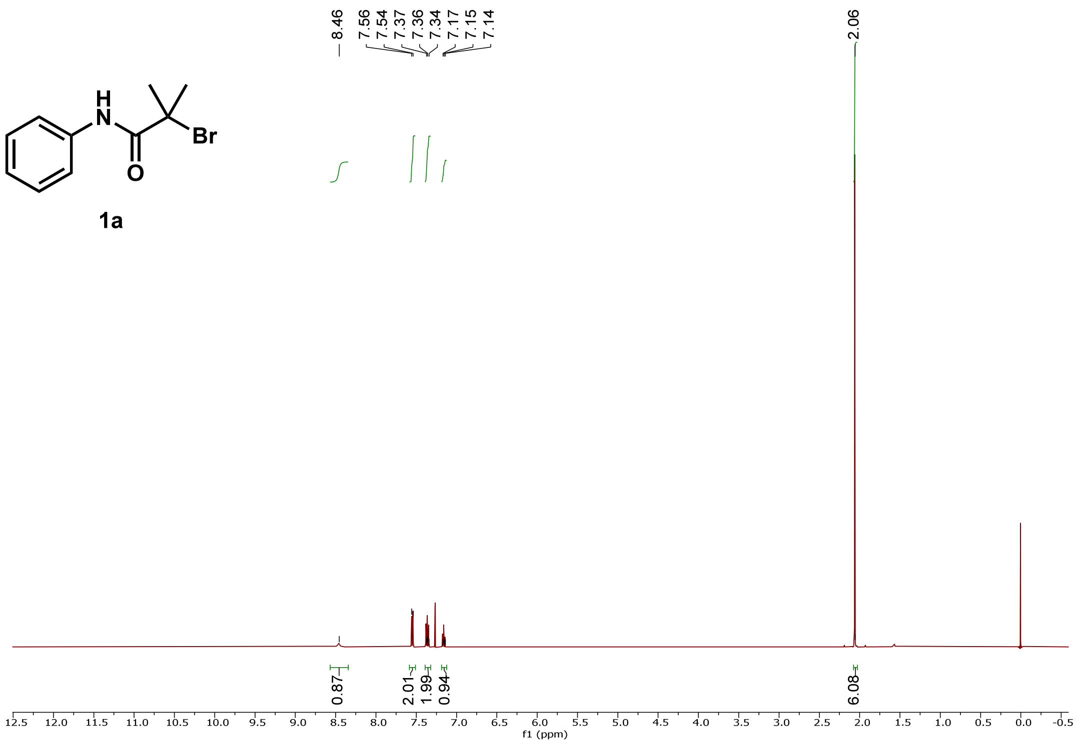
Substrate **1a** (121.1 mg, 0.50 mmol), substrate **2a** (0.17mL, 1.0 mmol, 2.0 equiv, *E* : *Z* = 100 : 0) and $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv) were sequentially added under air to a drum vial equipped with a stir bar and a screw cap. After flashing nitrogen gas (purity 99.95%), dried 1,4-dioxane (1.0 mL) and ${}^{i}Pr_2NEt$ (0.17 mL, 1.0 mmol, 2.0 equiv) were added by syringe and the resulting mixture was vigorously stirred under nitrogen atmosphere for 1-24 h at 110 °C. After each reaction time, the yields were determined by ^{1}H NMR analysis.

From *Z*-**2a**

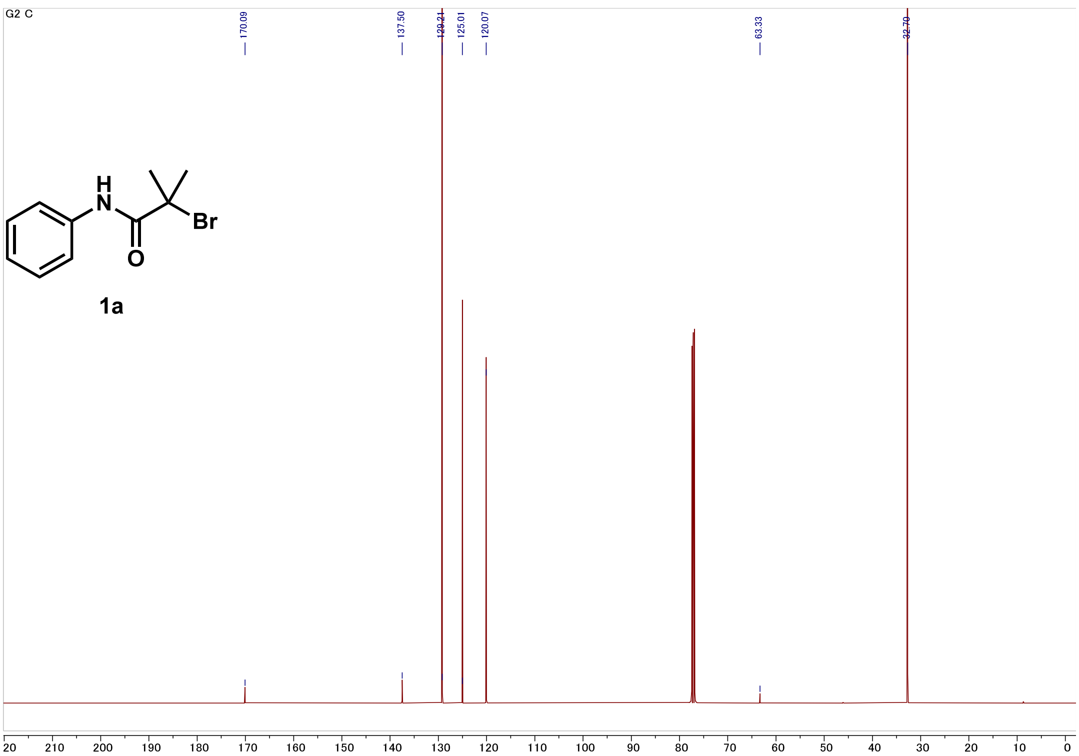
Substrate **1a** (121.1 mg, 0.50 mmol), substrate **2a** (0.17mL, 1.0 mmol, 2.0 equiv, *E* : *Z* = 0 : 100) and $FeCl_2$ (3.2 mg, 0.025 mmol, 0.05 equiv) were sequentially added under air to a drum vial equipped with a stir bar and a screw cap. After flashing nitrogen gas (purity 99.95%), dried 1,4-dioxane (1.0 mL) and $^i Pr_2NEt$ (0.17 mL, 1.0 mmol, 2.0 equiv) were added by syringe and the resulting mixture was vigorously stirred under nitrogen atmosphere for 1-24 h at 110 °C. After each reaction time, the yields were determined by ^{1}H NMR analysis.

4. Spectral charts for new compounds

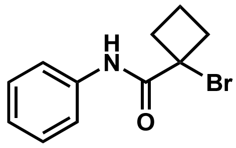
^{1}H NMR (500 MHz, $CDCl_3$)



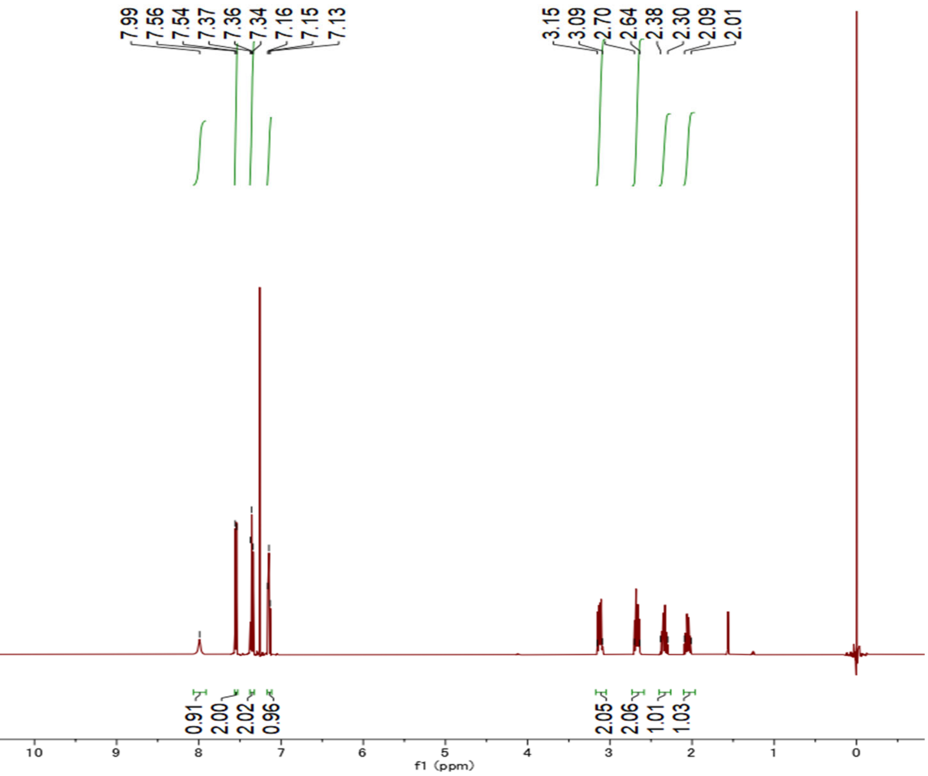
^{13}C NMR (125 MHz, $CDCl_3$)



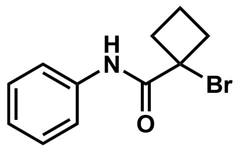
^{1}H NMR (500 MHz, $CDCl_3$)



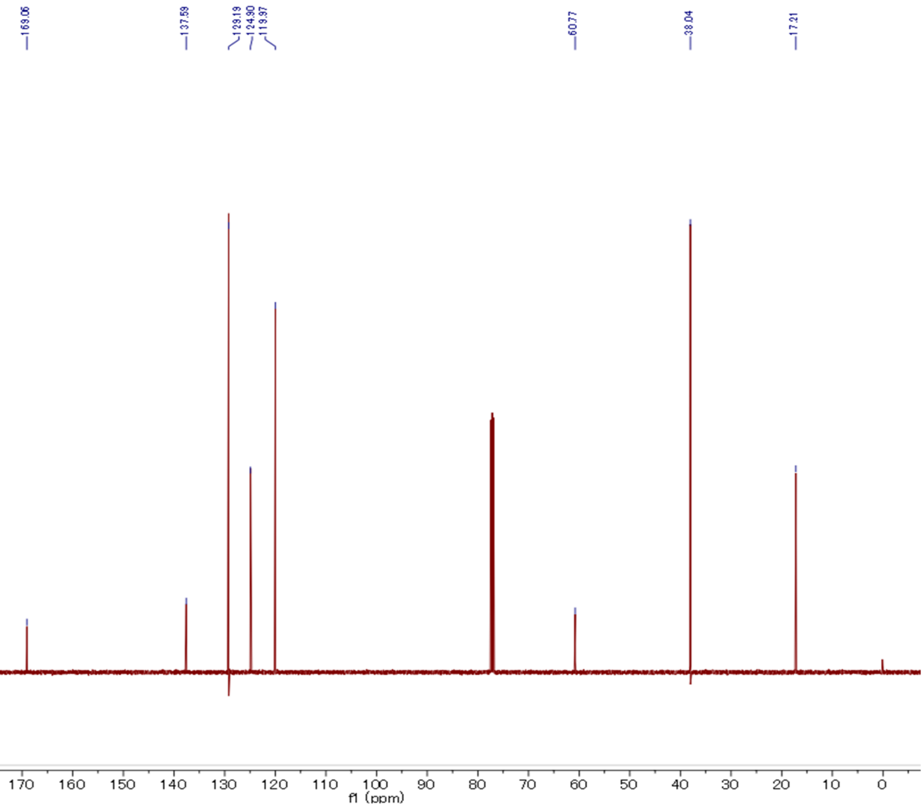
1b



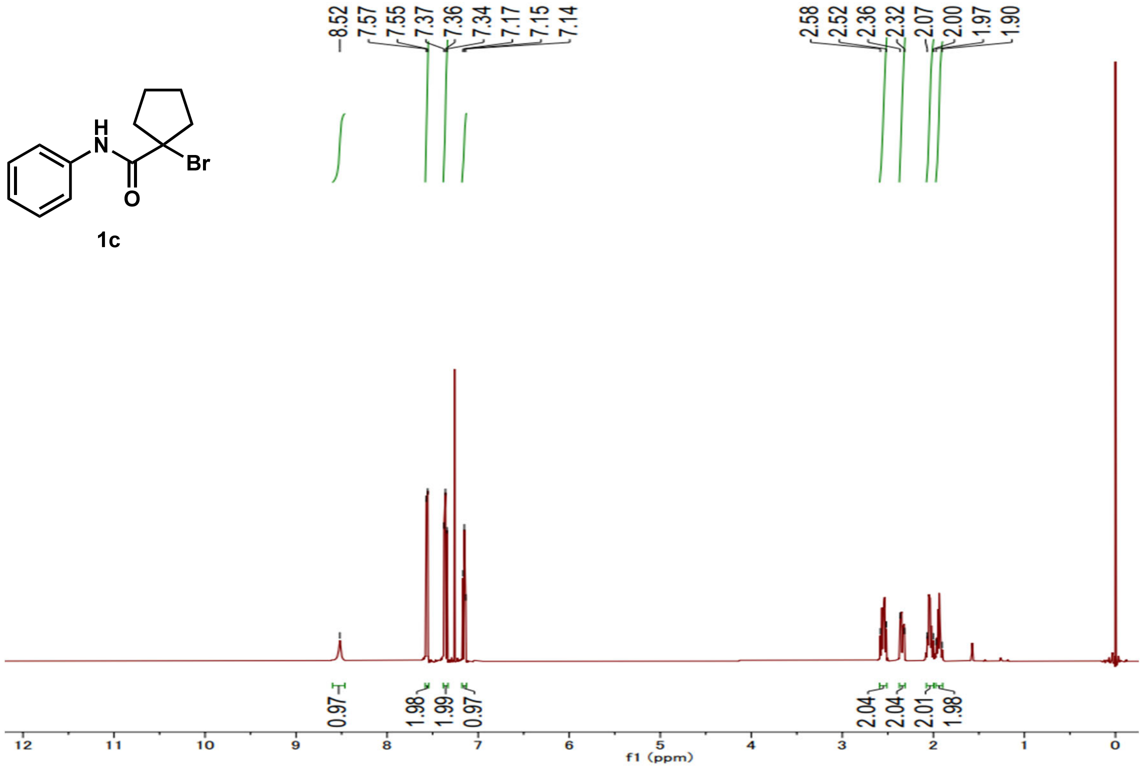
^{13}C NMR (125 MHz, $CDCl_3$)



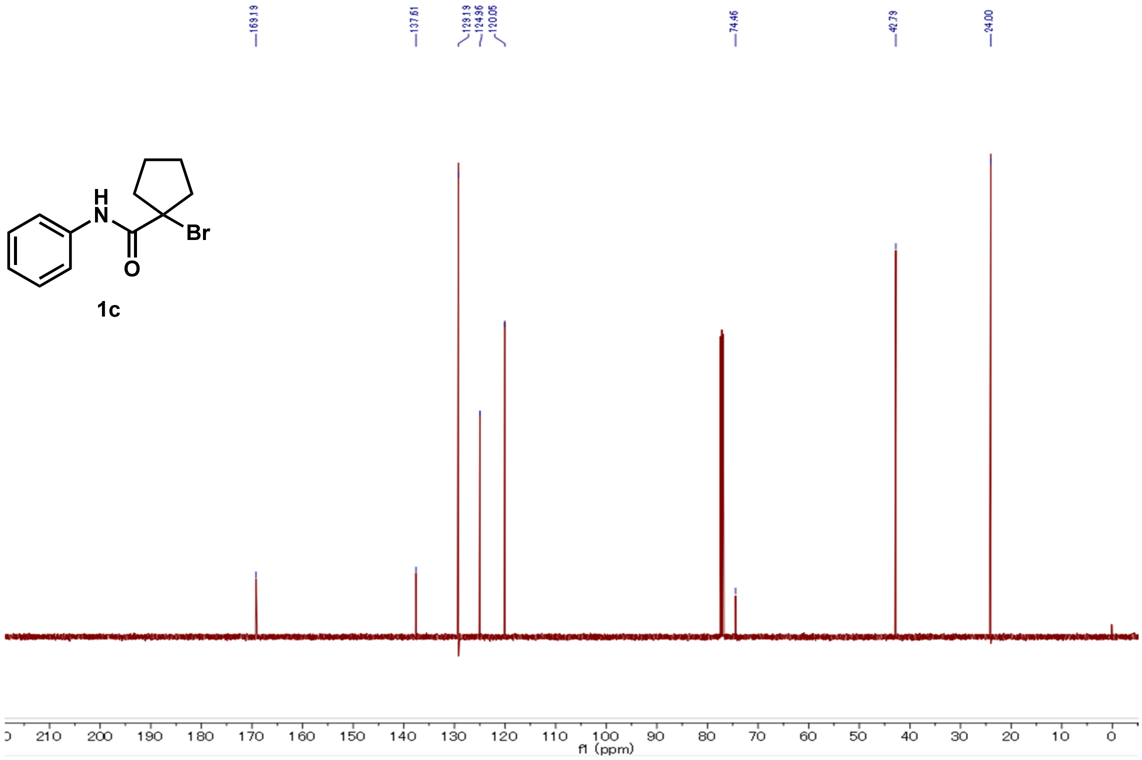
1b



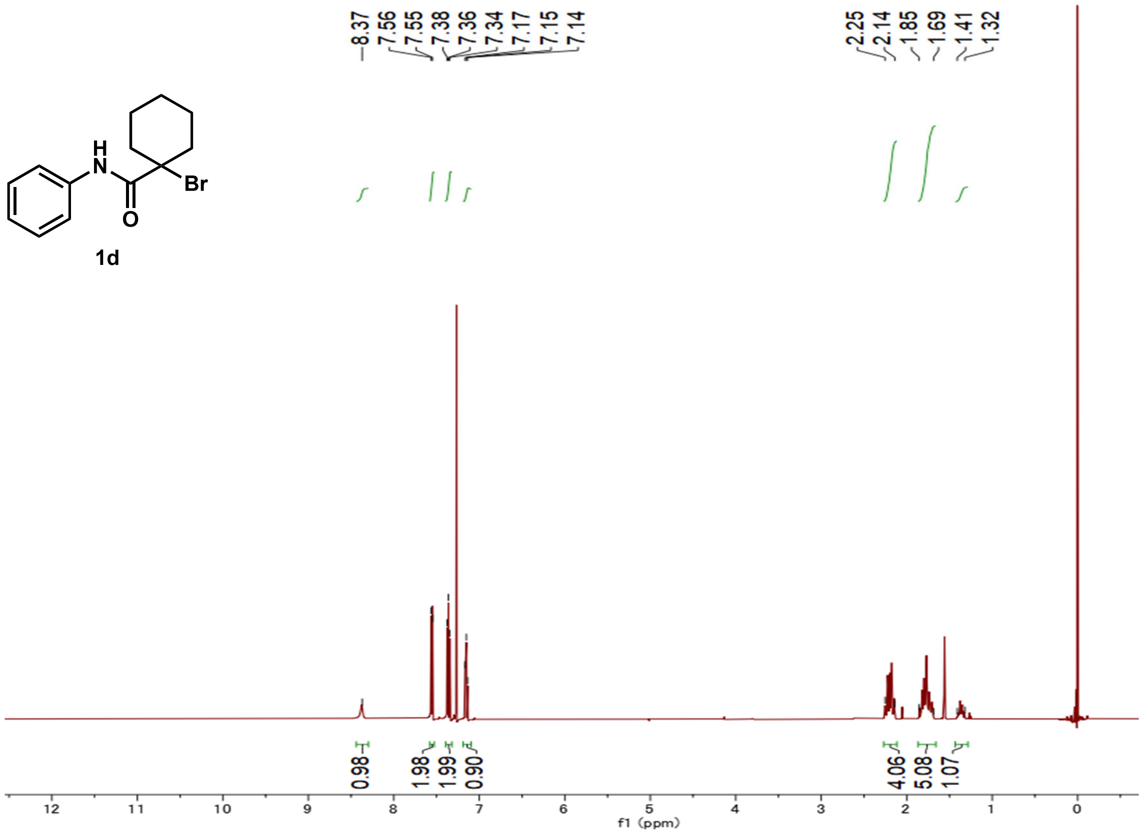
^{1}H NMR (500 MHz, $CDCl_3$)



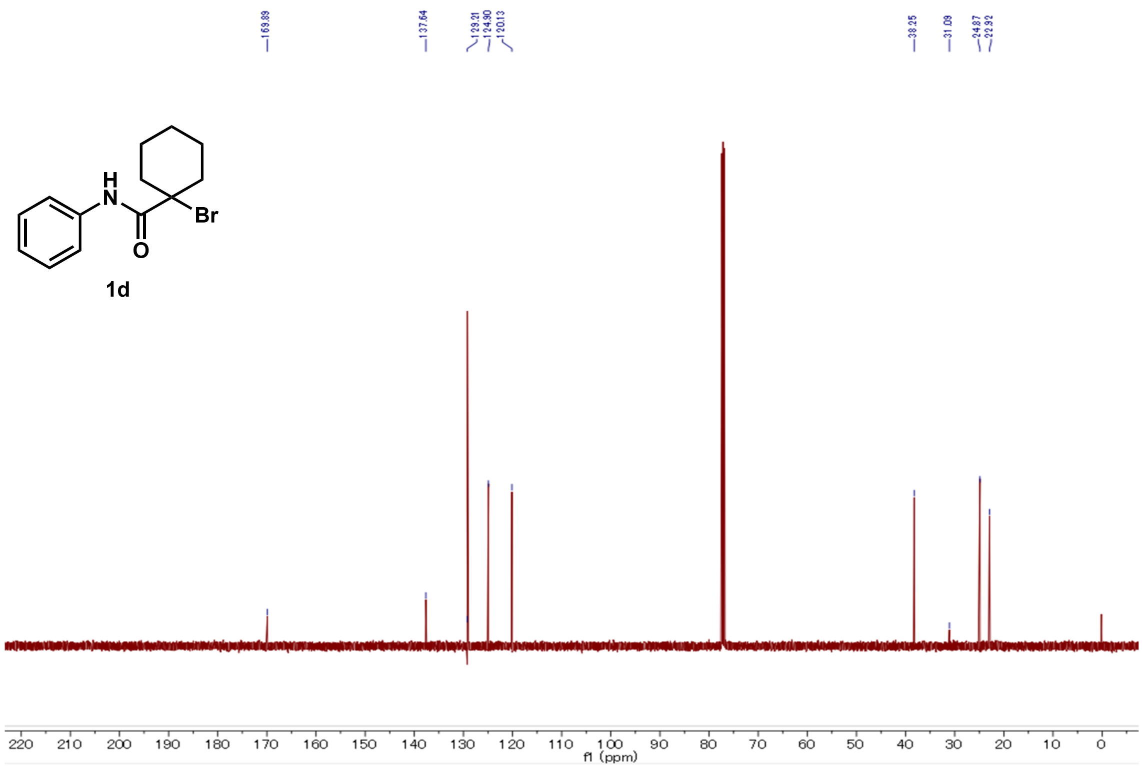
^{13}C NMR (125 MHz, $CDCl_3$)



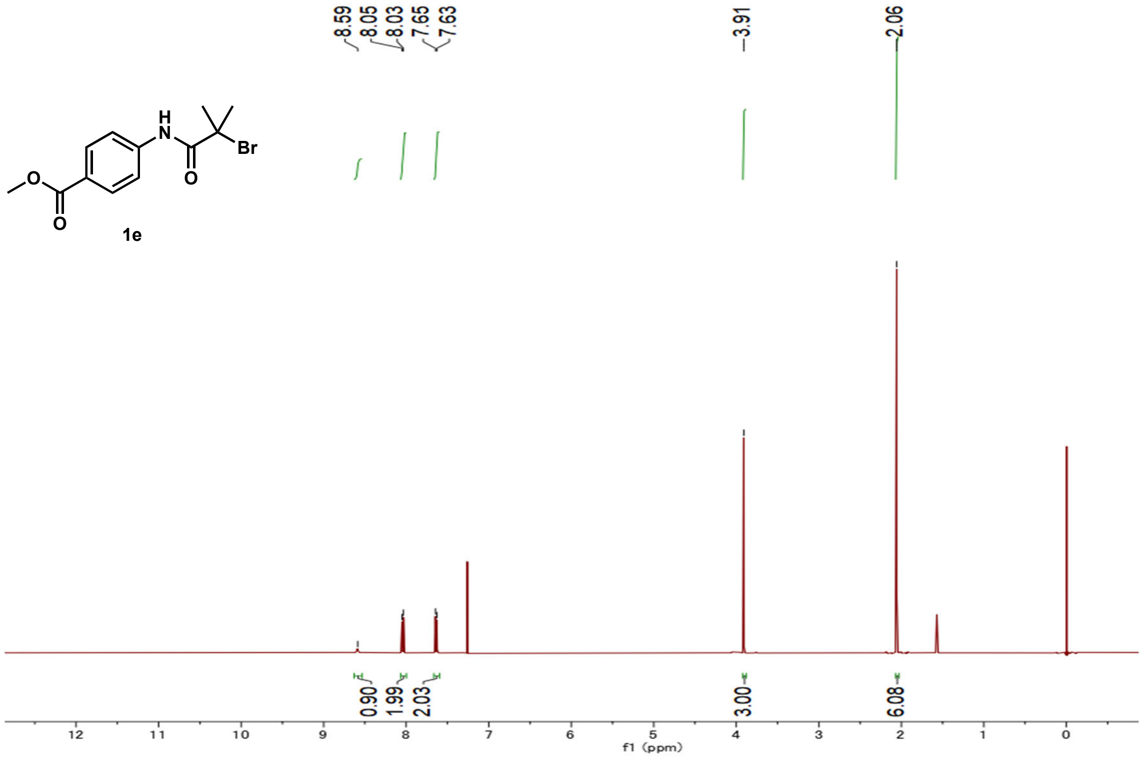
^{1}H NMR (500 MHz, $CDCl_3$)



