Supporting information

Stereoselective Palladium-Mediated Decarboxylative γ-Arylation of Acyclic, Unsaturated Carboxylic Acids

Ina Scheipers, Eva Koch and Armido Studer*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany, studer@uni-muenster.de

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1 General

Reactions involving air- or moisture-sensitive reagents or compounds were carried out in flame dried glass ware under argon atmosphere using standard *Schlenk* techniques.

Reagents and solvents were purified according to standard procedures or used as received from *Sigma Aldrich, Fluka, Acros Organics, TCI* or *ABCR*. Pd-catalyst and Cs_2CO_3 were used as received from *Sigma Aldrich*.

Melting points (MP) were measured on a *Stuart SMP10* and are uncorrected.

Infrared spectra (IR) were measured on a *Digilab FTS 4000* spectrometer and the intensity of the signals were described with *w* (weak), *m* (medium) and *s* (strong).

^{1}H NMR, ^{13}C NMR and NOE spectra were measured on *DPX 300*, *Bruker AV 300*, *Bruker AV 400* or *DD2 600* spectrometer. Chemical shifts (δ in ppm) were referenced on the residual peak of $CDCl_3$ (^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.0) and the multiplicity of all signals were reported as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). NOE spectra were measured in order to determine the stereoselectivity of the double bond.

Thin layer chromatography (TLC) was performed using *Merck* silica gel 60 F-254 plates, detection of compounds with UV light (λ = 254 nm) or dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$), followed by heating.

Column chromatography was performed on *Merck* silica gel 60 (40 – 63 µm) or *Acros Organics* silica gel (35 – 70 µm) with an excess argon pressure up to 0.5 bar. Enantiomeric excess was determined by HPLC analysis using a Chiralcel DJ-RH column (Agilent 1200 Series HPLC with auto sampler and UV DAD), with ACN:H_2O = 65:35 (isocratic) at a flow rate of 1.0 mL/min at 10 °C detected at 230 nm and 354 nm wavelength.

Mass spectra were recorded on a *Bruker Daltonics Micro Tof*, a Waters-*Micromass Quatro LCZ* (ESI), *Dalton Scientific Orbitrap LTQ XL* (APCI) or a Waters-Micromass Quatro Micro (EI); peaks are given in *m*/*z* (% of basis peak).

2 General procedures

General procedure for the alkylation of esters (GP1)

Based on a literature procedure by *Hill et al.*[1] freshly distilled diisopropylamine (DIPA) (1.8 mL, 13 mmol, 1.04 equiv.) in dry THF (18 mL) was cooled to 0 °C. After the addition of *n*-BuLi (1.6 M in hexane, 8.3 mL, 1.04 equiv.) the reaction mixture was stirred for 30 minutes at 0 °C. At -78 °C the ester (12.7 mmol, 1.0 equiv.) was added dropwise and directly after that DMPU (1.6 mL, 13 mmol, 1.0 equiv.). The reaction mixture was stirred for 30 minutes at -78 °C before adding 1-chloro-2-phenylacetylene (3.4 g, 25 mmol, 2.5 equiv.). The reaction mixture was allowed to warm up to room temperature overnight, water was added and the mixture extracted with EtOAc (3 x). The combined organic layers were washed with water and with aqueous NaCl-solution (sat.) before drying over $MgSO_4$ and concentrated under reduced pressure. The title compounds were isolated after purification by column chromatography (SiO_2, P/DEE = 100/1).

General procedure for the ester hydrolysis (GP2)

The corresponding ester compound was stirred in a 1/1-mixture of THF and aqueous NaOH-solution (15 M) at 80 °C overnight. After cooling to room temperature the phases were separated. Concentrated HCl-solution (37%) was added to the aqueous phase and the resulting solution extracted with DEE (3 x). The combined organic phases were washed with aqueous NaCl-solution (sat.), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was used for the next step without further purification.

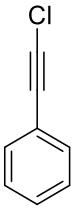
General procedure for the palladium coupling reactions (GP3)

To a flame-dried *Schlenk*-tube containing the carboxylic acid (0.286 mmol, 1.0 equiv.), $Pd(dba)_2$ (16.6 mg, 286 µmol, 10 mol%) and Cs_2CO_3 (103 mg, 0.318 mmol, 1.1 equiv.) in toluene (1.0 mL) the corresponding aryl iodide (0.318 mmol, 1.1 equiv.) was added and the reaction mixture was stirred at 110 °C for 24 h. After cooling to room temperature the mixture was filtered over Celite with Et_2O and concentrated *in vacuo*. The desired compound was obtained by column chromatography on silica gel.

