

Supporting Information

Triflimide-catalyzed allyl-allyl cross-coupling: a metal-free allylic alkylation

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General experimental

All the reactions were carried out in a flame or oven-dried glassware under an argon or nitrogen atmosphere with freshly distilled solvents under anhydrous conditions unless otherwise indicated. Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (0.010–0.063 mm). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using base solution of potassium permanganate. Technical grade solvents were used for chromatography and were distilled prior to use. IR spectra were recorded using FTIR Restige-21 (Shimadzu). NMR spectra were recorded at room temperature on 300 MHz Bruker ACF 300, 400 MHz Bruker DPX 400, 500 MHz Bruker AMX 500, and 400 MHz JEOL ECA 400 NMR spectrometers. The residual solvent signals were taken as the reference (7.26 ppm for ¹H NMR spectra and 77.0 ppm for ¹³C NMR spectra in CDCl₃, 2.5 ppm for ¹H NMR spectra and 39.5 ppm for ¹³C NMR spectra in MeOD). TMS signal at 0.0 ppm was used as an internal standard for partial ¹H NMR spectra. Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-ToF premierTM mass spectrometer.

Materials: All solvents were distilled under nitrogen from the following drying agents immediately before use: tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl; dichloromethane and 1, 2-dichloroethane were distilled from calcium hydride. The cinnamyl acetate (**1a**), cinnamyl alcohol (**1b**), cinnamyl bromide (**1f**), allyltrimethylsilane (**2a**), methallyltrimethylsilane (**2b**) and trimethylsilyl cyclopentadiene (**2e**) were purchased from commercial suppliers and used without further purification. Other cinnamyl acetate derivatives (**1c-1e**, **1g-1h**, **1bs-1ps**) and allyltrimethylsilane derivatives (**2c**, **2d**) were prepared from standard methods according to literature reported procedure. All the catalysts were purchased from commercial suppliers and used without further purification.

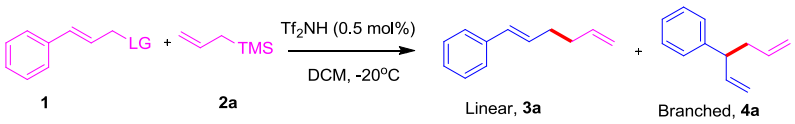
Table 1. Optimization studies.

1a + 2a $\xrightarrow{\text{Conditions}}$ Linear, 3a + Branched, 4a

Entry	Catalysts (mol%)	solvent	Temp (°C)	3a/4a ^a	Yield (%) ^b
1	B. A. (1) ^c	DCM ^d	r.t.	-	nr ^f
2	TFA (1)	DCM ^d	r.t.	-	trace
3	Amberlyst(1)	DCM ^d	r.t.	-	trace
4	MK-10 (1)	DCM ^d	r.t.	54/46	24
5	Tf ₂ NH (1)	DCM ^d	r.t.	69/31	39
6	Tf ₂ NH (1)	CH ₃ NO ₂ ^d	r.t.	-	trace
7	Tf ₂ NH (1)	THF ^d	r.t.	-	nr ^f
8	Tf ₂ NH (1)	Toluene ^d	r.t.	-	nr ^f
9	Tf ₂ NH (1)	DMF ^d	r.t.	-	nr ^f
10	Tf ₂ NH (1)	Dioxone ^d	r.t.	-	trace
11	Tf ₂ NH (1)	Benzene ^d	r.t.	78/22	29
12	Tf ₂ NH (1)	AcCN ^d	r.t.	-	nr ^f
13	Tf ₂ NH (1)	DCM ^e	r.t.	75/25	47
14	Tf ₂ NH (1)	DCM ^e	-40	77/23	42
15	Tf ₂ NH (1)	DCM ^e	-20	75/25	53
16	Tf ₂ NH (1)	DCM ^e	0	76/24	45
17	Tf ₂ NH (1)	DCM ^e	r.t.	75/25	47
18	Tf ₂ NH (1)	DCM ^e	40	79/21	33
19	Tf ₂ NH (0.5)	DCM ^e	r.t.	78/22	57
20	Tf ₂ NH (1)	DCM ^e	r.t.	75/25	53
21	Tf ₂ NH (2)	DCM ^e	r.t.	66/34	41
22 ^[g]	Tf ₂ NH (0.5)	DCM ^e	rt	78/22	64
23 ^[h]	Tf ₂ NH (0.5)	DCM ^e	rt	79/21	73
24^[i]	Tf₂NH (0.5)	DCM^e	-20	91/9	89

^aThe ration determined by crude NMR. ^bIsolated yield after purification. ^cB. A. = Brønsted acid (TsOH, H₃PO₄, HCl, AcOH, MeSO₃H). ^d[M] = 0.5 M. ^e[M] = 0.1 M. ^fnr = no reaction. ^gUsing 1.5 equiv. **2a**. ^hUsing 2.0 equiv. **2a**. ⁱUsing 3.0 equiv. **2a**.

Table 2. Scope of Leaving Group in triflimide-catalyzed allyl-allyl cross-coupling.

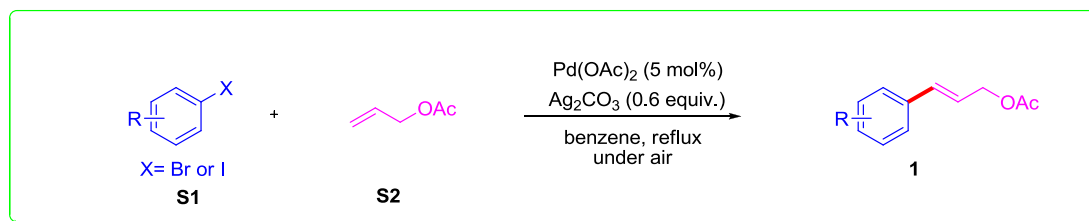


The reaction scheme shows the cross-coupling of allyl bromide (1) and allyltrimethylsilane (2a) catalyzed by Tf₂NH (0.5 mol%) in DCM at -20°C. The reaction yields a linear product (3a) and a branched product (4a).

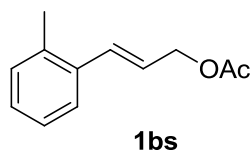
Entry	LG (mol%)	3a/4a ^a	Yield (%) ^b
1	OH (1b)	-	nr ^[c]
2	OMe (1c)	74/26	63
3	OEt (1d)	74/26	58
4	OTMS (1e)	79/21	68
5	Br (1f)	72/28	43
6	OCO ₂ Me (1g)	80/20	73
7	OBoc (1h)	81/19	93

^aThe ration determined by crude NMR. ^bIsolated yield after purification. ^cnr = no reaction. LG = Leaving Group. TMS = Trimethylsilane. Boc = tert-butyl- carbonate.

General procedures for the synthesis of cinnamyl acetates **1**, method A:¹



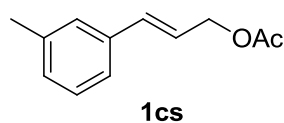
Aryl bromide or iodide **S1** (1.0 mmol) and then allyl acetate **S2** (200 mg, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1s** as a liquid.



(*E*)-3-*o*-tolylallyl acetate (**1bs**): The title compound was prepared according to the general procedure A. 2-Iodotoluene (218mg, 127 μ L, 1.0 mmol) and then allyl acetate **S2** (200 mg, 216 μ L, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1bs** (127 mg, 67%) as a liquid. The NMR datas obtained for **1bs** are in agreement with previously reported

1. Pan, D.; Chen, A.; Su, Y.; Zhou, W.; Li, S.; Jia, W.; Xiao, J.; Liu, Q.; Zhang, L.; Jiao, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4729–4732.
2. Su, Y.; Jiao, N. *Org. Lett.* **2009**, *11*, 2089.

literature values.² (*E*)-3-*o*-tolylallyl acetate (**1bs**): ¹H NMR (CDCl₃, 400MHz): δ 7.26-7.46 (m, 1H), 7.14-7.19 (m, 3H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.18 (dt, *J* = 6.4, 15.6 Hz, 1H), 4.75 (dd, *J* = 1.2, 16.4 Hz, 2H), 2.36 (s, 3H), 2.11 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 170.8, 135.7, 135.3, 132.1, 130.3, 128.0, 126.2, 125.8, 124.5, 65.3, 21.0, 19.8. FT-IR (CHCl₃): 3025, 1740, 1513, 1472, 1243, 975 cm⁻¹. ESI-MS *m/z* 213.3 [M+Na]⁺.



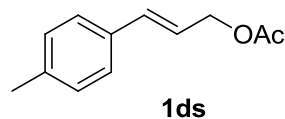
(*E*)-3-*m*-tolylallyl acetate (**1cs**): The title compound was prepared according to the general procedure A. 3-Iodotoluene (218mg, 127 μL, 1.0 mmol) and then allyl acetate **S2** (200 mg, 216 μL, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1cs** (158 mg, 83%) as a liquid. The NMR datas obtained for **1cs** are in agreement with previously reported literature values.³

(*E*)-3-*m*-tolylallyl acetate (**1cs**): ¹H NMR (CDCl₃, 400MHz): δ 7.19-7.25 (m, 3H), 7.06-7.08 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.26 (dt, *J* = 6.8, 16.0 Hz, 1H), 4.71 (dd, *J* = 1.2, 6.4 Hz, 2H), 2.34 (s, 3H), 2.09 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 170.9, 138.2, 136.2, 134.4, 128.9, 128.5, 127.3, 123.8, 123.0, 65.2, 21.4, 21.0.

3. Pan, D.; Yu, M.; Chen, W.; Jiao, N. *Chem. Asian J.* **2010**, *5*, 1090–1093.

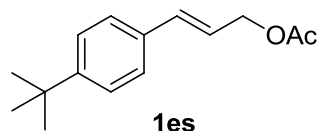
FT-IR (CHCl₃): 3020, 1735, 1591, 1470, 1211, 1018, 953 cm⁻¹. ESI-MS m/z 213.1

[M+Na]⁺.



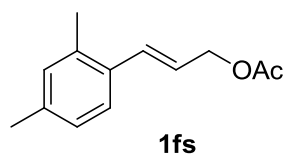
(*E*)-3-*p*-tolylallyl acetate (**1ds**): The title compound was prepared according to the general procedure A. 4-Iodotoluene (218mg, 127 μL, 1.0 mmol) and then allyl acetate **S2** (200 mg, 216 μL, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1ds** (169 mg, 89%) as a liquid. The NMR datas obtained for **1ds** are in agreement with previously reported literature values.²

(*E*)-3-*p*-tolylallyl acetate (**1ds**): ¹H NMR (CDCl₃, 300MHz): δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 6.6, 15.9 Hz, 1H), 4.74 (dd, *J* = 0.9, 6.3 Hz, 2H), 2.37 (s, 3H), 2.12 (s, 3H); ¹³C NMR (CDCl₃, 300MHz): δ 170.8, 138.0, 134.3, 133.5, 129.3, 126.6, 122.1, 65.2, 21.2, 21.0. FT-IR (CHCl₃): 3010, 1736, 1485, 1226, 1032 cm⁻¹. ESI-MS m/z 190.9 [M+H]⁺.



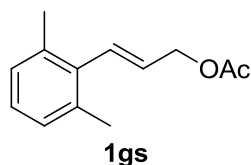
(*E*)-3-(4-*tert*-butylphenyl)allyl acetate (**1es**): The title compound was prepared according to the general procedure A. 4-*tert*-Butyliodobenzene (260mg, 177 μL, 1.0

mmol) and then allyl acetate **S2** (200 mg, 216 μ L, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1es** (183 mg, 79%) as a liquid. ¹H NMR (CDCl₃, 300MHz): δ 7.34-7.41 (m, 4H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.28 (dt, *J* = 6.6, 15.9 Hz, 1H), 4.75 (dd, *J* = 1.2, 6.3 Hz, 2H), 2.12 (s, 3H), 1.35 (s, 9H); ¹³C NMR (CDCl₃, 300MHz): δ 170.8, 151.2, 134.1, 133.5, 126.4, 125.5, 122.4, 65.2, 34.6, 31.3, 21.0. FT-IR (CHCl₃): 3023, 1745, 1456, 1325, 1012, 985 cm⁻¹. ESI-MS *m/z* 255.2 [M+Na]⁺.

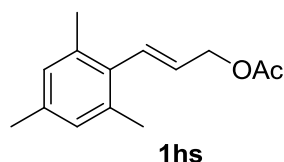


(*E*)-3-(2,4-dimethylphenyl)allyl acetate (**1fs**): The title compound was prepared according to the general procedure A. 1-Iodo-2,4-dimethylbenzene (232mg, 143 μ L, 1.0 mmol) and then allyl acetate **S2** (200 mg, 216 μ L, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1fs** (153 mg, 66%) as a liquid. ¹H NMR (CDCl₃, 400MHz): δ 7.37 (d, *J* = 8.0 Hz, 1H), 6.99-7.01 (m, 2H), 6.87 (d, *J* = 16 Hz, 1H), 6.16 (dt, *J* = 6.4, 15.6 Hz, 1H), 4.76 (dd, *J* = 1.2, 6.8 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.12 (s, 3H); ¹³C

NMR (CDCl₃, 400MHz): δ 170.8, 137.8, 135.5, 132.5, 132.1, 131.1, 126.9, 125.8, 123.5, 65.5, 21.1, 21.0, 19.7. FT-IR (CHCl₃): 3015, 1744, 1465, 1378, 1021, 956 cm⁻¹.
ESI-MS m/z 227.4 [M+Na]⁺.



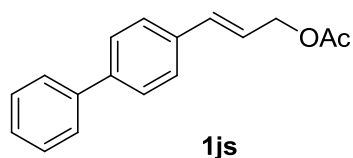
(*E*)-3-(2,6-dimethylphenyl)allyl acetate (**1gs**): The title compound was prepared according to the general procedure A. 1-Iodo-2,6-dimethylbenzene (232mg, 143 μ L, 1.0 mmol) and then allyl acetate **S2** (200 mg, 216 μ L, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1fs** (118 mg, 58%) as a liquid. ¹H NMR (CDCl₃, 400MHz): δ 7.02-7.07 (m, 3H), 6.65 (d, J = 16.4 Hz, 1H), 5.81 (dt, J = 6.4, 16.0 Hz, 1H), 4.76 (d, J = 6.4 Hz, 2H), 2.30 (s, 6H), 2.12 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 170.8, 136.0, 132.0, 131.9, 128.6, 127.8, 126.9, 65.3, 21.0, 20.9. FT-IR (CHCl₃): 3008, 1749, 1463, 1255, 1046, 890 cm⁻¹. ESI-MS m/z 227.2 [M+Na]⁺.



(*E*)-3-mesitylallyl acetate (**1hs**): The title compound was prepared according to the general procedure A. 2-Iodo-1,3,5-trimethylbenzene (246 mg, 160 μ L, 1.0 mmol) and

then allyl acetate **S2** (200 mg, 216 μ L, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1hs** (102 mg, 47%) as a liquid. The NMR datas obtained for **1hs** are in agreement with previously reported literature values.⁴

(*E*)-3-mesitylallyl acetate (**1hs**): ¹H NMR (CDCl₃, 400MHz): δ 6.82-6.85 (m, 2H), 6.62 (d, *J* = 16.4 Hz, 1H), 5.77(dt, *J* = 6.4, 16.4 Hz, 1H), 4.73 (dd, *J* = 1.6, 6.4 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 6H), 2.09 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 170.8, 136.5, 135.9, 133.0, 132.0, 129.0, 128.6, 65.4, 21.0, 21.0, 20.8. FT-IR (CHCl₃): 2985, 1747, 1458, 1229, 1044, 867 cm⁻¹. ESI-MS *m/z* 241.3 [M+Na]⁺.

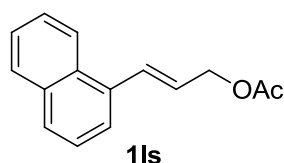


(*E*)-3-(biphenyl-4-yl)allyl acetate (**1js**): The title compound was prepared according to the general procedure A. 4-Iodobiphenyl (280 mg, 1.0 mmol) and then allyl acetate **S2** (200 mg, 216 μ L, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1js** (186 mg, 74%) as a liquid. The NMR datas obtained for **1js** are in agreement with previously reported

4. (a) Serra-Muns, A.; Guerinot, A.; Reymond, S.; Cossy, J. *Chem. Commun.*, **2010**, 46, 4178–4180;
(b) Wang, J.; Cui, Z.; Zhang, Y.; Li, H.; Wu L.; Liu, Z. *Org. Biomol. Chem.*, **2011**, 9, 663-666.

literature values.²

(*E*)-3-(biphenyl-4-yl)allyl acetate (**1js**): ¹H NMR (CDCl₃, 400MHz): δ 7.57-7.62 (m, 4H), 7.43-7.48 (m, 4H), 7.34-7.37 (m, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 6.4, 16.0 Hz, 1H), 4.76 (d, *J* = 6.4 Hz, 2H), 2.12 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 170.9, 140.8, 140.6, 135.2, 133.8, 128.8, 127.4, 127.3, 127.1, 127.0, 123.3, 65.1, 21.0. FT-IR (CHCl₃): 1744, 1478, 1385, 1243, 1026, 875 cm⁻¹. ESI-MS *m/z* 253.5 [M+H]⁺.

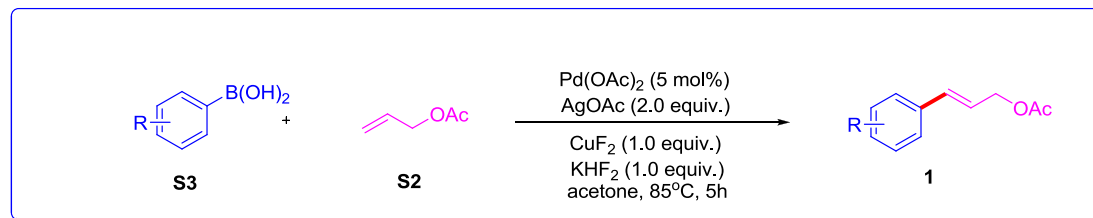


(*E*)-3-(naphthalen-1-yl)allyl acetate (**1ls**): The title compound was prepared according to the general procedure A. 1-Iodonaphthalene (254 mg, 146 μL, 1.0 mmol) and then allyl acetate **S2** (200 mg, 216 μL, 2.0 mmol) were added to a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol) and Ag₂CO₃ (166 mg, 0.6 mmol) in benzene (6 mL), and the resulting mixture was heated at reflux overnight. The reaction mixture was then concentrated by evaporation, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1ls** (149 mg, 66%) as a liquid. The NMR datas obtained for **1ls** are in agreement with previously reported literature values.⁵

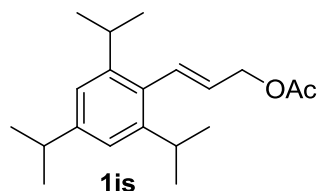
(*E*)-3-(naphthalen-1-yl)allyl acetate (**1ls**): ¹H NMR (CDCl₃, 300MHz): δ 8.11-8.13 (m, 1H), 7.81-7.89 (m, 1H), 7.63(d, *J* = 6.9 Hz, 1H), 7.42-7.62 (m, 4H), 6.75 (dt, *J* = 6.3, 15.6 Hz, 1H), 4.87 (dd, *J* = 1.2, 6.3 Hz, 2H), 2.17 (s, 3H); ¹³C NMR (CDCl₃, 300MHz): δ 170.8, 162.3, 134.0, 133.6, 131.4, 128.6, 128.4, 126.4, 126.2, 125.9, 125.6, 124.1, 123.7, 65.2, 21.0. FT-IR (CHCl₃): 1757, 1468, 1367, 1251, 1022, 890 cm⁻¹. ESI-MS *m/z* 249.2 [M+Na]⁺.

5. Rao, G.V.; Reddy, M. J. R.; Srinivas, K.; Reddy, M. J. R.; Bushan, K. M.; Rao, G. V. *Photochemistry and Photobiology* **2002**, 76, 29-34.

General procedures for the synthesis of cinnamyl acetates **1**, method B:²

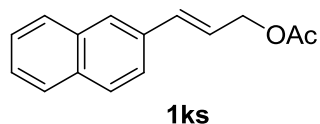


To a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol), AgOAc (334 mg, 2.0 mmol), CuF₂ (102 mg, 0.5 mmol), KHF₂ (156 mg, 2.0 mmol) and acetone (5 mL) was added arylboronic acid (1.0 mmol) and allyl acetate (200 mg, 216 μL, 2.0 mmol, 2.0 eq.) subsequently. The reaction mixture was vigorously stirred at 85°C for 5h. After cooling down to room temperature and concentrating in vacuum, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (E)-**1** as a liquid.



(E)-3-(2,4,6-triisopropylphenyl)allyl acetate (**1is**): The title compound was prepared according to the general procedure B. To a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol), AgOAc (334 mg, 2.0 mmol), CuF₂ (102 mg, 0.5 mmol), KHF₂ (156 mg, 2.0 mmol) and acetone (5 mL) was added 2,4,6-triisopropylphenylboronic acid (248 mg, 1.0 mmol) and allyl acetate (200 mg, 216 μL, 2.0 mmol, 2.0 eq.) subsequently. The reaction mixture was vigorously stirred at 85°C for 5h. After cooling down to room temperature and concentrating in vacuum, and the residue was purified carefully by

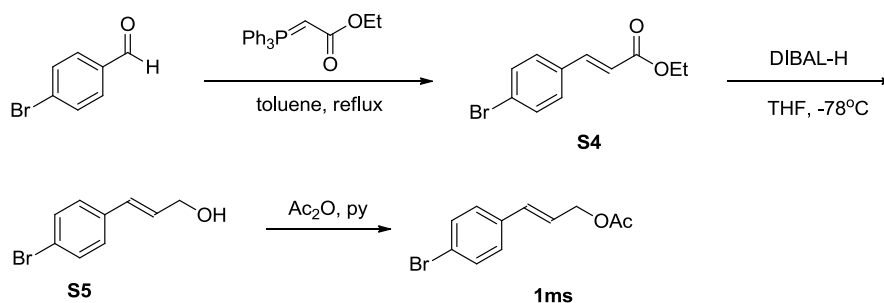
flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1is** (102 mg, 47%) as a liquid. ¹H NMR (CDCl₃, 400MHz): δ 6.99 (s, 2H), 6.72 (d, *J* = 16.4 Hz, 1H), 5.69 (dt, *J* = 6.0, 16.0 Hz, 1H), 4.75 (dd, *J* = 1.2, 6.4 Hz, 2H), 3.12-3.19 (m, 2H), 2.85-2.90 (m, 1H), 2.11 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 1.19 (s, 6H), 1.17 (s, 6H); ¹³C NMR (CDCl₃, 400MHz): δ 170.8, 147.8, 146.3, 132.1, 128.5, 121.1, 120.5, 65.1, 34.3, 30.0, 24.0, 23.8, 21.0. FT-IR (CHCl₃): 2995, 1756, 1437, 1348, 1208, 1031, 950 cm⁻¹. ESI-MS *m/z* 325.4 [M+Na]⁺.



(*E*)-3-(naphthalen-2-yl)allyl acetate (**1ks**): The title compound was prepared according to the general procedure B. To a mixture of Pd(OAc)₂ (11.2 mg, 0.05 mmol), AgOAc (334 mg, 2.0 mmol), CuF₂ (102 mg, 0.5 mmol), KHF₂ (156 mg, 2.0 mmol) and acetone (5 mL) was added 2-naphthylboronic acid (172 mg, 1.0 mmol) and allyl acetate (200 mg, 216 μL, 2.0 mmol, 2.0 eq.) subsequently. The reaction mixture was vigorously stirred at 85°C for 5h. After cooling down to room temperature and concentrating in vacuum, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1ks** (188 mg, 83%) as a liquid. The NMR datas obtained for **1ks** are in agreement with previously reported literature values.²

(*E*)-3-(naphthalen-2-yl)allyl acetate (**1ks**): ¹H NMR (CDCl₃, 400MHz): δ 8.05-8.07 (m, 1H), 7.79-7.82 (m, 1H), 7.74-7.76 (m, 1H), 7.55-7.57 (m, 1H), 7.35-7.50 (m, 4H), 6.27 (dt, *J* = 6.4, 15.6 Hz, 1H), 4.00 (dd, *J* = 1.2, 6.4 Hz, 2H), 2.10 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 170.9, 134.0, 133.6, 131.4, 131.2, 128.6, 128.5, 126.5, 126.3, 125.9, 125.6, 124.2, 123.7, 65.2, 21.1. FT-IR (CHCl₃): 1752, 1485, 1335, 1234, 1045 cm⁻¹. ESI-MS *m/z* 249.2 [M+Na]⁺.

Procedure for the synthesis of (*E*)-3-(4-bromophenyl)allyl acetate **1ms**,
method C:⁶



S4: The mixture of 4-bromobenzaldehyde (370 mg, 2.0 mmol) and $\text{EtO}_2\text{CCH}=\text{PPh}_3$ (835 mg, 2.4 mmol) in toluene (4 mL) was refluxed overnight. After reaction was complete, the reaction mixture was loaded to column chromatography to give the product **S4** as yellow oil (450 mg, 88%).

S5: To the ethyl ester **S4** (450 mg, 1.76 mmol) in anhydrous CH_2Cl_2 (15 mL) was added dropwise DIBAL-H (5.28 mL, 5.28 mmol) at -78°C . After reaction was over 2h, MeOH (5 mL) was added dropwise and EtOAc (20 mL) and sodium potassium tartrate (20% $\text{-H}_2\text{O}$, 15 mL) were added at -78°C . The mixture was stirred at rt for 1 h, extracted with EtOAc. The organic layers were washed with brine and dried over Na_2SO_4 . Filtration and evaporation of the solvent under reduced pressure gave a crude product, which was purified by flash column chromatography on silica gel (n-hexane/EtOAc = 6/1) to afford alcohol **S5** as pale yellow oil (326 mg, 87%).

4-Bromocinnamyl acetate **1ms**: Alcohol **S5** (326 mg, 1.53 mmol) and DMAP (9.3 mg, 0.0765 mmol) were dissolved in 10 mL pyridine at 0°C . Acetic anhydride (0.7 mL, 8 mmol) was added slowly at 0°C . The solution was stirred at room temperature for 24 h and quenched with NaHCO_3 solution (aq, 40 mL). It was then diluted with water (20 mL), extracted with CH_2Cl_2 (3×50 mL), dried (MgSO_4), evaporated and co-evaporated with toluene (2×10 mL) to remove pyridine, and the residue was

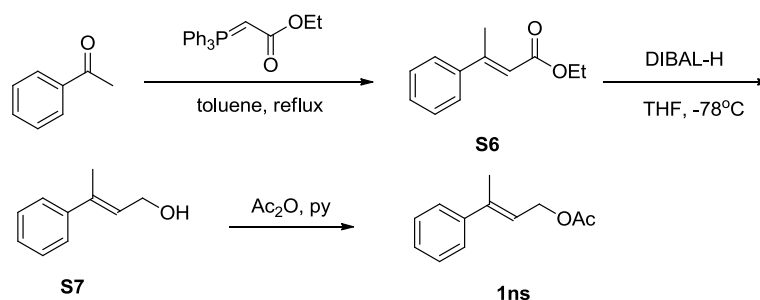
purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1ms** (188 mg, 83%) as a liquid. The NMR datas

6. Mattias Engman, Jarle S. Diesen, Alexander Paptchikhine and Pher G. Andersson. *J. Am. Chem. Soc.* **2007**, *129*, 4536 – 4537.

obtained for **1ks** are in agreement with previously reported literature values.⁷

4-Bromocinnamyl acetate **1ms**: ¹H NMR (CDCl₃, 400MHz): δ 7.42-7.45 (m, 2H), 7.23-7.26 (m, 2H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.27 (dt, *J* = 6.4, 15.6 Hz, 1H), 4.71 (dd, *J* = 1.2, 6.4 Hz, 2H), 2.10 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 171.8, 135.2, 132.8, 131.7, 128.1, 124.1, 121.9, 64.8, 21.0. FT-IR (CHCl₃): 1732, 1453, 1308, 1254, 1025, 675 cm⁻¹. ESI-MS *m/z* 277.6, 278.4 [M+Na]⁺.

Procedure for the synthesis of (*E*)-3-phenylbut-2-enyl acetate **1ns**, method C:⁶



S6: The mixture of acetophenone (240 mg, 2.0 mmol) and EtO₂CCH=PPh₃ (835 mg, 2.4 mmol) in toluene (4 mL) was refluxed overnight. After reaction was complete, the reaction mixture was loaded to column chromatography to give the product **S6** as a liquid (281 mg, 74%).

S7: To the ethyl ester **S6** (281 mg, 1.48 mmol) in anhydrous CH₂Cl₂ (15 mL) was added dropwise DIBAL-H (4.44 mL, 4.44 mmol) at -78°C. After reaction was over 2h, MeOH (4 mL) was added dropwise and EtOAc (15 mL) and sodium potassium tartrate (20%-H₂O, 10 mL) were added at -78°C. The mixture was stirred at rt for 1 h, extracted with EtOAc. The organic layers were washed with brine and dried over Na₂SO₄. Filtration and evaporation of the solvent under reduced pressure gave a crude product, which was purified by flash column chromatography on silica gel (n-hexane/EtOAc = 6/1) to afford alcohol **S7** as colorless oil (183 mg, 84%).

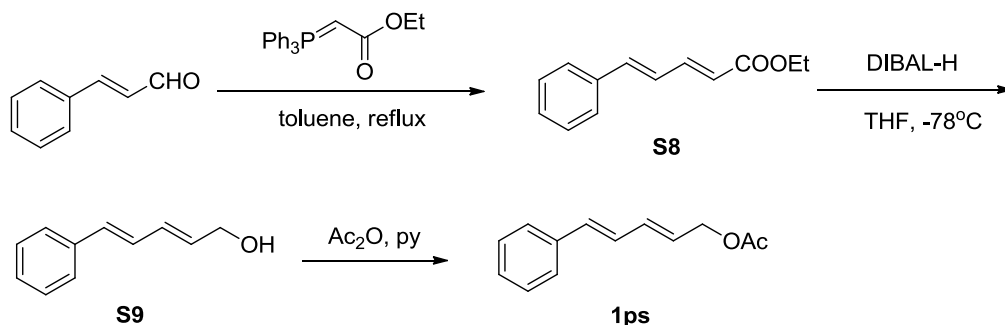
(*E*)-3-phenylbut-2-enyl acetate **1ns**: Alcohol **S7** (183 mg, 1.24 mmol) and DMAP (7.6 mg, 0.062 mmol) were dissolved in 8 mL pyridine at 0°C. Acetic anhydride (0.5 mL, 5.7 mmol) was added slowly at 0°C. The solution was stirred at room temperature for

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7. (a) Procopiou, P. A.; Baugh, S. P. D.; Flack, S.; Inglis, G. A. *J. Org. Chem.* **1998**, *63*, 2342-2347.
(b) Ouellette, R. J.; Shaw, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 1651.

24 h and quenched with NaHCO₃ solution (aq, 20 mL). It was then diluted with water (15 mL), extracted with CH₂Cl₂ (3×50 mL), dried (MgSO₄), evaporated and co-evaporated with toluene (2×10 mL) to remove pyridine, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1ns** (158 mg, 67%) as a liquid. The NMR datas obtained for **1ns** are in agreement with previously reported literature values.⁸

¹H NMR (CDCl₃, 300MHz): δ 7.27-7.45 (m, 5H), 5.93 (td, *J* = 1.2, 6.9 Hz, 1H), 4.82 (d, *J* = 6.9 Hz, 2H), 2.14 (s, 3H), 2.12 (s, 3H); ¹³C NMR (CDCl₃, 300MHz): δ 171.0, 142.6, 140.2, 128.3, 127.5, 125.9, 121.4, 61.7, 21.0, 16.2. FT-IR (CHCl₃): 2986, 1750, 1445, 1325, 1246, 978 cm⁻¹. ESI-MS *m/z* 213.3 [M+Na]⁺.

Procedure for the synthesis of (*E*)-3-phenylbut-2-enyl acetate **1ps**, method C:⁶



S8: The mixture of cinnamaldehyde (264 mg, 2.0 mmol) and EtO₂CCH=PPh₃ (835 mg, 2.4 mmol) in toluene (4 mL) was refluxed overnight. After reaction was complete, the reaction mixture was loaded to column chromatography to give the product **S8** as a liquid (355 mg, 88%).