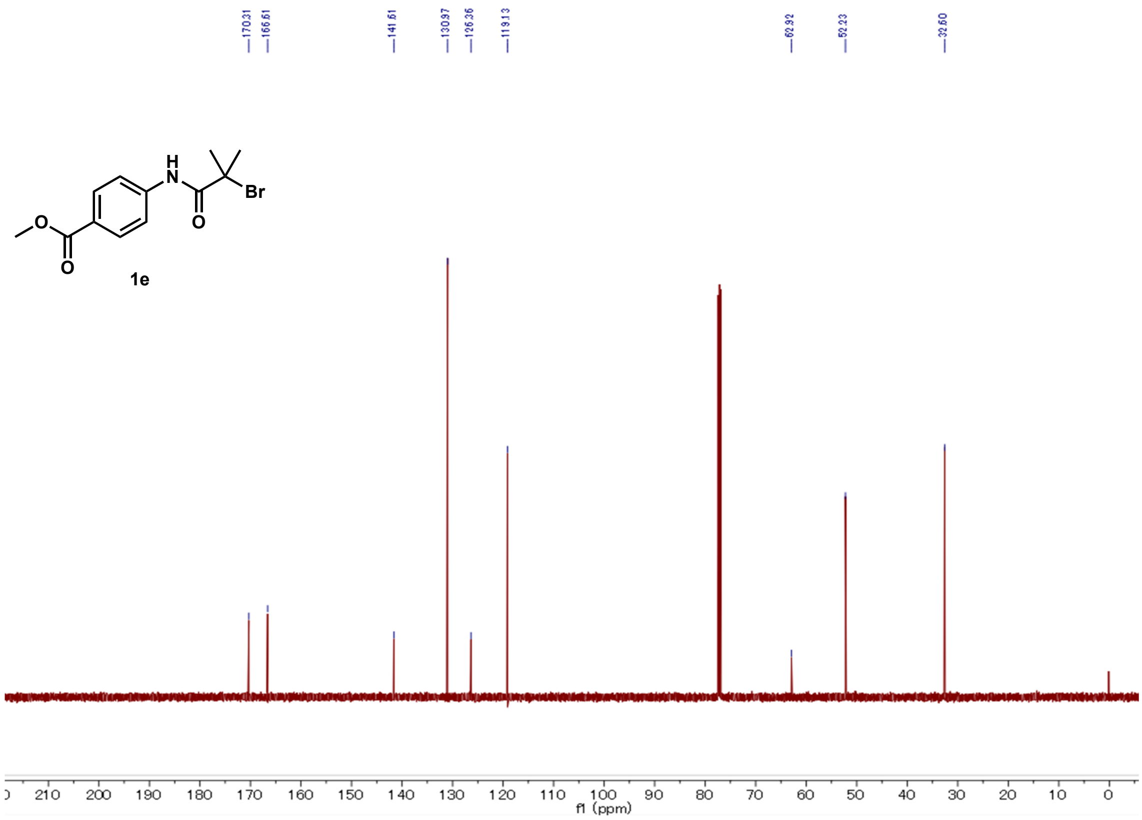
^{13}C NMR (125 MHz, $CDCl_3$)



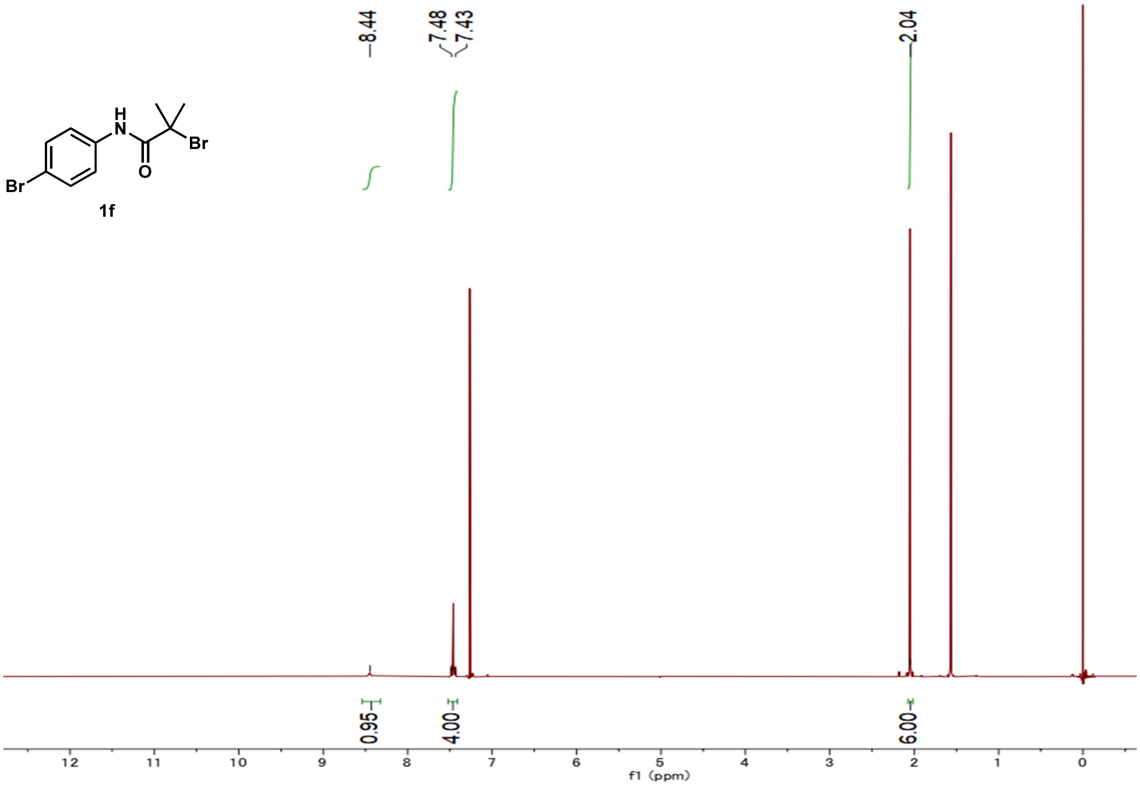
^{1}H NMR (500 MHz, $CDCl_3$)



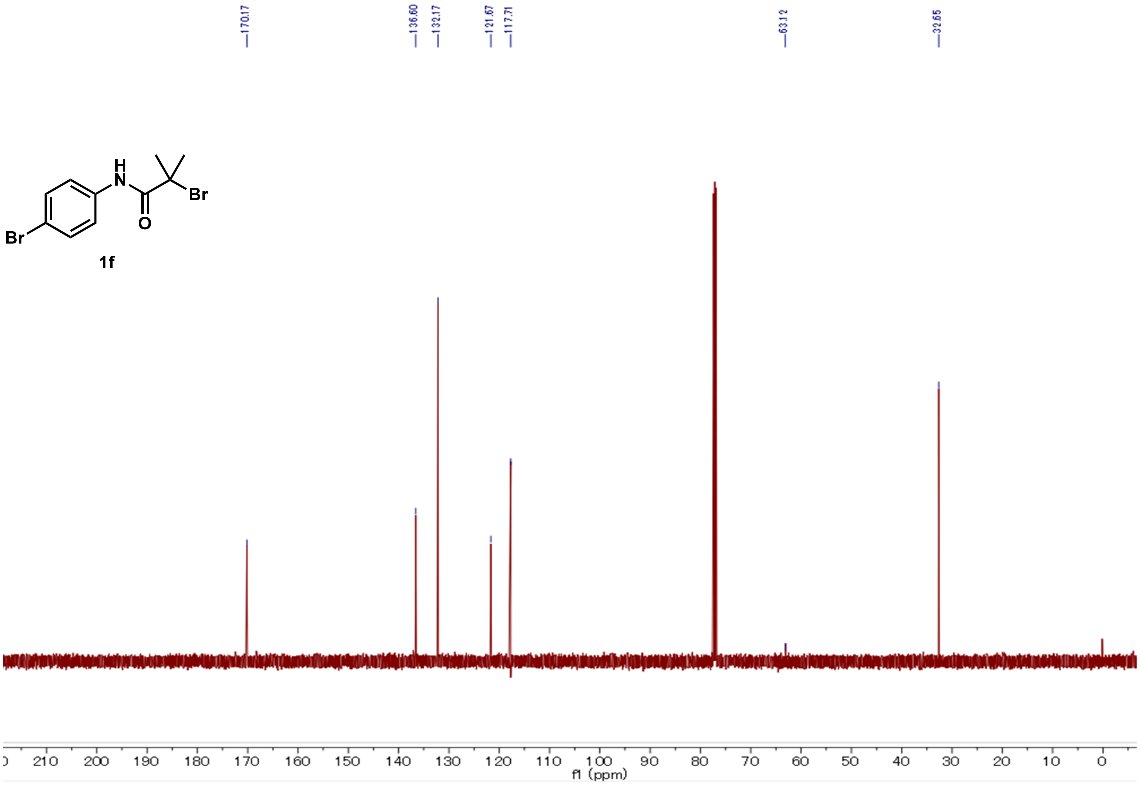
^{13}C NMR (125 MHz, $CDCl_3$)



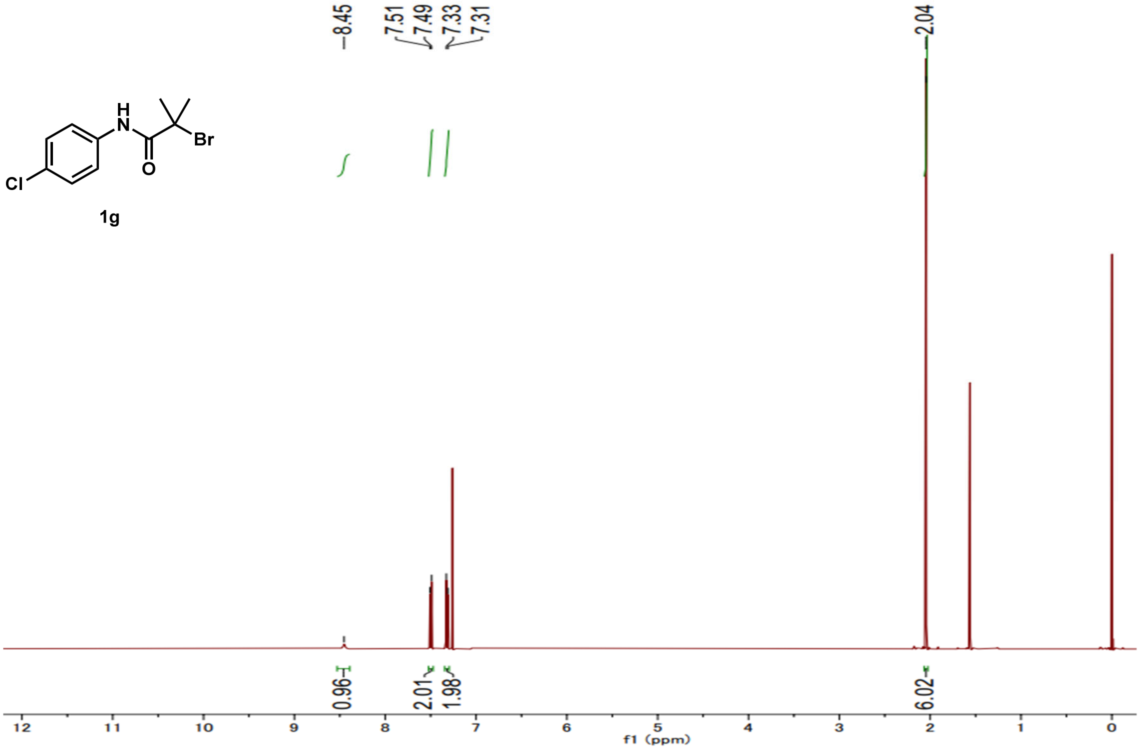
^{1}H NMR (500 MHz, $CDCl_3$)



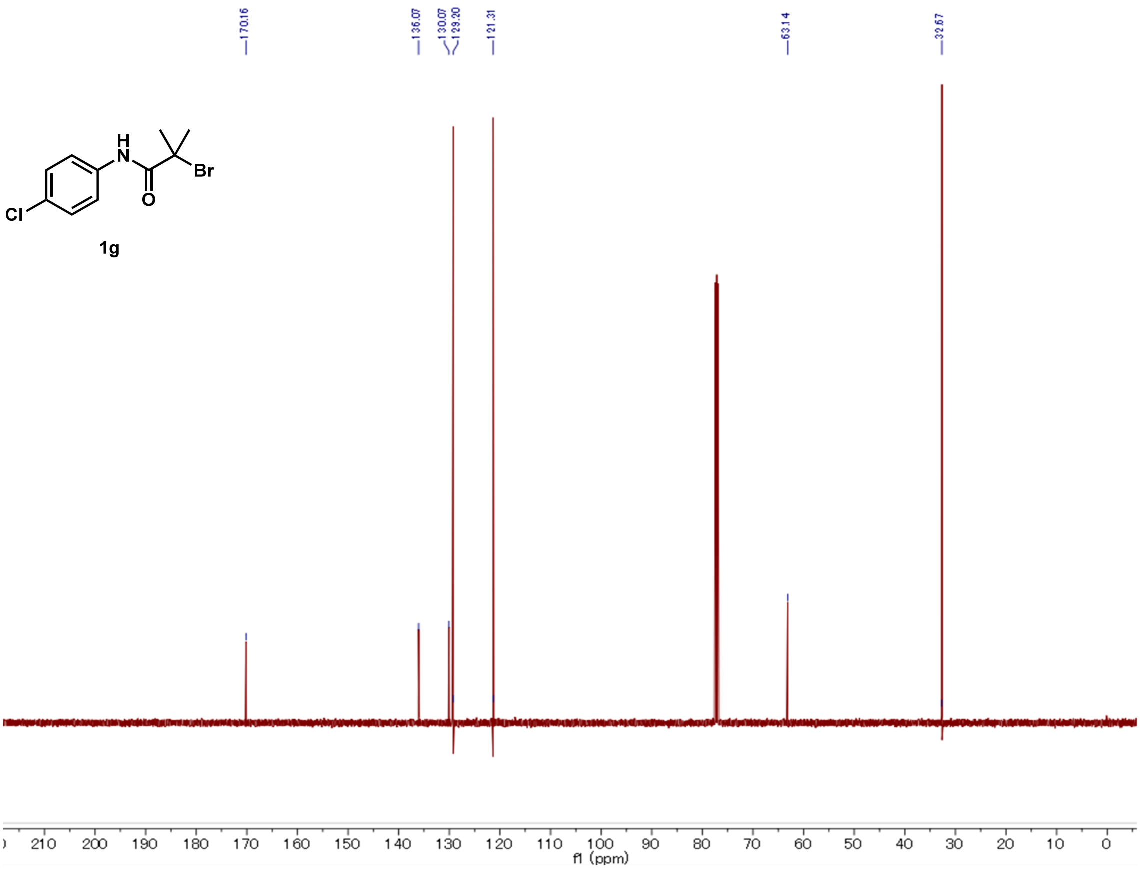
^{13}C NMR (125 MHz, $CDCl_3$)



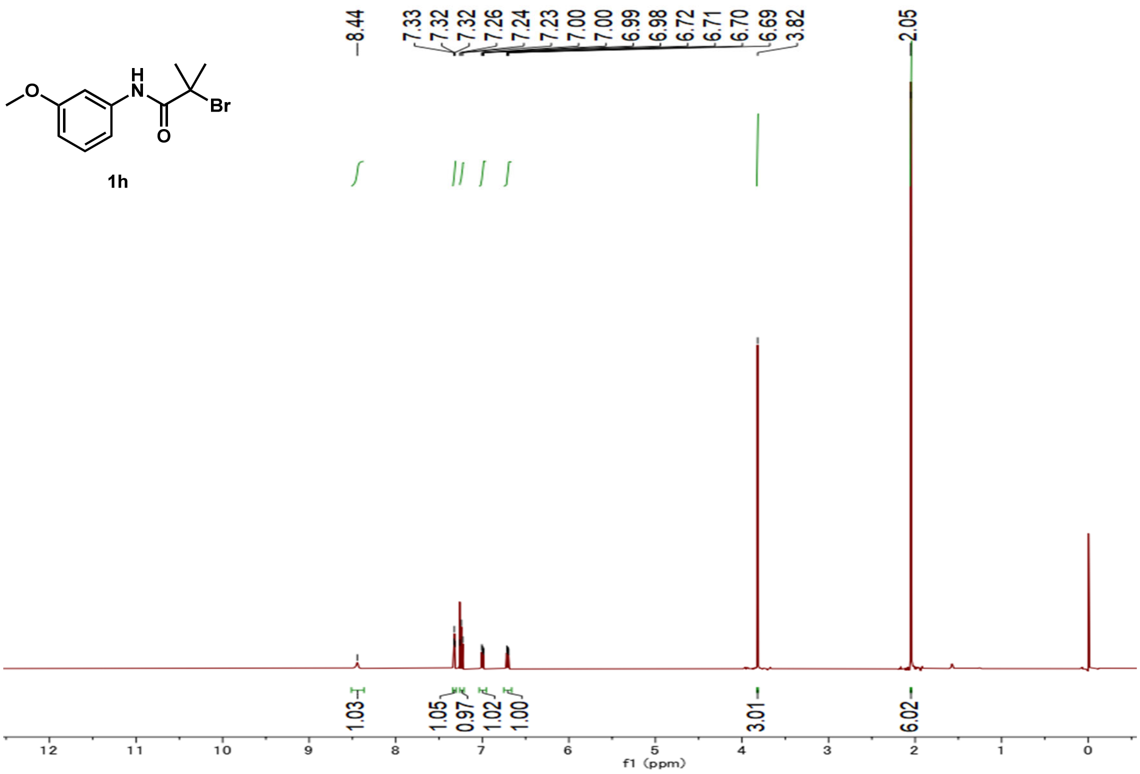
^{1}H NMR (500 MHz, $CDCl_3$)



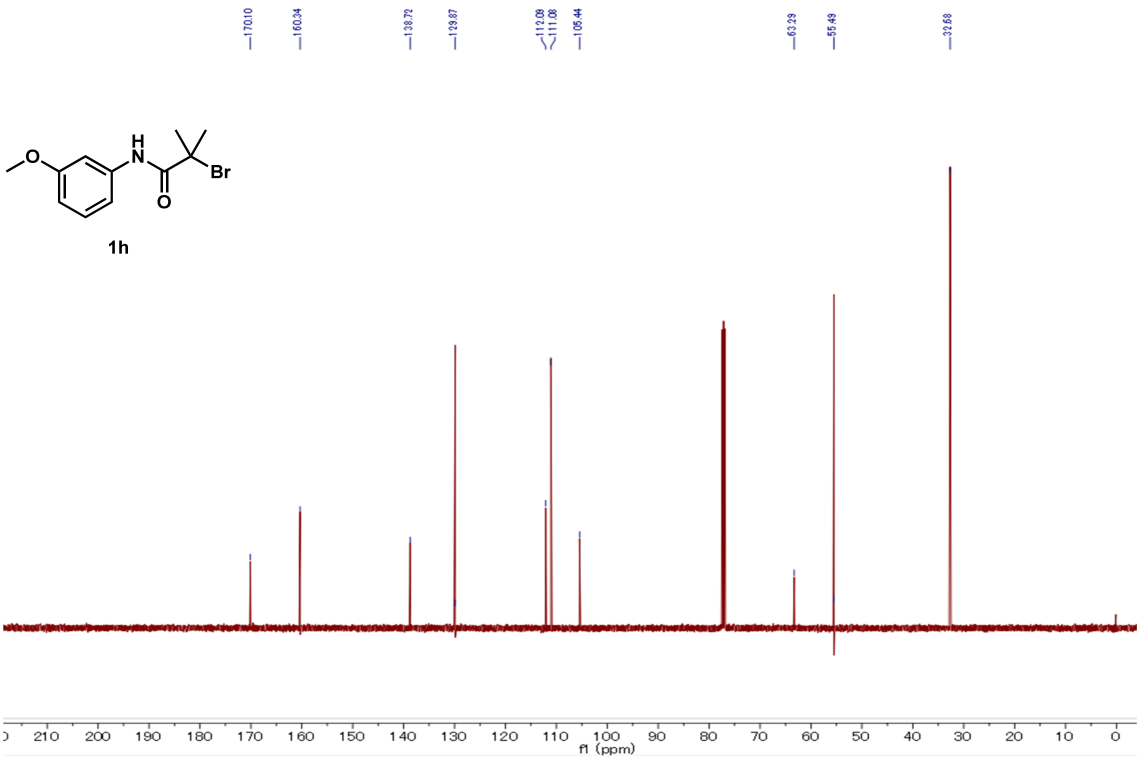
^{13}C NMR (125 MHz, $CDCl_3$)



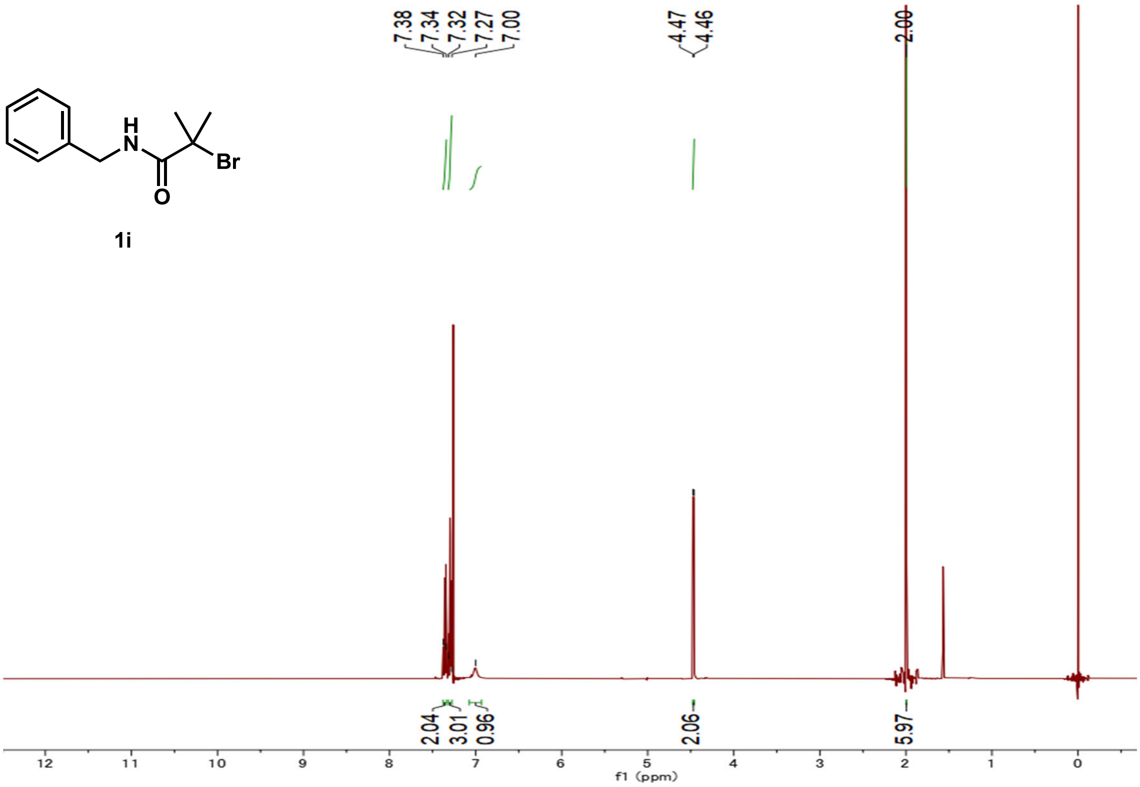
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

