

Supplementary Material (ESI) for RSC Advances
This journal is (C) The Royal Society of Chemistry 2013

Supporting information

Pd-Catalyzed Ligand-free Suzuki Reaction of β -Substituted Allylic Halides with Arylboronic Acids in Water

Chaonan Dong, Lingjuan Zhang, Xiao Xue, Huanrong Li, Zhiyong Yu, Weijun Tang and Lijin Xu*

Department of Chemistry, Renmin University of China, Beijing 100872, China.

Email: xulj@chem.ruc.edu.cn;

Table of Contents:

1. General information	S2
2. General procedure for allylation in water	S2
3. References	S14
4. NMR spectra of products	S15

1. General Information

Unless otherwise noted, all experiments were carried out in air, and all commercially available chemicals including solvents and organoboronic compounds were used as received without any further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer (^1H 400 MHz and ^{13}C 106 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. The β -arylated allylic halides (bromides and chlorides) (**1a-k**)¹ and methyl 2-(bromomethyl)acrylate (**1m**)² were prepared according to the previous reports.

2. General procedure for allylation of organoborons in water

A mixture of allyl halide **1** (1.0 mmol), arylboronic acid **2** (1.20 mmol), KOH (84.17 mg, 1.5 mmol), palladium trifluoroacetate (0.033 mg, 0.0001 mmol) in water (3.0 mL) in a round-bottom flask was stirred and heated at 90 °C for 3 h. Then the flask was removed from the oil bath and cooled to room temperature. Water (5.0 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 $\times$ 5.0 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 , concentrated in vacuo. The residue was then purified via flash chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product.

1-Methoxy-3-(2-phenyl-allyl)-benzene (3aa), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.81 (s, 3H), 3.88 (s, 2H), 5.11 (d, J = 1.28 Hz, 1H), 5.57 (d, J = 0.92 Hz, 1H), 6.80 (dd, J = 2.40, 8.16 Hz, 1H), 6.86 (m, 1H), 6.90 (d, J = 7.60 Hz, 1H), 7.24 (m, 1H), 7.35 (m, 3H), 7.51 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.7, 55.1, 111.5, 114.7, 114.8, 121.5, 126.2, 127.6, 128.4, 129.4, 140.8, 141.2, 146.7, 159.7; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{16}\text{NaO}[\text{M}+\text{Na}]^+$: 247.1093, found: 247.1089.

2,3-Diphenyl propene (3ab),³ yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.88 (s, 2H), 5.06 (d, J = 1.24 Hz, 1H), 5.54 (d, J = 0.52 Hz, 1H), 7.22 (m, 1H), 7.28 (m, 4H), 7.33 (m, 3H), 7.48 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.8, 114.7, 126.3, 127.6,

128.4, 128.5, 129.1, 138.9, 139.6, 140.9, 147.0; HRMS (ESI) calcd. for $C_{15}H_{14}Na[M+Na]^+$: 217.0988, found: 217.0986.

1-Methoxy-4-(2-phenylallyl)-benzene (3ac), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.81(s, 3H), 3.82 (s, 2H), 5.05 (d, $J = 1.32$ Hz, 1H), 5.52 (m, 1H), 6.86 (m, 2H), 7.20 (m, 2H), 7.32 (m, 3H), 7.49 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 40.8, 55.2, 113.8, 114.3, 126.2, 127.4, 128.3, 129.9, 131.5, 140.9, 147.4, 158.0; HRMS (ESI) calcd. for $C_{16}H_{17}O[M+H]^+$: 225.1274, found: 225.1271.

1-Methyl-4-(2-phenyl-allyl)-benzene (3ad),⁴ yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.83 (s, 2H), 5.05 (d, $J = 1.24$ Hz, 1H), 5.52 (s, 1H), 7.14 (dd, $J = 8.08, 18.28$ Hz, 4H), 7.30 (m, 3H), 7.48 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.8, 41.3, 114.5, 126.2, 127.5, 128.3, 128.9, 129.2, 135.6, 136.5, 140.9, 147.2; HRMS (ESI) calcd. for $C_{16}H_{16}Na[M+Na]^+$: 231.1144, found: 231.1141.

1-Methyl-2-(2-phenyl-allyl)-benzene (3ae),⁵ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.82 (s, 2H), 4.79 (s, 1H), 5.50 (d, $J = 0.96$ Hz, 1H), 7.20 (m, 3H), 7.38 (m, 3H), 7.46 (m, 1H), 7.54 (d, $J = 8.04$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.5, 38.9, 114.0, 126.0, 126.5, 127.6, 128.4, 130.0, 130.2, 136.8, 137.7, 138.8, 141.5, 146.4; HRMS (ESI) calcd. for $C_{16}H_{17}[M+H]^+$: 209.1325, found: 209.1321.

1-Methoxy-2-(2-phenylallyl)benzene (3af),⁶ yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 5H), 4.97 (s, 1H), 5.52 (s, 1H), 6.90 (m, 2H), 7.21 (m, 3H), 7.34 (m, 2H), 7.54 (d, $J = 7.92$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 34.9, 55.4, 110.3, 113.8, 120.5, 126.1, 126.2, 127.4, 128.1, 128.2, 130.3, 141.1, 146.5, 157.4; HRMS (ESI) calcd. for $C_{16}H_{17}O[M+H]^+$: 225.1274, found: 225.1270.

1-Fluoro-3-(2-phenyl-allyl)-benzene (3ag), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 2H), 5.09 (d, $J = 1.20$ Hz, 1H), 5.55 (s, 1H), 6.90 (td, $J = 2.36, 8.48$ Hz, 1H), 6.98 (m, 1H), 7.05 (d, $J = 7.68$ Hz, 1H), 7.26 (m, 2H), 7.33 (m, 2H), 7.45 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.4, 112.9, 113.2, 115.0, 115.6, 115.8, 124.6, 126.1, 127.6, 128.3, 129.7, 129.8, 140.4, 142.2, 146.2; HRMS (ESI) calcd. for $C_{15}H_{13}FNa[M+Na]^+$: 235.0893, found: 235.0888.

1,2-Difluoro-4-(2-phenyl-allyl)-benzene (3ah), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 3.83 (s, 2H), 5.09 (d, $J = 1.20$ Hz, 1H), 5.55 (s, 1H), 6.97 (m, 1H), 7.07 (m, 2H), 7.33 (m, 3H), 7.43 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 40.8, 115.1, 116.9, 117.1, 117.5, 117.6, 124.6, 126.1, 127.7, 128.4, 136.5, 140.2, 146.2; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{Na}[\text{M}+\text{Na}]^+$: 253.0799, found: 253.0798.

1-Chloro-4-(2-phenyl-allyl)-benzene (3ai),⁷ pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.84 (s, 2H), 5.07 (d, $J = 1.20$ Hz, 1H), 5.54 (s, 1H), 7.20 (d, $J = 8.36$ Hz, 2H), 7.27 (m, 3H), 7.34 (m, 2H), 7.45 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.0, 114.9, 126.1, 127.6, 128.3, 128.5, 130.3, 131.9, 138.0, 140.4, 146.5; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{13}\text{ClNa}[\text{M}+\text{Na}]^+$: 251.0598, found: 251.0596.

1-Chloro-2-(2-phenyl-allyl)-benzene (3aj), pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.98 (s, 2H), 4.93 (d, $J = 1.20$ Hz, 1H), 5.56 (d, $J = 0.52$ Hz, 1H), 7.20 (m, 2H), 7.28 (m, 2H), 7.36 (m, 2H), 7.41 (m, 1H), 7.52 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 38.7, 114.6, 126.0, 126.8, 127.6, 127.7, 128.4, 129.4, 130.9, 134.4, 137.2, 140.7, 145.5; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{13}\text{ClNa}[\text{M}+\text{Na}]^+$: 251.0598, found: 251.0593.

1-Bromo-4-(2-phenyl-allyl)-benzene (3ak), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.82 (s, 2H), 5.07 (d, $J = 1.04$ Hz, 1H), 5.54 (s, 1H), 7.15 (d, $J = 8.28$ Hz, 2H), 7.33 (m, 3H), 7.43 (m, 4H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.1, 114.9, 120.0, 126.1, 127.6, 128.4, 130.7, 131.5, 138.5, 140.4, 146.4; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{14}\text{Br}[\text{M}+\text{H}]^+$: 273.0273, found: 273.0270.

1-Bromo-2-(2-phenyl-allyl)-benzene (3al), colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 3.99 (s, 2H), 4.92 (s, 1H), 5.58 (s, 1H), 7.13 (m, 1H), 7.28 (m, 3H), 7.39 (m, 2H), 7.54 (d, $J = 7.96$ Hz, 2H), 7.63 (d, $J = 7.96$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.4, 114.7, 125.2, 126.0, 127.4, 127.7, 128.0, 128.4, 131.0, 132.8, 139.0, 140.7, 145.5; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{14}\text{Br}[\text{M}+\text{H}]^+$: 273.0273, found: 273.0268.

[4-(2-Phenyl-allyl)-phenyl]-methanol (3am), white solid, mp: 31-32 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.06 (s, 1H), 3.89 (s, 2H), 4.63 (s, 2H), 5.09 (d, $J = 1.0$ Hz, 1H), 5.56 (s, 1H), 7.28 (m, 5H), 7.33 (m, 2H), 7.50 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3)

δ 41.4, 65.1, 114.7, 126.2, 127.2, 127.5, 128.3, 129.1, 138.7, 139.0, 140.7, 146.9; HRMS (ESI) calcd. for $C_{16}H_{16}ONa[M+Na]^+$: 247.1093, found: 247.1096.

2-(2-Phenyl-allyl)-naphthalene (3an),⁸ yellow solid, mp: 56-57 °C; 1H NMR (400 MHz, $CDCl_3$) δ 4.09 (s, 2H), 5.17 (s, 1H), 5.65 (s, 1H), 7.36 (m, 3H), 7.51 (m, 3H), 7.58 (d, J = 7.88 Hz, 2H), 7.77 (s, 1H), 7.86 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.9, 115.0, 125.4, 126.0, 126.2, 127.4, 127.6, 127.6, 127.7, 128.0, 128.3, 128.4, 132.2, 133.7, 137.2, 140.9, 146.9; HRMS (ESI) calcd. for $C_{19}H_{16}Na[M+Na]^+$: 267.1144., found: 267.1142.

4-(2-Phenyl-allyl)-benzaldehyde (3ao), yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 2H), 5.10 (s, 1H), 5.57 (s, 1H), 7.32 (m, 3H), 7.43 (m, 4H), 7.82 (d, J = 8.12 Hz, 2H), 9.98 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.9, 115.3, 126.1, 127.7, 128.4, 129.5, 129.9, 134.8, 140.2, 145.9, 147.0, 192.0; HRMS (ESI) calcd. for $C_{16}H_{14}ONa[M+Na]^+$: 245.0937, found: 245.0936.

1-(4-(2-phenylallyl)phenyl)ethanone (3ap),⁹ yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 3.92 (s, 2H), 5.09 (d, J = 0.92 Hz, 1H), 5.55 (s, 1H), 7.28 (m, 2H), 7.33 (m, 3H), 7.44 (m, 2H), 7.89 (d, J = 8.20 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.9, 41.7, 115.2, 126.1, 127.7, 128.4, 128.5, 129.1, 135.3, 140.3, 145.4, 146.1, 197.9; HRMS (ESI) calcd. for $C_{17}H_{16}ONa[M+Na]^+$: 259.1093, found: 259.1091.

4-(2-Phenyl-allyl)-benzoic acid methyl ester (3aq),¹⁰ yellow solid, mp: 57-59 °C ; 1H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 5H), 5.09 (d, J = 0.92 Hz, 1H), 5.56 (s, 1H), 7.28 (m, 2H), 7.34 (m, 3H), 7.45 (m, 2H), 7.99 (d, J = 8.24 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.7, 52.0, 115.1, 126.1, 127.7, 128.2, 128.4, 129.0, 129.7, 140.4, 145.1, 146.2, 167.1; HRMS (ESI) calcd. for $C_{17}H_{17}O_2[M+H]^+$: 253.1223, found: 253.1221.

4-(2-Phenyl-allyl)-benzonitrile (3ar), orange oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 2H), 5.09 (d, J = 0.92 Hz, 1H), 5.57 (s, 1H), 7.29 (m, 2H), 7.34 (m, 3H), 7.42 (m, 2H), 7.56 (d, J = 8.28 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.8, 110.1, 115.5, 119.0, 126.1, 127.9, 128.5, 129.6, 132.2, 139.9, 145.3, 145.6; HRMS (ESI) calcd. for $C_{16}H_{13}NNa[M+Na]^+$: 242.0940, found: 242.0939.

1-(2-Phenyl-allyl)-4-trifluoromethyl-benzene (3as), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.95 (s, 2H), 5.10 (d, $J = 0.96$ Hz, 1H), 5.59 (s, 1H), 7.38 (m, 5H), 7.48 (m, 2H), 7.58 (d, $J = 8.04$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.4, 115.3, 125.31, 125.4, 126.1, 127.8, 128.2, 128.4, 129.2, 138.8, 140.2, 143.7, 146.1; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{14}\text{F}_3[\text{M}+\text{H}]^+$: 263.1042, found: 263.1034.

1-(2-phenylallyl)-2-(trifluoromethyl)benzene (3at), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 4.06 (s, 2H), 4.92 (d, $J = 1.08$ Hz, 1H), 5.60 (s, 1H), 7.32 (m, 5H), 7.46 (m, 3H), 7.69 (d, $J = 7.80$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 37.7, 115.5, 123.4, 125.9, 126.0, 126.3, 127.6, 128.4, 128.7, 131.2, 131.7, 138.0, 140.5, 145.9; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{14}\text{F}_3[\text{M}+\text{H}]^+$: 263.1042, found: 263.1038.

1-Nitro-3-(2-phenyl-allyl)-benzene (3au), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.97 (s, 2H), 5.12 (s, 1H), 5.59 (s, 1H), 7.31 (m, 3H), 7.44 (m, 3H), 7.57 (d, $J = 7.56$ Hz, 1H), 8.07 (d, $J = 7.56$ Hz, 1H), 8.13 (s, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.3, 115.7, 121.4, 123.7, 126.1, 127.9, 128.5, 129.2, 135.1, 139.9, 141.6, 145.7, 148.4; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2\text{Na} [\text{M}+\text{Na}]^+$: 262.0838, found: 262.0835.

2-(2-Phenyl-allyl)-thiophene (3av), colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 4.06 (s, 2H), 5.21 (d, $J = 1.16$ Hz, 1H), 5.53 (s, 1H), 6.86 (m, 1H), 6.93 (m, 1H), 7.15 (dd, $J = 1.16, 5.12$ Hz, 1H), 7.33 (m, 3H), 7.49 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 35.9, 114.6, 123.8, 125.4, 126.2, 126.8, 127.6, 128.3, 140.3, 142.6, 146.5; HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{13}\text{S}[\text{M}+\text{H}]^+$: 201.0732, found: 201.0729.

3-(2-Phenyl-allyl)-thiophene (3aw), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 3.90 (s, 2H), 5.14 (d, $J = 1.28$ Hz, 1H), 5.54 (m, 1H), 7.02 (m, 2H), 7.28 (m, 1H), 7.36 (m, 3H), 7.50 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 36.4, 114.2, 121.5, 125.3, 126.1, 127.6, 128.3, 128.6, 140.1, 140.8, 146.6; HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{13}\text{S}[\text{M}+\text{H}]^+$: 201.0732, found: 201.0730.

(E)-Penta-1,4-diene-1,4-diyl dibenzene (3ax),¹¹ yellow solid, mp: 52-53 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.47 (d, $J = 6.64$ Hz, 2H), 5.22 (s, 1H), 5.50 (s, 1H), 6.38 (m, 1H), 6.56 (d, $J = 15.88$ Hz, 1H), 7.35 (m, 4H), 7.40 (m, 4H), 7.55 (d, $J = 7.92$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 14.0, 22.2, 31.7, 32.2, 38.3, 112.7, 116.1,

126.1, 127.4, 128.3, 132.9, 141.3, 147.3; HRMS (ESI) calcd. for $C_{17}H_{16}Na[M+Na]^+$: 243.1144, found: 243.1143.

(E)-1-methyl-4-(4-phenylpenta-1,4-dienyl)benzene (3ay), pale yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.45 (d, $J = 6.72$ Hz, 2H), 5.20 (d, $J = 1.28$ Hz, 1H), 5.48 (s, 1H), 6.30 (m, 1H), 6.52 (d, $J = 15.84$ Hz, 1H), 7.15 (d, $J = 7.96$ Hz, 2H), 7.32 (m, 3H), 7.38 (m, 2H), 7.54 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.2, 38.7, 113.3, 126.0, 127.0, 127.5, 128.3, 128.5, 129.2, 131.5, 134.8, 136.9, 141.0, 146.6; HRMS (ESI) calcd. for $C_{18}H_{18}Na[M+Na]^+$: 257.1301, found: 257.1299.

(E)-nona-1,4-dien-2-ylbenzene (3az),¹² colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, $J = 7.08$ Hz, 3H), 1.39 (m, 4H), 2.05 (m, 2H), 3.22 (d, $J = 4.36$ Hz, 2H), 5.11 (d, $J = 1.28$ Hz, 1H), 5.39 (s, 1H), 5.53 (m, 2H), 7.29 (m, 1H), 7.37 (m, 2H), 7.48 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.2, 31.7, 32.2, 38.3, 112.7, 116.1, 126.1, 127.4, 128.3, 132.9, 141.3, 147.3; HRMS (ESI) calcd. for $C_{15}H_{20}Na[M+Na]^+$: 223.1457, found: 223.1455.

3,3'-(Prop-2-ene-1,2-diyl)bis(methoxybenzene) (3ba), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.81 (s, 3H), 3.83 (s, 2H), 5.08 (d, $J = 1.24$ Hz, 1H), 5.54 (d, $J = 1.0$ Hz, 1H), 6.77 (dd, $J = 2.18, 8.32$ Hz, 1H), 6.83 (m, 2H), 6.87 (d, $J = 7.52$ Hz, 1H), 7.00 (t, $J = 2.28$ Hz, 1H), 7.07 (m, 1H), 7.24 (dd, $J = 8.00, 15.92$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.7, 55.1, 55.2, 111.5, 112.1, 112.7, 114.6, 114.9, 118.7, 121.4, 129.2, 129.3, 141.1, 142.3, 146.6, 159.5, 159.6; HRMS (ESI) calcd. for $C_{17}H_{19}O_2[M+H]^+$: 255.1380, found: 255.1376.

1-Methoxy-3-(3-phenylprop-1-en-2-yl)benzene (3bb), yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.84 (d, $J = 1.20$ Hz, 3H), 3.91 (s, 2H), 5.12 (d, $J = 1.28$ Hz, 1H), 5.59 (s, 1H), 6.89 (m, 1H), 7.07 (m, 1H), 7.14 (m, 1H), 7.29 (m, 2H), 7.36 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.8, 55.2, 112.2, 112.8, 114.9, 118.8, 126.2, 128.4, 129.0, 129.3, 139.6, 142.4, 146.9, 159.5; HRMS (ESI) calcd. for $C_{16}H_{17}O[M+H]^+$: 225.1274, found: 225.1273.

1-(3-(4-Bromophenyl)prop-1-en-2-yl)-3-methoxybenzene (3bk), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 2H), 3.82 (s, 3H), 5.07 (s, 1H), 5.54 (s, 1H), 6.84 (m, 1H), 6.98 (m, 1H), 7.05 (m, 1H), 7.14 (d, $J = 8.20$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz,

1H), 7.43 (d, $J = 8.24$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.1, 55.2, 112.2, 112.7, 115.1, 118.7, 120.0, 129.3, 130.7, 131.5, 138.5, 141.9, 146.3, 159.5; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{BrNaO}[\text{M}+\text{Na}]^+$: 325.0198, found: 325.0202.

4-(2-(3-Methoxyphenyl)allyl)benzaldehyde (3bo), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.80 (s, 3H), 3.93 (s, 2H), 5.10 (d, $J = 1.04$ Hz, 1H), 5.57 (s, 1H), 6.83 (m, 1H), 6.97 (t, $J = 2.24$ Hz, 1H), 7.04 (m, 1H), 7.24 (t, $J = 7.96$ Hz, 1H), 7.43 (d, $J = 8.04$ Hz, 2H), 7.81 (d, $J = 8.12$ Hz, 2H), 9.97 (s, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.9, 55.2, 112.2, 112.8, 115.6, 118.6, 129.4, 129.5, 130.0, 134.7, 141.7, 145.8, 147.0, 159.5, 192.0; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{17}\text{O}_2[\text{M}+\text{H}]^+$: 253.1223, found: 253.1222.

1-Methoxy-3-(3-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)benzene (3bs), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 3.82 (s, 3H), 3.92 (s, 2H), 5.10 (d, $J = 1.08$ Hz, 1H), 5.58 (s, 1H), 6.86 (dd, $J = 1.88, 8.20$ Hz, 1H), 7.00 (t, $J = 2.16$ Hz, 1H), 7.06 (m, 1H), 7.27 (t, $J = 7.80$ Hz, 1H), 7.39 (d, $J = 8.00$ Hz, 2H), 7.57 (d, $J = 8.04$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.5, 55.2, 112.2, 112.8, 113.5, 115.4, 117.1, 118.6, 125.3, 129.2, 129.4, 141.8, 143.7, 146.0, 159.6; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{ONa}[\text{M}+\text{Na}]^+$: 315.0967, found: 315.0963.

1-Methoxy-3-(3-(3-nitrophenyl)prop-1-en-2-yl)benzene (3bu), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.81 (s, 3H), 3.95 (s, 2H), 5.12 (d, $J = 1.04$ Hz, 1H), 5.59 (s, 1H), 6.82 (m, 1H), 6.96 (t, $J = 2.28$ Hz, 1H), 7.03 (m, 1H), 7.26 (m, 1H), 7.44 (t, $J = 7.92$ Hz, 1H), 7.59 (d, $J = 7.56$ Hz, 1H), 8.07 (dd, $J = 1.20, 8.16$ Hz, 1H), 8.13 (m, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.3, 55.2, 112.2, 112.9, 115.9, 118.6, 121.5, 123.7, 129.3, 129.5, 135.1, 141.4, 141.6, 145.6, 148.4, 159.6; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_3\text{Na}[\text{M}+\text{Na}]^+$: 292.0944., found: 292.0938.

1-(3-(4-Methoxyphenyl)prop-1-en-2-yl)-2-methylbenzene (3cc), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 2.29 (s, 3H), 3.59 (s, 2H), 3.82 (s, 3H), 4.95 (m, 1H), 5.11 (m, 1H), 6.85 (m, 2H), 7.04 (d, $J = 7.00$ Hz, 1H), 7.08 (m, 2H), 7.14 (m, 1H), 7.19 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 19.8, 43.6, 55.2, 113.6, 115.0, 125.3, 126.8, 128.4, 130.0, 130.3, 131.1, 134.9, 142.7, 149.8, 158.0; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{19}\text{O}[\text{M}+\text{H}]^+$: 239.1430., found: 239.1426.

Methyl 4-(2-*o*-tolylallyl)benzoate (3cq), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 2.27 (s, 3H), 3.70 (s, 2H), 3.93 (s, 3H), 5.00 (m, 1H), 5.16 (m, 1H), 7.01(d, $J = 7.28$ Hz, 1H), 7.13 (m, 1H), 7.18 (m, 2H), 7.24 (d, $J = 8.20$ Hz, 2H), 7.97(d, $J = 8.28$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 19.7, 44.6, 52.0, 115.9, 125.4, 127.1, 128.4, 129.4, 129.6, 130.1, 132.9, 134.8, 142.1, 144.5, 148.5, 167.1; $\text{C}_{18}\text{H}_{18}\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$: 289.1199, found: 289.1198.

2-(3-Phenylprop-1-en-2-yl)naphthalene (3db), white solid, mp: 43-44 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.99 (s, 2H), 5.16 (d, $J = 1.20$ Hz, 1H), 5.67 (s, 1H), 7.21 (m, 1H), 7.29 (m, 4H), 7.46 (m, 2H), 7.66 (dd, $J = 1.80, 8.64$ Hz, 1H), 7.80 (m, 3H), 7.88 (d, $J = 1.24$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.7, 115.2, 124.6, 125.0, 125.9, 126.1, 126.2, 127.5, 127.8, 128.3, 128.4, 129.0, 132.8, 133.4, 138.0, 139.6, 146.8; HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{17}[\text{M}+\text{H}]^+$: 245.1325, found: 245.1331.

2-(3-(4-Methoxyphenyl)prop-1-en-2-yl)naphthalene (3dc), pale yellow solid, mp: 48-49 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.82 (s, 3H), 3.97 (s, 2H), 5.20 (d, $J = 0.88$ Hz, 1H), 5.70 (s, 1H), 6.90 (d, $J = 8.56$ Hz, 2H), 7.27 (d, $J = 8.52$ Hz, 2H), 7.52 (m, 2H), 7.70 (dd, $J = 1.76, 8.60$ Hz, 1H), 7.86 (m, 3H), 7.93 (s, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 40.8, 55.2, 113.9, 114.9, 124.7, 125.0, 125.9, 126.1, 127.6, 127.8, 128.3, 129.9, 131.6, 132.9, 133.4, 138.1, 147.2, 158.0; HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{19}\text{O}[\text{M}+\text{H}]^+$: 275.1430, found: 275.1424.

Methyl 4-(2-(naphthalen-2-yl)allyl)benzoate (3dq), white solid, mp: 72-73 °C, ^1H NMR (400 MHz, CDCl_3) δ 3.91 (s, 3H), 4.04 (s, 2H), 5.19 (d, $J = 1.04$ Hz, 1H), 5.70 (s, 1H), 7.38 (d, $J = 8.24$ Hz, 2H), 7.48 (m, 2H), 7.64 (dd, $J = 1.80, 8.64$ Hz, 1H), 7.84 (m, 4H), 7.98 (d, $J = 8.24$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.7, 52.0, 115.7, 124.4, 125.0, 126.0, 126.2, 127.5, 127.9, 128.3, 128.9, 129.8, 130.9, 132.9, 133.3, 137.5, 145.1, 146.0, 167.1; $\text{C}_{21}\text{H}_{18}\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$: 325.1199, found: 325.1193.

4-(2-(4-Fluorophenyl)allyl)benzonitrile (3er), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 2H), 5.08 (s, 1H), 5.50 (s, 1H), 6.99 (m, 2H), 7.36 (m, 4H), 7.58 (d, $J = 8.16$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.9, 115.2, 115.4, 115.5, 118.9, 127.7, 127.8, 128.9, 129.6, 132.3, 144.6, 145.0; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{12}\text{FNNa}[\text{M}+\text{Na}]^+$: 260.0846, found: 260.0845.

(E)-1-Fluoro-4-(5-phenylpenta-1,4-dien-2-yl)benzene (3ex), pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.45 (d, $J = 6.76$ Hz, 2H), 5.23 (d, $J = 0.80$ Hz, 1H), 5.46 (s, 1H), 6.36 (m, 1H), 6.57 (d, $J = 15.84$ Hz, 1H), 7.10 (m, 2H), 7.28 (m, 1H), 7.37 (t, $J = 7.32$ Hz, 2H), 7.43 (m, 2H), 7.52 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 38.9, 113.4, 115.3 ($J = 21.2$ Hz), 126.2, 127.2, 127.6, 127.7, 127.8, 128.6, 131.9, 137.5, 145.5, 163.7; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{16}\text{F}[\text{M}+\text{H}]^+$: 239.1231, found: 239.1227.

(E)-1-Fluoro-4-(5-p-tolylpenta-1,4-dien-2-yl)benzene (3ey), pale yellow solid, mp: 76-77 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.35 (s, 3H), 3.40 (d, $J = 6.68$ Hz, 2H), 5.17 (s, 1H), 5.40 (s, 1H), 6.25 (m, 1H), 6.48 (d, $J = 15.84$ Hz, 1H), 7.04 (m, 2H), 7.14 (d, $J = 7.92$ Hz, 2H), 7.28 (m, 2H), 7.47 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 21.2, 38.8, 113.2, 115.0, 115.2, 126.0, 126.7, 127.6, 127.7, 129.2, 131.6, 134.6, 137.0, 145.6; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{17}\text{FNa}[\text{M}+\text{Na}]^+$: 275.1206, found: 275.1205.

(E)-1-Fluoro-4-(nona-1,4-dien-2-yl)benzene (3ez), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.90 (t, $J = 7.08$ Hz, 3H), 1.38 (m, 4H), 2.03 (q, $J = 6.68$ Hz, 2H), 3.18 (d, $J = 5.32$ Hz, 2H), 5.08 (d, $J = 1.12$ Hz, 1H), 5.32 (s, 1H), 5.50 (m, 2H), 7.02 (m, 2H), 7.42 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 13.9, 22.1, 31.6, 32.2, 38.5, 112.6, 114.8, 115.1, 127.1, 127.6, 127.7, 133.0, 146.2; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{19}\text{FNa}[\text{M}+\text{Na}]^+$: 241.1363, found: 241.1358.