S7: To the ethyl ester **S8** (355 mg, 1.76 mmol) in anhydrous CH₂Cl₂ (15 mL) was added dropwise DIBAL-H (5.28 mL, 5.28 mmol) at -78°C. After reaction was over 2h, MeOH (4 mL) was added dropwise and EtOAc (15 mL) and sodium potassium

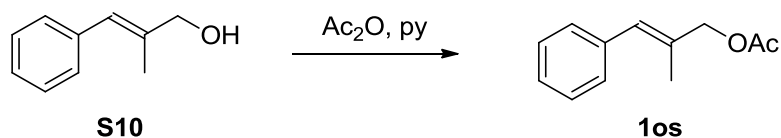
tartrate (20%-H₂O, 10 mL) were added at -78°C. The mixture was stirred at rt for 1 h, extracted with EtOAc. The organic layers were washed with brine and dried over Na₂SO₄. Filtration and evaporation of the solvent under reduced pressure gave a crude product, which was purified by flash column chromatography on silica gel (n-hexane/

8. Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, *9*, 2653-2656.

EtOAc = 6/1) to afford alcohol **S9** as colorless oil (222 mg, 79%).
(*E*)-3-phenylbut-2-enyl acetate **1ps**: Alcohol **S9** (222 mg, 1.4 mmol) and DMAP (7.6 mg, 0.062 mmol) were dissolved in 8 mL pyridine at 0°C. Acetic anhydride (0.5 mL, 5.7 mmol) was added slowly at 0°C. The solution was stirred at room temperature for 24 h and quenched with NaHCO₃ solution (aq, 20 mL). It was then diluted with water (15 mL), extracted with CH₂Cl₂ (3×50 mL), dried (MgSO₄), evaporated and co-evaporated with toluene (2×10 mL) to remove pyridine, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1ps** (200 mg, 1.0 mmol, 72%) as a liquid. The NMR datas obtained for **1ps** are in agreement with previously reported literature values.¹

¹H NMR (CDCl₃, 300MHz): δ 7.20-7.39 (m, 5H), 6.75 (dd, *J* = 7.8, 11.7 Hz, 1H), 6.57 (d, *J* = 11.7 Hz, 1H), 5.93 (q, *J* = 7.8 Hz, 1H), 5.86 (dt, *J* = 4.8, 9.9 Hz, 1H), 4.63 (d, *J* = 4.8 Hz, 2H), 2.06 (s, 3H); ¹³C NMR (CDCl₃, 300MHz): δ 171.8, 137.0, 134.6, 133.8, 128.7, 127.9, 127.7, 126.9, 126.5, 64.7, 21.0. FT-IR (CHCl₃): 1755, 1468, 1320, 1241, 1021, 750 cm⁻¹. ESI-MS *m/z* 225.1 [M+Na]⁺.

Procedure for the synthesis of (*E*)-2-methyl-3-phenylallyl acetate **1os**:

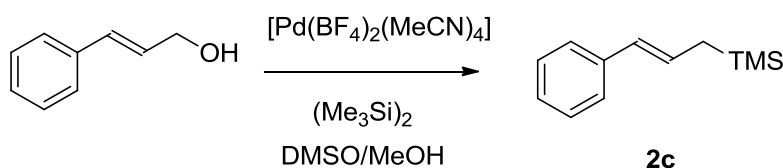


(*E*)-2-methyl-3-phenylallyl acetate **1os**: Trans-2-Methyl-3-phenyl-2-propen-1-ol **S10** (296 mg, 2.0 mmol) and DMAP (12 mg, 0.1 mmol) were dissolved in 10 mL pyridine

at 0°C. Acetic anhydride (0.7 mL, 8 mmol) was added slowly at 0°C. The solution was stirred at room temperature for 24 h and quenched with NaHCO₃ solution (aq, 40 mL). It was then diluted with water (20 mL), extracted with CH₂Cl₂ (3×50 mL), dried (MgSO₄), evaporated and co-evaporated with toluene (2×10 mL) to remove pyridine, and the residue was purified carefully by flash chromatography on silica gel (eluent: petroleum ether/diethyl ether 10:1) to afford (*E*)-**1os** (213 mg, 56%) as a liquid. The NMR datas obtained for **1ks** are in agreement with previously reported literature values.⁸

¹H NMR (CDCl₃, 400MHz): δ 7.20-7.35 (m, 5H), 6.53 (s, 1H), 4.63 (s, 2H), 2.11(s, 3H), 1.89 (s, 3H); ¹³C NMR (CDCl₃, 400MHz): δ 170.9, 137.1, 132.8, 127.4, 128.3, 125.1, 126.8, 70.2, 21.0, 15.6. FT-IR (CHCl₃): 2974, 1752, 1473, 1225, 1034, 957 cm⁻¹. ESI-MS m/z 213.4 [M+Na]⁺.

Procedures for the synthesis of (*E*)-3-Trimethylsilyl-1-phenyl-1-propene **2c**:⁹

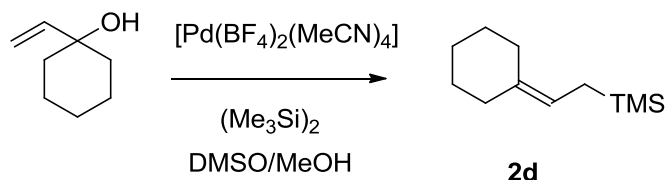


(*E*)-3-Trimethylsilyl-1-phenyl-1-propene **2c**: The cinnamyl alcohol (212 mg, 1.58 mmol) was dissolved in a mixture of methanol and DMSO (2.1 mL/2.1 mL), followed by the addition of hexamethyldisilane (278 mg, 390 μL, 1.9 mmol) and palladium catalyst [Pd(BF₄)₂(MeCN)₄] (35 mg, 0.08 mmol, 5 mol%). Then, this reaction mixture was stirred at 50°C for 15h. The crude reaction mixture was extracted with 3 x 20 mL pentane, followed by drying and evaporation of the organic phase, and the residue was purified carefully using pentane as eluent for silica gel chromatography to afford (*E*)-**2c** (213 mg, 56%) as a liquid. The ¹H NMR data obtained for **2c** is in agreement with previously reported literature values.⁹

(*E*)-3-Trimethylsilyl-1-phenyl-1-propene **2c**: ^1H NMR (CDCl_3 , 300MHz): δ 7.21-7.55 (m, 5H), 6.33-6.35 (m, 2H), 1.75 (d, $J = 5.7$ Hz, 2H), 0.04 (s, 9H). ESI-MS m/z 213.2 $[\text{M}+\text{H}]^+$.

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9. (a) Selander, N.; Paasch, J. R.; Szabo, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409–411;
(b) Moser, R.; Nishikata, T.; Lipshutz, B. H. *Org. Lett.* **2010**, *12*, 28-31.

Procedure for the synthesis of [2-(Trimethylsilyl)ethylidene]cyclohexane **2d**:⁹

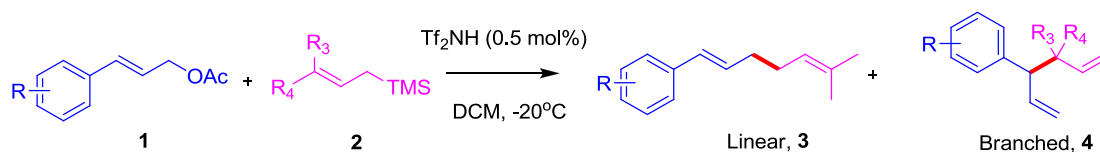


[2-(Trimethylsilyl)ethylidene]cyclohexane **2d**: The 1-vinyl cyclohexanol (200 mg, 1.58 mmol) was dissolved in a mixture of methanol and DMSO (2.1 mL/2.1 mL), followed by the addition of hexamethyldisilane (278 mg, 390 μL , 1.9 mmol) and palladium catalyst $[\text{Pd}(\text{BF}_4)_2(\text{MeCN})_4]$ (35 mg, 0.08 mmol, 5 mol%). Then, this reaction mixture was stirred at 65°C for 15h. The crude reaction mixture was extracted with 3 x 20 mL pentane, followed by drying and evaporation of the organic phase, and the residue was purified carefully using pentane as eluent for silica gel chromatography to afford (*E*)-**2d** (120 mg, 43%) as a liquid. The NMR datas obtained for **1ks** are in agreement with previously reported literature values.^{9, 10}

[2-(Trimethylsilyl)ethylidene]cyclohexane **2d**: ^1H NMR (CDCl_3 , 300MHz): δ 5.12 (t, $J = 8.7$ Hz, 1H), 2.09-2.12 (m, 4H), 1.52-1.55 (m, 6H), 1.42 (d, $J = 8.4$ Hz, 2H), 0.02 (s, 9H); ^{13}C NMR (CDCl_3 , 400MHz): δ 136.9, 116.7, 37.3, 28.8, 28.4, 27.6, 27.1, 17.7, -1.8.

10. Hsiao, C.-N.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2688.

General procedures for the Triflimide-catalyzed Allyl-Allyl Cross-coupling:



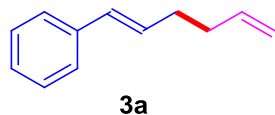
Making a triflimide solution (0.1 M in DCM):^{11d}

Step 1: Bring the flame-dried, argon-flushed schlenk flask with rubber septum, HNTf₂ and spatula into dry box.

Step 2: Weigh out desired mass of triflimide (e.g., 562 mg, 2 mmol) into schlenk flask, cap with rubber septa and remove from dry box.

Step 3: Add desired amount of dichloromethane (20 ml) to make a 0.1 M solution.

General Procedure: To a solution of allylic acetate **1** (0.2 mmol) in DCM (3 ml) was added allylic silane **2** (3 equiv) under N_2 atmosphere. The solution was cooled down to -20°C , then 0.5 mol% Tf_2NH (, mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20°C under N_2 atmosphere. After reaction the mixture was quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product.

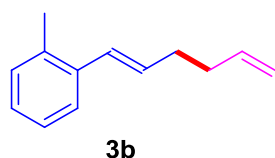


(*E*)-Hexa-1,5-dien-1-ylbenzene (**3a**): To a solution of (*E*)-cinnamyl acetate (**1a**) (88 mg, 0.5 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (171mg, 238 μ L,

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11. (a) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, 103, 1969–1975;
(b) Antonsson, T.; Moberg, C.; Tottie, L.; Heumann, A. *J. Org. Chem.* **1989**, 54,4914–4929;
(c) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* **1977**, 99, 4417–4424;
(d) Boxer, M. B.; Yamamoto, Y. *Nature Proto.* **2006**, 1, 2434.

1.5 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled down to $-20\text{ }^\circ\text{C}$, then 0.5 mol% Tf_2NH (25 μ L, 0.0025 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at $-20\text{ }^\circ\text{C}$ under N_2 atmosphere. After reaction the mixture was quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3a** (70 mg, 89%) as a liquid. The NMR datas obtained for **3a** are in agreement with previously reported literature values.¹²

(*E*)-Hexa-1,5-dien-1-ylbenzene (**3a**): ^1H NMR (CDCl_3 , 400MHz): δ 7.30-7.48 (m, 5H), 6.53 (d, $J = 16.0$ Hz, 1H), 6.35 (dt, $J = 6.4, 15.6$ Hz, 1H), 5.94-6.04 (m, 1H), 5.16 (dt, $J = 1.6$ Hz, 13.4 Hz, 1H), 5.12 (dd, $J = 1.6$ Hz, 13.4 Hz, 1H), 2.35-2.45 (m, 4H); ^{13}C NMR (CDCl_3 , 400MHz): δ 138.1, 137.8, 130.2, 130.1, 128.5, 126.9, 126.0, 114.9, 33.6, 32.5; FT-IR (CHCl_3): 1635, 1610, 995, 910 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{Na}$ 181.0993, found 181.0997.



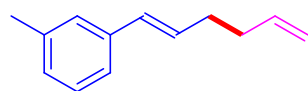
(*E*)-1-(Hexa-1,5-dienyl)-2-methylbenzene (**3b**): To a solution of (*E*)-3-*o*-tolylallyl acetate (**1bs**) (95 mg, 0.5 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (171mg, 238 μ L, 1.5 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled

down to -20 °C, then 0.5 mol% Tf₂NH (25 μL, 0.0025 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to

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12. (a) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969–1975;
(b) Antonsson, T.; Moberg, C.; Tottie, L.; Heumann, A. *J. Org. Chem.* **1989**, *54*, 4914–4929;
(c) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* 1977, *99*, 4417–4424;
(d) Hatakeyama, T.; Nakagawa, N.; Nakamura, M. *Org. Lett.* **2009**, *11*, 4496–4499;
(e) Sumida, Y.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 1629–1632.

column chromatography (silica gel, pentane-diethyl ether=20:1) to obtain the isomers of product **3b** (75 mg, 88%) as a liquid. The NMR datas obtained for **1ks** are in agreement with previously reported literature values.^{12d}

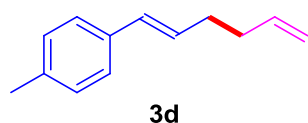
(*E*)-1-(Hexa-1,5-dienyl)-2-methylbenzene (**3b**): ¹H NMR (CDCl₃, 400MHz): δ 7.40 (d, *J* = 6.4 Hz, 1H), 7.12- 7.19 (m, 3H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.10 (dt, *J* = 6.4, 15.6 Hz, 1H), 5.83-5.93 (m, 1H), 5.08 (dd, *J* = 1.6 Hz, 13.4 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 2.32-2.37 (m, 5H), 2.23-2.28 (m, 2H); ¹³C NMR (CDCl₃, 400MHz): δ 138.1, 136.9, 135.0, 131.5, 130.1, 128.1, 126.8, 126.0, 125.5, 114.9, 33.7, 32.7, 19.8; FT-IR (CHCl₃): 3010, 1613, 1553, 1462, 995, 905 cm⁻¹; HRMS (ESI) *m/z* [M+Na]⁺ calcd for C₁₃H₁₆Na 195.1150, found 195.1143.



3c

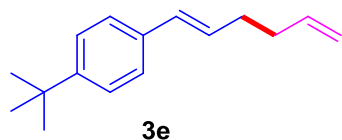
(*E*)-1-(hexa-1,5-dienyl)-3-methylbenzene (**3c**): To a solution of (*E*)-3-*m*-tolylallyl acetate (**1cs**) (95 mg, 0.5 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (171mg, 238 μL, 1.5 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (25 μL, 0.0025 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to

column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3c** (60 mg, 80%) as a liquid. ^1H NMR (CDCl_3 , 400MHz): δ 7.15-7.19 (m, 3H), 7.01 (d, $J = 7.2$ Hz, 1H), 6.37 (d, $J = 15.6$ Hz, 1H), 6.21 (d, $J = 2.4$, 15.6 Hz, 1H), 5.82-5.92 (m, 1H), 4.98-5.09 (m, 2H), 2.34 (s, 3H), 2.26-2.32 (m, 2H), 2.22-2.25 (m, 2H); ^{13}C NMR (CDCl_3 , 400MHz): δ 138.2, 138.0, 137.7, 130.3, 129.9, 128.4, 127.7, 126.7, 123.1, 114.9, 33.6, 32.5, 21.4; FT-IR (CHCl_3): 2997, 1642, 1504, 1460, 993, 917 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}$ 173.1330, found 173.1333.



(*E*)-1-(hexa-1,5-dienyl)-4-methylbenzene (**3d**): To a solution of (*E*)-3-*p*-tolylallyl acetate (**1ds**) (95 mg, 0.5 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (171mg, 238 μL , 1.5 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled down to -20 $^\circ\text{C}$, then 0.5 mol% Tf_2NH (25 μL , 0.0025 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 $^\circ\text{C}$ under N_2 atmosphere. After reaction the mixture was quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3d** (63 mg, 84%) as a liquid. The NMR datas obtained for **3d** are in agreement with previously reported literature values.^{12d,13}

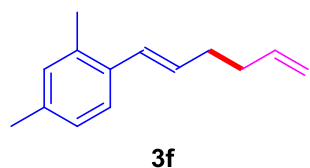
(*E*)-1-(hexa-1,5-dienyl)-4-methylbenzene (**3d**): ^1H NMR (CDCl_3 , 400MHz): δ 7.24 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.37 (d, $J = 16.0$ Hz, 1H), 6.17 (dt, $J = 6.4$, 15.6 Hz, 1H), 5.81-5.91 (m, 1H), 5.06 (dq, $J = 1.6$, 17.2 Hz, 1H), 4.98 (dq, $J = 0.8$, 17.2 Hz, 1H), 2.32 (s, 3H), 2.21-2.31 (m, 4H); ^{13}C NMR (CDCl_3 , 400MHz): δ 138.2, 136.6, 135.0, 130.0, 129.2, 129.1, 125.9, 114.9, 33.6, 32.4, 21.1; FT-IR (CHCl_3): 2990, 1645, 1468, 990, 910 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{16}\text{Na}$ 195.1150, found 195.1140.



(E)-1-tert-butyl-4-(hexa-1,5-dienyl)benzene (**3e**): To a solution of (*E*)-3-(4-tert-butylphenyl)allyl acetate (**1es**) (116 mg, 0.5 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (171mg, 238 μ L, 1.5 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (25 μ L, 0.0025 mmol,

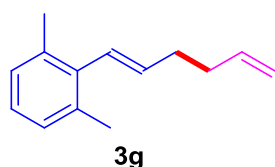
13. Nakamura, H.; Bao, M.; Yamamoto, Y. *Angewandte Chemie, International Edition*, **2001**, *40*, 3208-3210.

0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 48 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 \times 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3e** (54 mg, 57%) as a liquid. ¹H NMR (CDCl₃, 300MHz): δ 7.17-7.36 (m, 4H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 6.3, 15.9 Hz, 1H), 5.82-5.96 (m, 1H), 4.99-5.11 (m, 2H), 2.19-2.37 (m, 4H), 1.34 (s, 9H); ¹³C NMR (CDCl₃, 300MHz): δ 162.3, 150.0, 138.2, 129.9, 129.3, 125.7, 125.4, 114.8, 34.5, 33.6, 32.4, 31.4; FT-IR (CHCl₃): 3023, 291, 1647, 1526, 1483, 998, 896 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₆H₂₃ 215.1800, found 215.1809



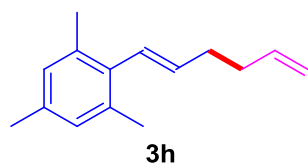
(*E*)-1-(hexa-1,5-dienyl)-2,4-dimethylbenzene (**3f**): To a solution of (*E*)-3-(2,4-dimethylphenyl)allyl acetate (**1fs**) (102 mg, 0.5 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (171mg, 238 μ L, 1.5 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (25 μ L, 0.0025 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred

for 48 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3f** (52 mg, 64%) as a liquid. ¹H NMR (CDCl₃, 400MHz): δ 7.30 (d, *J* = 6.4 Hz, 1H), 6.95-6.98 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.05 (dt, *J* = 6.8, 15.6 Hz, 1H), 5.84-5.92 (m, 1H), 4.98-5.09 (m, 2H), 2.31-2.35 (m, 2H), 2.29 (s, 6H), 2.23-2.26 (m, 2H); ¹³C NMR (CDCl₃, 400MHz): δ 138.2, 136.5, 131.0, 130.5, 127.9, 126.7, 125.4, 114.8, 33.7, 32.7, 30.3, 29.7, 21.0, 19.7; FT-IR (CHCl₃): 3015, 2907, 1624, 1463, 998, 913 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₄H₁₉ 187.1487, found 187.1491.

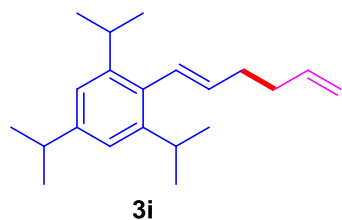


(*E*)-2-(hexa-1,5-dienyl)-1,3-dimethylbenzene (**3g**): To a solution of (*E*)-3-(2,6-dimethylphenyl)allyl acetate (**1gs**) (102 mg, 0.5 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (171mg, 238 μL, 1.5 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (25 μL, 0.0025 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 48 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3g** (63 mg, 77%) as a liquid. ¹H NMR (CDCl₃, 400MHz): δ 7.03 (s, 3H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.86-5.96 (m, 1H), 5.67 (dt, *J* = 6.8, 12.0 Hz, 1H), 5.08 (dq, *J* = 1.6, 17.2 Hz, 1H), 5.01 (dq, *J* = 1.2, 10.4 Hz, 1H), 2.33-2.37 (m, 2H), 2.29 (s, 6H), 2.25-2.27 (m, 2H); ¹³C NMR (CDCl₃, 400MHz): δ 138.2, 137.6, 135.9, 134.9, 127.8, 127.6, 126.2, 114.9, 33.8, 32.8, 21.0; FT-IR

(CHCl₃): 3004, 2913, 1606, 1455, 998, 904 cm⁻¹; HRMS (ESI) m/z [M+H]⁺ calcd for C₁₄H₁₉ 187.1487, found 187.1474.

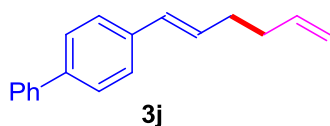


(*E*)-2-(hexa-1,5-dienyl)-1,3,5-trimethylbenzene (**3h**): To a solution of (*E*)-3-mesitylallyl acetate (**1hs**) (54 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μL, 0.75 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (12.5 μL, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 48 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3h** (27 mg, 60%) as a liquid. ¹H NMR (CDCl₃, 400MHz): δ 6.85 (s, 2H), 6.30 (d, *J* = 16.4 Hz, 1H), 5.83-5.93 (m, 1H), 5.64 (dt, *J* = 6.8, 16.4 Hz, 1H), 4.98-5.09 (m, 2H), 2.29-2.35 (m, 2H), 2.22-2.27 (m, 11H); ¹³C NMR (CDCl₃, 400MHz): δ 138.2, 135.8, 135.6, 134.6, 128.4, 127.7, 114.9, 33.8, 32.8, 20.9; FT-IR (CHCl₃): 3021, 1603, 1466, 1002, 907 cm⁻¹; HRMS (ESI) m/z [M+H]⁺ calcd for C₁₅H₂₁ 201.1643, found 201.1643.



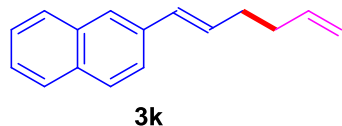
(*E*)-2-(hexa-1,5-dienyl)-1,3,5-triisopropylbenzene (**3i**): To a solution of (*E*)-3-(2,4,6-tri-isopropylphenyl)allyl acetate (**1is**) (75 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μL, 0.75 mmol, 3 equiv) under N₂

atmosphere. The solution was cooled down to $-20\text{ }^{\circ}\text{C}$, then 0.5 mol% Tf_2NH (12.5 μL , 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 48 hours at $-20\text{ }^{\circ}\text{C}$ under N_2 atmosphere. After reaction the mixture was quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3i** (58 mg, 82%) as a liquid. ^1H NMR (CDCl_3 , 400MHz): δ 6.97 (s, 2H), 6.39 (d, $J = 16.0$ Hz, 1H), 5.82-5.92 (m, 1H), 5.54 (dt, $J = 6.4, 16.0$ Hz, 1H), 5.06 (dq, $J = 1.2, 16.8$ Hz, 1H), 4.98-5.01 (m, 1H), 3.20-3.27 (m, 2H), 2.84-2.91 (m, 1H), 2.32-2.37 (m, 2H), 2.24-2.27 (m, 2H), 1.26 (s, 3H), 1.24 (s, 3H), 1.18 (s, 6H), 1.16 (s, 6H); ^{13}C NMR (CDCl_3 , 400MHz): δ 147.1, 146.5, 138.3, 134.5, 133.6, 127.3, 120.3, 114.9, 34.2, 33.8, 32.6, 29.9, 24.1, 23.8; FT-IR (CHCl_3): 3004, 1627, 1528, 1463, 990, 900 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{32}\text{Na}$ 307.2402, found 307.2412.

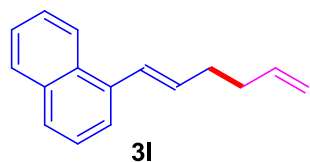


(*E*)-4-(hexa-1,5-dienyl)biphenyl (**3j**): To a solution of (*E*)-3-(biphenyl-4-yl) allyl acetate (**1js**) (63 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μL , 0.75 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled down to $-20\text{ }^{\circ}\text{C}$, then 0.5 mol% Tf_2NH (12.5 μL , 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at $-20\text{ }^{\circ}\text{C}$ under N_2 atmosphere. After reaction the mixture was quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3j** (44 mg, 75%) as a liquid. ^1H NMR (CDCl_3 , 400MHz): δ 7.59 (dd, $J = 1.2, 8.4$ Hz, 2H), 7.54 (dd, $J = 1.6, 6.4$ Hz, 2H), 7.31-7.45 (m, 5H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.28 (dt, $J = 6.4, 16.0$ Hz, 1H), 5.83-5.93 (m, 1H), 5.02-5.10 (m, 2H),

2.32-2.36 (m, 2H), 2.25-2.28 (m, 2H); ^{13}C NMR (CDCl_3 , 400MHz): δ 140.9, 138.1, 136.8, 130.3, 129.8, 128.8, 127.2, 127.0, 126.9, 126.4, 115.0, 77.2, 33.6, 32.5; FT-IR (CHCl_3): 2927, 1613, 1546, 1483, 987, 895 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{18}\text{Na}$ 257.1306, found 257.1306.



(E)-2-(hexa-1,5-dienyl)naphthalene (**3k**): To a solution of (E)-3-(naphthalen-2-yl)allyl acetate (**1ks**) (57 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μL , 0.75 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled down to $-20\text{ }^\circ\text{C}$, then 0.5 mol% Tf_2NH (12.5 μL , 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at $-20\text{ }^\circ\text{C}$ under N_2 atmosphere. After reaction the mixture was quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 ($3 \times 5\text{ mL}$). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3k** (35 mg, 68%) as a liquid. ^1H NMR (CDCl_3 , 400MHz): δ 8.12 (d, $J = 7.6\text{ Hz}$, 1H), 7.83-7.87 (m, 1H), 7.72-7.76 (m, 1H), 7.39-7.56 (m, 4H), 7.14 (d, $J = 15.6\text{ Hz}$, 1H), 6.24 (dt, $J = 6.8, 15.6\text{ Hz}$, 1H), 5.87-5.96 (m, 1H), 5.00-5.13 (m, 2H), 2.42-2.47 (m, 2H), 2.30-2.35 (m, 2H); ^{13}C NMR (CDCl_3 , 400MHz): δ 138.1, 133.4, 128.9, 128.4, 127.4, 127.3, 125.8, 125.7, 125.6, 125.4, 124.0, 123.6, 116.2, 115.0, 33.6, 32.8; FT-IR (CHCl_3): 2988, 1625, 1534, 1476, 995, 902 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{Na}$ 231.1150, found 231.1167.

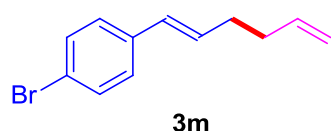


(E)-1-(5-methylhexa-1,5-dienyl)naphthalene (**3l**): To a solution of (E)-3-(naphthalen-1-yl)allyl acetate (**1ls**) (57 mg, 0.25 mmol) in DCM (5 ml) was added

allyltrimethylsilane **2a** (85 mg, 119 μ L, 0.75 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (12.5 μ L, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 \times 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3l** (40 mg, 76%) as a liquid. The NMR datas obtained for **3l** are in agreement with previously reported literature values.¹⁴

14. Azemi, T.; Kitamura, M.; Narasaka, K. *Tetrahedron*, **2004**, *60*, 1339-1344.

(*E*)-1-(5-methylhexa-1,5-dienyl)naphthalene (**3l**): ¹H NMR (CDCl₃, 400MHz): δ 8.12 (d, *J* = 6.8 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.40-7.56 (m, 3H), 7.14 (d, *J* = 15.2 Hz, 1H), 6.24 (dt, *J* = 2.8, 15.6 Hz, 1H), 5.87-5.97 (m, 1H), 5.00-5.14 (m, 3H), 2.42-2.47 (m, 2H), 2.29-2.35 (m, 2H); ¹³C NMR (CDCl₃, 400MHz): δ 141.1, 138.1, 135.6, 133.6, 133.4, 128.5, 127.5, 127.3, 125.8, 125.7, 125.6, 124.0, 123.6, 115.0, 33.6, 32.8; FT-IR (CHCl₃): 3014, 2913, 1606, 1510, 1457, 993, 906 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₆H₁₆Na 231.1150, found 231.1155.

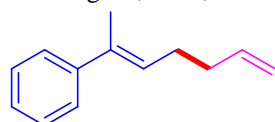


(*E*)-1-bromo-4-(hexa-1,5-dienyl)benzene (**3m**): To a solution of 4-Bromocinnamyl acetate **1ms** (70 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μ L, 0.75 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (12.5 μ L, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 48 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 \times 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to

column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3m** (29 mg, 54%) as a liquid. The NMR datas obtained for **3m** are in agreement with previously reported literature values.¹⁵

(E)-1-bromo-4-(hexa-1,5-dienyl)benzene (**3m**): ¹H NMR (CDCl₃, 300MHz): δ 7.40-7.46 (m, 2H), 7.21-7.28 (m, 2H), 6.37 (d, *J* = 16.2 Hz, 1H), 6.19-6.28 (m, 1H), 5.81-5.98 (m, 1H), 4.99-5.12 (m, 2H), 2.22-2.37 (m, 4H); ¹³C NMR (CDCl₃, 300MHz): δ 137.9, 136.7, 131.6, 131.0, 139.1, 127.5, 120.5, 115.1, 33.4, 32.4; FT-IR (CHCl₃): 2998, 1615, 1578, 1453, 998, 912, 576 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₂H₁₄Br 237.0279, found 237.0275.

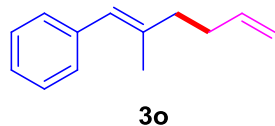
15. Flegeau, E. F.; Schneider, U.; Kobayashi, S. *Chem. Eur. J.* **2009**, *15*, 12247-12254.



3n

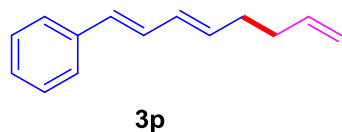
(E)-hepta-2,6-dien-2-ylbenzene (**3n**): To a solution of (*E*)-3-phenylbut-2-enyl acetate **1ns** (48 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μL, 0.75 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (12.5 μL, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 48 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3n** (18 mg, 43%) as a liquid. The NMR datas obtained for **3n** are in agreement with previously reported literature values.¹⁴

¹H NMR (CDCl₃, 300MHz): δ 7.21-7.42 (m, 5H), 5.86-5.97 (m, 1H), 5.80-5.84 (m, 1H), 5.09 (dq, *J* = 1.5, 18.5 Hz, 1H), 5.00-5.04 (m, 1H), 2.23-2.35 (m, 4H), 2.07 (s, 3H); ¹³C NMR (CDCl₃, 300MHz): δ 143.9, 138.4, 135.1, 128.1, 127.7, 126.5, 125.6, 114.8, 33.7, 28.2, 15.9; HRMS (ESI) *m/z* [M+Na]⁺ calcd for C₁₃H₁₆Na 195.1150, found 195.1159.



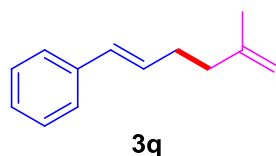
(E)-(2-methylhexa-1,5-dien-1-yl)benzene (**3o**): To a solution of (*E*)-2-methyl-3-phenylallyl acetate **1os** (48 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μ L, 0.75 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled down to -20 $^{\circ}C$, then 0.5 mol% Tf_2NH (12.5 μ L, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 $^{\circ}C$ under N_2 atmosphere. After reaction the mixture was quenched with saturated $NaHCO_3$ (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3o** (37 mg, 87%) as a liquid. The NMR datas obtained for **3o** are in agreement with previously reported literature values.^{15a}

(E)-(2-methylhexa-1,5-dien-1-yl)benzene (**3o**): 1H NMR ($CDCl_3$, 400MHz): δ 7.21-7.38 (m, 5H), 6.33 (s, 1H), 5.87-5.98 (m, 1H), 5.14 (dt, $J = 3.2, 16.2$ Hz, 1H), 5.04 (dd, $J = 2.0, 10.4$ Hz, 1H), 2.28-2.36 (m, 4H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 138.4, 138.3, 128.8, 128.0, 125.9, 126.9, 125.2, 114.7, 40.0, 32.4, 17.8; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{13}H_{16}Na$ 195.1150, found 195.1154.