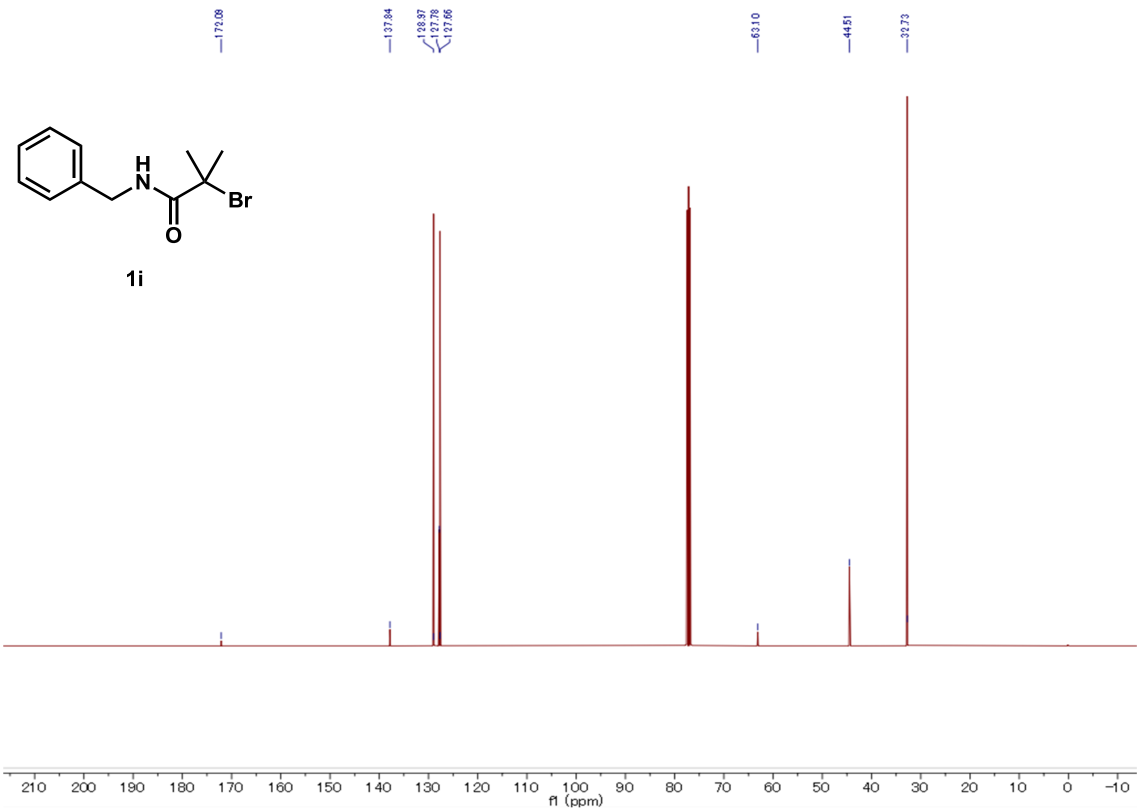


^{1}H NMR (500 MHz, $CDCl_3$)



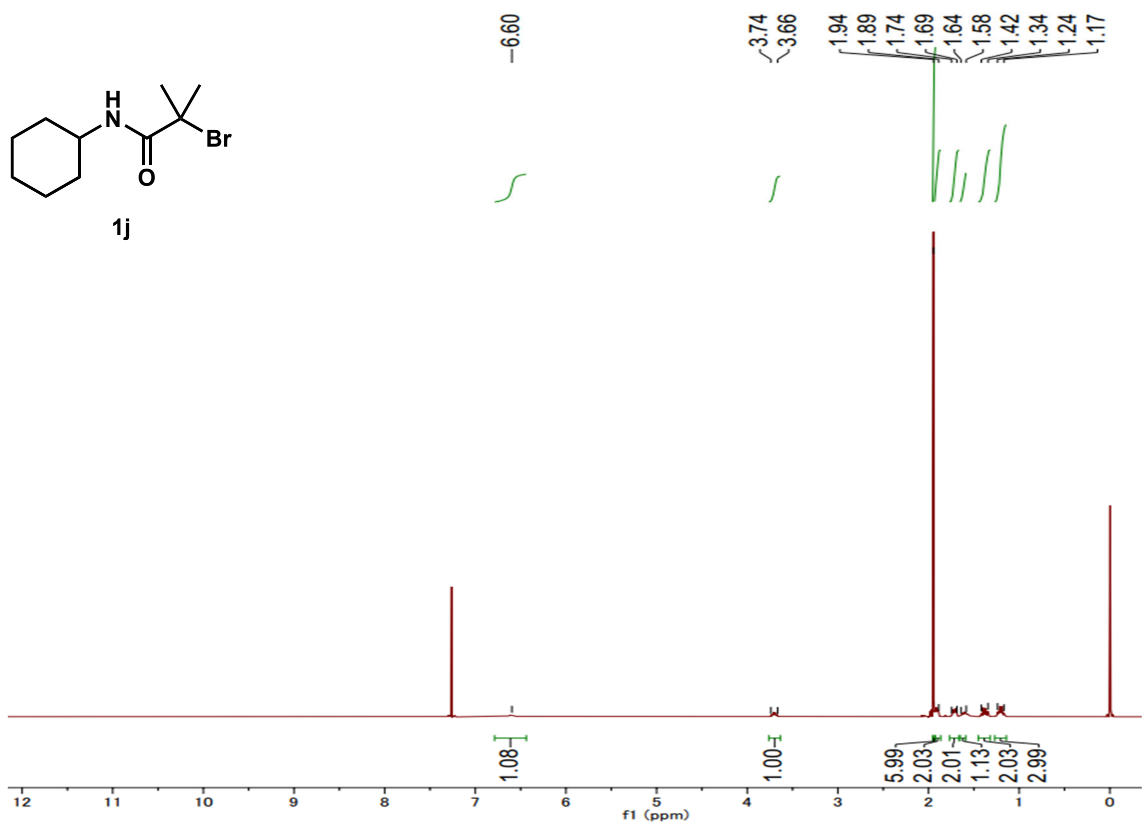
1i

^{13}C NMR (125 MHz, $CDCl_3$)

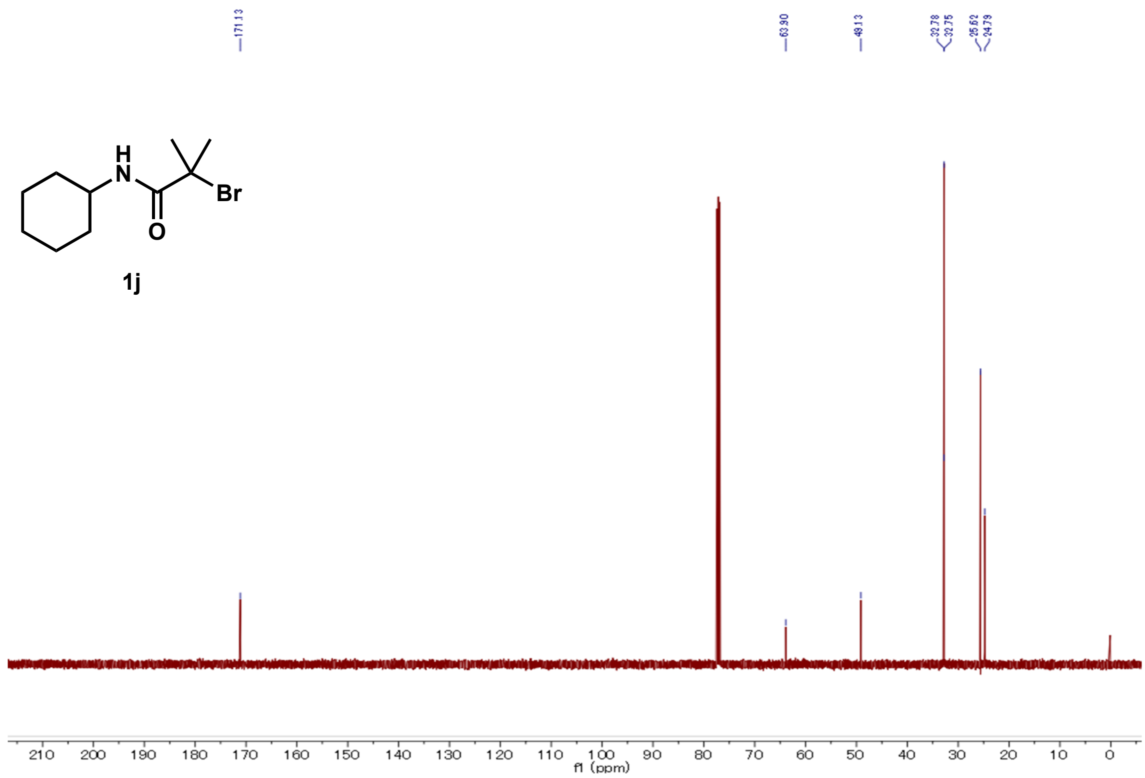


1i

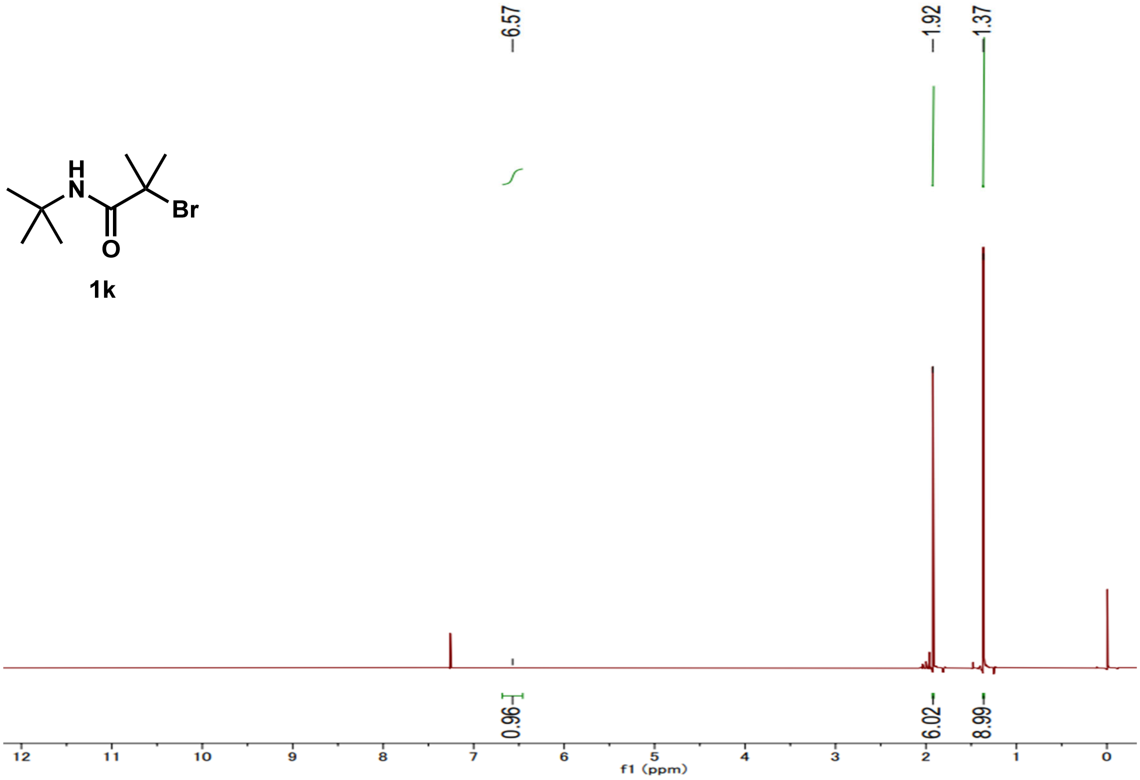
^{1}H NMR (500 MHz, $CDCl_3$)



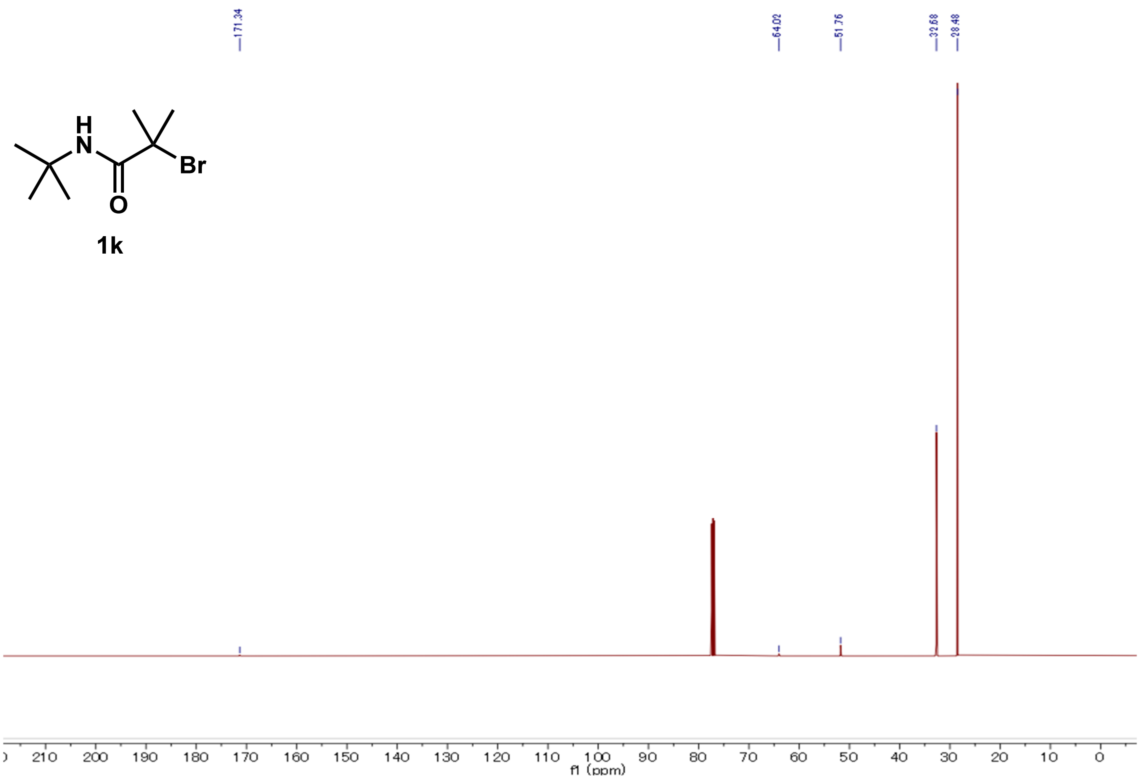
^{13}C NMR (125 MHz, $CDCl_3$)



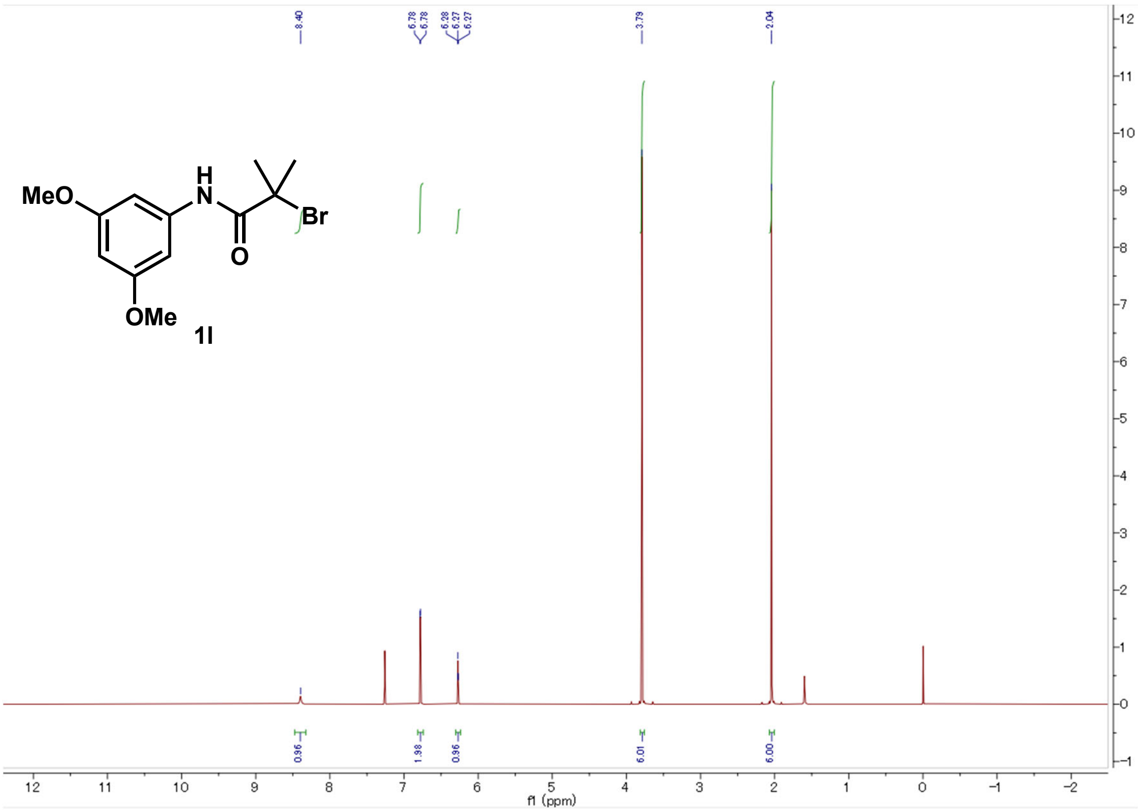
^{1}H NMR (500 MHz, $CDCl_3$)



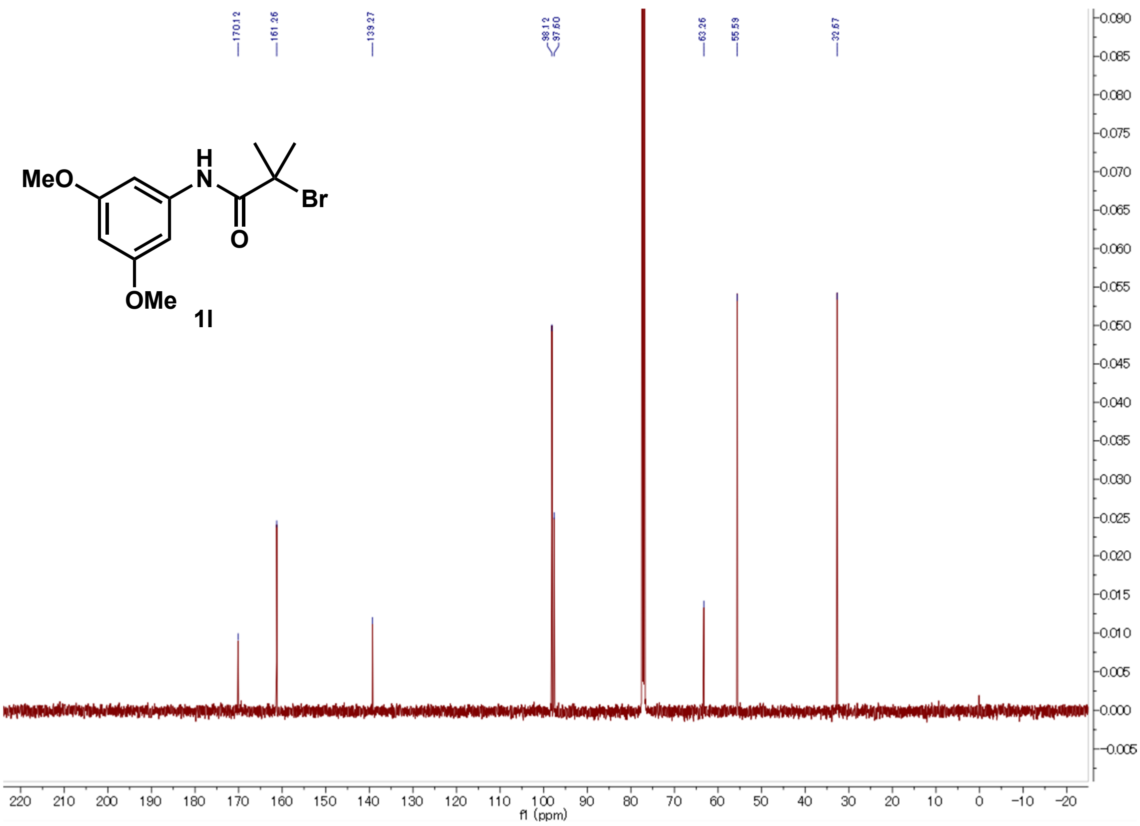
^{13}C NMR (125 MHz, $CDCl_3$)



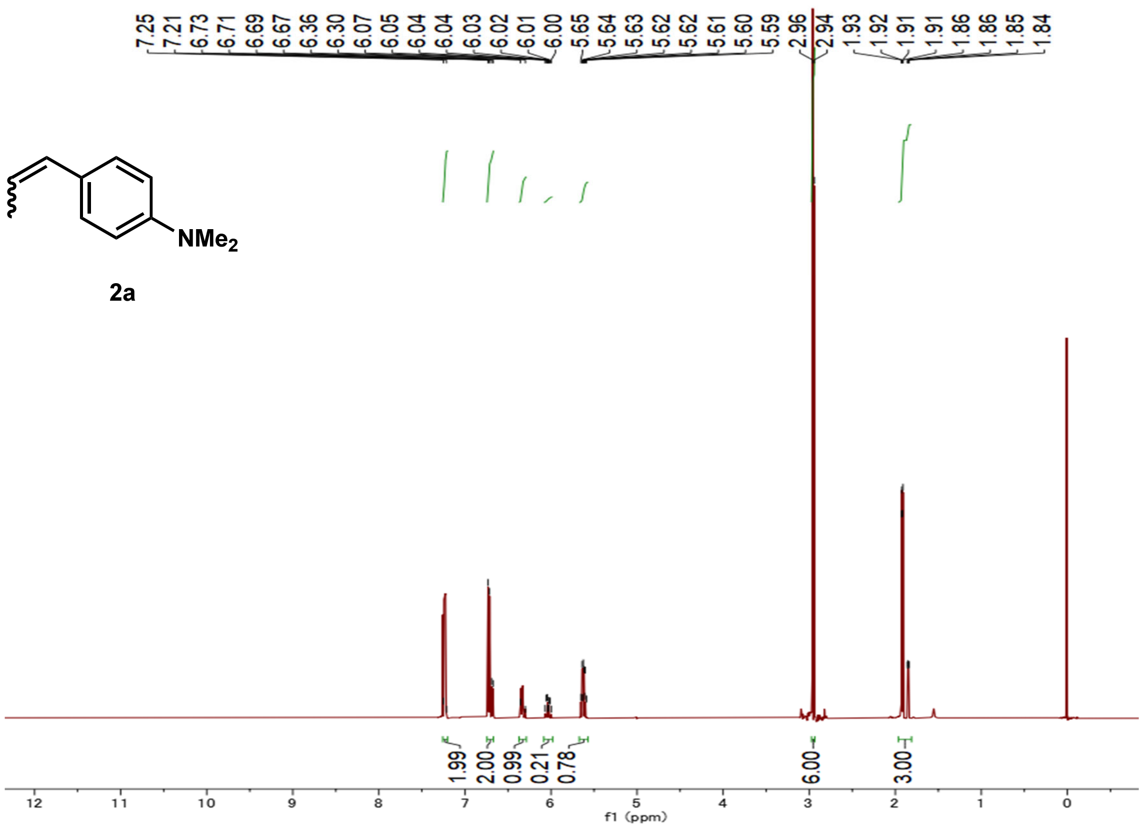
^{1}H NMR (500 MHz, $CDCl_3$)