3 Analytical data and spectra

3.1 Synthesis of starting materials

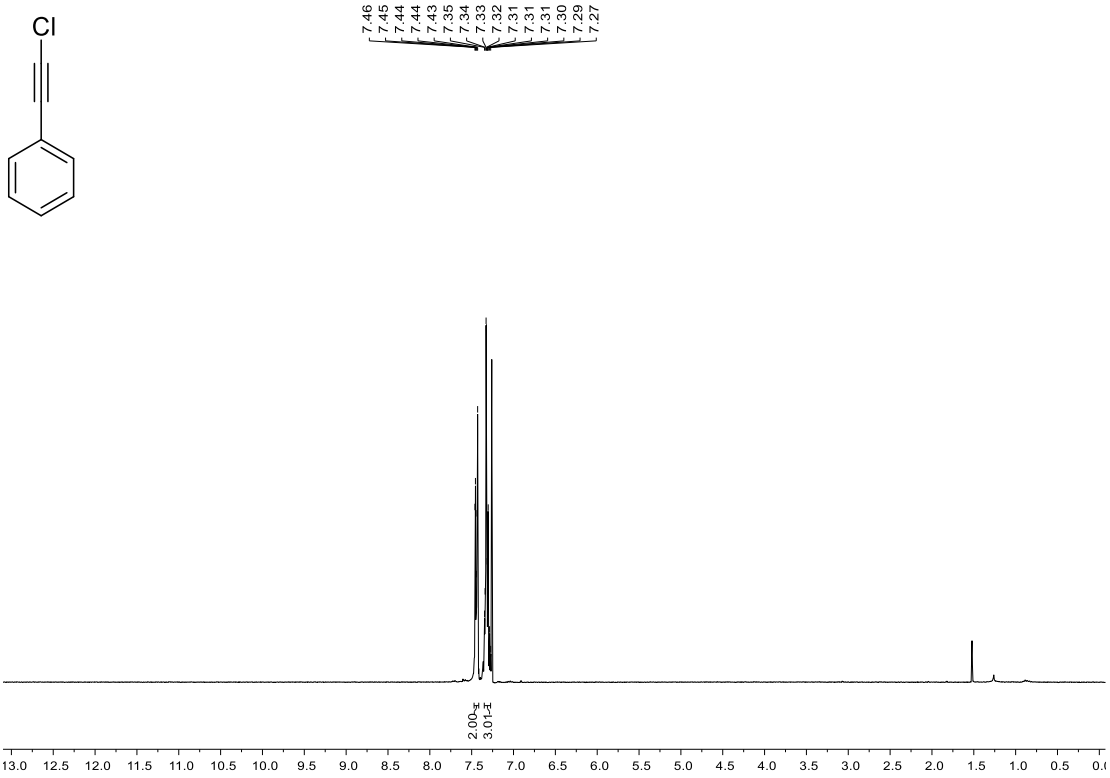
1-Chloro-2-phenylacetylene

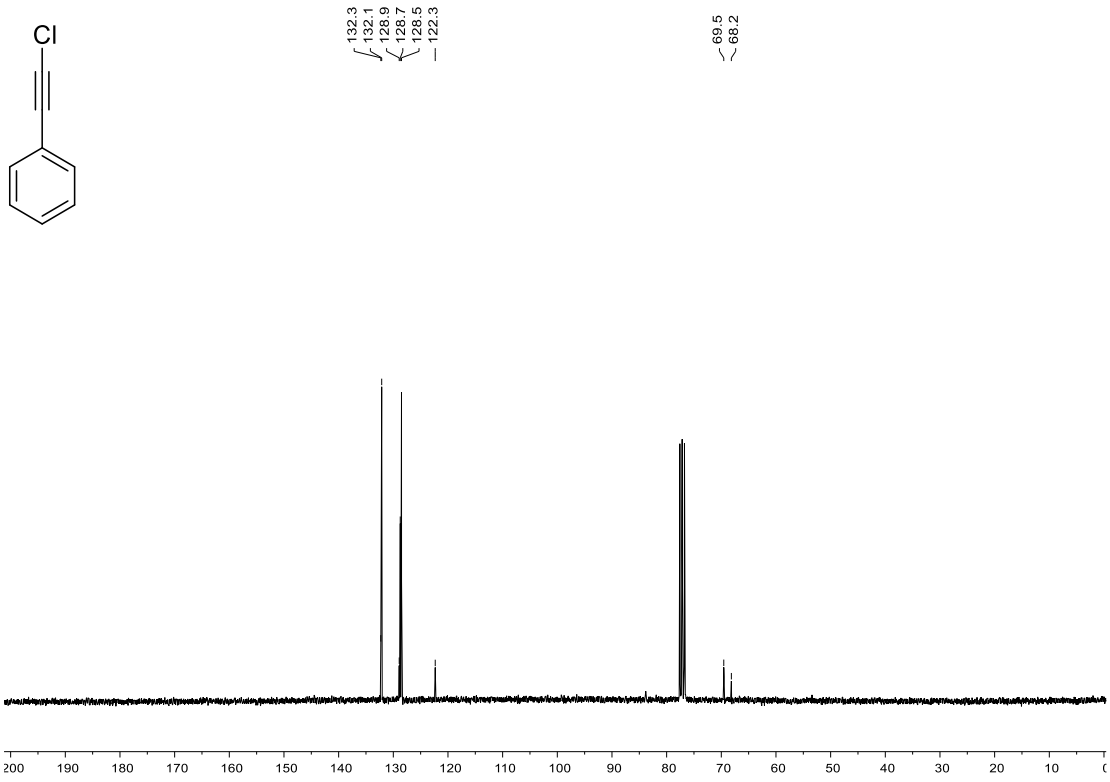


Phenylacetylene (5.5 mL, 50 mmol, 1.0 equiv.), K_2CO_3 (6.9 mL, 50 mmol, 10 mol%) and tetrabutylammonium fluoride trihydrate (1.6 mL, 5.0 mmol, 1.0 equiv.) in CCl_4 (30 mL) were stirred at room temperature overnight. The reaction mixture was filtered through a short pad of silica with pentane, concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane) to provide the analytical pure product as colourless oil.

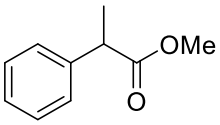
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.48 – 7.40 (m, 2H, CH_{arom}), 7.38 – 7.27 (m, 3H, CH_{arom}). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 132.3 (CH), 132.1 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 122.3 (C), 69.5 (C), 68.2 (C).

The analytical data are in accordance with those described in the literature.[2]





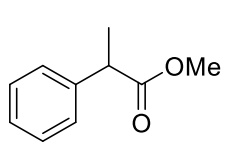
Methyl 2-phenylpropanoate



Concentrated sulfuric acid (0.17 mL, 3.3 mmol, 0.1 equiv.) was added to a solution of 2-phenylpropionic acid (4.5 mL, 33 mmol, 1.0 equiv.) in MeOH (20 mL). The solution was stirred at 65 °C overnight, cooled to room temperature and aqueous Na_2CO_3-solution was added. Pentane was added to the mixture before phase separation. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product was used for the next synthesis step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.31 – 7.12 (m, 5H, CH_{arom}), 3.65 (q, *J* = 7.2 Hz, 1H, CH), 3.59 (s, 3H, OCH_3), 1.43 (d, *J* = 7.2 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 175.1 (C), 140.7 (C), 128.8 (CH), 127.6 (2 x CH), 127.3 (2 x CH), 52.1 (CH_3), 45.6 (CH), 18.8 (CH_3).

