Supplementary Information

Mechanochemical Indium(0)-mediated Barbier allylation of Carbonyl Compounds: Unexpected Immiscible Water Additive Effect for Hydrophobic Reagents

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1. General Considerations

Materials

All reagents were purchased from Alfa Aesar, Aldrich, or TCI and used without further purification. The ball-milling experiments were performed using a Retsch Mixer Mill MM 400 instrument with a stainless, zirconia, or Teflon vessel and stainless-steel balls with diameters of 7 mm or zirconia balls with diameters of 8 mm.

Measurements

The ^{1}H and ^{13}C NMR spectra were measured by a Bruker AVANCE III HD-400 MHz Fourier transform NMR spectrometer at the Future Energy Convergence Core Center (FECC). Infrared spectra were recorded on an ABB MB3000 Fourier-transform infrared (FT-IR) spectrometer equipped with an attenuated total reflectance module.

2. Experimental

General Procedure A for Reactions of Allylation

A 10 mL Teflon milling jar was filled with the carbonyl compound (0.50 mmol, 1.0 equiv.), indium powder (325 mesh; 1.0 mmol, 116 mg, 2.0 equiv.), allyl bromide (0.75 mmol, 65 µL, 1.5 equiv.), deionized water (40 µL), and three stainless steel balls (7 mm diameter) under an air atmosphere. And the mixture was milled at 30 Hz for 5 min. After the reaction was finished, the crude mixture transferred with chloroform (10 mL), quenched with 1 M HCl (10 mL), and stirred for 30 min until the organic layer becomes transparent. The organic layer was separated and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was then purified by silica gel flash chromatography.

Scale-up experiment

A 25 mL Teflon milling jar was filled with the 4-phenylbenzaldehyde (5.3 mmol, 1.0 g, 1.0 equiv.), indium powder (325 mesh; 1.1 mmol, 1.2 g, 2.0 equiv.), allyl bromide (8.0 mmol, 712 µL, 1.5 equiv.), deionized water (0.20 mL), and three stainless steel balls (7 mm diameter) under an air atmosphere. And the mixture was milled at 30 Hz for 5 minutes and rested for 5 minutes. Repeat this process six times. After the reaction was finished, the crude mixture transferred with chloroform (100 mL), quenched with 1 M HCl (100 mL), and stirred for 5 h until the organic layer becomes transparent. The organic layer was separated and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was then purified by silica gel flash chromatography.

General Procedure B for Reactions of Propargylation

A 10 mL Teflon milling jar was filled with the aldehyde (0.50 mmol, 1.0 equiv.), indium powder (325 mesh; 1.0 mmol, 116 mg, 2.0 equiv.), propargyl bromide (0.75 mmol, 61 µL, 1.5 equiv.), deionized water (40 µL), and three stainless steel balls (7 mm diameter) under an air atmosphere. And the mixture was milled at 30 Hz for 5 min. After the reaction was finished, the crude mixture transferred with chloroform (10 mL), quenched with 1 M HCl (10 mL), and stirred for 30 min until the organic layer becomes transparent. The organic layer was separated and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was then purified by silica gel flash chromatography.

General Procedure C for Reactions of Crotylation

A 10 mL Teflon milling jar was filled with the aldehyde (0.50 mmol, 1.0 equiv.), indium powder (325 mesh; 1.0 mmol, 116 mg, 2.0 equiv.), crotyl bromide (0.75 mmol, 77 µL, 1.5 equiv.), deionized water (40 µL), and three stainless steel balls (7 mm diameter) under an air atmosphere. And the mixture was milled at 30 Hz for 30 min. After the reaction was finished, the crude mixture transferred with chloroform (10 mL), quenched with 1 M HCl (10 mL), and stirred for 30 min until the organic layer becomes transparent. The organic layer was separated and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was then purified by silica gel flash chromatography.

Table S1. Scope of carbonyl compounds.

Entry	Product	NMR Conv. (%)	NMR Yield. (%)	Isolated Yield
2a-1	1-([1,1'-biphenyl]-4-yl)but-3-en-1-ol	>99	95	96.3mg (86%)
2a-2		>99	97	102 mg (91%)
2b-1	1-Phenyl-3-buten-1-ol	>99	99	70.7 mg (95.4 %)
2b-2		>99	99	69.8 mg (94.2 %)
2c-1	1-(4- Chlorophenyl)-3-buten-1-ol	>99	98	86.2 mg (94.3 %)
2c-2		>99	99	87.9 mg (96.2 %)
2d-1	1-(4-Methoxyphenyl)-3-buten-1-ol	99	80	69.6 mg (78%)
2d-2		98	79	64.0 mg (72%)
2e-1	1-(4-Nitrophenyl)-3-buten-1-ol	99	0	-
2e-2		99	0	-
2f-1	1-(pyren-2-yl)but-3-en-1-ol	100	97	109.6 mg (81%)
2f-2		100	99	136 mg (100%)
2g-1	1-(Anthracen-9-yl)but-3-en-1-ol	>99	99	118 mg (95 %)
2g-2		99	99	120 mg (96.8 %)
2h-1	1-Phenyl-1,5-hexadien-3-ol	>99	85	67.0 mg (77%)
2h-2		>99	99	78.2 mg (89%)
2i-1	1-(Cyclohexen-1-yl)-3-buten-1-ol	irreproducible	irreproducible	27.0 mg (35%)
2i-2		irreproducible	irreproducible	12.2 mg (16%)
2i-3		irreproducible	irreproducible	64.2 mg (84%)
2i-4		irreproducible	irreproducible	37.6 mg (49%)
2j-1	1-Phenyl-5-hexen-3-ol	>99	98	78.9 mg (90%)
2j-2		>99	95	76.4 mg (87%)
2k-1	1-Cyclohexyl-3-buten-1-ol	99	99	57.6 mg (74.6 %)
2k-2		99	98	60.3 mg (78.2 %)
2l-1	Dodec-1-en-4-ol	96	95	71.6 mg (77.7 %)
2l-2		96	96	77.0 mg (83.5 %)
2m-1	1,1'-(1,4-Phenylene)dibut-3-en-1-ol	>99	69	37.0 mg (67.7 %)
2m-2		>99	65	33.3 mg (61 %)
2n-1	2-Phenylpent-4-en-2-ol	91	85	67.3 mg (82.9 %)
2n-2		88	82	61.9 mg (77.5 %)

Table S2. Scale-up experiment

Entry	Product	NMR Conv. (%)	NMR Yield. (%)	Isolated Yield
2a-3	1-([1,1'-biphenyl]-4-yl)but-3-en-1-ol	>99	94	1.12 g (91.1%)
2a-4		>99	90	1.09 g (88.7%)

Table S3. Mechanochemical indium propargylation

Entry	Product	NMR Conv. (%)	NMR Yield. (%)	Propargyl(3) : Allenyl(4) (%)	Isolated Yield
3a(4a)-1	1-([1,1'-Biphenyl]-4-yl)but-3-yn-1-ol	77	77	81 : 19	78.7 mg (70.8 %)
3a(4a)-2	1-([1,1'-biphenyl]-4-yl)buta-2,3-dien-1-ol	77	76	81 : 19	75.1 mg (67.6 %)
3b(4b)-1	1-(4-Chloro-phenyl)-but-3-yn-1-ol	87	87	79 : 21	71.7 mg (79.4 %)
3b(4b)-2	1-(4-(chlorophenyl)buta-2,3-dien-1-ol	88	86	82: 18	74 mg (81.9 %)
3c(4c)-1	1-Phenylhex-5-yn-3-ol	91	91	81 : 19	68.4 mg (78.5 %)
3c(4c)-2	1-Phenylhexa-4,5-dien-3-ol	92	91	80 : 20	71.5 mg (82 %)

Table S4. Mechanochemical indium crotylation

Entry	Product	NMR Conv. (%)	NMR Yield. (%)	Syn(5) : anti(5') (%)	Isolated Yield
5a-1	1-([1,1'-biphenyl]-4-yl)-2-methylbut-3-en-1-ol	>99	91	54 : 46	103 mg (87%)
5a-2		>99	99	54 : 46	115.9 mg (97%)
5b-1	1-(4-Chlorophenyl)-2-methylbut-3-en-1-ol	99	96	53 : 47	73.1 mg (74%)
5b-2		>99	94	51 : 49	81.6 mg (83%)
5c-1	4-Methyl-1-phenyl-hex-5-en-3-ol	100	90	50 : 50	84.6 mg (89%)
5c-2		>99	95	52 : 48	85.5 mg (90%)

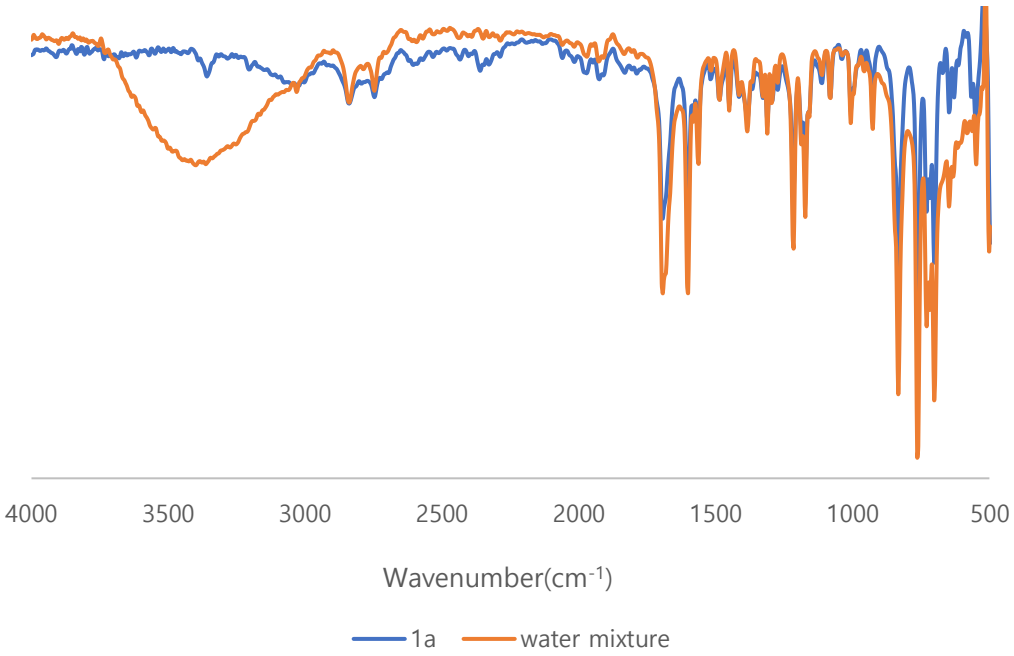
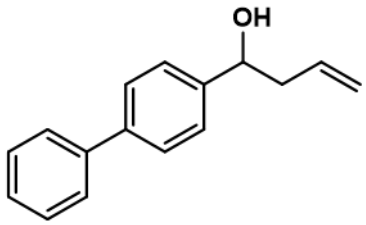


Figure S1. Infrared spectra for aldehyde **1a** and water mixture ball-milling

3. ^{1}H & ^{13}C NMR of obtained products



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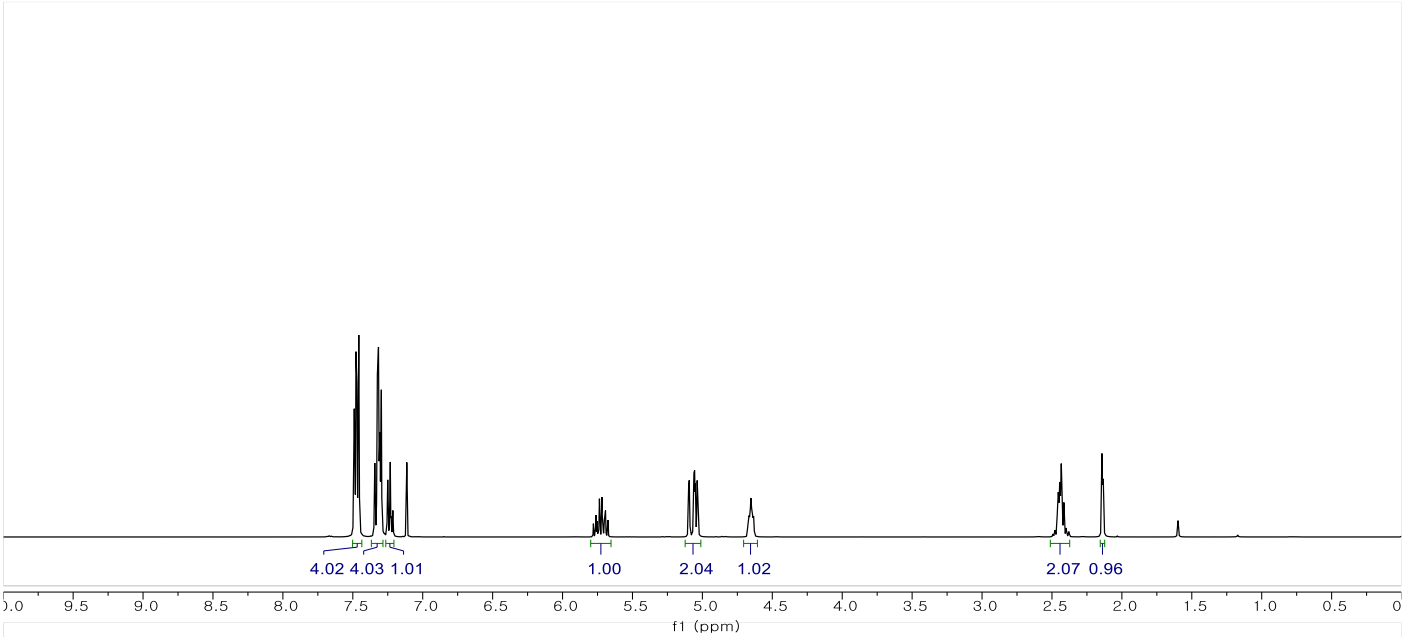
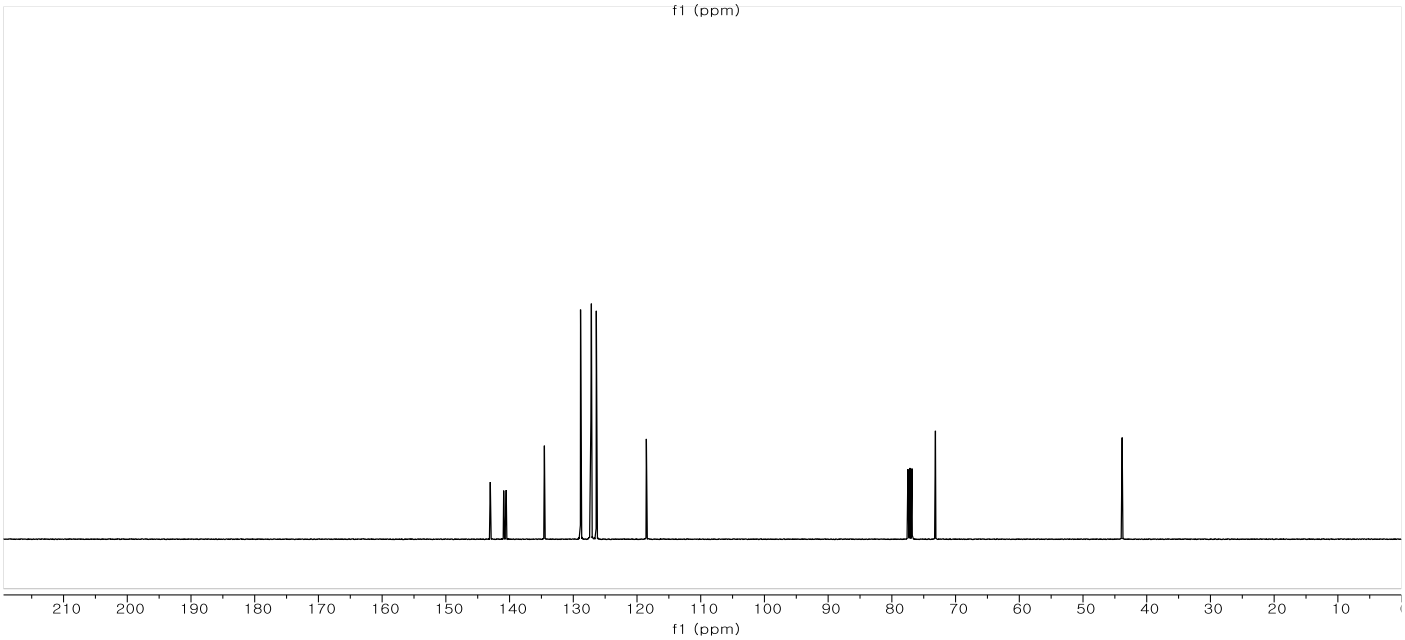
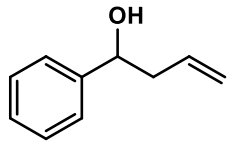