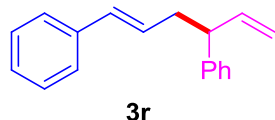
(1*E*, 3*E*)-octa-1,3,7-trienylbenzene (**3p**): To a solution of (*E*)-3-phenylbut-2-enyl acetate **1ps** (50 mg, 0.25 mmol) in DCM (5 ml) was added allyltrimethylsilane **2a** (85 mg, 119 μ L, 0.75 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled down to -20 $^{\circ}C$, then 0.5 mol% Tf_2NH (12.5 μ L, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 $^{\circ}C$ under N_2 atmosphere. After reaction the mixture was quenched with saturated $NaHCO_3$ (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was

dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3p** (25 mg, 55%) as a liquid. ^1H NMR (CDCl_3 , 400MHz): δ 7.38 (d, $J = 7.6$ Hz, 2H), 7.26-7.32 (m, 2H), 7.18-7.22 (m, 1H), 6.76 (dd, $J = 10.4, 15.6$ Hz, 1H), 6.46 (d, $J = 15.6$ Hz, 1H), 6.24 (d, $J = 10.4, 15.2$ Hz, 1H), 5.80-5.88 (m, 2H), 5.06 (d, $J = 12.2$ Hz, 1H), 5.00 (d, $J = 10.0$ Hz, 1H), 2.20-2.29 (m, 4H); ^{13}C NMR (CDCl_3 , 400MHz): δ 138.1, 137.6, 134.8, 131.0, 130.3, 129.3, 128.6, 127.1, 126.2, 114.9, 33.5, 32.3; FT-IR (CHCl_3): 2995, 2837, 1643, 1511, 1462, 909 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{Na}$ 207.1150, found 207.1158.



(*E*)-(5-methylhexa-1,5-dienyl)benzene (**3q**): To a solution of (*E*)-cinnamyl acetate (**1a**) (44 mg, 0.25 mmol) in DCM (5 ml) was added methallyltrimethylsilane **2b** (96 mg, 131 μL , 0.75 mmol, 3 equiv) under N_2 atmosphere. The solution was cooled down to -20 $^\circ\text{C}$, then 0.5 mol% Tf_2NH (12.5 μL , 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 $^\circ\text{C}$ under N_2 atmosphere. After reaction the mixture was quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 (3×5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3q** (28 mg, 66%) as a liquid. The NMR datas obtained for **3q** are in agreement with previously reported literature values.^{12e, 15a, 16}

^1H NMR (CDCl_3 , 300MHz): δ 7.31-7.41 (m, 5H), 6.46 (d, $J = 15.9$ Hz, 1H), 6.26 (dt, $J = 6.6, 15.9$ Hz, 1H), 4.78-4.80 (m, 2H), 2.37-2.49 (m, 2H), 2.21-2.26 (m, 2H), 1.81 (s, 3H); ^{13}C NMR (CDCl_3 , 300MHz): δ 130.4, 130.0, 128.5, 128.4, 127.7, 126.9, 126.0, 110.3, 37.5, 31.2, 22.5; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{16}\text{Na}$ 195.1150, found 195.1150.



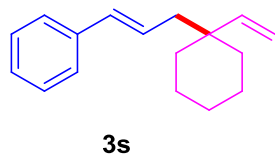
(*S, E*)-hexa-1,5-diene-1,4-diylidibenzene (**3r**): To a solution of (*E*)-cinnamyl acetate (**1a**) (44 mg, 0.25 mmol) in DCM (5 ml) was added (*E*)-3-Trimethylsilyl-1-phenyl-1-propene **2c** (159 mg, 0.75 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (12.5 μL, 0.00125 mmol, 0.1M solution

16. Crowe, W. E.; Zhang, Z. J. *J. Am. Chem. Soc.* **1993**, *115*, 10998-10999.

17. (a) Barrero, A. F.; Herrador, M. M.; Moral, J. F.; Arteaga, P.; Arteaga, J. F.; Dieguez, H. R.; Sanchez, E. M, *J. Org. Chem.* **2007**, *72*, 2988 – 2995; (b) Médéjan, S.; Hélicon, F.; Namy, J. L. *Eur. J. Org. Chem.* **2005**, 4715–472.

in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3r** (37 mg, 70%) as a liquid. The NMR datas obtained for **3r** are in agreement with previously reported literature values.¹⁷

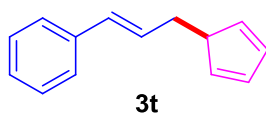
(*S, E*)-hexa-1,5-diene-1,4-diylidibenzene (**3r**): ¹H NMR (CDCl₃, 400MHz): δ 7.16-7.38 (m, 10H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.13 (dt, *J* = 7.2, 15.6 Hz, 1H), 5.98-6.06 (m, 1H), 5.04-5.09 (m, 2H), 3.43 (q, *J* = 7.6 Hz, 1H), 2.62-2.66 (m, 2H); ¹³C NMR (CDCl₃, 400MHz): δ 145.6, 143.3, 133.2, 130.6, 130.3, 130.2, 129.5, 128.8, 128.2, 127.9, 127.5, 116.5, 51.8, 40.8; HRMS (ESI) *m/z* [M+Na]⁺ calcd for C₁₈H₁₉ 235.1487, found 235.1479.



(*E*)-(3-(1-vinylcyclohexyl)prop-1-enyl)benzene (**3s**): To a solution of (*E*)-cinnamyl acetate (**1a**) (44 mg, 0.25 mmol) in DCM (5 ml) was added [2-(Trimethylsilyl)ethylidene]cyclohexane **2d** (136 mg, 0.75 mmol, 3 equiv) under N₂ atmosphere. The

solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (12.5 μL, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 48 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3s** (20 mg, 36%) as a liquid. The NMR datas obtained for **3r** are in agreement with previously reported literature values.^{12e}

(E)-(3-(1-vinylcyclohexyl)prop-1-enyl)benzene (**3s**): ¹H NMR (CDCl₃, 400MHz): δ 7.15-7.34 (m, 5H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 7.2, 11.2 Hz, 1H), 5.71 (dd, *J* = 11.2, 18.0 Hz, 1H), 5.11 (dd, *J* = 1.2, 10.8 Hz, 1H), 4.93 (dd, *J* = 1.2, 16.0 Hz, 1H), 2.20 (dd, *J* = 1.2, 6.8 Hz, 2H), 1.26-1.60 (m, 10H); ¹³C NMR (CDCl₃, 400MHz): δ 146.3, 137.9, 131.8, 128.4, 127.3, 126.8, 126.0, 112.9, 40.3, 35.5, 26.4, 22.1, 22.0; HRMS (ESI) *m/z* [M+Na]⁺ calcd for C₁₇H₂₂Na 249.1619, found 249.1609.



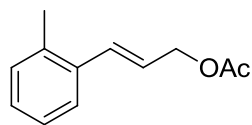
(E)-(3-(cyclopenta-2,4-dienyl)prop-1-enyl)benzene (**3t**): To a solution of (*E*)-cinnamyl acetate (**1a**) (44 mg, 0.25 mmol) in DCM (5 ml) was added trimethylsilyl cyclopentadiene **2e** (103 mg, 0.75 mmol, 3 equiv) under N₂ atmosphere. The solution was cooled down to -20 °C, then 0.5 mol% Tf₂NH (12.5 μL, 0.00125 mmol, 0.1M solution in DCM) was added to this mixture. The reaction mixture was stirred for 36 hours at -20 °C under N₂ atmosphere. After reaction the mixture was quenched with saturated NaHCO₃ (3 mL) and subsequently extracted with CH₂Cl₂ (3 × 5 mL). The extract was dried and concentrated in vacuo in ice-water bath. The residue was subjected to column chromatography (silica gel, pentane-diethyl ether = 20:1) to obtain the isomers of product **3t** (25 mg, 63%) as a liquid. ¹H NMR (CDCl₃, 400MHz): δ 7.29-7.31 (m, 2H), 7.17-7.26 (m, 3H), 6.42-6.45 (m, 1H), 6.29-6.31 (m, 1H), 6.20-6.24 (m, 2H), 5.12 (dt, *J* = 1.2, 10.0 Hz, 1H), 5.00(dt, *J* = 1.6, 17.2 Hz, 1H),

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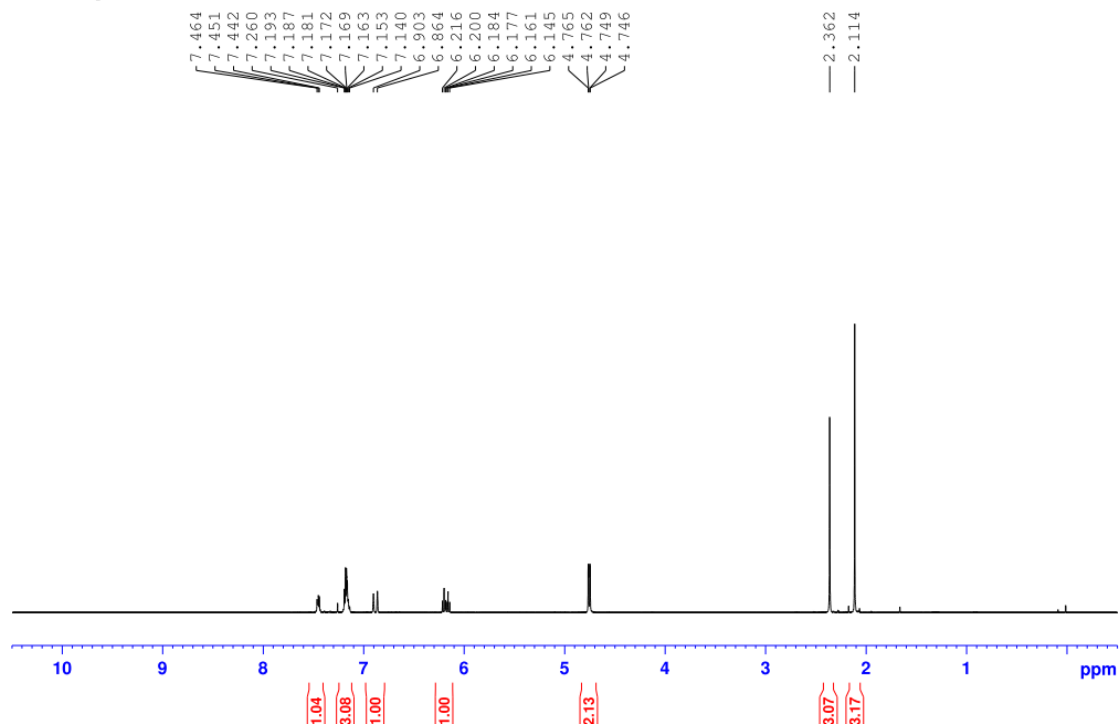
Supporting Information

4.45 (d, $J = 7.6$ Hz, 1H), 2.85 (d, $J = 1.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 400MHz): δ 150.7, 143.4, 140.6, 132.1, 131.8, 128.3, 126.3, 115.3, 51.5, 42.6; FT-IR (CHCl_3): 3013, 2894, 1652, 1521, 1467, 903, 785 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}$ 183.1174, found 183.1171.

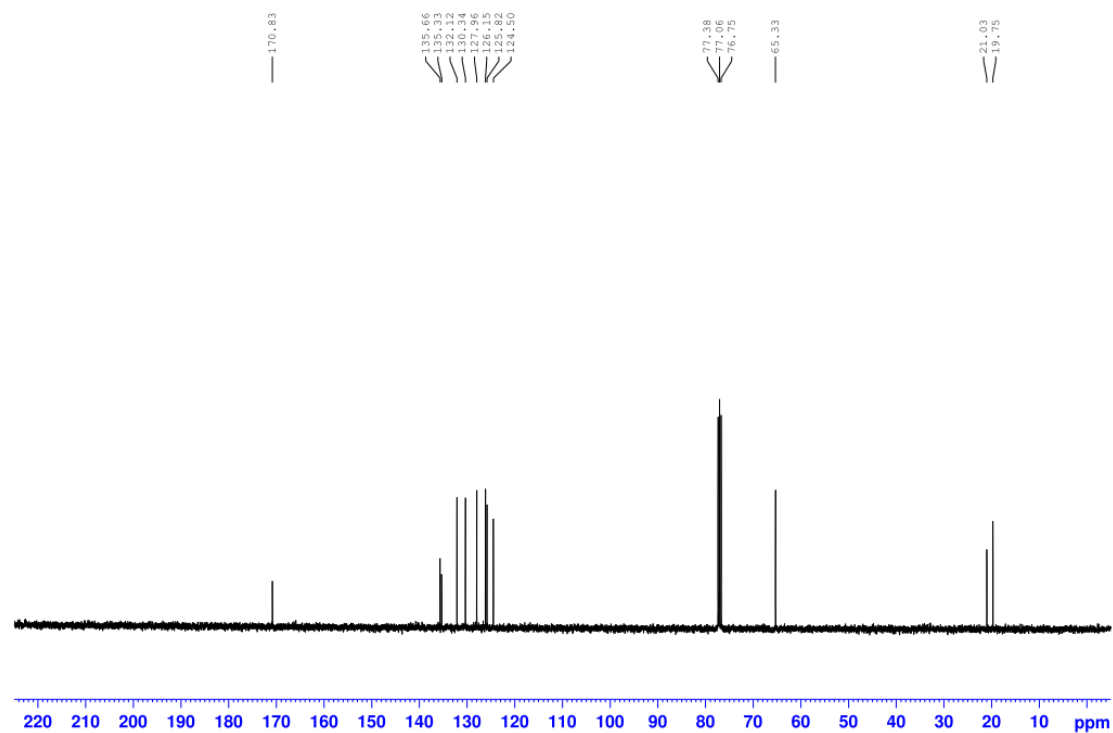
^1H and ^{13}C NMR spectra for all compounds