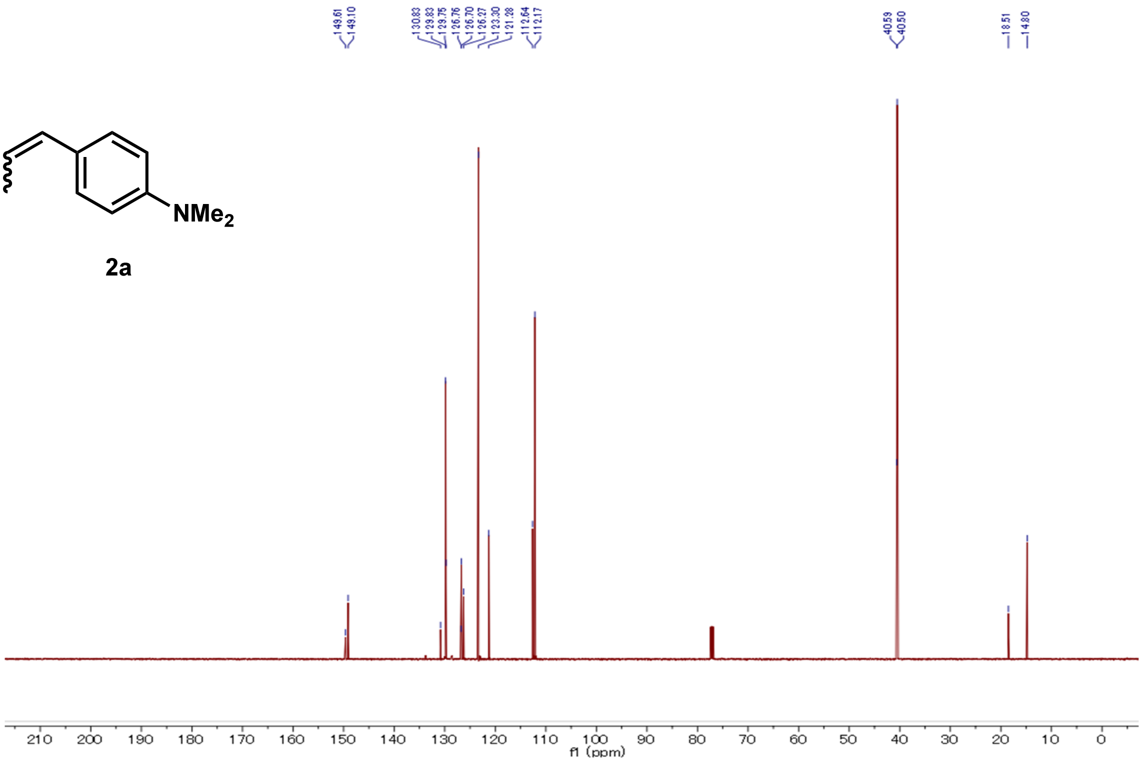
^{13}C NMR (125 MHz, $CDCl_3$)



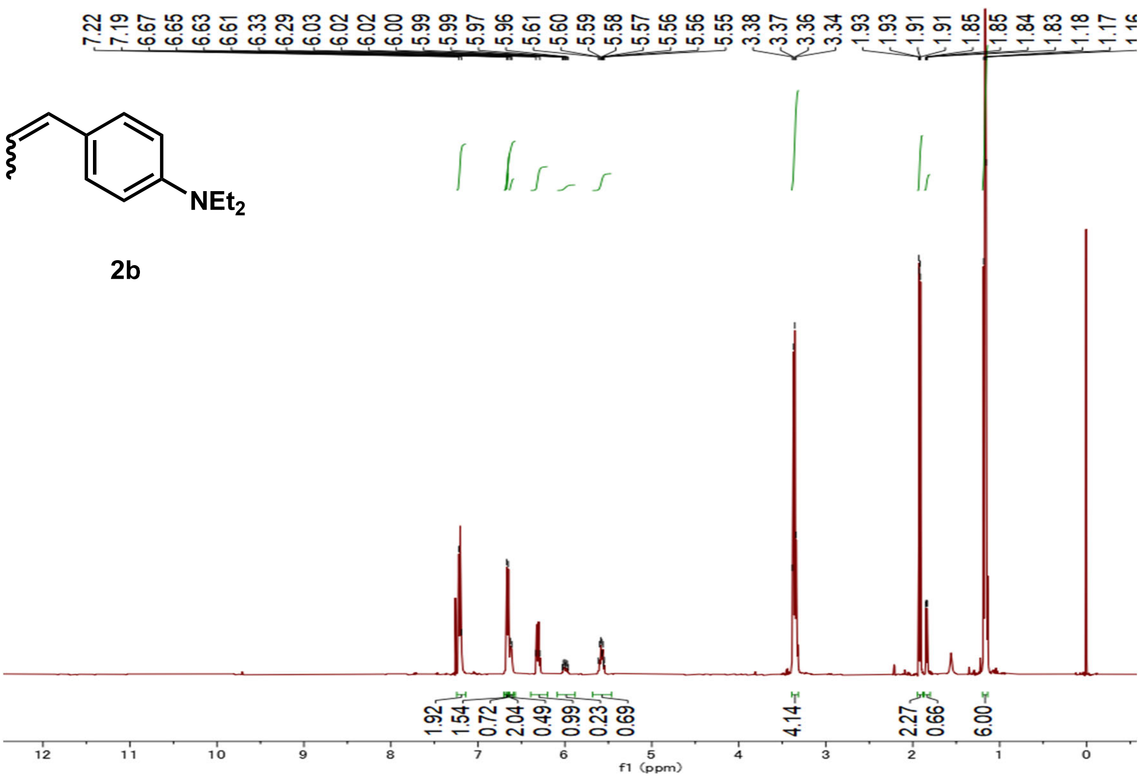
^{1}H NMR (500 MHz, $CDCl_3$)



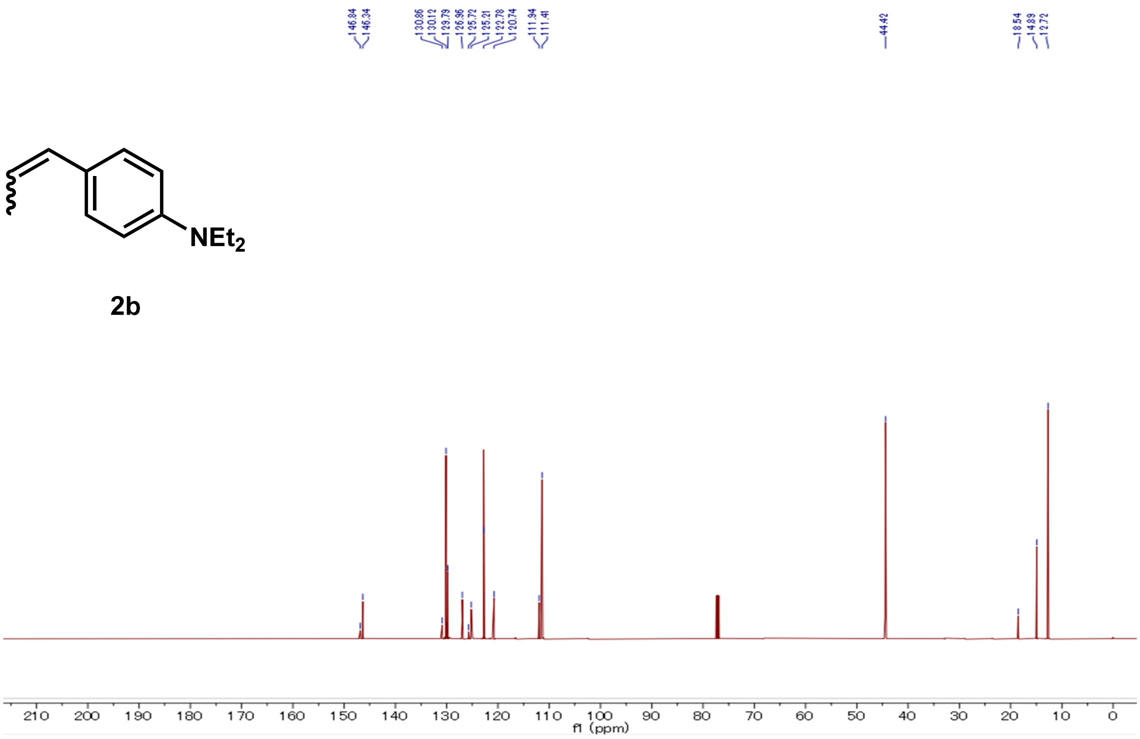
^{13}C NMR (125 MHz, $CDCl_3$)



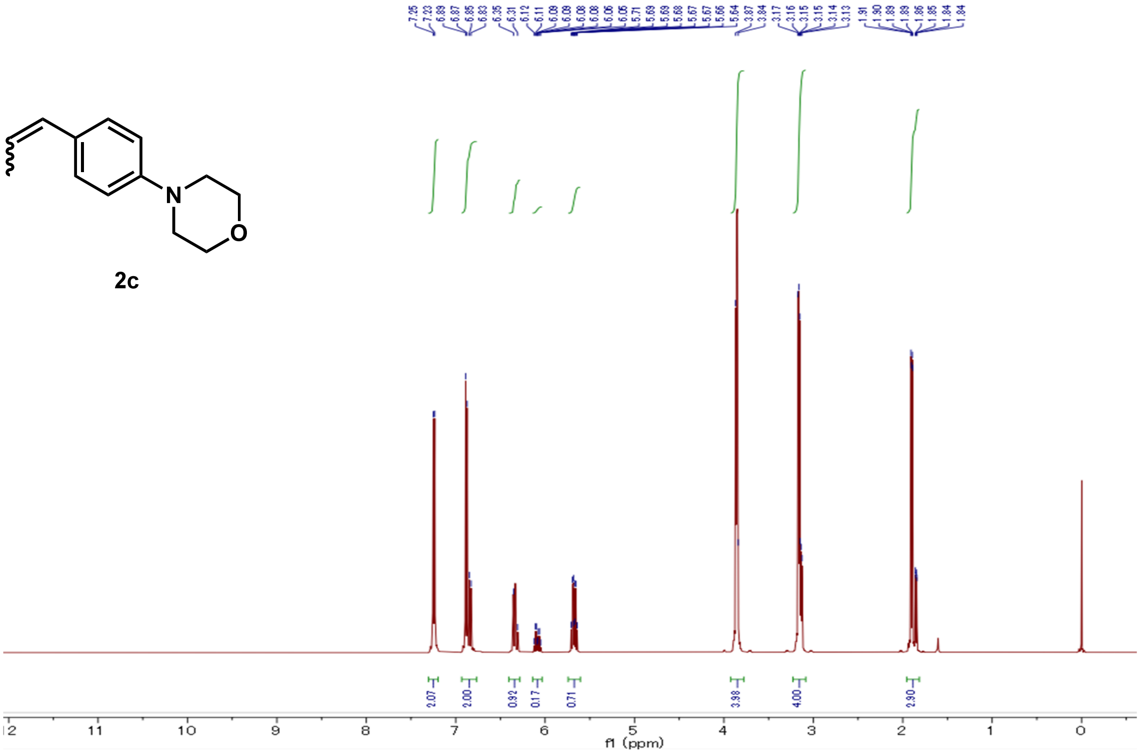
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

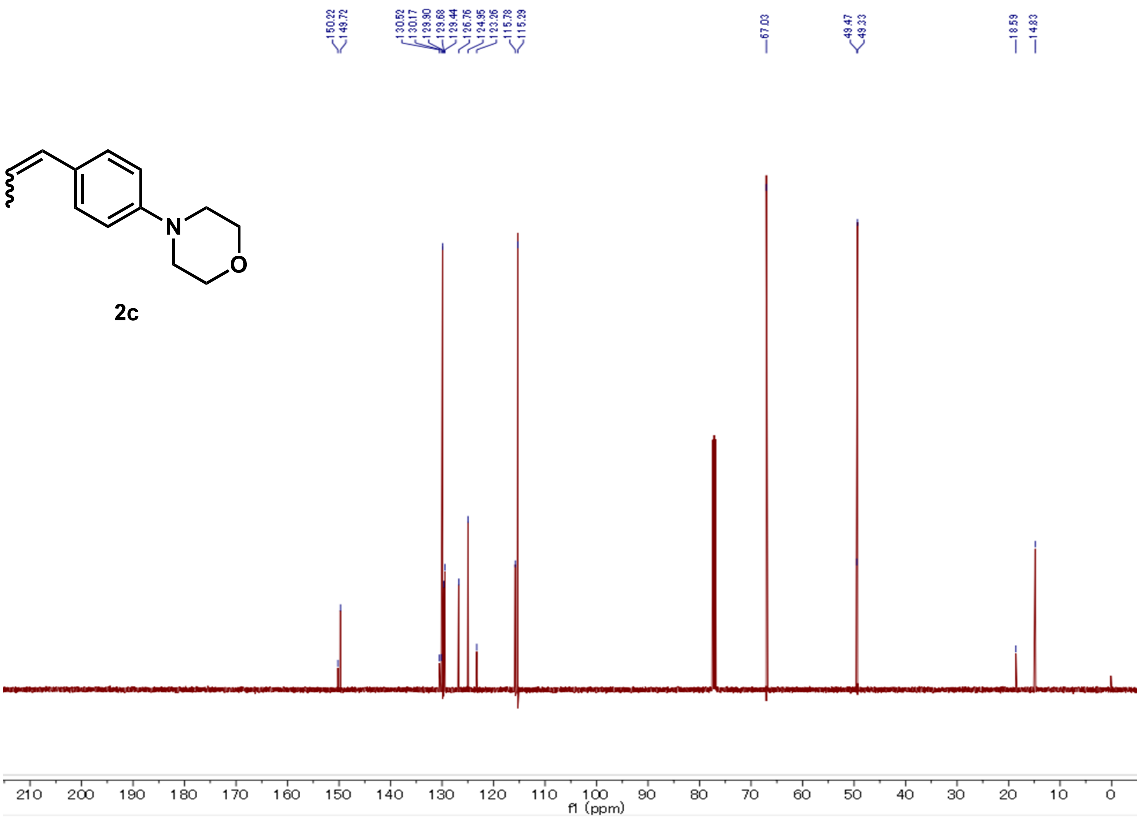


^{1}H NMR (500 MHz, $CDCl_3$)



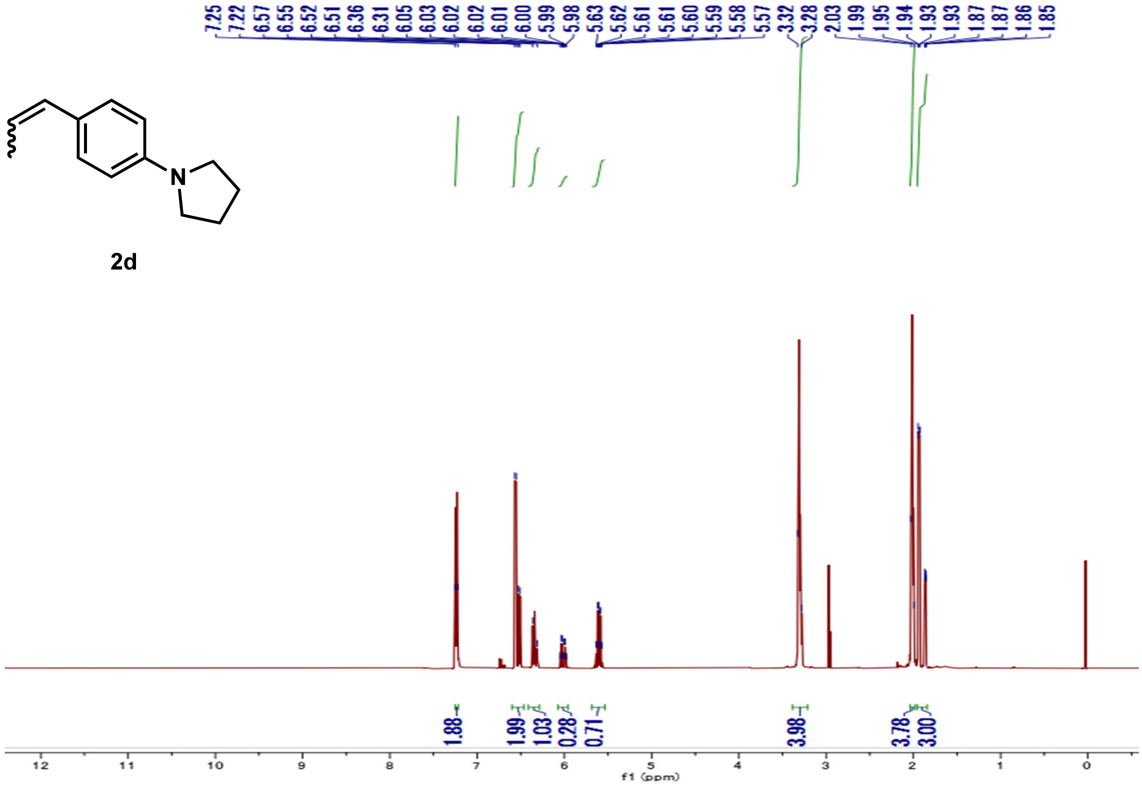
2c

^{13}C NMR (125 MHz, $CDCl_3$)

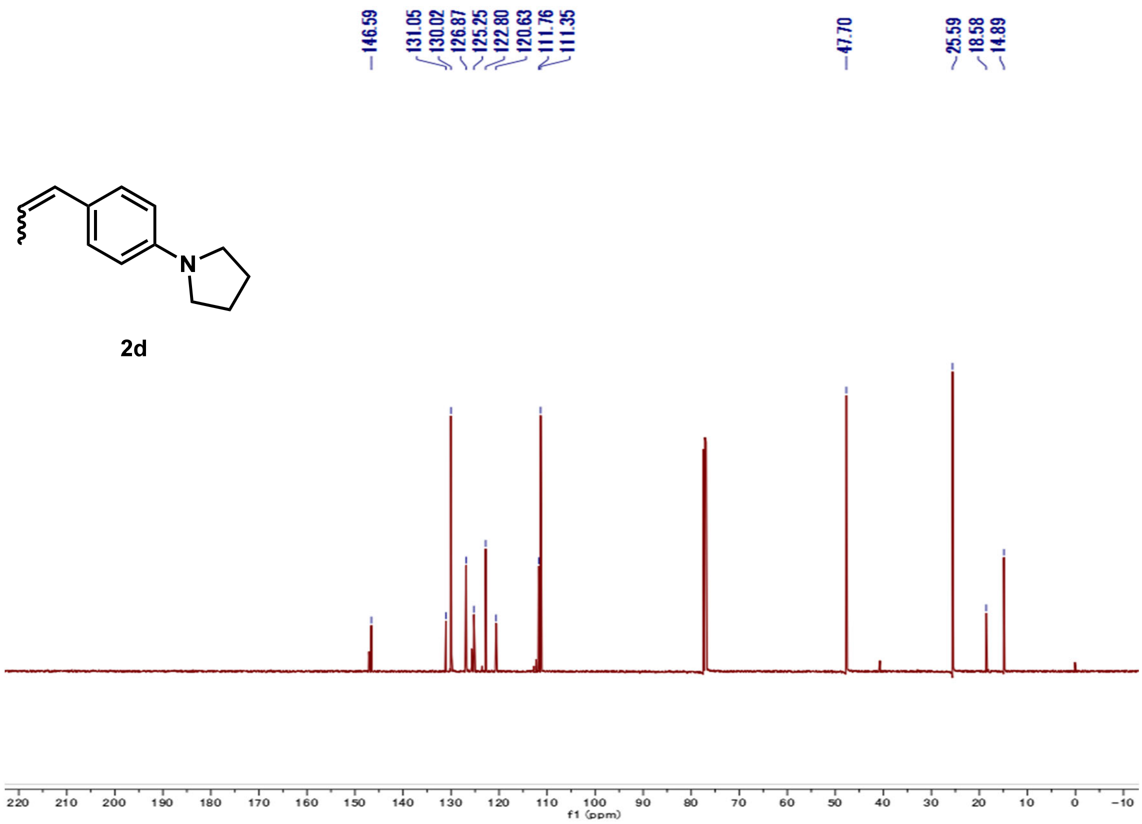


2c

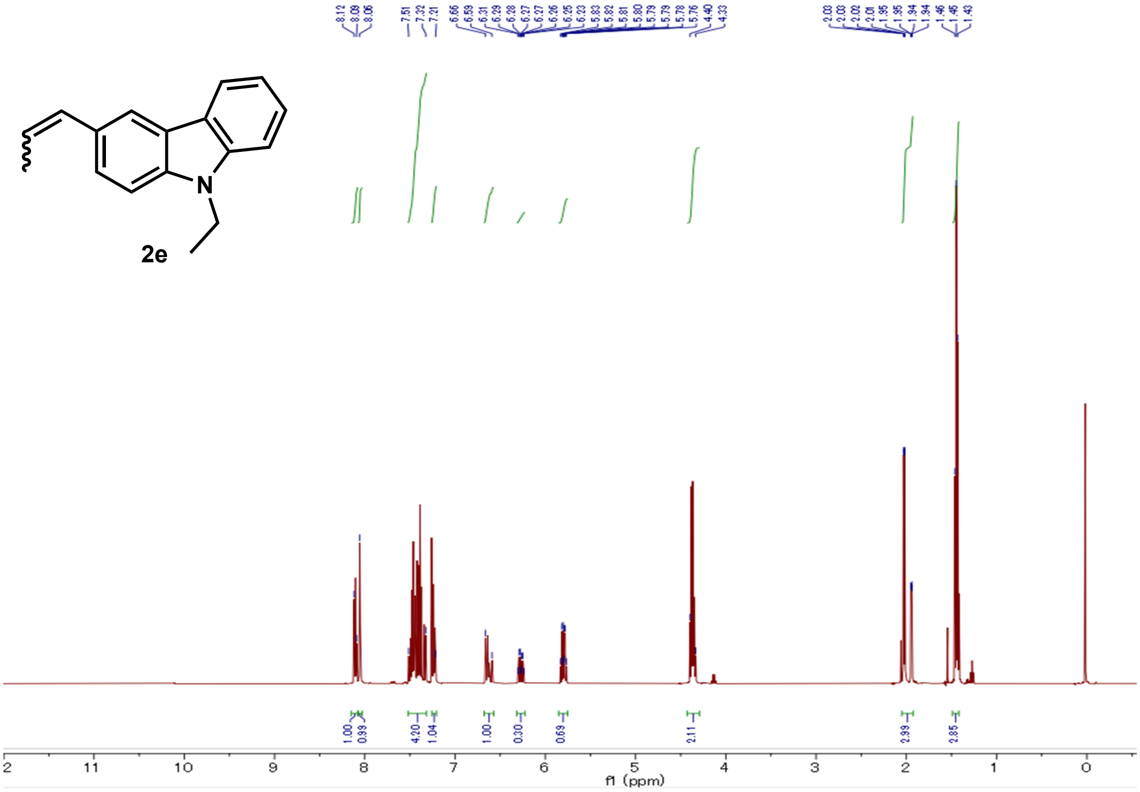
^{1}H NMR (500 MHz, $CDCl_3$)