Analytical data are in accordance with those reported in the literature.[3]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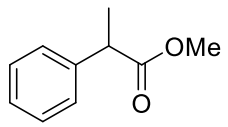
OMe
O

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128.8
127.6
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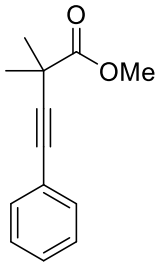
45.6
18.8

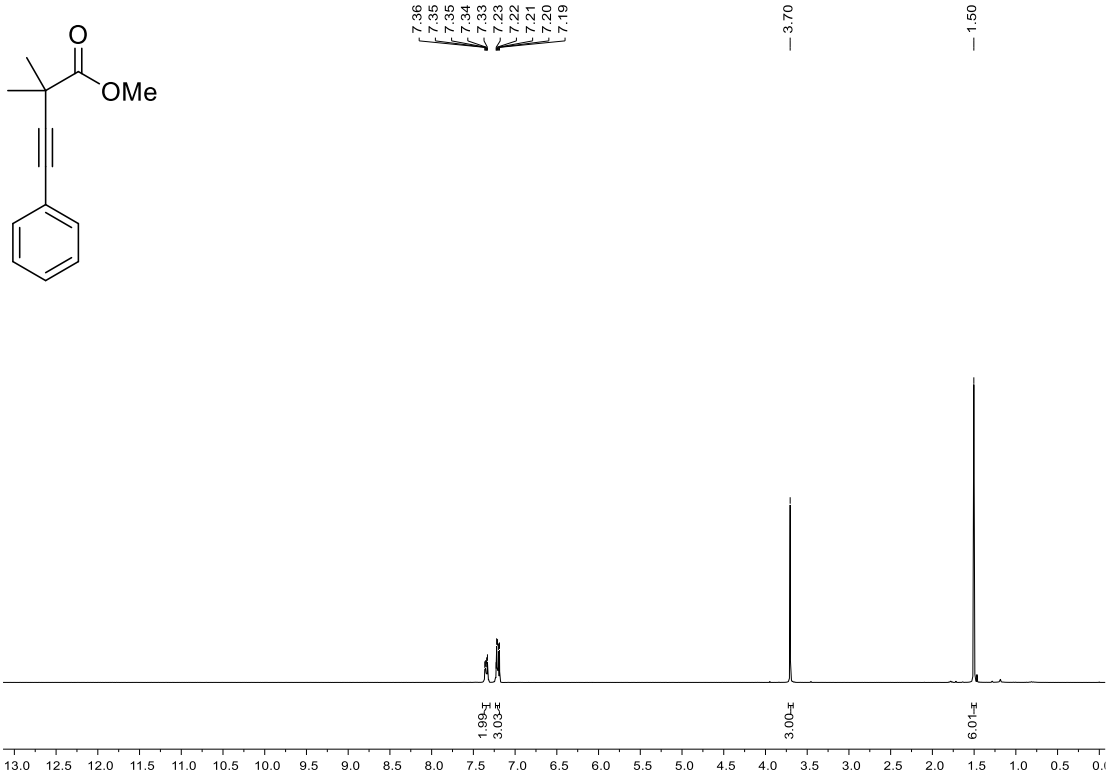
3.2 Analytical data of the ester alkylation products

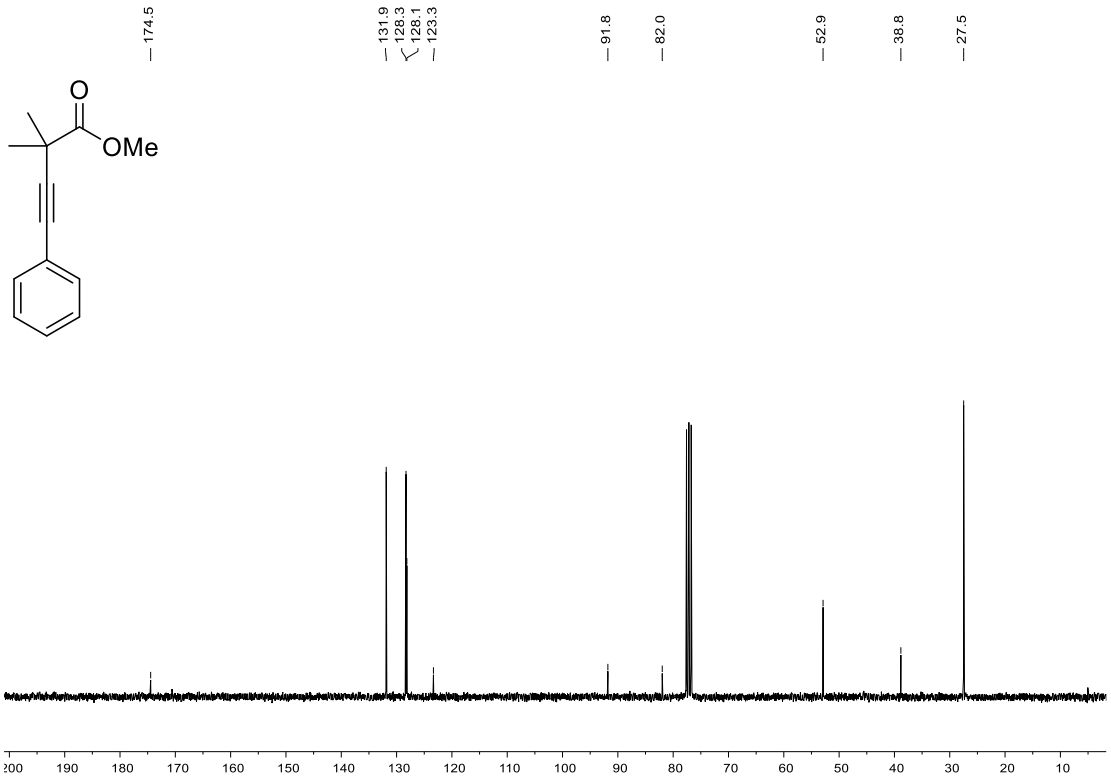
Methyl 2,2-dimethyl-4-phenylbut-3-ynoate