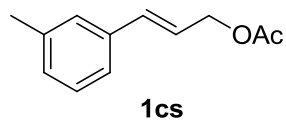


R2-114-1p, BBF01-400Hz, ^1H , cdCl_3

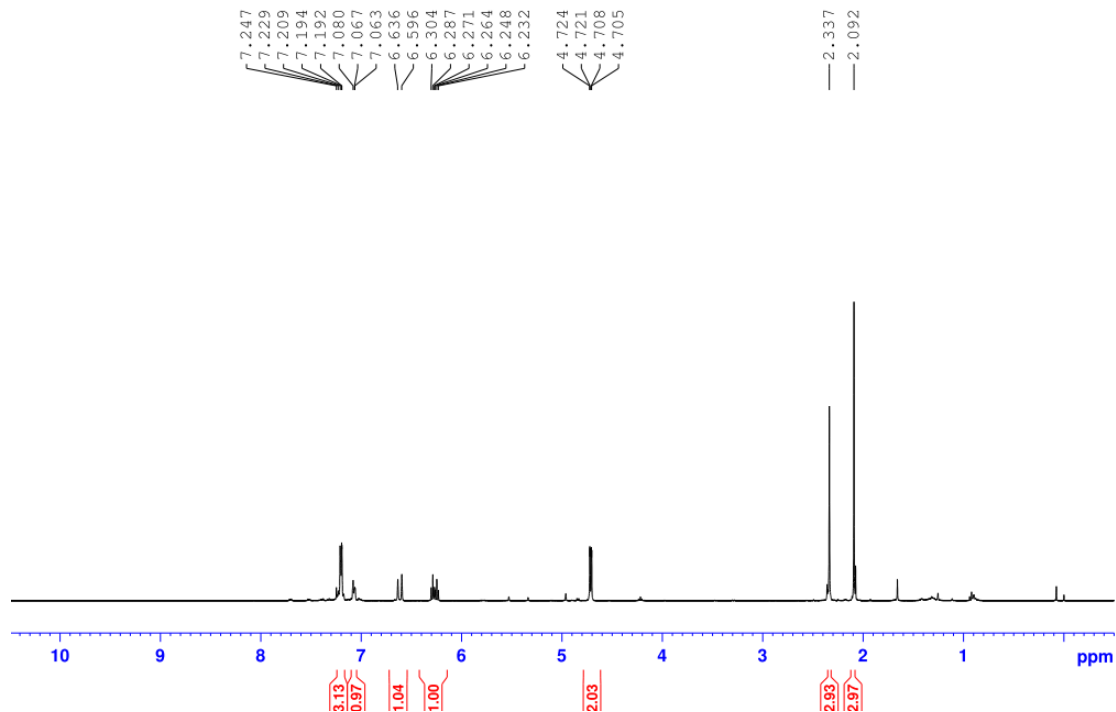


R2-114-1p, BBF01-400Hz, ^{13}C , cdCl_3

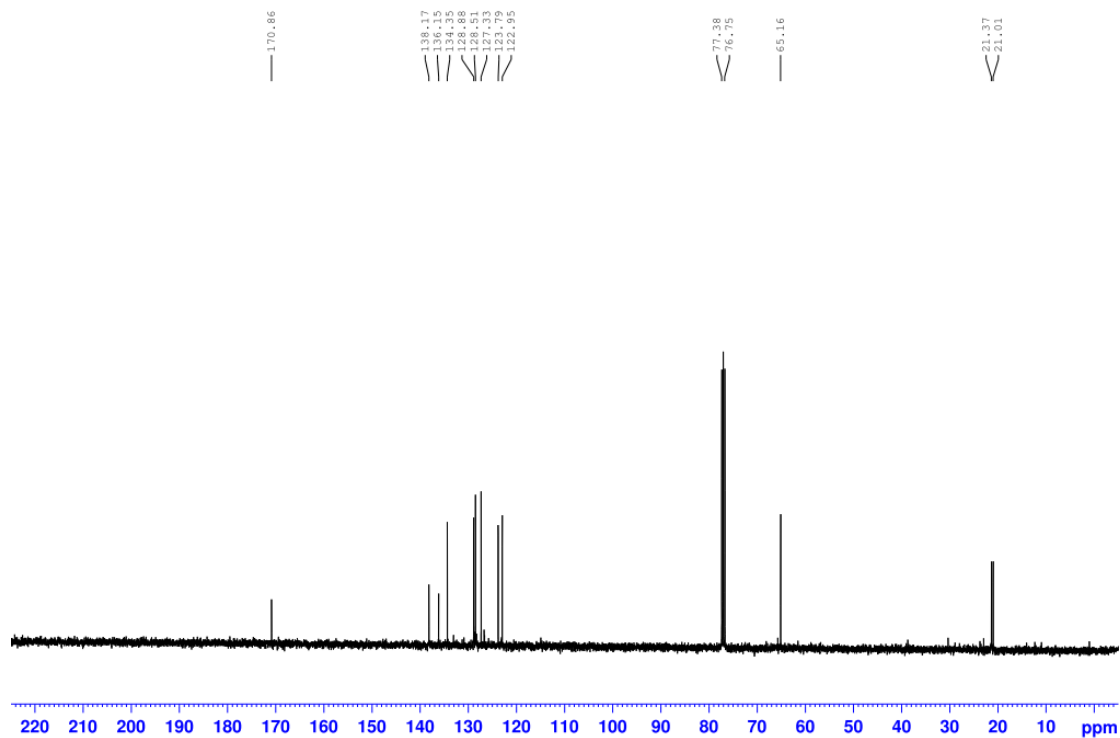


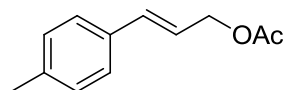


R2-135-1, BBF01-400Hz, 1H, cdcl3

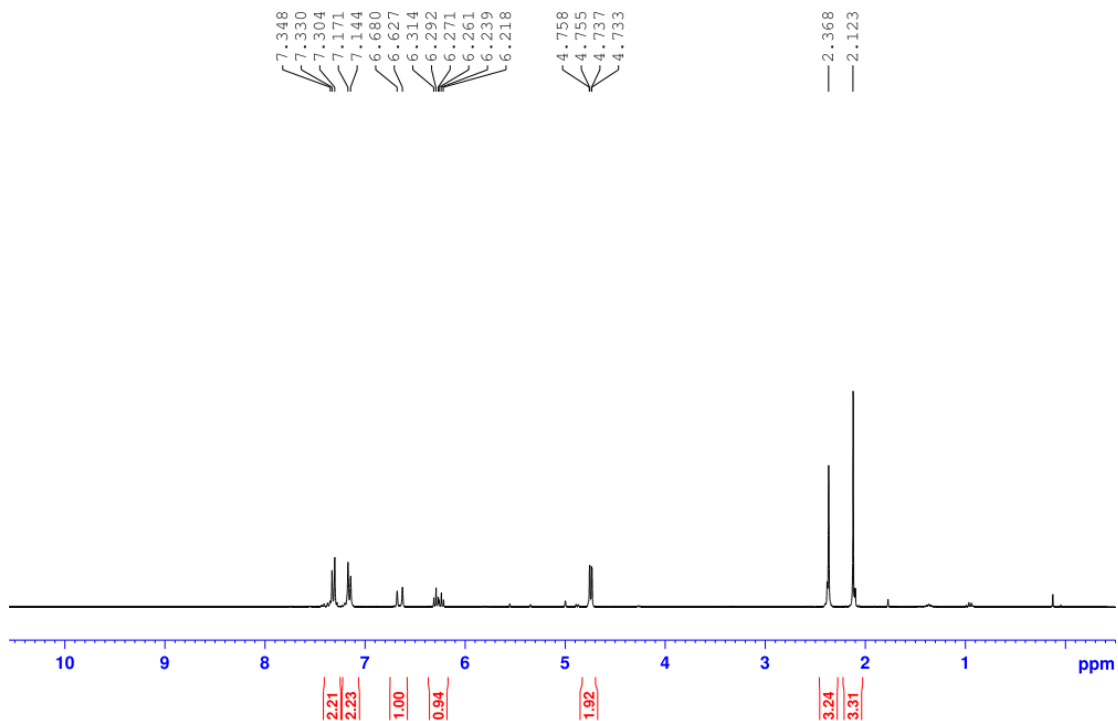


R2-135-1, BBF01-400Hz, 13C, cdcl3

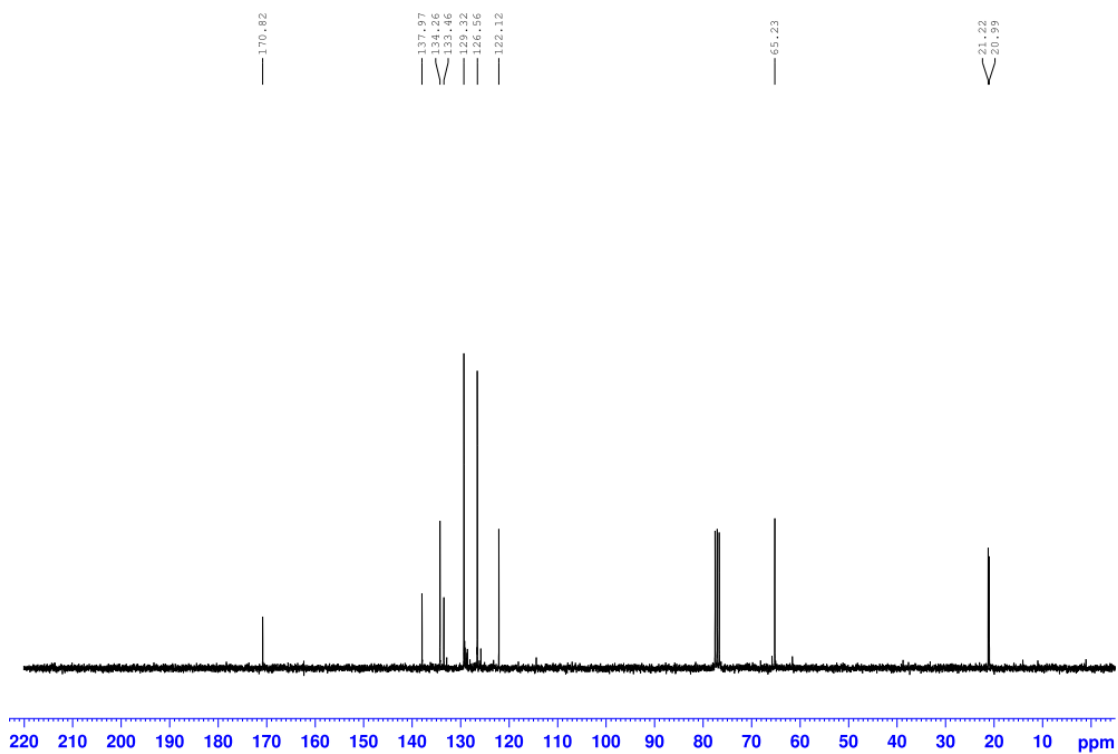




R3010-p, 300 MHz, ¹H NMR, CDCl₃

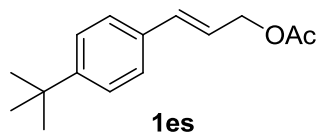


.3010-p, 300 MHz, ¹³C NMR, CDCl₃

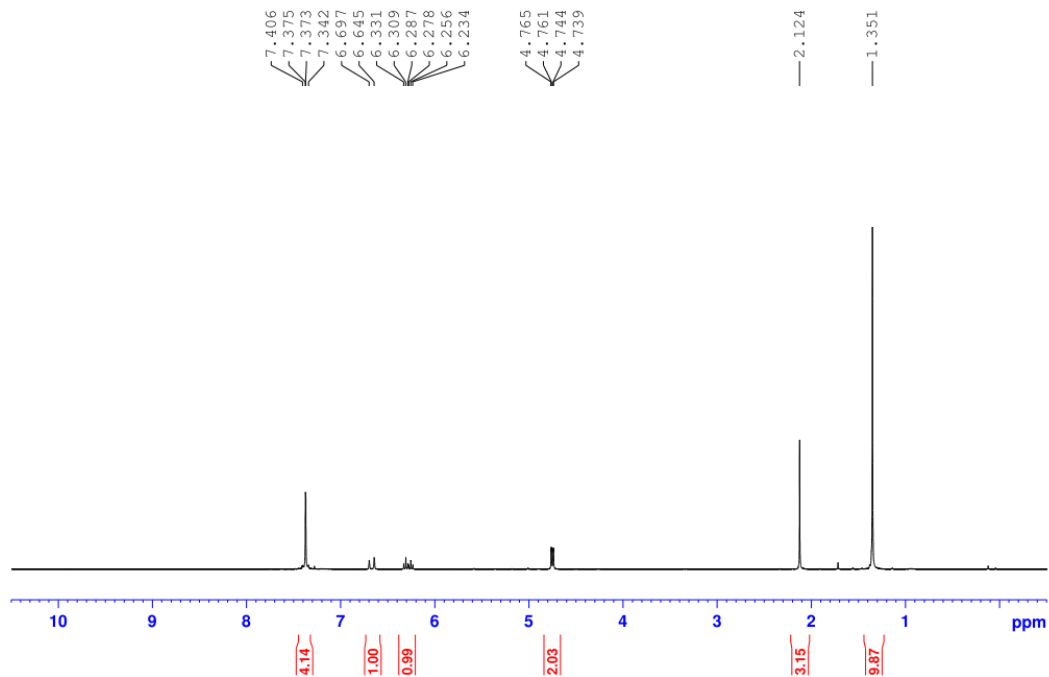


F. Ding et al.

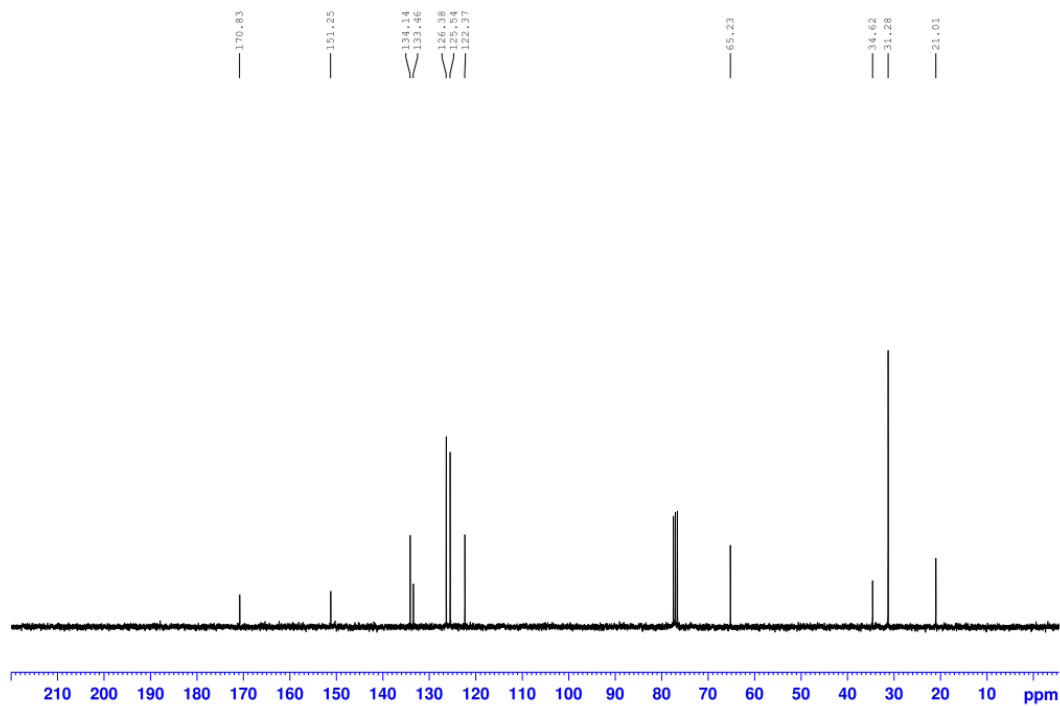
Supporting Information

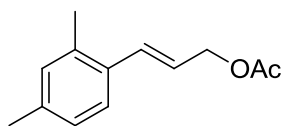


R3014-p, 300 MHz, ¹HNMR, CDCl₃

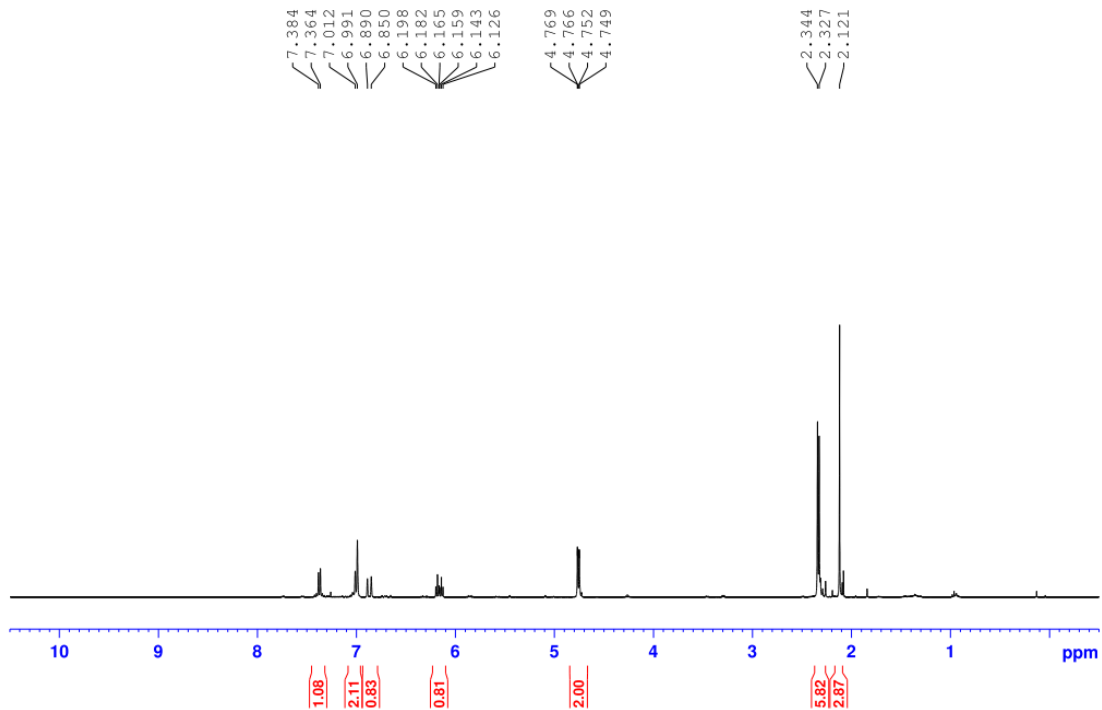


R3014-p, 300 MHz, ¹³CNMR, CDCl₃

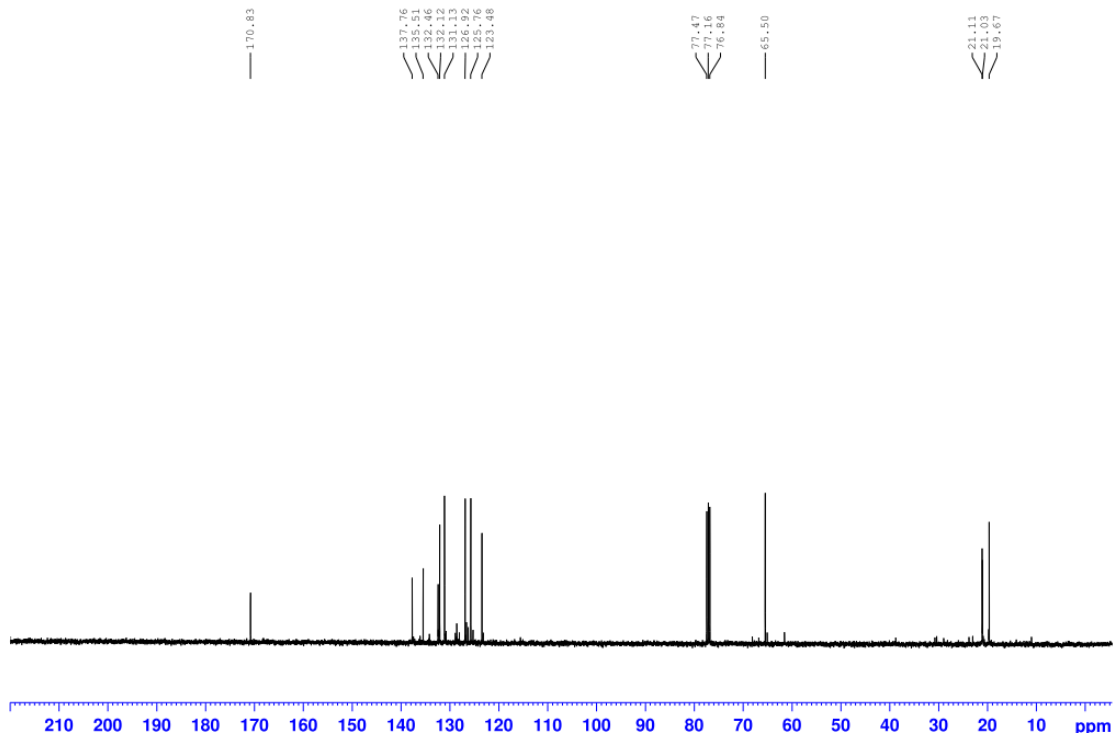


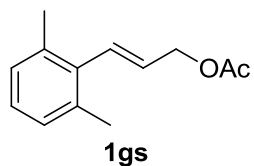


R2-139-1P, BBFO1-400Hz, 1H, cdc13

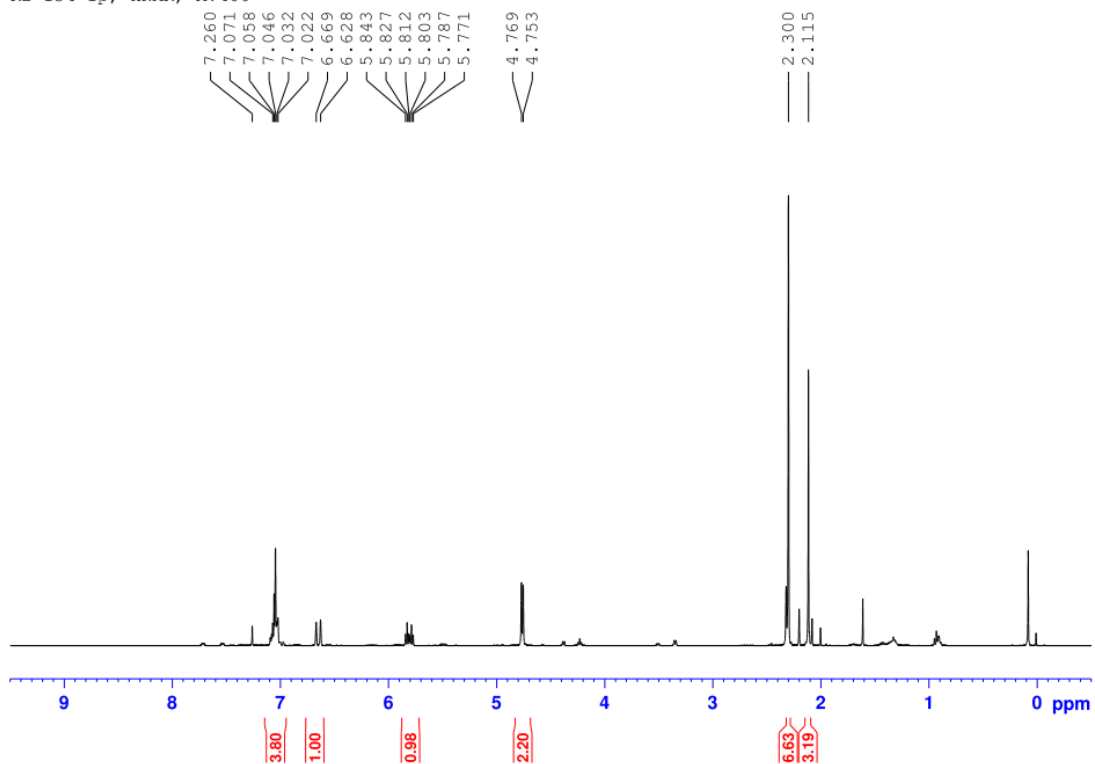


R2-139-1P, BBFO1-400Hz, 13C, cdc13

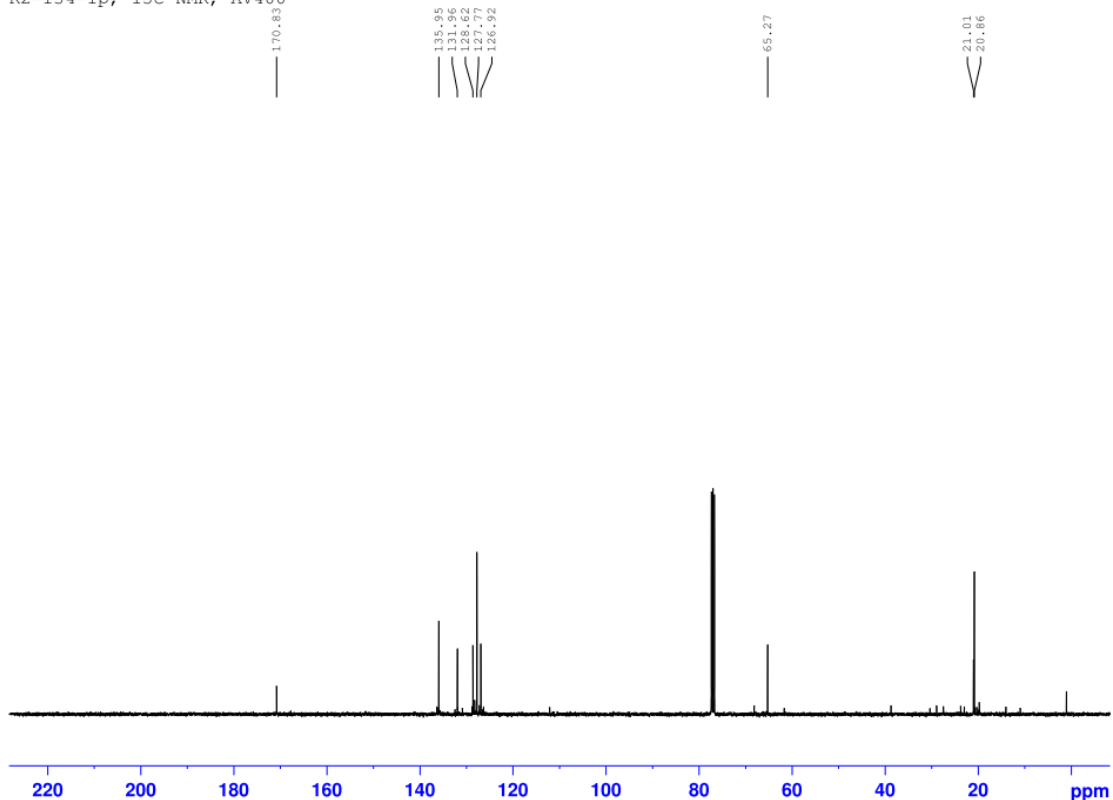


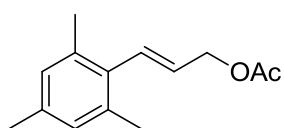


R2-134-1p, HNMR, AV400



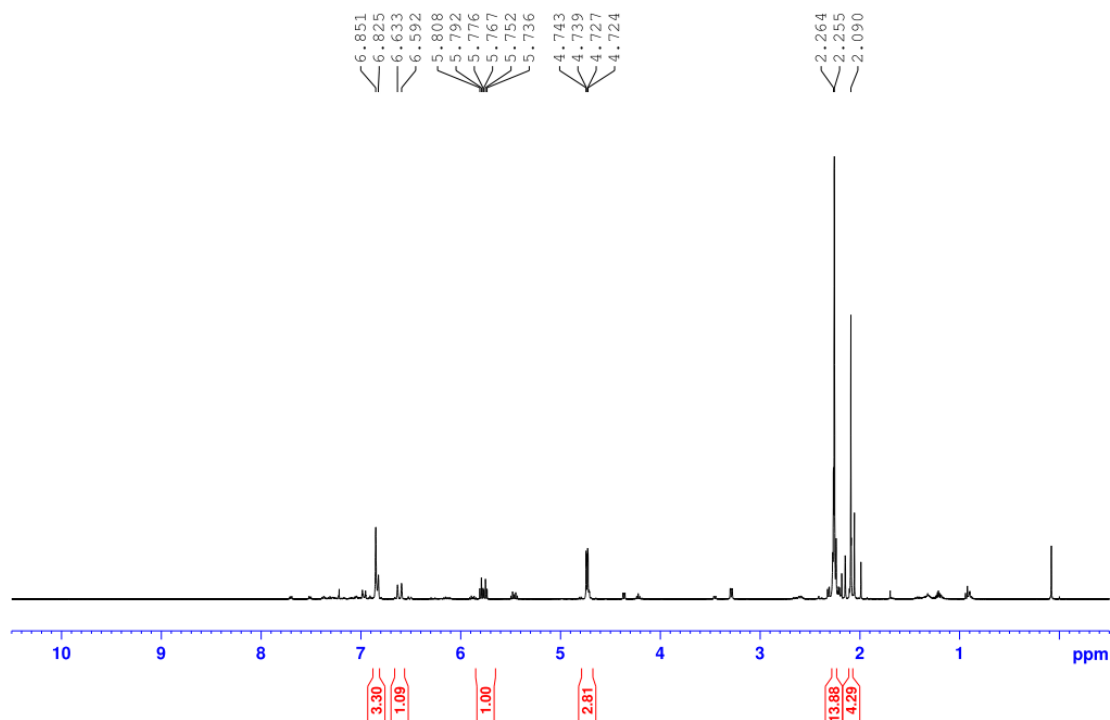
R2-134-1p, ¹³C NMR, AV400



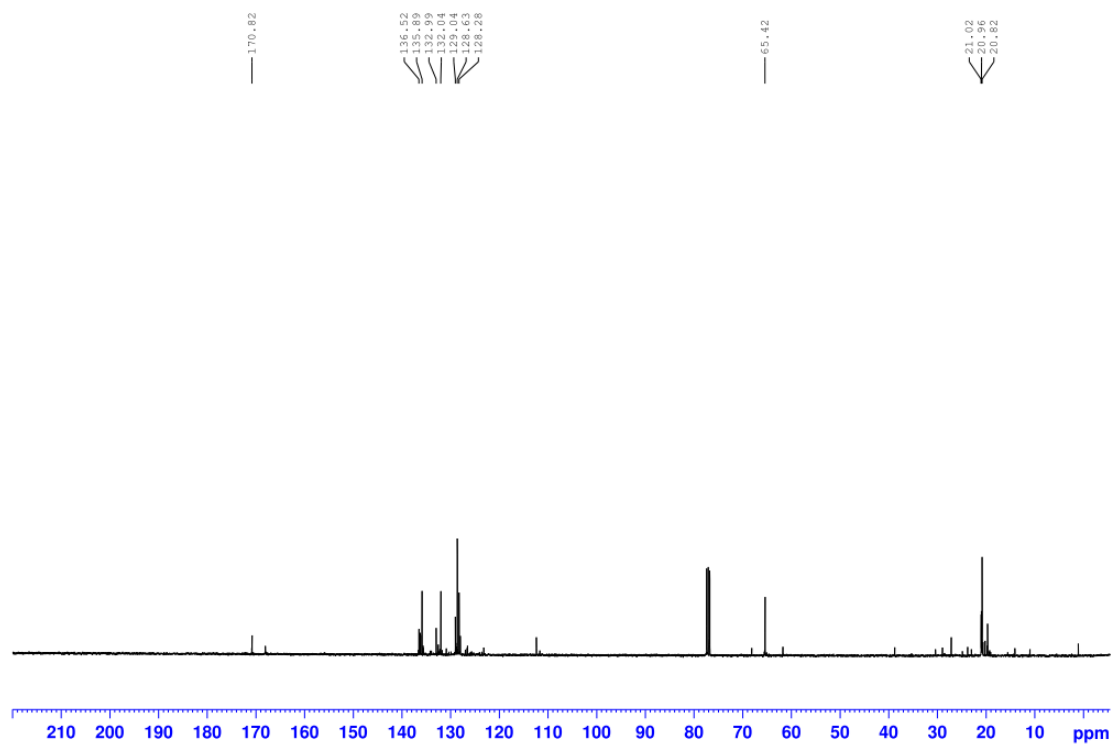


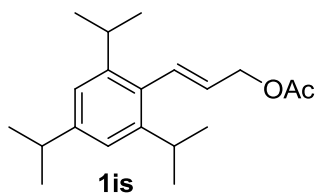
1hs

R2-140-1P, BBF01-400Hz, 1H, cdc13

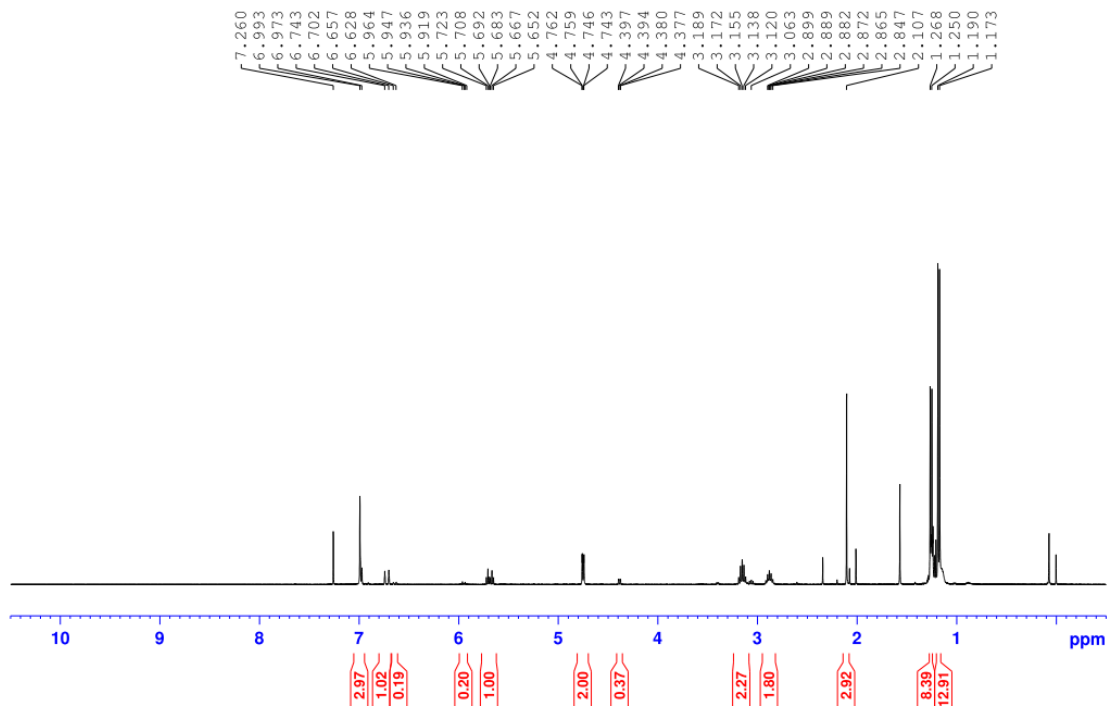


R2-140-1P, BBF01-400Hz, 13C, cdc13

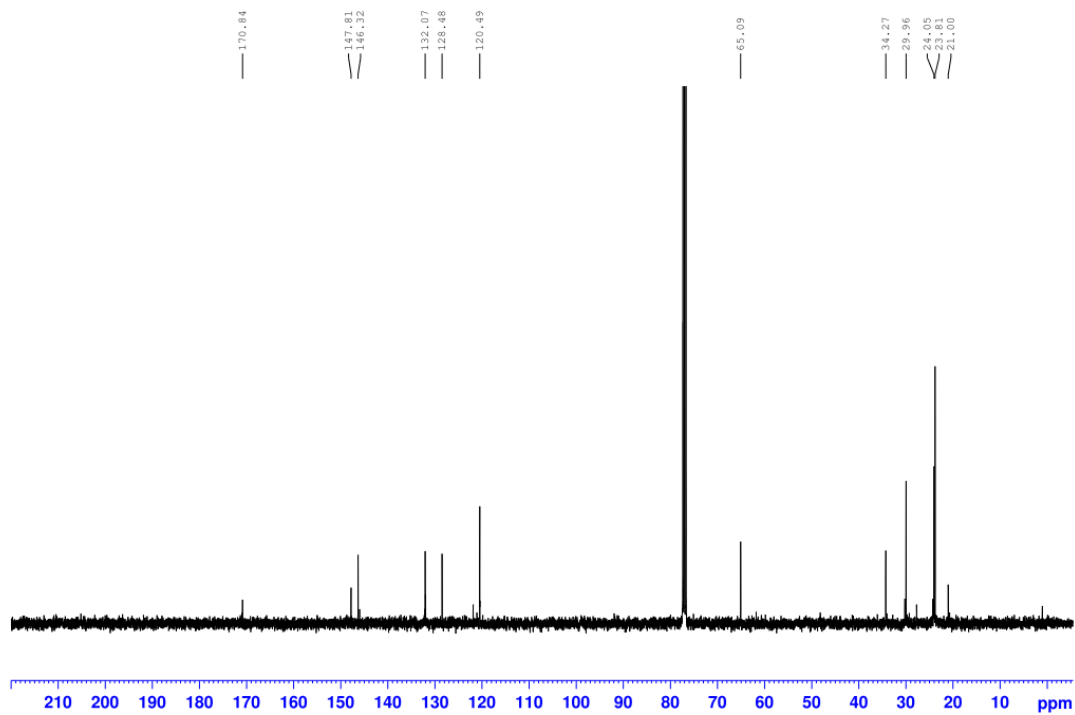


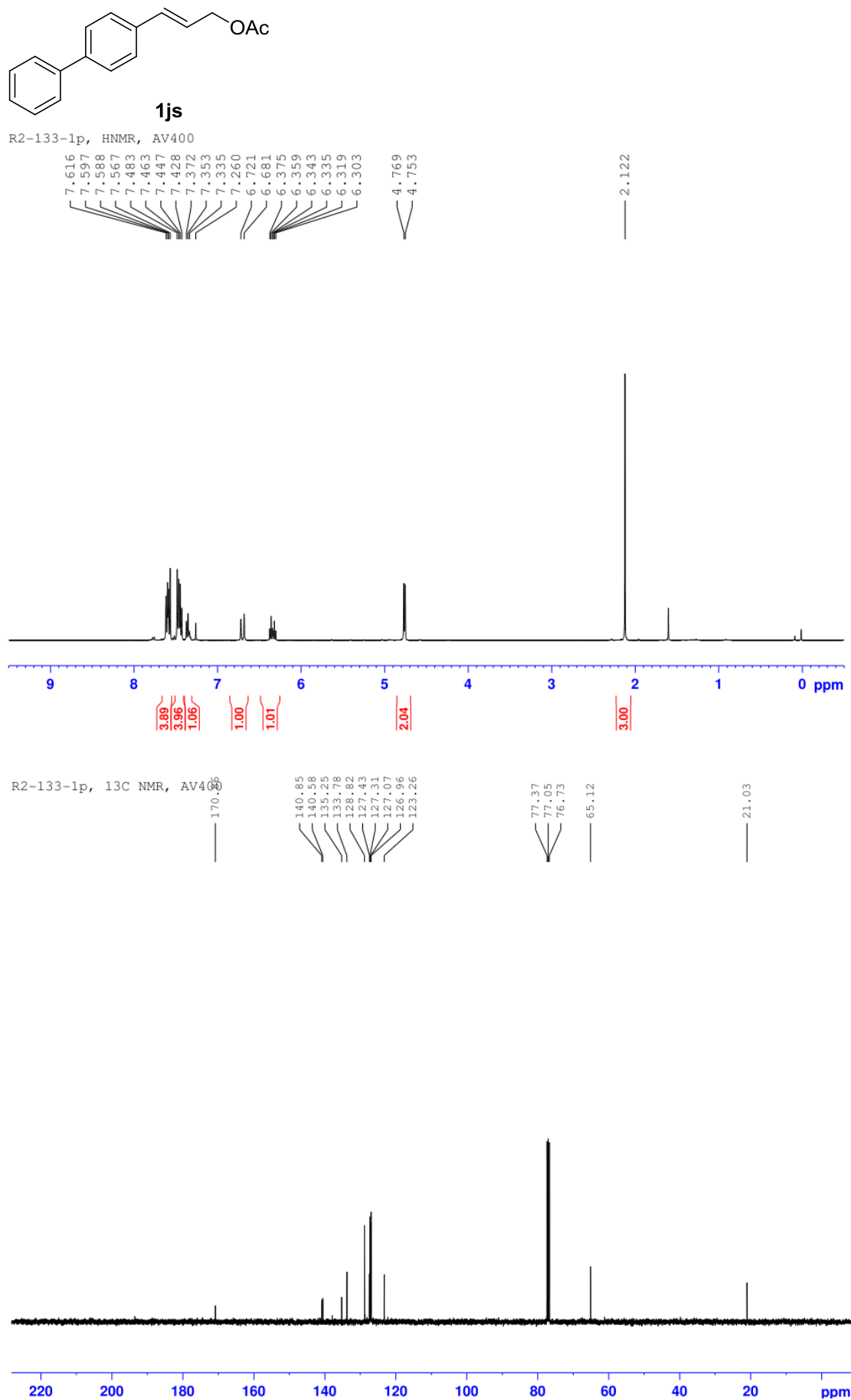


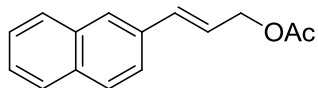
R3-019-1p, ¹H, Bruker 400 BBF01, CDCl₃



R3-019-1p, ¹³C, Bruker 400 BBF01, CDCl₃

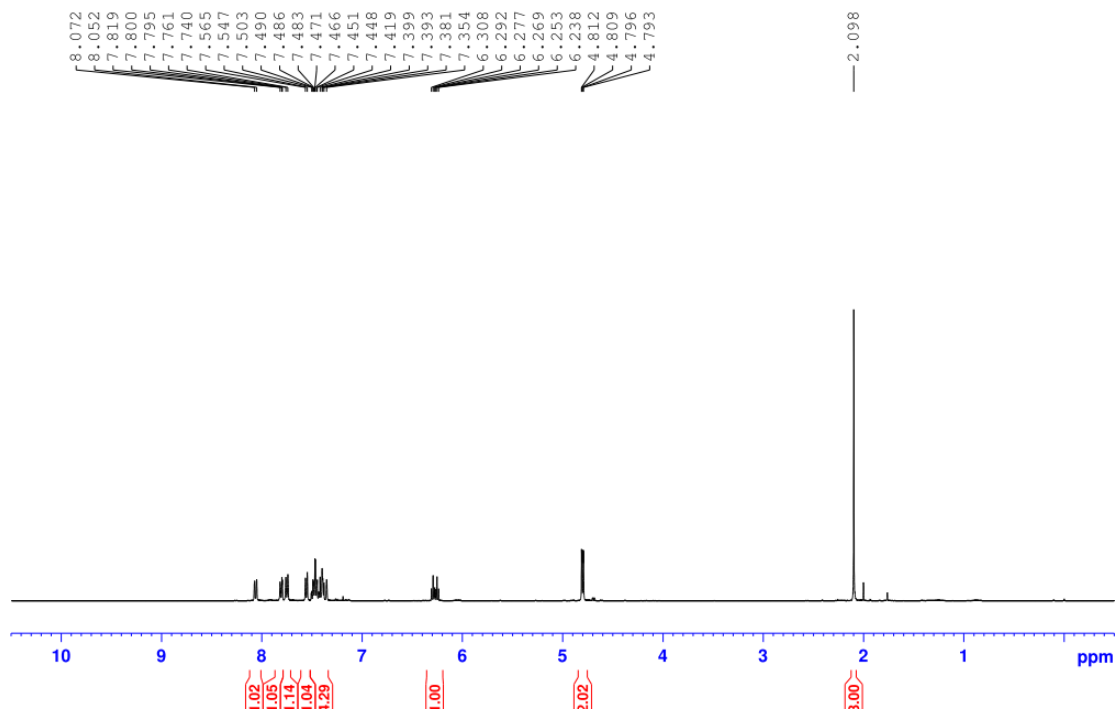




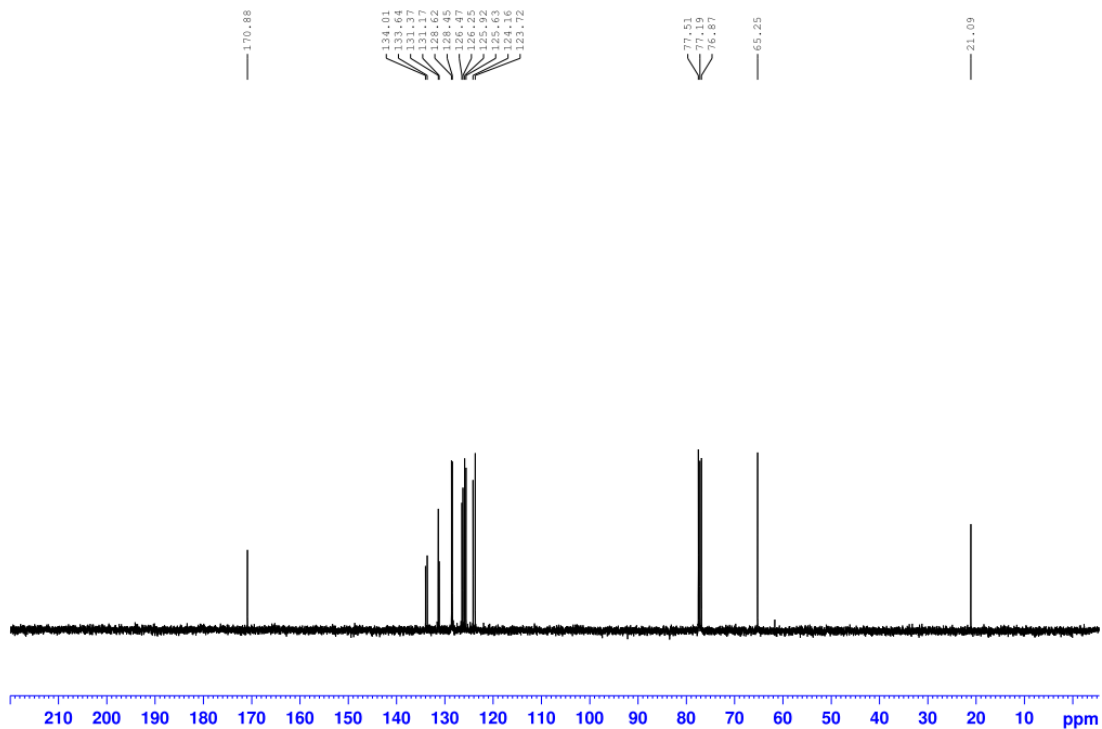