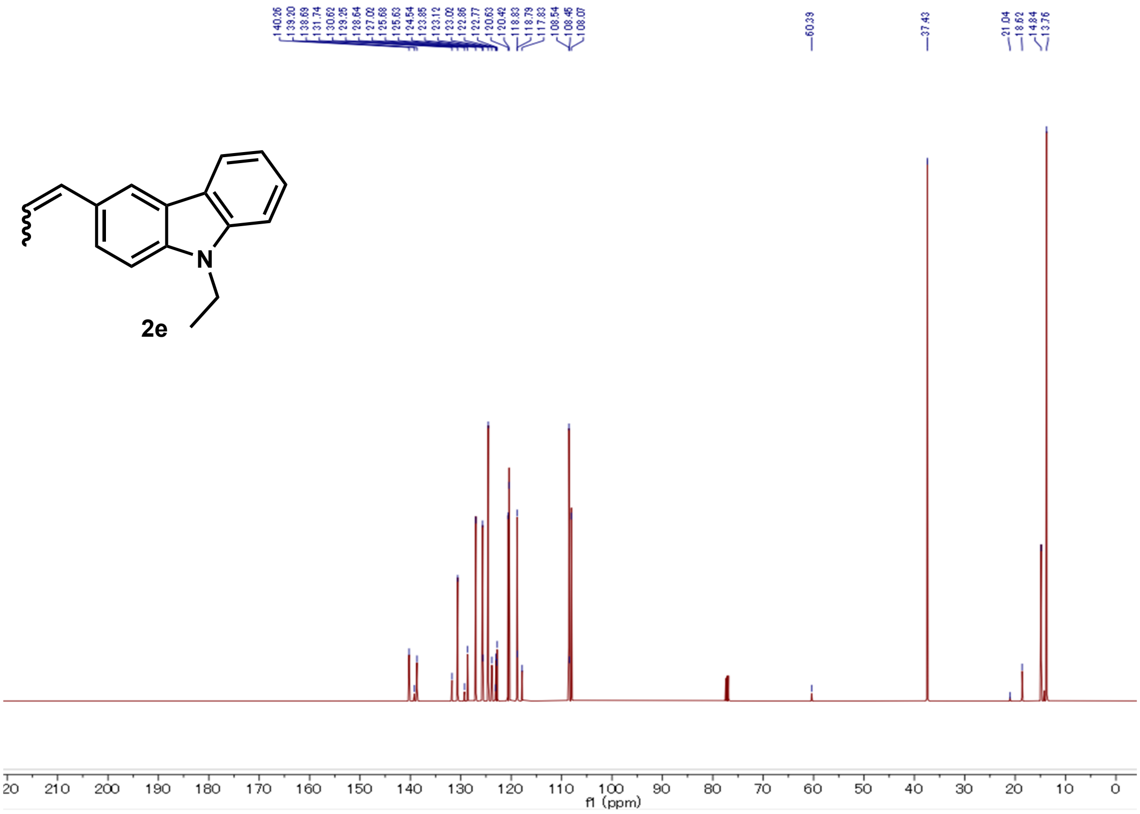
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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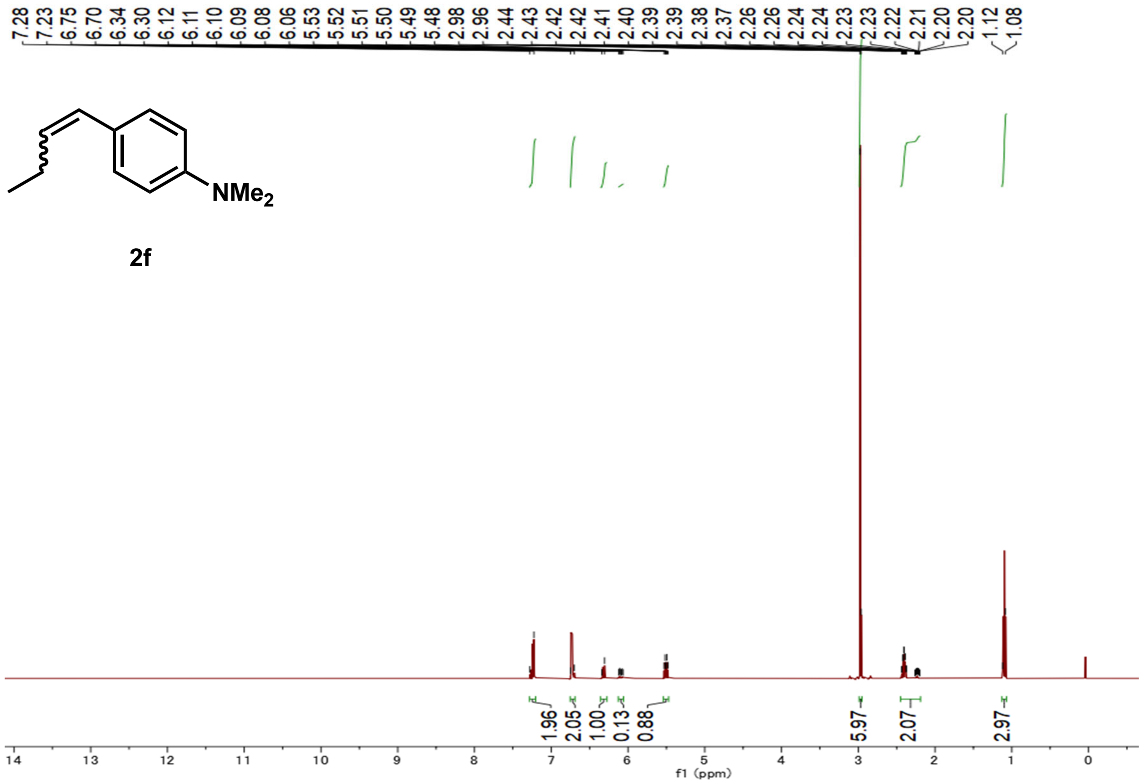
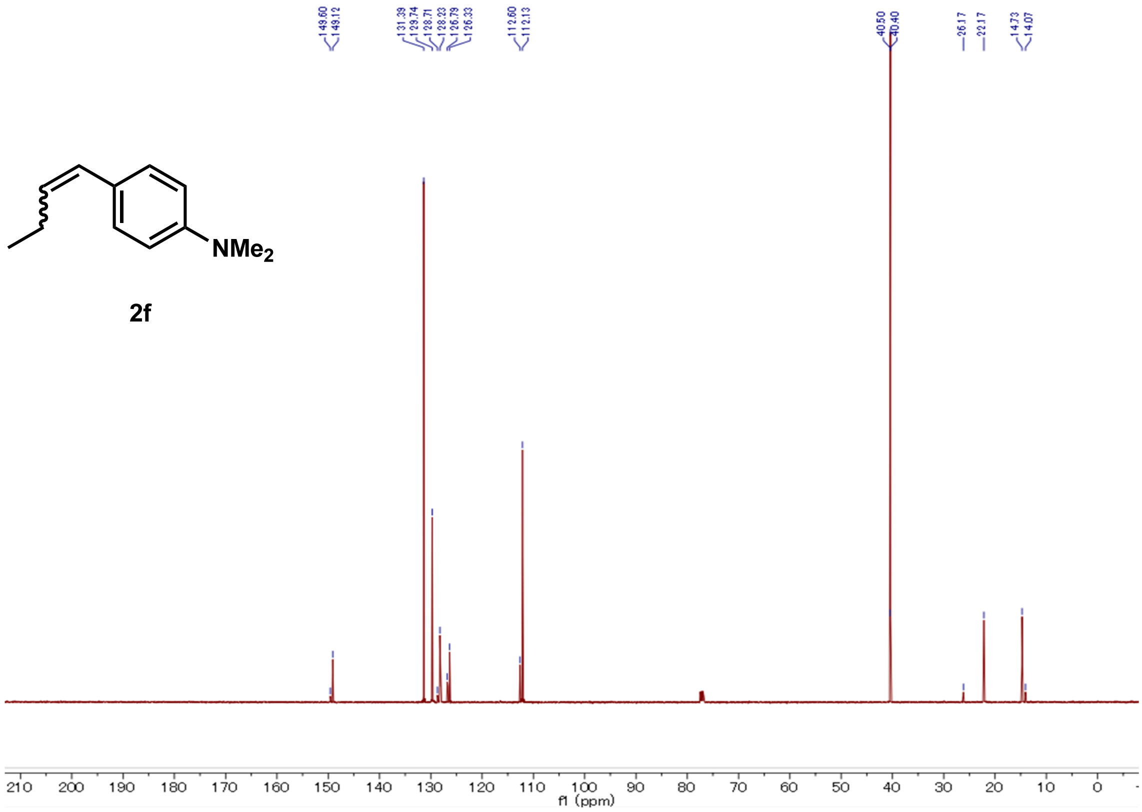
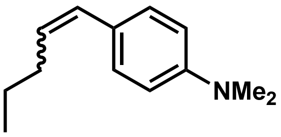


^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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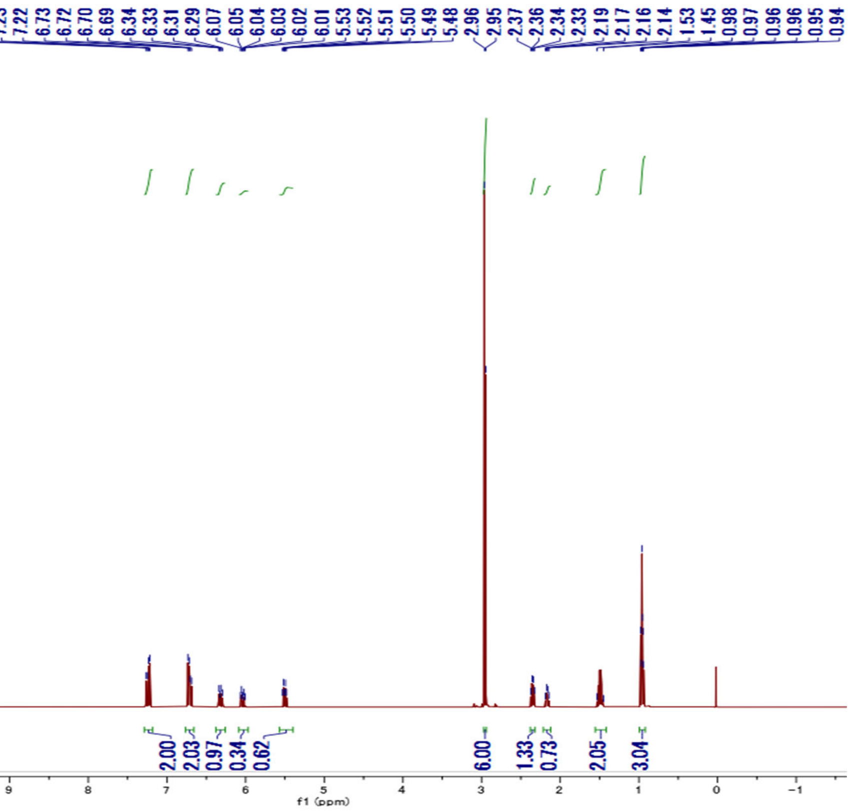
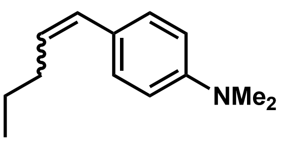


^{13}C NMR (125 MHz, $CDCl_3$)



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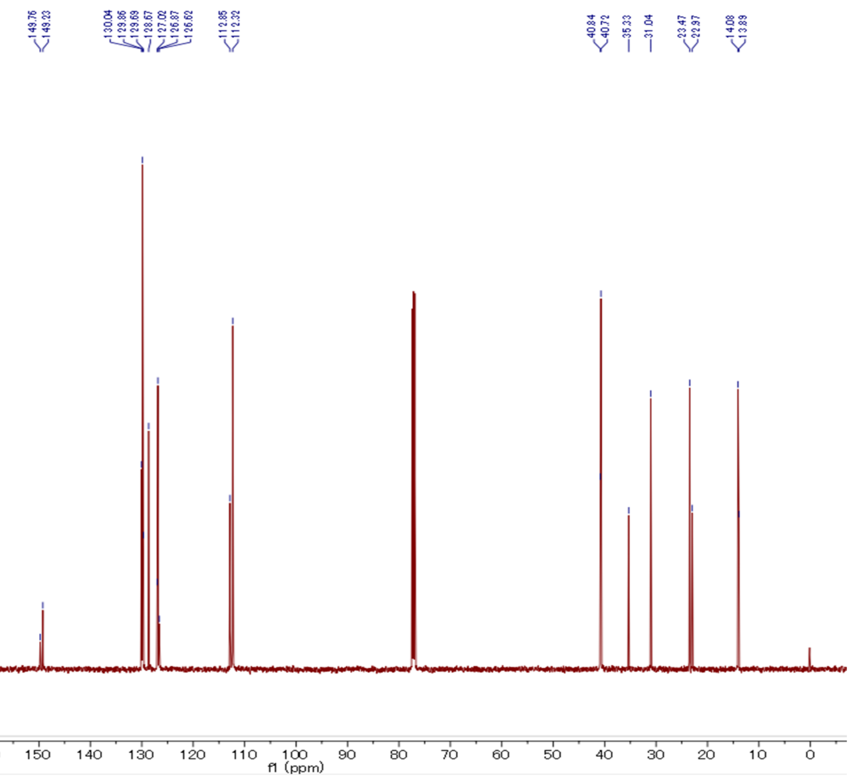

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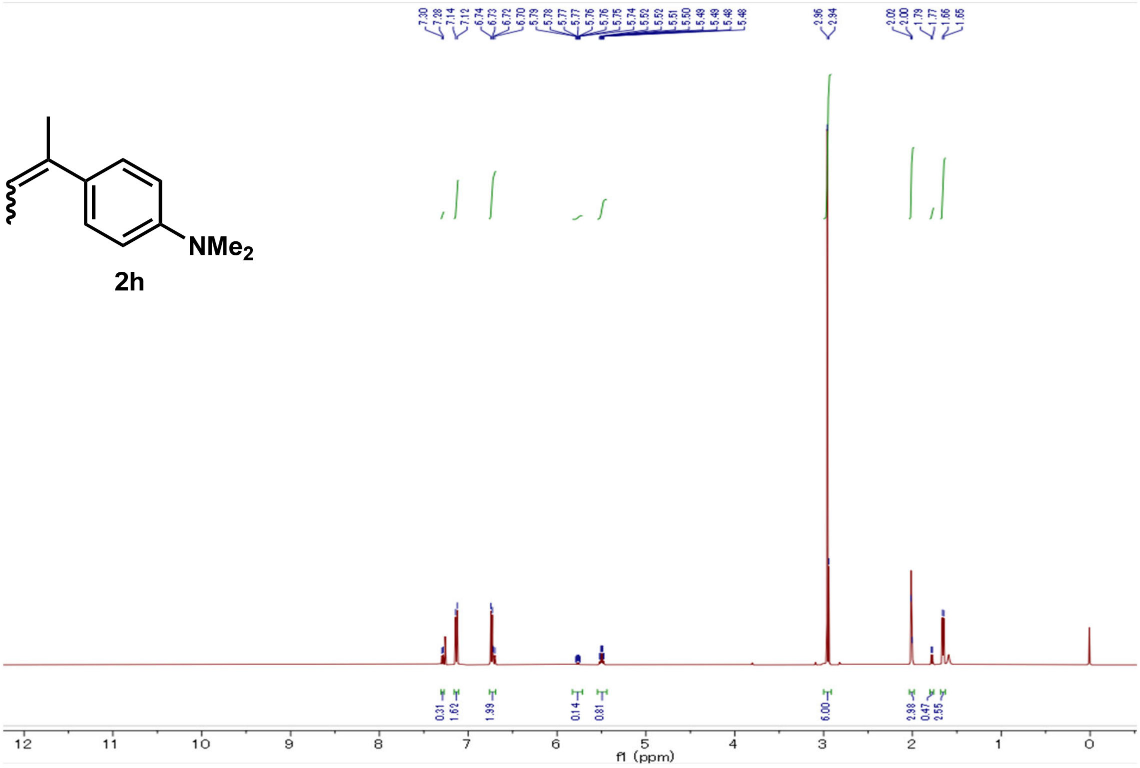

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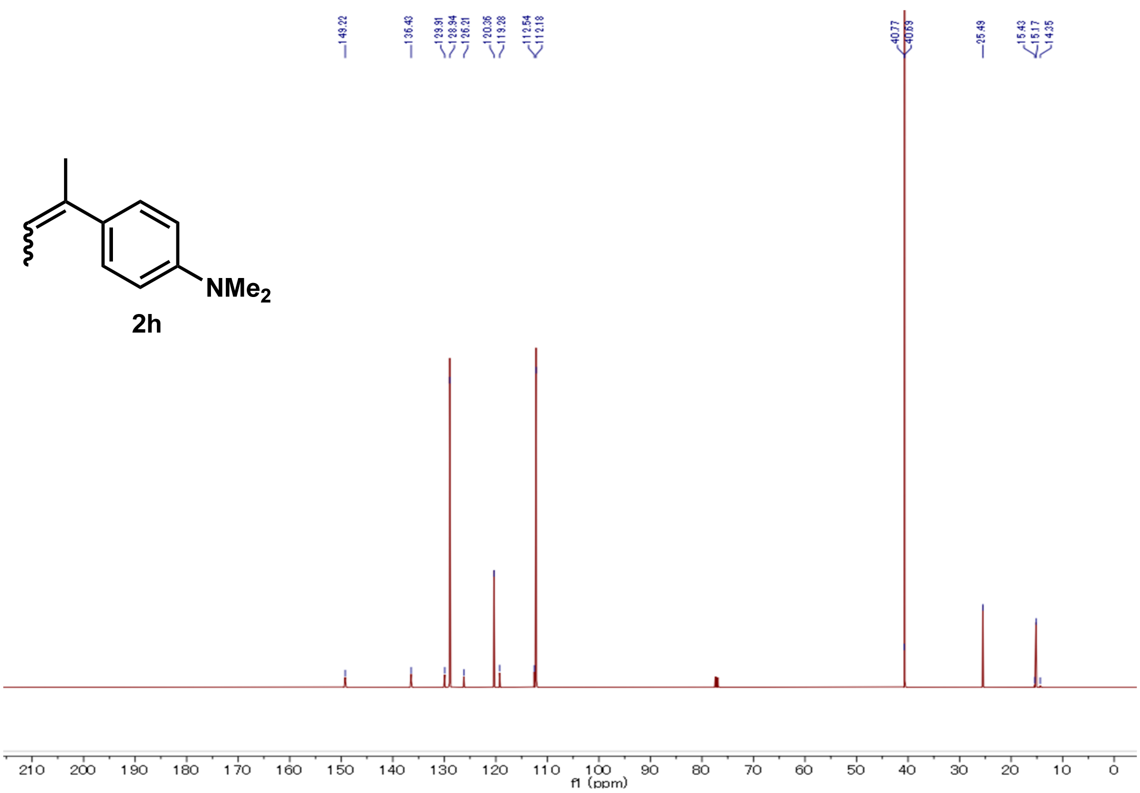
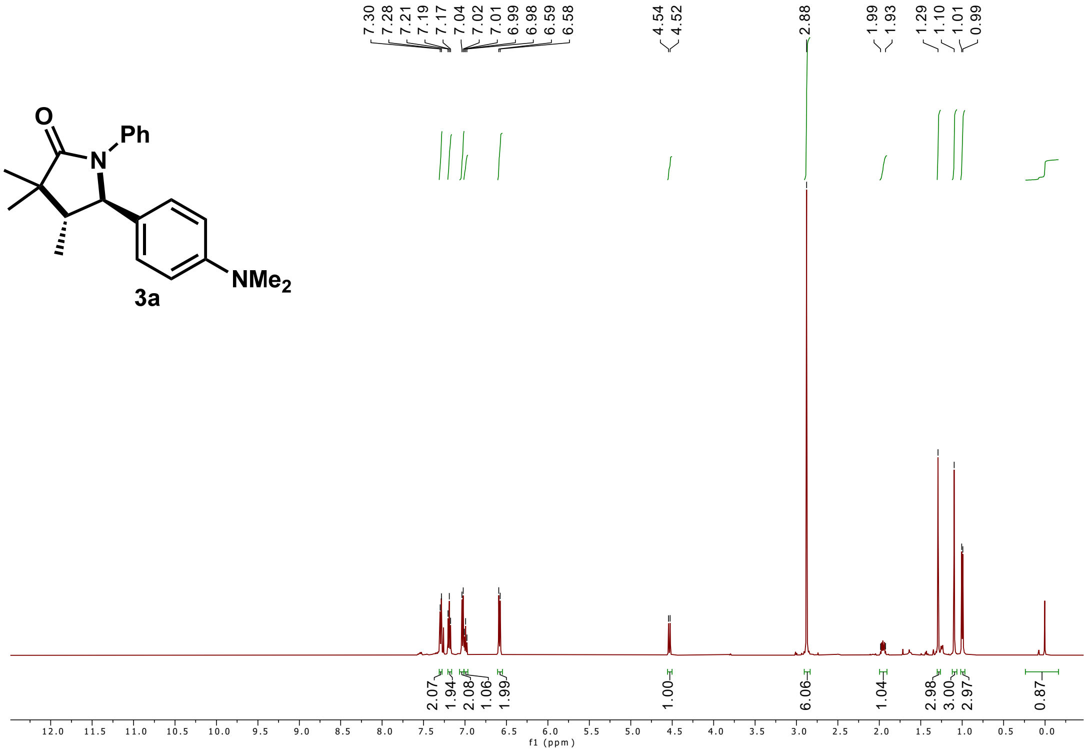


[1]H NMR (500 MHz, $CDCl_3$)



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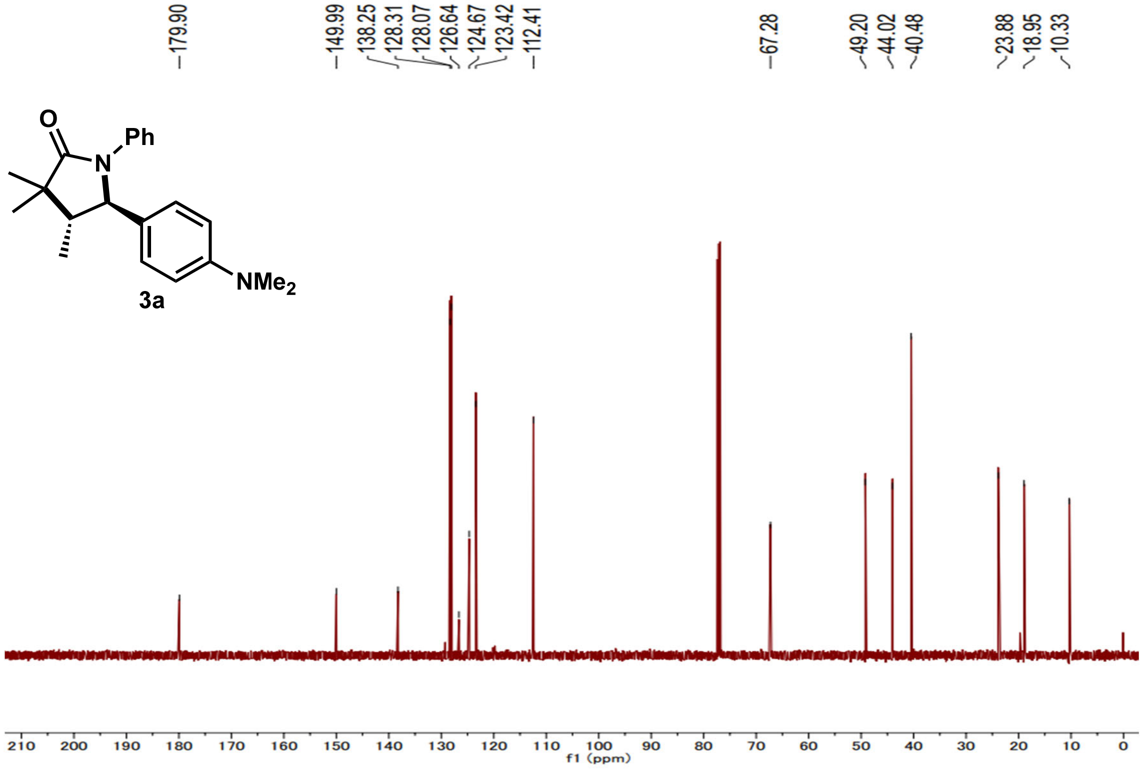

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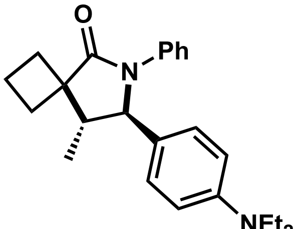
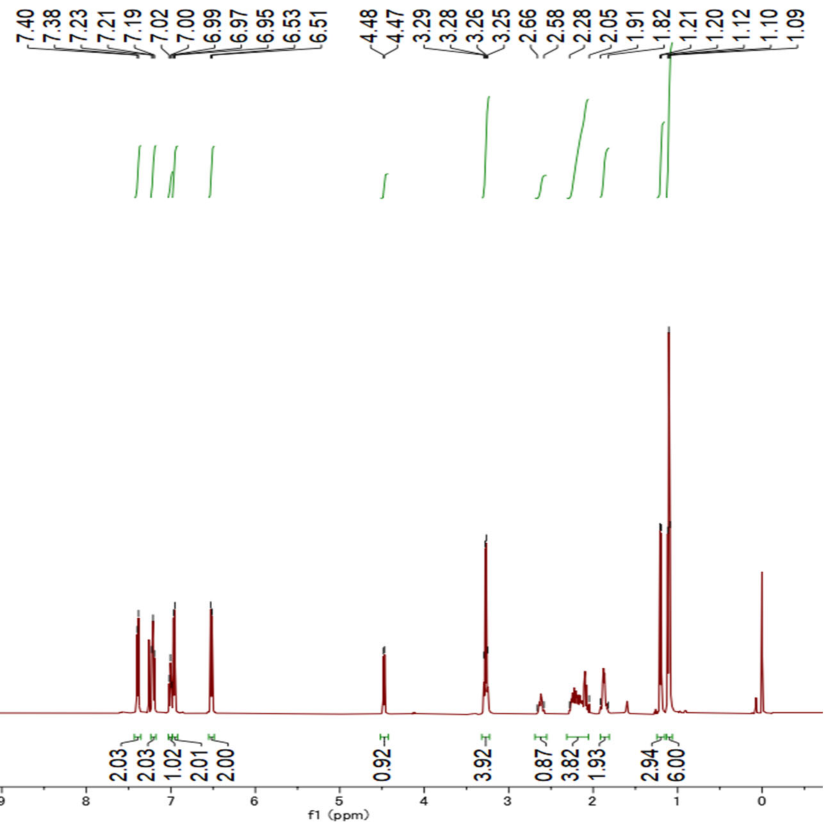