(E)-1-Chloro-4-(5-phenylpenta-1,4-dien-2-yl)benzene (3fx), white solid, mp: 68-69 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 3.43 (d, $J = 6.68$ Hz, 2H), 5.23 (d, $J = 1.00$ Hz, 1H), 5.48 (s, 1H), 6.33 (m, 1H), 6.54 (d, $J = 15.84$ Hz, 1H), 7.26 (m, 1H), 7.35 (m, 4H), 7.40 (m, 2H), 7.46 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 38.6, 114.0, 126.2, 127.3, 127.4, 127.6, 128.5, 128.6, 131.9, 133.3, 137.4, 139.3, 145.4; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{16}\text{Cl}[\text{M}+\text{H}]^+$: 255.0935, found: 255.0932.

4,4'-(Prop-2-ene-1,2-diyl)bis(bromobenzene) (3gk), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 3.78 (s, 2H), 5.10 (d, $J = 1.08$ Hz, 1H), 5.52 (s, 1H), 7.11 (d, $J = 8.40$ Hz, 2H), 7.29 (m, 2H), 7.42 (m, 4H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.0, 115.5, 120.1, 121.6, 127.8, 130.6, 131.45, 131.54, 138.1, 139.2, 145.4; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{13}\text{Br}_2[\text{M}+\text{H}]^+$: 350.9379, found: 350.9379.

(E)-1-bromo-4-(5-phenylpenta-1,4-dien-2-yl)benzene (3gx), white solid, mp: 79-80 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.41 (d, $J = 6.64$ Hz, 2H), 5.52 (s, 1H), 5.46 (s, 1H), 6.30 (m, 1H), 6.52 (d, $J = 15.84$ Hz, 1H), 7.24 (m, 1H), 7.32 (m, 2H), 7.38 (d, $J = 8.20$ Hz, 4H), 7.50 (d, $J = 8.48$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 38.6, 114.0, 121.5, 126.1, 127.2, 127.6, 127.7, 128.5, 131.4, 131.9, 137.4, 139.8, 145.4; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{16}\text{Br}[\text{M}+\text{H}]^+$: 299.0430, found: 299.0425.

1-(4-(3-Phenylprop-1-en-2-yl)phenyl)ethanone (3hb), white solid, mp: 59-60 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.59 (s, 3H), 3.90 (s, 2H), 5.21 (d, $J = 1.04$ Hz, 1H), 5.64 (s, 1H), 7.26 (m, 5H), 7.56 (m, 2H), 7.92 (d, $J = 8.48$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 26.6, 41.5, 116.8, 126.3, 128.4, 128.5, 128.9, 131.0, 136.0, 139.0, 145.3, 146.0, 197.7; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{16}\text{ONa}[\text{M}+\text{Na}]^+$: 259.1093, found: 259.1090.

Methyl 4-(3-(3-methoxyphenyl)prop-1-en-2-yl)benzoate (3ia), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.78 (s, 3H), 3.86 (s, 2H), 3.92 (s, 3H), 5.20 (s, 1H), 5.62 (s, 1H), 6.77 (m, 2H), 6.84 (d, $J = 7.60$ Hz, 1H), 7.21 (dt, $J = 7.80, 15.84$ Hz, 1H), 7.53 (d, $J = 8.44$ Hz, 2H), 7.99 (d, $J = 8.40$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.5, 52.1, 55.1, 111.5, 114.7, 116.6, 121.3, 126.1, 129.0, 129.4, 129.6, 140.6, 145.2, 145.9, 159.7, 166.9; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{Na}[\text{M}+\text{Na}]^+$: 305.1148, found: 305.1145.

Methyl 4-(3-phenylprop-1-en-2-yl)benzoate (3ib), white solid, mp: 50-51 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 2H), 3.93 (s, 3H), 5.18 (d, $J = 0.92$ Hz, 1H), 5.62 (s, 1H), 7.24 (m, 3H), 7.31 (m, 2H), 7.54 (d, $J = 8.52$ Hz, 2H), 8.00 (d, $J = 8.52$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.5, 52.1, 116.5, 126.2, 126.3, 128.5, 128.9, 129.0, 129.6, 139.0, 145.3, 146.2, 166.9; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Na}[\text{M}+\text{Na}]^+$: 275.1043, found: 275.1043.

Methyl 4-(3-(3-nitrophenyl)prop-1-en-2-yl)benzoate (3iu), white solid, mp: 117-118 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.91 (s, 3H), 3.97 (s, 2H), 5.22 (s, 1H), 5.66 (s, 1H), 7.46 (m, 3H), 7.56 (d, $J = 7.20$ Hz, 1H), 7.98 (d, $J = 7.92$ Hz, 2H), 8.06 (d, $J = 7.96$ Hz, 1H), 8.10 (s, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 41.0, 52.1, 117.5, 121.6,

123.7, 126.1, 129.35, 129.40, 129.8, 135.0, 141.1, 144.3, 145.0, 148.4, 166.7; HRMS (ESI) calcd. for $C_{17}H_{16}NO_4[M+H]^+$: 298.1074, found: 298.1068.

4-(3-(3-Methoxyphenyl)prop-1-en-2-yl)benzonitrile (3ja), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.84 (s, 2H), 5.27 (s, 1H), 5.62 (s, 1H), 6.77 (m, 2H), 6.83 (d, $J = 7.64$ Hz, 1H), 7.22 (m, 1H), 7.53 (d, $J = 8.48$ Hz, 2H), 7.59 (d, $J = 8.44$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.3, 55.2, 111.0, 111.5, 114.7, 117.7, 118.9, 121.2, 126.8, 129.5, 132.1, 140.2, 145.1, 145.2, 159.8; HRMS (ESI) calcd. for $C_{17}H_{15}NNaO[M+Na]^+$: 272.1046., found: 272.1044.

4-(3-Phenylprop-1-en-2-yl)benzonitrile (3jb), white solid, mp: 50-51 °C; 1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 2H), 3.25 (d, $J = 0.92$ Hz, 1H), 5.63 (s, 1H), 7.23 (m, 3H), 7.31 (m, 2H), 7.54 (m, 2H), 7.58 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.3, 111.0, 117.6, 118.9, 126.5, 126.8, 128.6, 128.8, 132.2, 128.5, 145.2, 145.5; HRMS (ESI) calcd. for $C_{16}H_{13}NNa[M+Na]^+$: 242.0940., found: 242.0937.

4-(3-(3-Nitrophenyl)prop-1-en-2-yl)benzonitrile (3ju), yellow solid, mp: 85-86 °C; 1H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 2H), 5.28 (s, 1H), 5.68 (s, 1H), 7.52 (m, 4H), 7.61 (d, $J = 8.32$ Hz, 2H), 8.08 (d, $J = 8.28$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 40.8, 111.4, 118.6, 121.8, 123.6, 126.8, 129.5, 132.3, 135.0, 140.6, 144.28, 144.32, 148.5; HRMS (ESI) calcd. for $C_{16}H_{12}N_2NaO_2[M+Na]^+$: 287.0791, found: 287.0785.

(2-Methyl-allyl)-benzene (3lb),¹³ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 3H), 3.40 (s, 2H), 4.81 (s, 1H), 4.89 (d, $J = 0.52$ Hz, 1H), 7.28 (m, 3H), 7.36 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.1, 44.7, 112.0, 126.1, 128.3, 129.0, 139.8, 145.2; HRMS (ESI) calcd. for $C_{10}H_{13}[M+H]^+$: 133.1012, found: 133.1011.

1-Methoxy-4-(2-methyl-allyl)-benzene (3lc),¹⁴ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.73 (s, 3H), 3.31 (s, 2H), 3.84 (s, 3H), 4.77 (s, 1H), 4.84 (d, $J = 0.32$ Hz, 1H), 6.90 (d, $J = 8.60$ Hz, 2H), 7.17 (d, $J = 8.60$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.0, 43.8, 55.2, 111.6, 113.7, 129.8, 131.9, 145.6, 158.0; HRMS (ESI) calcd. for $C_{11}H_{14}NaO[M+Na]^+$: 185.0937, found: 185.0933.

Methyl 4-(2-methylallyl)benzoate (3lq),¹⁰ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 3H), 3.38 (s, 2H), 3.92 (s, 3H), 4.76 (s, 1H), 4.86 (s, 1H), 7.29 (d, $J = 8.24$ Hz, 2H), 7.80 (d, $J = 8.28$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.0, 44.6, 52.0,

112.6, 128.1, 129.0, 129.7, 144.2, 145.3, 167.2; HRMS (ESI) calcd. for $C_{12}H_{14}NaO_2[M+Na]^+$: 213.0886, found: 213.0885.

(E)-(4-Methylpenta-1,4-dienyl)benzene (3lx),¹⁵ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.96 (d, $J = 7.00$ Hz, 2H), 4.84 (m, 2H), 6.28 (m, 1H), 6.49 (d, $J = 15.8$ Hz, 1H), 7.27 (m, 1H), 7.35 (t, $J = 7.36$ Hz, 2H), 7.42 (d, $J = 7.52$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.5, 41.5, 111.1, 126.1, 127.0, 128.2, 128.5, 131.4, 137.6, 144.6; HRMS (ESI) calcd. for $C_{12}H_{14}Na[M+Na]^+$: 181.0988, found: 181.0983.

Ethyl 2-benzylacrylate (3mb),¹⁶ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, $J = 7.12$ Hz, 3H), 3.67 (s, 2H), 4.22 (q, $J = 7.16$ Hz, 2H), 5.48 (d, $J = 1.40$ Hz, 1H), 6.26 (d, $J = 0.44$ Hz, 1H), 7.24 (m, 3H), 7.32 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 38.1, 60.7, 126.0, 126.3, 128.4, 129.1, 138.8, 140.4, 166.9; HRMS (ESI) calcd. for $C_{12}H_{14}NaO_2[M+Na]^+$: 213.0886, found: 213.0882.

Methyl 4-(2-(ethoxycarbonyl)allyl)benzoate (3mq),¹⁷ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, $J = 7.12$ Hz, 3H), 3.70 (s, 2H), 3.92 (s, 3H), 4.20 (q, $J = 7.16$ Hz, 2H), 5.51 (d, $J = 1.24$ Hz, 1H), 6.29 (s, 1H), 7.30 (d, $J = 8.28$ Hz, 2H), 7.99 (d, $J = 8.28$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 38.2, 52.0, 60.9, 126.6, 128.3, 129.0, 129.7, 139.6, 144.3, 166.6, 167.1; HRMS (ESI) calcd. for $C_{14}H_{16}NaO_4[M+Na]^+$: 271.0941, found: 271.0937.

(E)-Ethyl 2-methylene-5-phenylpent-4-enoate (3mx),¹⁸ colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, $J = 7.12$ Hz, 3H), 3.26 (m, 2H), 4.26 (q, $J = 7.12$ Hz, 2H), 5.66 (d, $J = 1.40$ Hz, 1H), 6.29 (m, 2H), 6.51 (d, $J = 15.80$ Hz, 1H), 7.25 (m, 1H), 7.35 (m, 2H), 7.40 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2, 35.2, 60.8, 125.4, 126.1, 126.9, 127.2, 128.5, 132.1, 137.4, 139.5, 166.9; HRMS (ESI) calcd. for $C_{14}H_{16}NaO_2[M+Na]^+$: 239.1043, found: 239.1042.

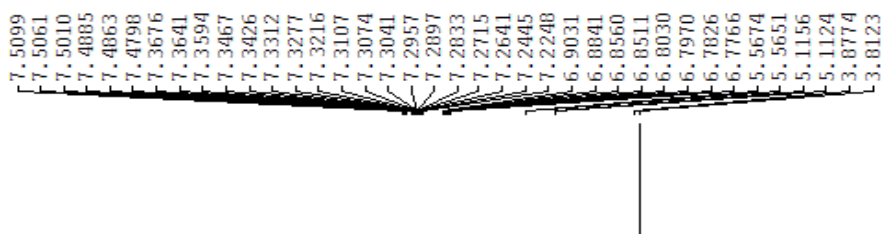
Dimethyl 4,4'-(prop-2-ene-1,2-diyl)dibenzoate (3nq), white solid, mp:; 1H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.91 (s, 3H), 3.92 (s, 2H), 5.18 (d, $J = 0.84$ Hz, 1H), 5.62 (s, 1H), 7.30 (d, $J = 8.20$ Hz, 2H), 7.48 (d, $J = 8.48$ Hz, 2H), 7.96 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.5, 52.0, 52.1, 117.0, 126.1, 128.3, 128.9, 129.2, 129.7, 129.8, 144.5, 144.8, 145.5, 166.8, 167.0; HRMS (ESI) calcd. for $C_{19}H_{18}NaO_4[M+Na]^+$: 333.1097, found: 333.1095.

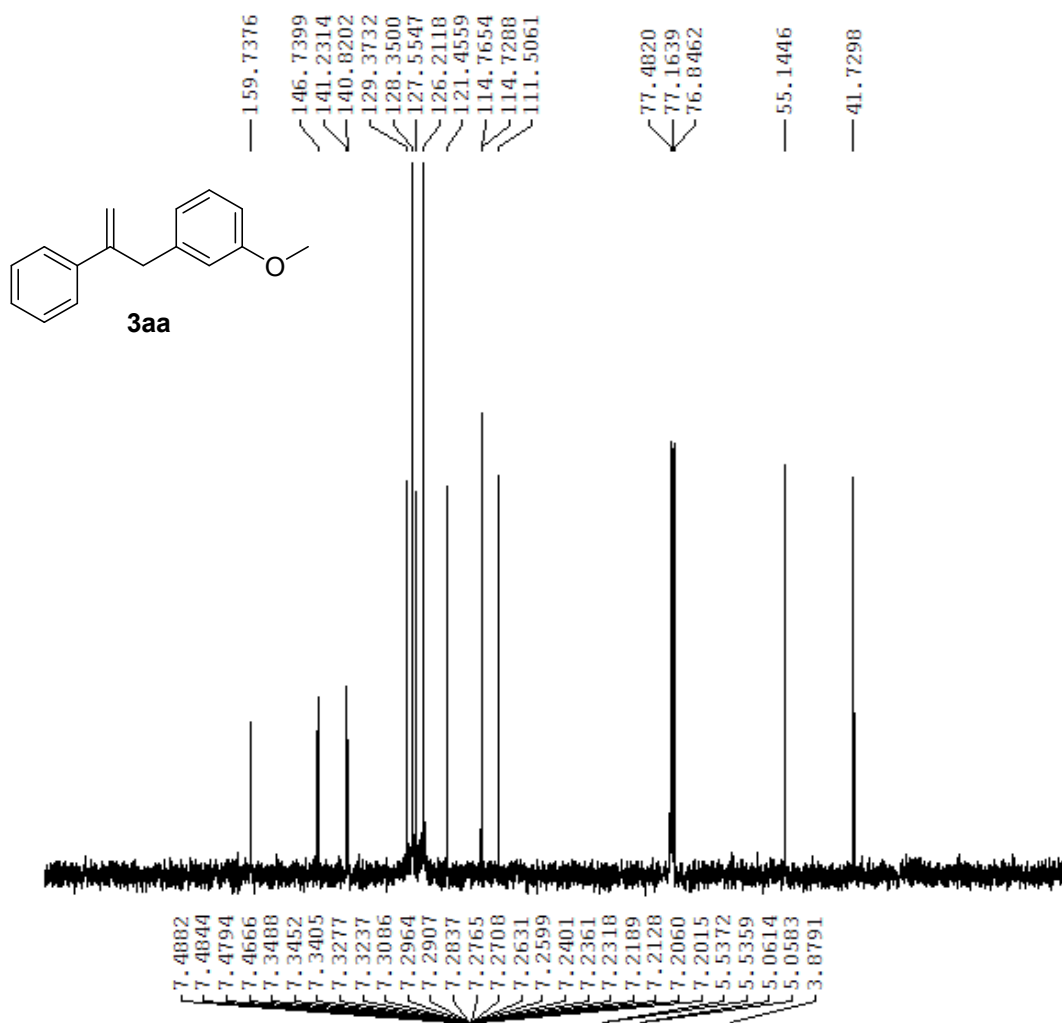
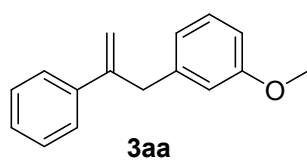
3. Reference

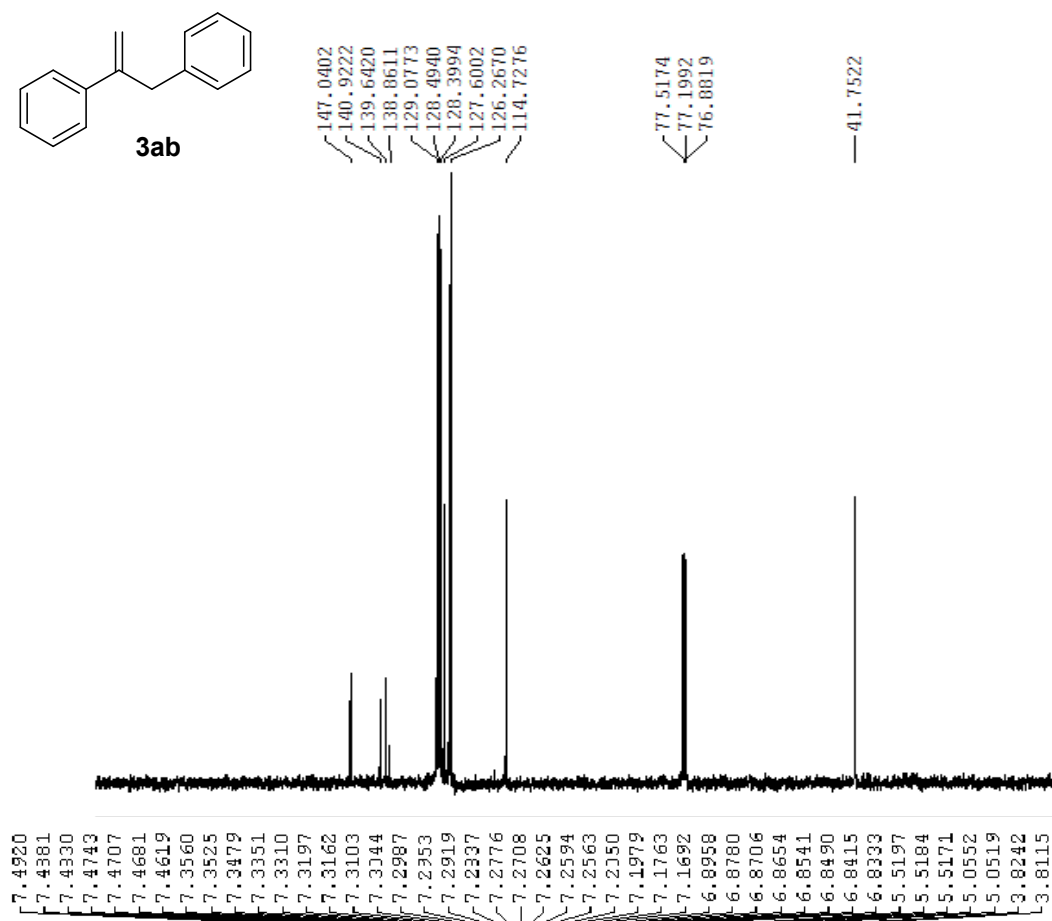
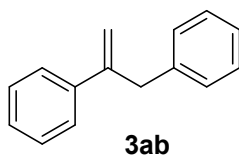
1. (a) M. Yamanaka, M. Arisawa, A. Nishida and M. Nakagawa, *Tetrahedron Lett.* 2002, **43**, 2403-2406; (b) A. Garzan, A. Jaganathan, N. S. Marzijarani, R. Yousefi, D. C. Whitehead, J. E. Jackson and B. Borhan, *Chem. Eur. J.* 2013, **19**, 9015-9021; (c) K. Fukamizu, Y. Miyake and Y. Nishibayashi, *Angew. Chem. Int. Ed.* 2009, **48**, 2534-2537; (d) Z.-C. Duan, X.-P. Hu, C. Zhang, D.-Y. Wang, S.-B. Yu and Z. Zheng, *J. Org. Chem.* 2009, **74**, 9191-9194.
2. (a) H. Huang, X. Liu, J. Deng, M. Qiu and Z. Zheng, *Org. Lett.* 2006, **8**, 3359-3362; (b) G. Sudhakar, K. Satish and J. Raghavaiah, *J. Org. Chem.* 2012, **77**, 10010-10020.
3. E. A. Standley and T. F. Jamison, *J. Am. Chem. Soc.* 2013, **135**, 1585-1592.
4. S. Nadri, M. Joshaghani and E. Rafiee, *Tetrahedron Lett.* 2009, **50**, 5470-5473.
5. I. Kondolff, H. Doucet and M. Santelli, *Tetrahedron Lett.* 2003, **44**, 8487-8491.
6. M. Kirihara, T. Noguchi, H. Kakuda, T. Akimoto, A. Shimajiri, M. Morishita, A. Hatano and Y. Hirai, *Tetrahedron Lett.* 2006, **47**, 3777-3780.
7. T. Mino, T. Koizumi, S. Suzuki, K. Hirai, K. Kajiwarra, M. Sakamoto and T. Fujita, *Eur. J. Org. Chem.* 2012, 678-680.
8. A. R. Ehle, Q. Zhou and M. P. Watson, *Org. Lett.* 2012, **14**, 1202-1205.
9. V. Calo, A. Nacci, A. Monopoli, A. Detomaso and P. Iliade, *Organometallics* 2003, **22**, 4193-4197.
10. X. Cui, S. Wang, Y. Zhang, W. Deng, Q. Qian and H. Gong, *Org. Biomol. Chem.*, 2013, **11**, 3094-3097.
11. H. Tsukamoto, T. Uchiyama, T. Suzuki and Y. Kondo, *Org. Biomol. Chem.*, 2008, **6**, 3005-3013.
12. K. S. Yoo, C. H. Yoon and K. W. Jung, *J. Am. Chem. Soc.* 2006, **128**, 16384-16393.
13. C. Najera, J. Gil-Molto, S. Karlstrom, *Adv. Synth. Catal.* 2004, **346**, 1798-1811.
14. M.-B. Li, X.-L. Tang and S.-K. Tian, *Adv. Synth. Catal.* 2011, **353**, 1980-1984.
15. E. Alacid and C. Najera, *J. Org. Chem.* 2009, **74**, 2321-2327.

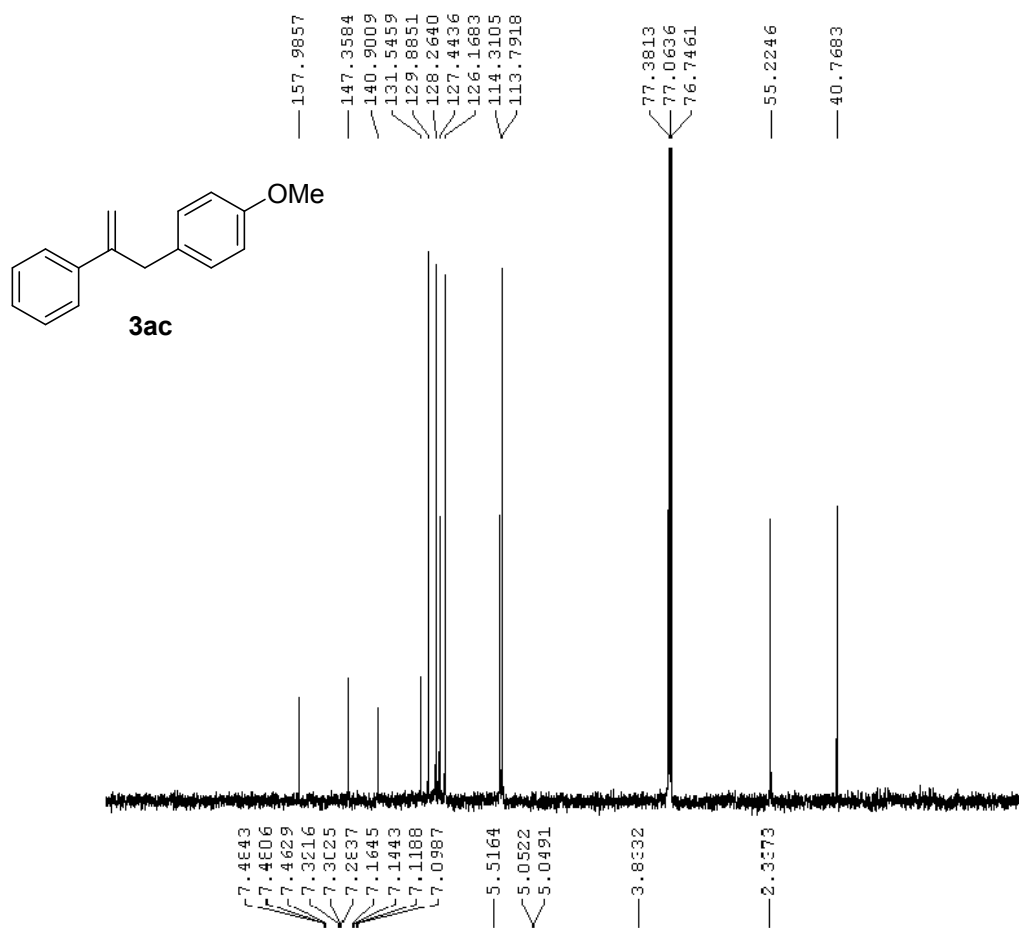
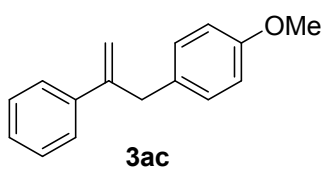
16. H.-S. Lee, J.-S. Park, B. M. Kim and S. H. Gellman, *J. Org. Chem.* 2003, **68**, 1575-1578.
17. C. J. Rohbogner, C. R. Diene, T. J. Korn and P. Knochel, *Angew. Chem. Int. Ed.* 2010, **49**, 1874-1877.
18. W.-B. Liu, H. He, L.-X. Dai and S.-L. You, *Chem. Eur. J.* 2010, **16**, 7376-7379.