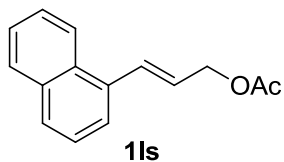
1ks

R2-142-1P, BBFO1-400Hz, 1H, cdcl3

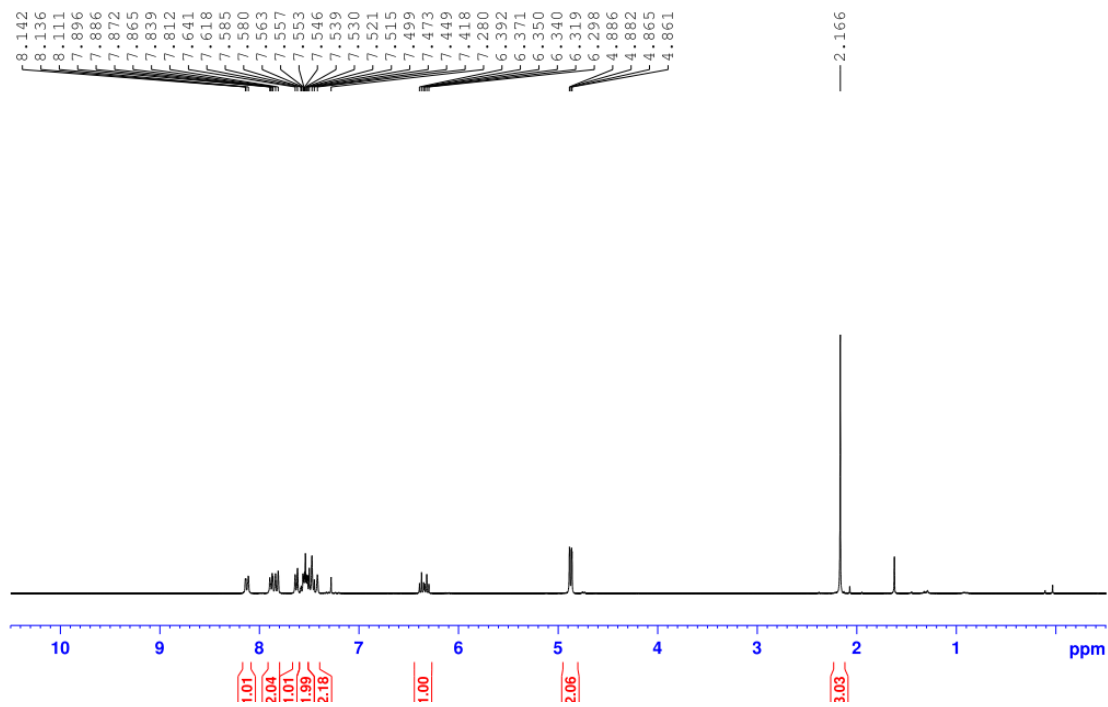


R2-142-1P, BBFO1-400Hz, 13C, cdcl3

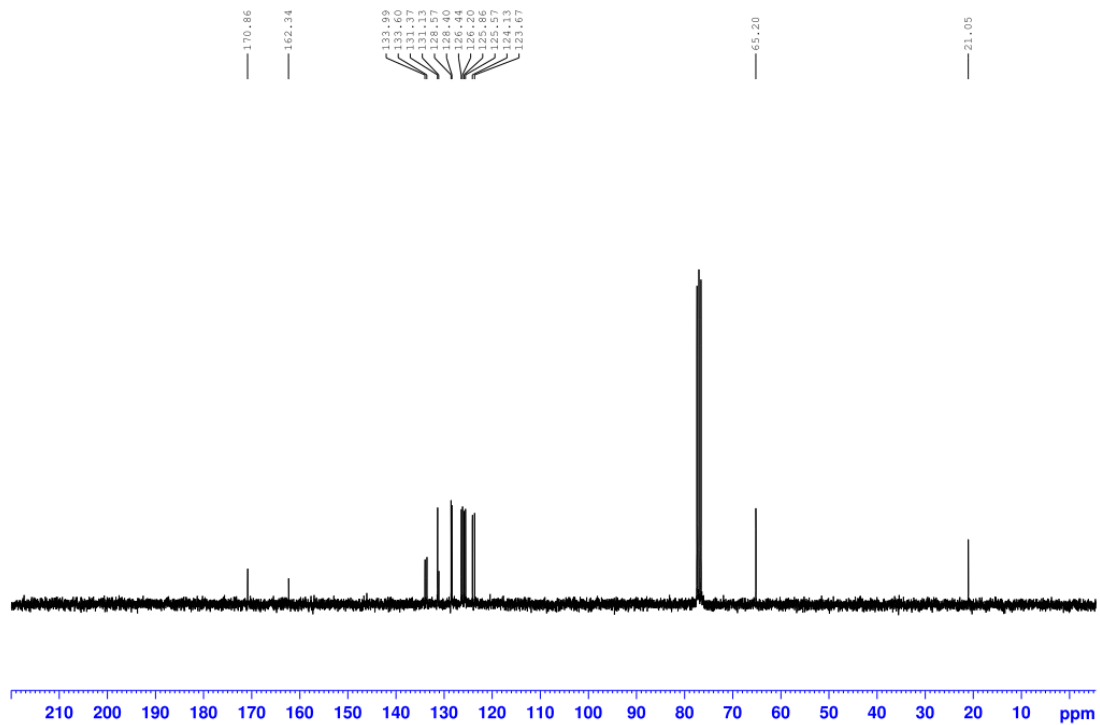


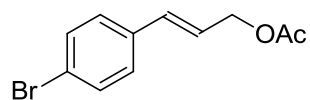


R3015-p, 300 MHz, ¹HNMR, CDCl₃



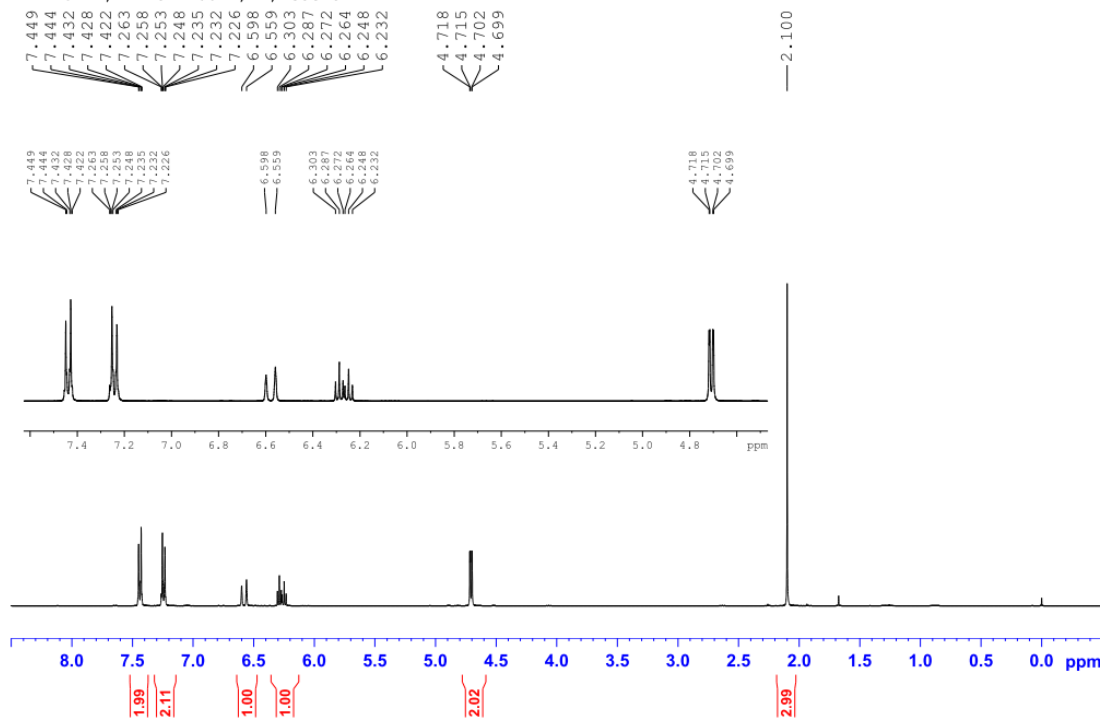
R3015-p, 300 MHz, ¹³CNMR, CDCl₃



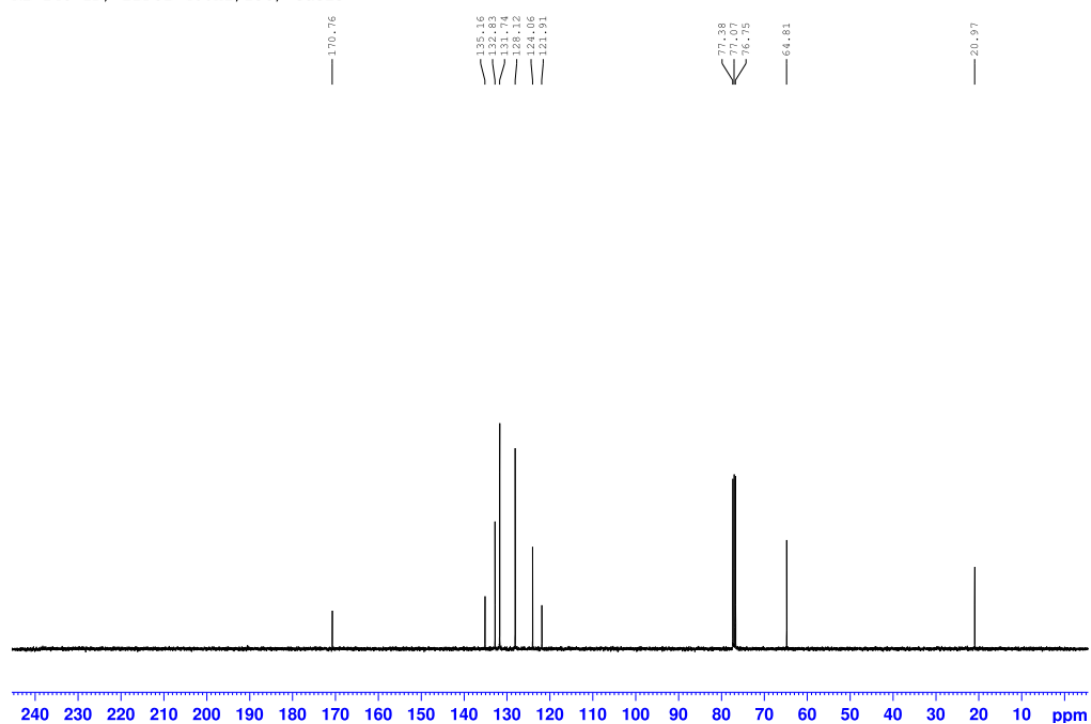


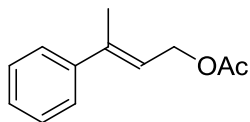
1ms

R2-148-1P, BBFO1-400Hz, 1H, cdcl3



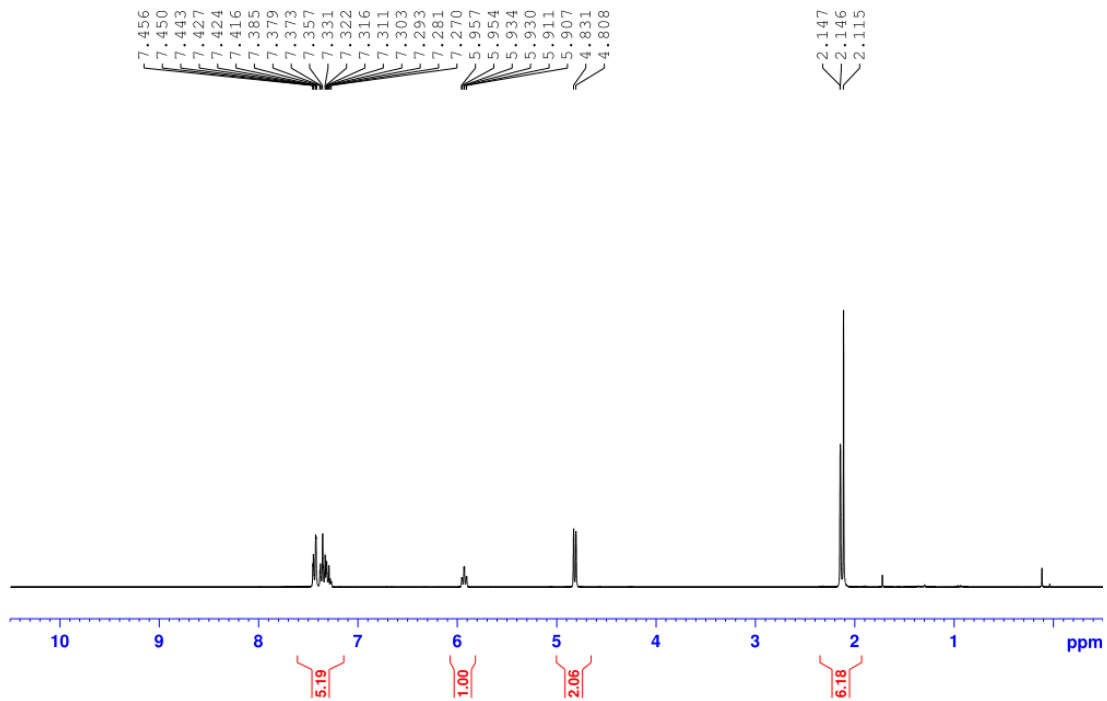
R2-148-1P, BBFO1-400Hz, 13C, cdcl3



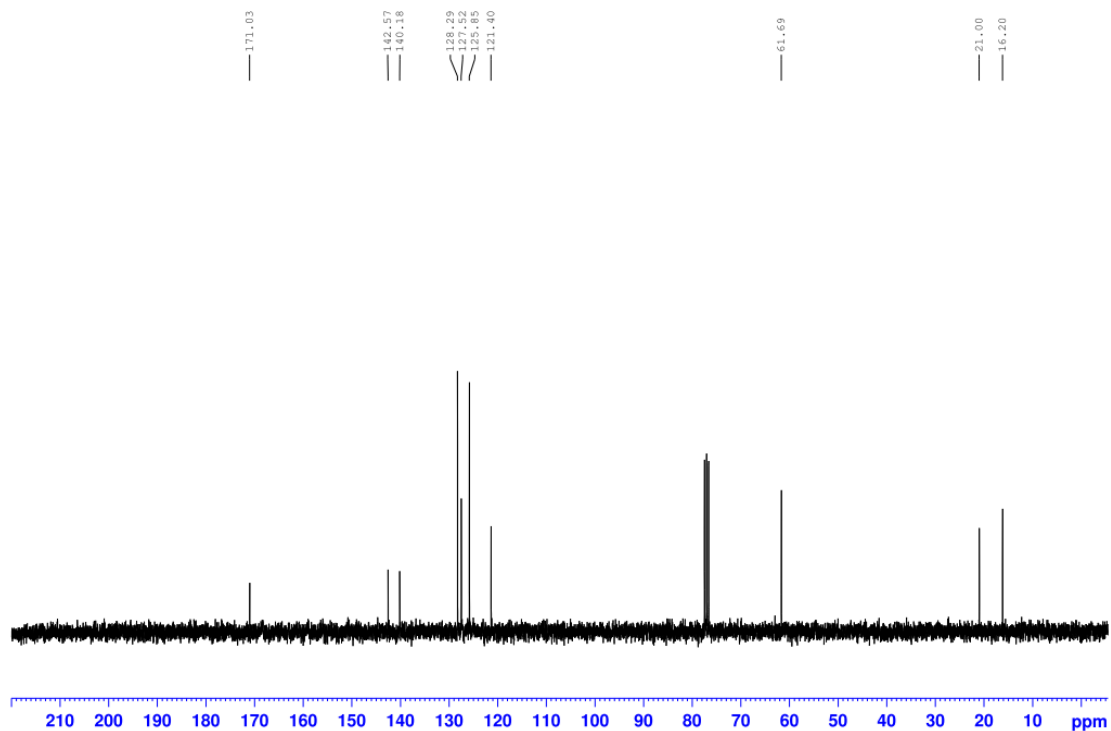


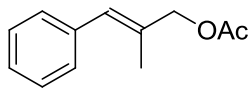
1ns

R3038-p, ¹HNMR, CDCL₃, 300 MHz



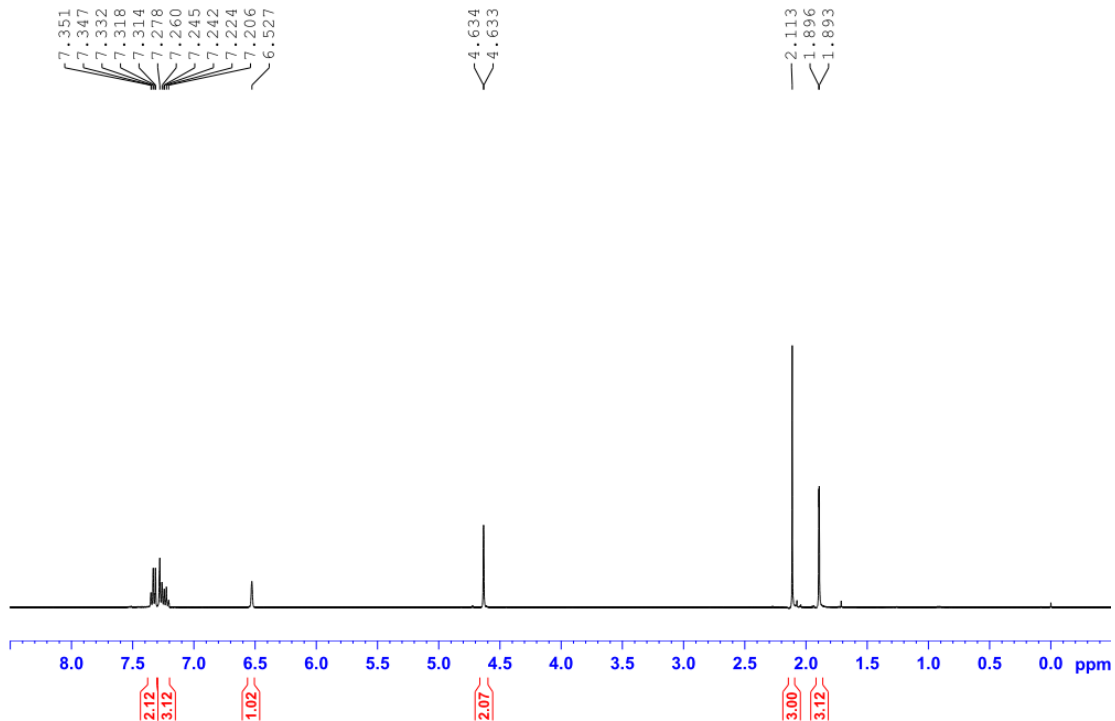
R3038-p, ¹³CNMR, CDCL₃, 300 MHz



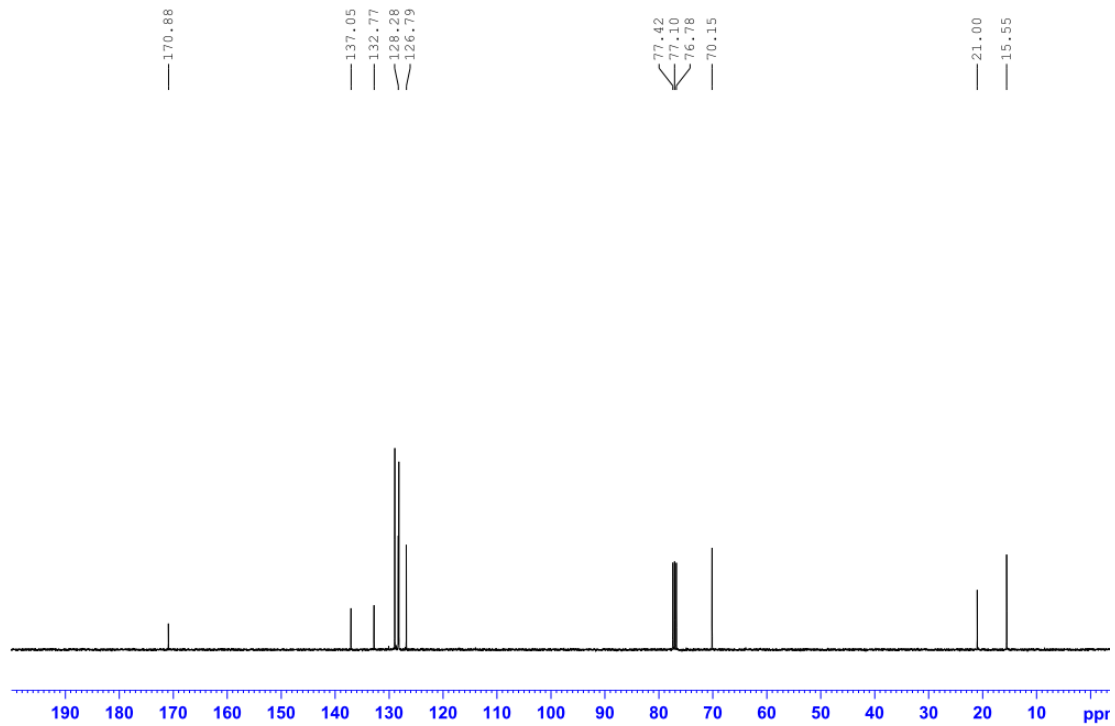


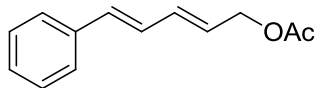
1os

R2-147-1P, BBFO1-400Hz, 1H, cdcl3



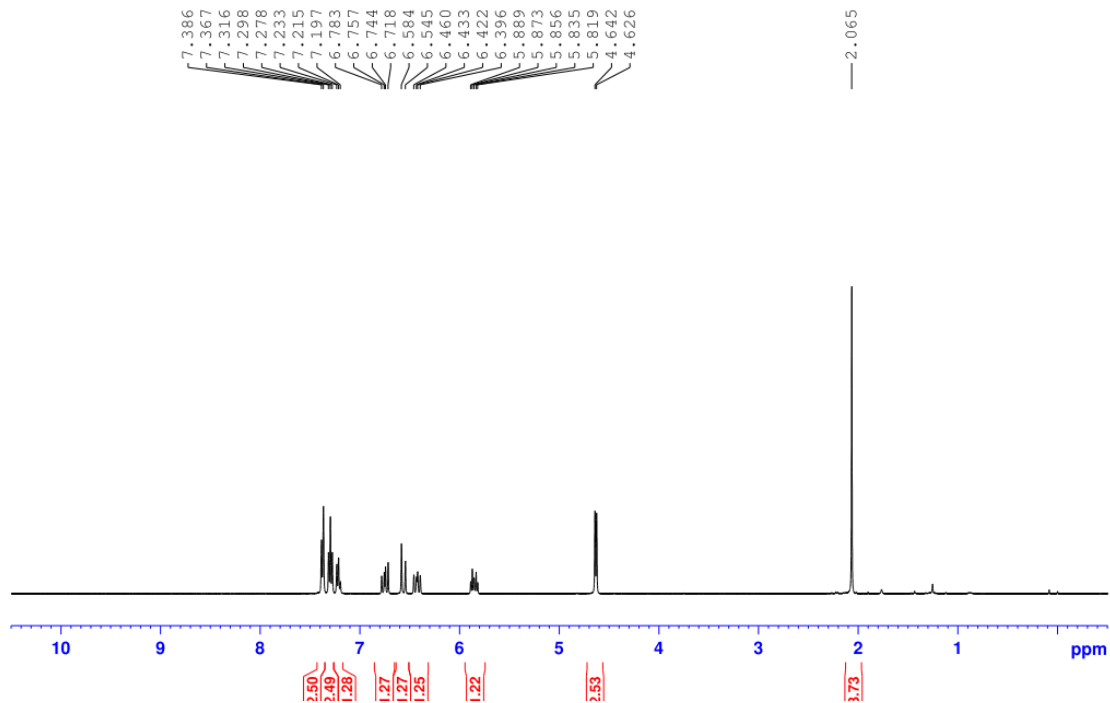
R2-147-1P, BBFO1-400Hz, 13C, cdcl3



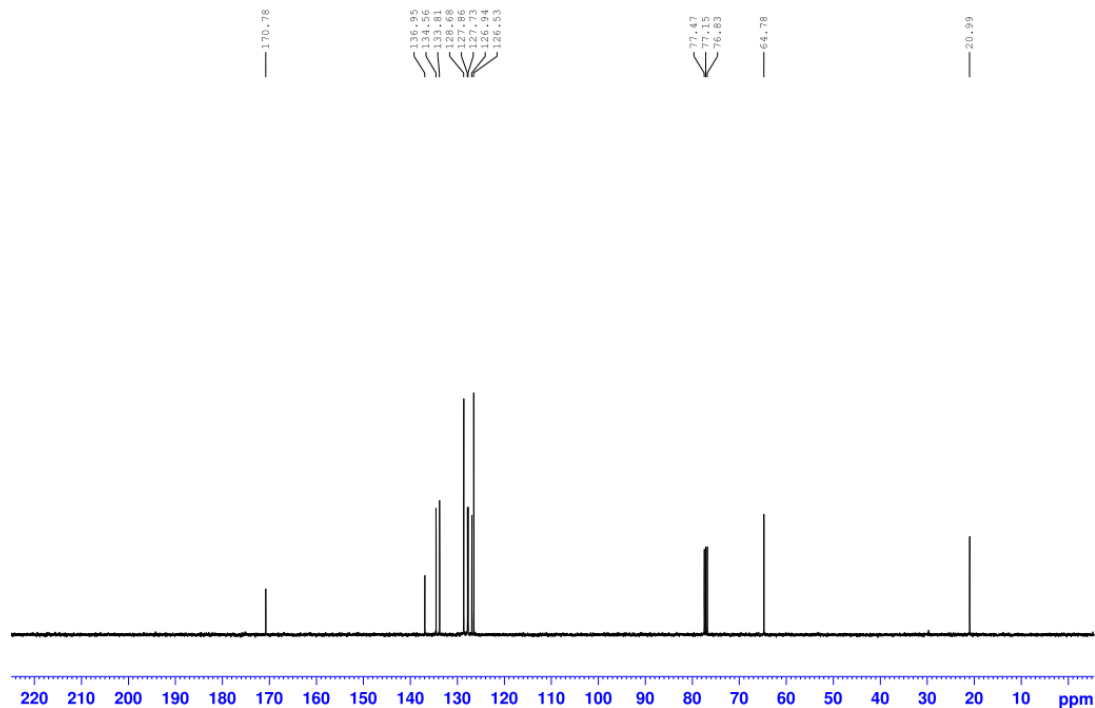


1ps

D2-106-1p, ¹H NMR, AV400MHz, CDCl₃

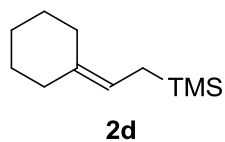


D2-106-1p, ¹³C NMR, AV400MHz, CDCl₃

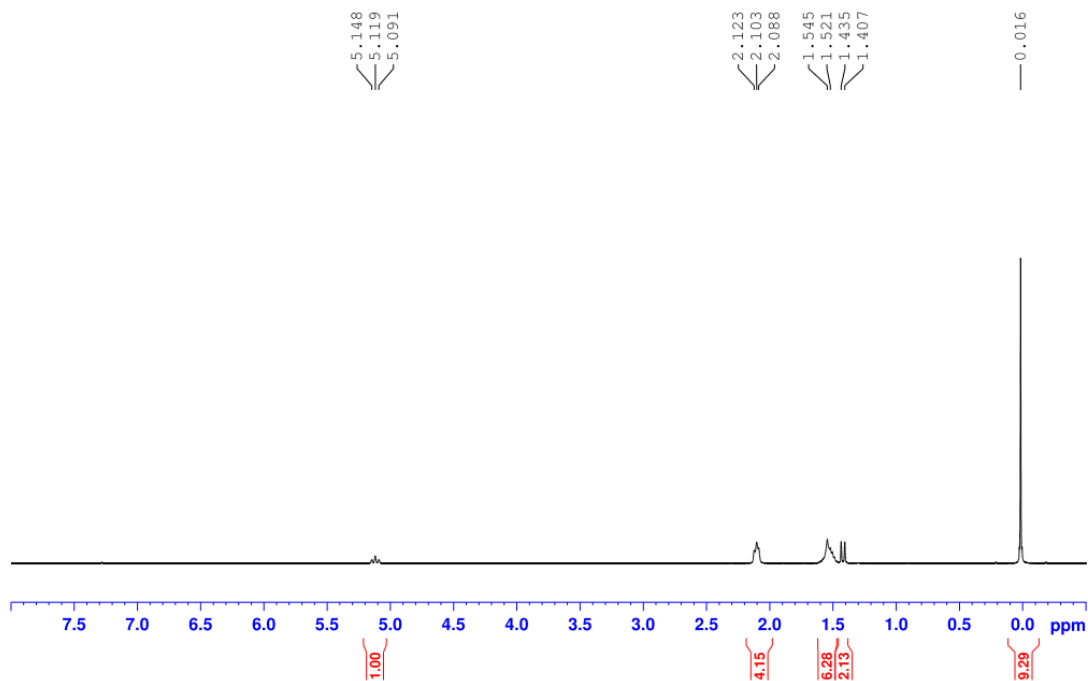


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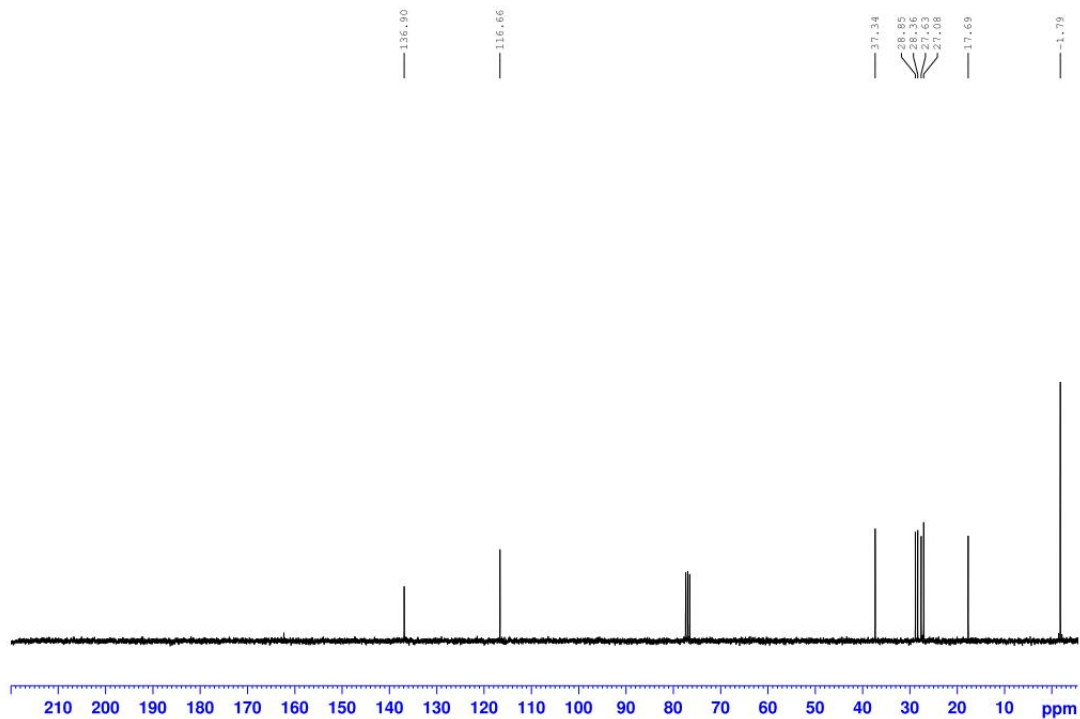
Supporting Information

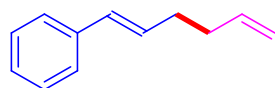


R3036-1p, ¹HNMR, CDCL₃, 300 MHz



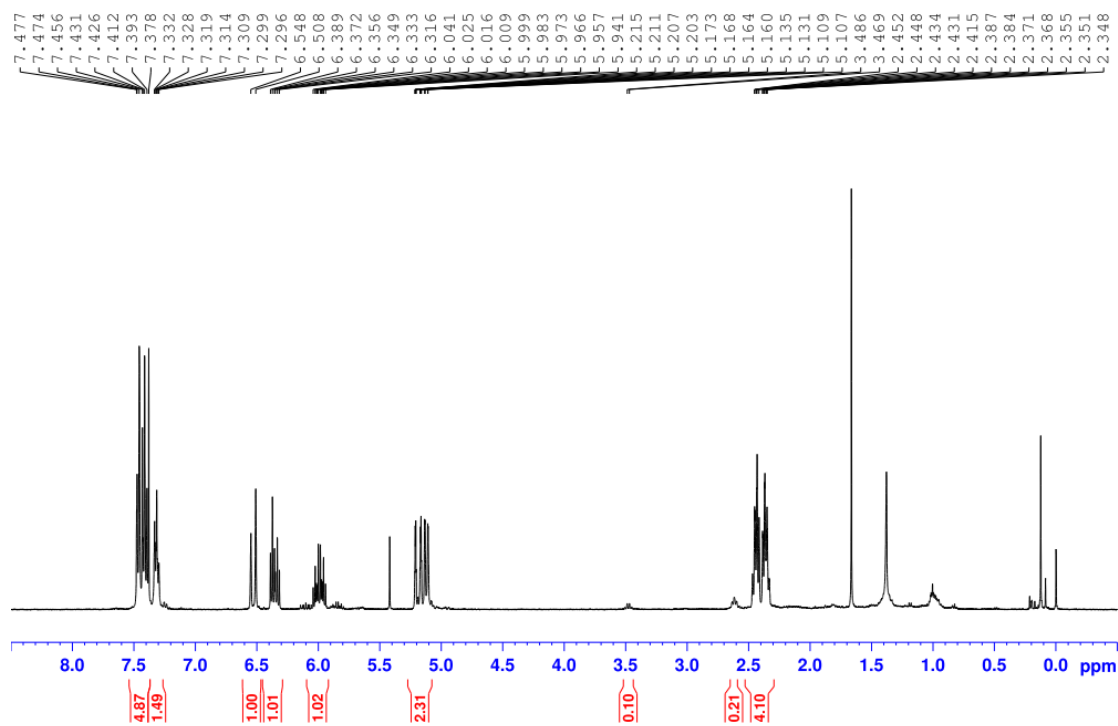
R3036-1p, ¹³CNMR, CDCL₃, 300 MHz



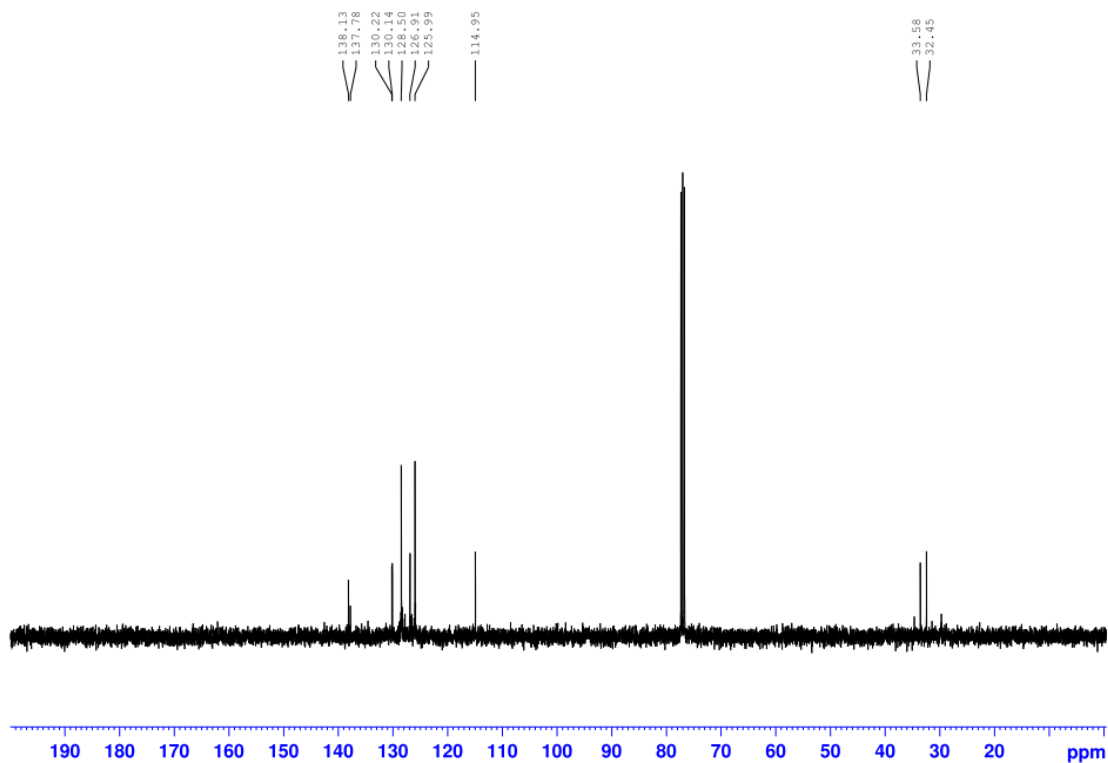


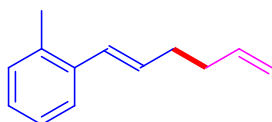
3a

D2-067-1, CDCl₃, 400Mz, HNMR, bbf1,



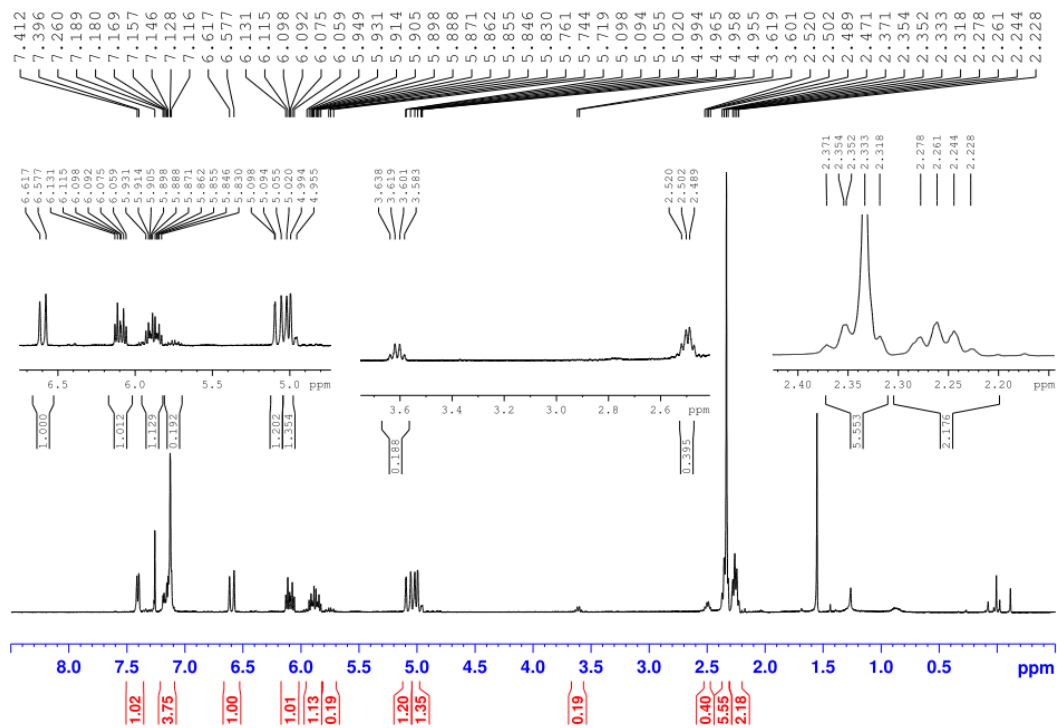
D2-067-1p, CDCl₃, AV400, ¹³C NMR, AUG-2011