^{1}H NMR (400 MHz, chloroform-*d*) δ 7.50 – 7.44 (m, 4H), 7.37 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 5.73 (m, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.12 – 5.01 (m, 2H), 4.65 (m, *J* = 8.0, 5.3, 2.8 Hz, 1H), 2.51 – 2.37 (m, 2H), 2.14 (d, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.0, 140.9, 140.5, 134.5, 128.9, 127.4, 127.2, 127.2, 126.4, 118.5, 73.2, 43.9.

Following the general procedure A. Spectra were matched to a previous report.[1]



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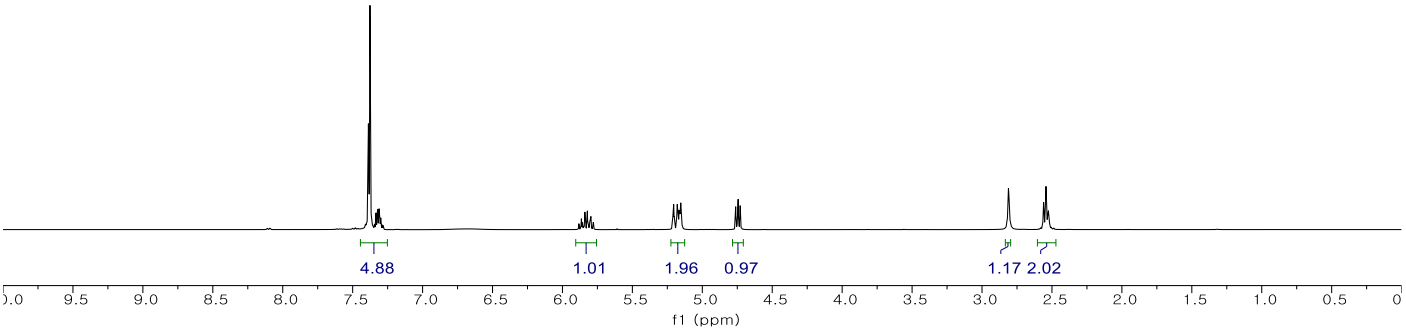
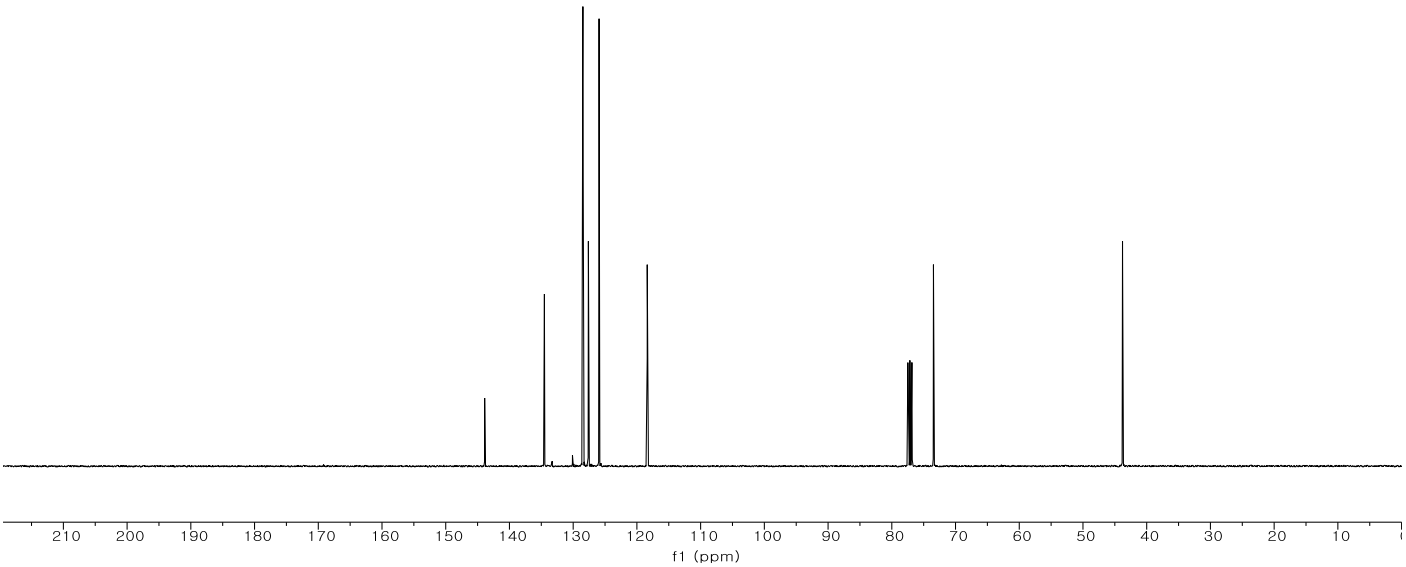
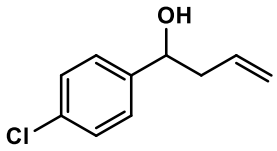




^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.13 (m, 5H), 5.71 (m, J = 17.2, 10.2, 7.1 Hz, 1H), 5.11 – 5.01 (m, 2H), 4.63 (dd, J = 7.2, 5.8 Hz, 1H), 2.69 (s, 1H), 2.43 (m, J = 7.2, 6.1, 1.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.9, 134.5, 128.5, 127.6, 125.9, 118.4, 73.5, 43.8.

Following the general procedure A. Spectra were matched to a previous report.[2]



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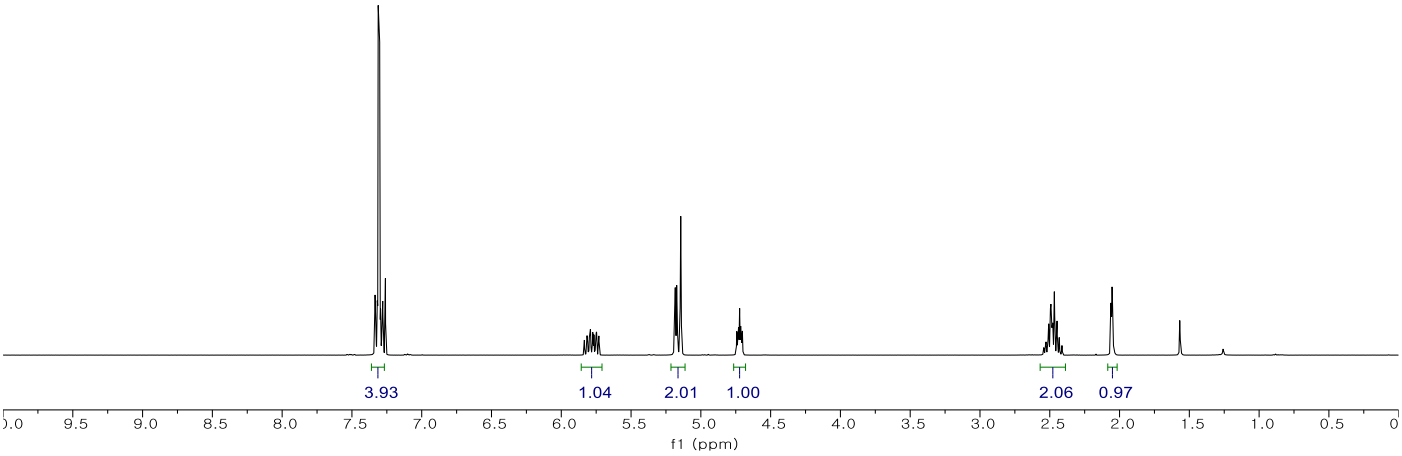
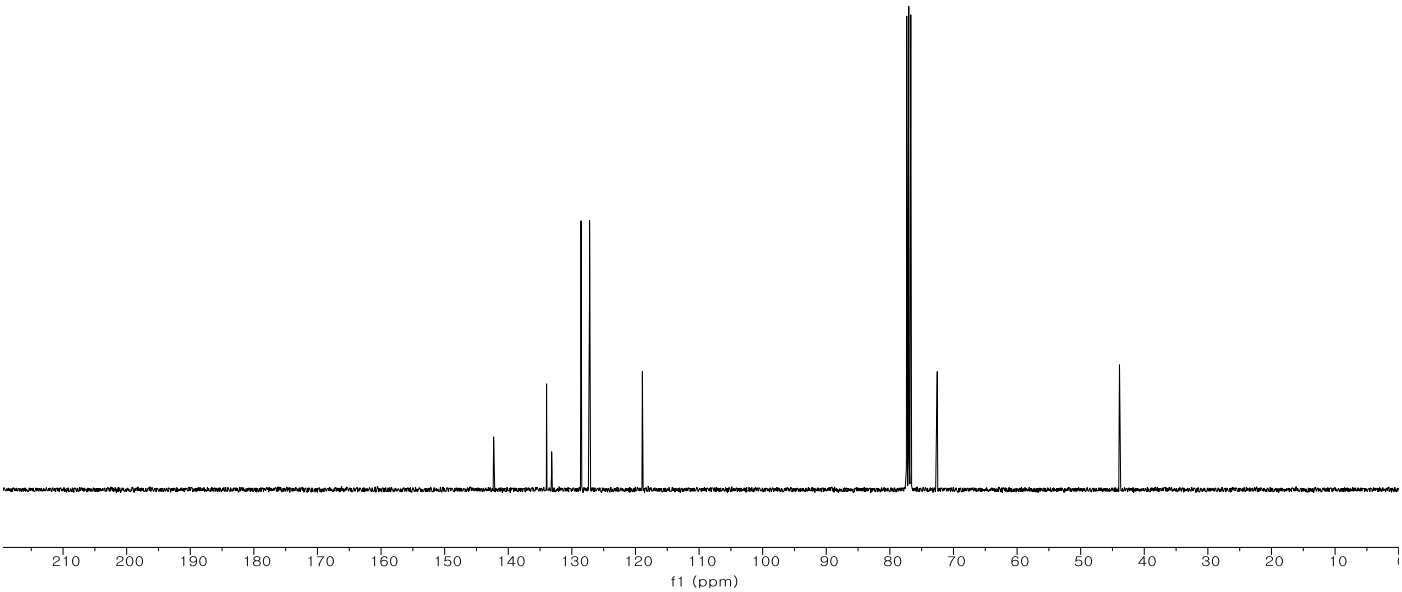
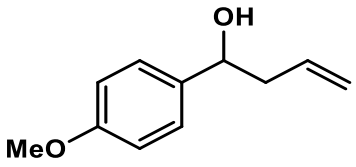




^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.27 (m, 4H), 5.86 – 5.71 (m, 1H), 5.21 – 5.11 (m, 2H), 4.72 (m, J = 8.0, 5.0, 3.2 Hz, 1H), 2.57 – 2.39 (m, 2H), 2.05 (m, J = 2.7, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 142.4, 134.1, 133.3, 128.7, 127.3, 119.1, 72.7, 44.0.