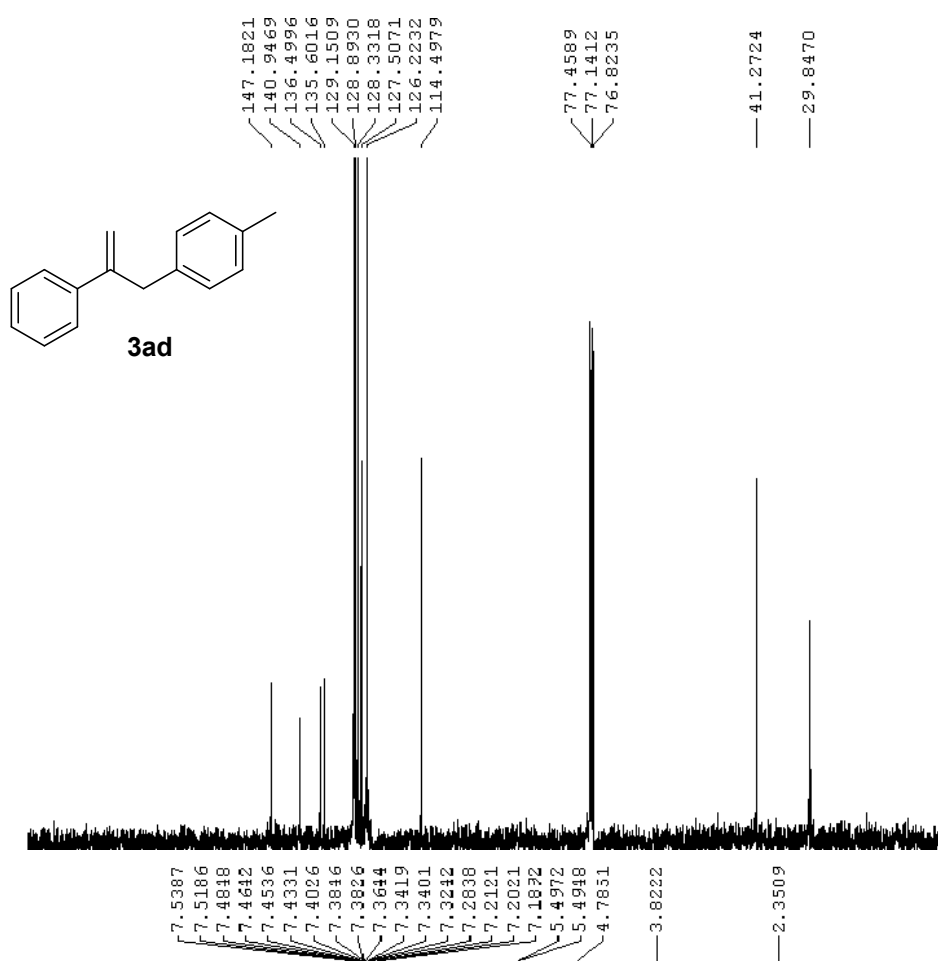
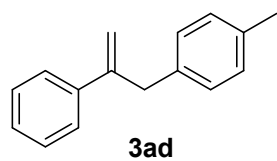
4. NMR spectra of allylated products

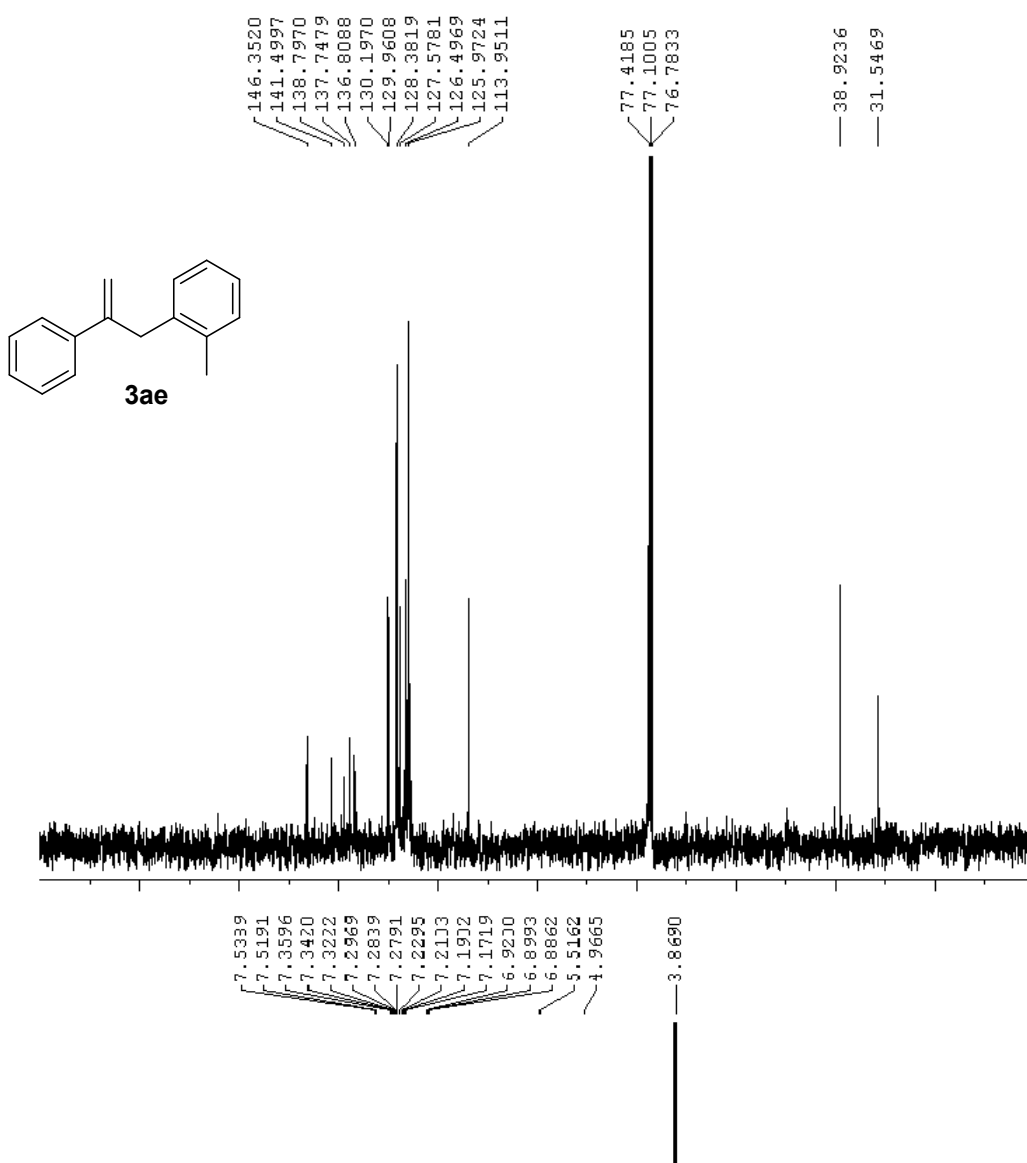
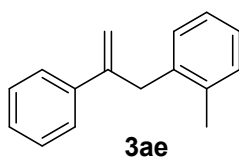


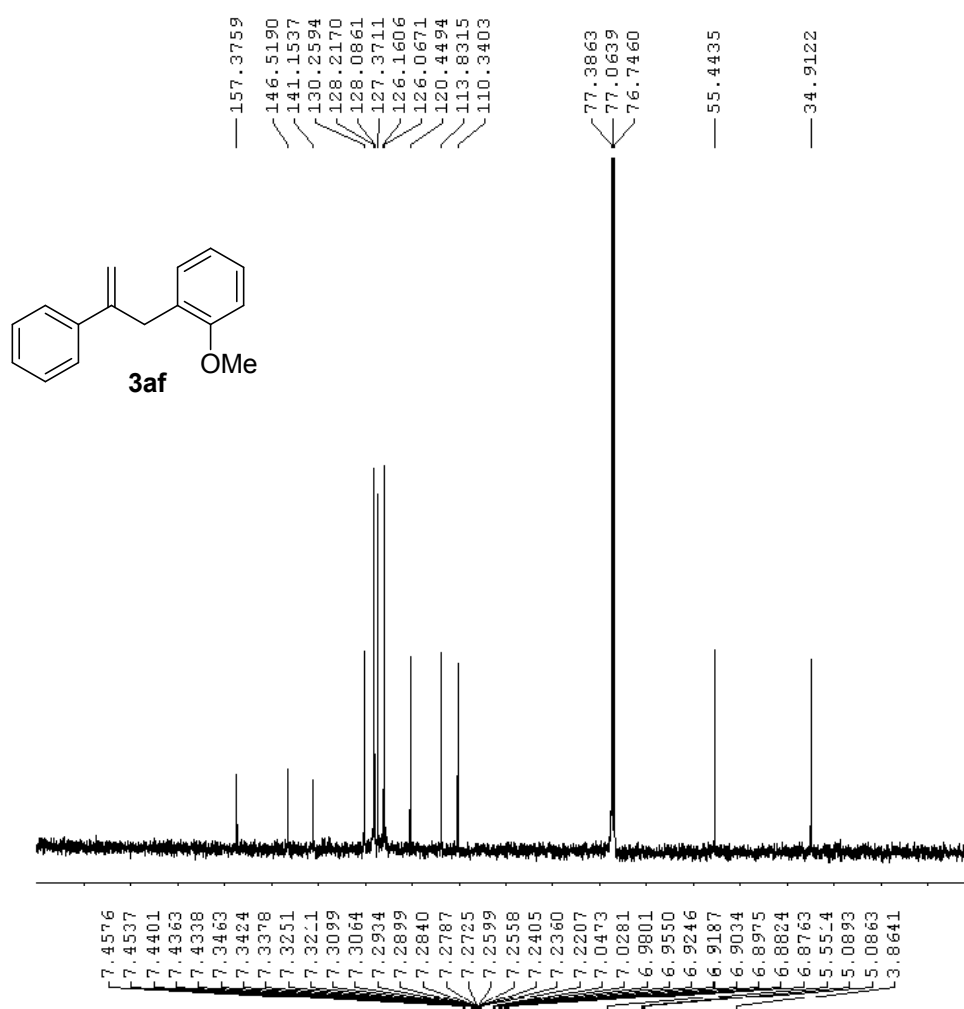
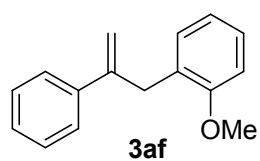


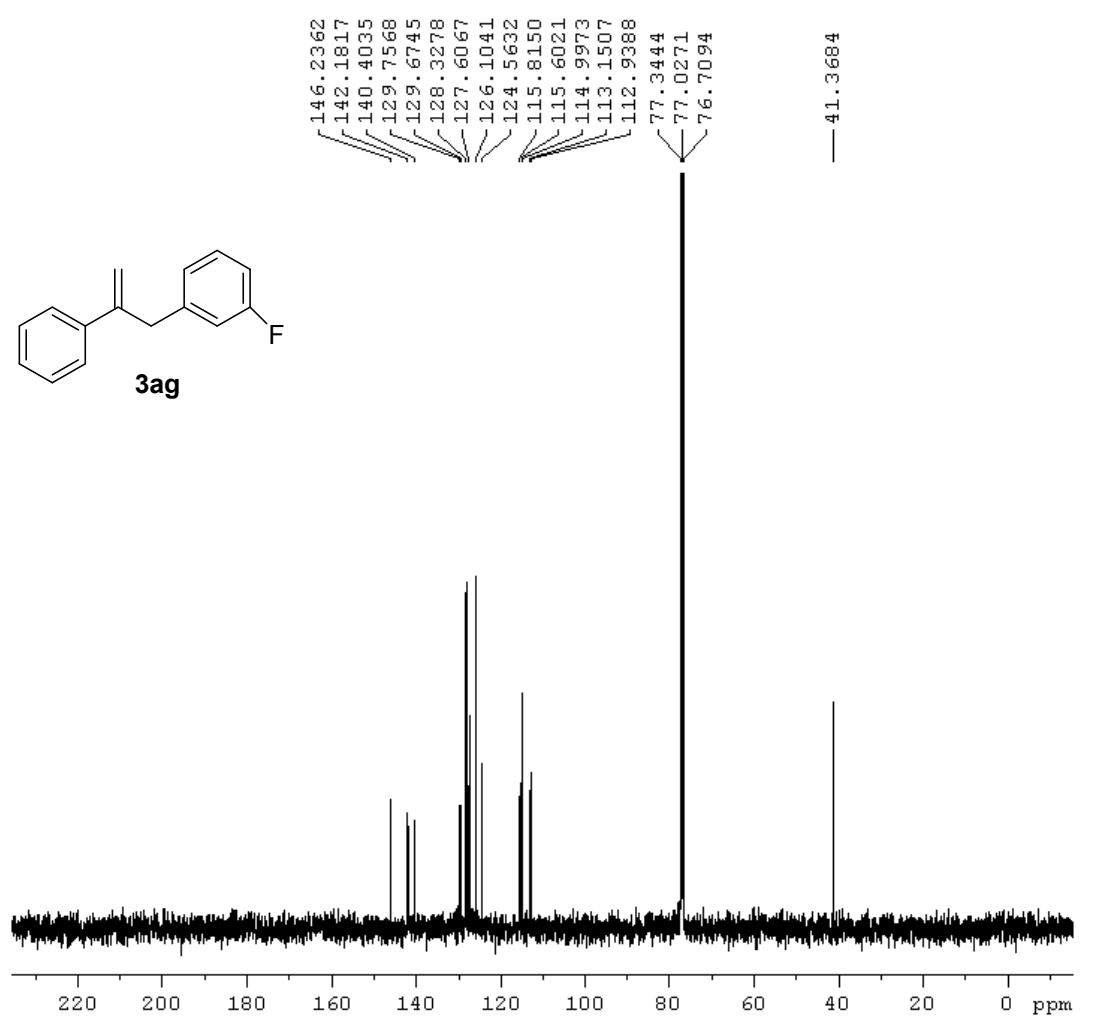
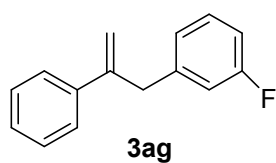


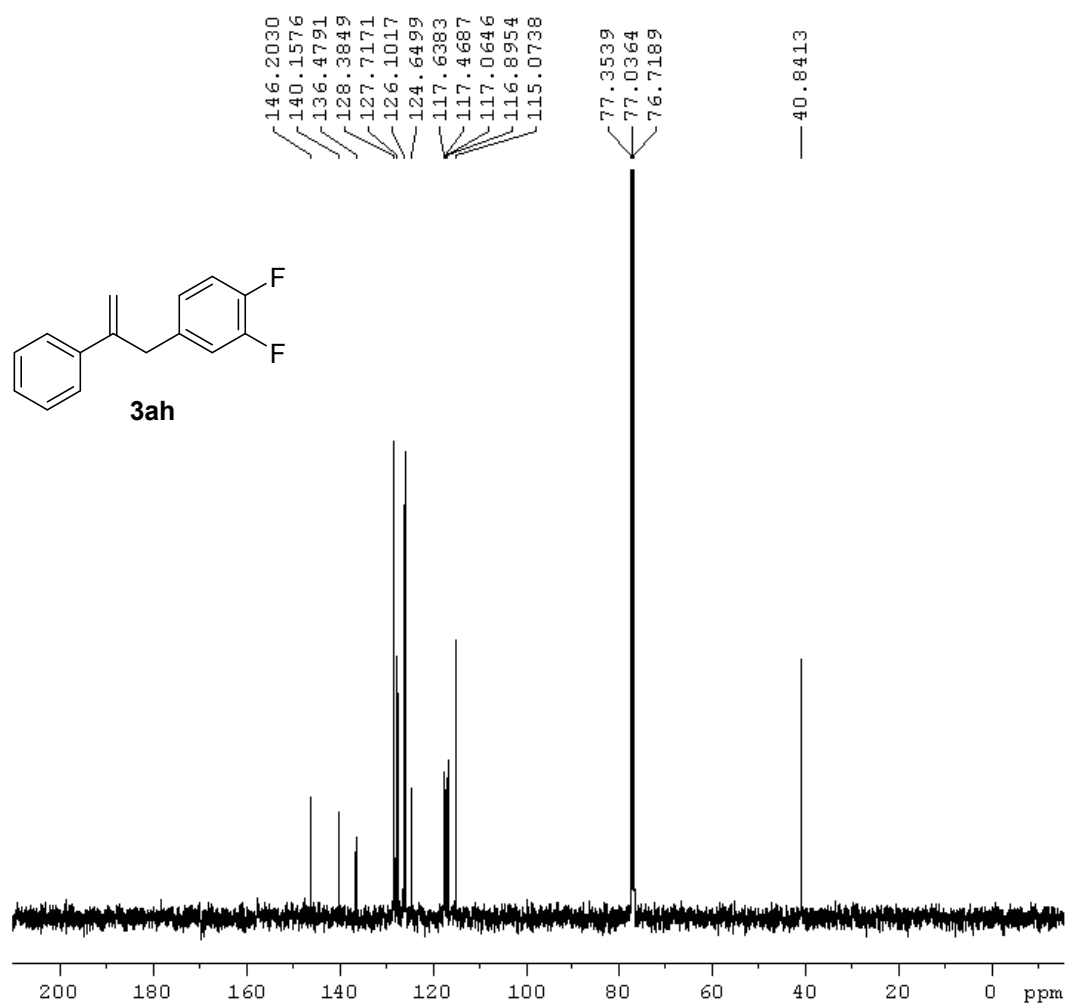
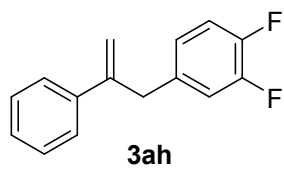


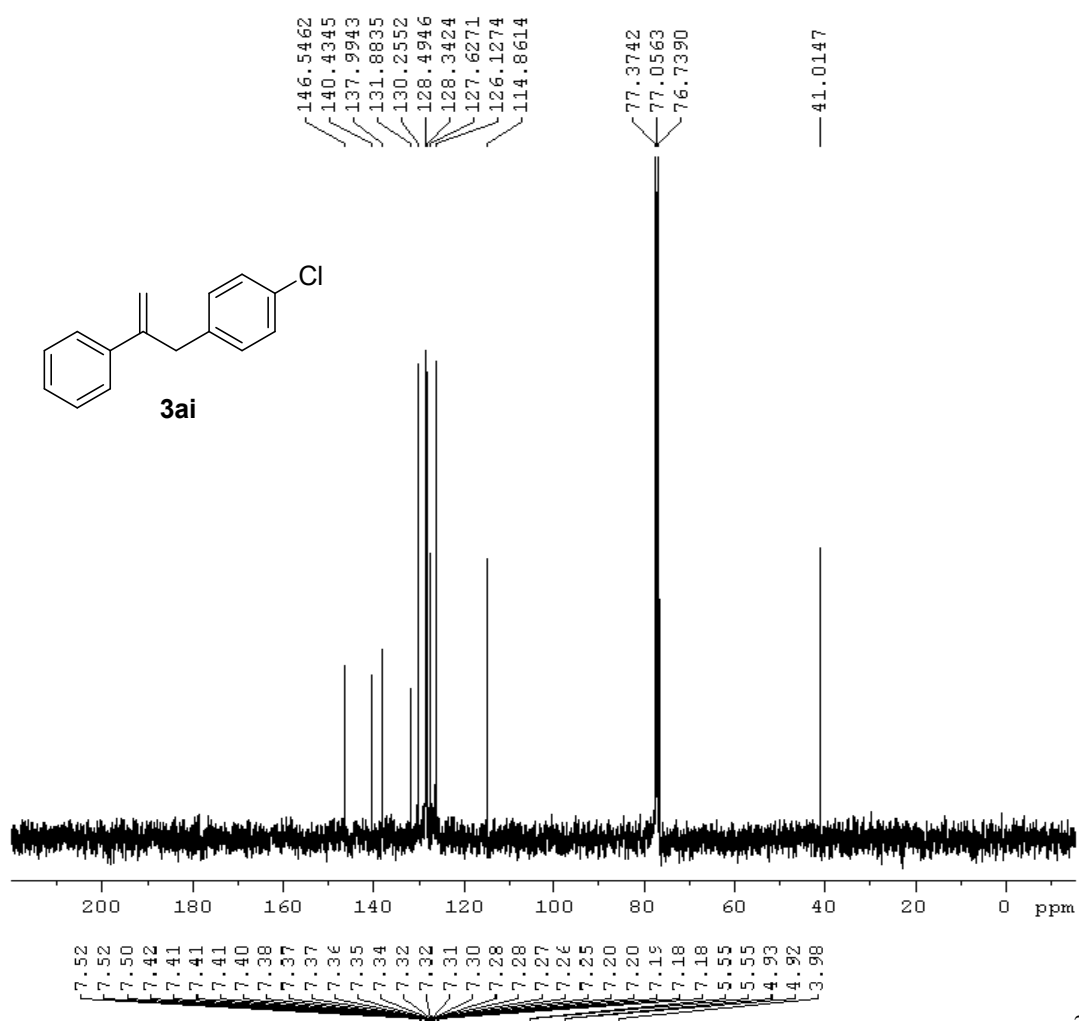
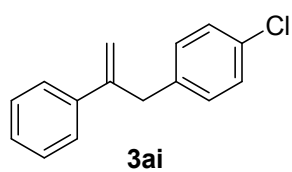


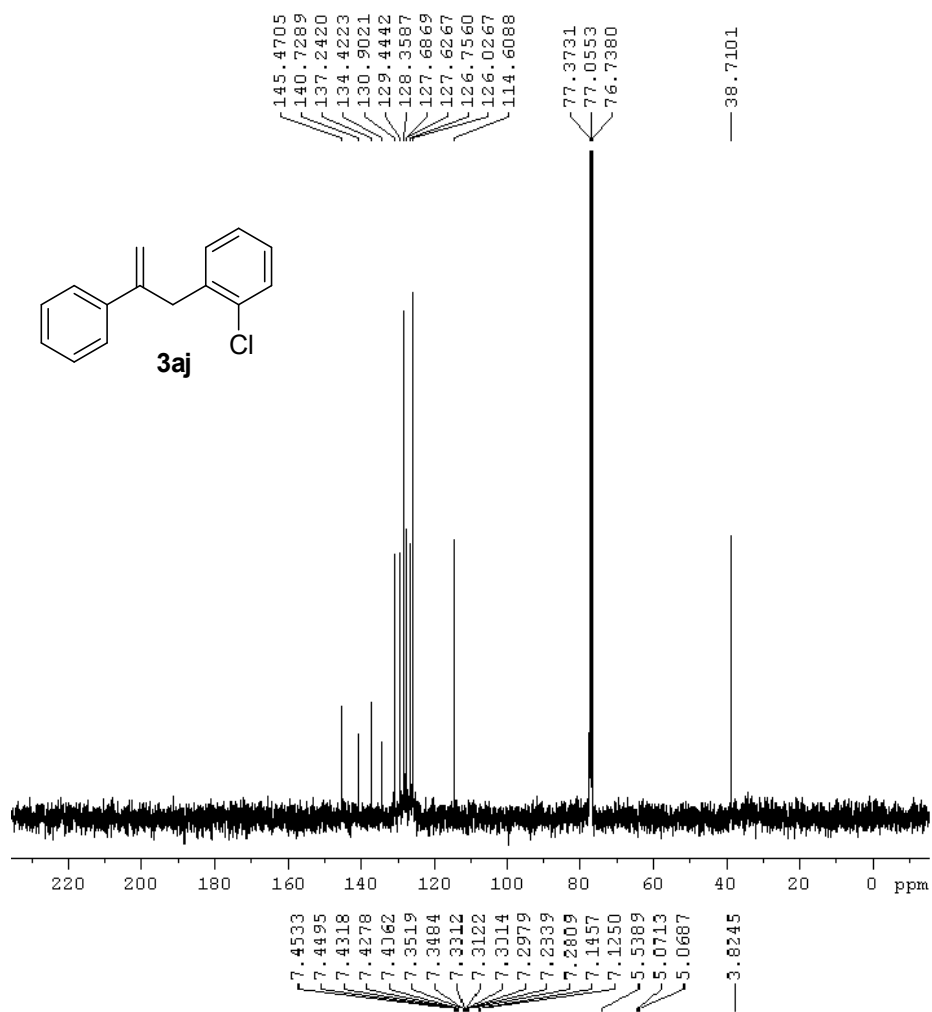
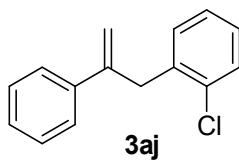




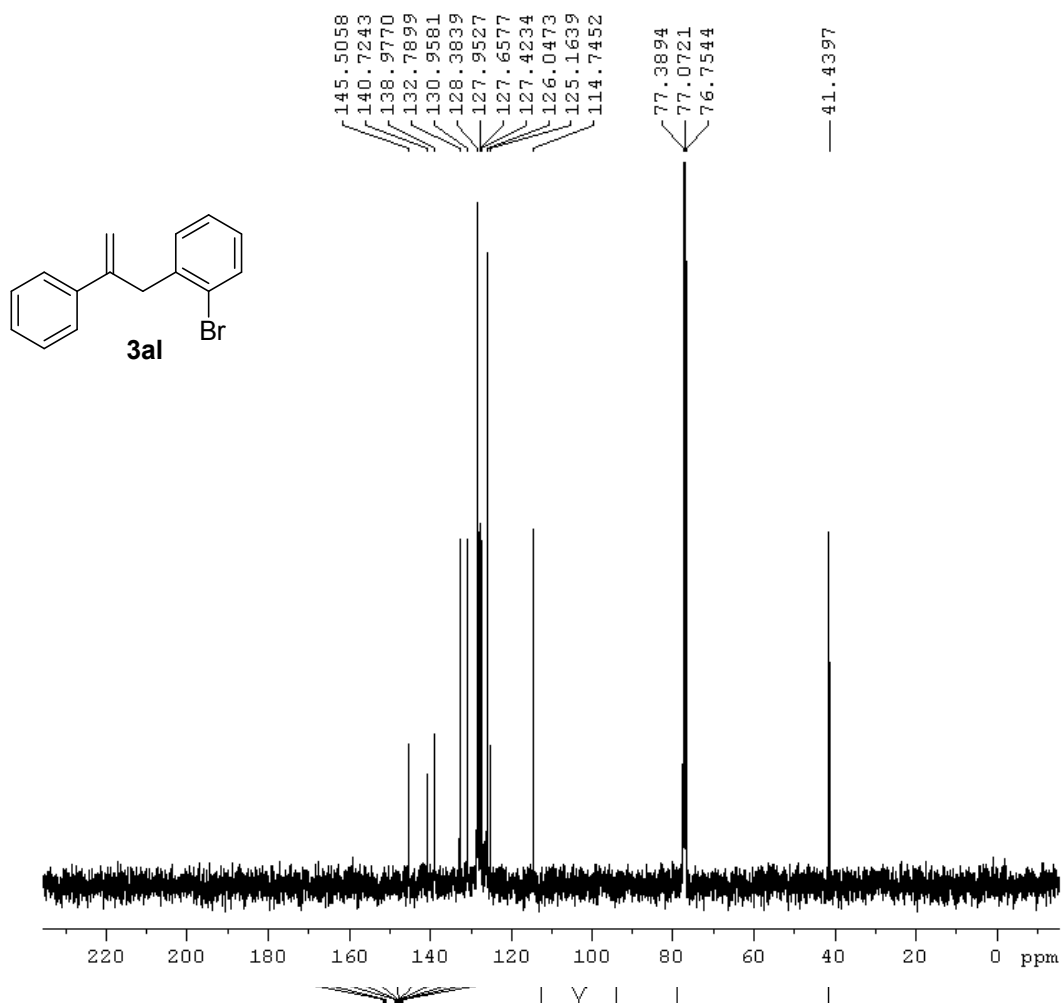
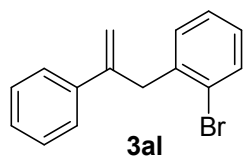


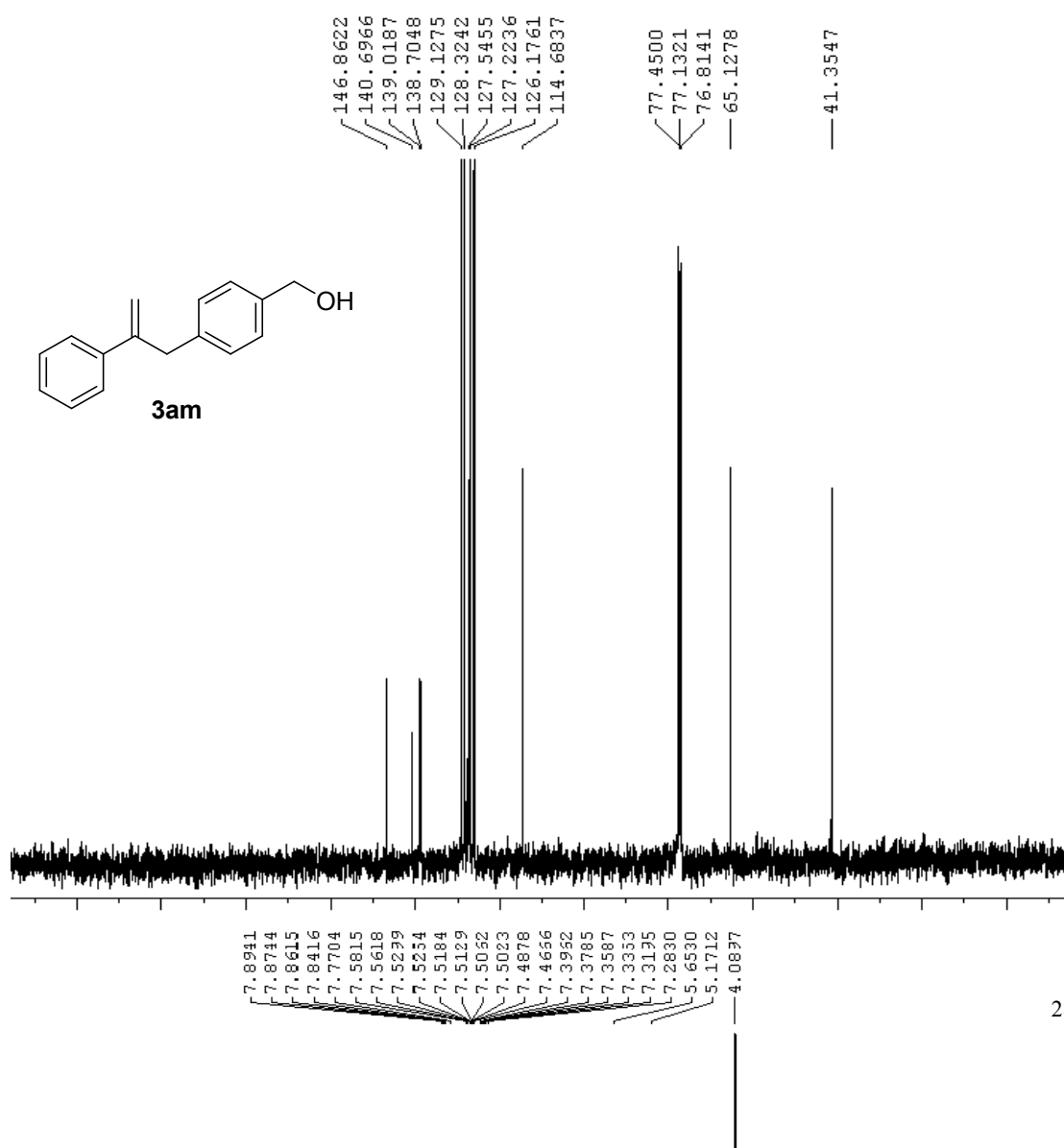
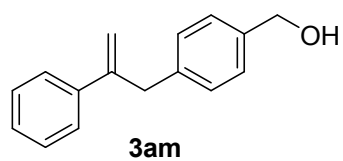