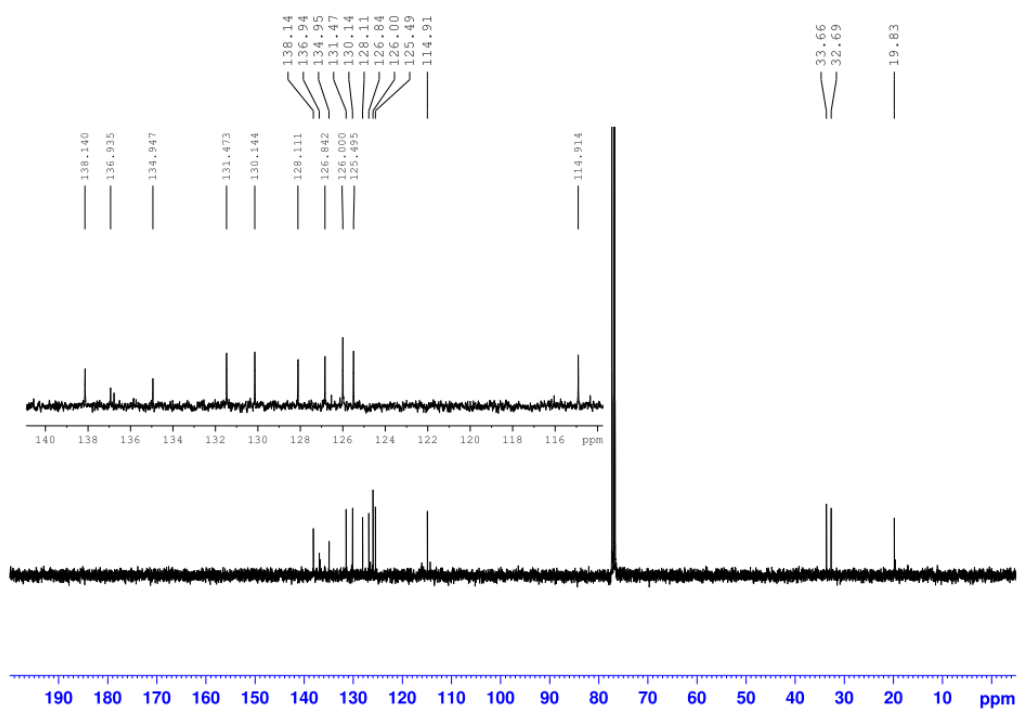


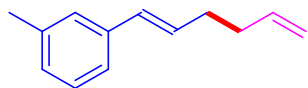
3b

R2-130-1p, ¹H NMR, AV400, CDCl₃



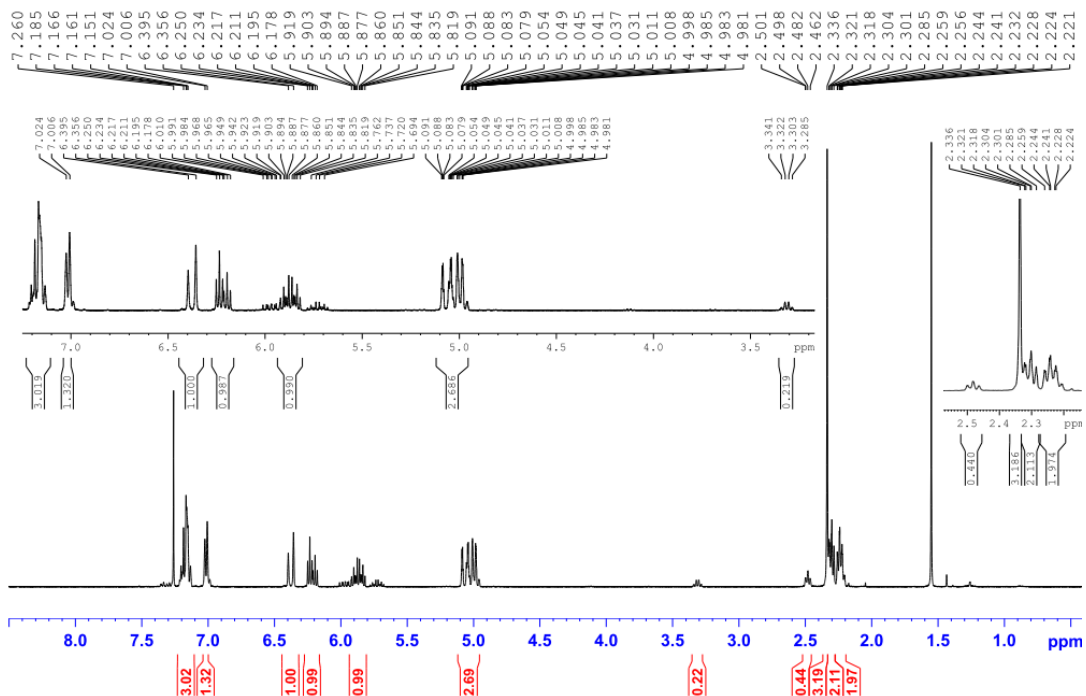
R2-130-1p, ¹³C NMR, AV400, CDCl₃



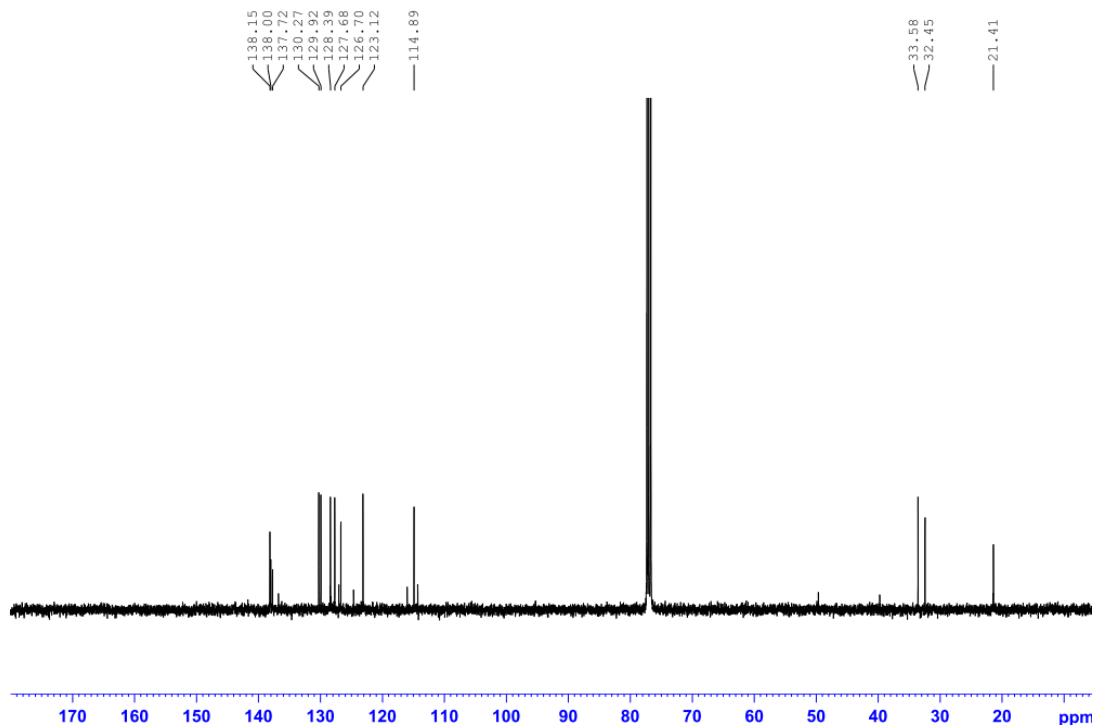


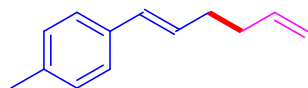
3c

W1-060-1, 400MHz(BBFO2), 1H NMR, CDCl3



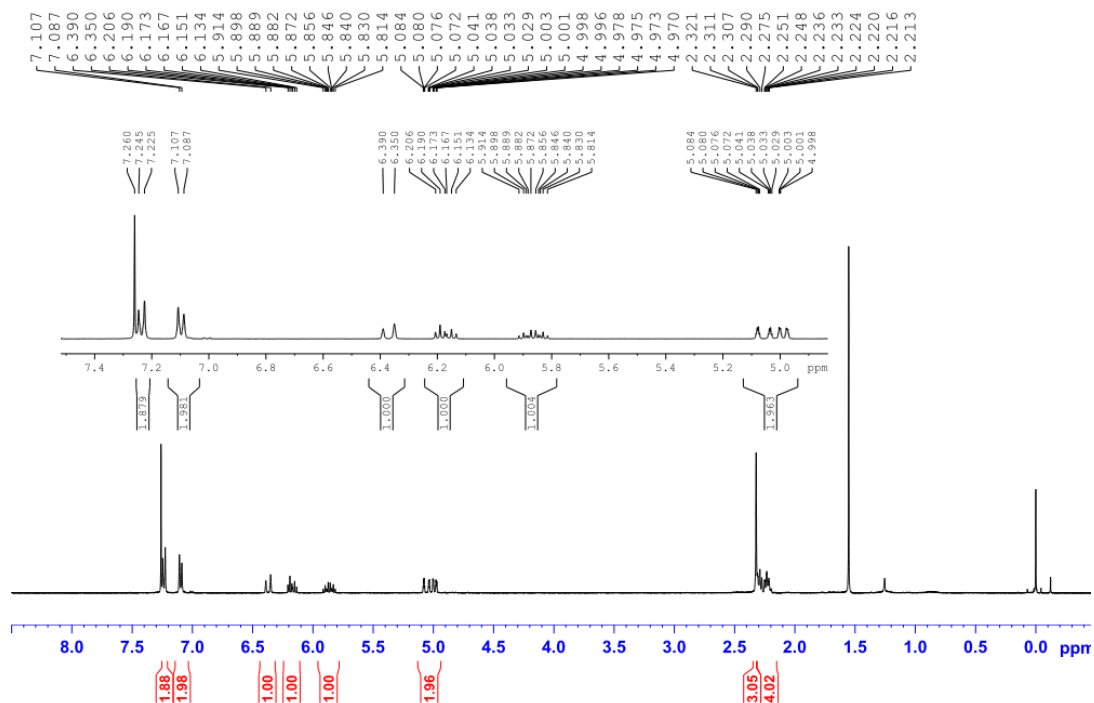
W1-060-1, 400MHz(BBFO2), 13C NMR, CDCl3



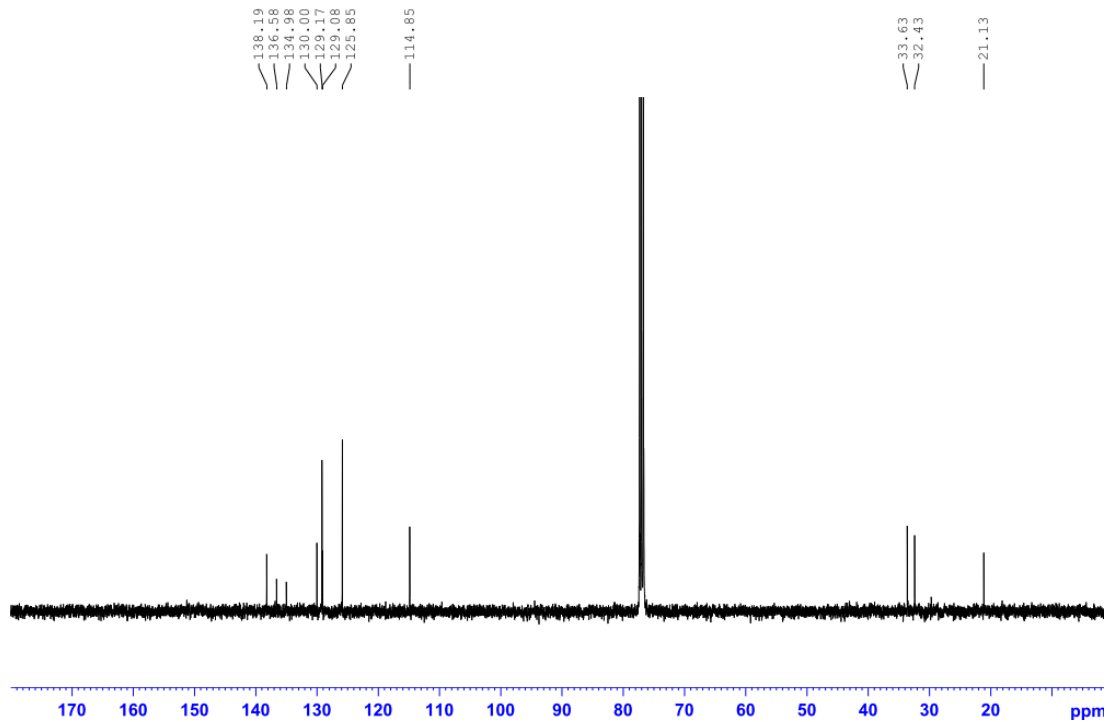


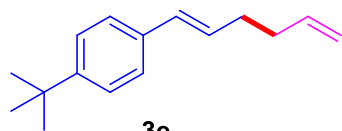
3d

R3-011-1, 1H, Bruker 400 BBF01, CDCl₃

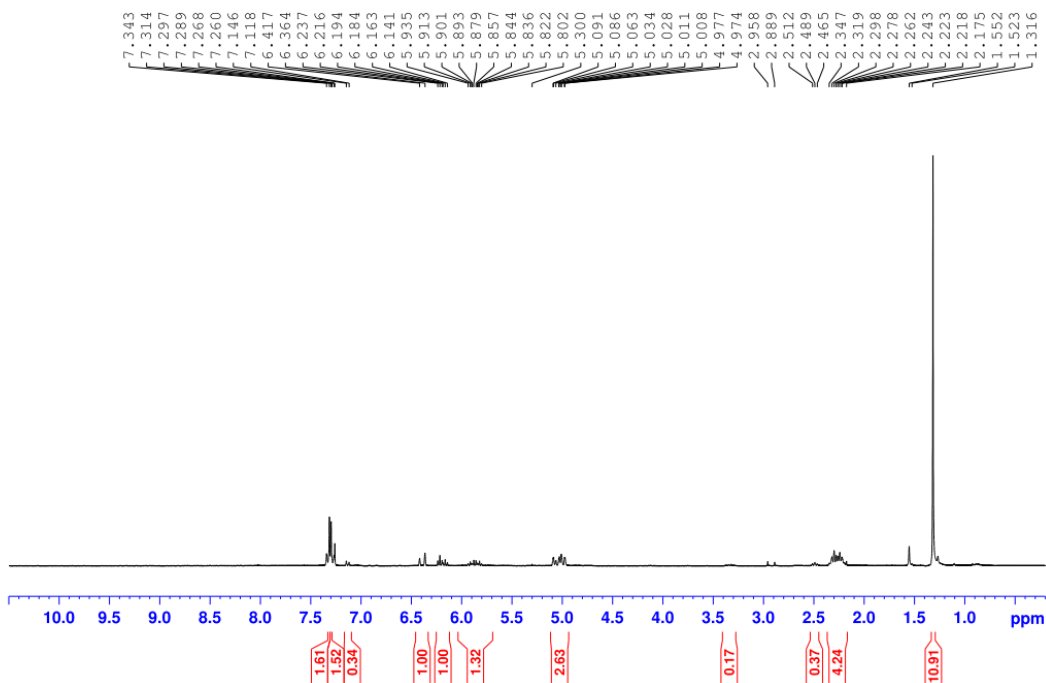


R3-011-1, 13C, Bruker 400 BBF01, CDCl₃

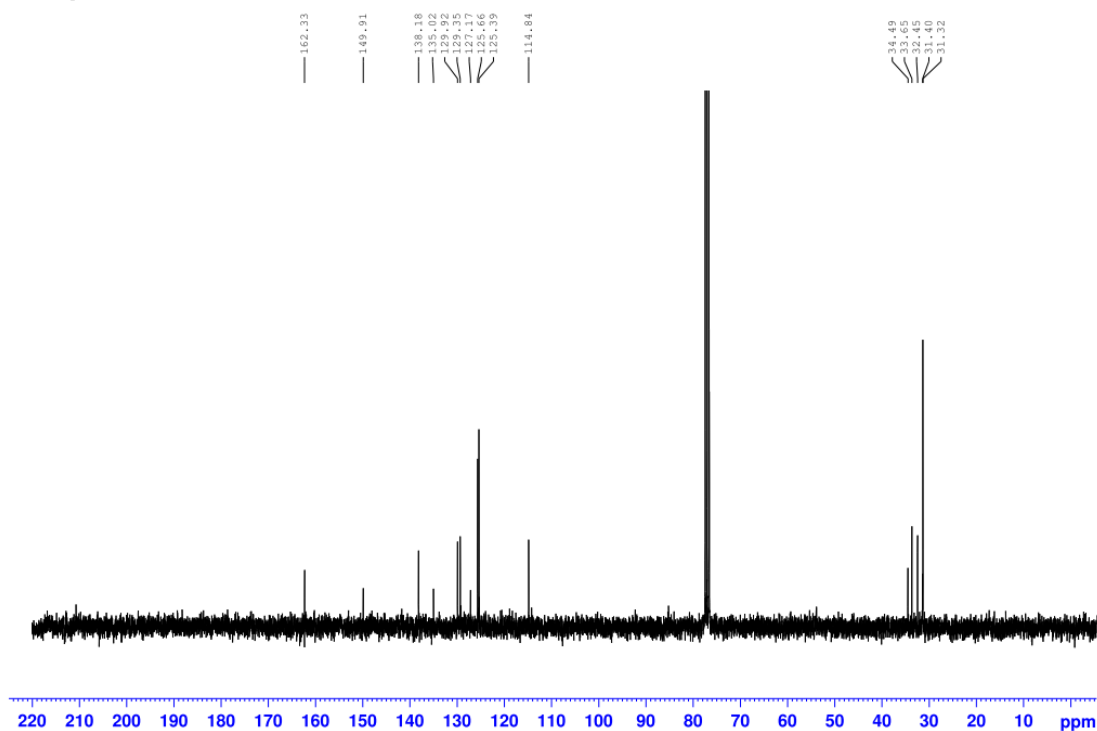


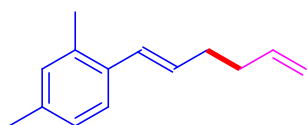


R3016-p, 300 MHz, ¹HNMR, CDCl₃



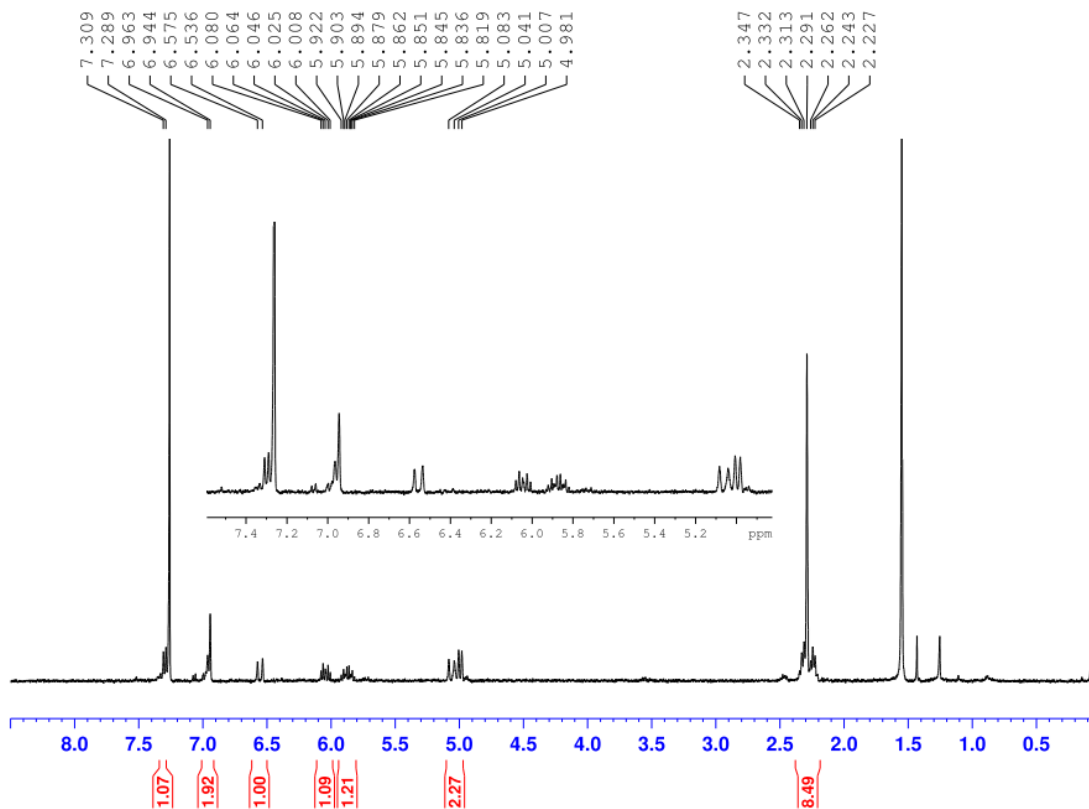
R3016-p, 300 MHz, ¹³CNMR, CDCl₃



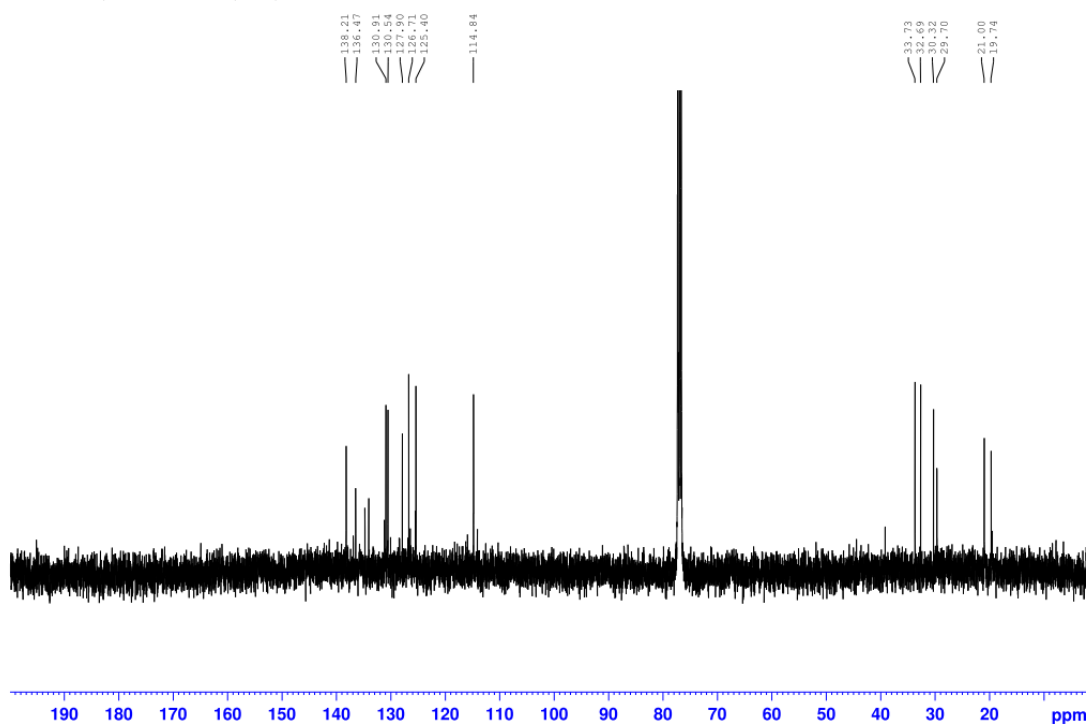


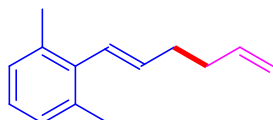
3f

R2-143-1p, HNMR, AV400

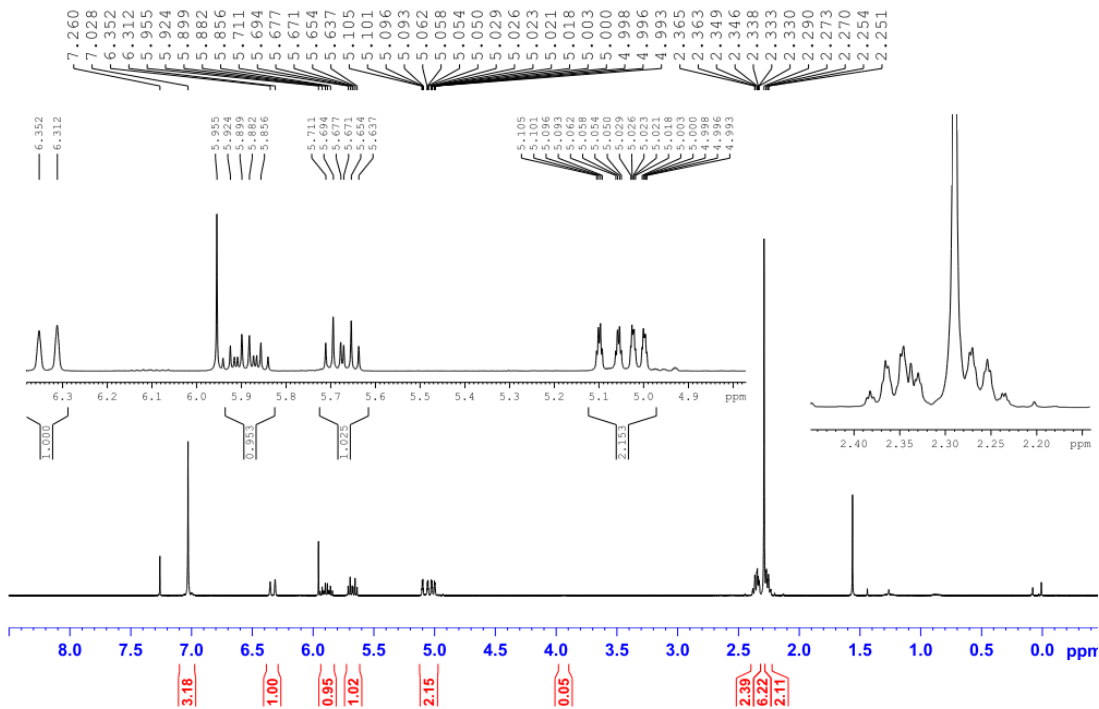


R2-143-1p, BBF01-400Hz, 13C, cdcl3

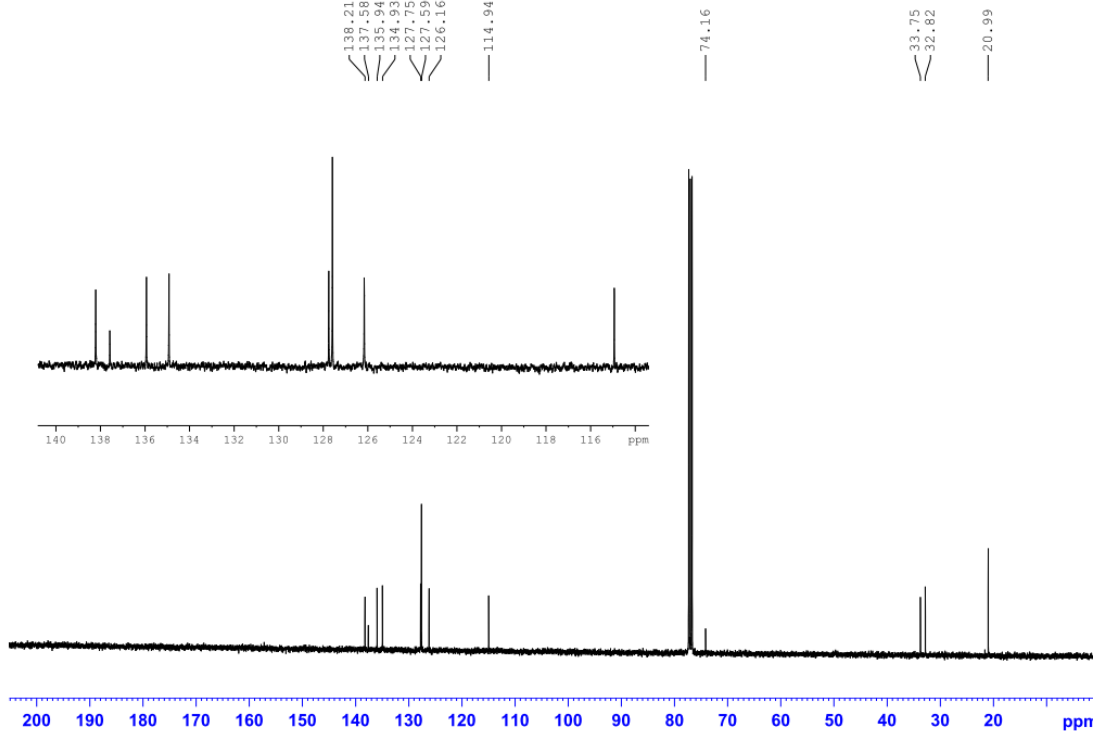


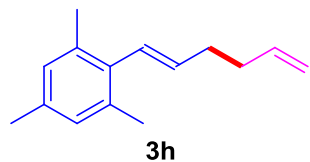


R2-137-1, BBF01-400Hz, 1H, cdcl3

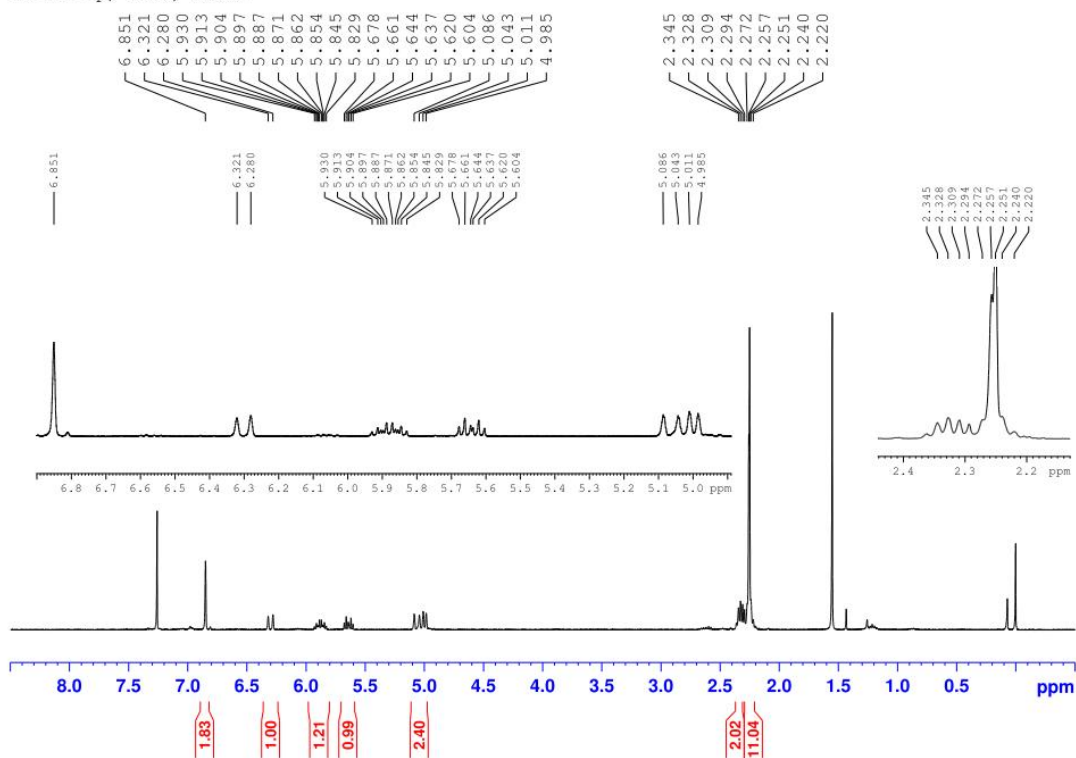


R2-137-1, BBF01-400Hz, 13C, cdcl3