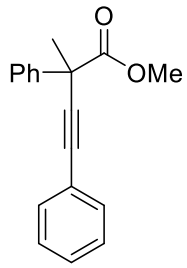
According to **GP1** with methyl isobutyrate (1.5 mL, 13 mmol, 1.0 equiv.). Column chromatography (SiO_2, P/DEE = 100/1) afforded the desired product (2.07 g, 10.2 mmol, 81%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.38 – 7.31 (m, 2H, CH_{arom}), 7.24 – 7.17 (m, 3H, CH_{arom}), 3.70 (s, 3H, OCH_3), 1.50 (s, 6H, 2 x CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 174.5 (C), 131.9 (CH), 128.3 (2 x CH), 128.1 (2 x CH), 123.3 (C), 91.8 (C), 82.0 (C), 52.9 (CH_3), 38.8 (C), 27.5 (2 x CH_3). **IR** (neat): 2989*m*, 2951*w*, 2363*w*, 1736*s*, 1491*s*, 1467*m*, 1385*w*, 1255*s*, 1142*s*, 1071*w*, 990*w*, 822*m*, 756*s*, 691*s*. **HRMS** (ESI) *m*/*z* = 225.0891 calcd. for $C_{13}H_{14}O_2Na$ $[M+Na]^+$, found: 225.0886.