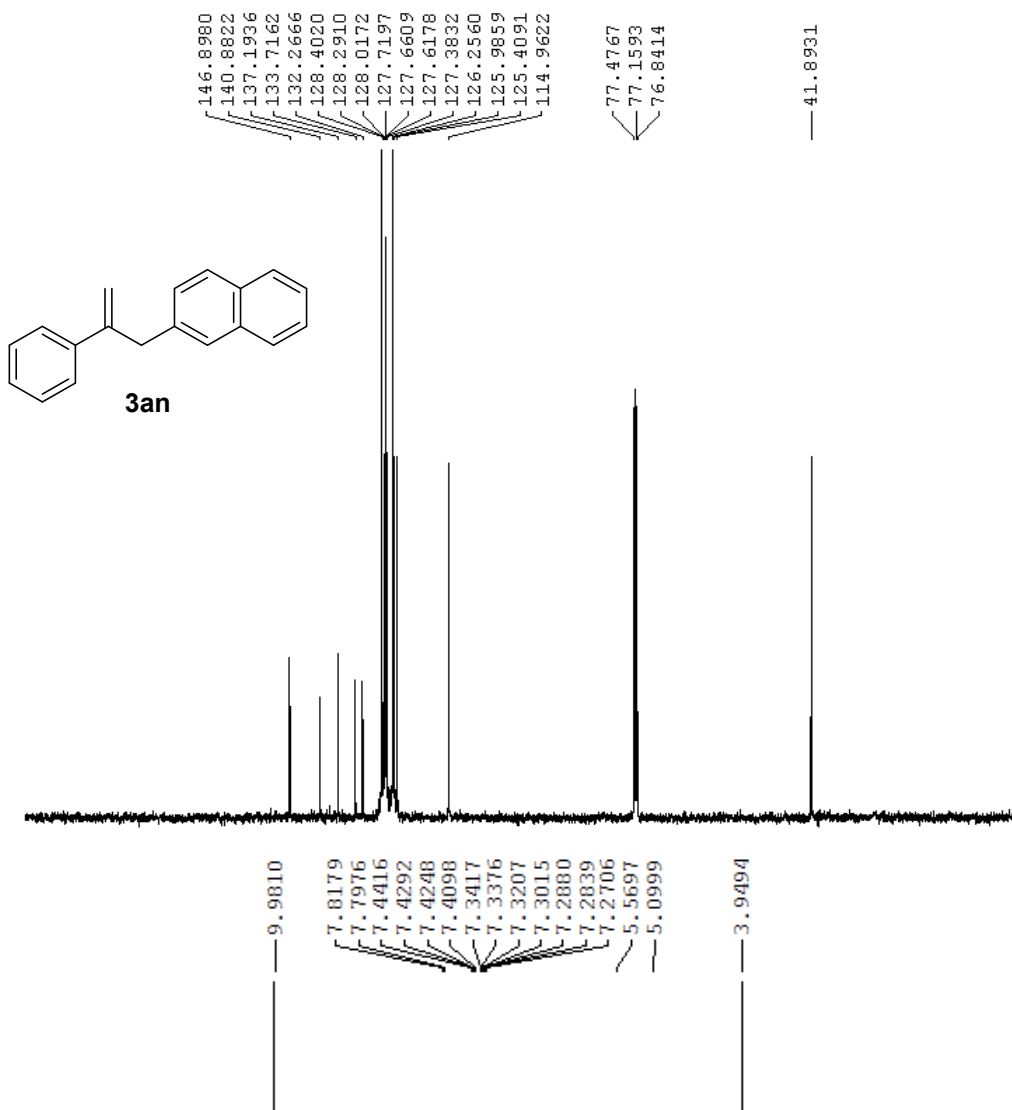
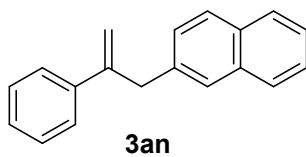


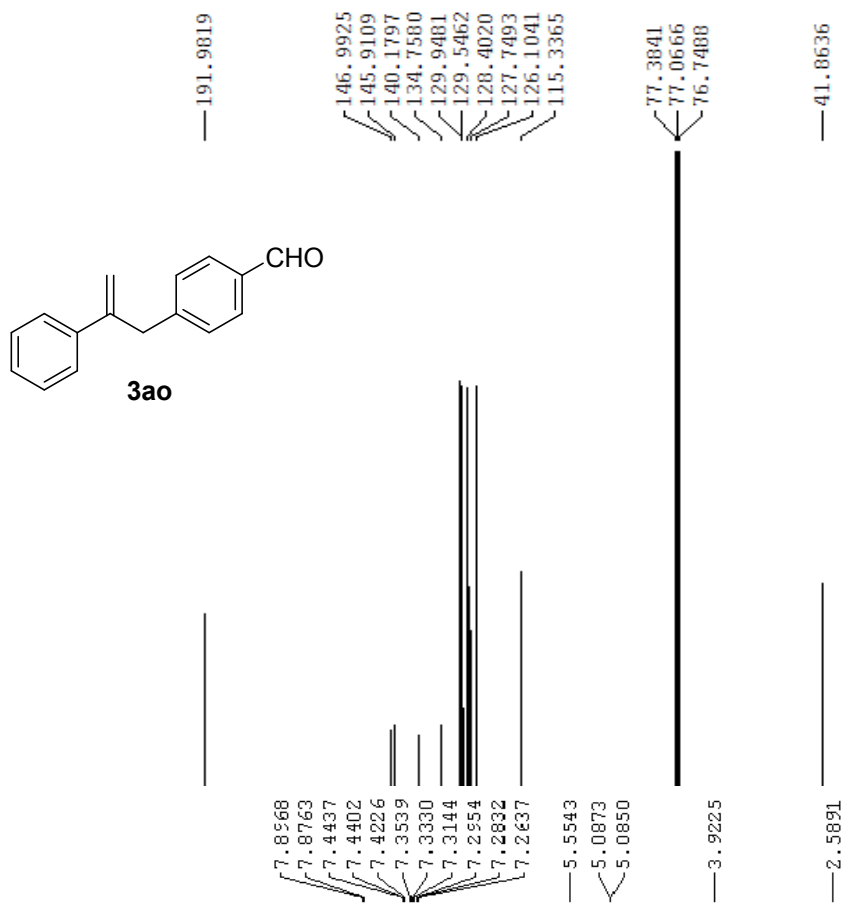
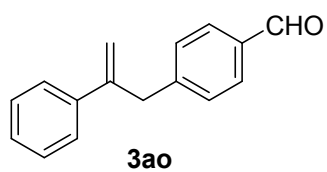


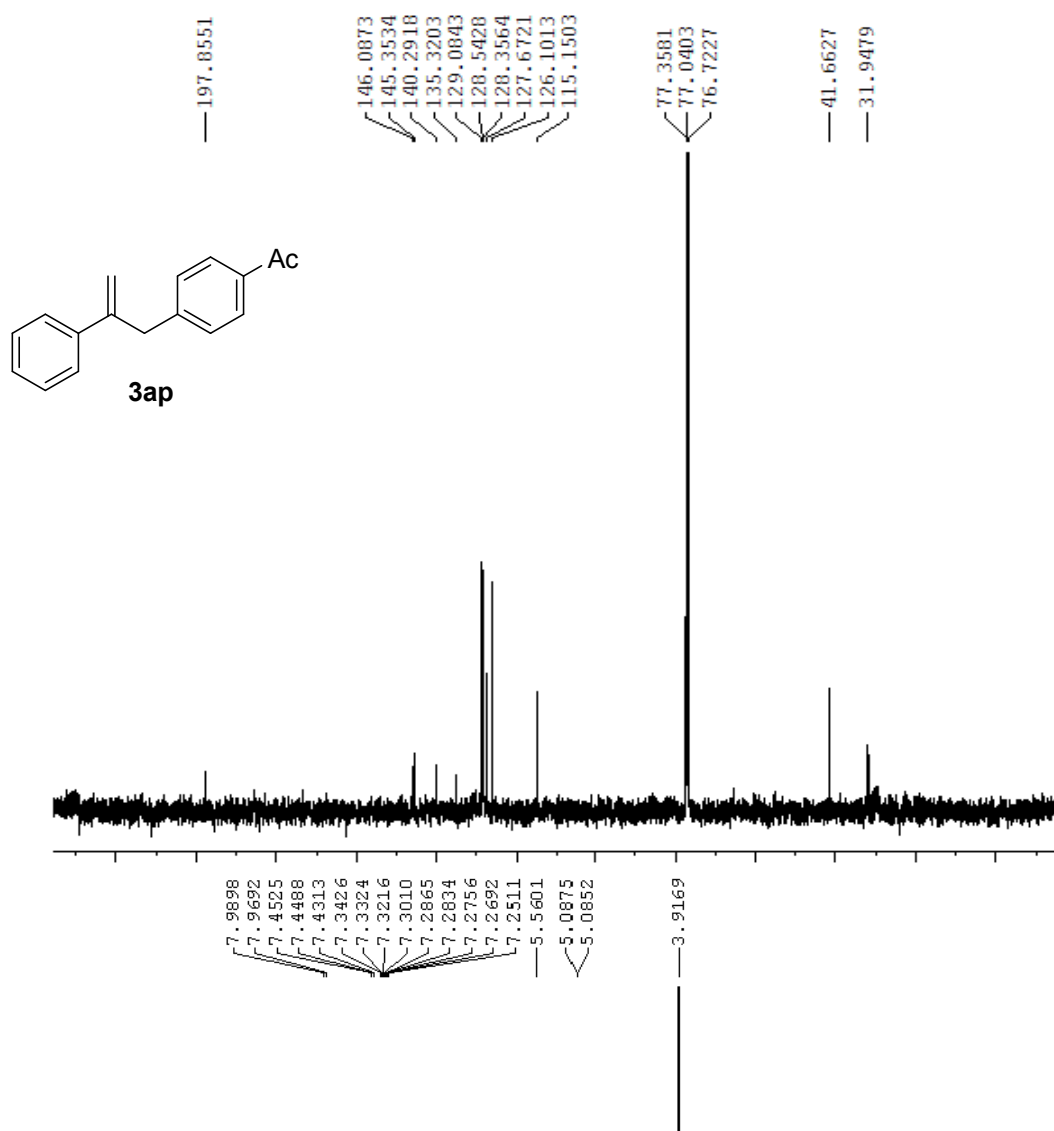
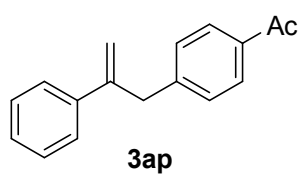


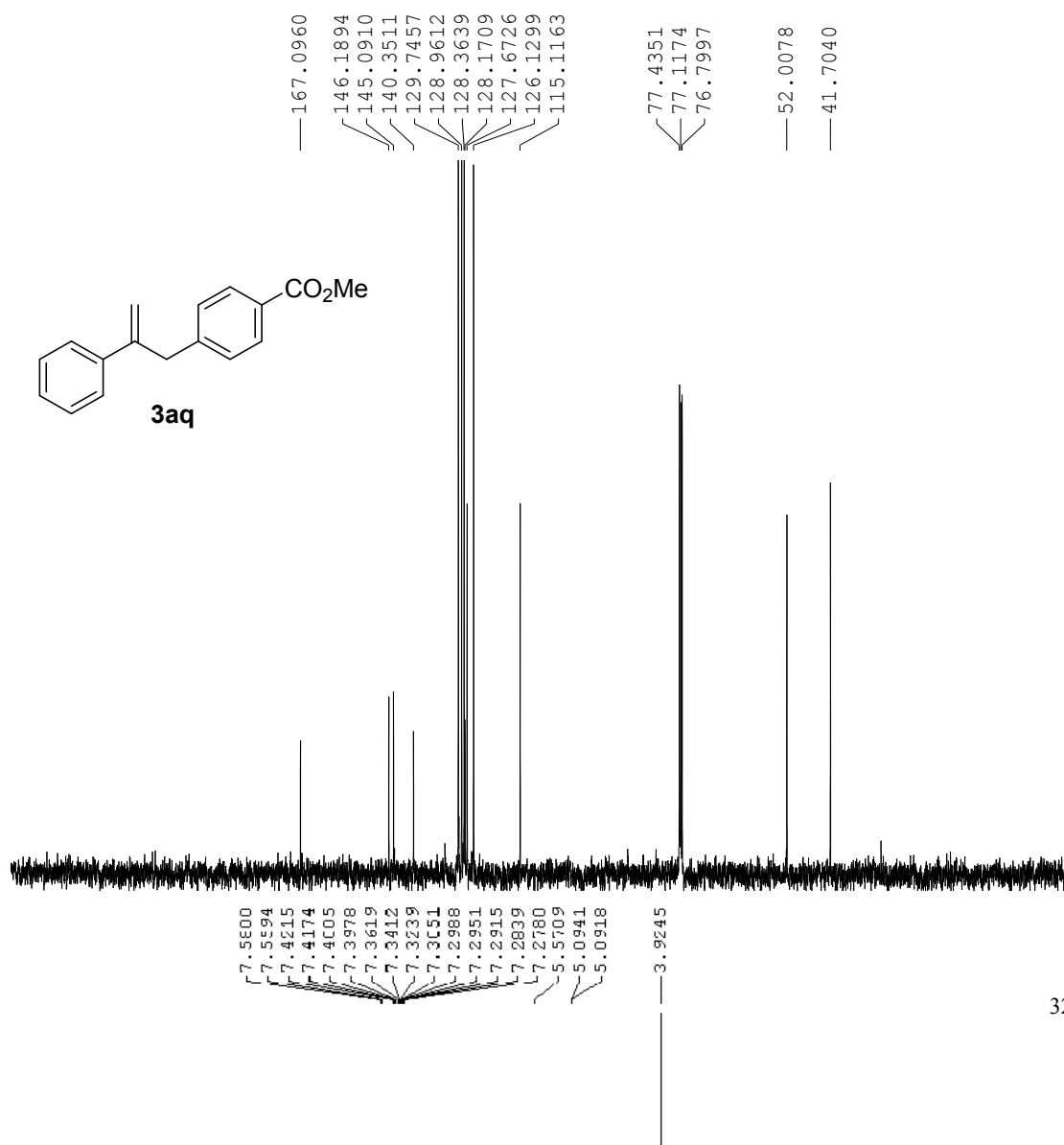
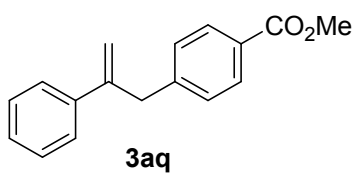


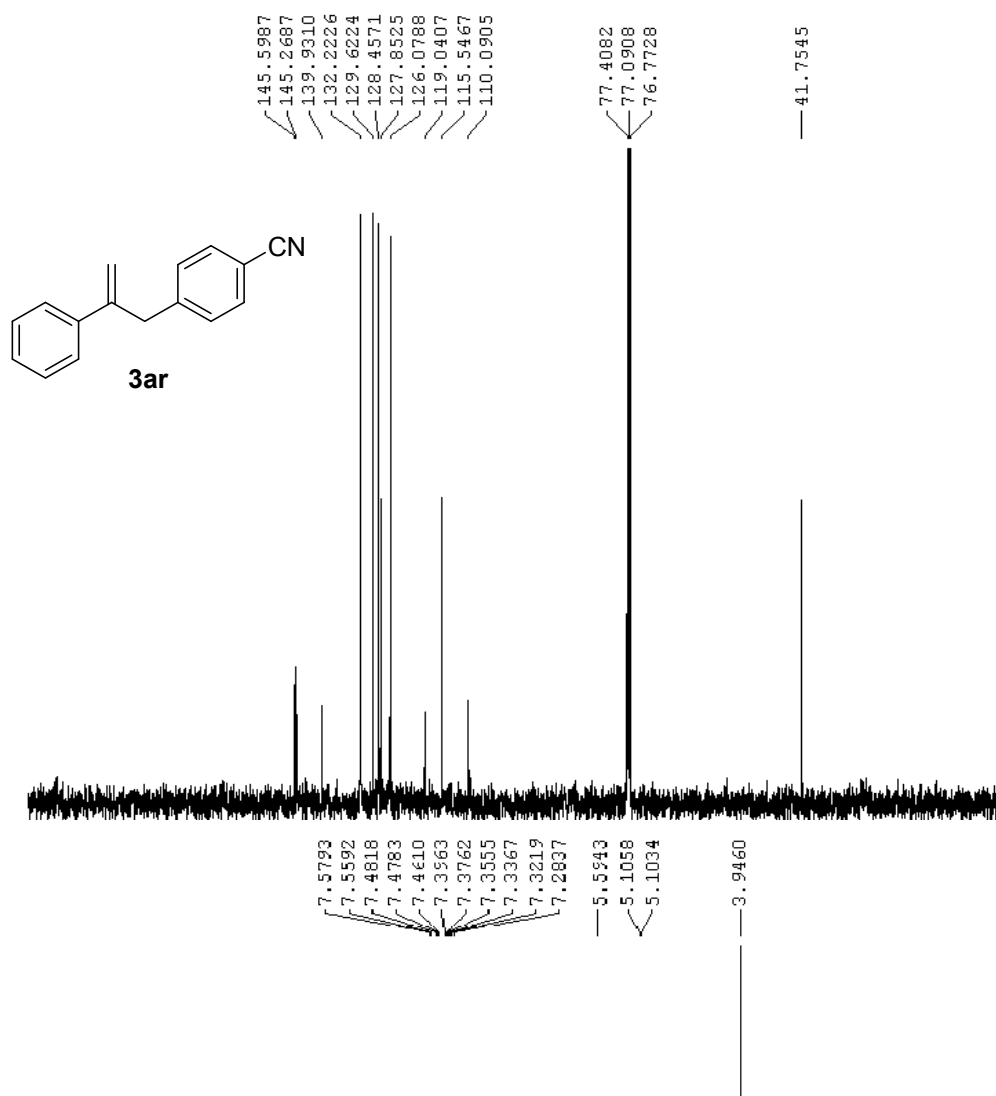
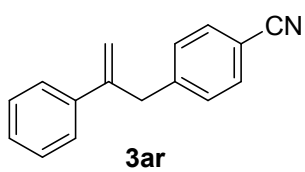


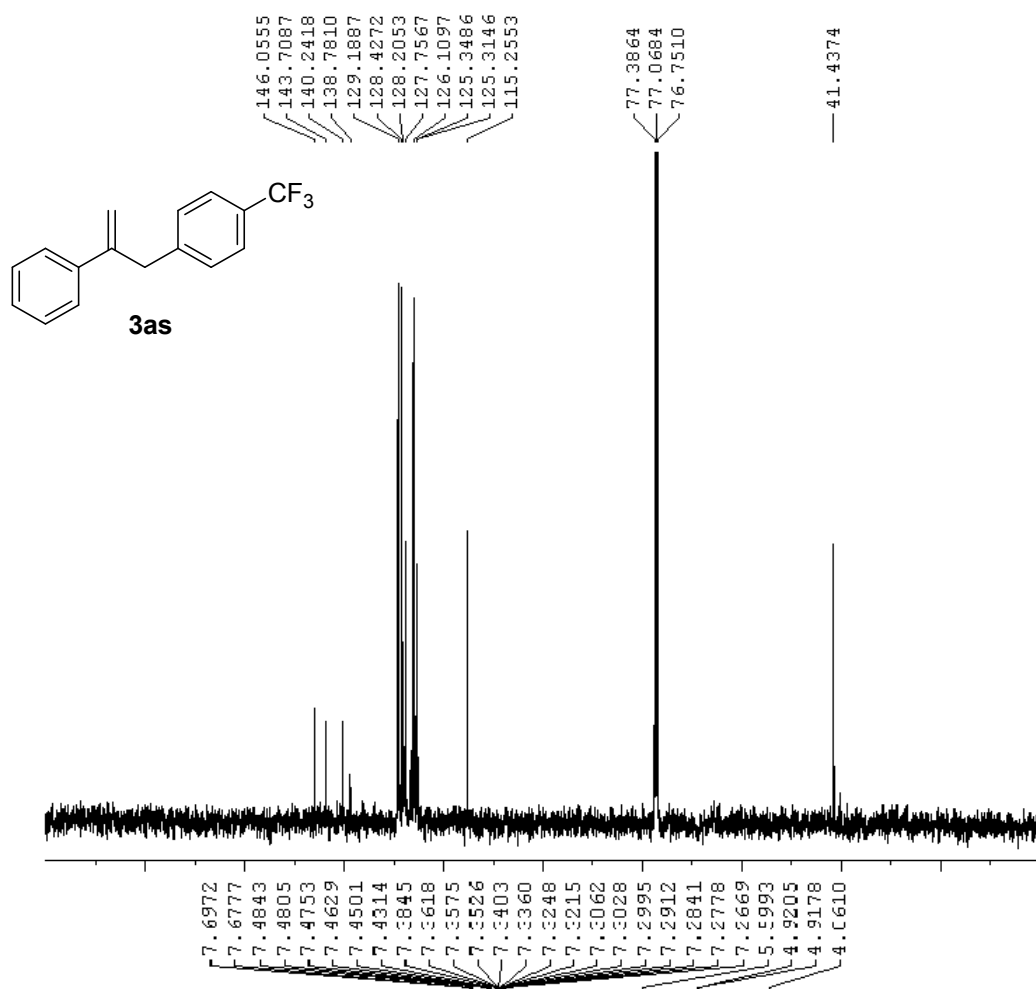
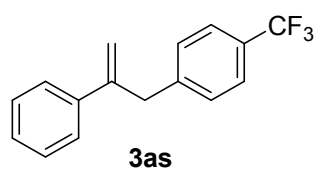


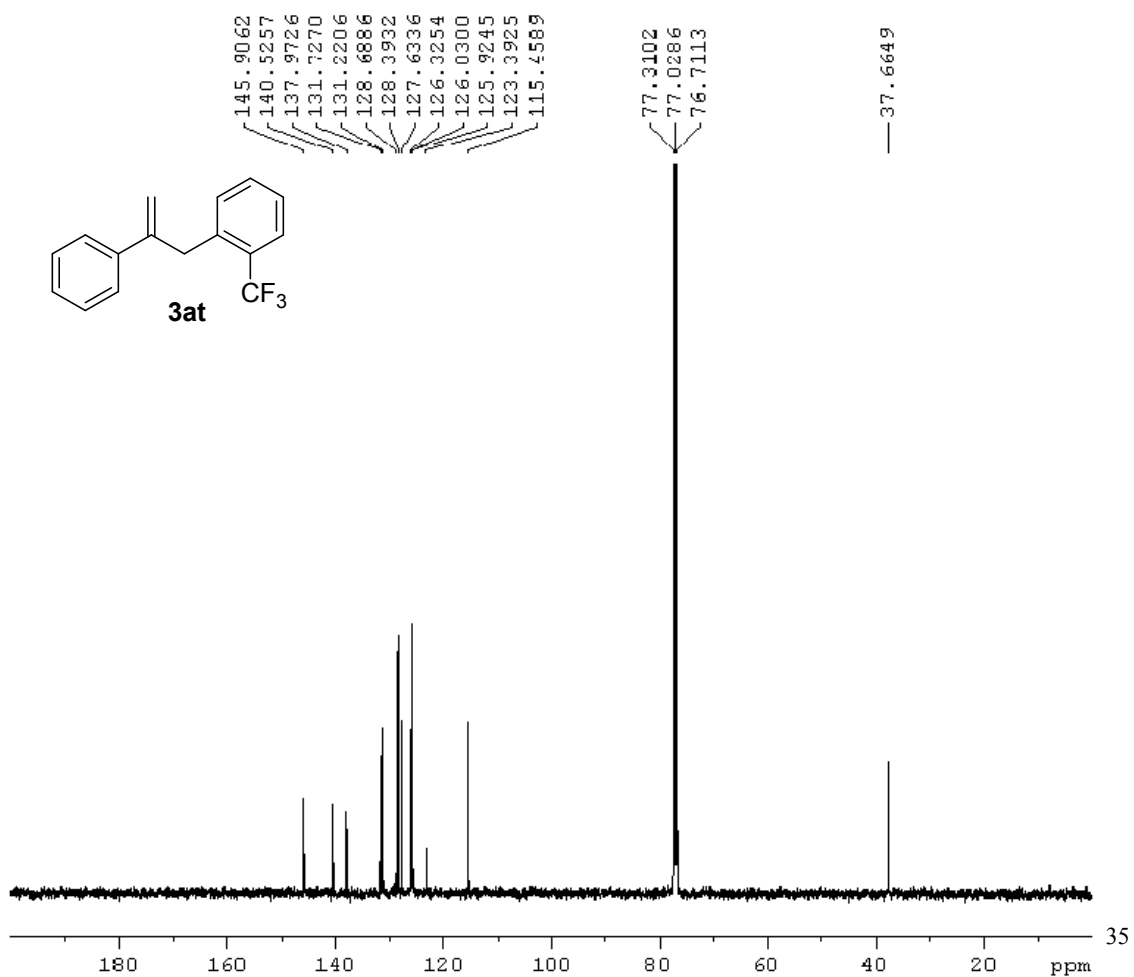
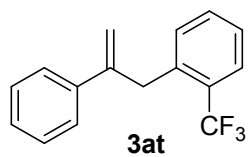


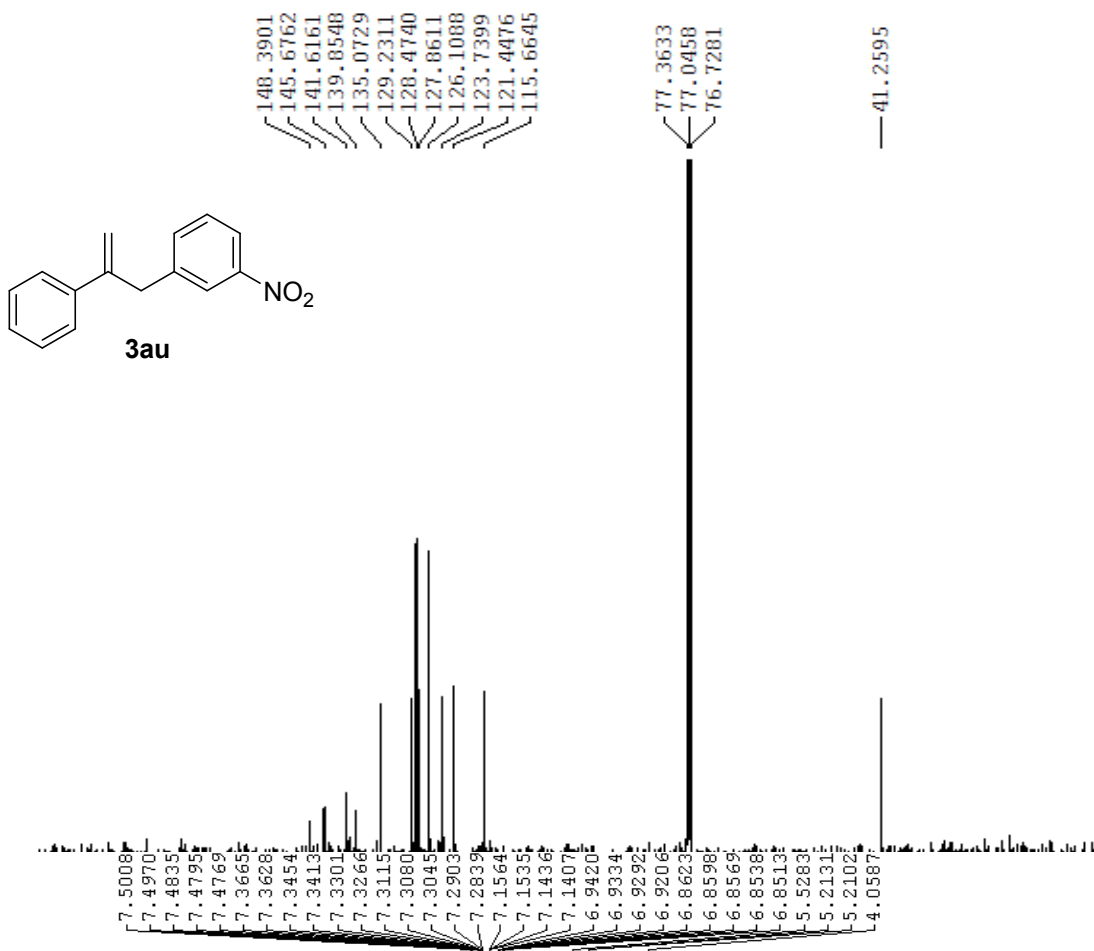
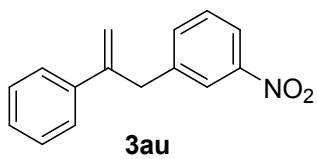