Following the general procedure A. Spectra were matched to a previous report.[2]



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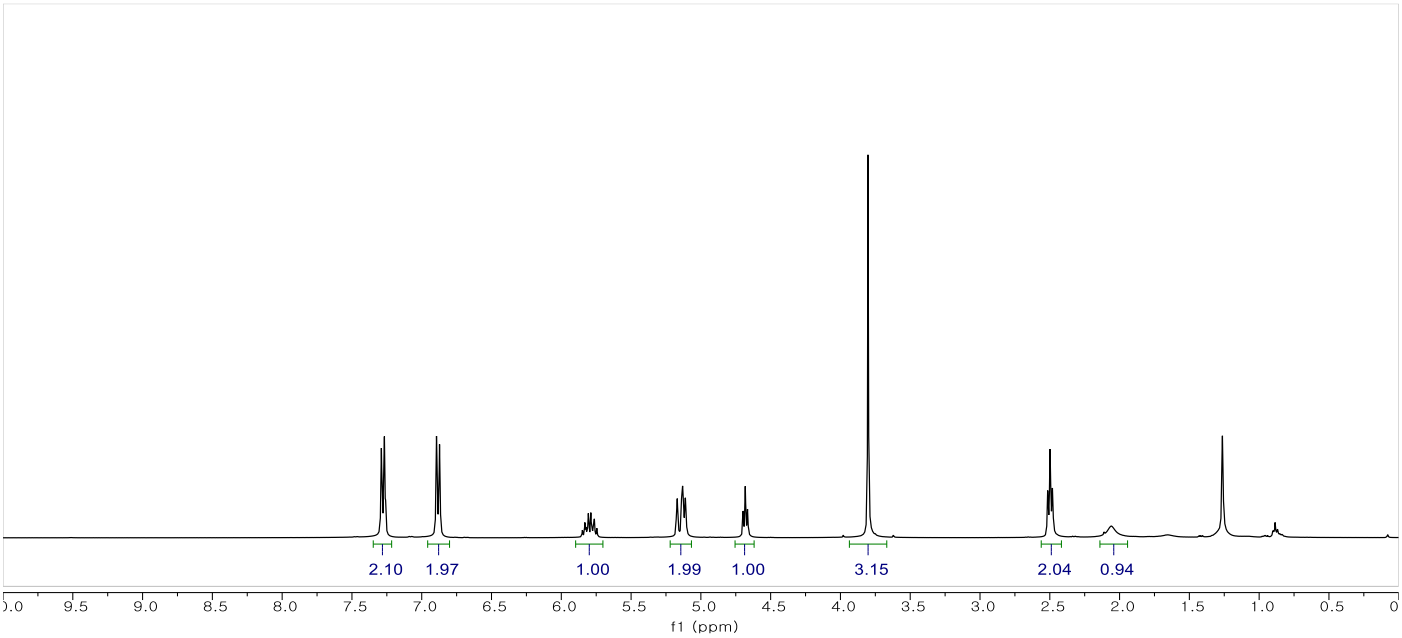
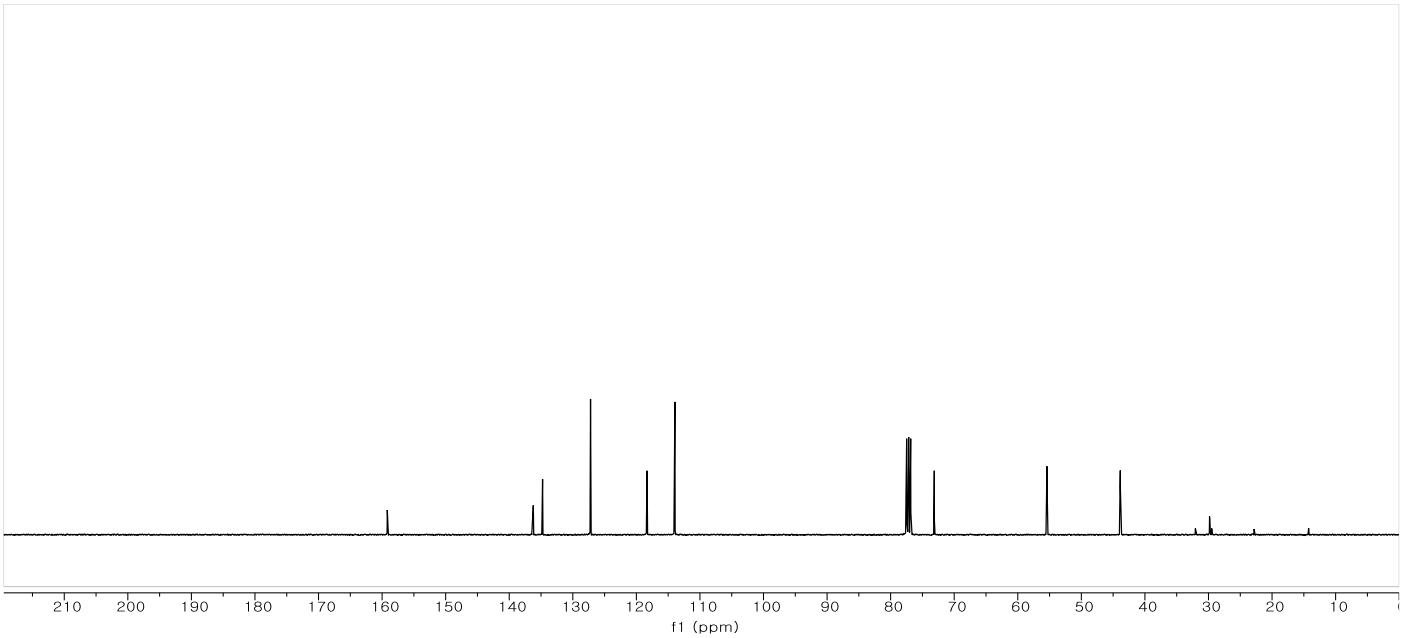
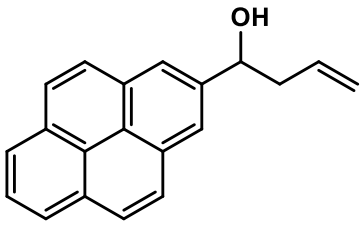




^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.22 (m, 2H), 6.96 – 6.80 (m, 2H), 5.80 (m, *J* = 17.2, 10.3, 7.1 Hz, 1H), 5.22 – 5.07 (m, 2H), 4.68 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 2.50 (t, *J* = 6.9 Hz, 2H), 2.11 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 136.2, 134.8, 127.2, 118.3, 113.9, 73.1, 55.4, 43.9.

Following the general procedure A. Spectra were matched to a previous report.[3]



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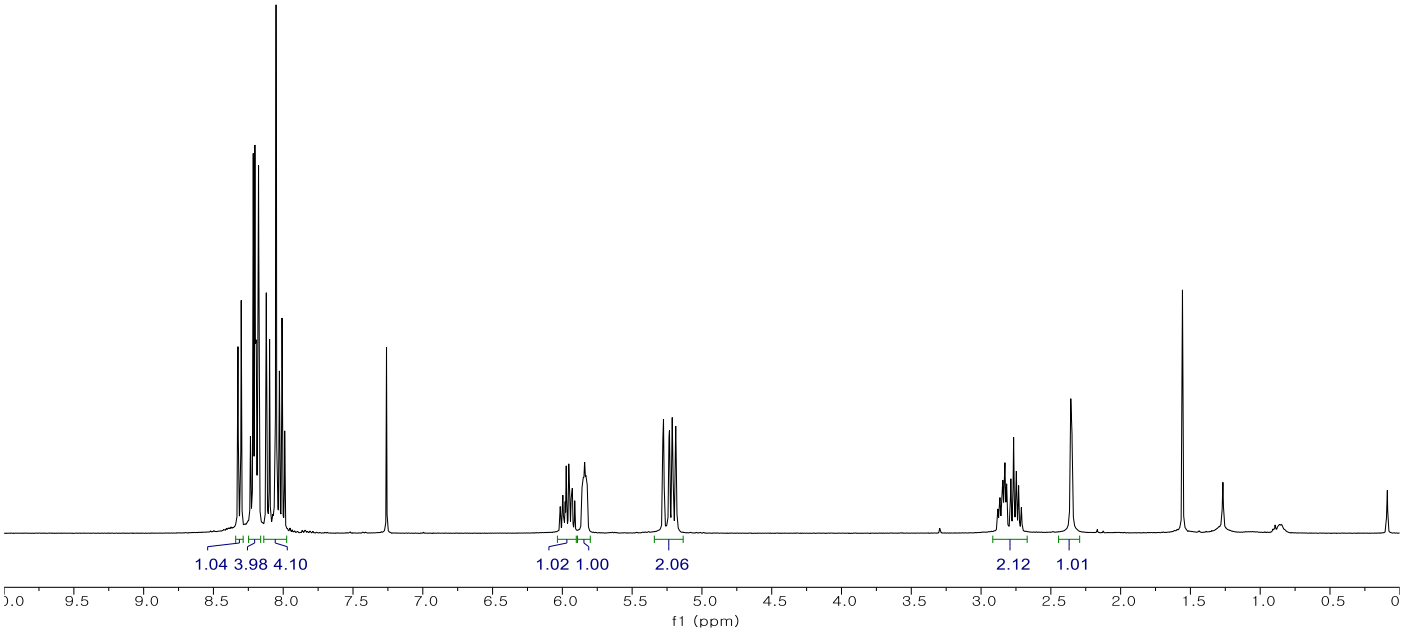
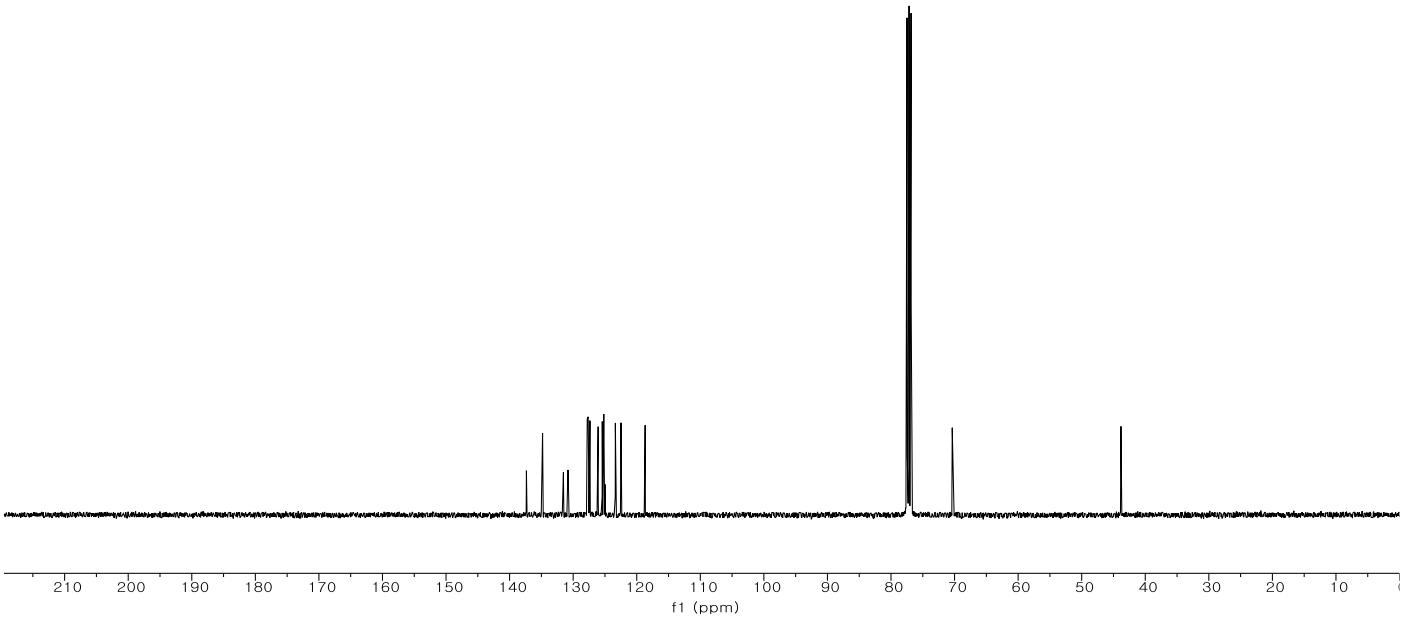


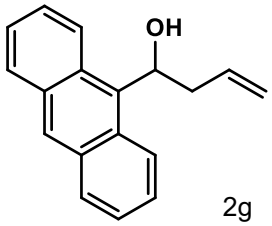


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 9.3 Hz, 1H), 8.25 – 8.16 (m, 4H), 8.14 – 7.98 (m, 4H), 6.04 – 5.90 (m, 1H), 5.84 (m, *J* = 7.6, 4.4, 2.3 Hz, 1H), 5.34 – 5.13 (m, 2H), 2.92 – 2.67 (m, 2H), 2.35 (d, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.4, 134.8, 131.5, 130.8, 130.8, 127.8, 127.6, 127.5, 127.4, 126.1, 125.4, 125.2, 125.2, 125.1, 125.0, 123.4, 122.5, 118.7, 70.4, 43.8.

HRMS (ESI) m/z: [M+H] + calcd. for $C_{20}H_{16}O$ + 272.1201; found: 272.1198

Following the general procedure A.



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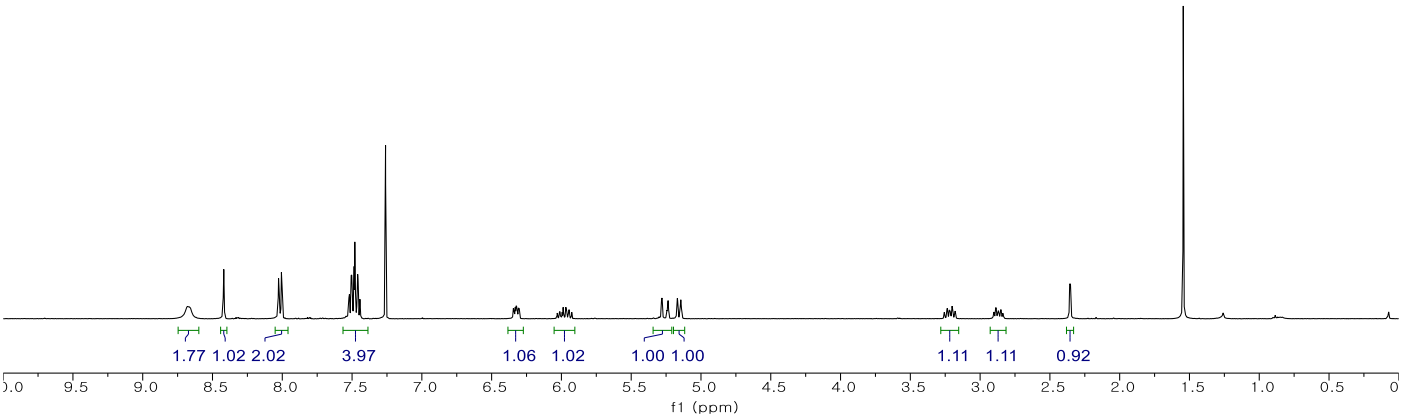
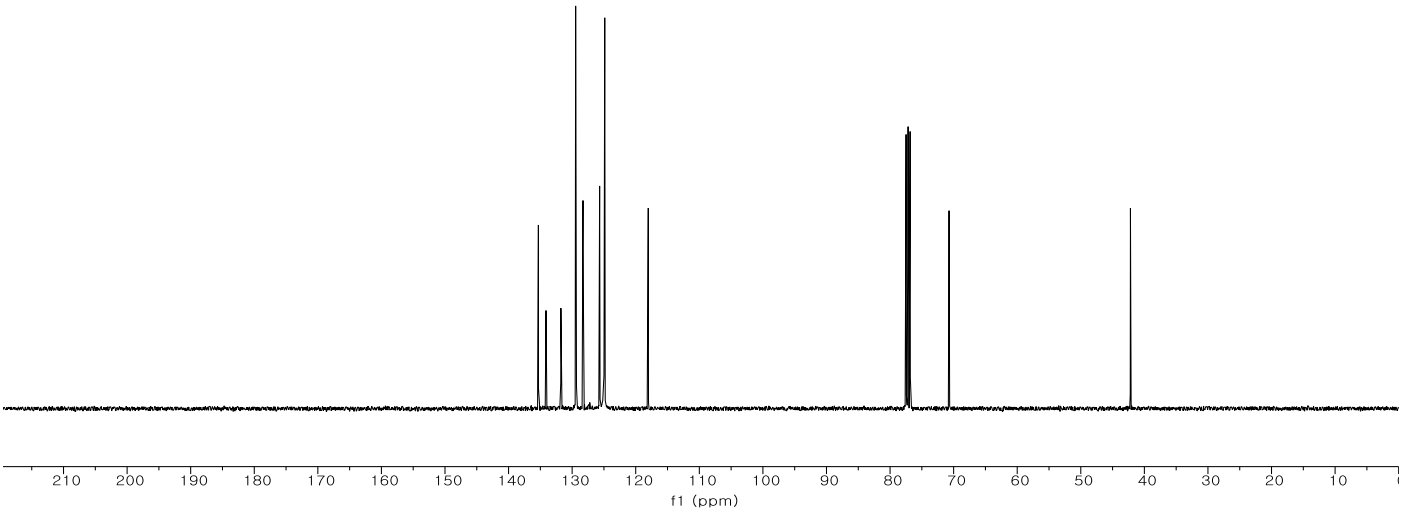
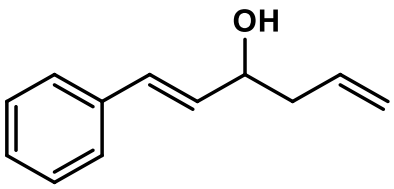