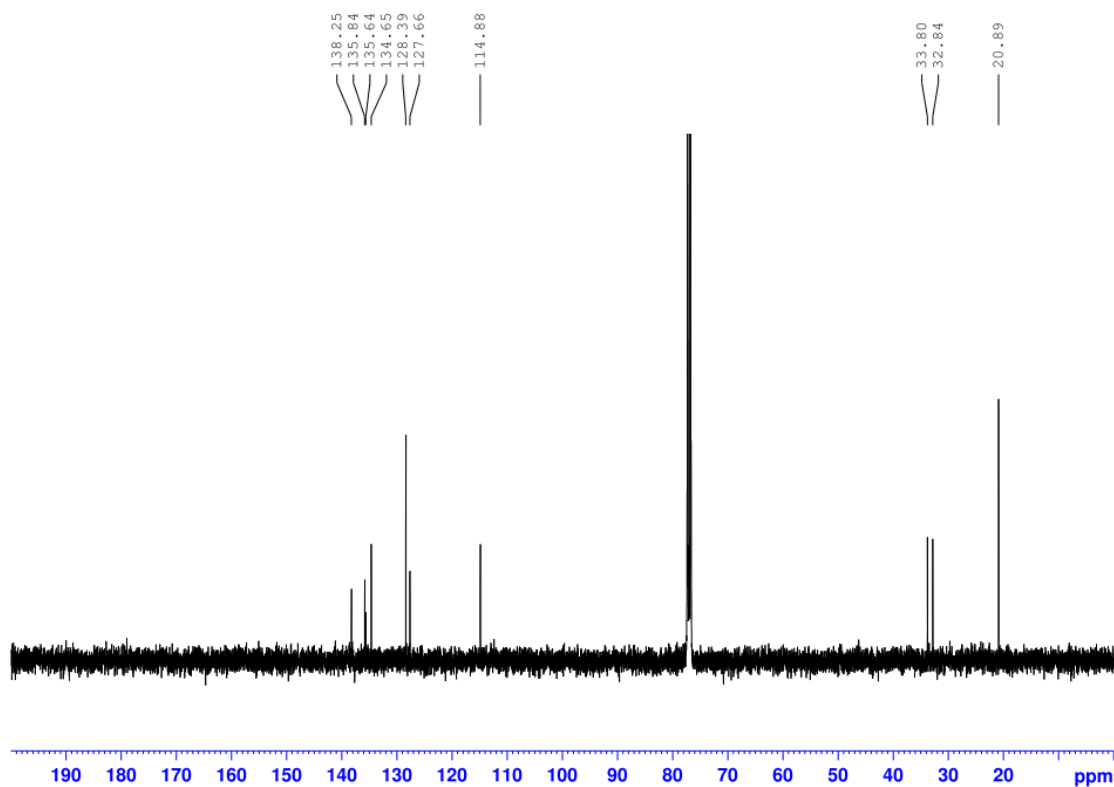


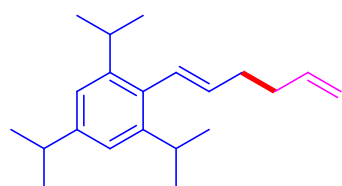


R2-144-1p, HNMR, AV400



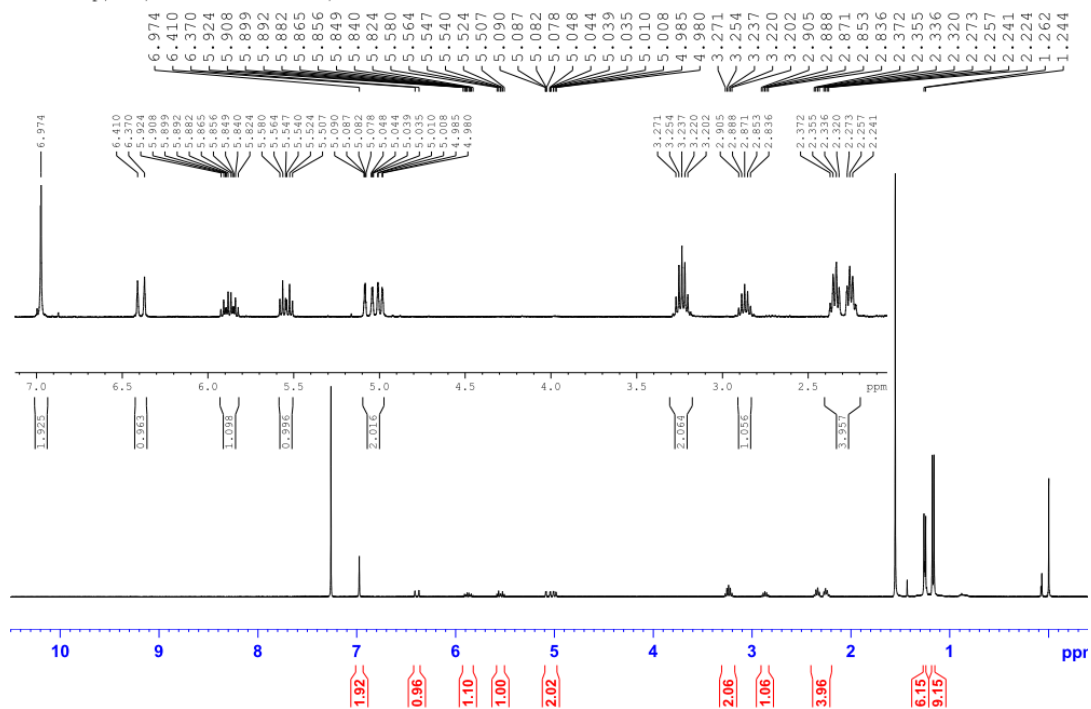
R2-144-1p, 13C NMR, AV400, cdcl3



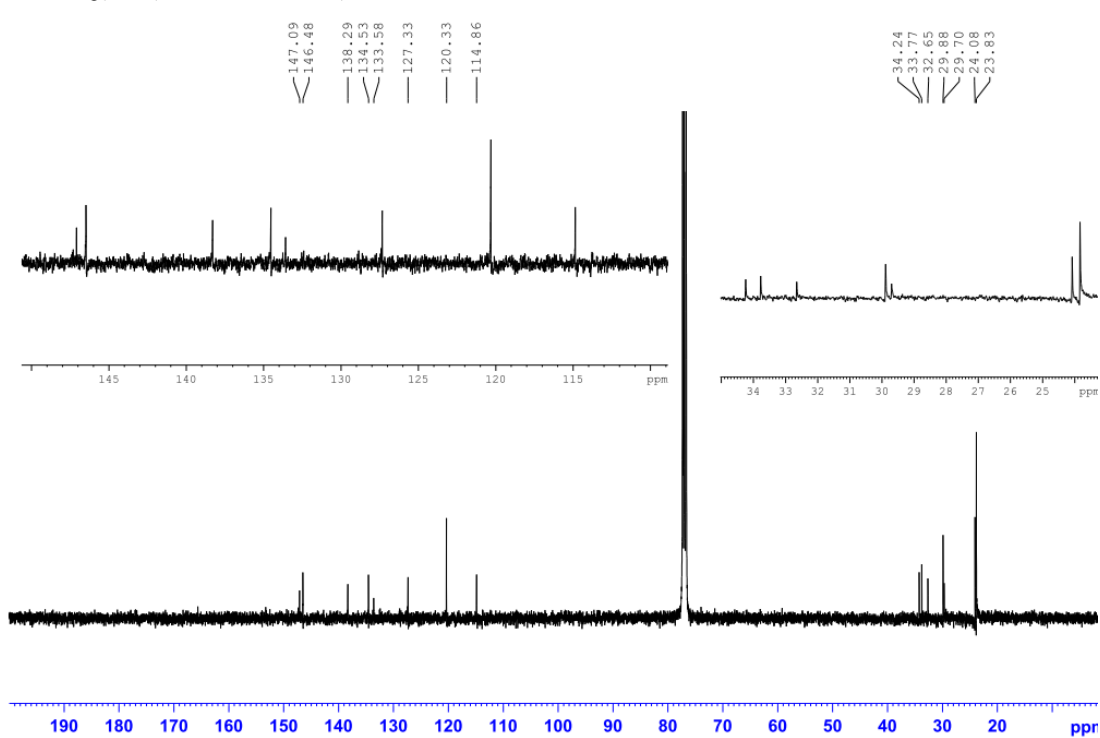


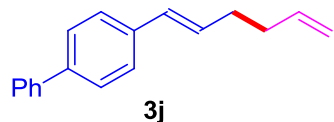
3i

R3-022-1p, 1H, Bruker 400 BBF01, CDCl3

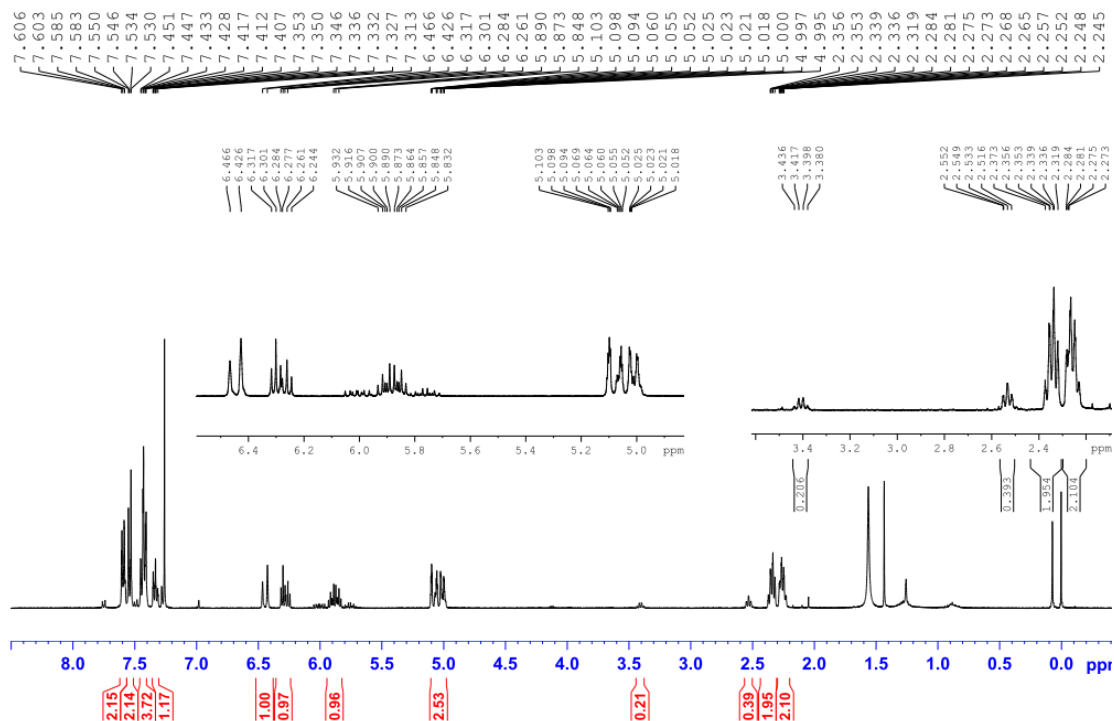


R3-022-1p, 13C, Bruker 400 BBF01, CDCl3

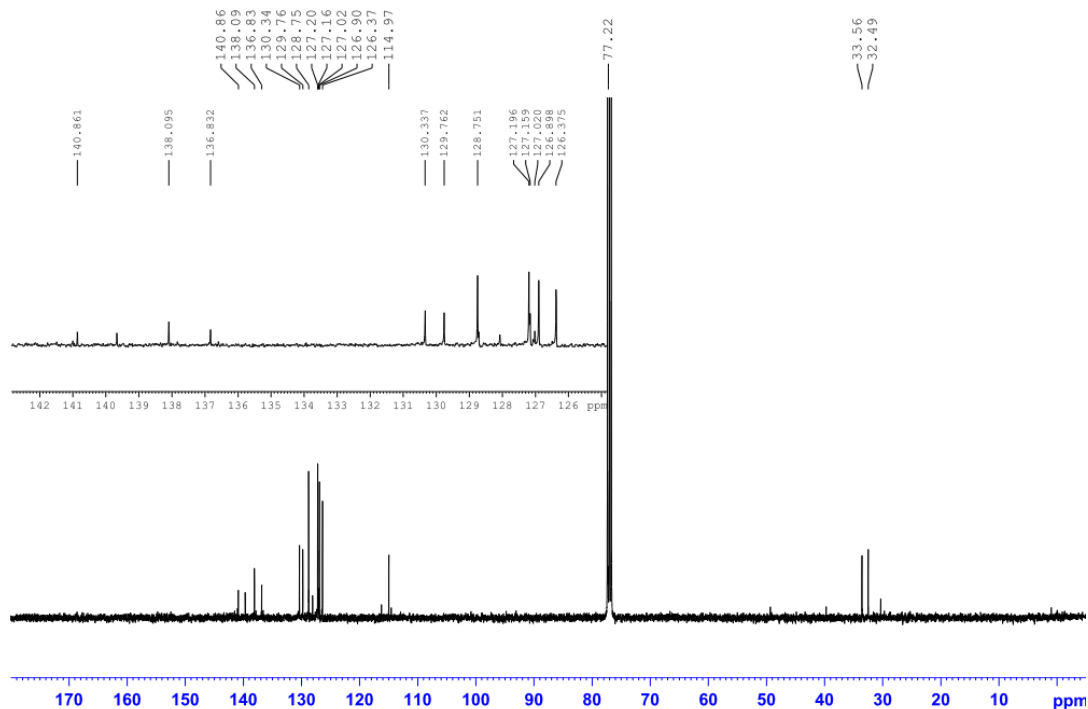


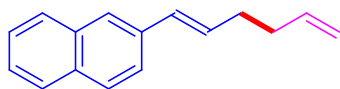


R2-138-1P, BBFO1-400Hz, 1H, cdcl3



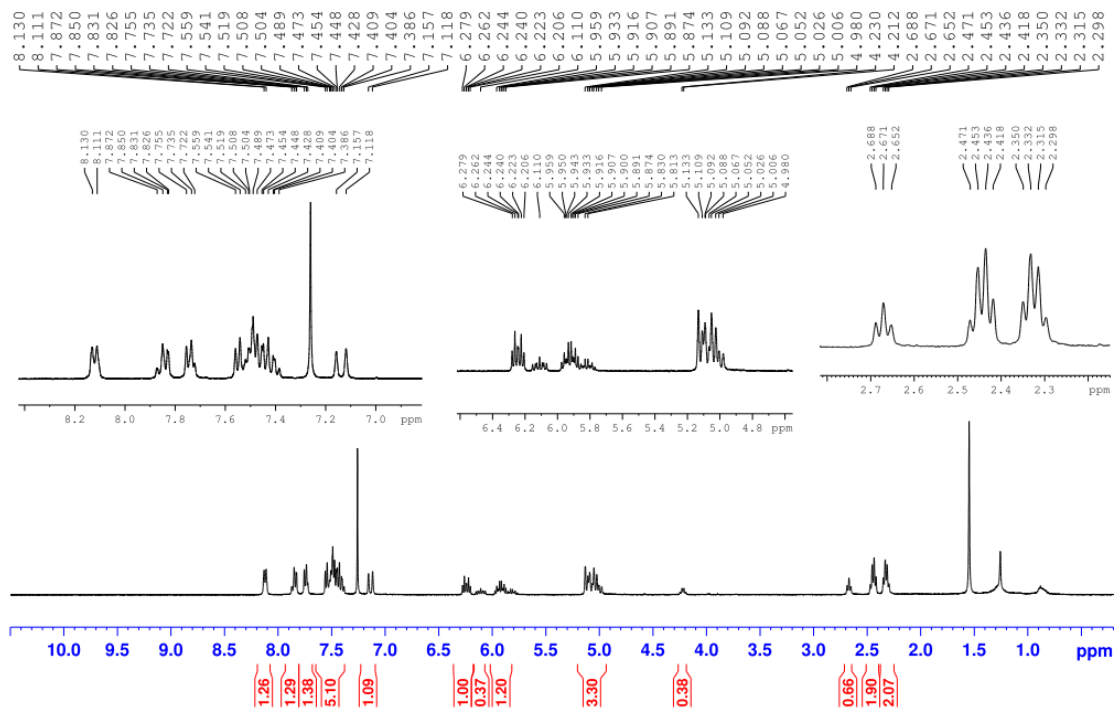
R2-138-1P, BBFO1-400Hz, 13C, cdcl3



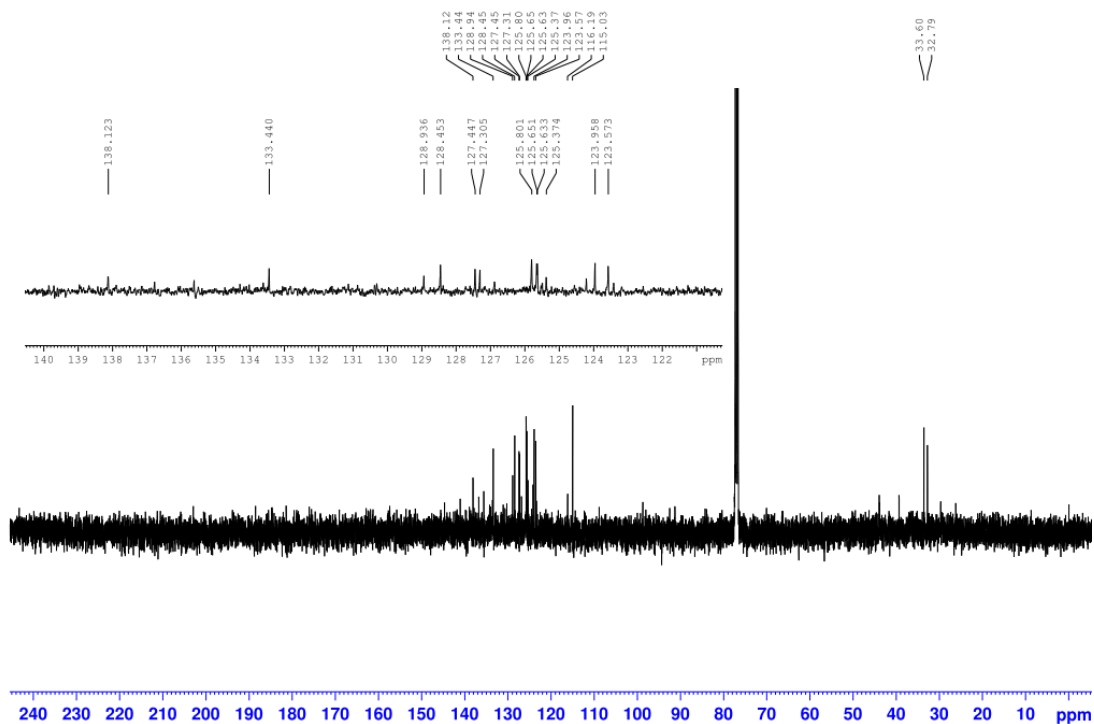


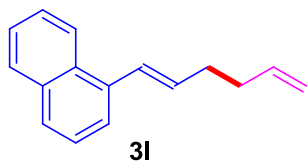
3k

R2-145-1, BBFO1-400Hz, 1H, cdcl3

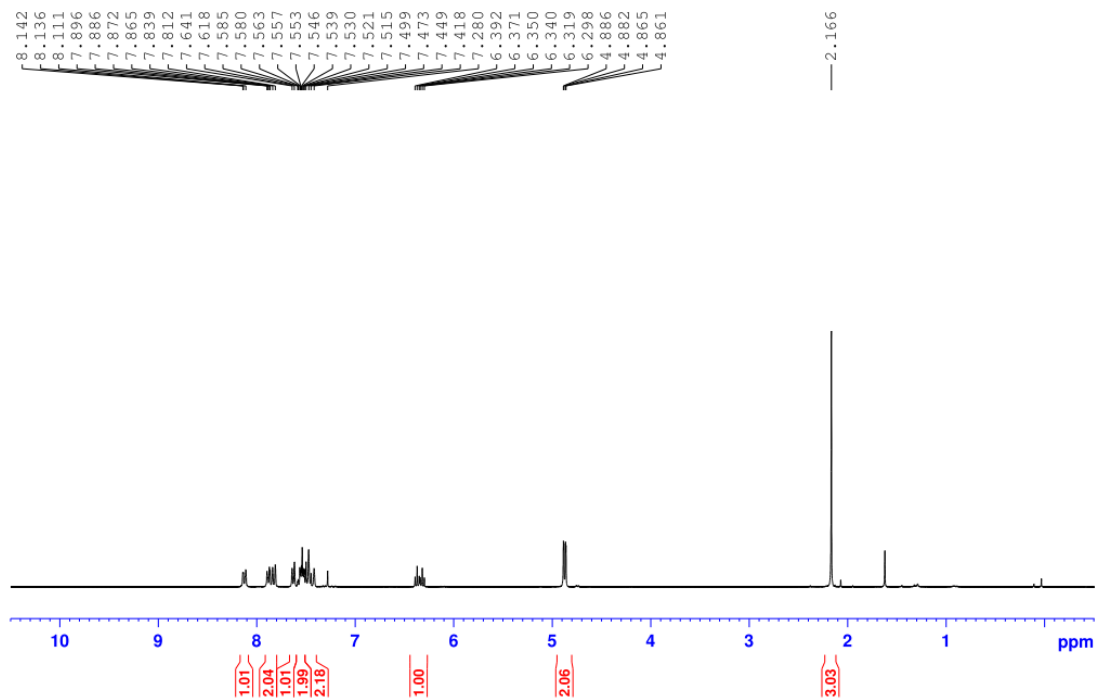


R2-145-1, BBFO1-400Hz, 13C, cdcl3

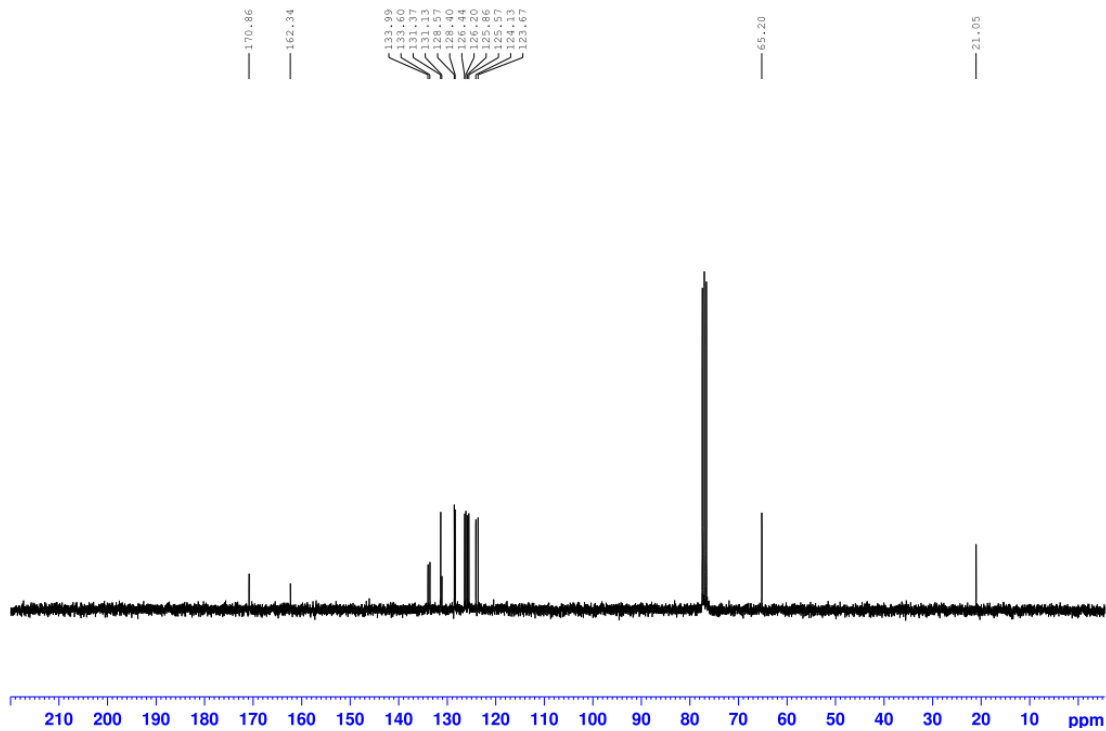


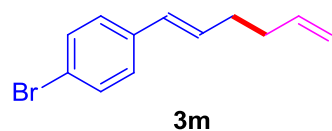


R3015-p, 300 MHz, ¹H NMR, CDCl₃

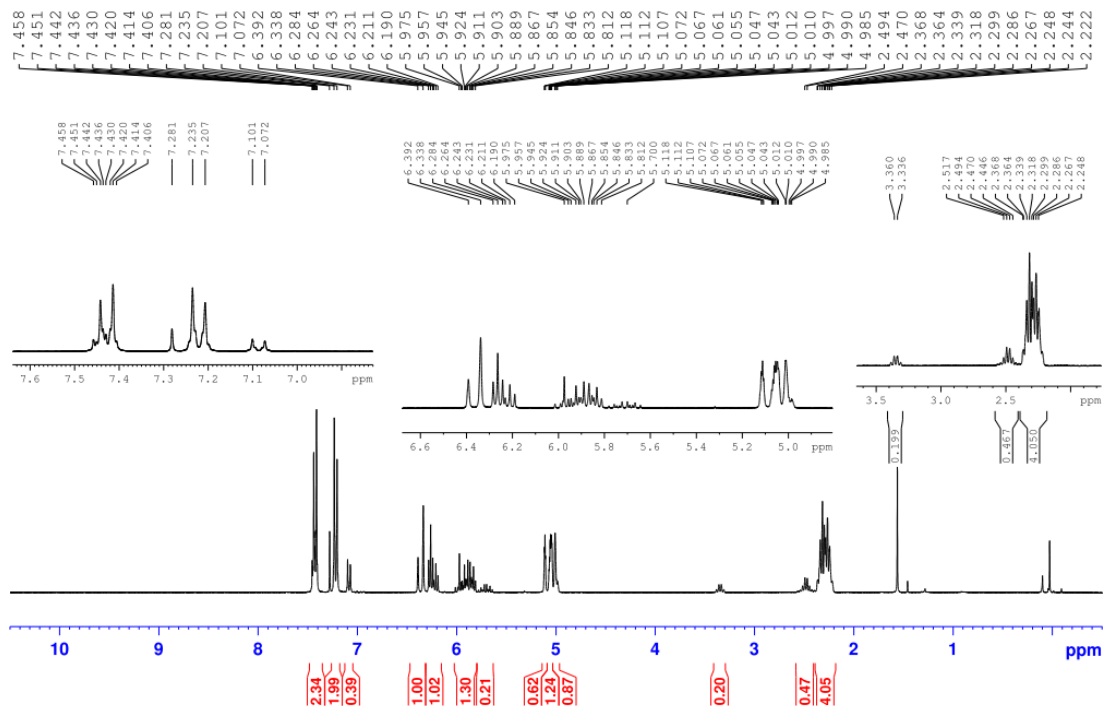


R3015-p, 300 MHz, ¹³C NMR, CDCl₃

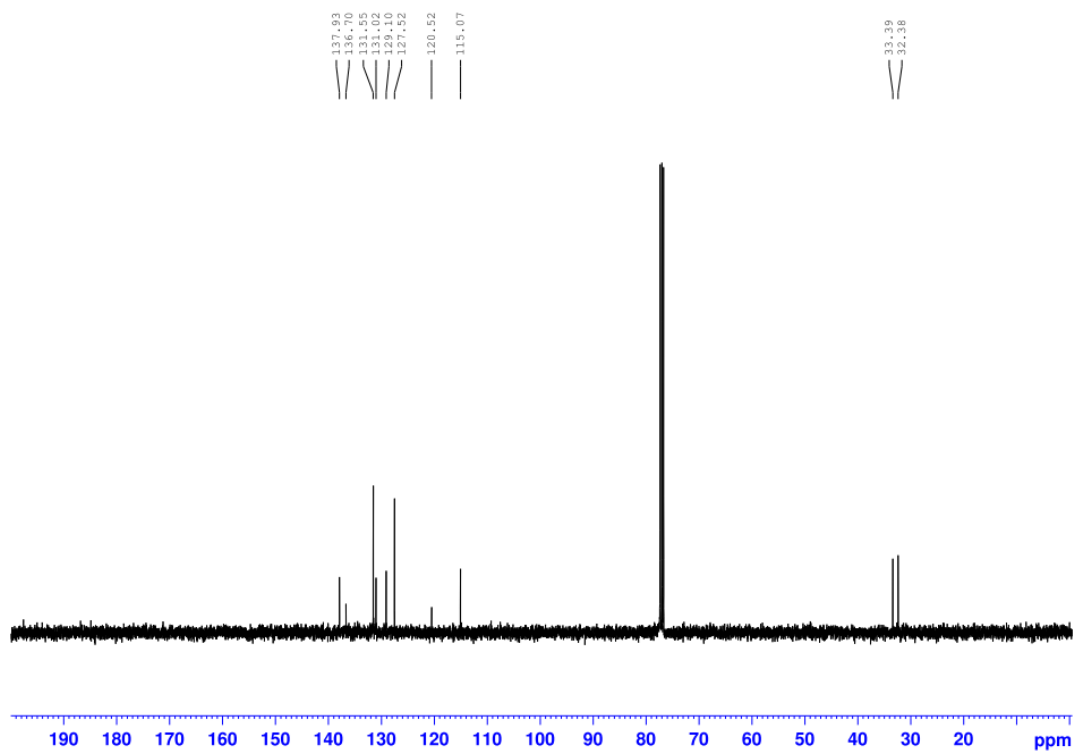


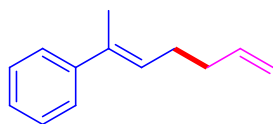


R2-150-2, 1H NMR, 300 MHz, CDCl₃



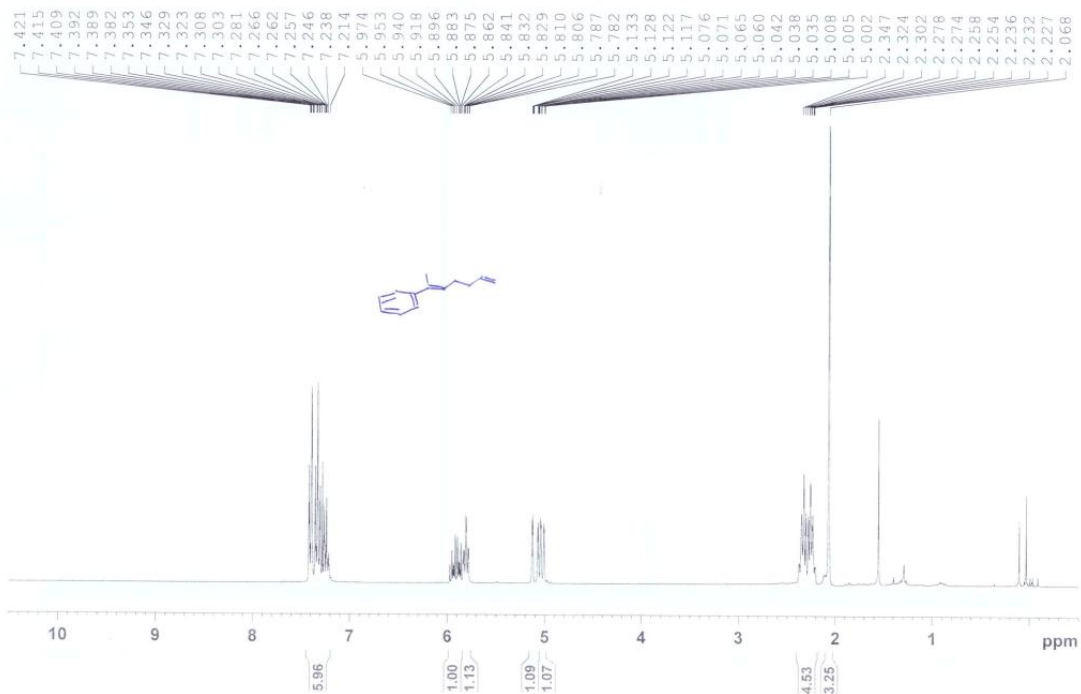
R2-150-1p, CDCl₃, AV400, 13C NMR, AUG-2011