3b



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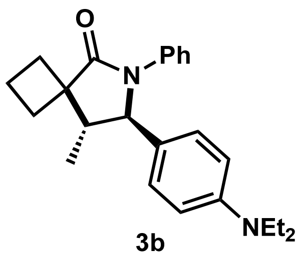

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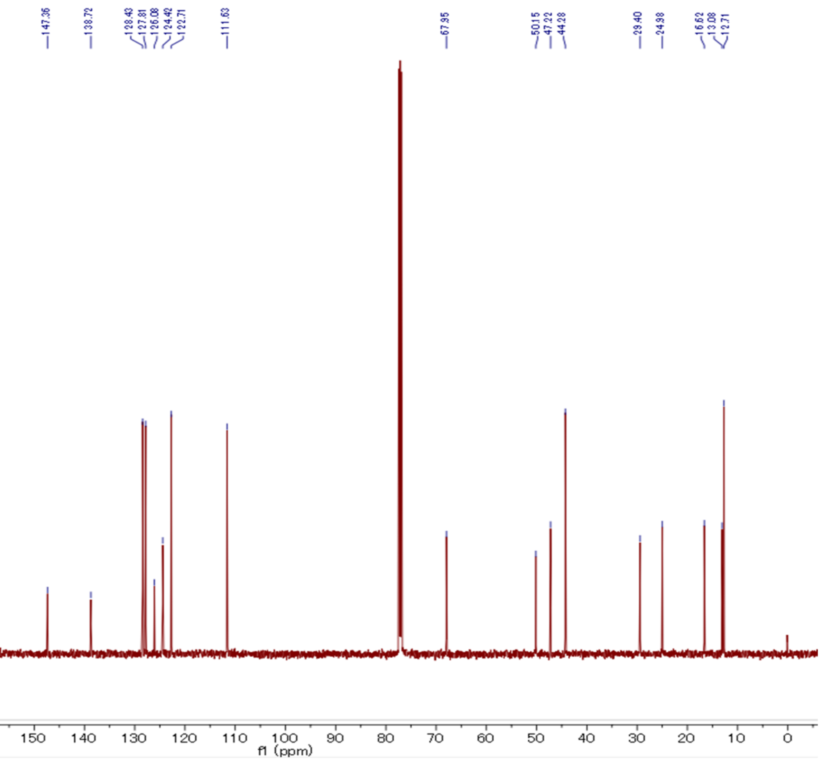

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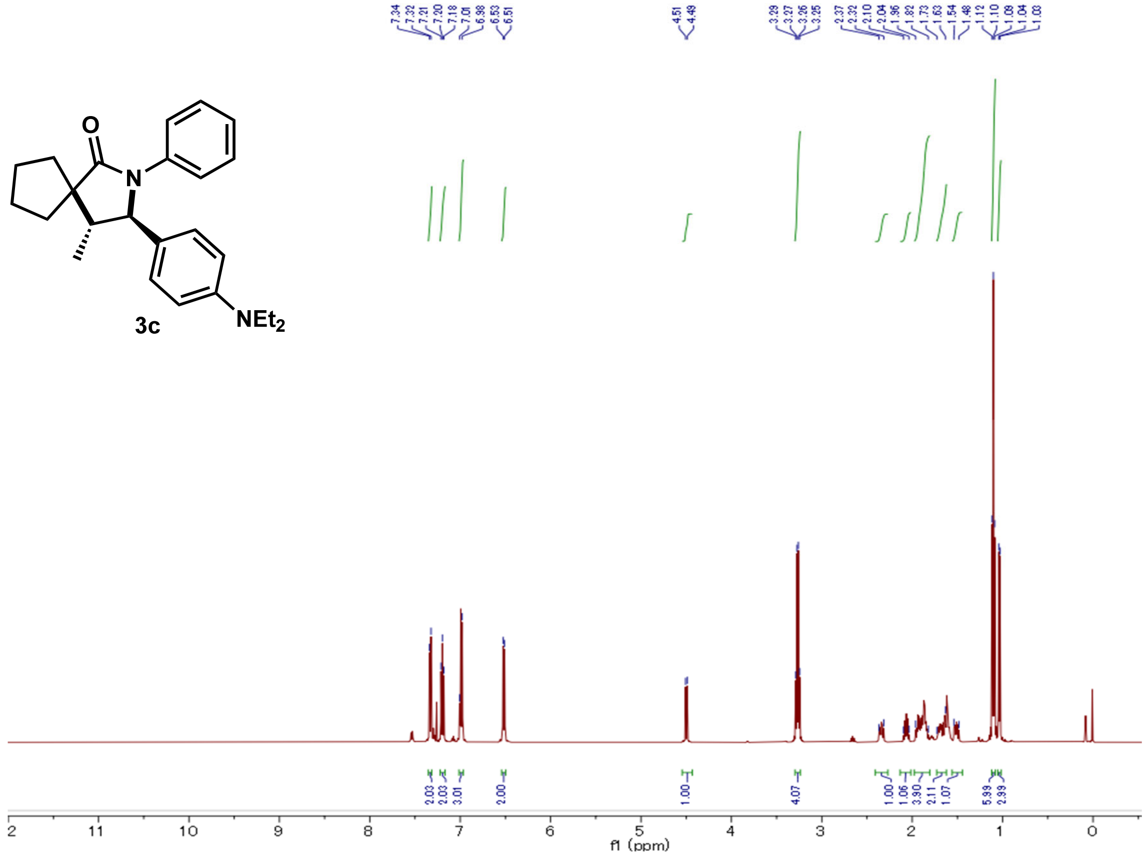

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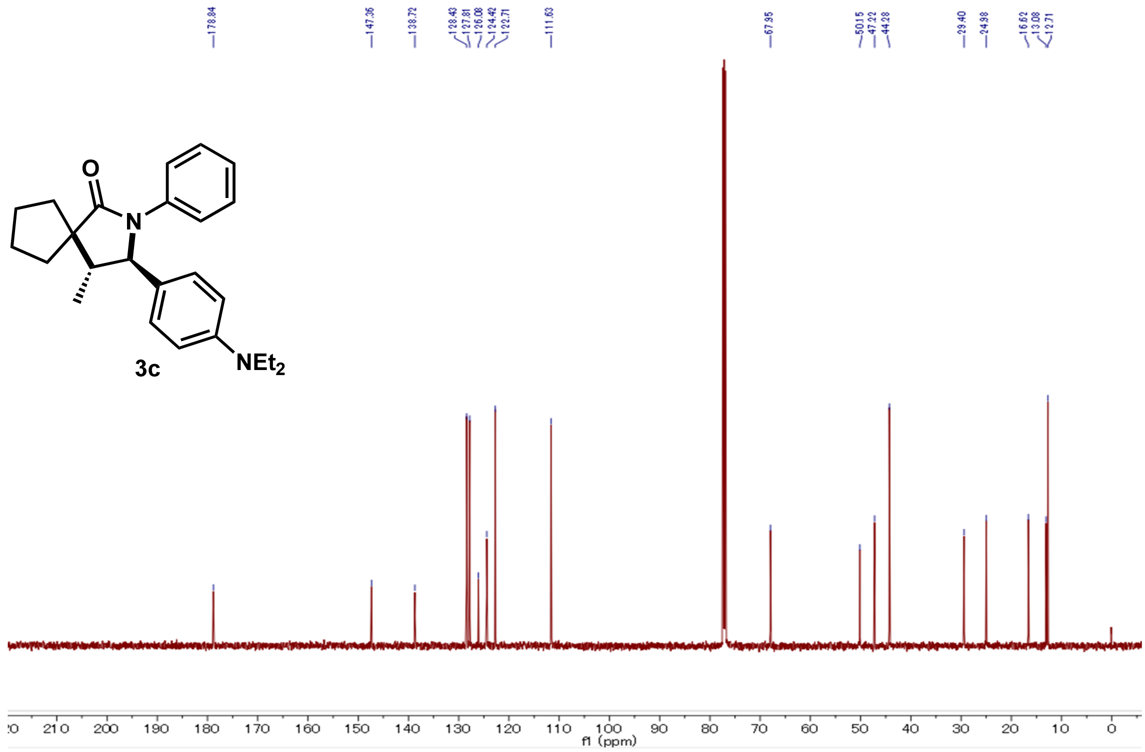

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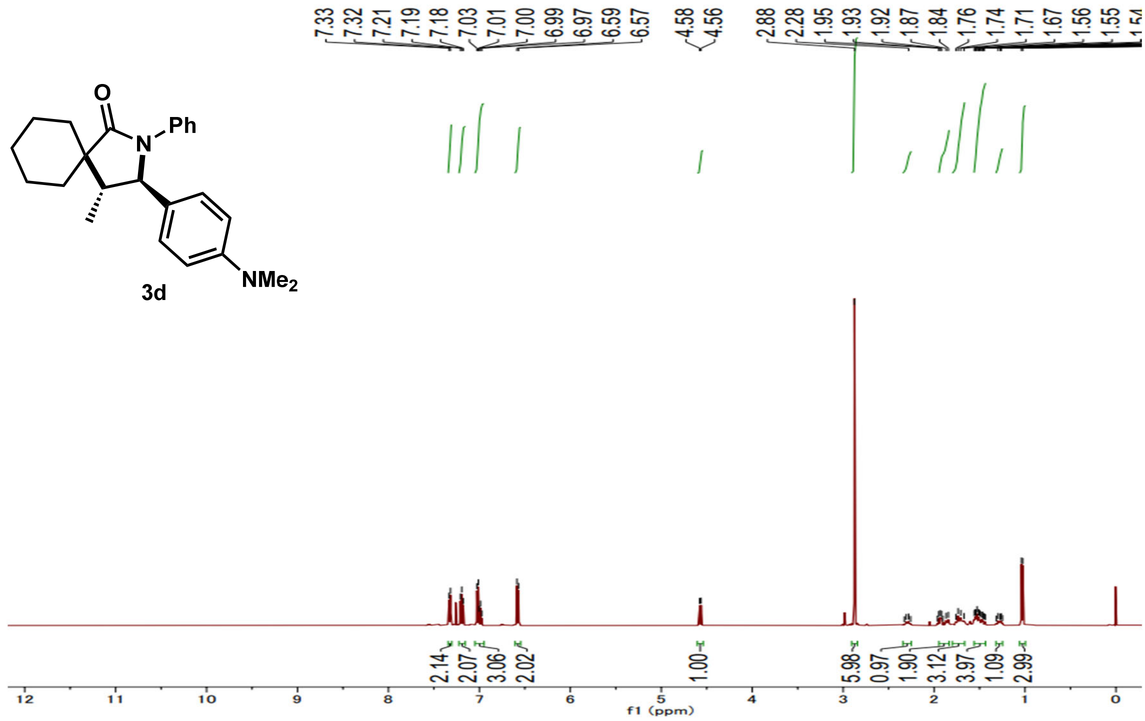

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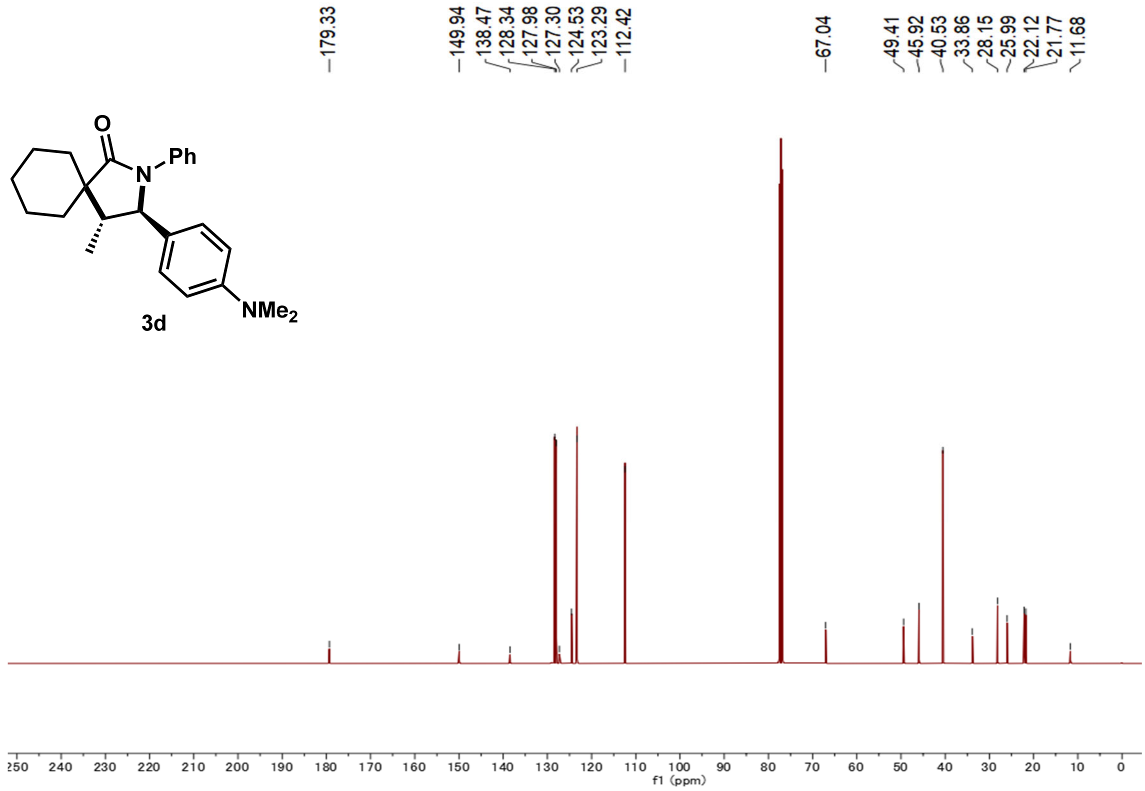

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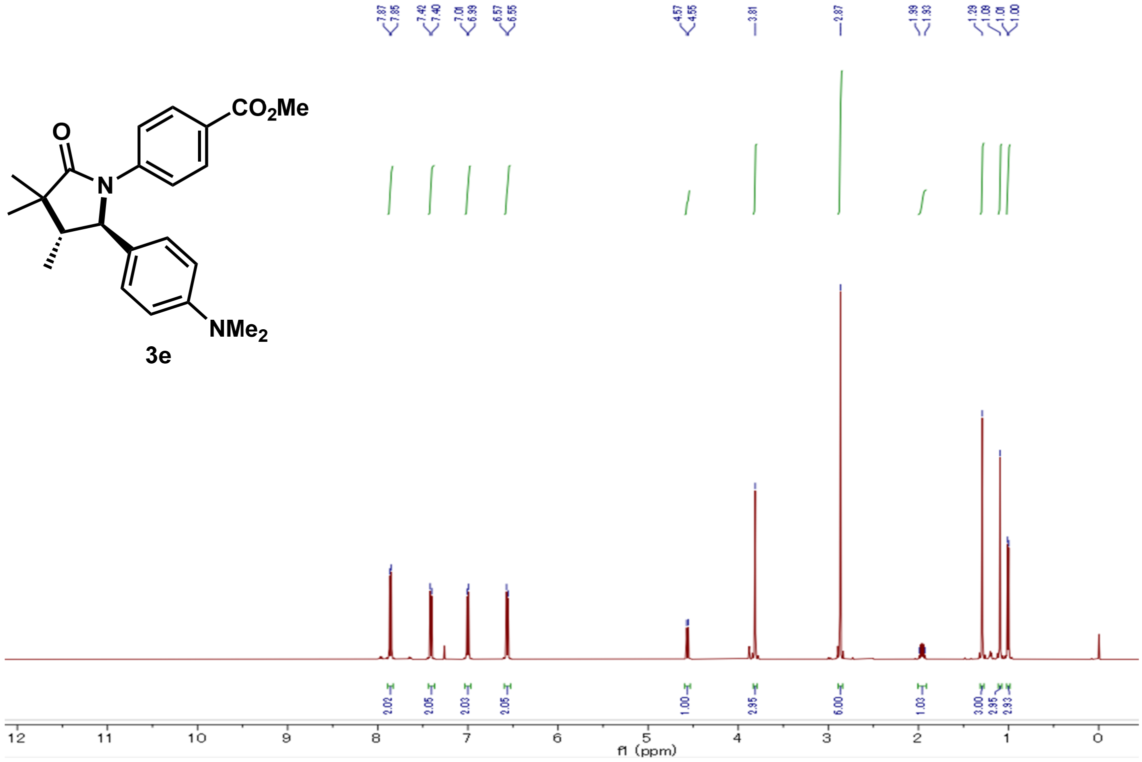

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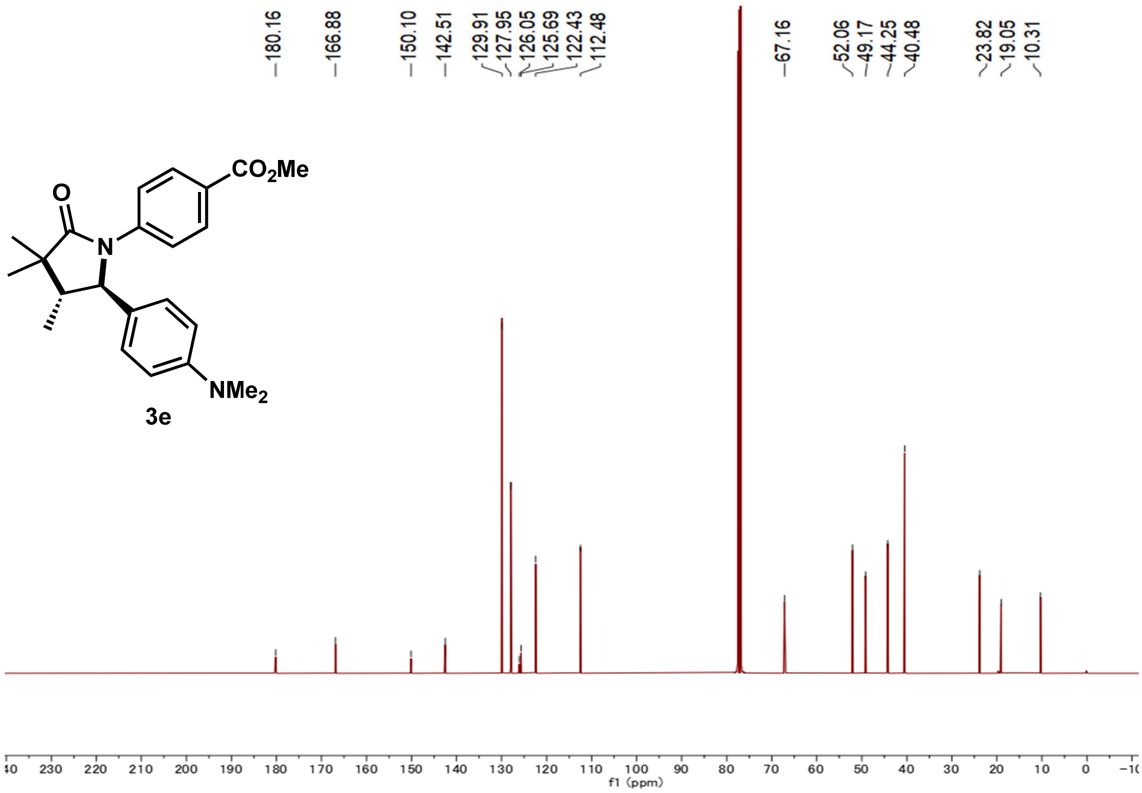

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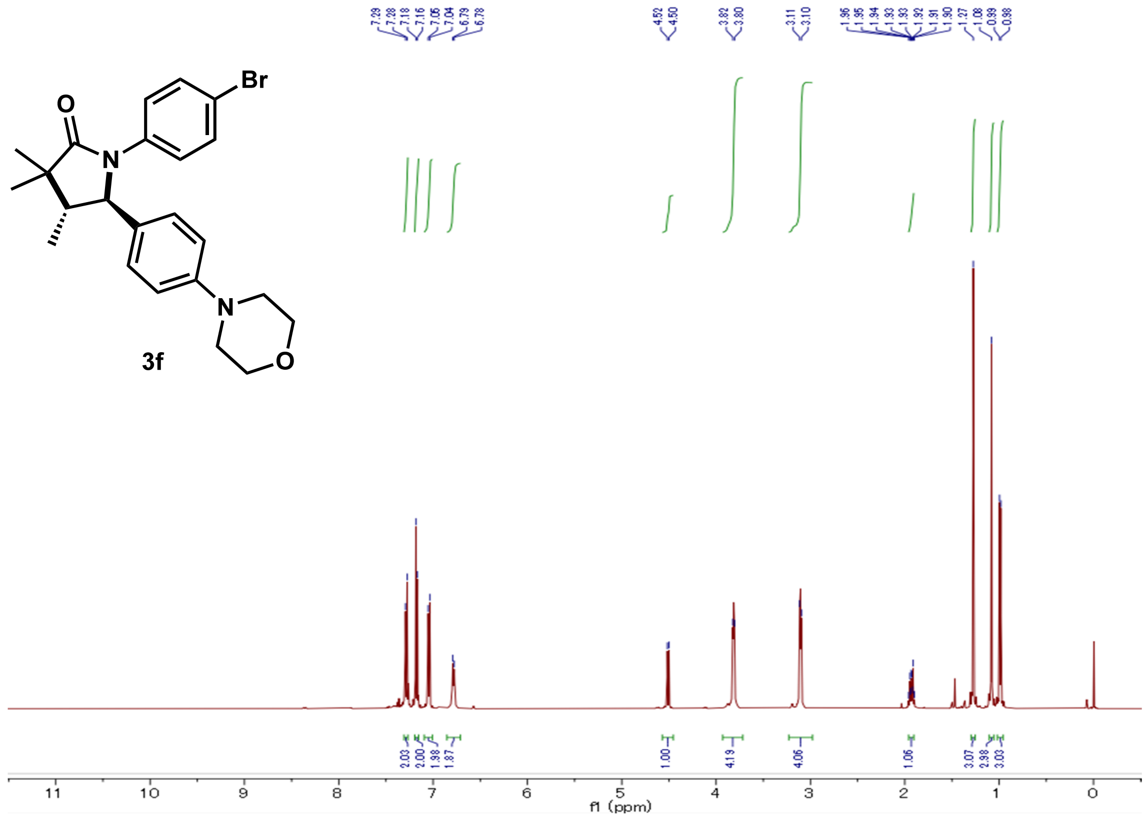

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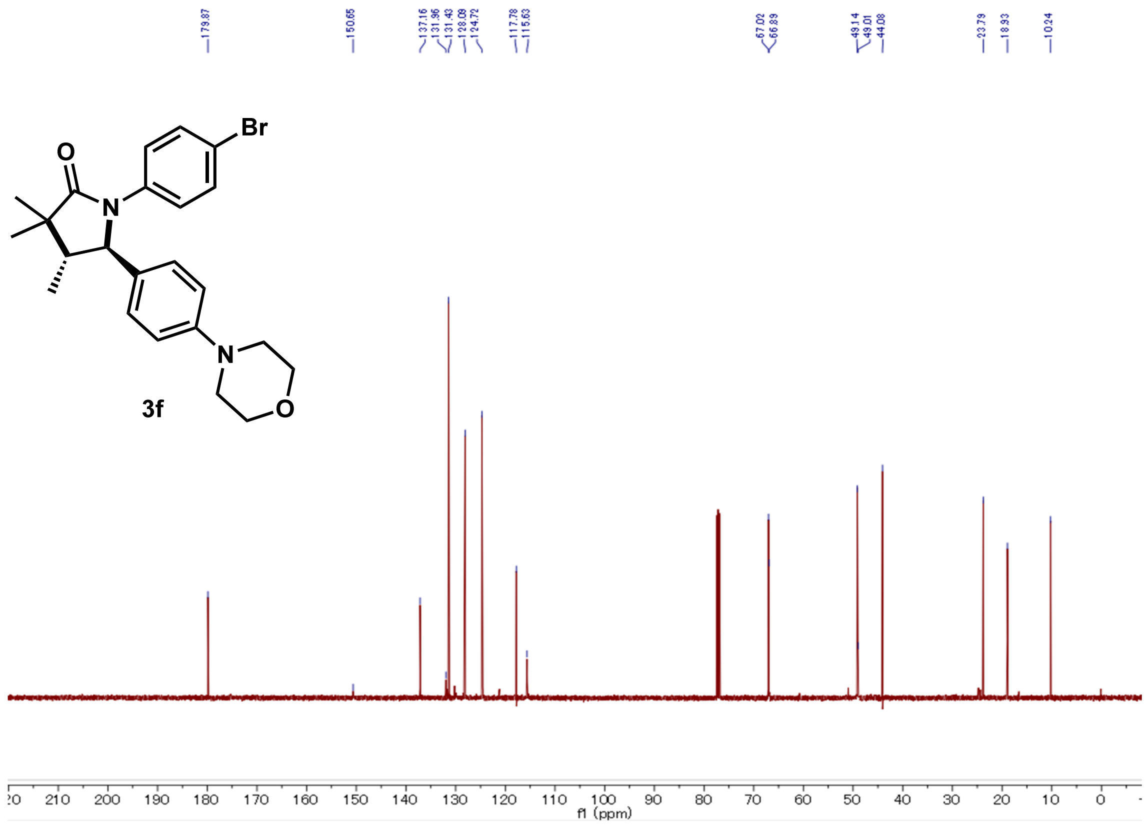