^{1}H NMR (400 MHz, Chloroform-d) δ 8.68 (s, 2H), 8.42 (s, 1H), 8.05 – 7.96 (m, 2H), 7.56 – 7.42 (m, 4H), 6.32 (m, J = 9.1, 5.3, 2.3 Hz, 1H), 5.98 (m, J = 16.8, 10.1, 7.8, 6.4 Hz, 1H), 5.26 (m, J = 17.1, 1.6 Hz, 1H), 5.16 (m, J = 10.1, 2.0, 1.0 Hz, 1H), 3.22 (m, J = 14.2, 9.0, 7.9, 1.1 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.36 (d, J = 2.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 135.3, 134.1, 131.8, 129.5, 129.3, 128.3, 125.7, 124.9, 118.0, 70.7, 42.2.

Following the general procedure A. Spectra were matched to a previous report.[4]



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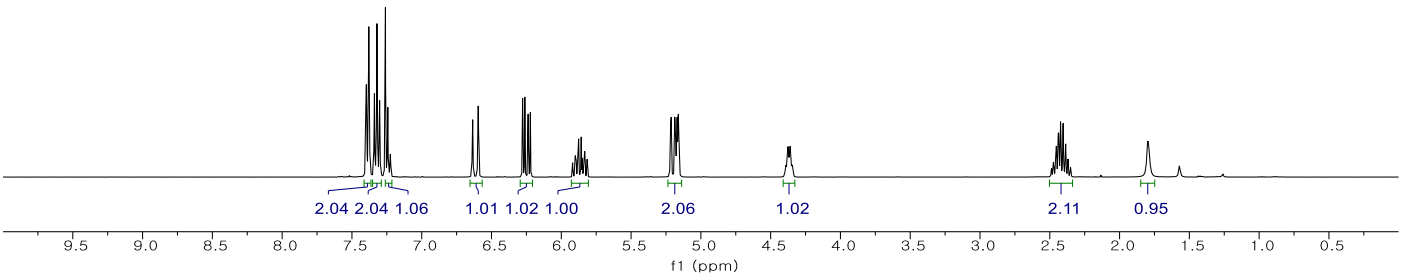
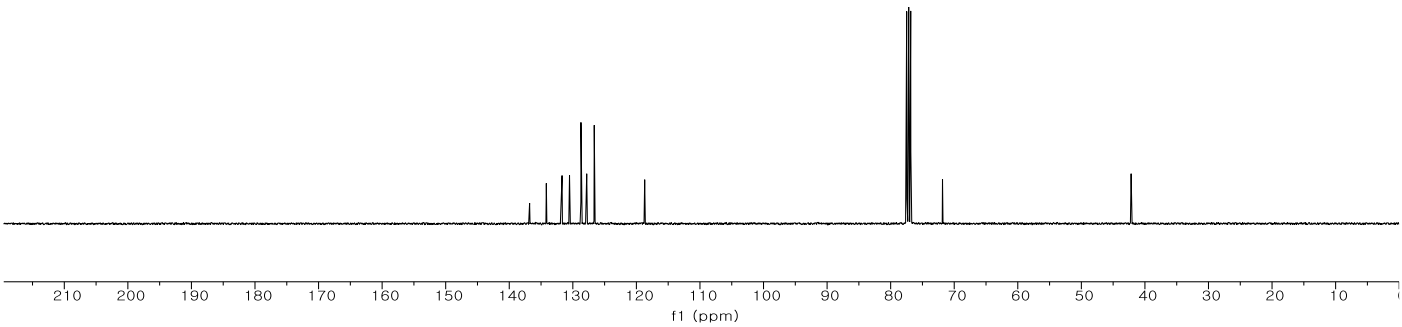
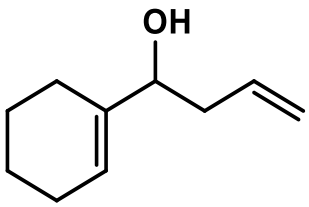




^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 6.62 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.93 – 5.81 (m, 1H), 5.24 – 5.14 (m, 2H), 4.37 (q, *J* = 6.3 Hz, 1H), 2.50 – 2.34 (m, 2H), 1.80 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.8, 134.2, 131.7, 130.5, 128.7, 127.8, 126.6, 118.7, 71.8, 42.2.

Following the general procedure A. Spectra were matched to a previous report.[3]



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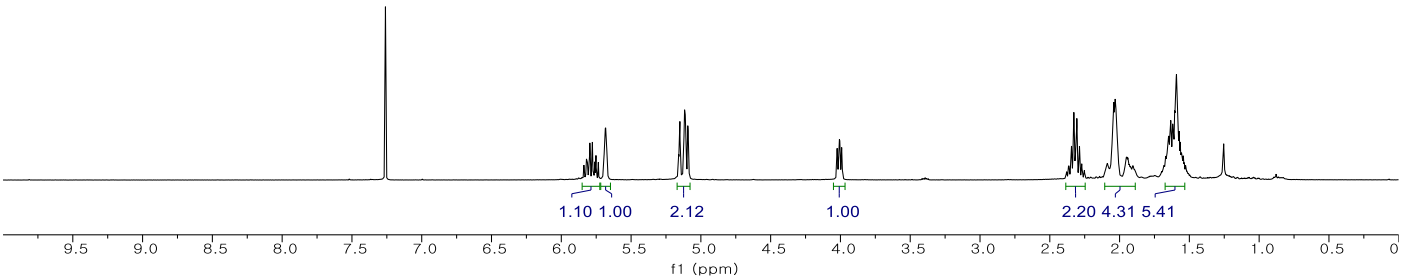
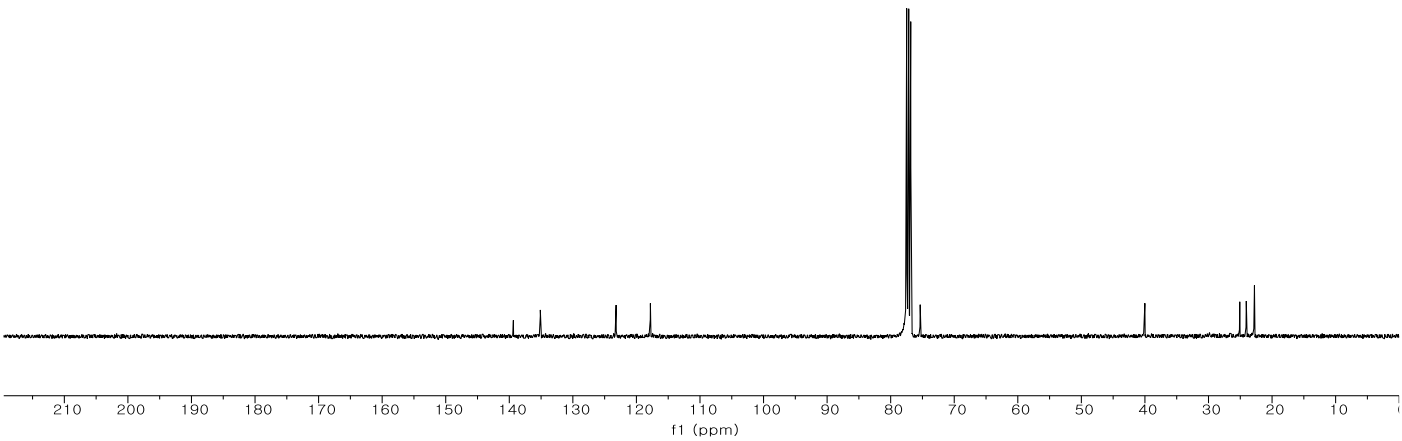
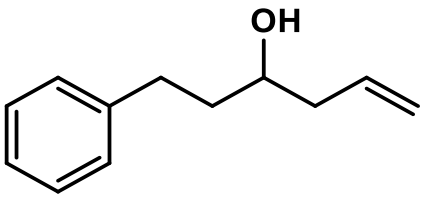




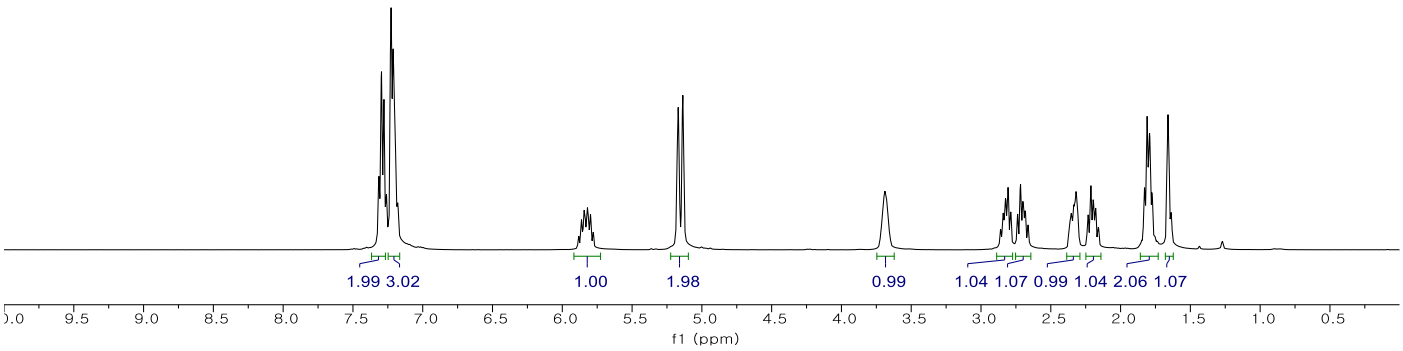
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.79 (m, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.69 (m, *J* = 4.6, 3.1, 2.2 Hz, 1H), 5.17 – 5.08 (m, 2H), 4.01 (m, *J* = 7.6, 5.4 Hz, 1H), 2.39 – 2.25 (m, 2H), 2.11 – 1.89 (m, 4H), 1.67 – 1.53 (m, 5H).

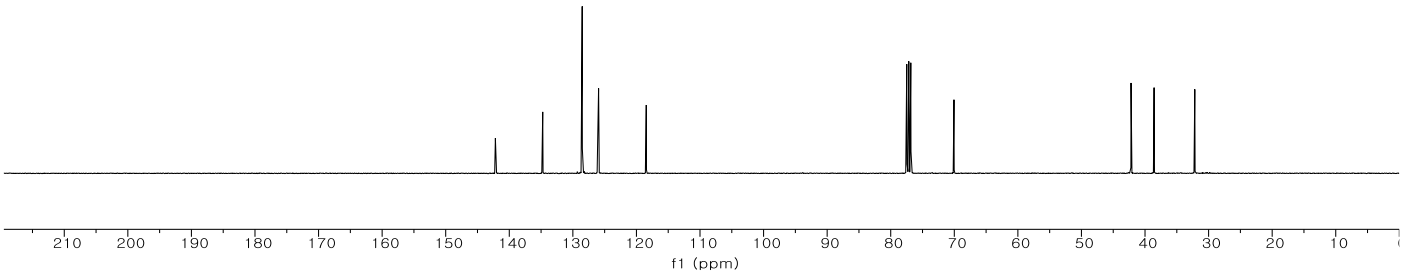
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.4, 135.1, 123.2, 117.8, 75.4, 40.0, 25.1, 24.1, 22.8, 22.8.