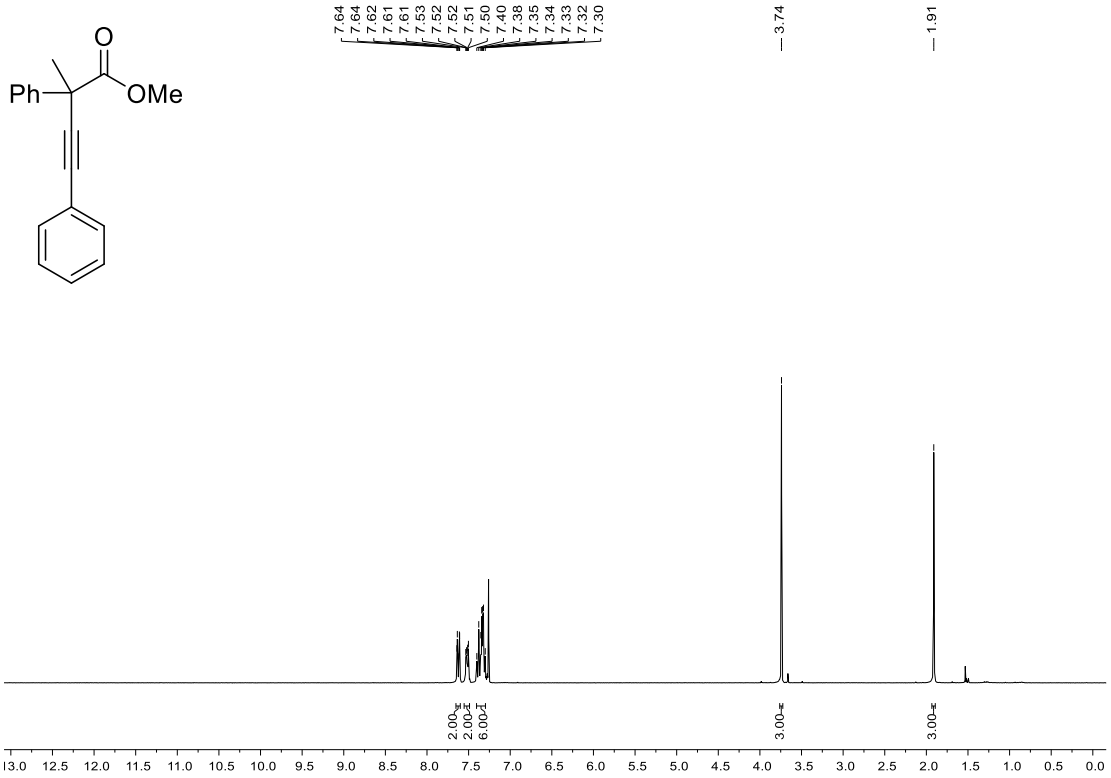


Methyl 2-methyl-2,4-diphenylbut-3-ynoate



According to **GP1** with methyl 2-phenylpropanoate (2.1 mL, 13 mmol, 1.0 equiv.). Column chromatography (SiO_2, P/DEE = 100/1) afforded the desired product (2.89 g, 10.9 mmol, 86%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.67 – 7.57 (m, 2H, CH_{arom}), 7.54 – 7.49 (m, 2H, CH_{arom}), 7.41 – 7.29 (m, 6H, CH_{arom}), 3.74 (s, 3H, OCH_3), 1.91 (s, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 172.8 (C), 141.3 (C), 132.0 (CH), 128.7 (2 x CH), 128.4 (2 x CH), 128.4 (CH), 127.7 (2 x CH), 126.3 (2 x CH), 123.2 (C), 89.8 (C), 85.3 (C), 53.3 (CH_3), 48.2 (C), 28.2 (CH_3). **IR** (neat): 2976*w*, 2364*w*, 1737*s*, 1599*w*, 1491*m*, 1444*m*, 1373*w*, 1234*s*, 1139*m*, 1098*m*, 1006*m*, 865*w*, 788*m*, 756*s*, 691*s*. **HRMS** (ESI) *m*/*z* = 287.1048 calcd. for $C_{18}H_{16}O_2Na$ $[M+Na]^+$, found: 287.1039.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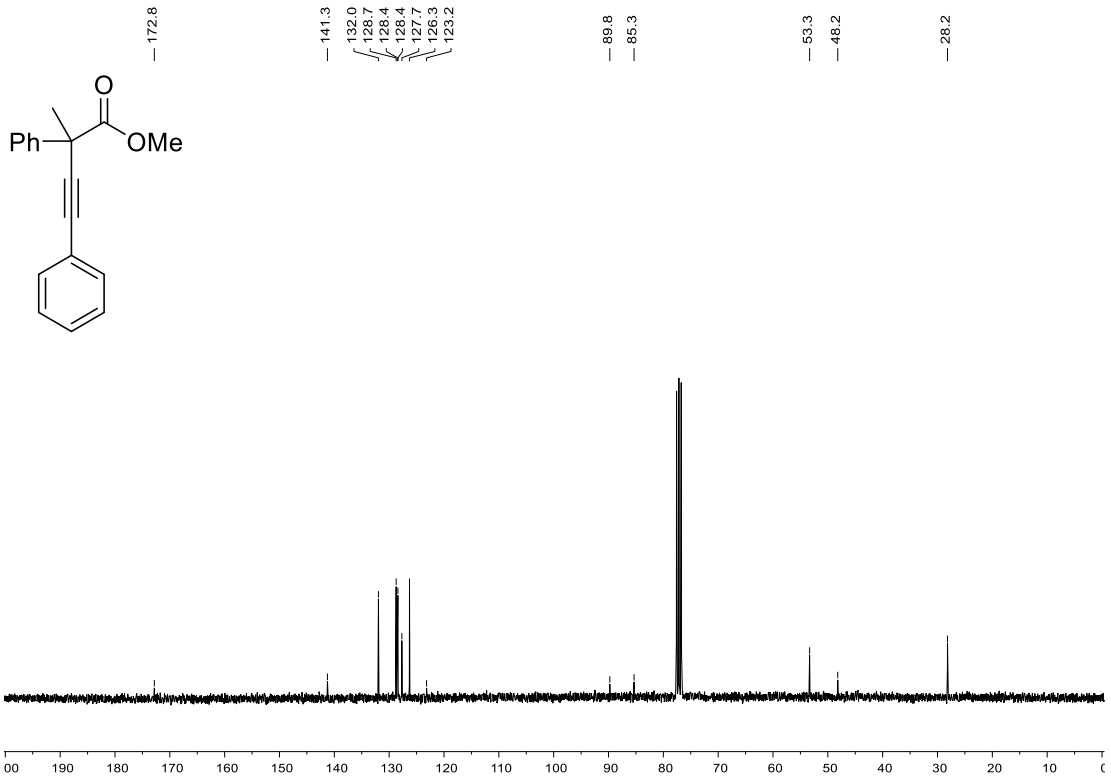
3.00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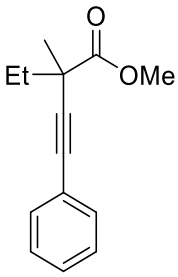
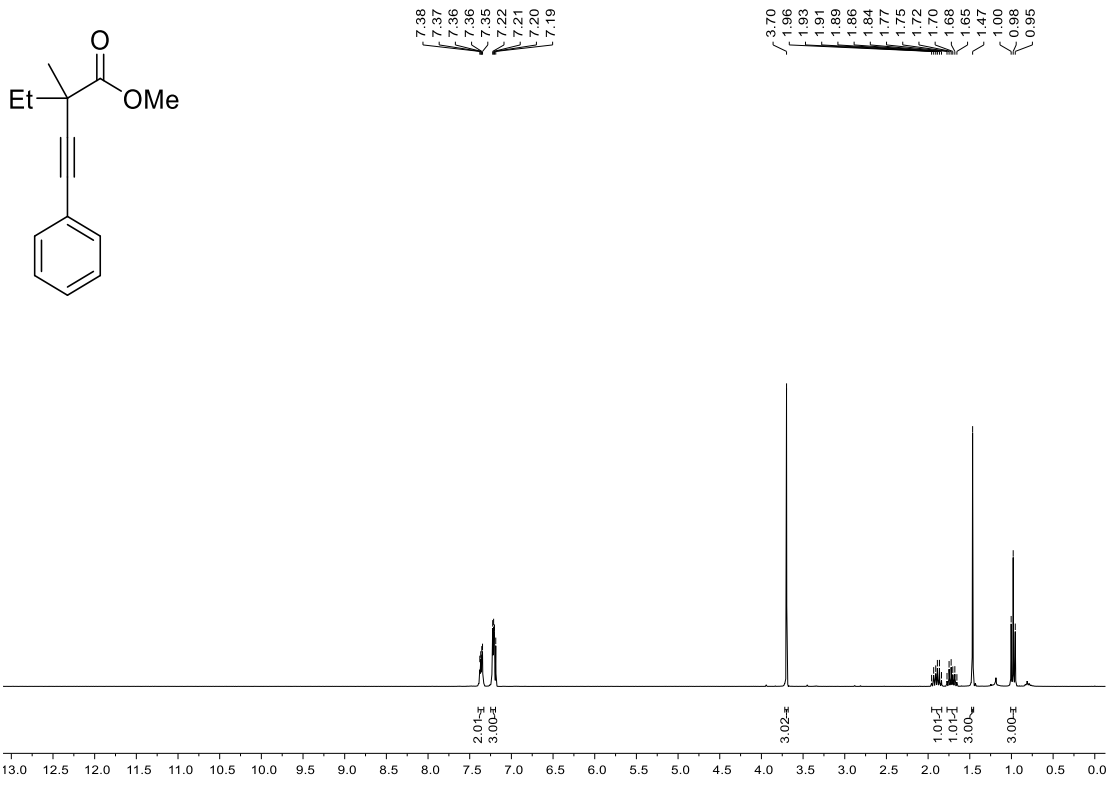
53.3
48.2
28.2