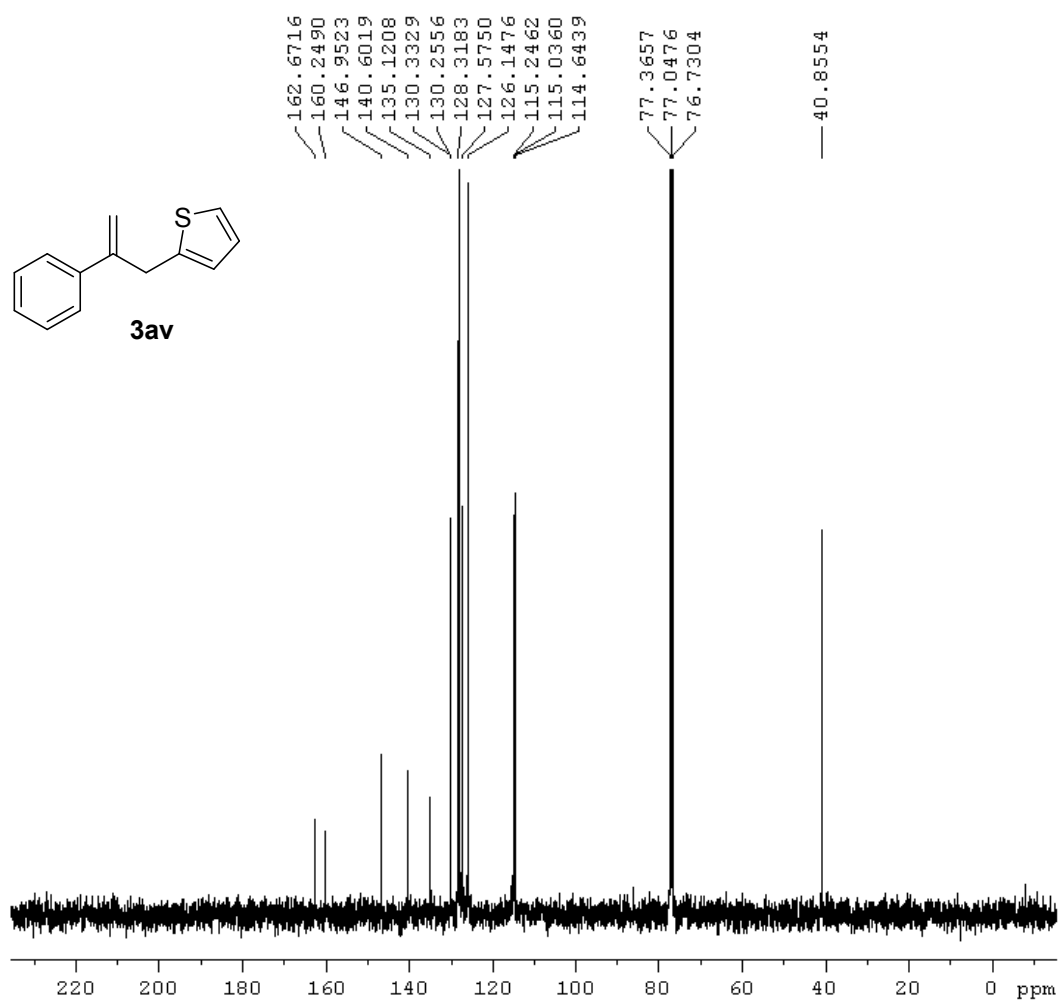
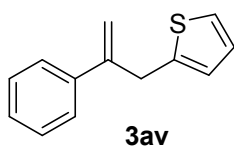


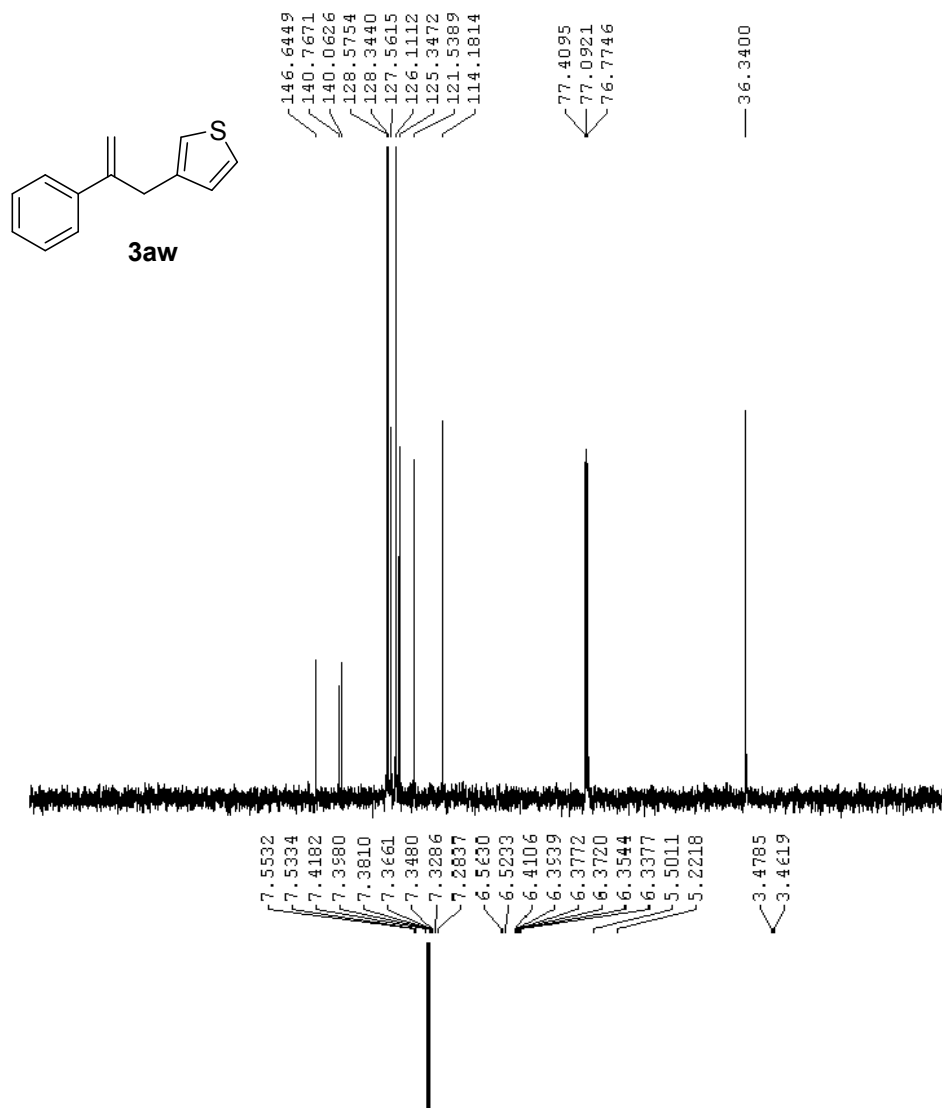
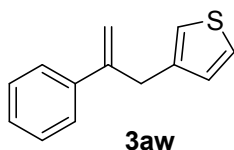


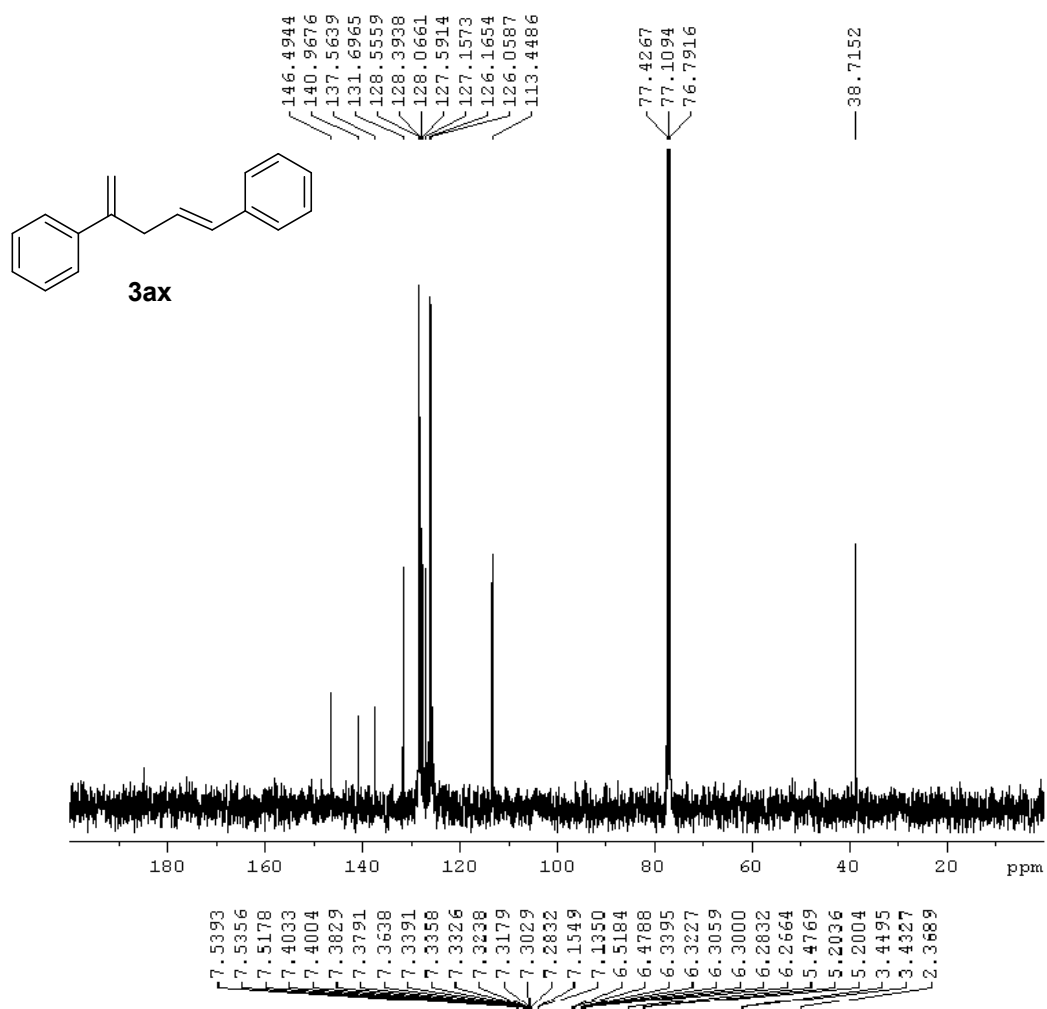
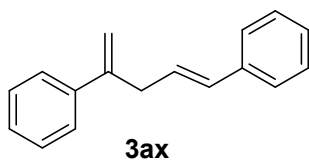


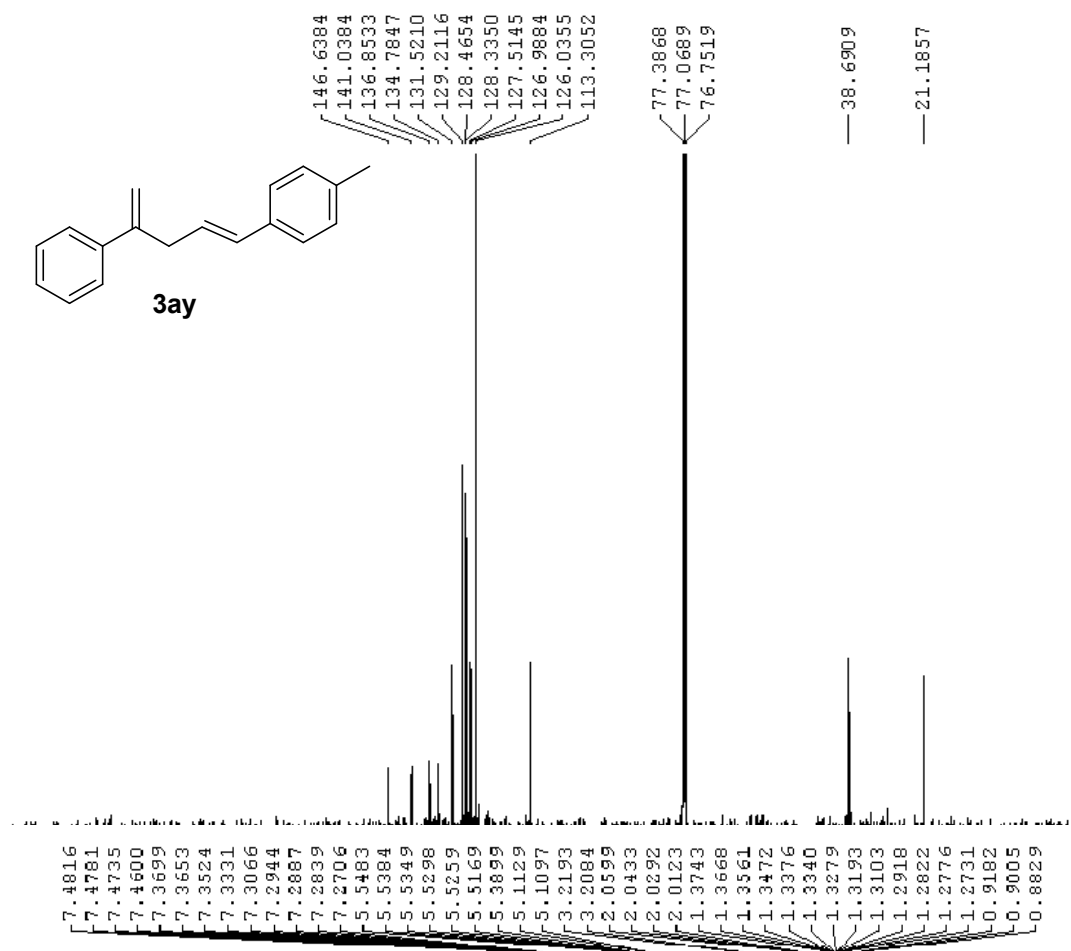
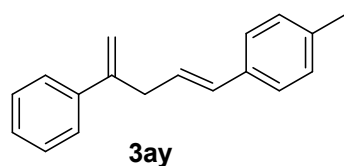


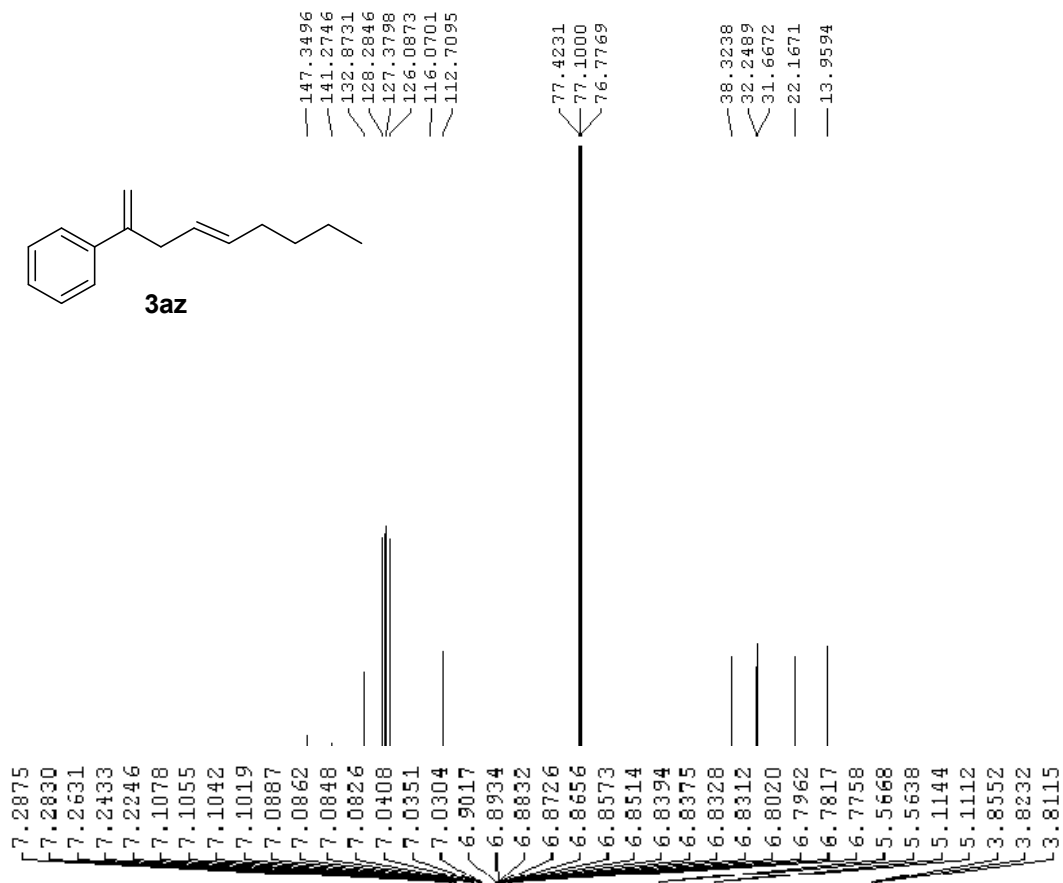
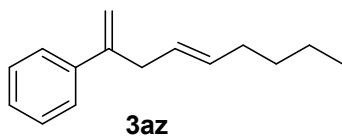


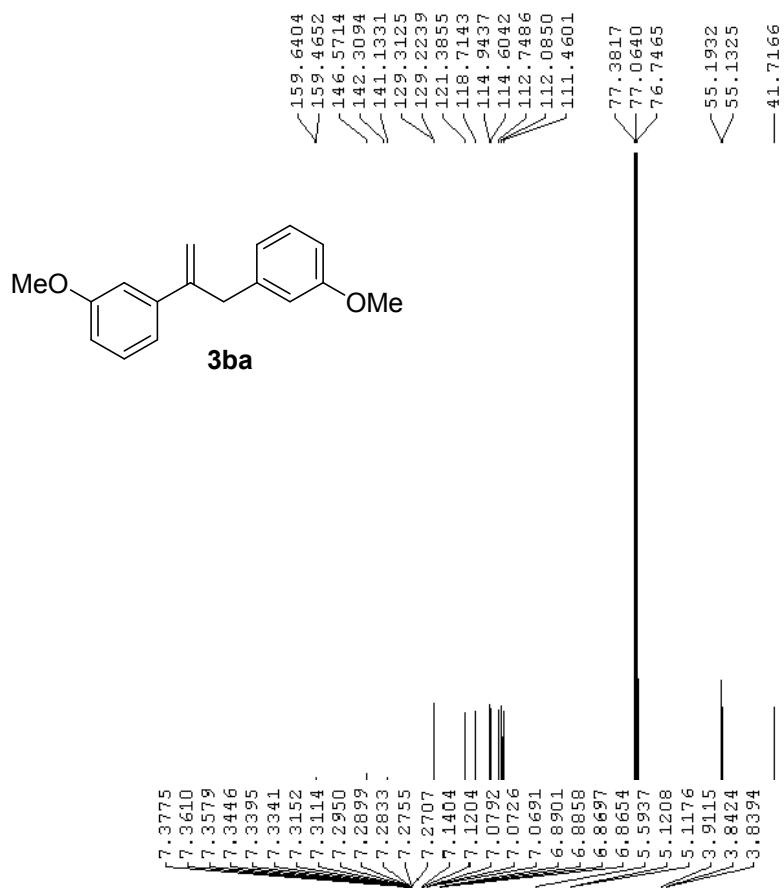
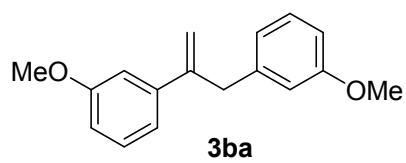


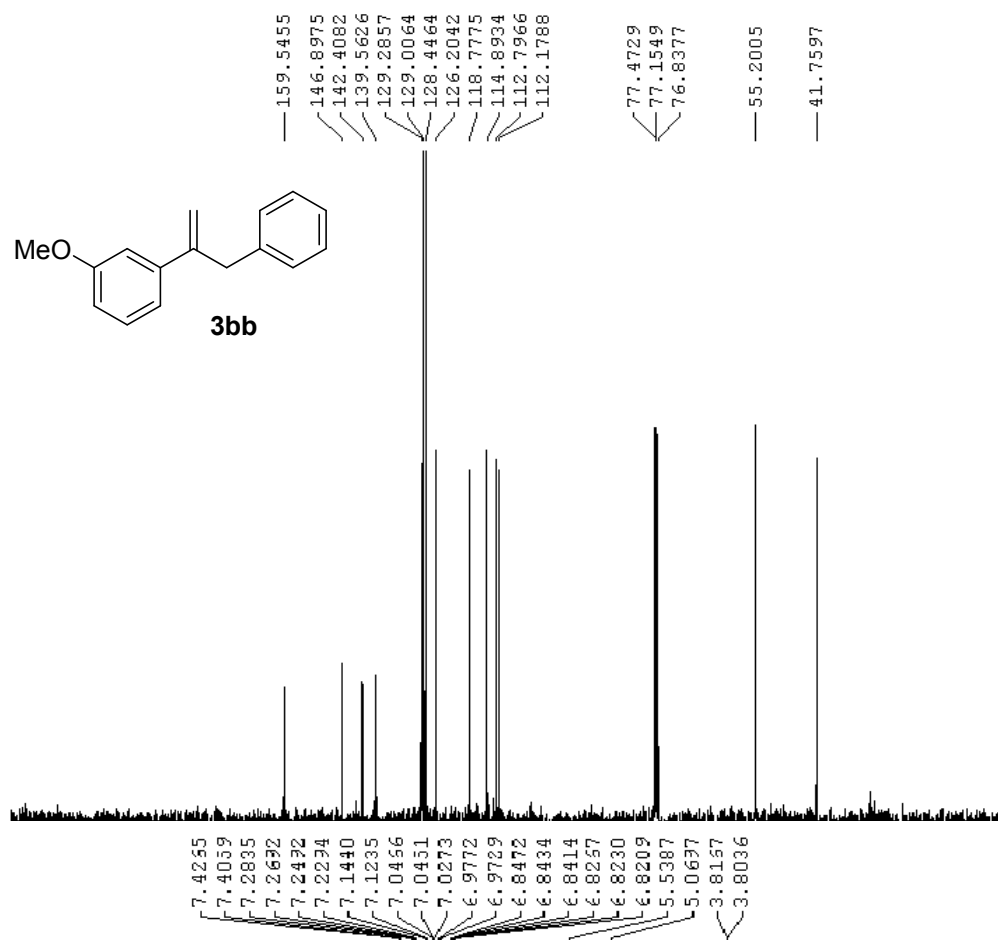
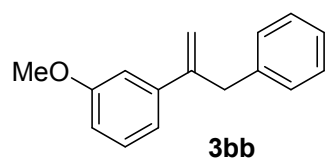


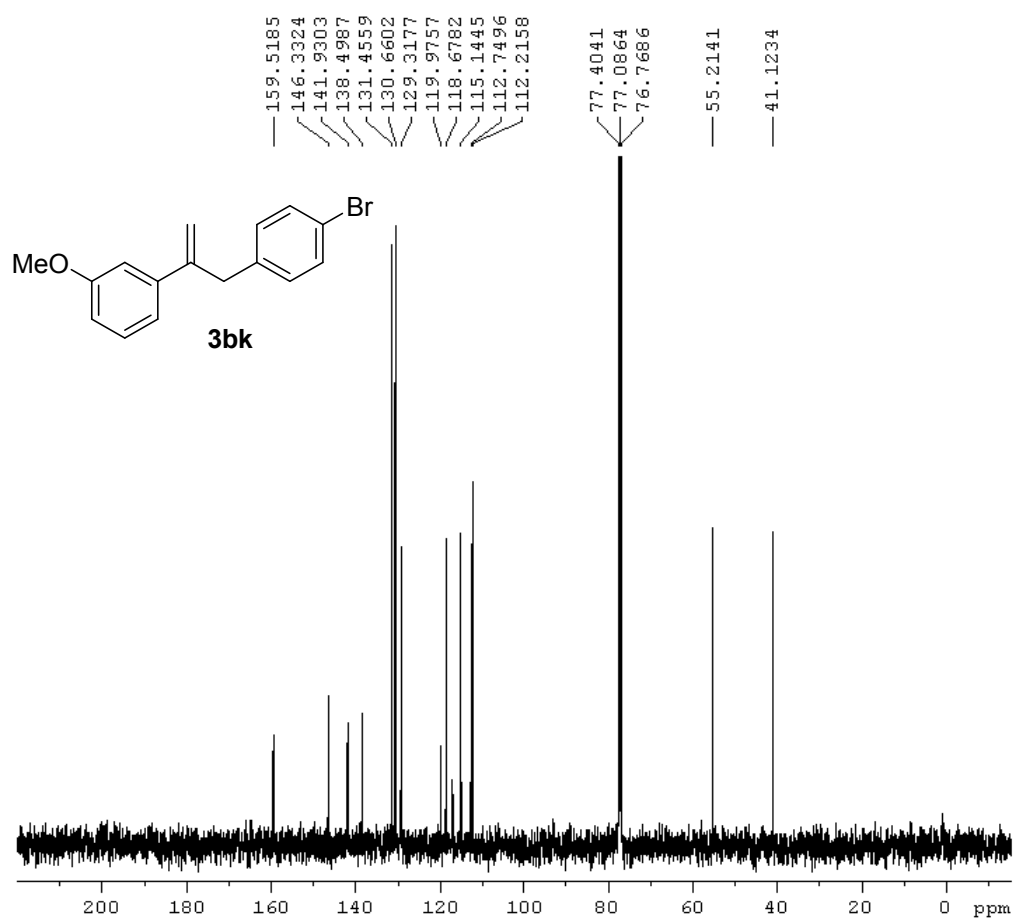
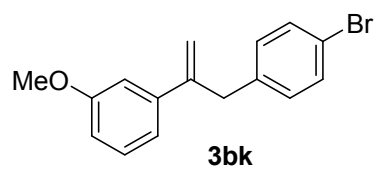


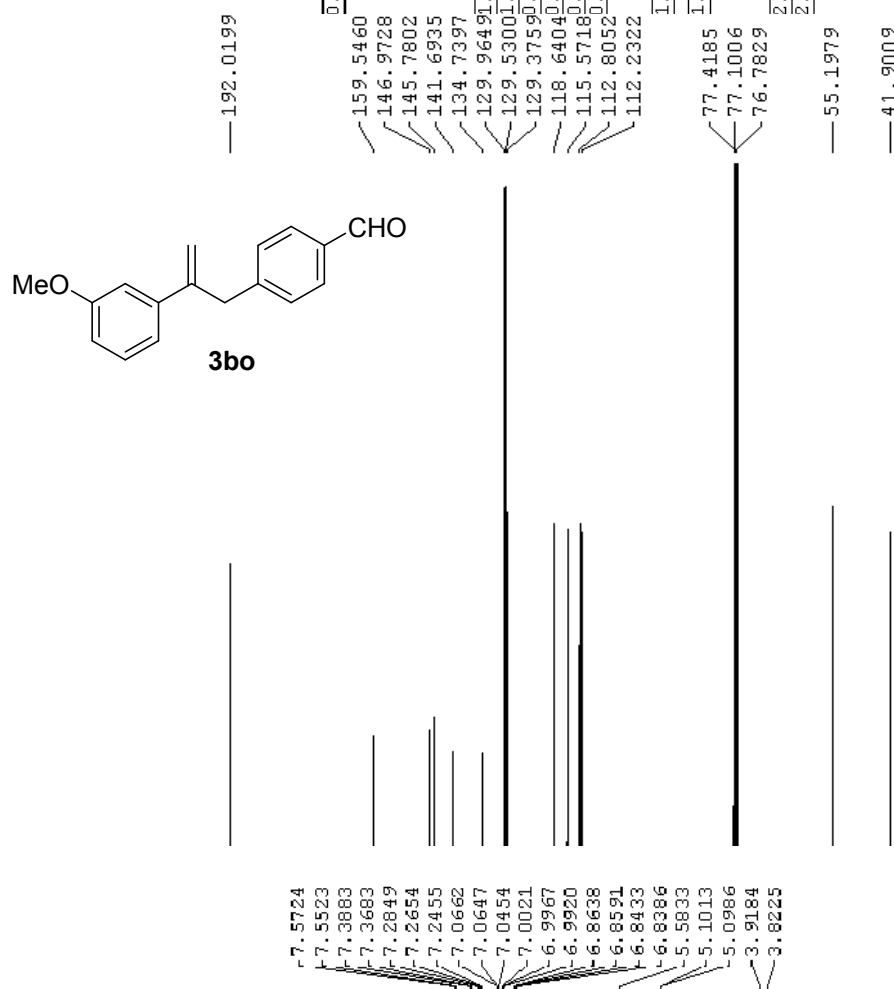
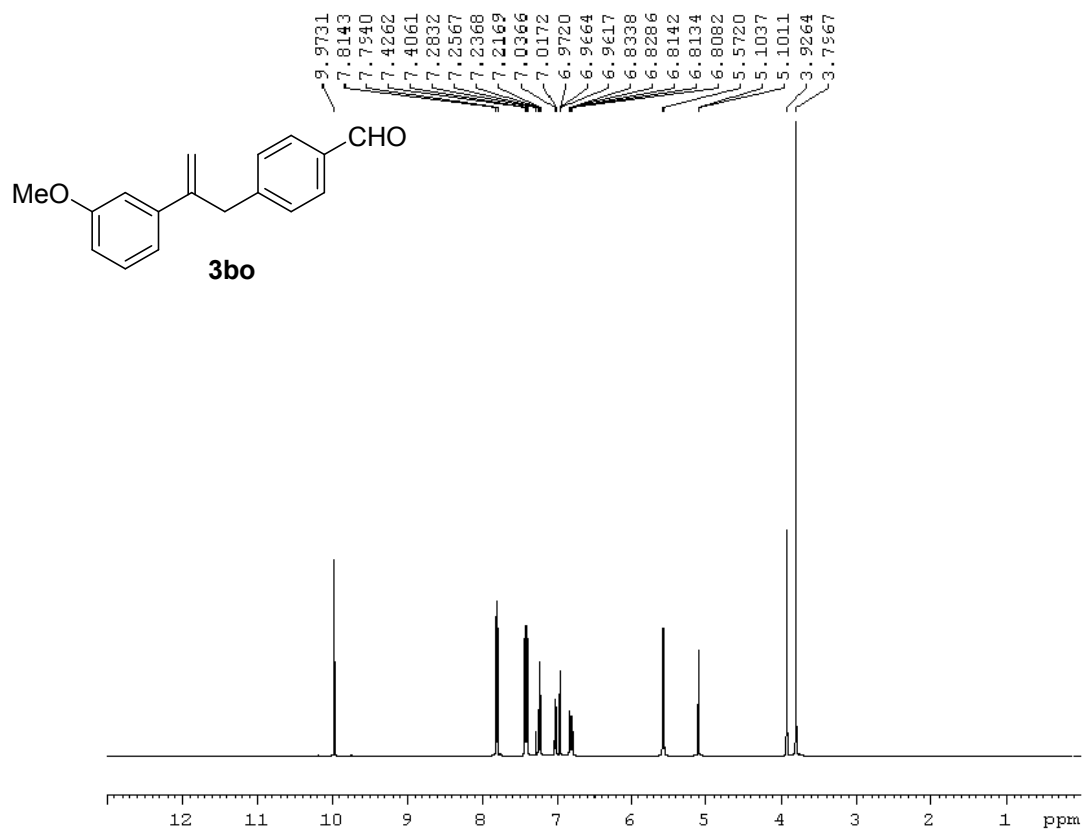