Following the general procedure A. Spectra were matched to a previous report.[3]



2j

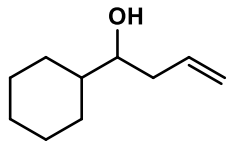




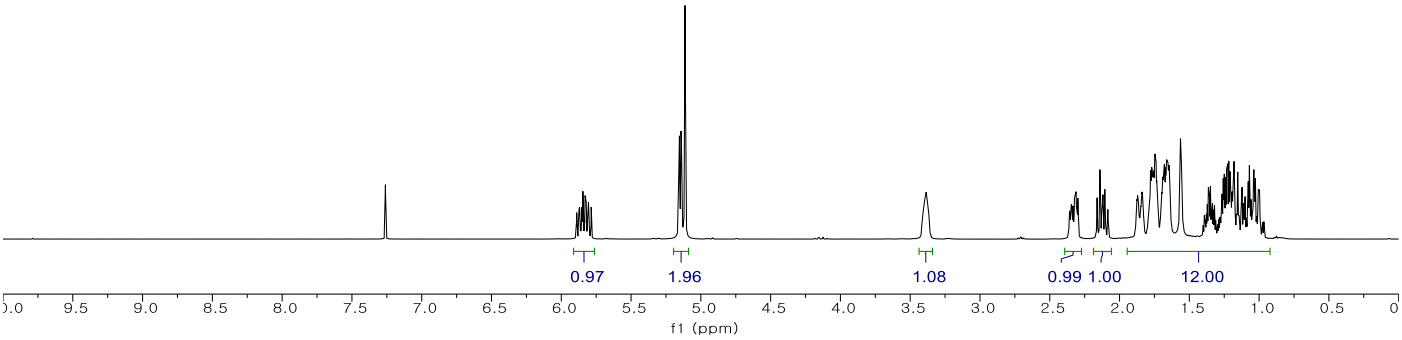
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 2H), 7.20 (m, *J* = 9.6, 7.4 Hz, 3H), 5.92 – 5.73 (m, 1H), 5.22 – 5.10 (m, 2H), 3.69 (m, *J* = 7.7, 4.0 Hz, 1H), 2.82 (m, *J* = 14.3, 8.2, 7.4, 2.4 Hz, 1H), 2.70 (m, *J* = 12.5, 8.2, 7.7, 2.5 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.25 – 2.14 (m, 1H), 1.80 (m, *J* = 9.0, 4.1, 2.1 Hz, 2H), 1.65 (t, *J* = 4.6 Hz, 1H).

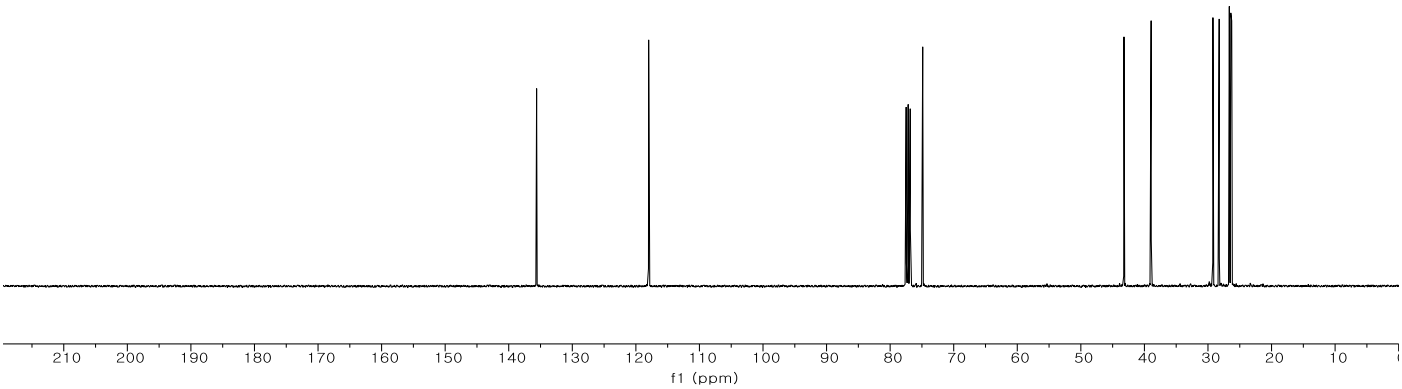
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 134.7, 128.6, 128.5, 126.0, 118.5, 70.1, 42.2, 38.6, 32.2.

Following the general procedure A. Spectra were matched to a previous report.[3]



2k

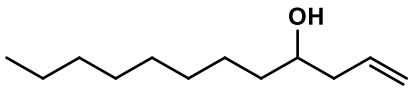




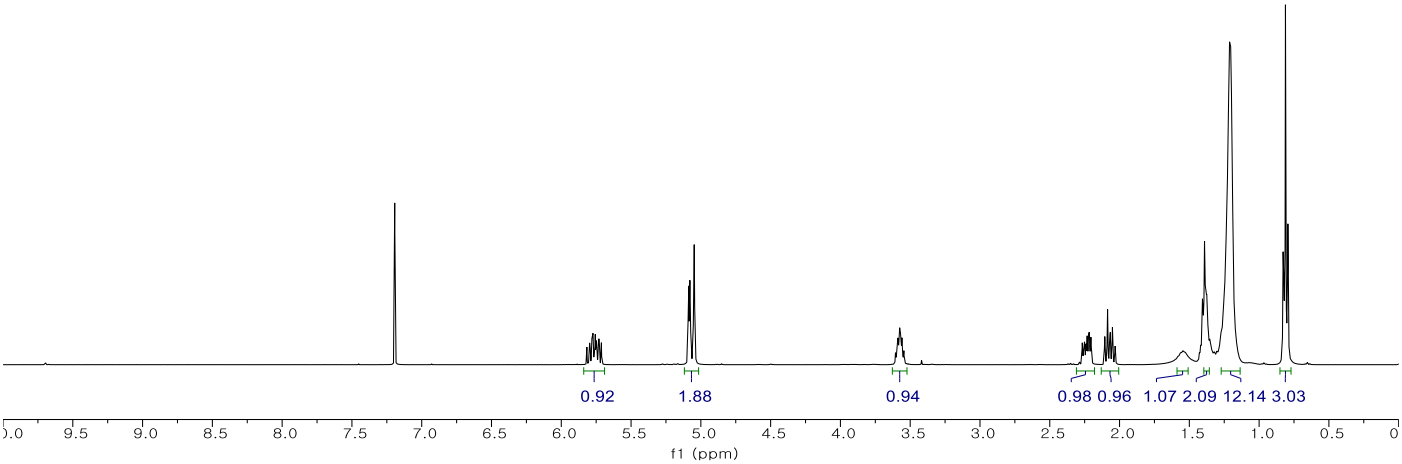
^{1}H NMR (400 MHz, Chloroform-d) δ 5.91 – 5.76 (m, 1H), 5.20 – 5.09 (m, 2H), 3.39 (m, J = 8.8, 5.7, 2.7 Hz, 1H), 2.33 (m, J = 14.1, 6.4, 3.2, 1.5 Hz, 1H), 2.19 – 2.06 (m, 1H), 1.95 – 0.92 (m, 12H).

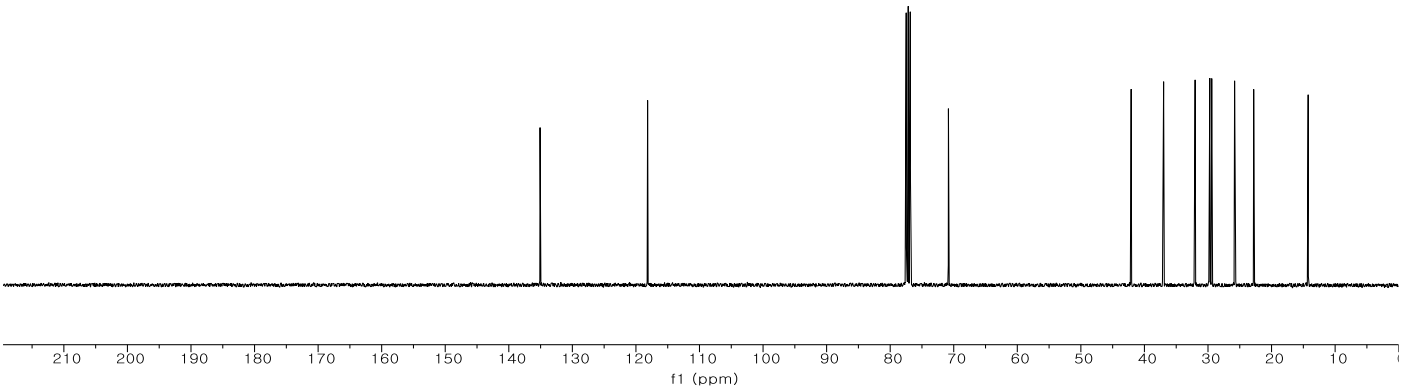
^{13}C NMR (101 MHz, Chloroform-d) δ 135.6, 118.0, 74.9, 43.2, 38.9, 29.2, 28.2, 26.7, 26.4, 26.3.

Following the general procedure A. Spectra were matched to a previous report.[2]



2l

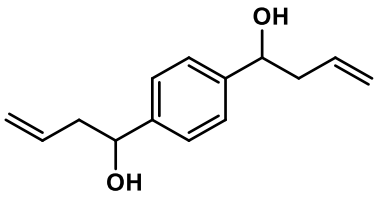




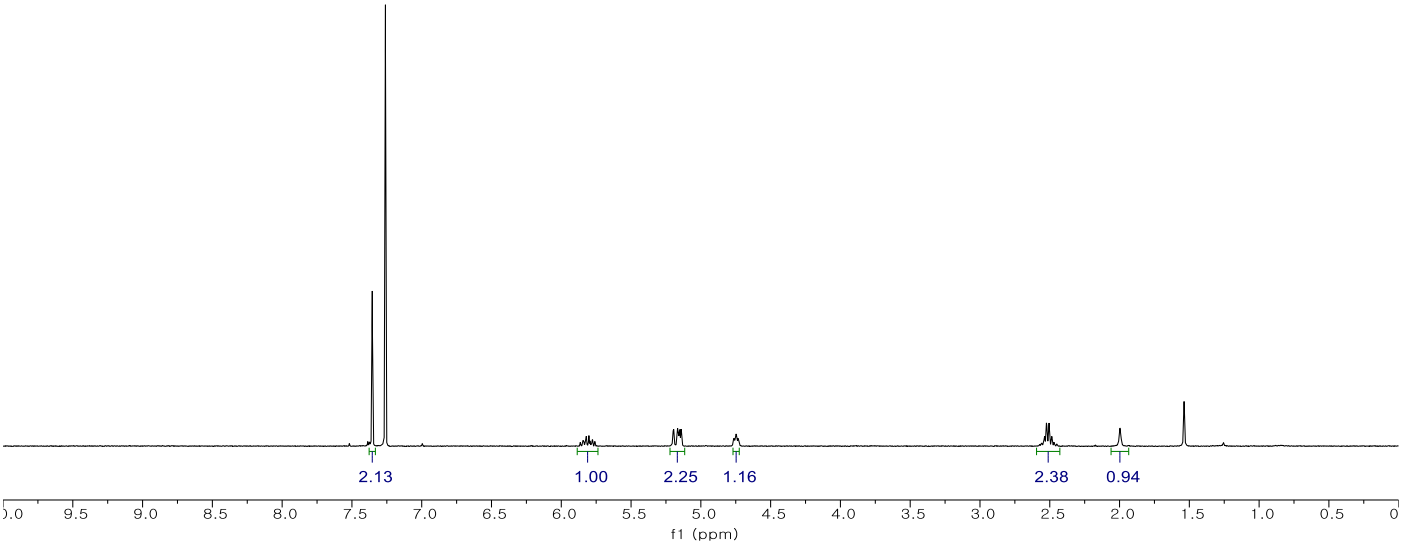
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.91 – 5.76 (m, 1H), 5.18 – 5.08 (m, 2H), 3.64 (m, *J* = 7.8, 5.9, 4.1 Hz, 1H), 2.38 – 2.25 (m, 1H), 2.20 – 2.07 (m, 1H), 1.62 (m, *J* = 9.7 Hz, 1H), 1.45 (m, *J* = 6.9 Hz, 2H), 1.28 (m, *J* = 4.8 Hz, 12H), 0.92 – 0.84 (m, 3H).

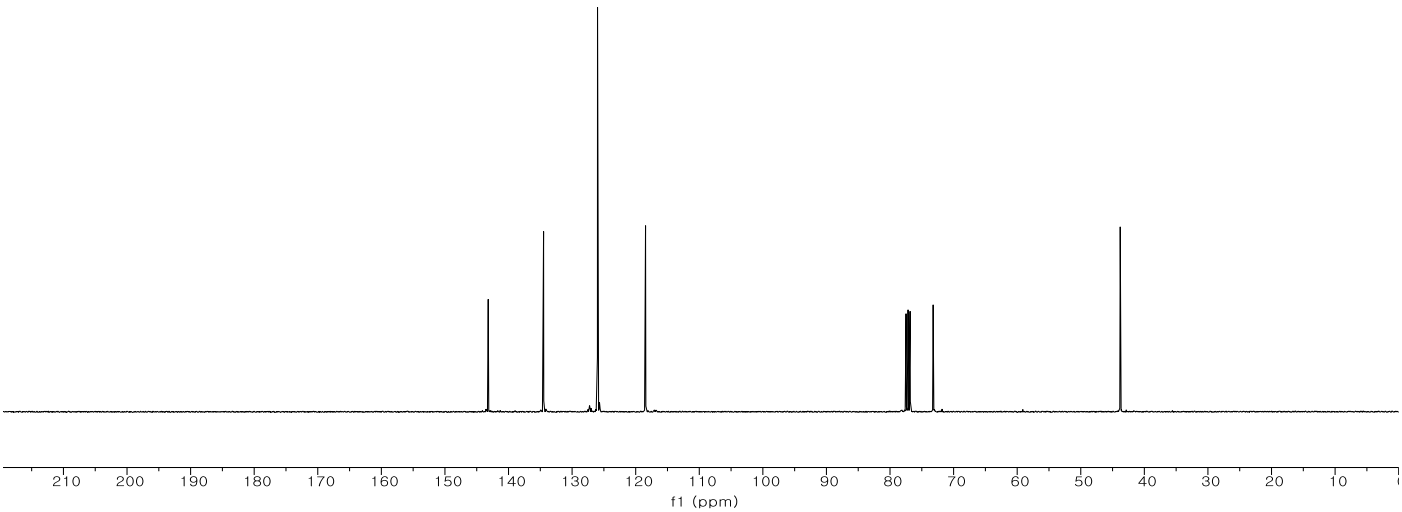
^{13}C NMR (101 MHz, Chloroform-d) δ 135.1, 118.2, 70.8, 42.1, 37.0, 32.0, 29.8, 29.7, 29.4, 25.8, 22.8, 14.2.