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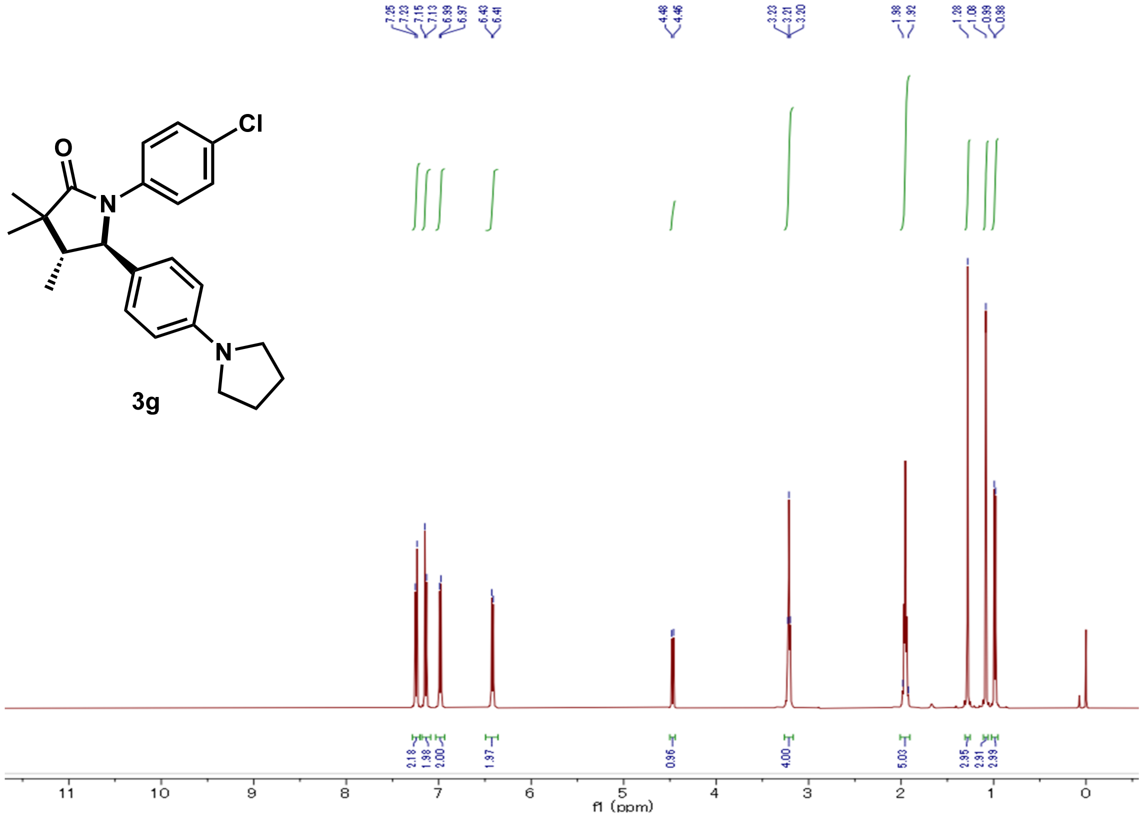

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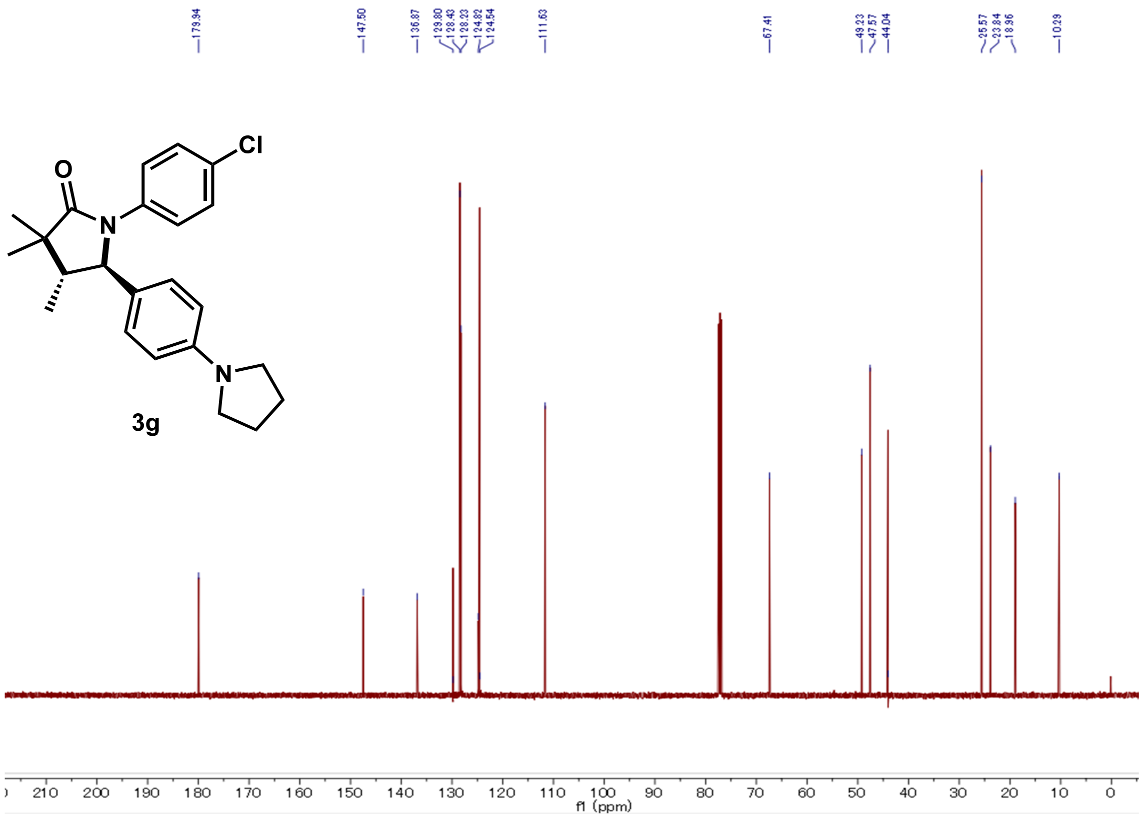

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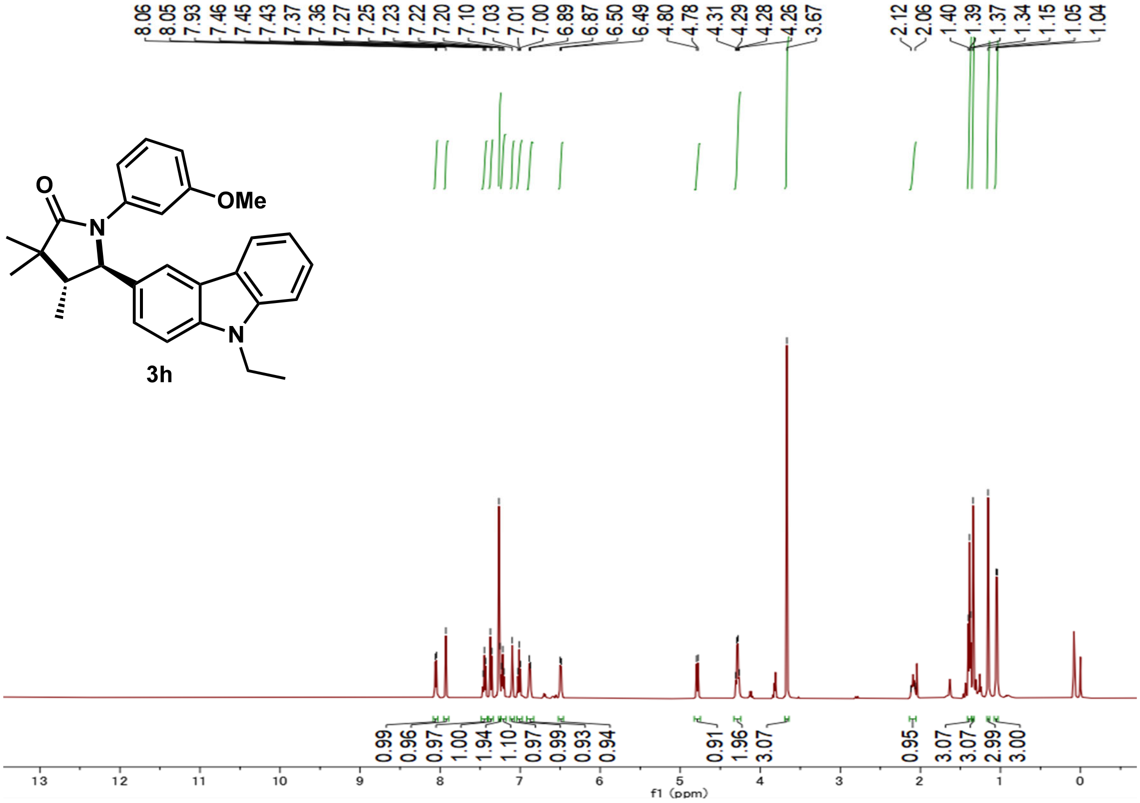

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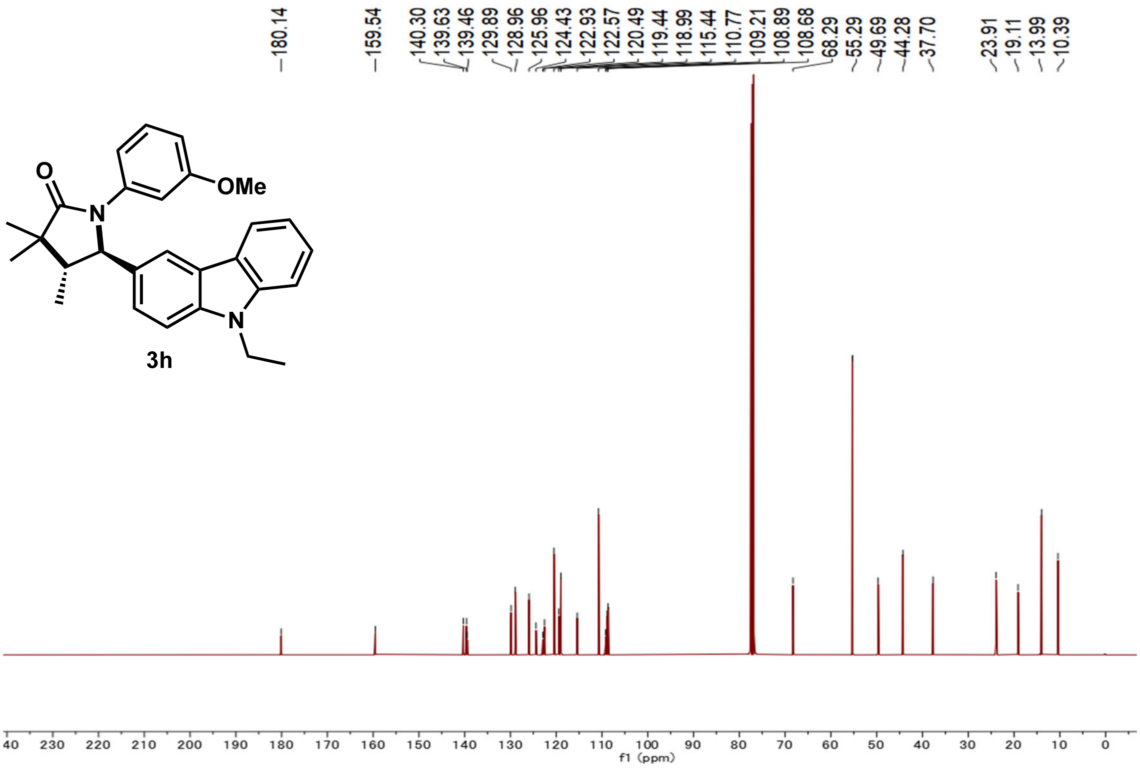

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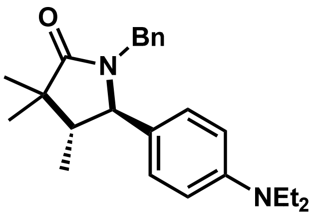

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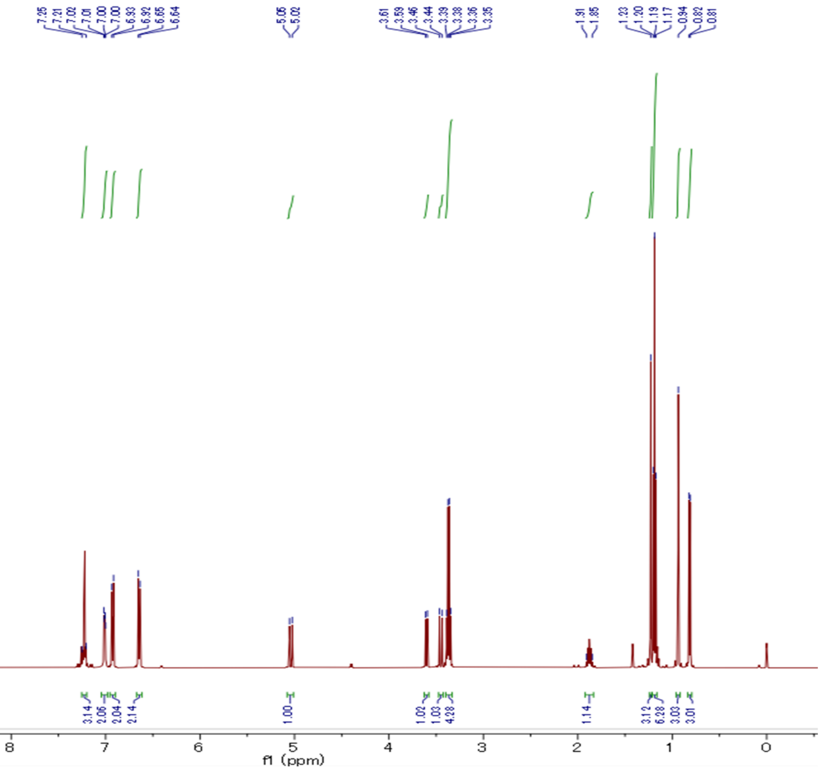

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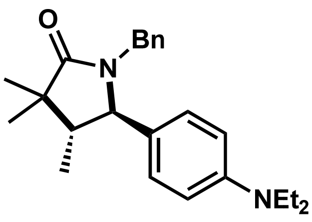

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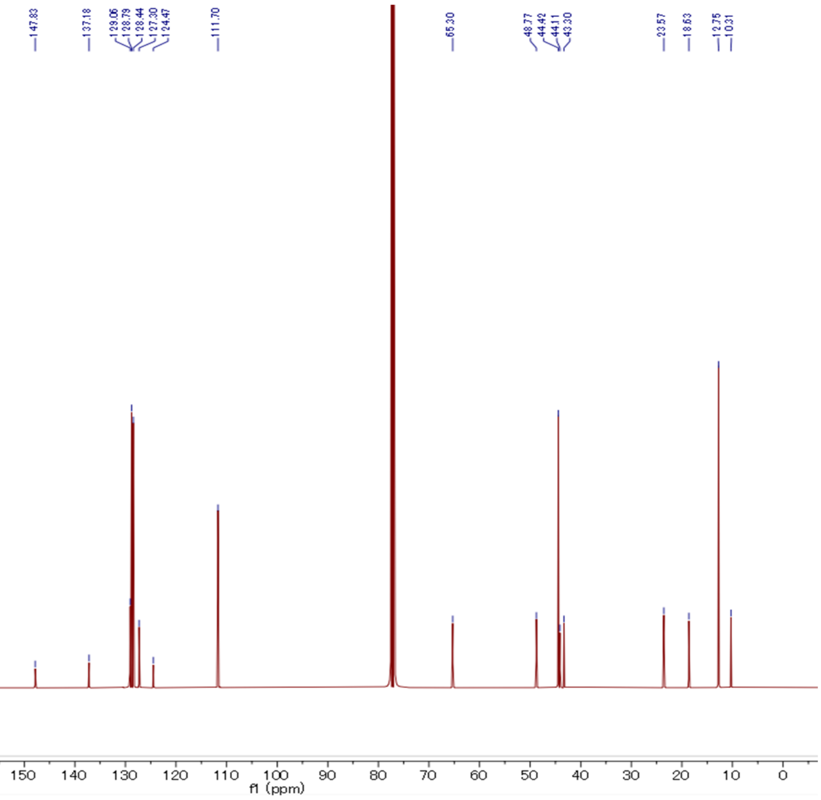

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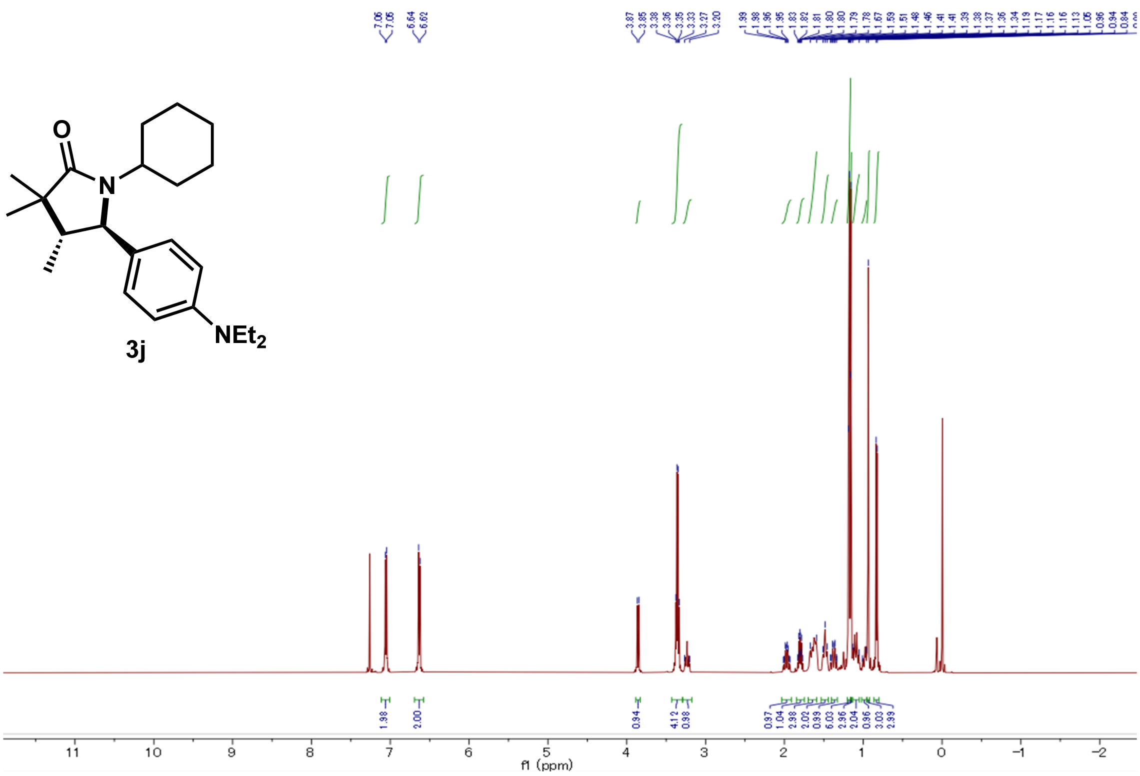

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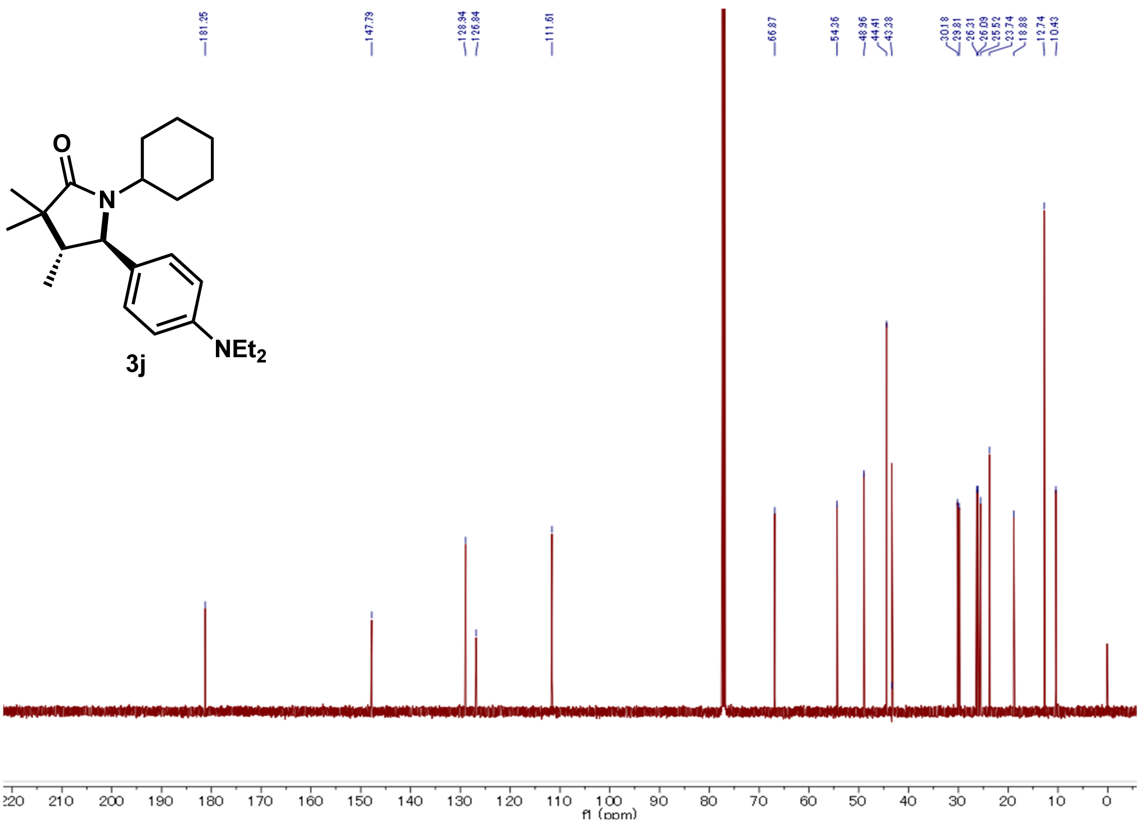

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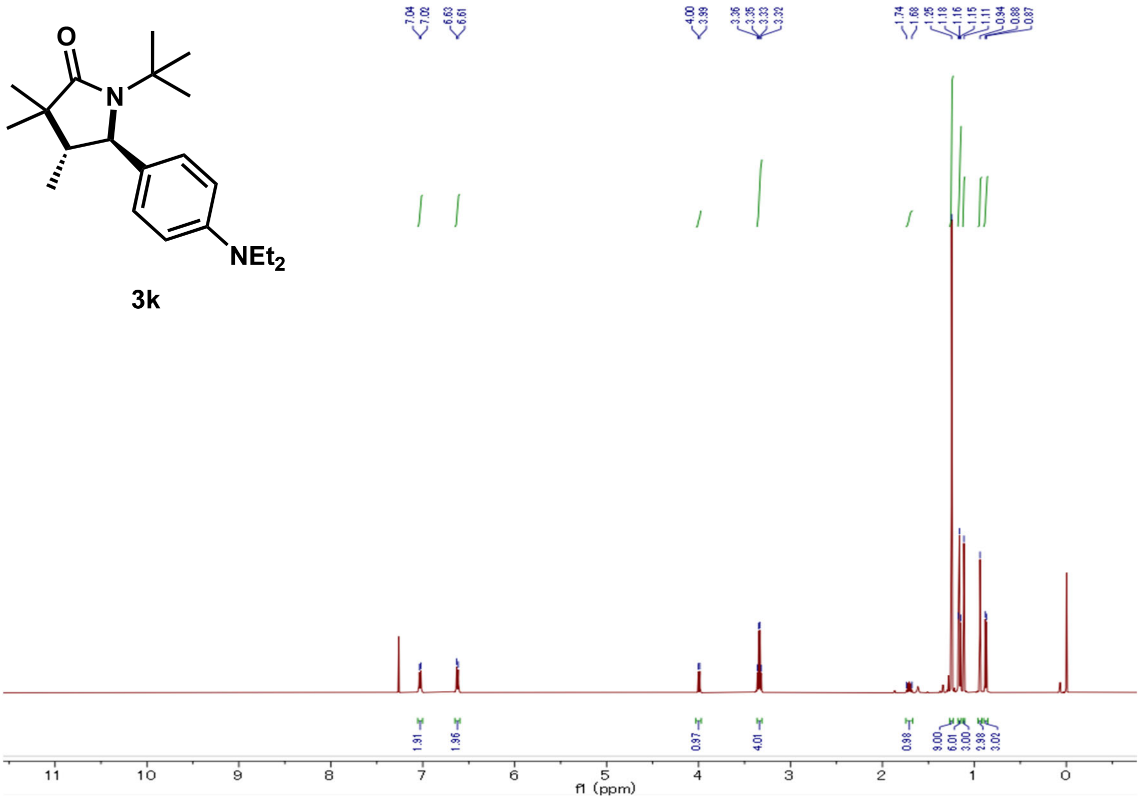