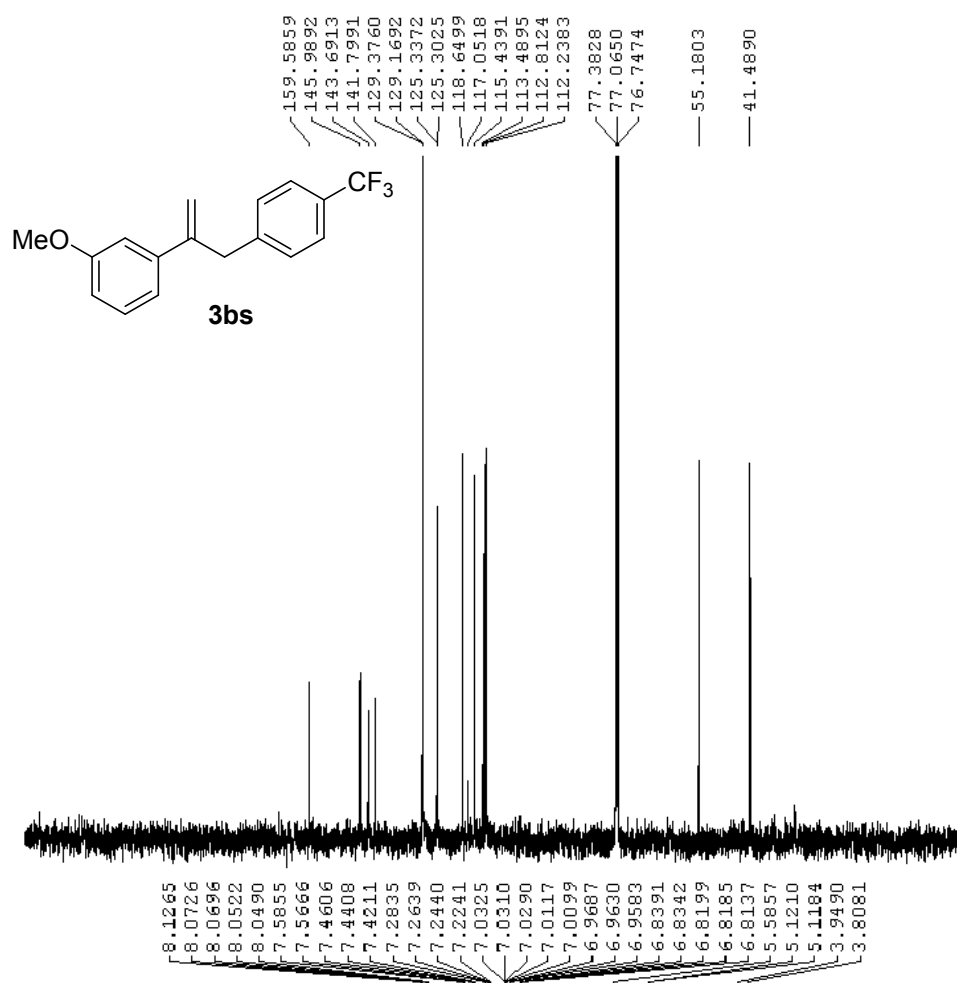
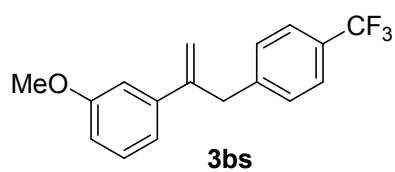


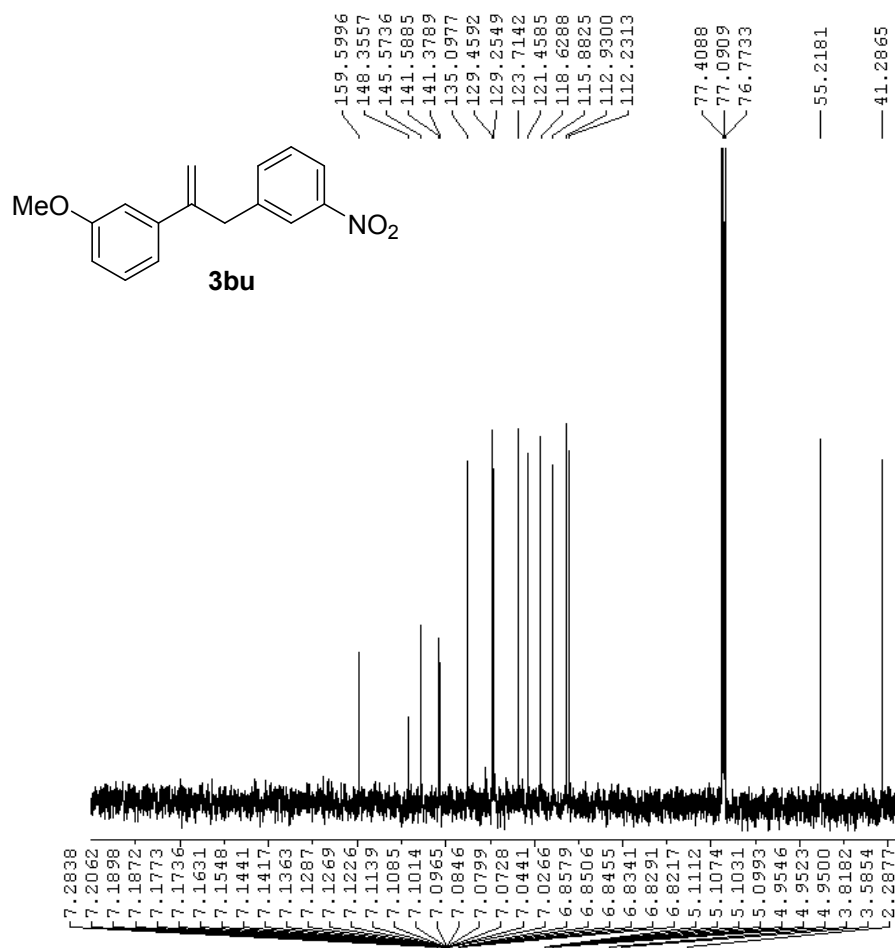
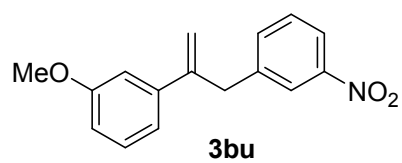


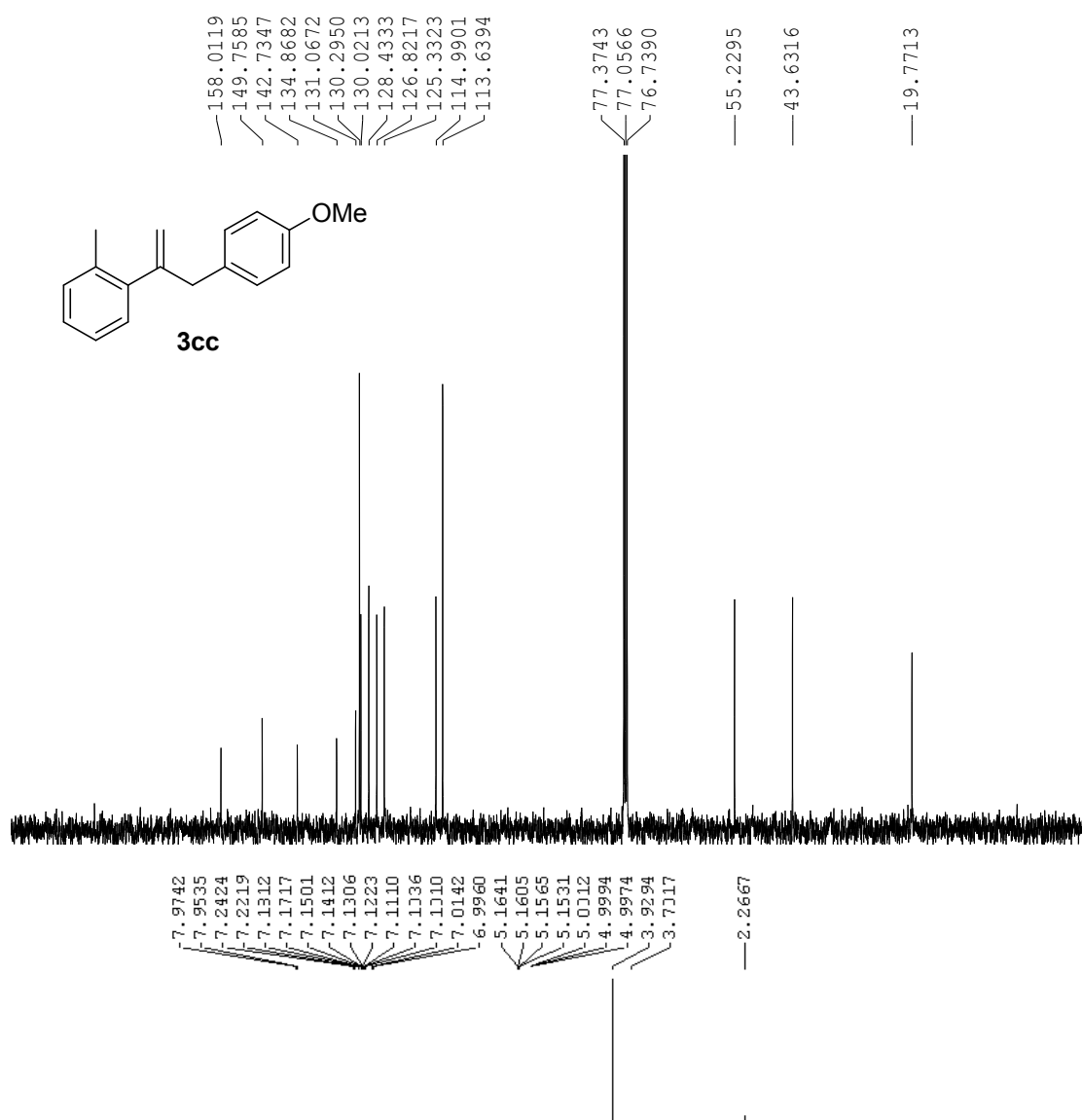
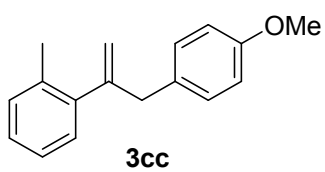


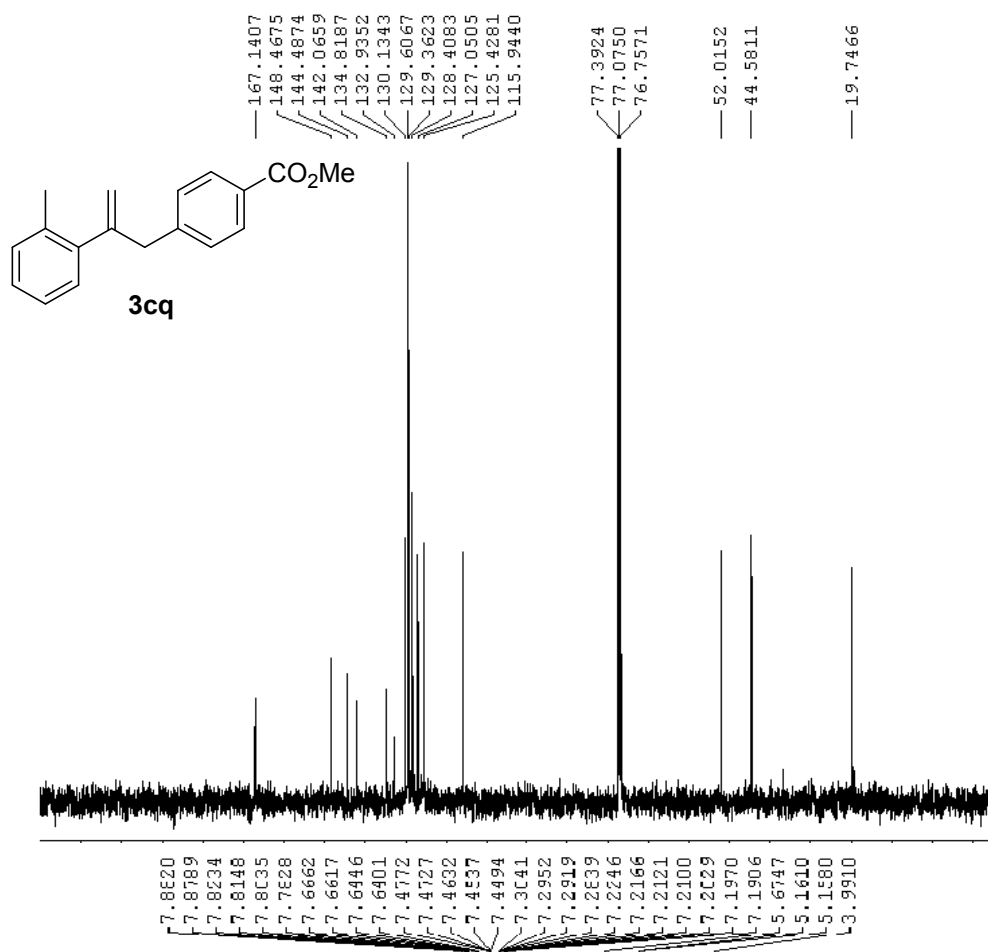
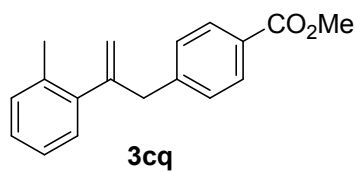


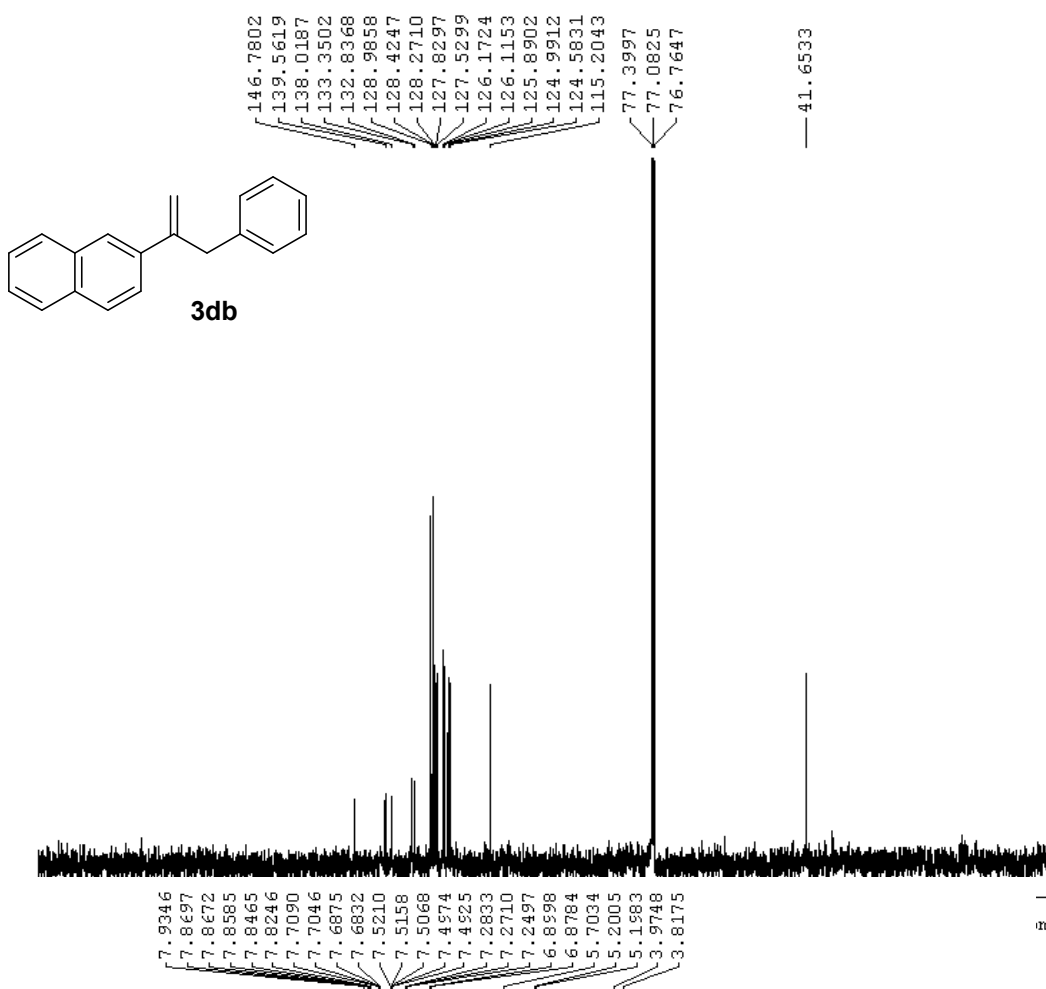
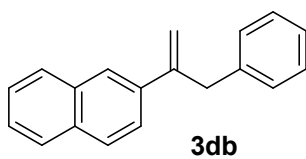


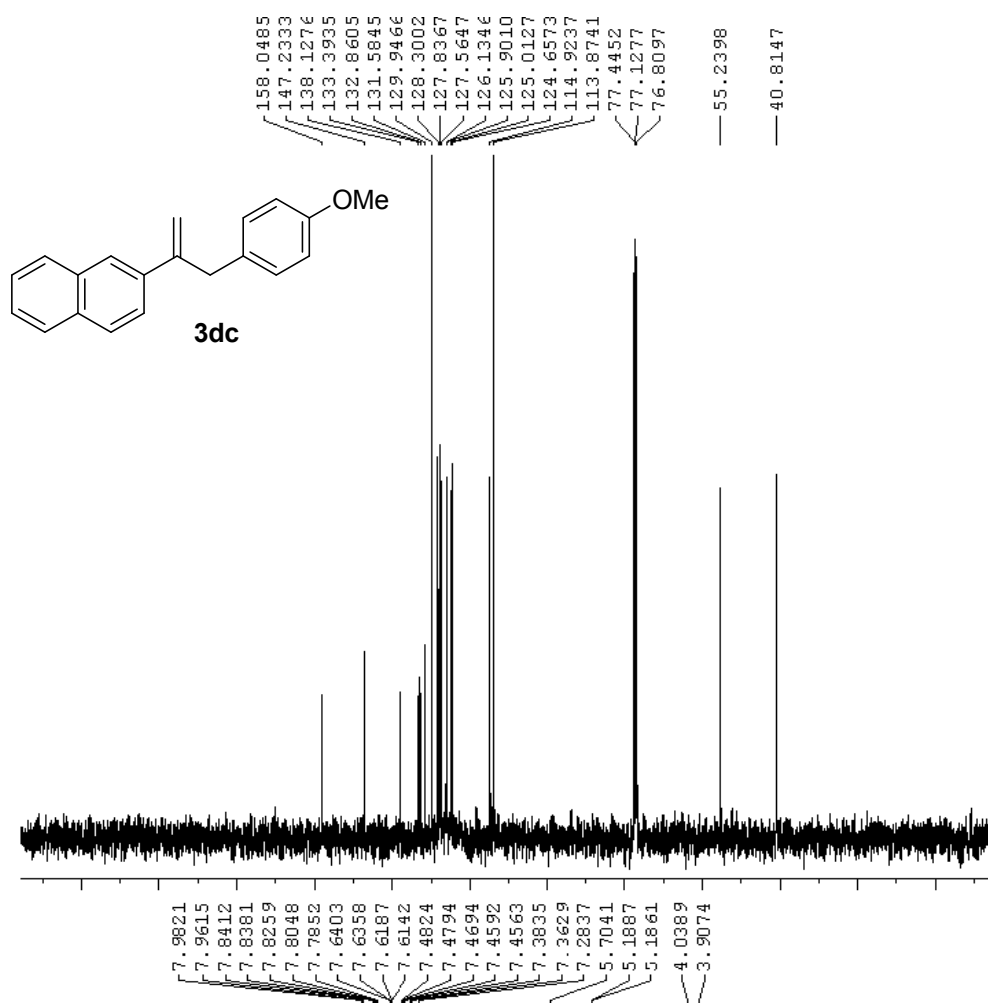
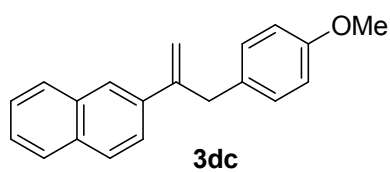


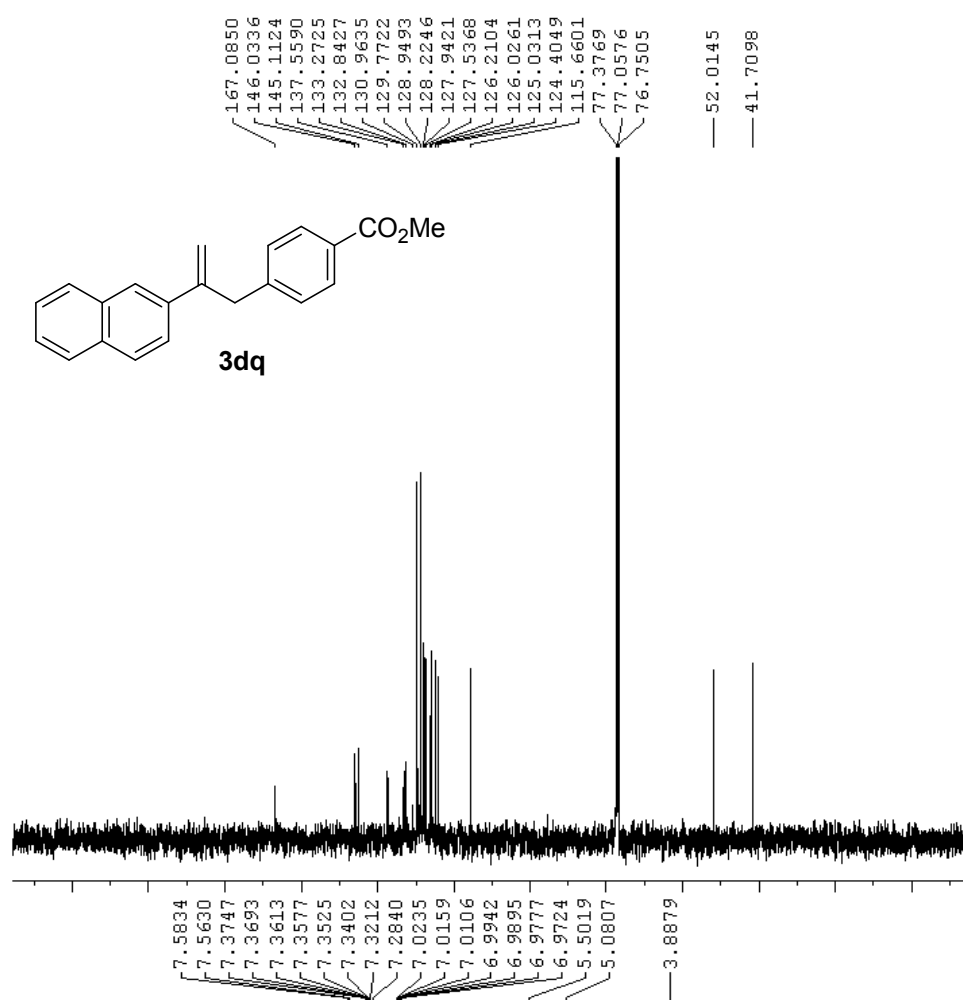
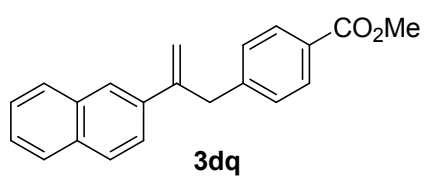


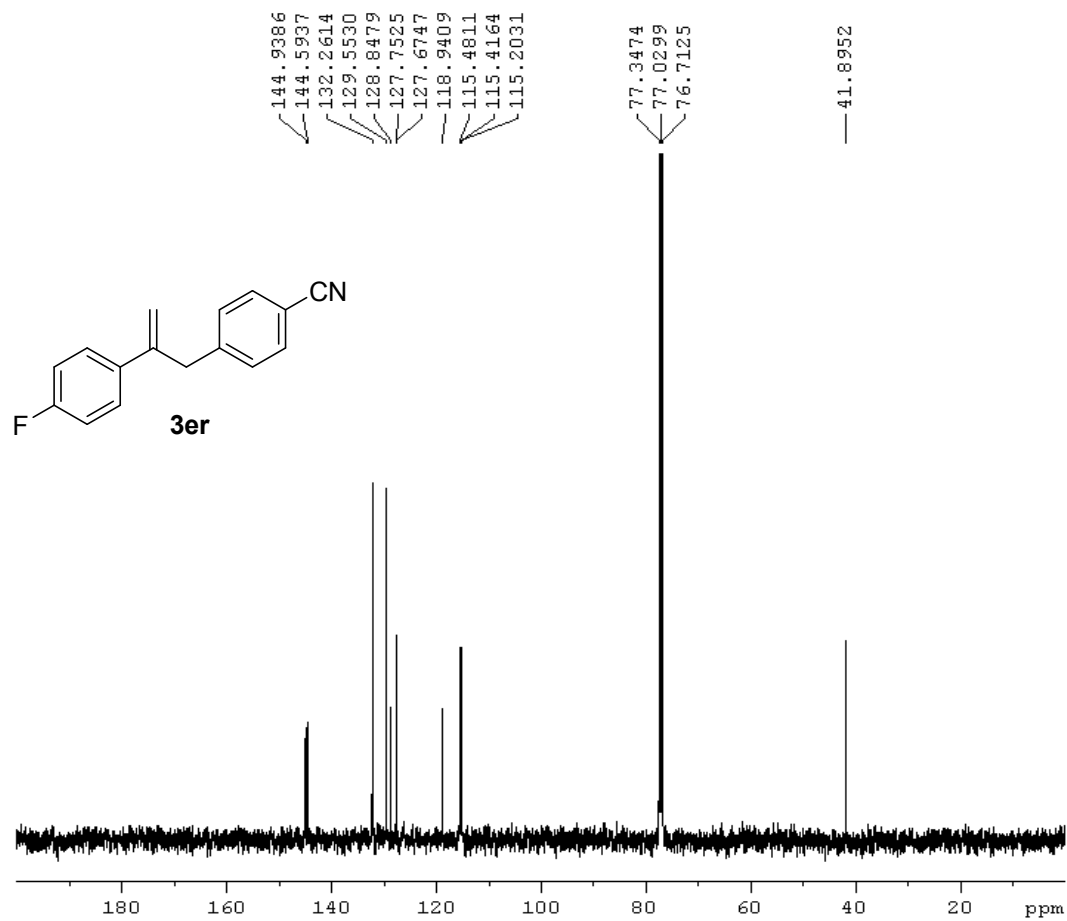
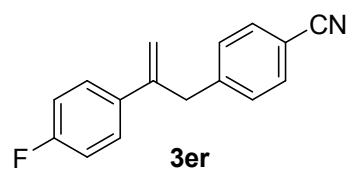