Following the general procedure A. Spectra were matched to a previous report.[5]



2m

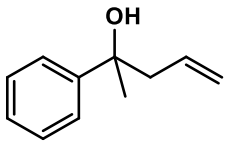




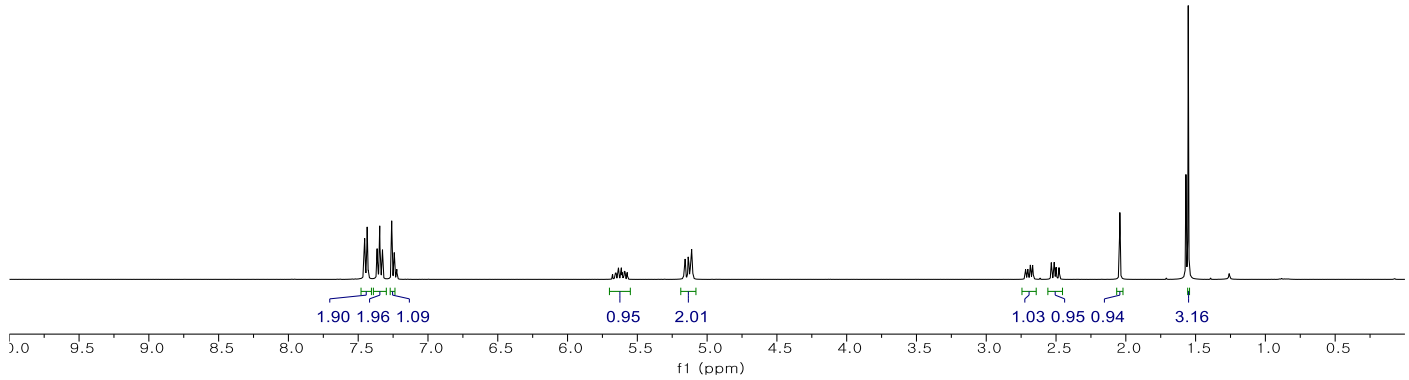
^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (s, 2H), 5.81 (m, J = 17.2, 10.1, 7.1 Hz, 1H), 5.22 – 5.12 (m, 2H), 4.75 (t, 1H), 2.59 – 2.43 (m, 2H), 2.00 (s, 1H).

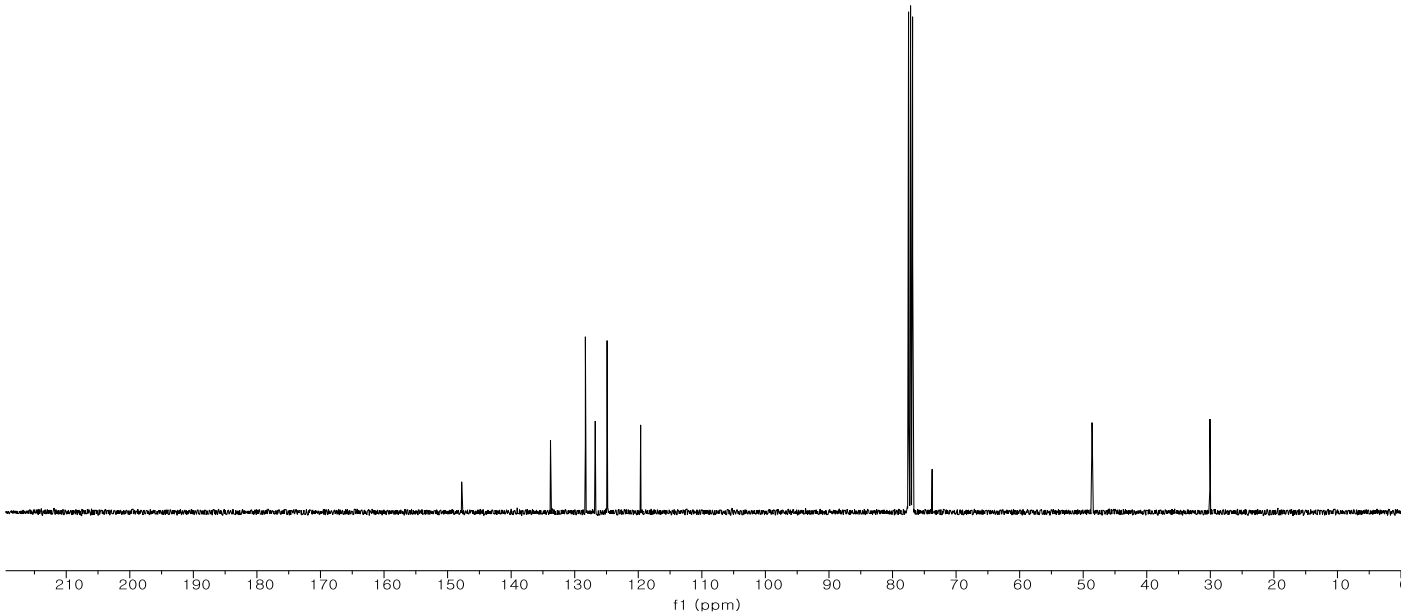
^{13}C NMR (101 MHz, Chloroform-d) δ 143.2, 134.5, 126.0, 118.5, 73.2, 43.8.

Following the general procedure A. Spectra were matched to a previous report.[5]



2n

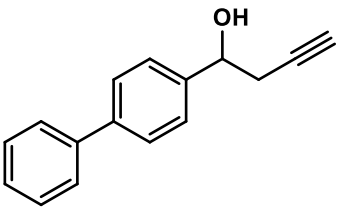




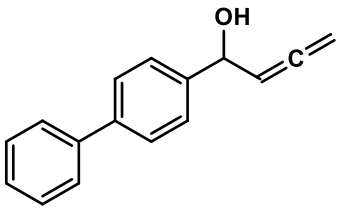
^{1}H NMR (400 MHz, Chloroform-d) δ 7.48 – 7.41 (m, 2H), 7.34 (m, J = 8.5, 6.9 Hz, 2H), 7.26 – 7.23 (m, 1H), 5.62 (m, J = 16.8, 10.1, 8.3, 6.4 Hz, 1H), 5.19 – 5.08 (m, 2H), 2.69 (m, J = 13.8, 6.4, 1.3 Hz, 1H), 2.51 (m, J = 13.7, 8.3, 1.0 Hz, 1H), 2.04 (s, 1H), 1.55 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 147.8, 133.8, 128.3, 126.8, 124.9, 119.6, 73.8, 48.6, 30.1.

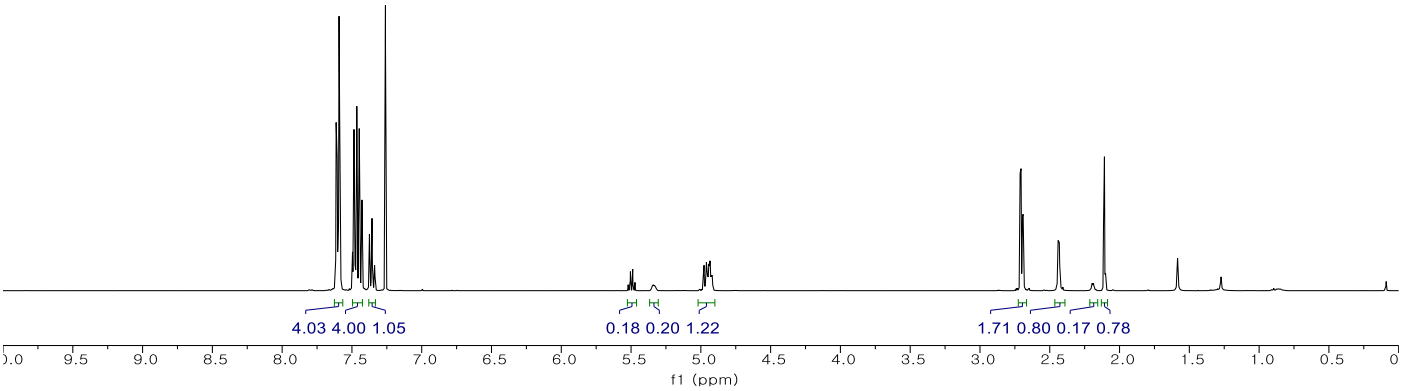
Following the general procedure A. Spectra were matched to a previous report.[2]

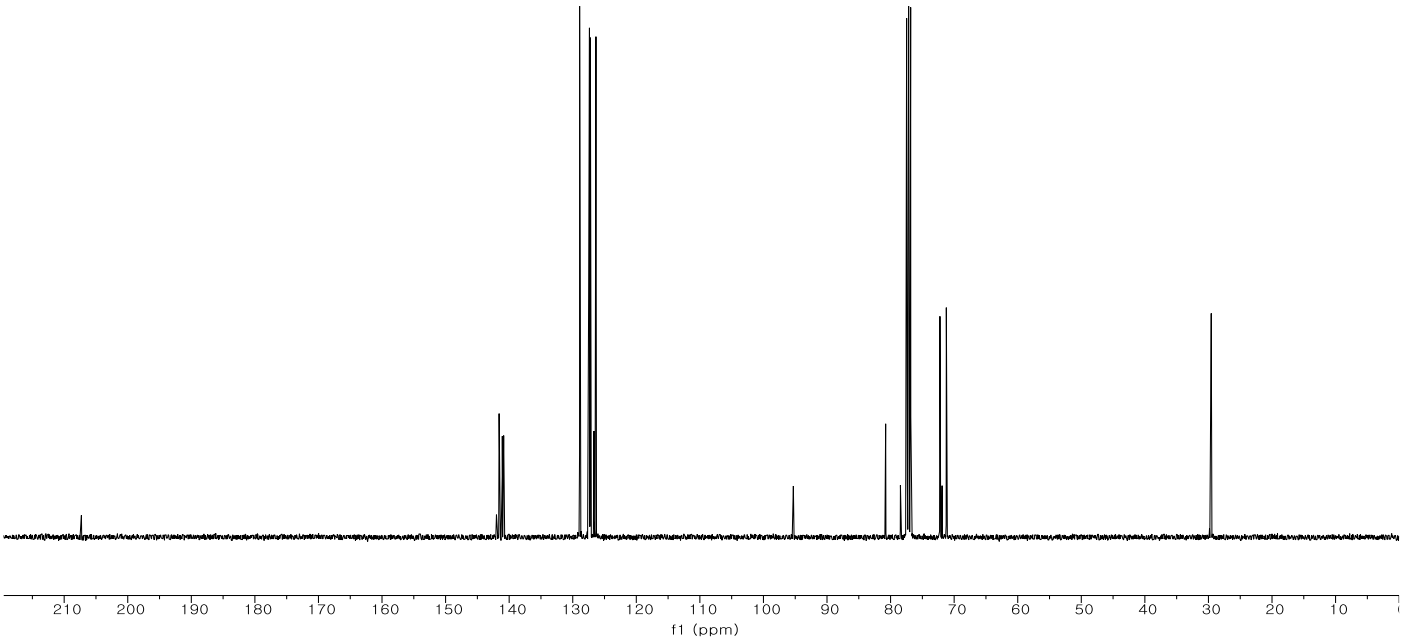


3a



4a





3a

^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.56 (m, 4H), 7.52 – 7.40 (m, 4H), 7.40 – 7.32 (m, 1H), 4.94 (m, J = 6.0, 2.5 Hz, 1H), 2.76 – 2.64 (m, 2H), 2.44 (m, J = 3.4 Hz, 1H), 2.11 (t, J = 2.6 Hz, 1H).

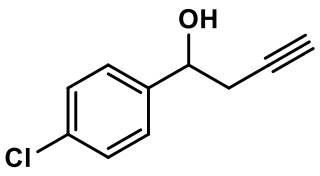
^{13}C NMR (101 MHz, Chloroform-d) δ 141.6, 141.1, 140.9, 128.9, 127.5, 127.4, 127.2, 126.6, 80.8, 72.2, 71.2, 29.6.

4a

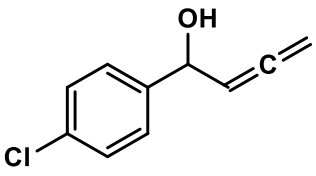
^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.56 (m, 4H), 7.52 – 7.40 (m, 4H), 7.40 – 7.32 (m, 1H), 5.49 (q, J = 6.5 Hz, 1H), 5.37 – 5.29 (m, 1H), 5.02 – 4.96 (m, 2H), 2.19 (d, J = 4.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 207.3, 142.0, 140.9 (d, J = 1.7 Hz), 128.9, 127.5, 127.4, 127.2, 126.7, 95.3, 78.5, 77.4, 71.9, 29.8.

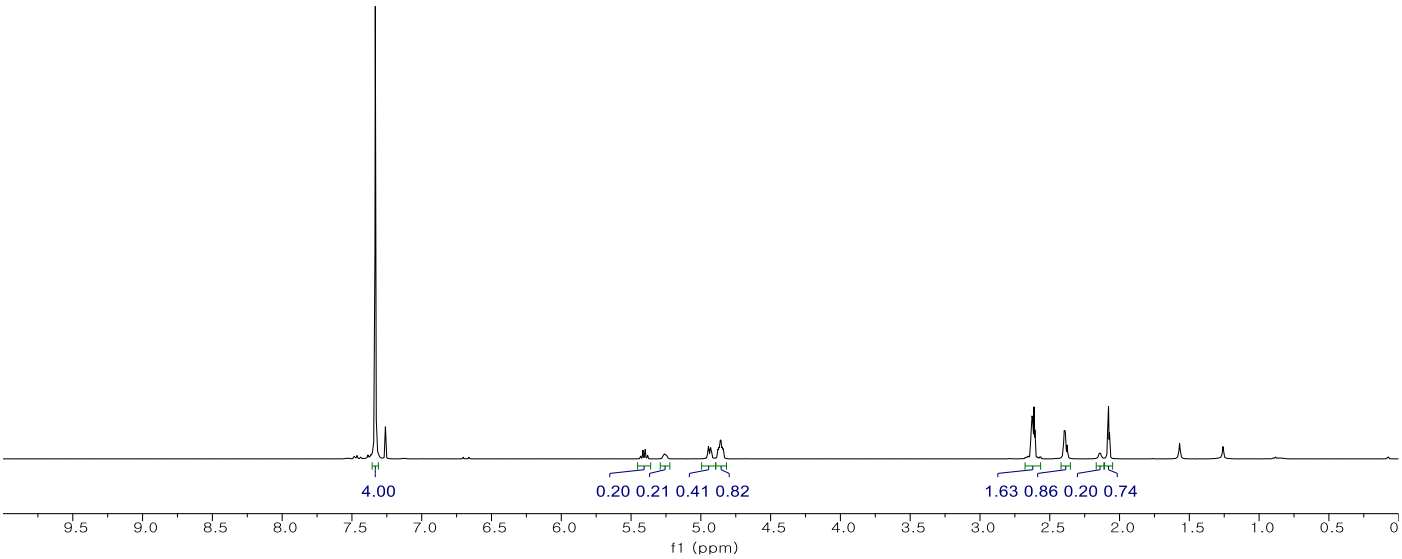
Following the general procedure B. Spectra were matched to a previous report.[6,7]