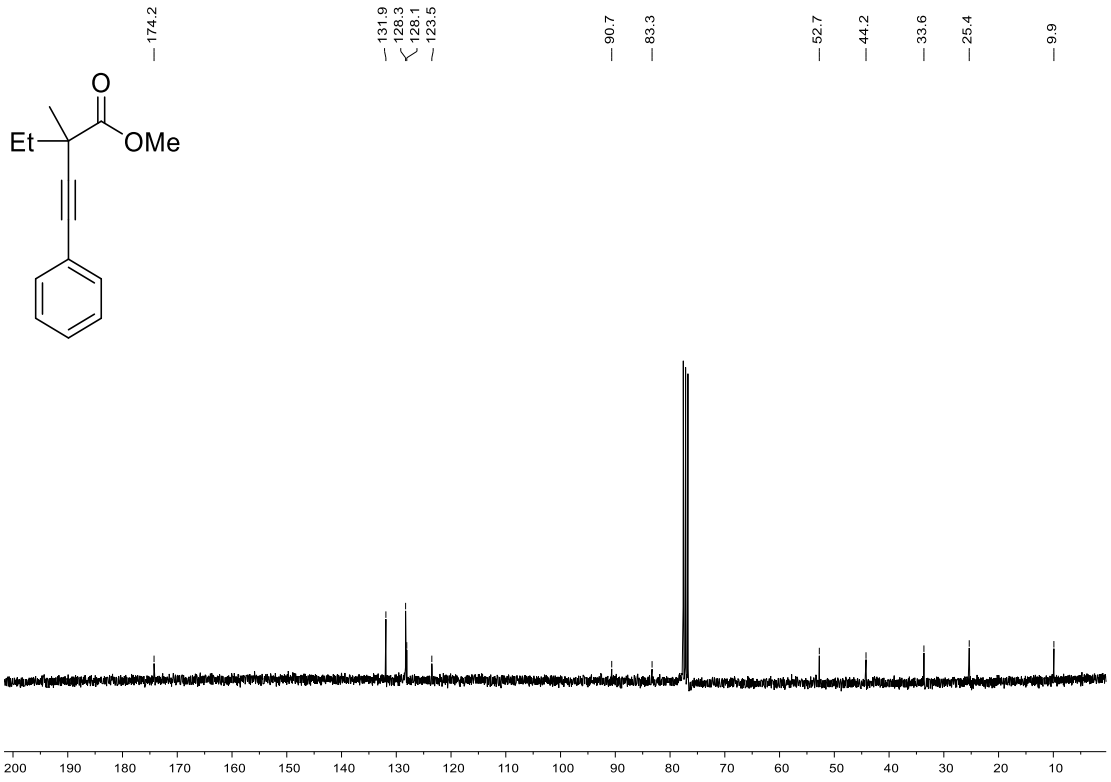
Methyl 2-ethyl-2-methyl-4-phenylbut-3-ynoate



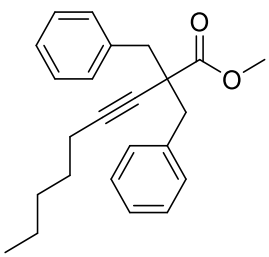
According to **GP1** with methyl 2-methylbutanoate (0.13 mL, 0.98 mmol, 1.0 equiv.). Column chromatography (SiO_2, P/DEE = 100/1) afforded the desired product (132 mg, 0.611 mmol, 62%) as colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.40 – 7.33 (m, 2H, CH_{arom}), 7.24 – 7.18 (m, 3H, CH_{arom}), 3.70 (s, 3H, OCH_3), 1.96 – 1.83 (m, 1H, CH_2), 1.78 – 1.65 (m, 1H, CH_2), 1.47 (s, 3H, CH_3), 0.98 (t, *J* = 7.4 Hz, 3H, $CH_2C\mathit{H}_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 174.2 (C), 131.9 (CH), 128.3 (2 x CH), 128.1 (2 x CH), 123.5 (C), 90.7 (C), 83.3 (C), 52.7 (CH_3), 44.2 (C), 33.6 (CH_2), 25.4 (CH_3), 9.9 (CH_3). **IR** (neat): 2965*w*, 2361*w*, 1734*m*, 1261*m*, 1095*m*, 1013*m*, 904*s*, 804*m*, 724*s*, 650*m*. **HRMS** (ESI) *m*/*z* = 239.1048 calcd. for $C_{14}H_{16}O_2Na$ $[M+Na]^+$, found: 239.1043.