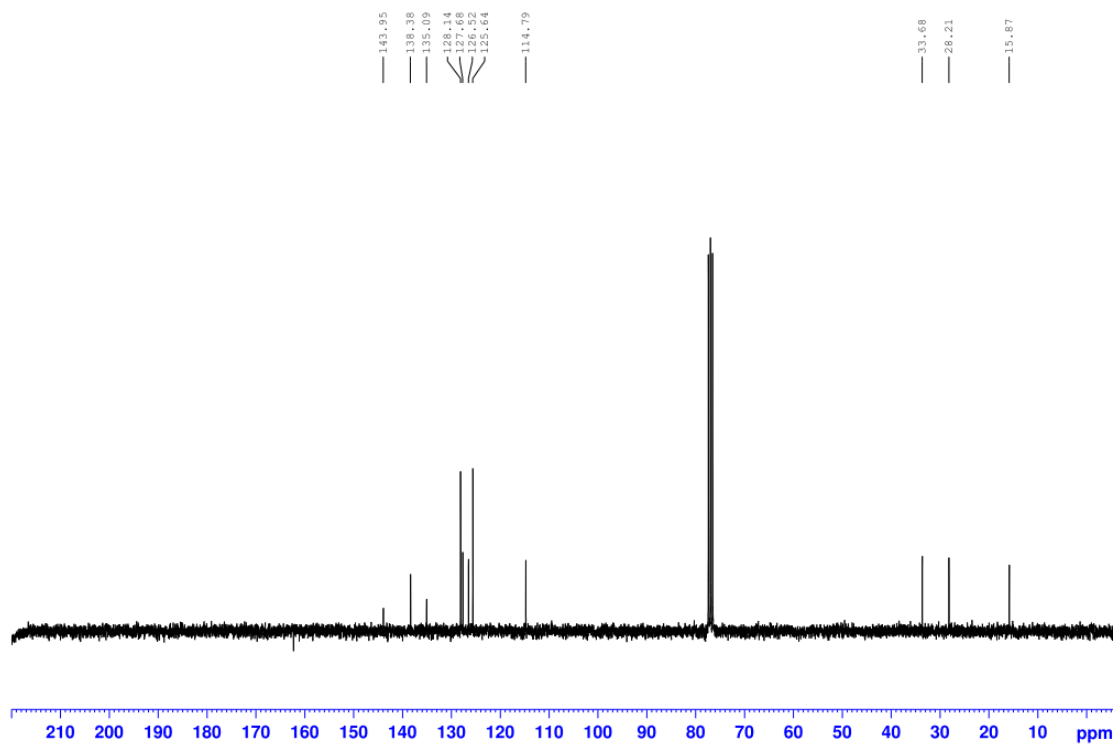


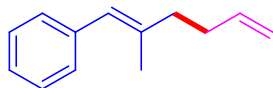
3n

R3042-1p, ¹H NMR, CDCl₃, 300 MHz



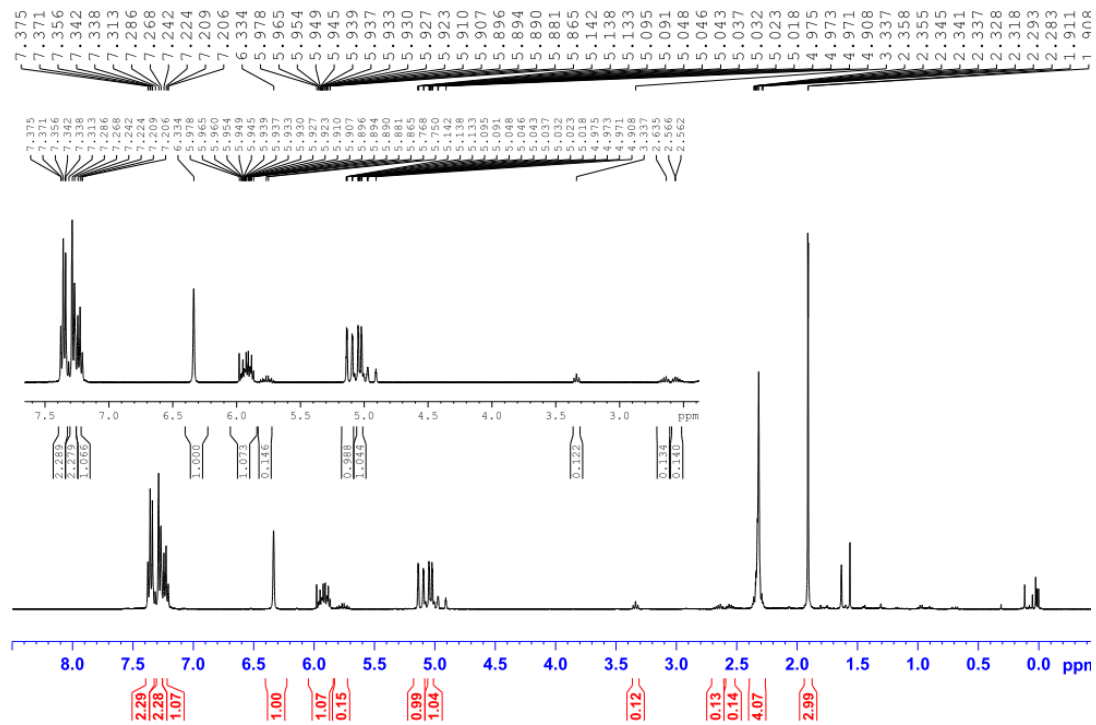
R3042-1p, ¹³C NMR, CDCl₃, 300 MHz



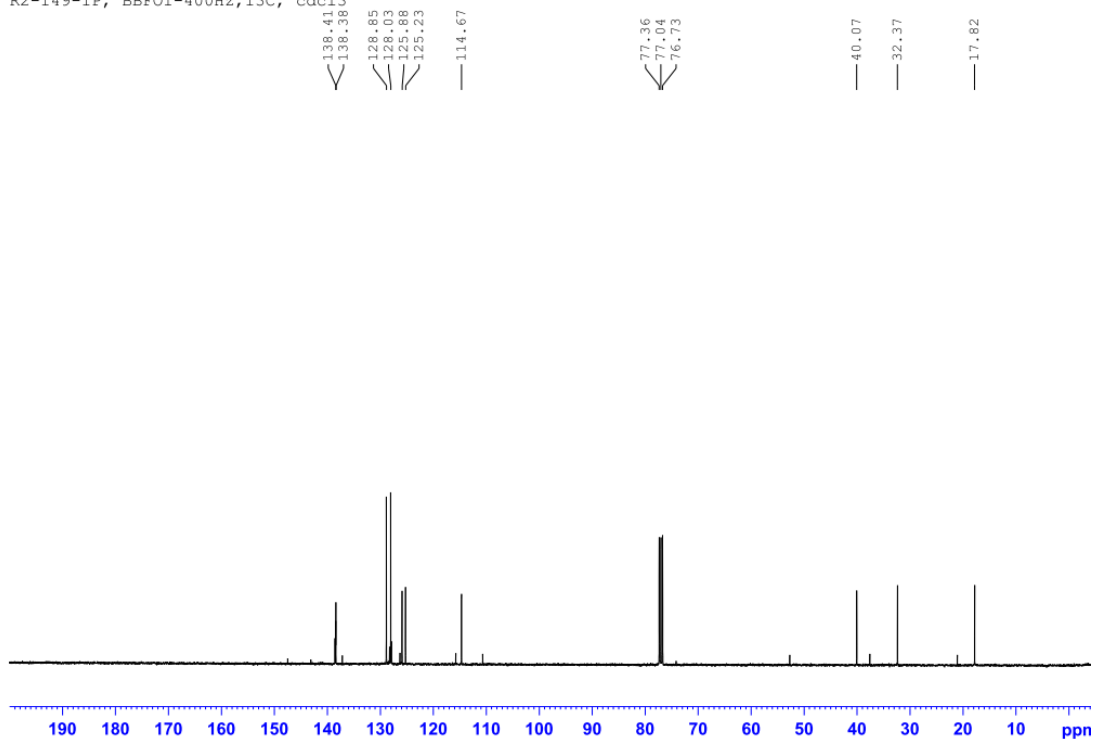


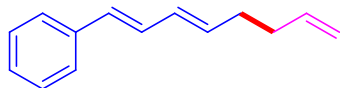
3o

R2-149-1P, BBFO1-400Hz, 1H, cdcl3



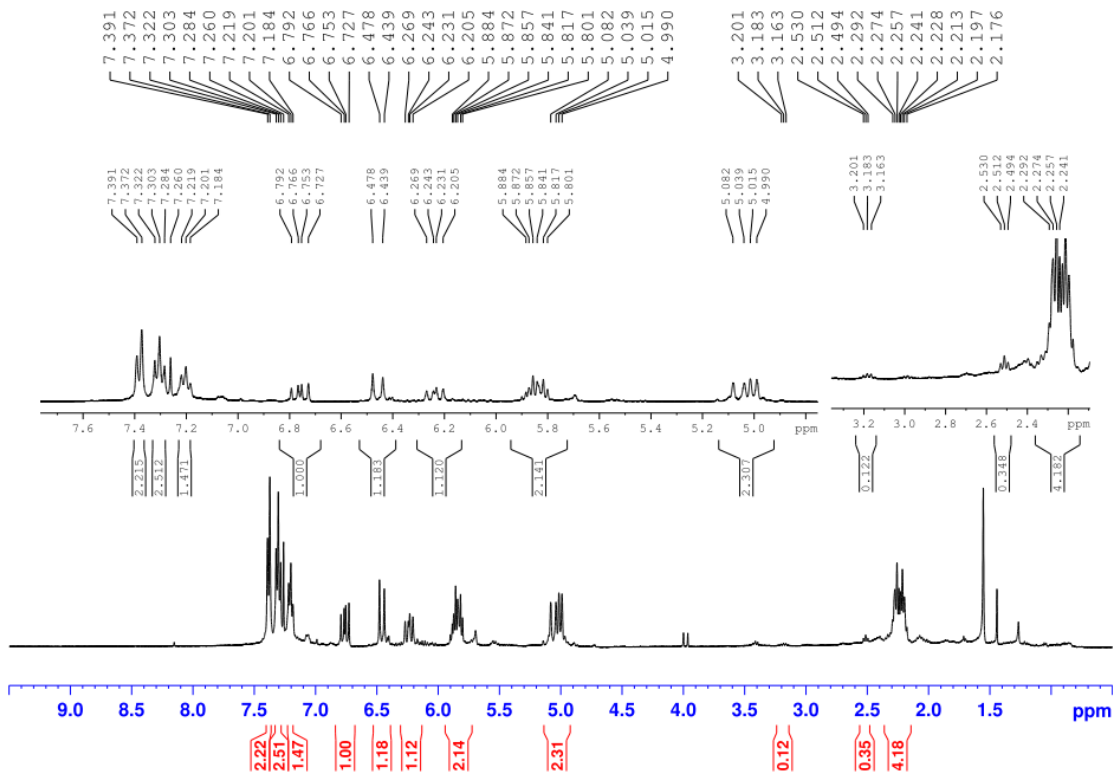
R2-149-1P, BBFO1-400Hz, 13C, cdcl3



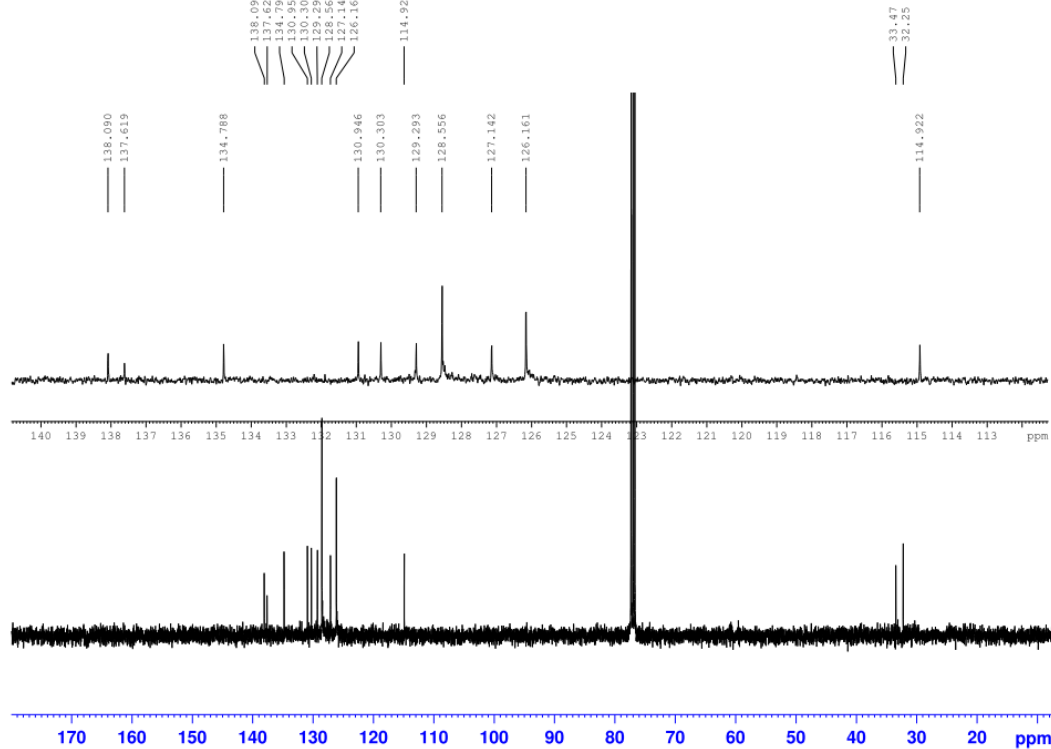


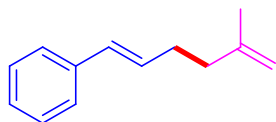
3p

D2-107-1p, ¹H NMR, AV400MHz, CDCl₃



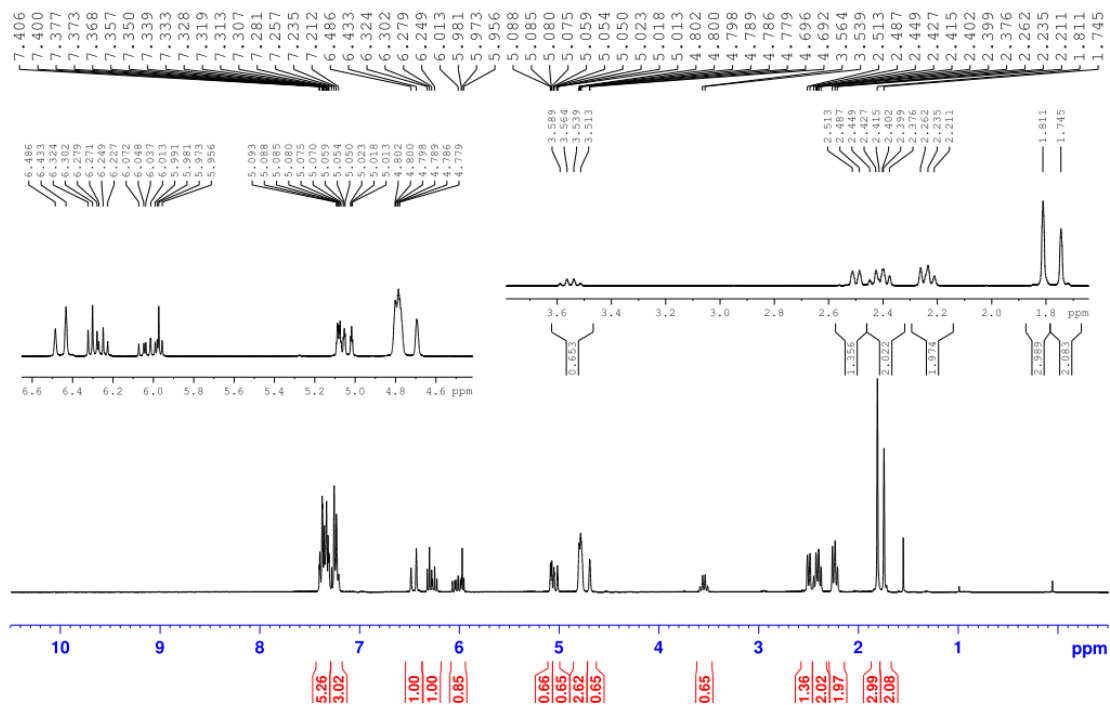
D2-107-1p, ¹³C NMR, AV400MHz, CDCl₃



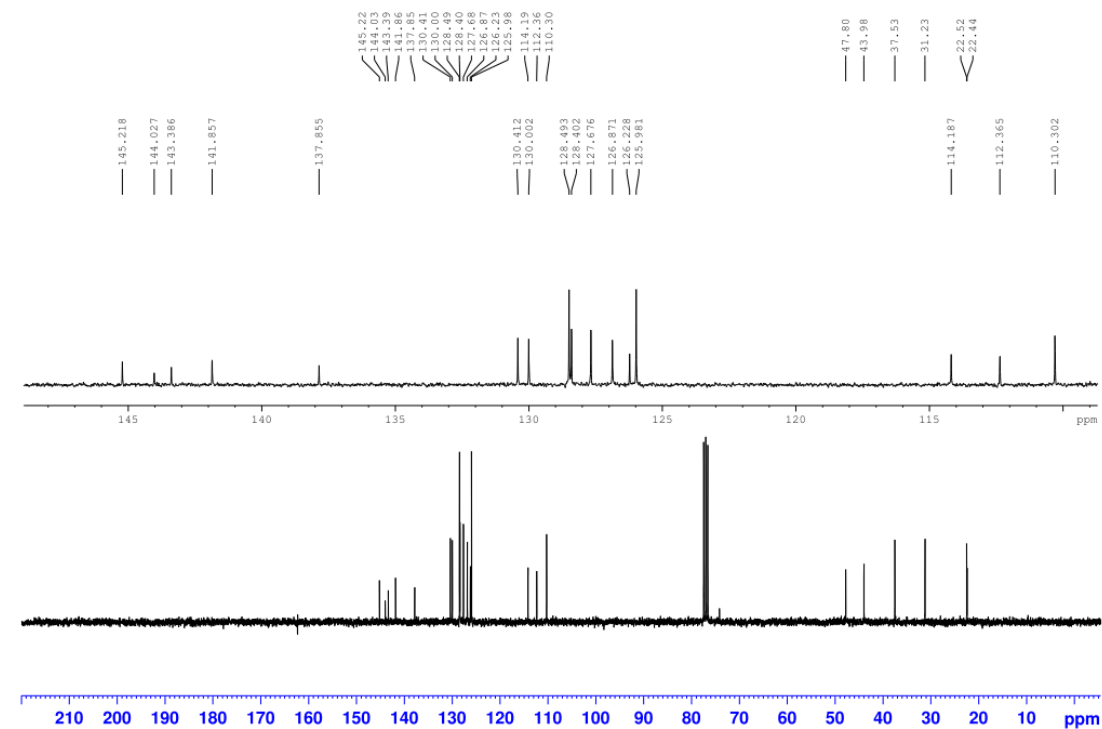


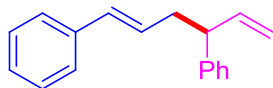
3q

R3005-p, 300 MHz, ¹HNMR, CDCl₃



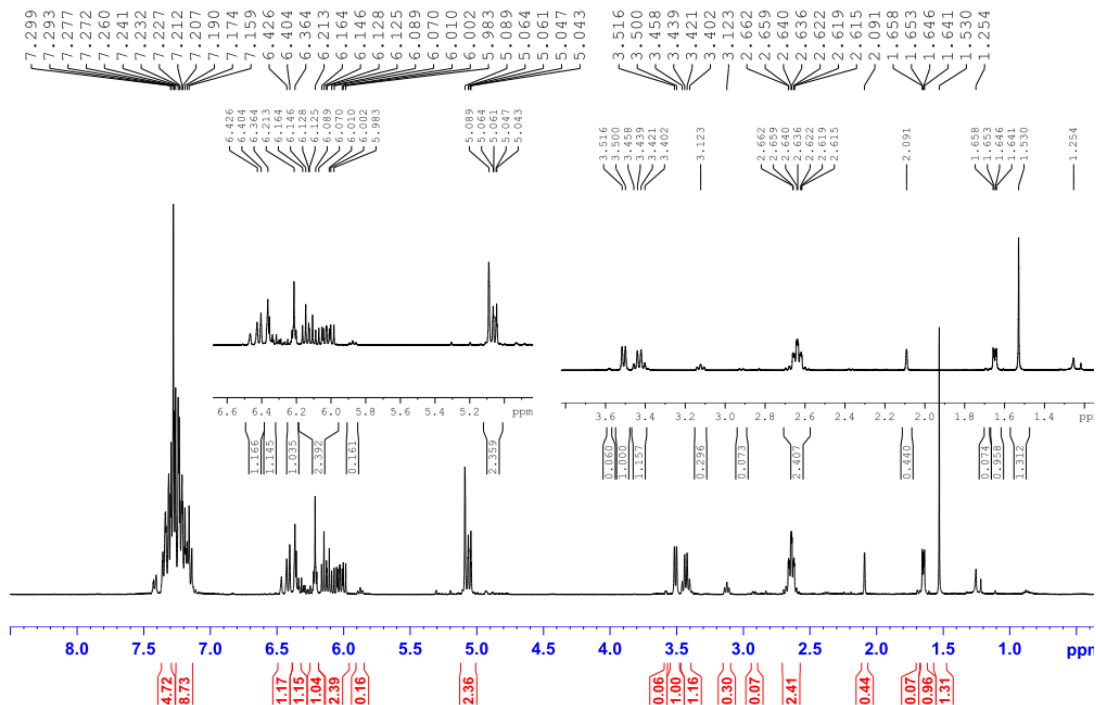
R3005-p, 300 MHz, ¹³CNMR, CDCl₃



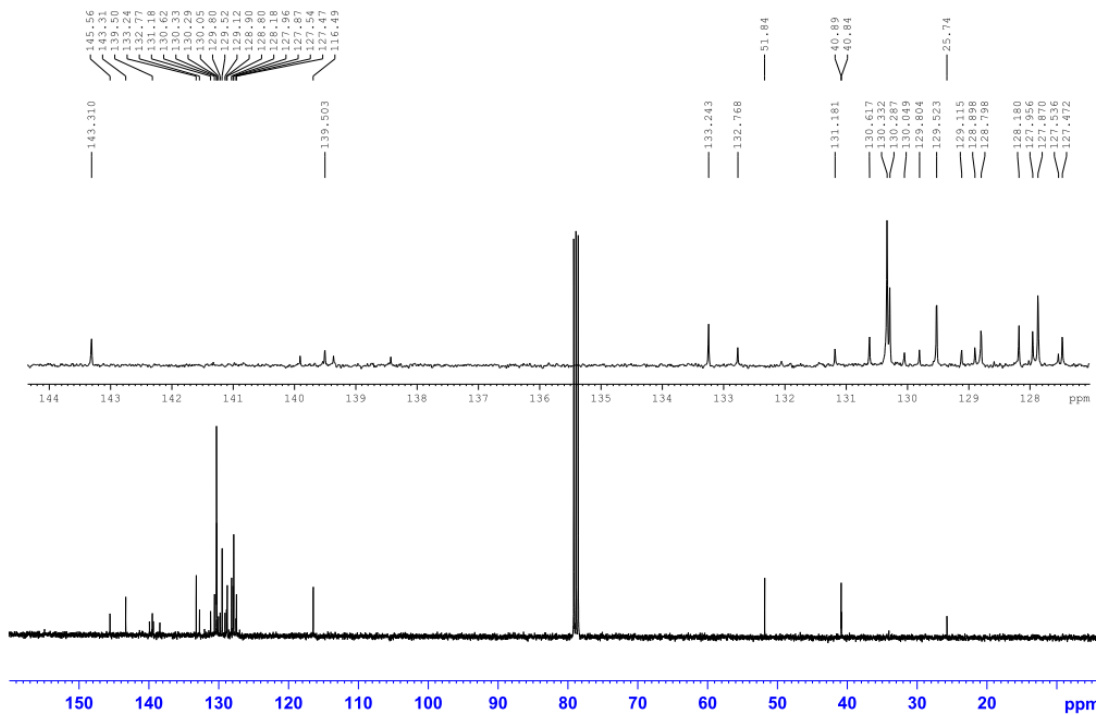


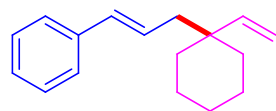
3r

R3-008-1, 1H, Bruker 400 BBFO1, CDCl₃



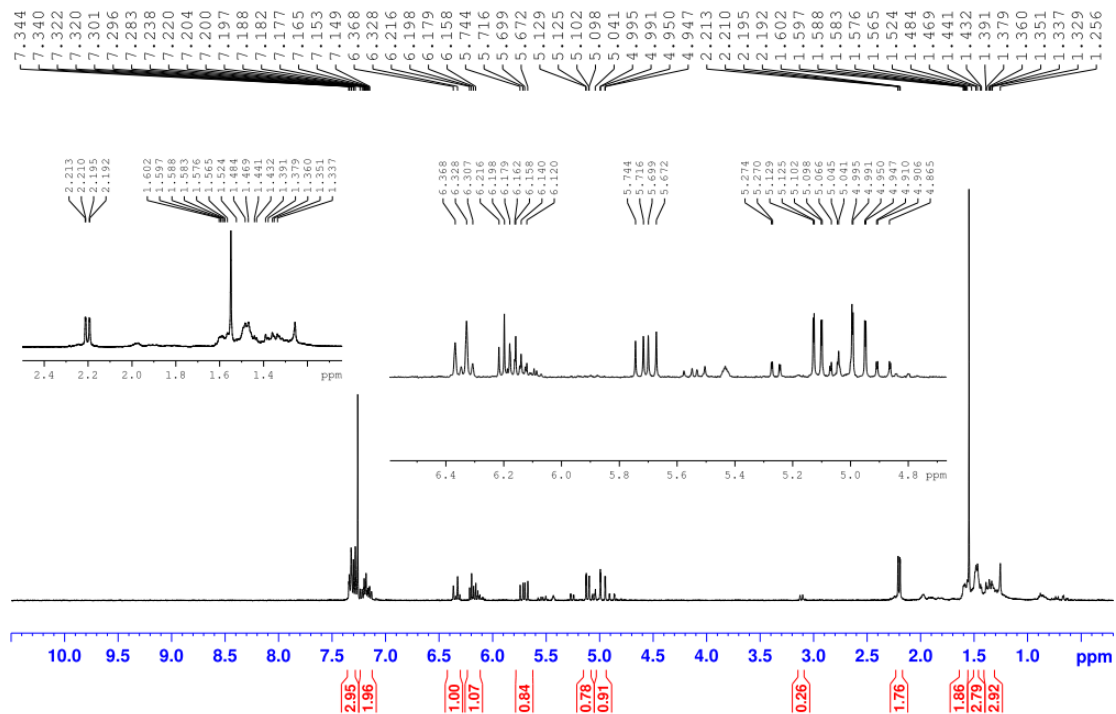
R3-008-1, 13C, Bruker 400 BBFO1, CDCl₃



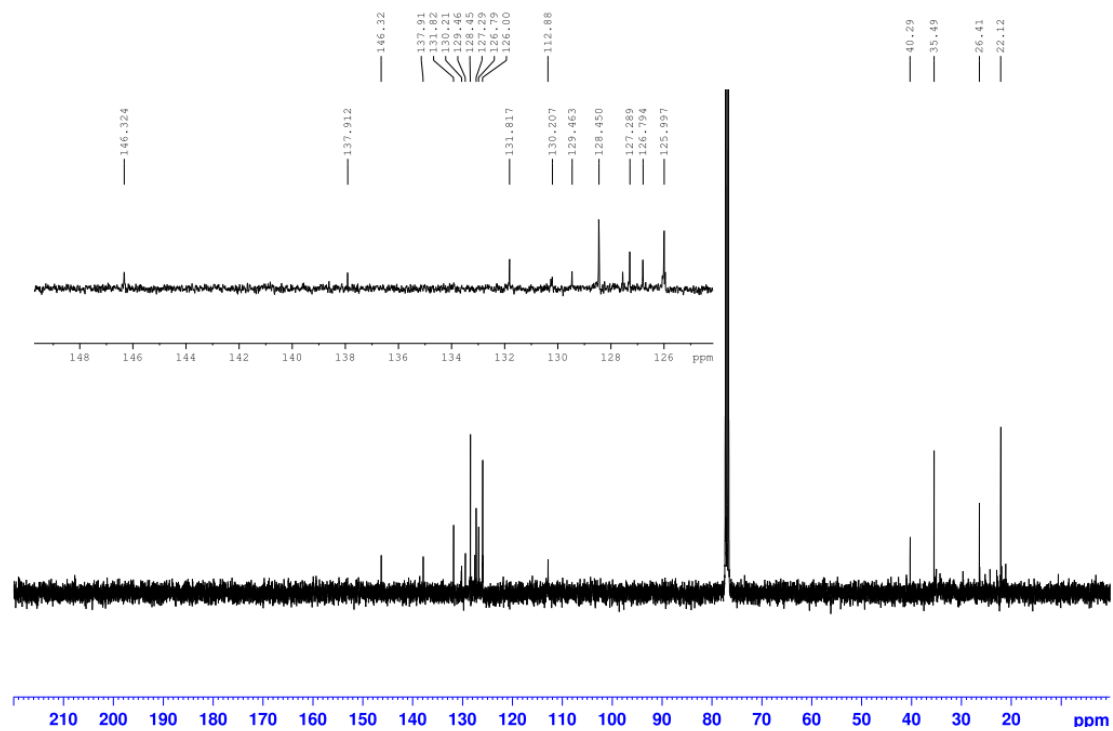


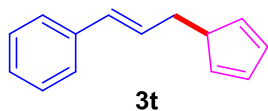
3s

R3-040-1p, 1H, BBFO1,400 Hz, CDC13

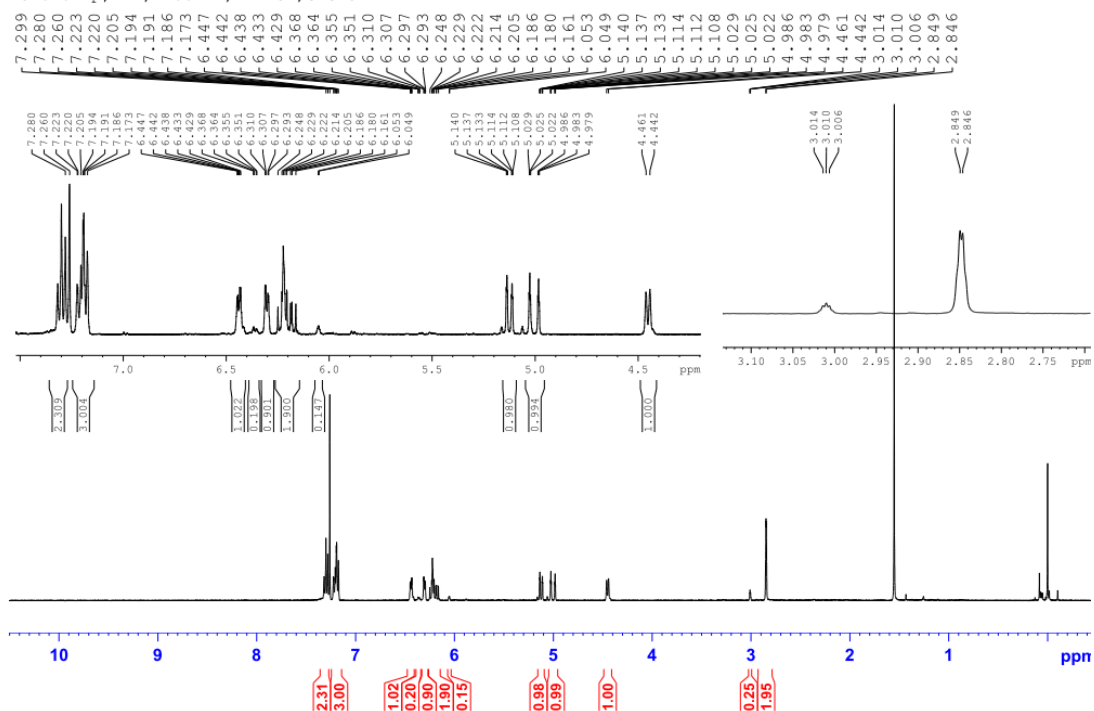


R3-040-1p, 13C, BBFO1,400 Hz, CDC13





R3-018-1p, ¹H, 400MHZ, BBFO2, CDC13



R3-018-1p, ¹³C, 400MHZ, BBFO2, CDC13