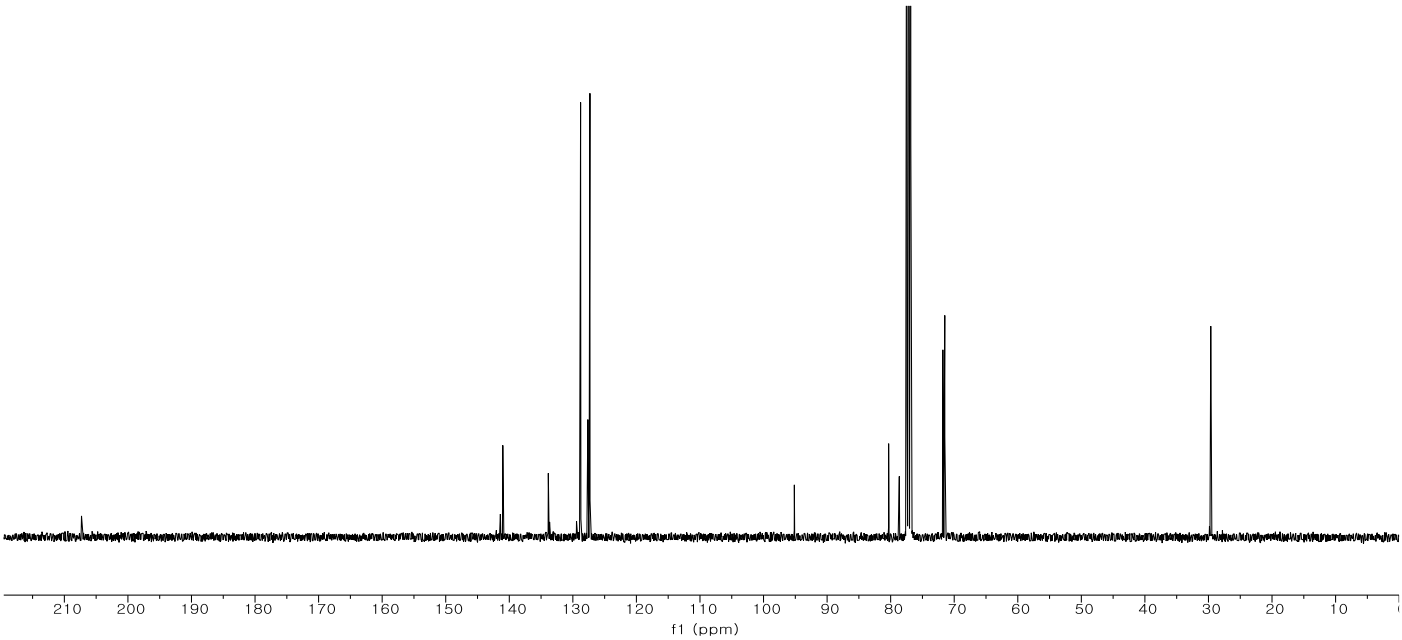


3b



4b





3b

^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (s, 4H), 4.86 (m, J = 6.3, 2.8 Hz, 1H), 2.68 – 2.57 (m, 2H), 2.42 – 2.35 (m, 1H), 2.08 (t, J = 2.6 Hz, 1H).

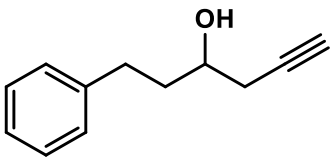
^{13}C NMR (101 MHz, Chloroform-d) δ 141.0, 133.9, 128.8, 127.3, 80.3, 71.8, 71.5, 29.6.

4b

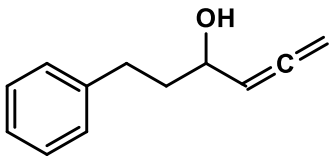
^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (s, 4H), 5.41 (q, J = 6.5 Hz, 1H), 5.26 (dd, J = 6.4, 3.1 Hz, 1H), 5.00 – 4.91 (m, 2H), 2.14 (d, J = 3.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 207.3, 141.4, 133.7, 128.8, 127.6, 95.2, 78.6, 71.5.

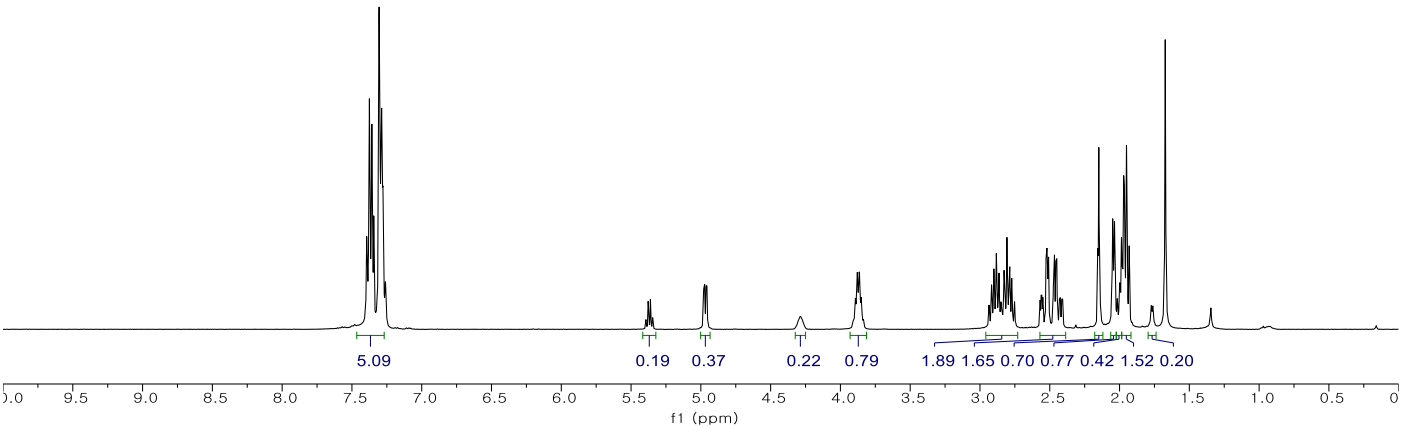
Following the general procedure B. Spectra were matched to a previous report.[8,9]

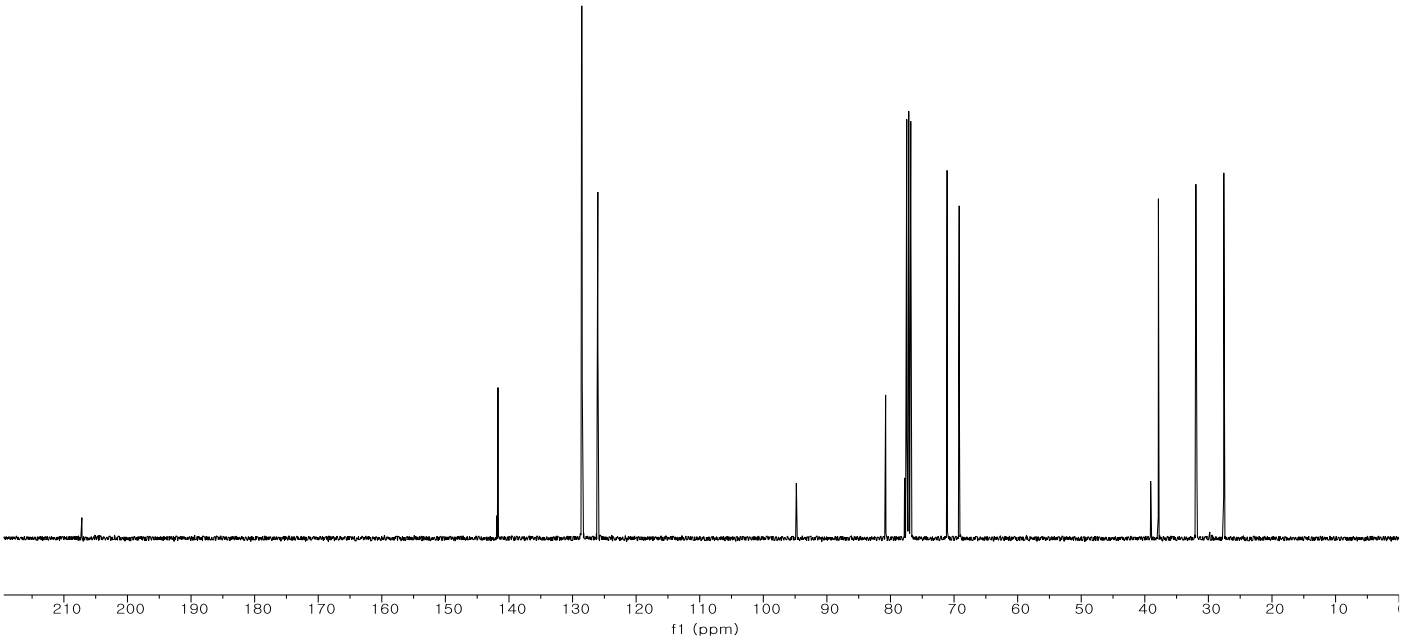


3c



4c





3c

^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.26 (m, 5H), 3.93 – 3.81 (m, 1H), 2.91-2.73 (m, 2H), 2.59 – 2.39 (m, 2H), 2.15 (t, J = 2.7 Hz, 1H), 2.04 (d, J = 5.1 Hz, 1H), 1.97 – 1.92 (m, 2H).

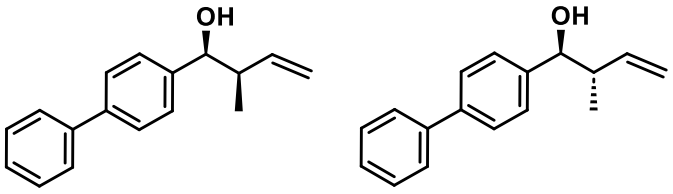
^{13}C NMR (101 MHz, Chloroform-d) δ 141.7, 128.5, 128.5, 126.0, 80.8, 71.1, 69.2, 37.9, 32.0, 27.6.

4c

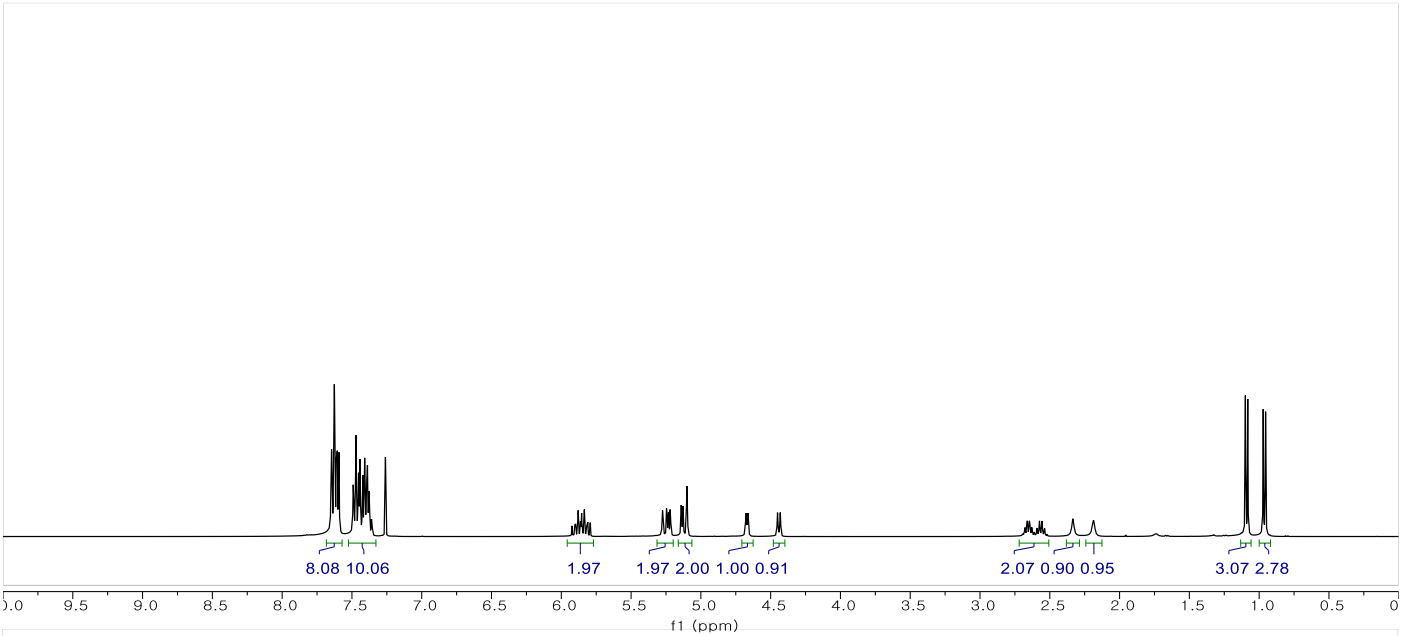
^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.26 (m, 5H), 5.37 (q, J = 6.5 Hz, 1H), 4.97 (dd, J = 6.6, 2.4 Hz, 2H), 4.39 – 4.15 (m, 1H), 2.86 – 2.83 (m, 2H), 1.99 (m, J = 5.4 Hz, 2H), 1.77 (d, J = 4.8 Hz, 1H).