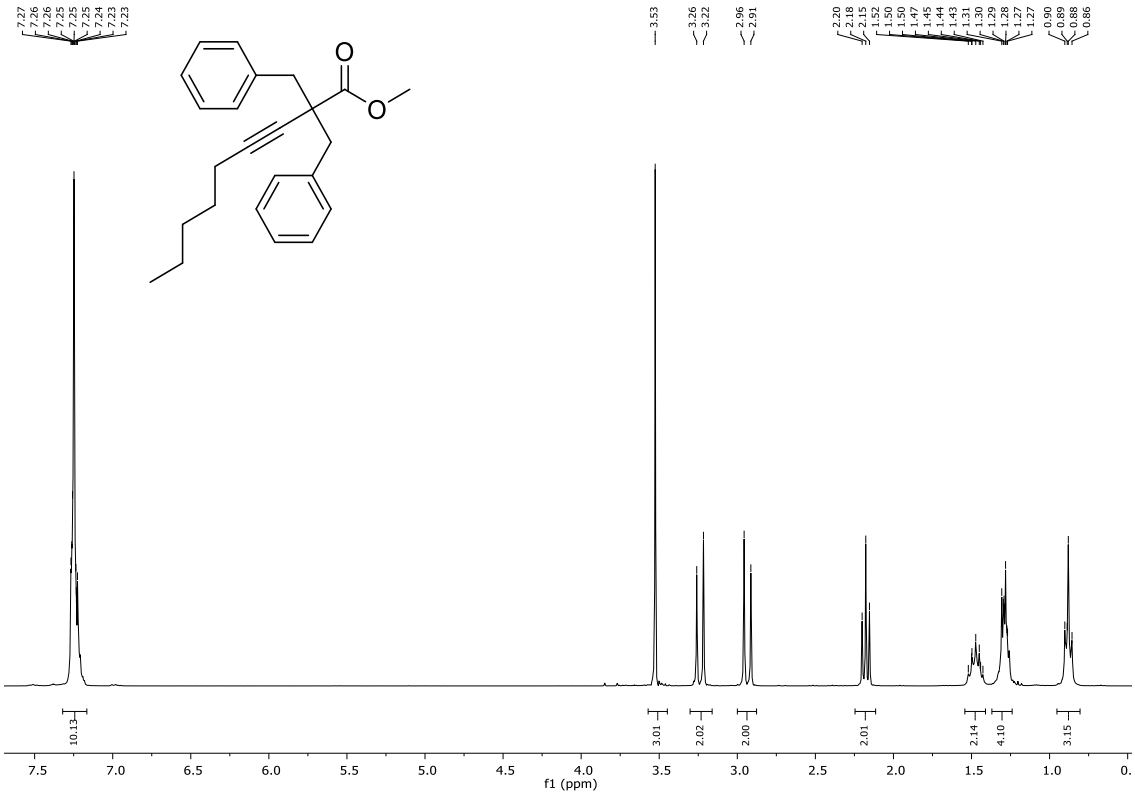
Methyl 2,2-dibenzylnon-3-inoate

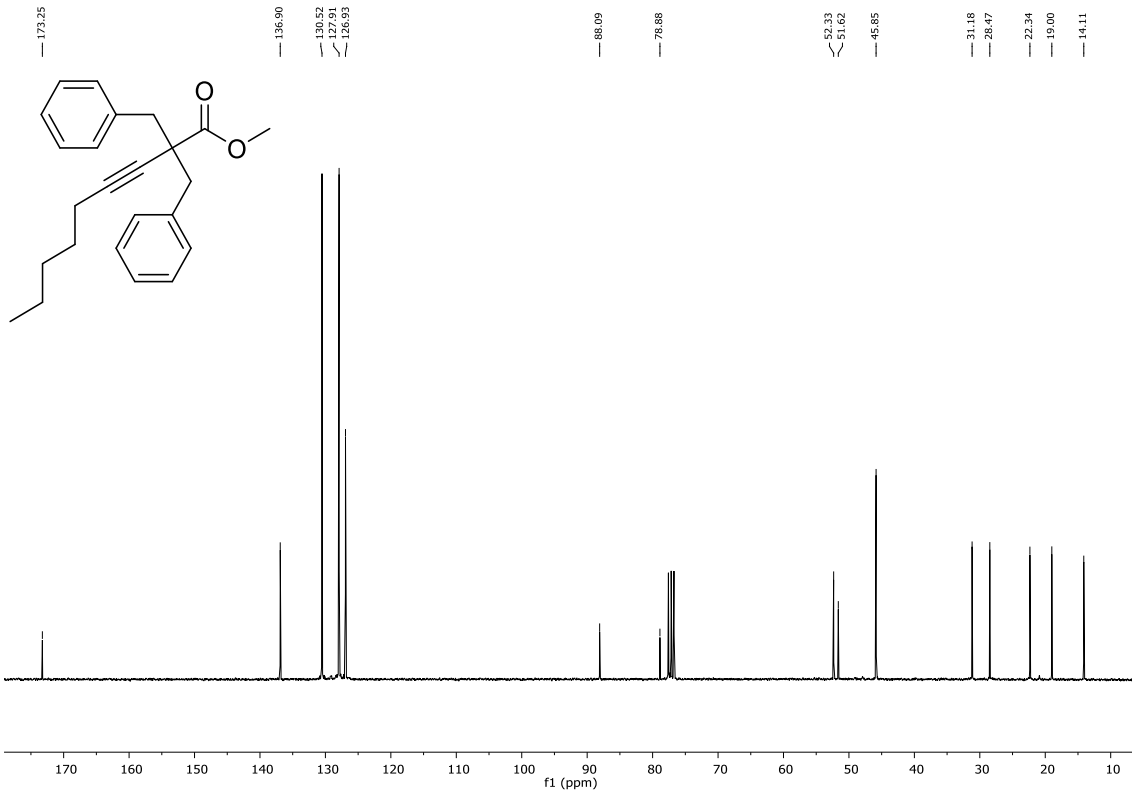


According to a literature procedure by *Nishio*[4] and *Larock*[5], *n*-BuLi (1.5 M solution in hexane, 44 mL, 66 mmol, 2.2 equiv.) was added to a solution of DIPA (9.3 mL, 66 mmol, 2.2 equiv.) in THF (8.0 mL) at 0 °C and stirred for 30 minutes. DMPU (8.0 mL, 66 mmol, 2.2 equiv.) and methyl non-3-ynoate (5.5 mL, 30 mmol, 1.0 equiv.) in THF (40 mL) were prepared in a separated *Schlenk*-tube before adding the synthesized LDA-solution at -98 C. After 30 minutes benzyl bromide (28 mL, 0.24 mol, 8.0 equiv.) was added at -98 °C and the reaction mixture was allowed to warm up to room temperature overnight before quenching with water. The aqueous phase was extracted with DEE (2 x). The combined organic layers were washed with aqueous HCl-solution (2 M), aqueous NaCl-solution (sat.), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, P/DEE = 40/1 → 8/1) affording the desired product (6.36 g, 18.2 mmol, 61%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.32 – 7.17 (m, 10H, CH_{arom}), 3.53 (s, 3H, CH_3), 3.24 (d, *J* = 13.0 Hz, 2H, CH_2), 2.93 (d, *J* = 13.0 Hz, 2H, CH_2), 2.18 (t, *J* = 7.0 Hz, 2H, CH_2), 1.47 (p, *J* = 7.0 Hz, 2H, CH_2), 1.29 (td, *J* = 4.0, 2.0 Hz, 4H, 2 x CH_2), 0.95 – 0.81 (m, 3H,