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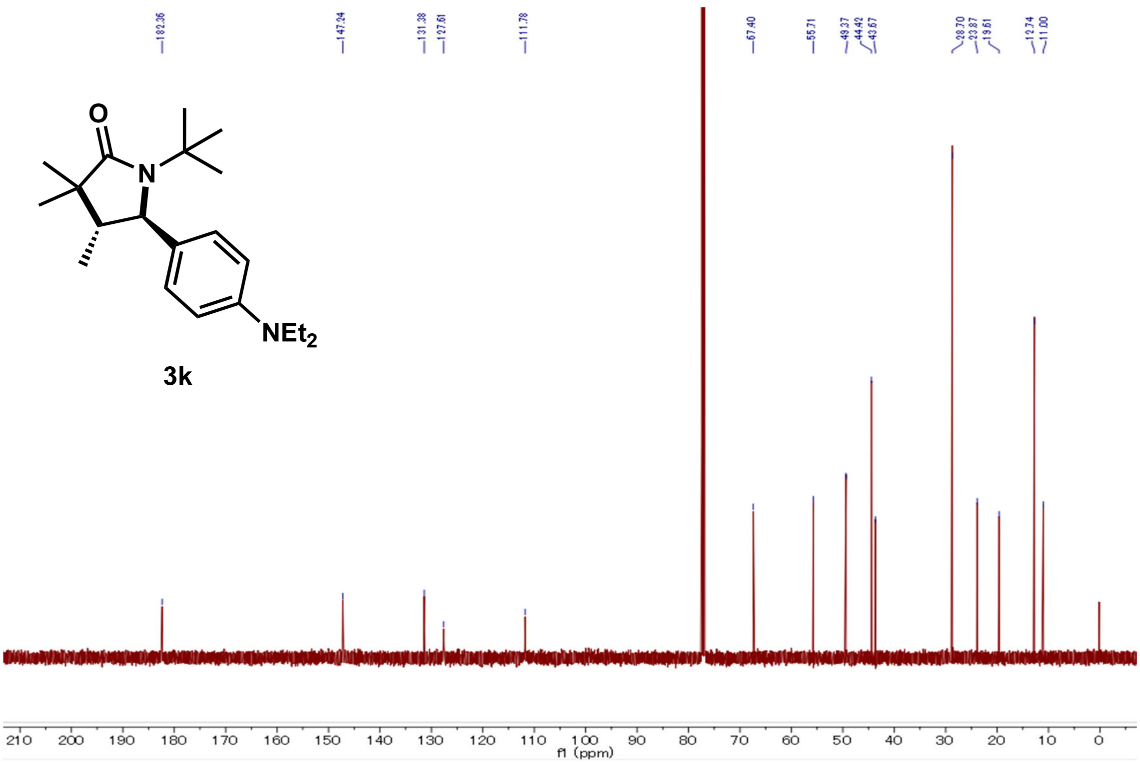

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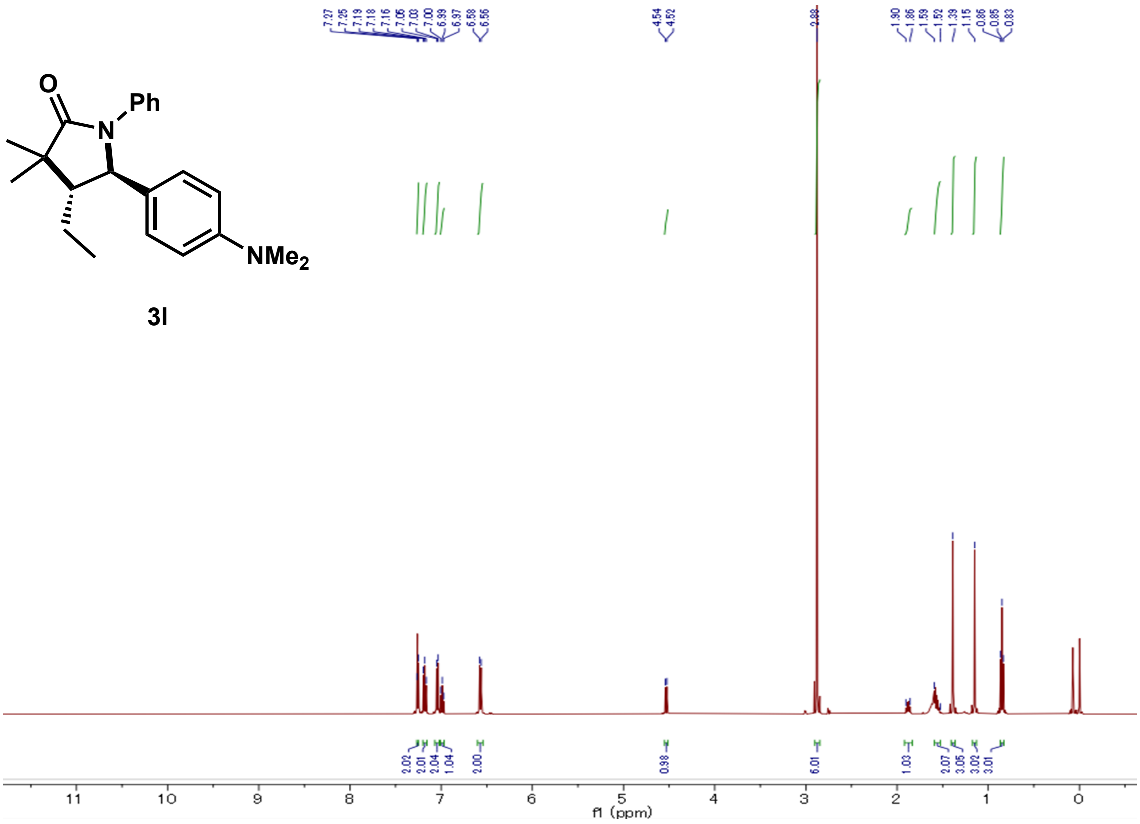

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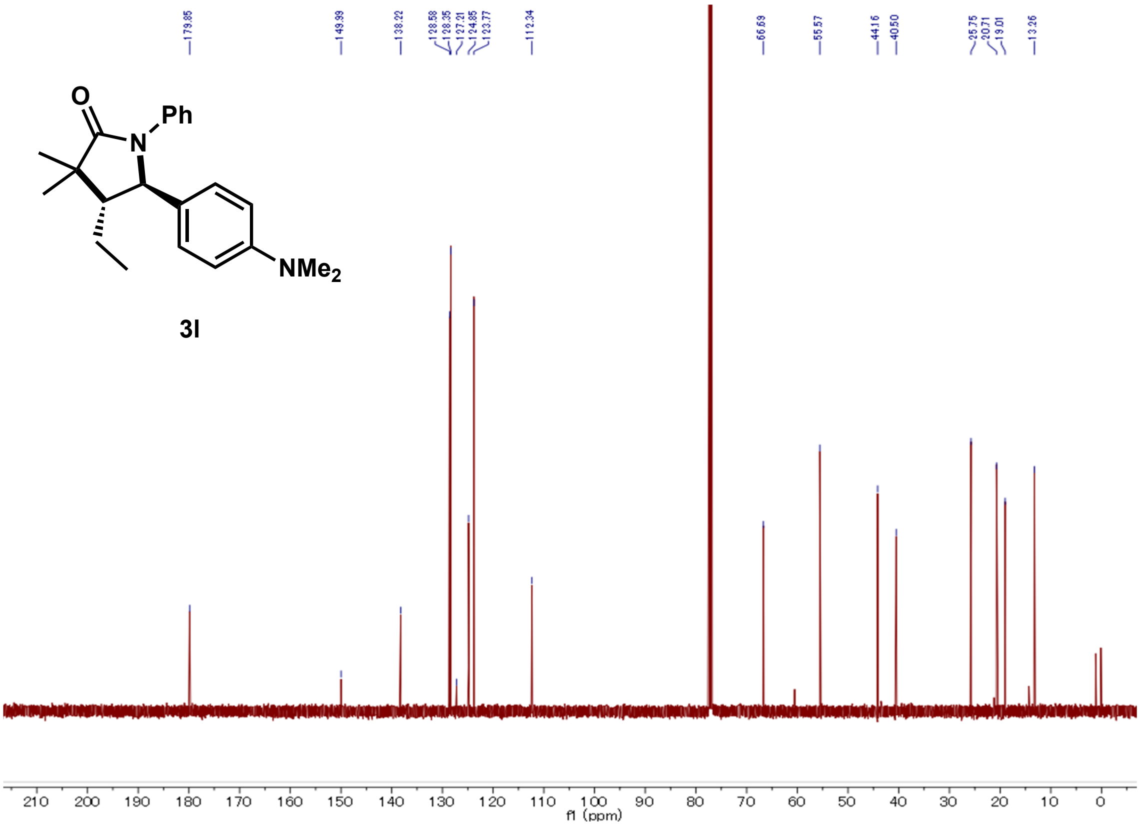
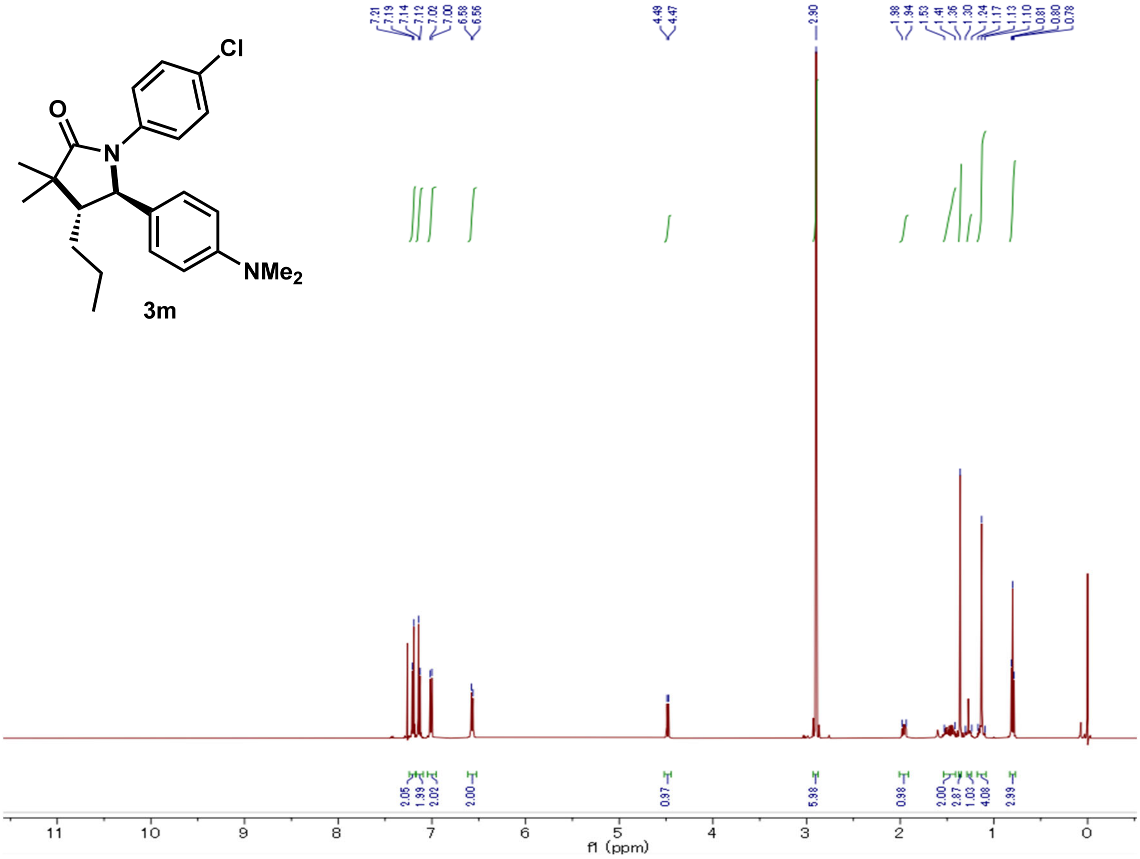


[1]H NMR (500 MHz, $CDCl_3$)



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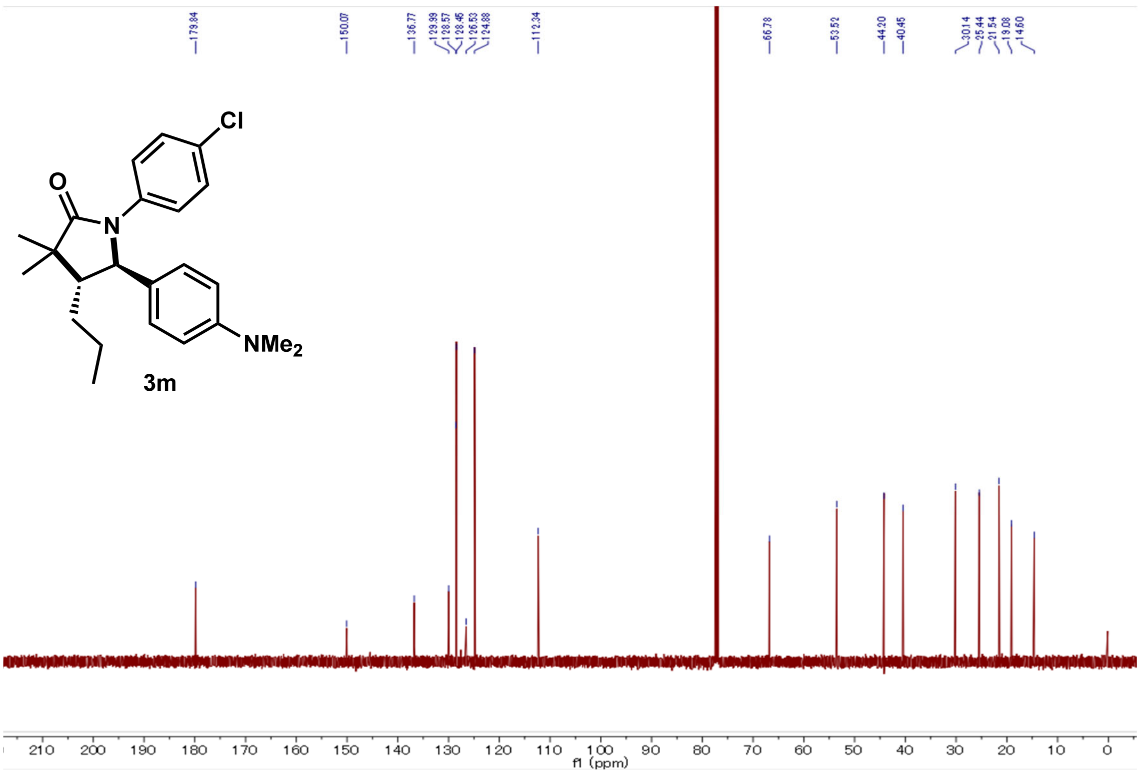

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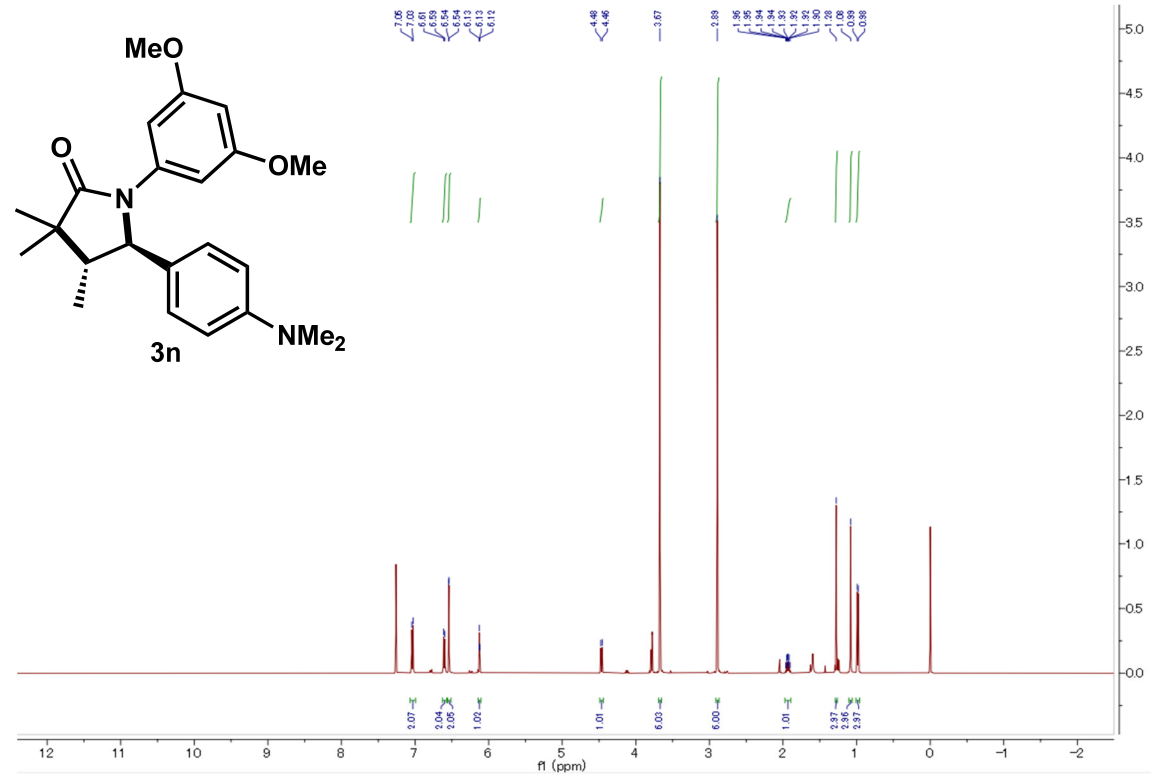

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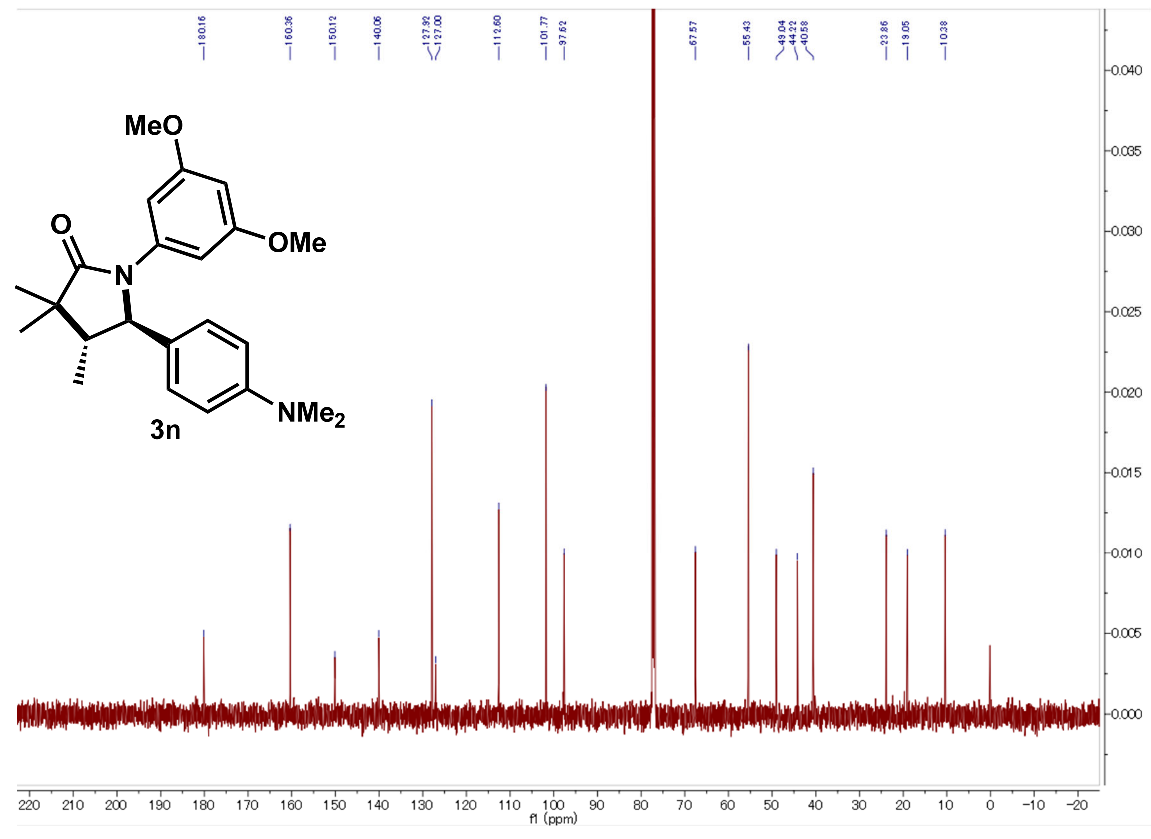

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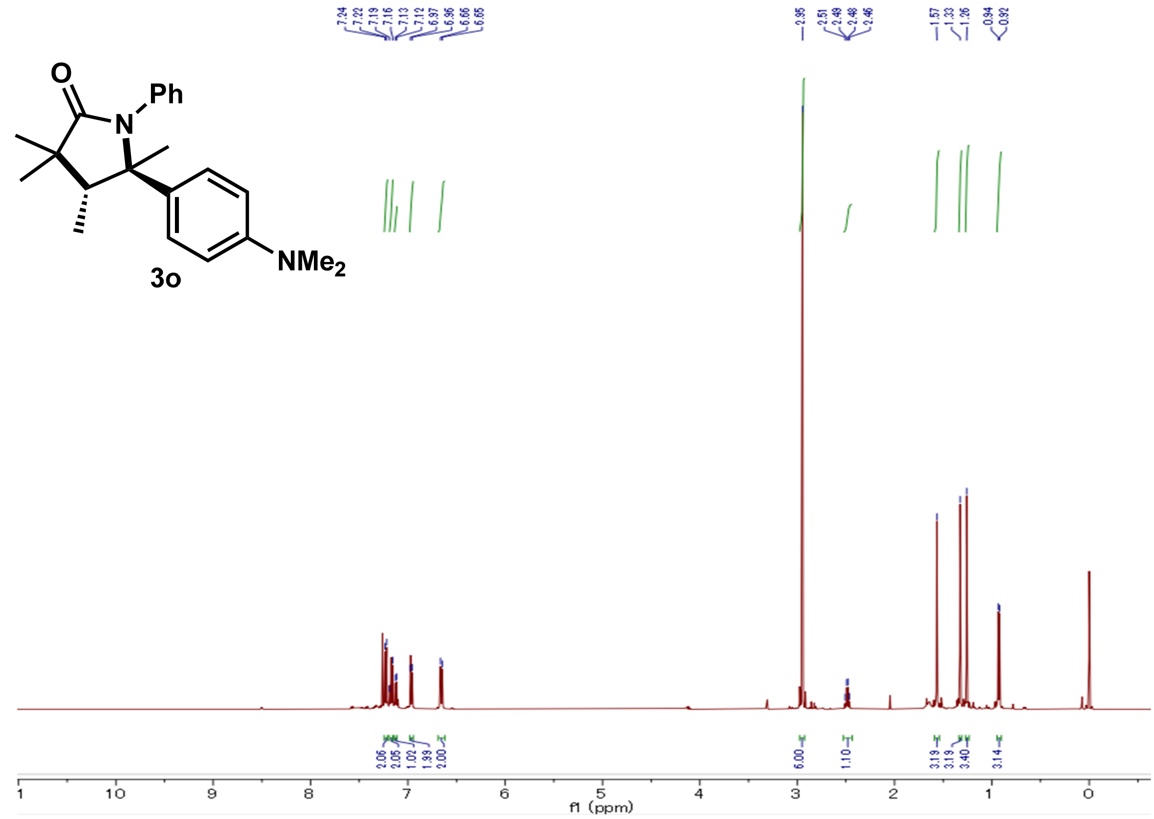

^{13}C NMR (125 MHz, $CDCl_3$)