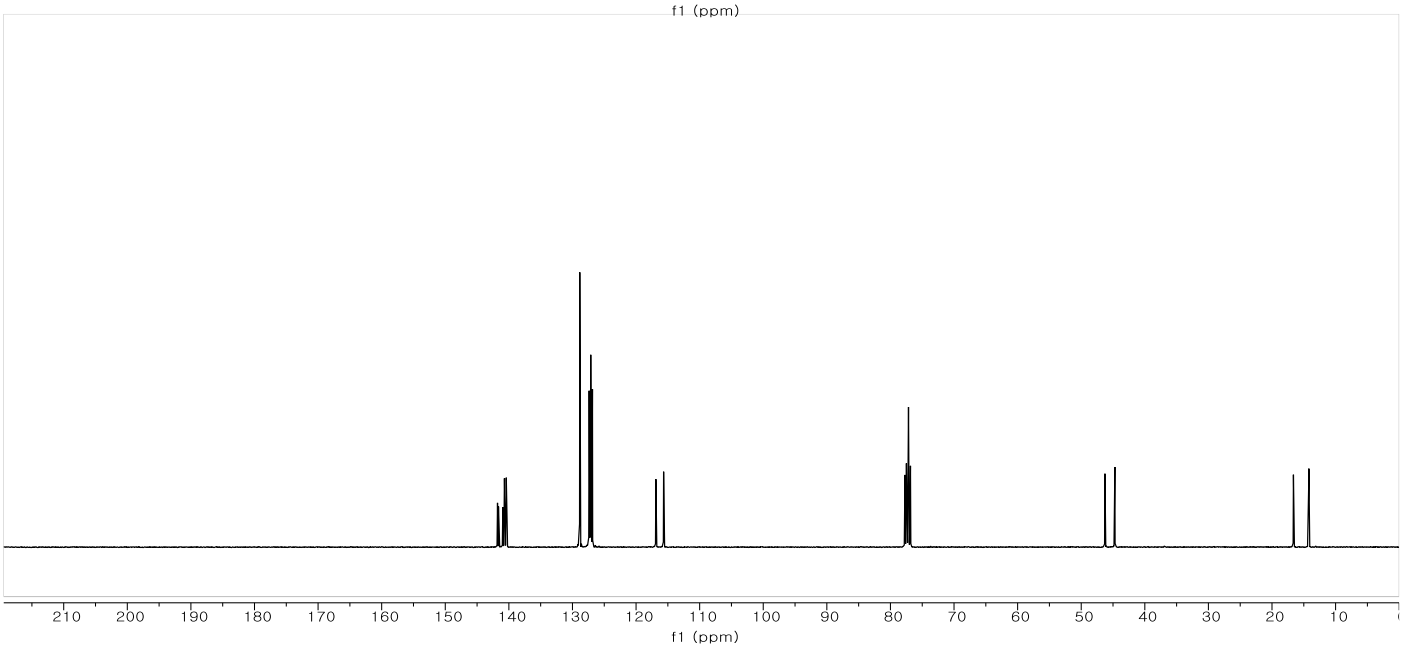
^{13}C NMR (101 MHz, Chloroform-d) δ 207.2, 141.9, 128.6, 128.5, 126.0, 94.8, 77.8, 69.0, 39.1, 31.8.

Following the general procedure B. Spectra were matched to a previous report.[10]



5a 5'a





5a

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 4H), 7.53 – 7.33 (m, 5H), 5.86 (m, *J* = 17.0, 10.1, 7.5 Hz, 1H), 5.31 – 5.20 (m, 2H), 4.44 (d, *J* = 7.7 Hz, 1H), 2.56 (m, *J* = 7.0 Hz, 1H), 2.33 (s, 1H), 1.09 (d, *J* = 6.8 Hz, 3H).

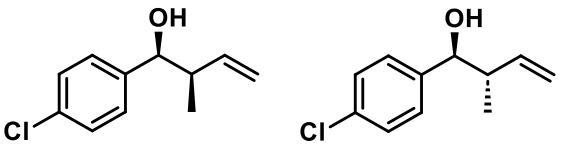
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.6, 141.0, 140.7, 140.6, 140.4, 128.9, 127.4, 127.2, 127.1, 127.1, 127.0, 126.9, 116.9, 77.7, 46.3, 16.6.

5'a

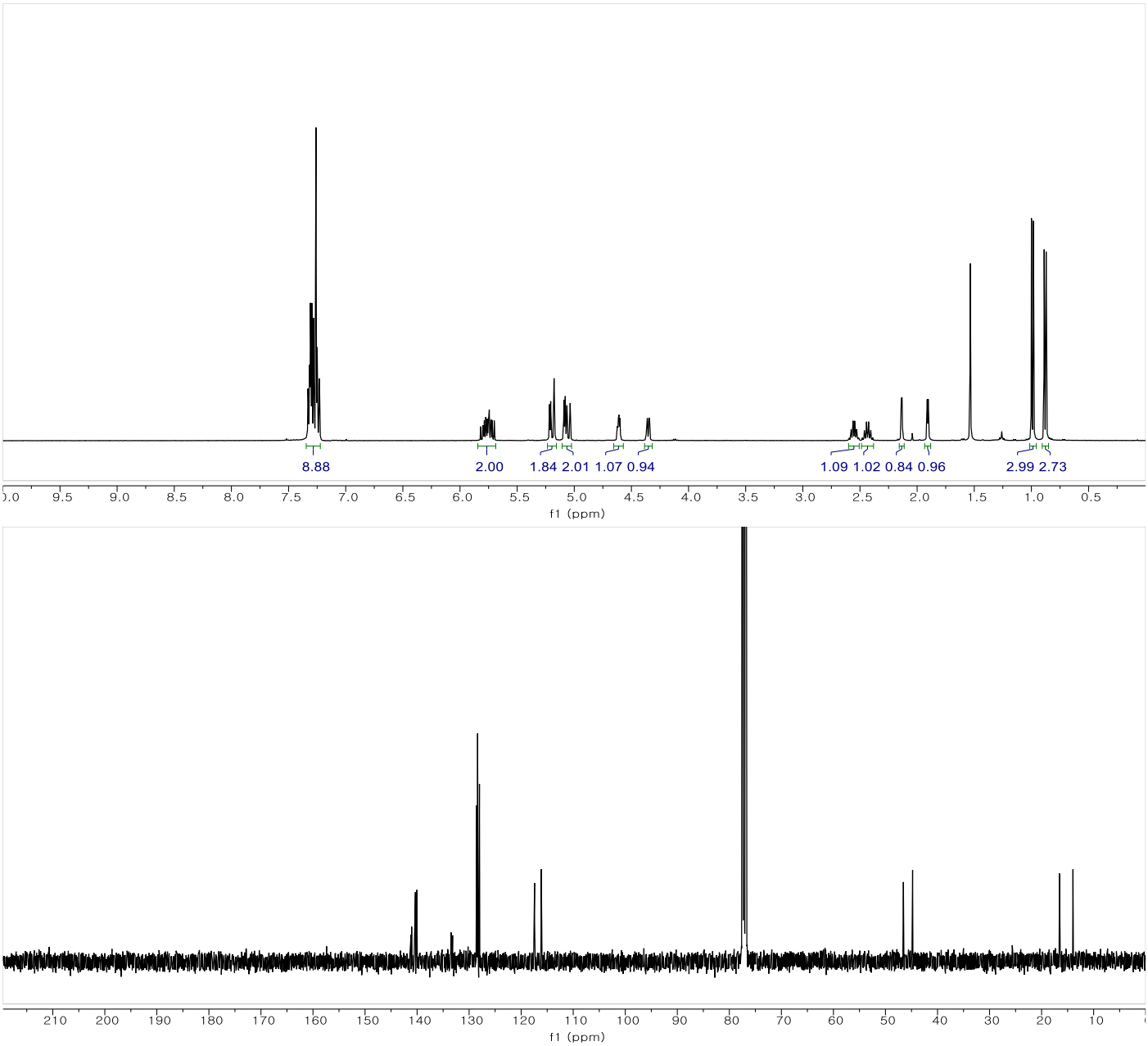
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 4H), 7.53 – 7.33 (m, 5H), 5.86 (m, *J* = 17.0, 10.1, 7.5 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.67 (d, *J* = 5.5 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.19 (s, 1H), 0.96 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8, 141.0, 140.4, 140.3, 128.9, 127.4, 127.2, 127.1, 127.1, 127.0, 126.9, 115.7, 77.4, 44.7, 14.2.

Following the general procedure C. Spectra were matched to a previous report.[11]



5b 5'b



5b

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.22 (m, 4H), 5.84 – 5.69 (m, 1H), 5.11 – 5.02 (m, 2H), 4.61 (dd, *J* = 5.4, 3.4 Hz, 1H), 2.55 (m, *J* = 6.9, 5.5, 1.3 Hz, 1H), 1.91 (d, *J* = 3.6 Hz, 1H),), 0.99 (d, *J* = 6.8 Hz, 3H).

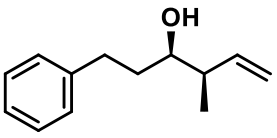
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.2, 140.1, 133.2, 128.5, 128.4, 128.0, 116.1, 76.7, 44.8, 16.6.

5'b

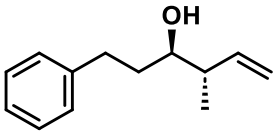
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.22 (m, 4H), 5.84 – 5.69 (m, 1H), 5.23 – 5.16 (m, 2H), 4.35 (dd, *J* = 7.8, 2.4 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.13 (d, *J* = 2.7 Hz, 1H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.0, 140.3, 133.5, 128.5, 128.4, 128.0, 117.4, 77.3, 46.5, 14.0.

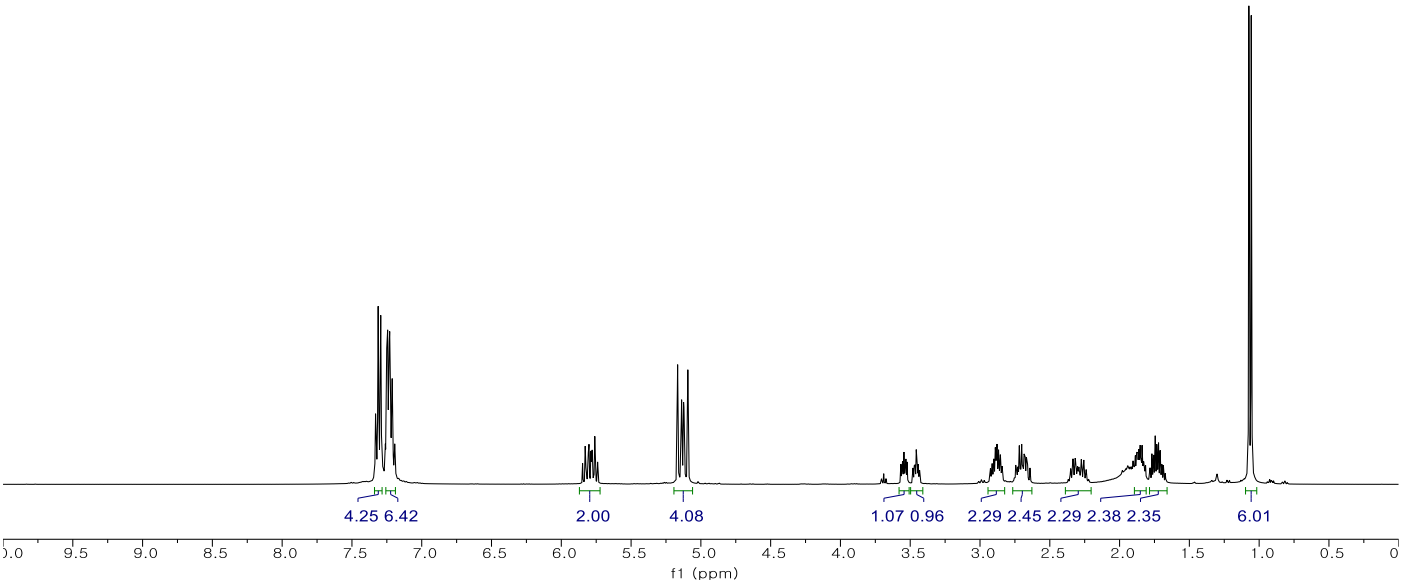
Following the general procedure C. Spectra were matched to a previous report.[11]

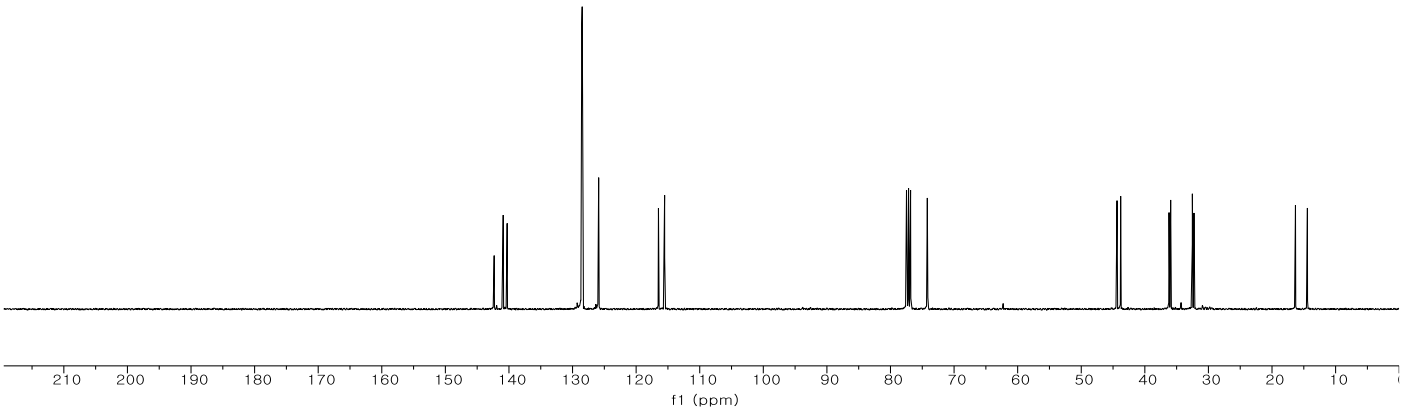


5c



5'c





5c

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 5.79 (m, *J* = 17.2, 11.3, 7.7 Hz, 1H), 5.19 – 5.06 (m, 2H), 3.55 (m, *J* = 9.4, 5.2, 3.2 Hz, 1H), 2.94 – 2.82 (m, 2H), 2.39 – 2.20 (m, 1H), 1.79 – 1.66 (m, 2H), 1.07 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.3, 140.9, 128.6, 128.6, 128.5, 128.5, 125.9, 115.5, 74.2, 43.8, 35.9, 32.5, 14.4.

5'c

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 5.79 (m, *J* = 17.2, 11.3, 7.7 Hz, 1H), 5.19 – 5.06 (m, 2H), 3.46 (m, *J* = 9.1, 5.9, 3.3 Hz, 1H), 2.69 (m, *J* = 13.8, 10.3, 6.7 Hz, 2H), 2.39 – 2.20 (m, 1H), 1.85 (m, *J* = 10.0, 6.7, 5.4, 3.5 Hz, 2H), 1.07 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.3, 140.3, 128.6, 128.6, 128.5, 128.5, 125.9, 116.5, 74.2, 44.4, 36.2, 32.3, 16.3.

Following the general procedure C. Spectra were matched to a previous report.[13]

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