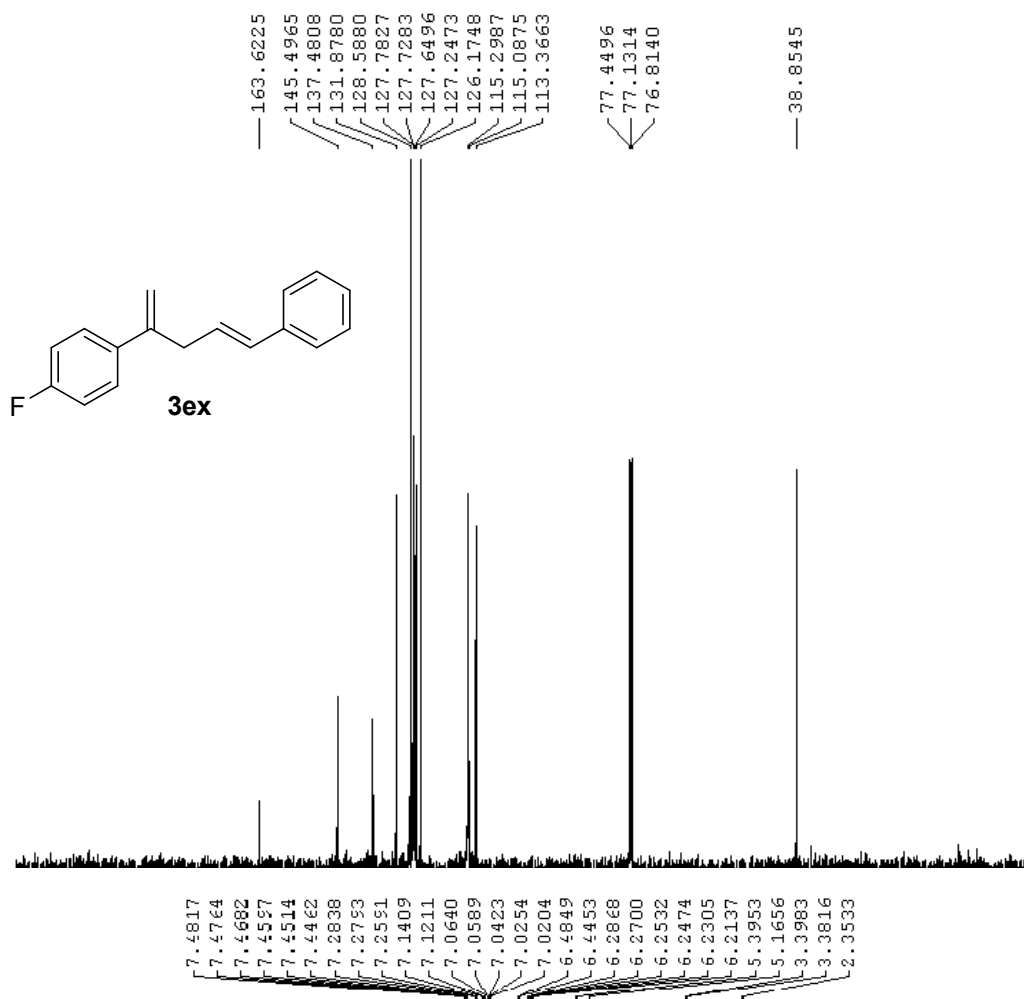
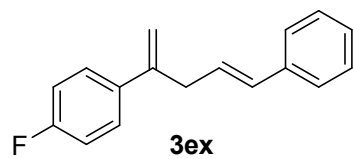


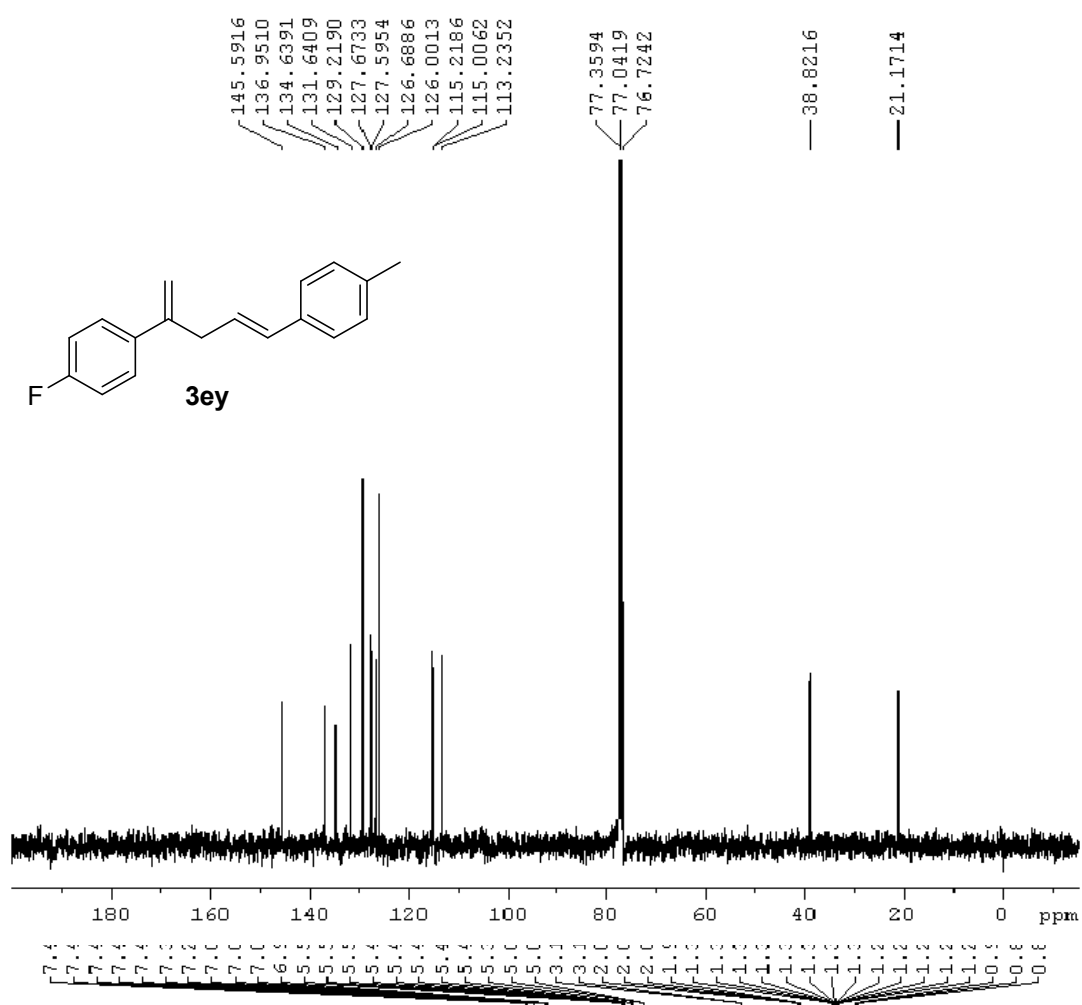
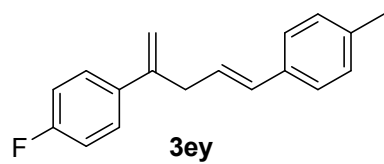


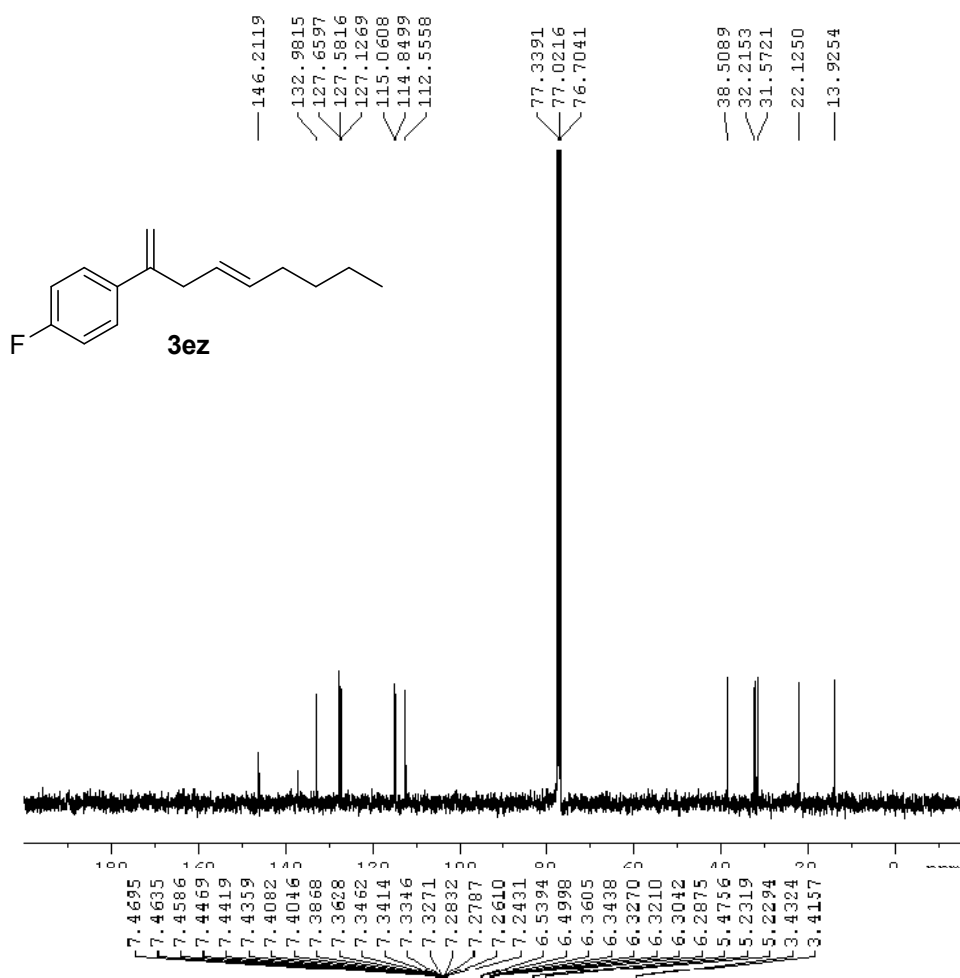
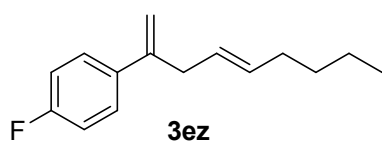


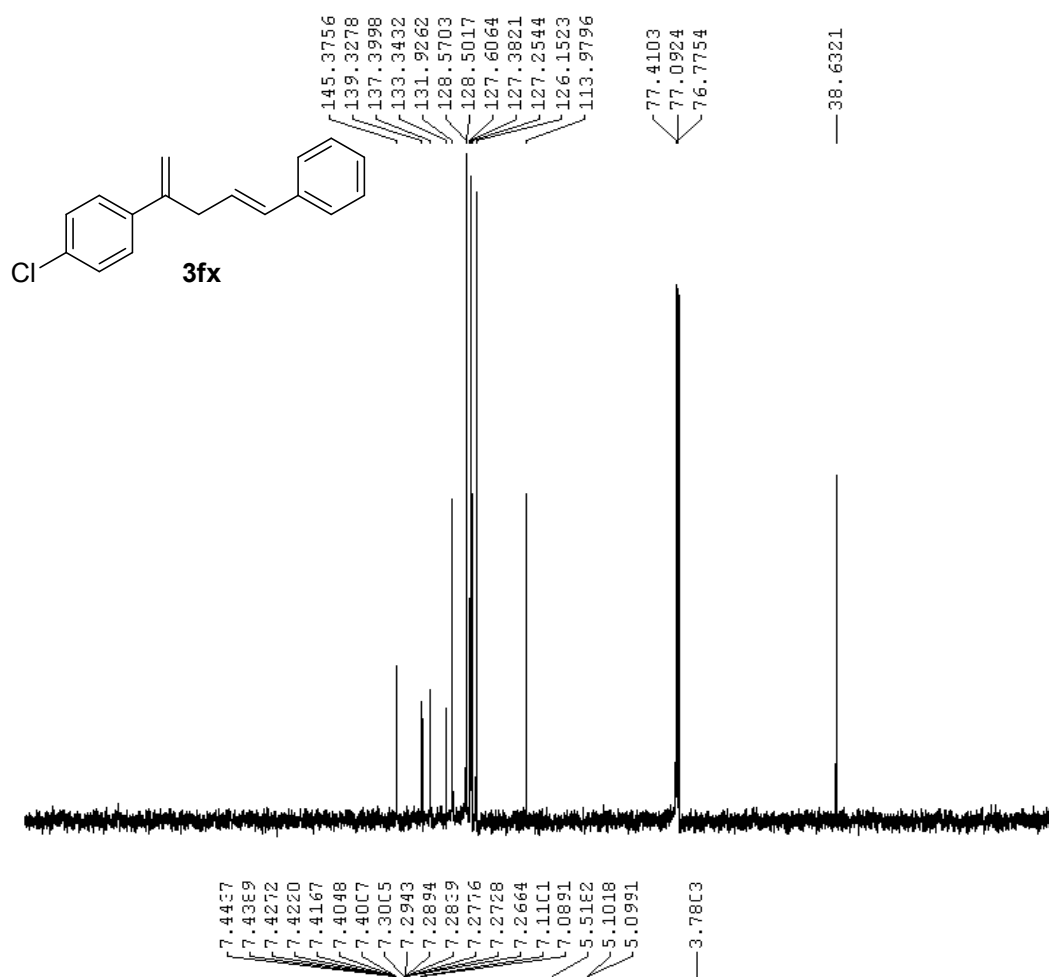
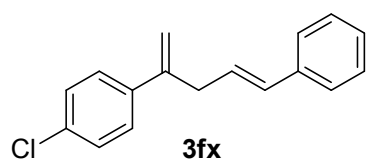


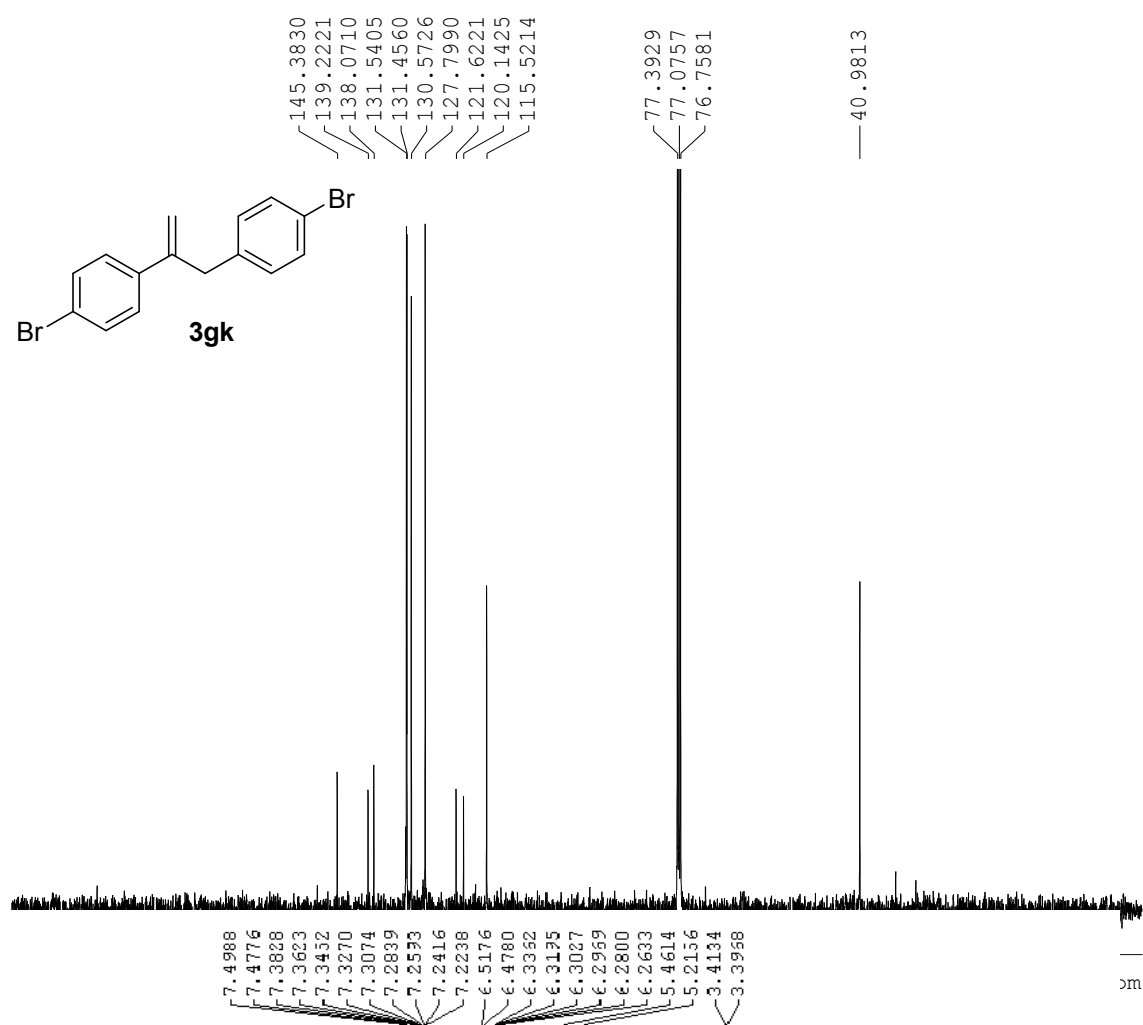
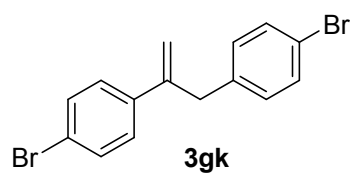


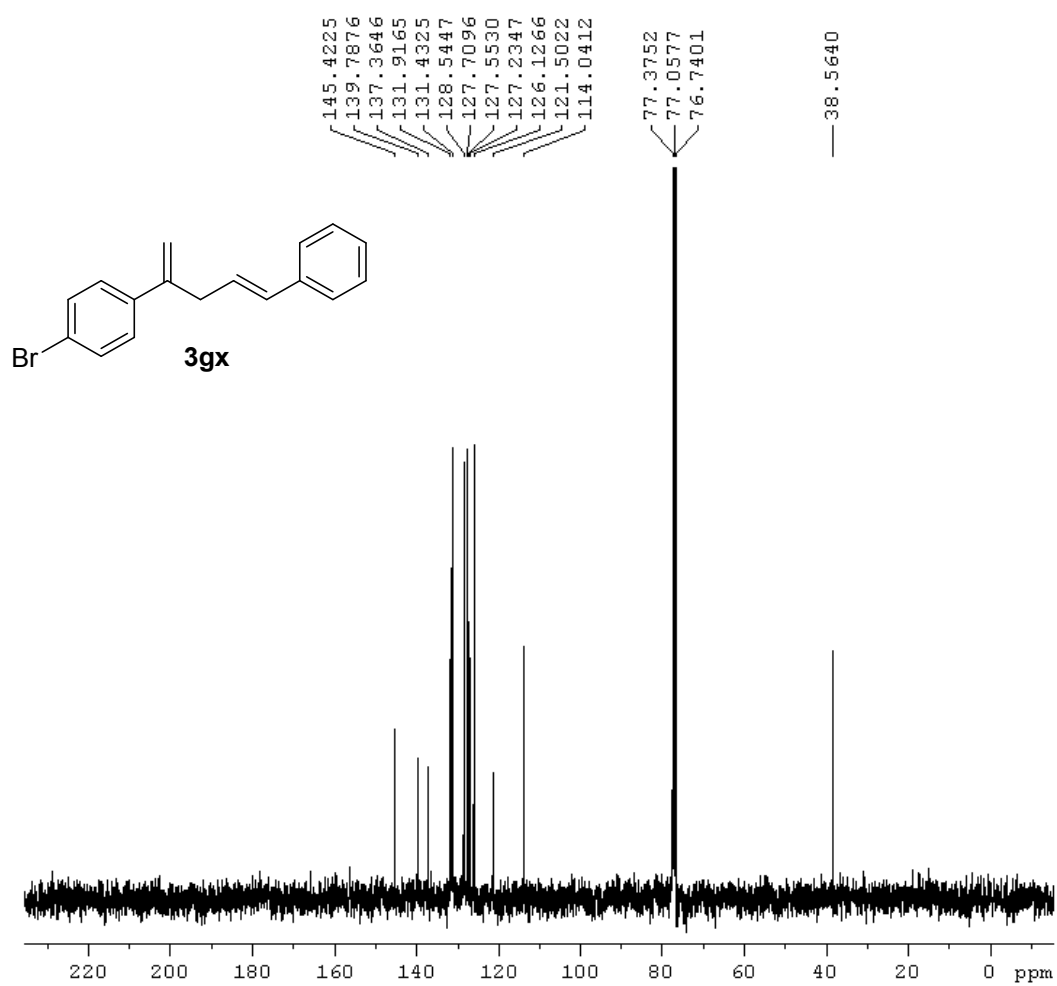
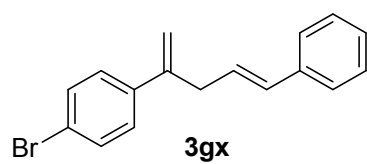


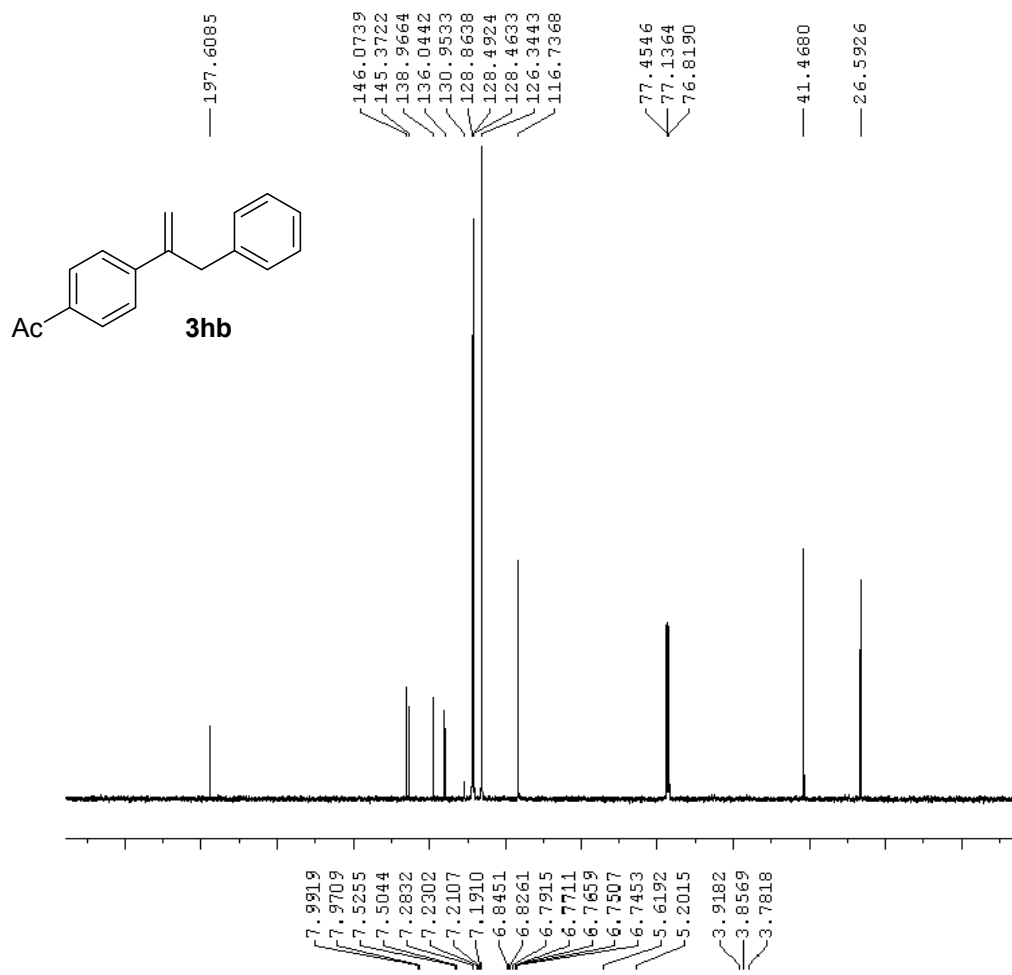
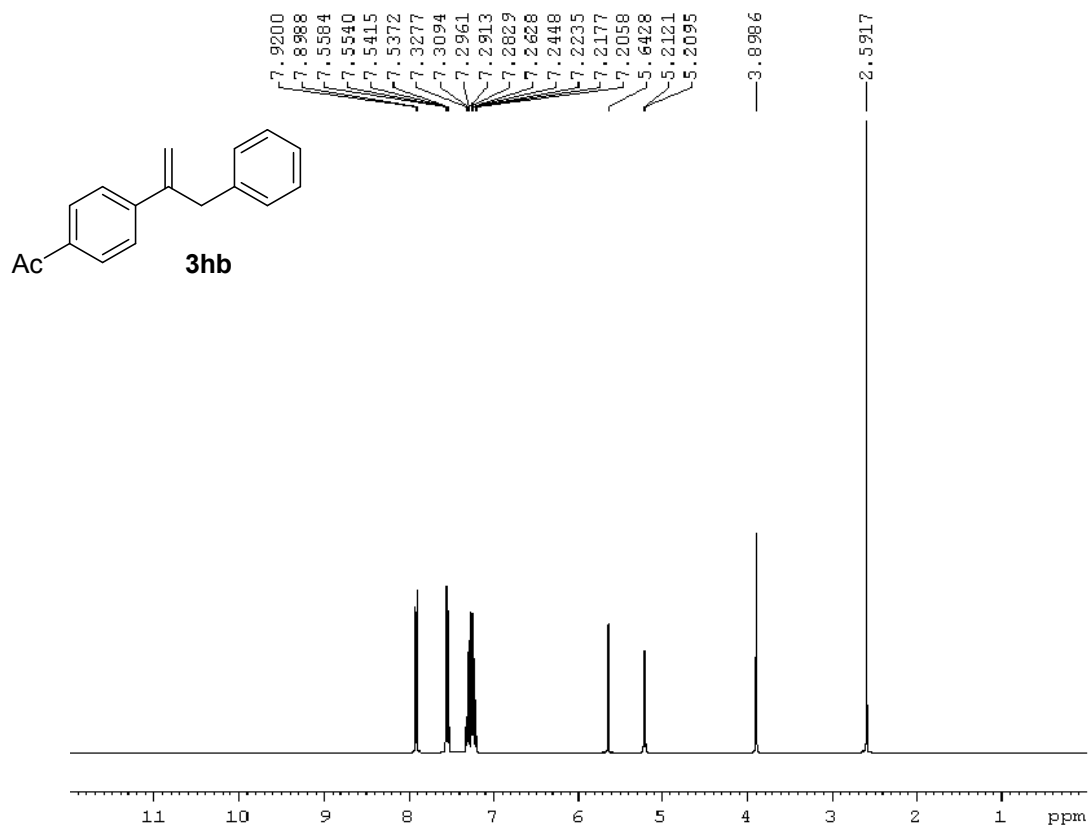


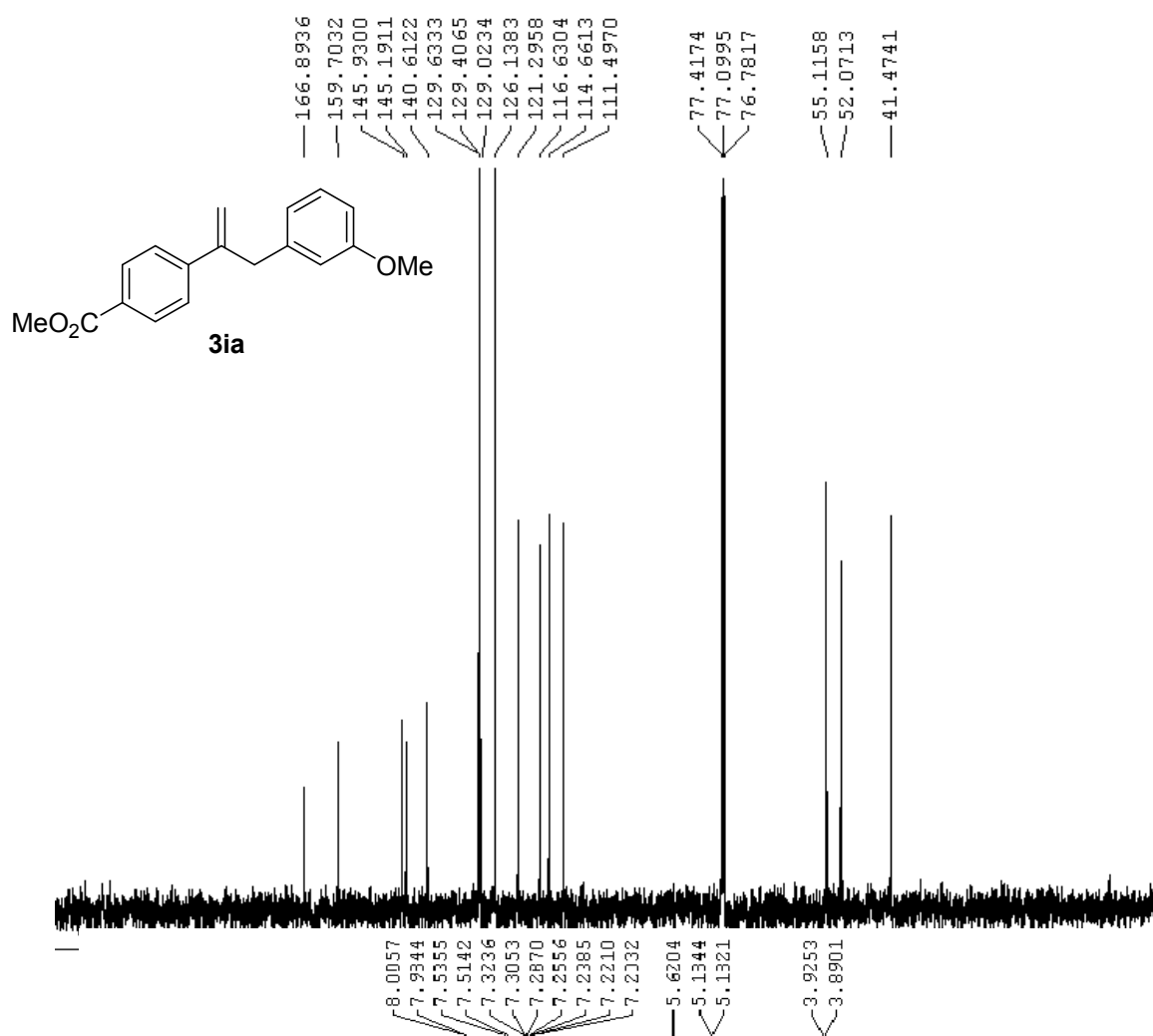
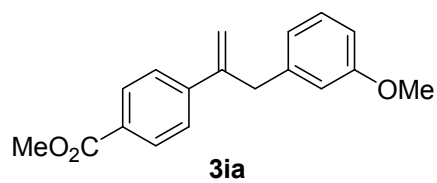


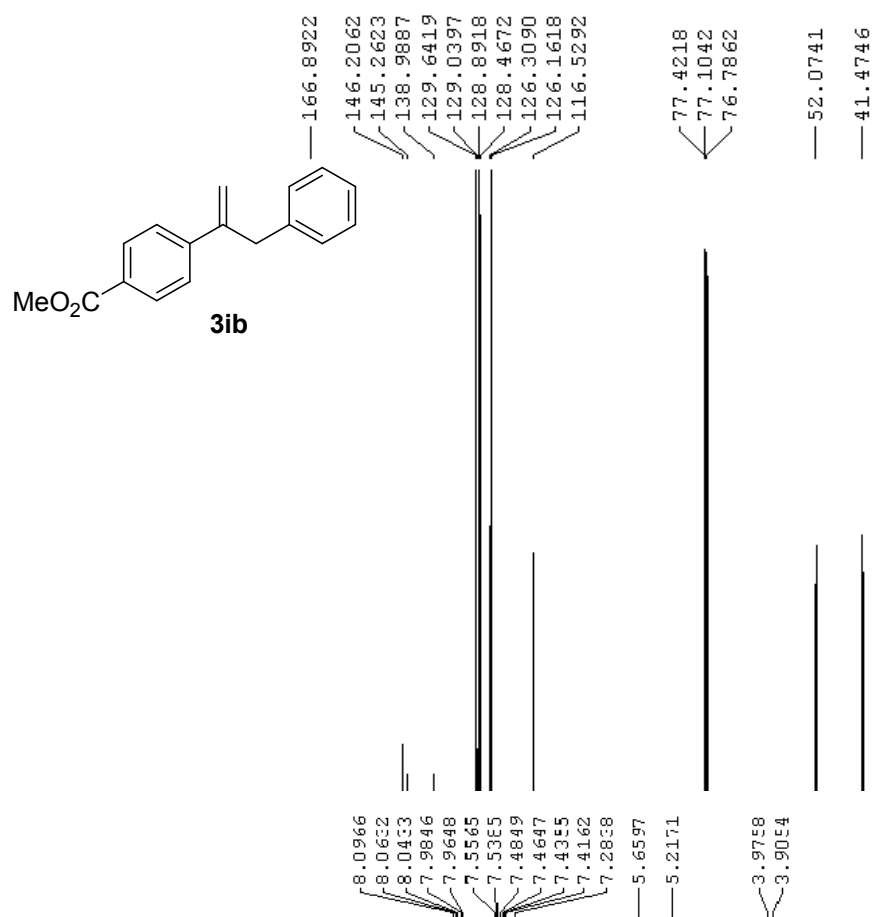
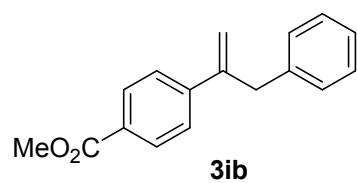


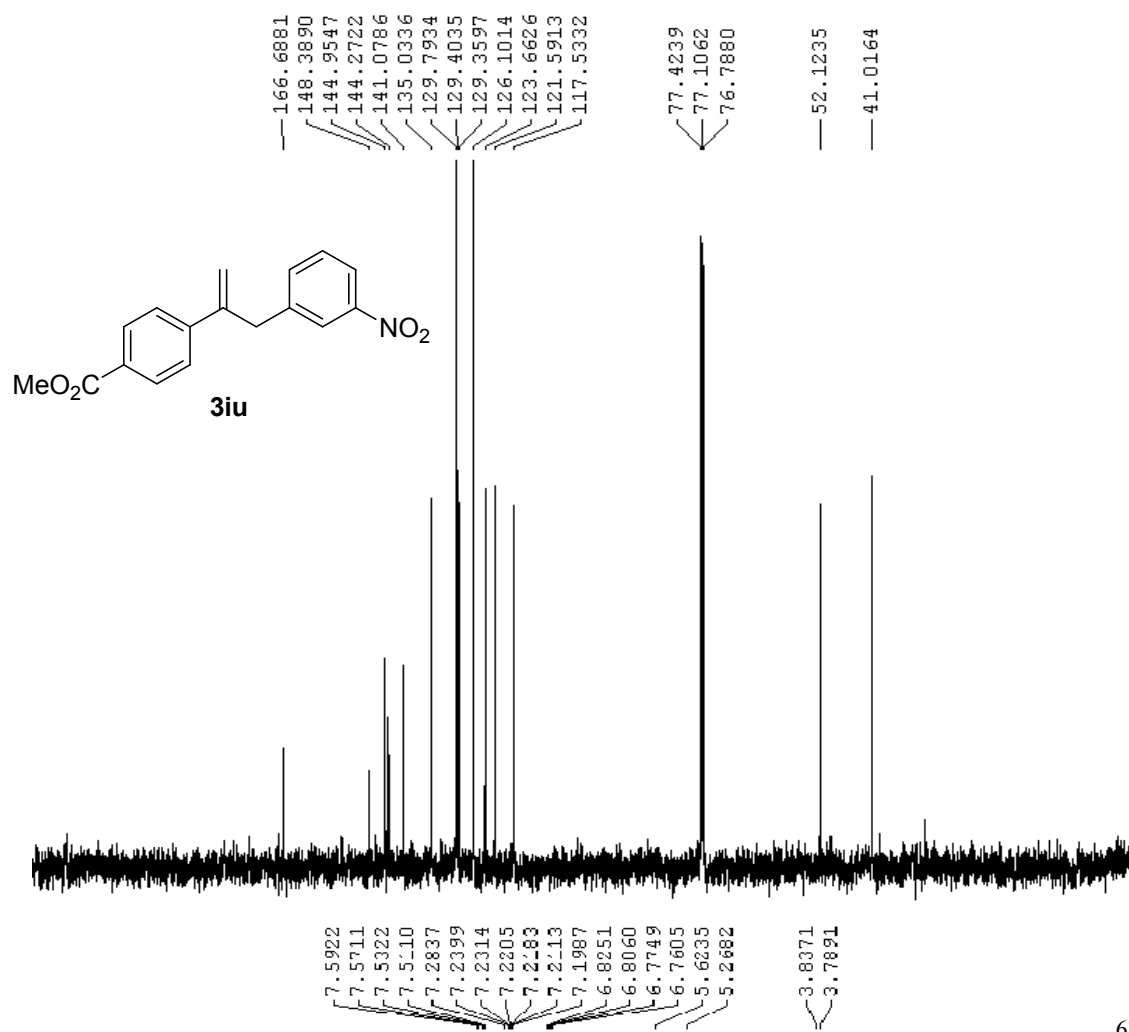
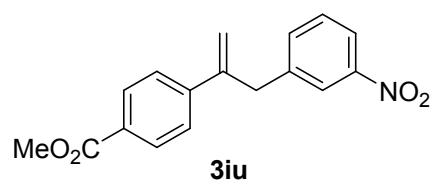


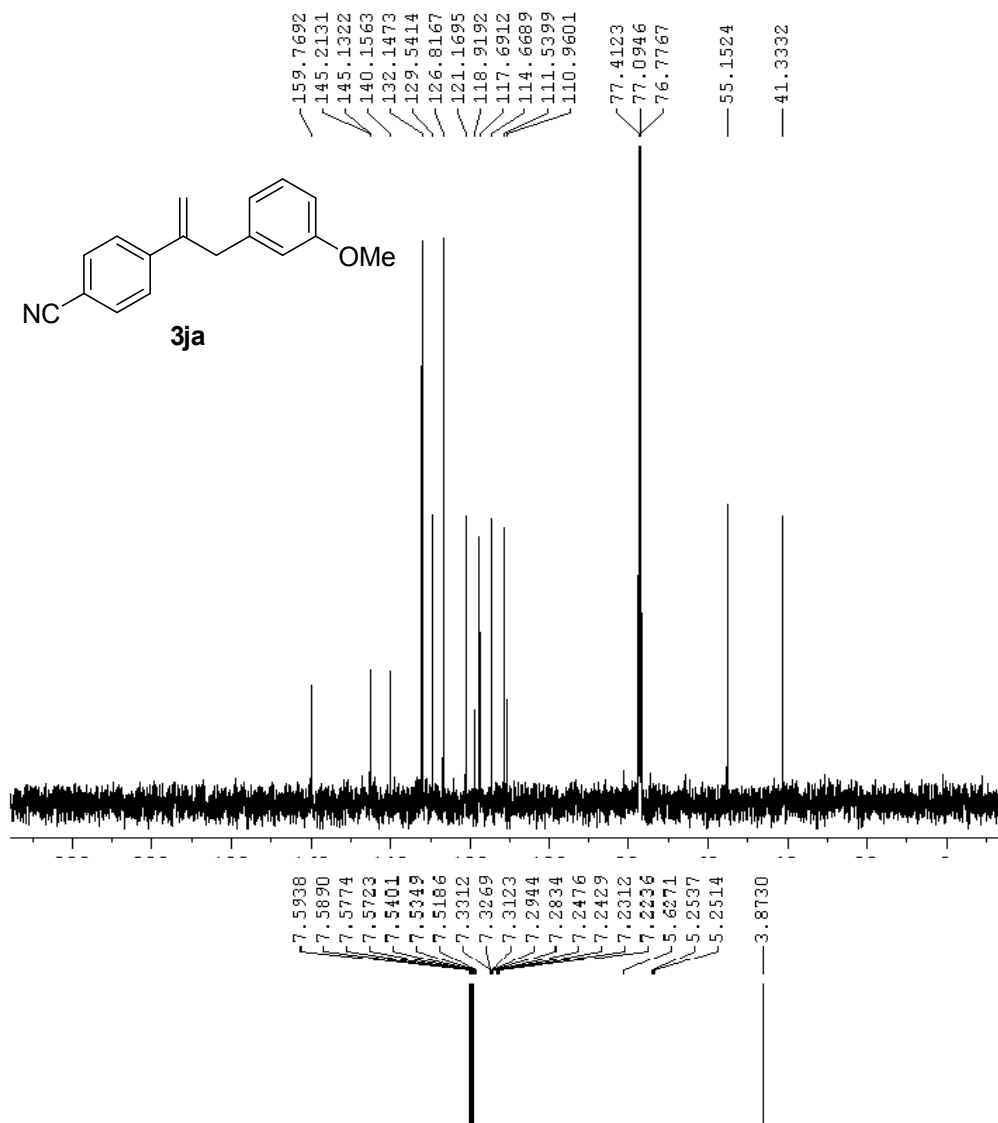
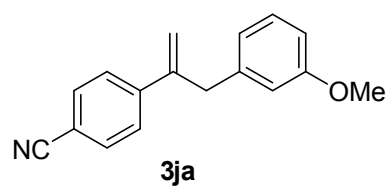


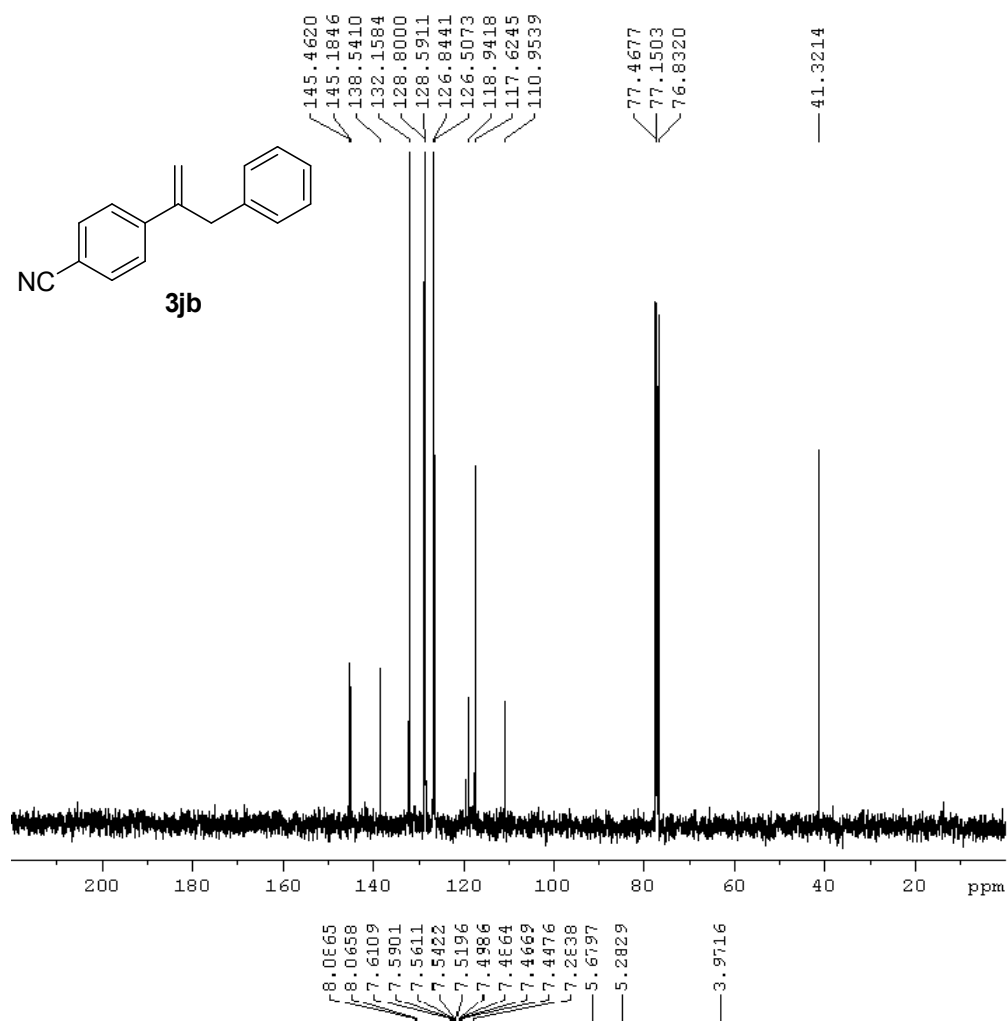
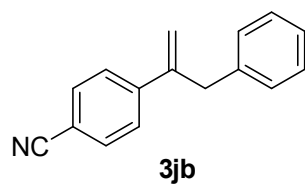


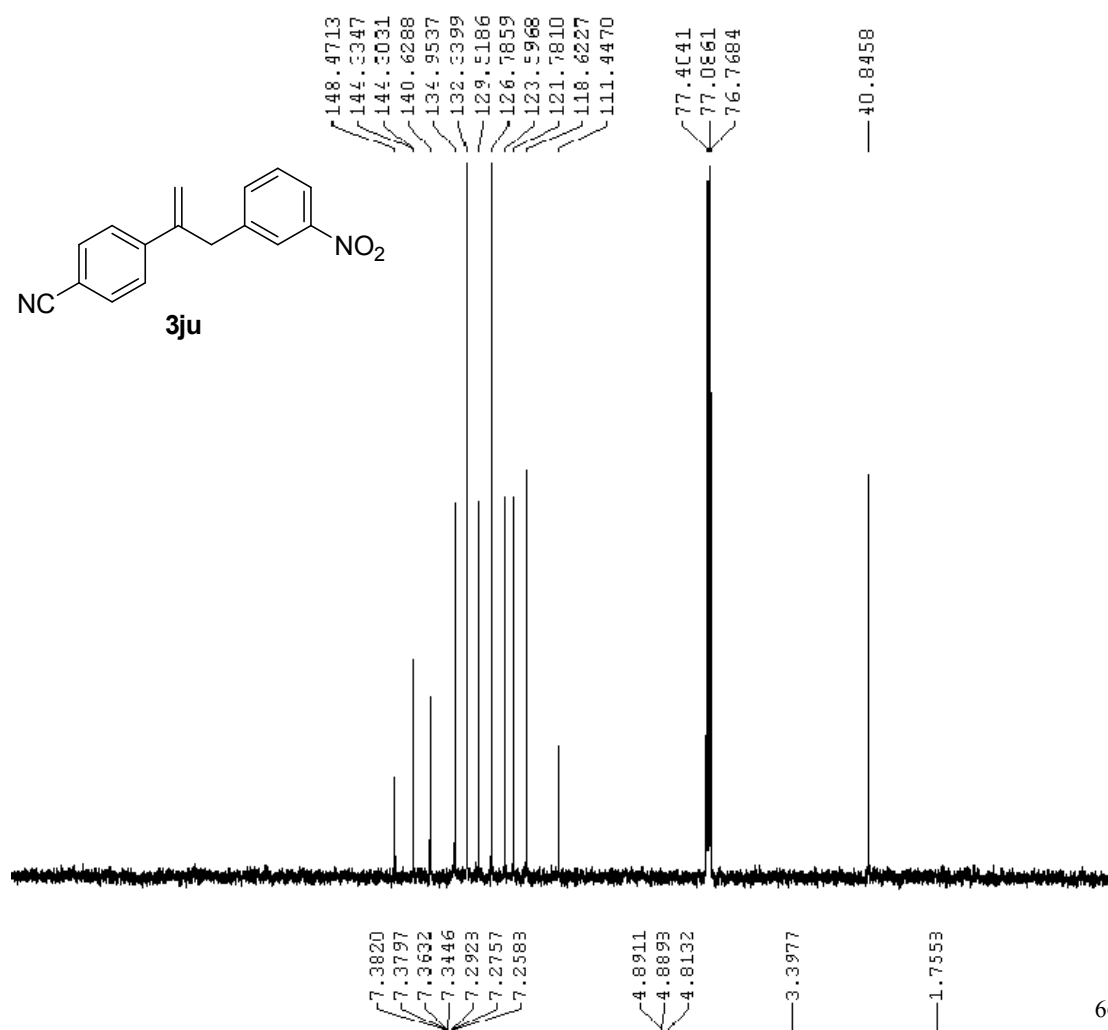
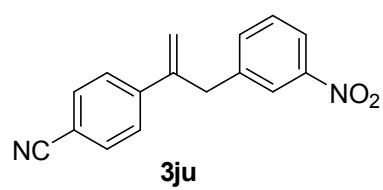


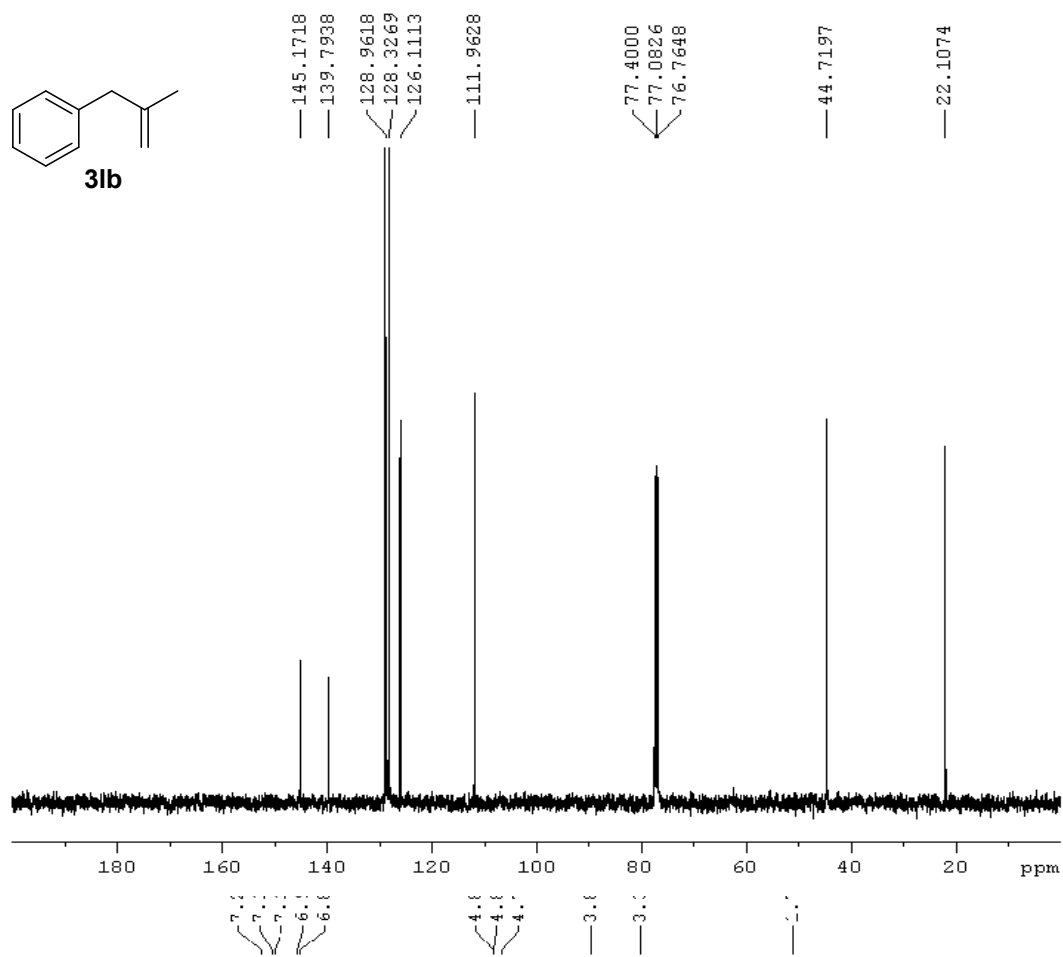
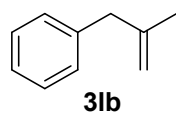


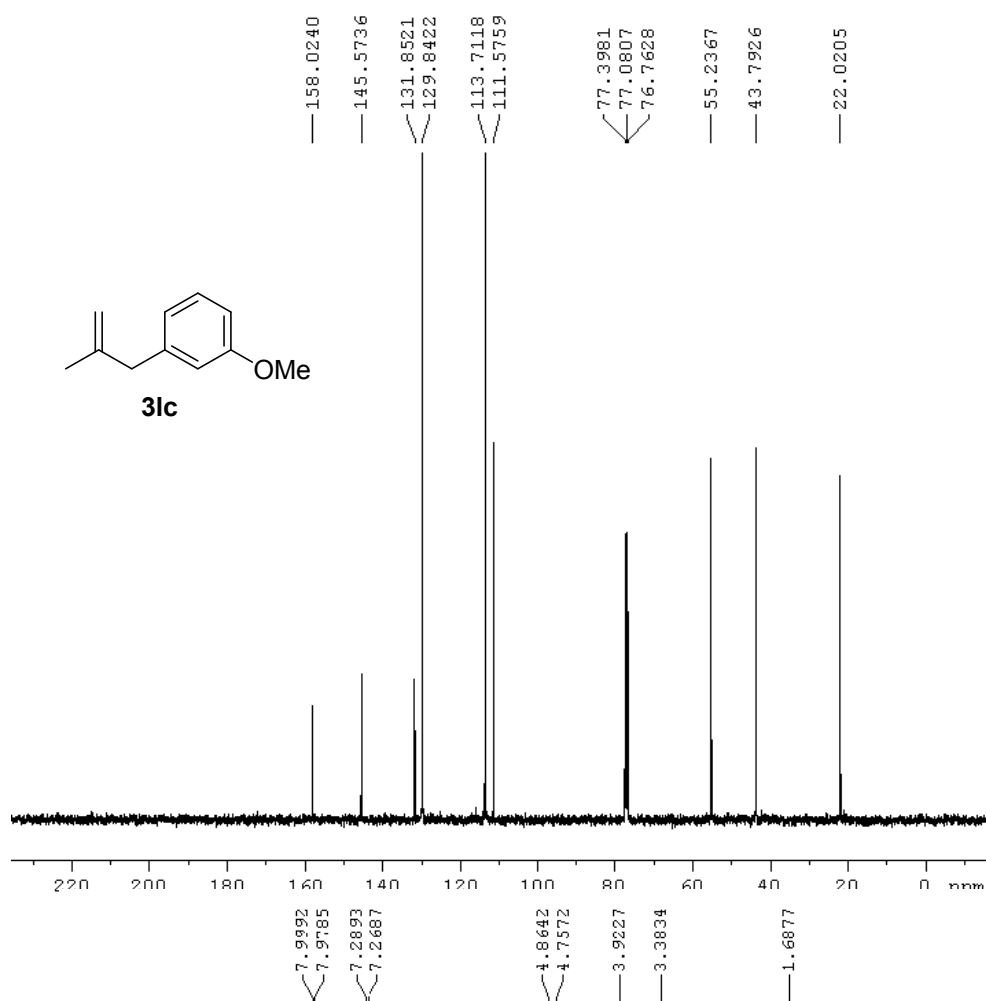
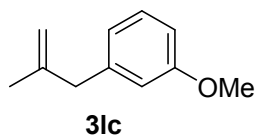


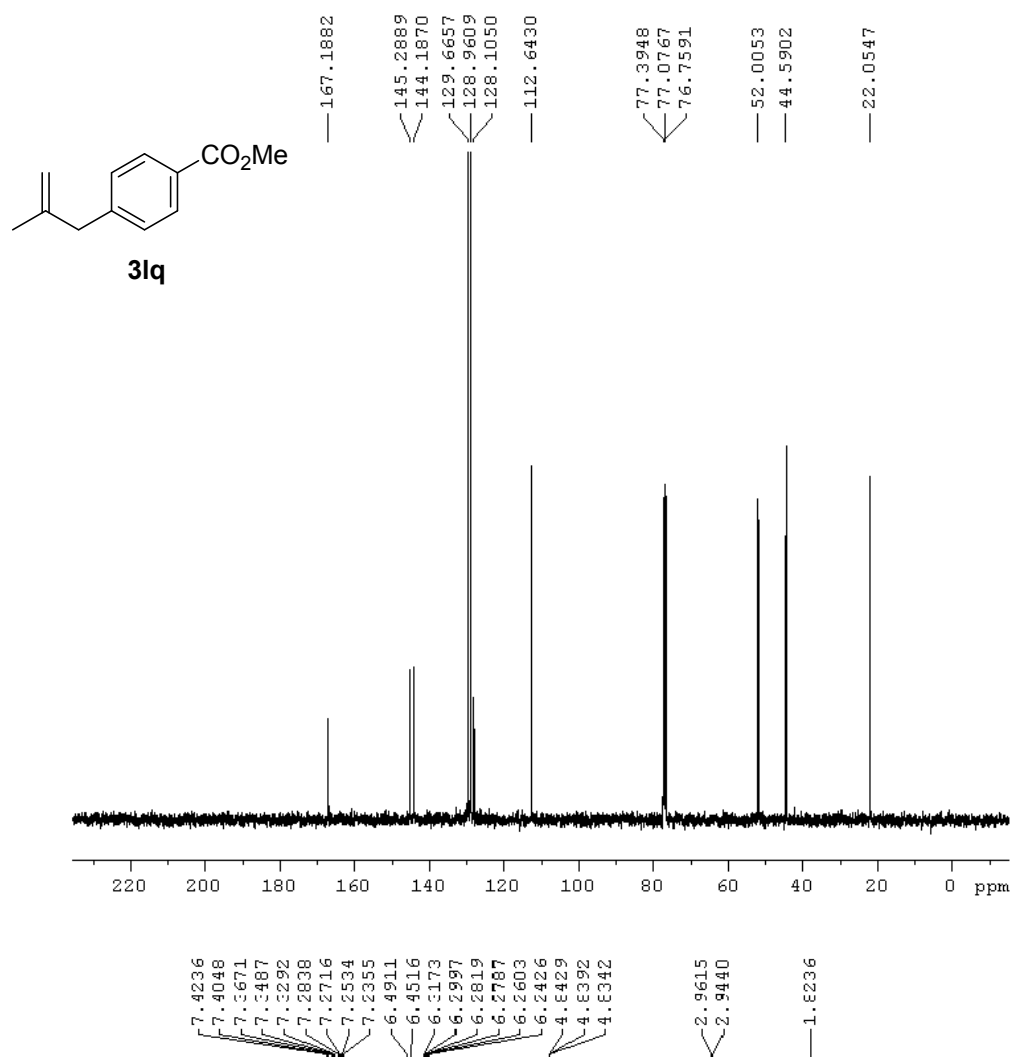
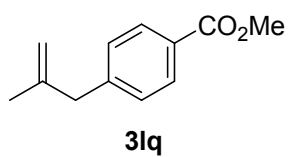


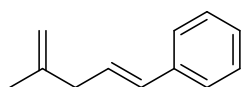




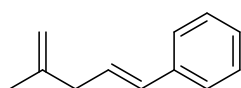








3lx



3lx