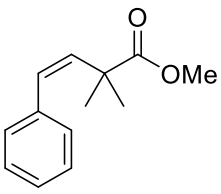
CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 173.3 (C), 136.9 (C), 130.5 (CH), 127.9 (CH), 126.9 (CH), 88.1 (C), 78.9 (C), 52.3 (CH_3), 51.6 (C), 45.9 (CH_2), 31.2 (CH_2), 28.5 (CH_2), 22.3 (CH_2), 19.0 (CH_2), 14.1 (CH_3). **IR** (neat): 2929*w*, 1727*m*, 1496*m*, 1232*m*, 1177*m*, 1084*m*, 1031*w*, 963*w*, 912*w*, 753*m*, 738*m*, 697*s*, 624*w*. **HRMS** (ESI) *m*/*z* = 371.1982 calcd. for $C_{24}H_{28}O_2Na$ $[M+Na]^+$, found: 371.1979.





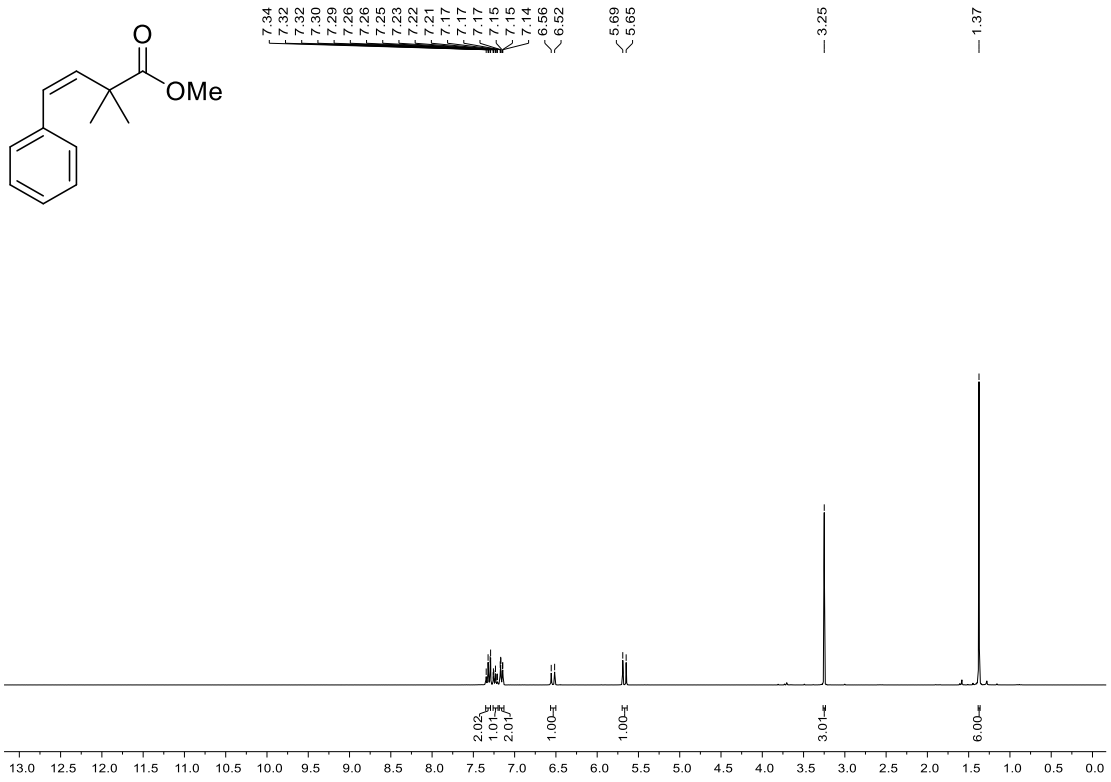
3.3 Analytical data of the hydrogenation products

Methyl (*Z*)-2,2-dimethyl-4-phenylbut-3-enoate



Methyl 2,2-dimethyl-4-phenylbut-3-ynoate (100 mg, 0.495 mmol, 1.0 equiv.) was added to a mixture of DIPA/quinoline (1/2, 2.0 equiv.) and *Lindlar* catalyst (117 mg, 0.119 mmol, 24 mol%) in MeOH (4.9 mL). The reaction mixture was stirred under H_2-atmosphere (atmospheric pressure) for 2 h. The reaction mixture was filtered through a short pad of Celite and purification by column chromatography (SiO_2, P/DEE = 100/1) afforded the desired product (92.9 mg, 0.455 mmol, 90%) as colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.36 – 7.28 (m, 2H, CH_{arom}), 7.27 – 7.20 (m, 1H, CH_{arom}), 7.18 – 7.13 (m, 2H, CH_{arom}), 6.54 (d, *J* = 12.3 Hz, 1H, CH_{olefin}), 5.67 (d, *J* = 12.3 Hz, 1H, CH_{olefin}), 3.25 (s, 3H, OCH_3), 1.37 (s, 6H, 2 x CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 176.9 (C), 137.4 (C), 136.7 (CH), 129.4 (CH), 128.6 (2 x CH), 128.0 (2 x CH), 126.9 (CH), 51.6 (CH_3), 43.8 (C), 27.8 (2 x CH_3). **IR** (neat): 2979*w*, 1730*s*, 1468*w*, 1444*w*, 1239*w*, 1190*w*, 1136*s*, 926*w*, 786*w*, 759*m*, 730*w*, 700*s*. **HRMS** (ESI) *m*/*z* = 227.1048 calcd. for $C_{13}H_{16}O_2Na$ $[M+Na]^+$, found: 227.1055.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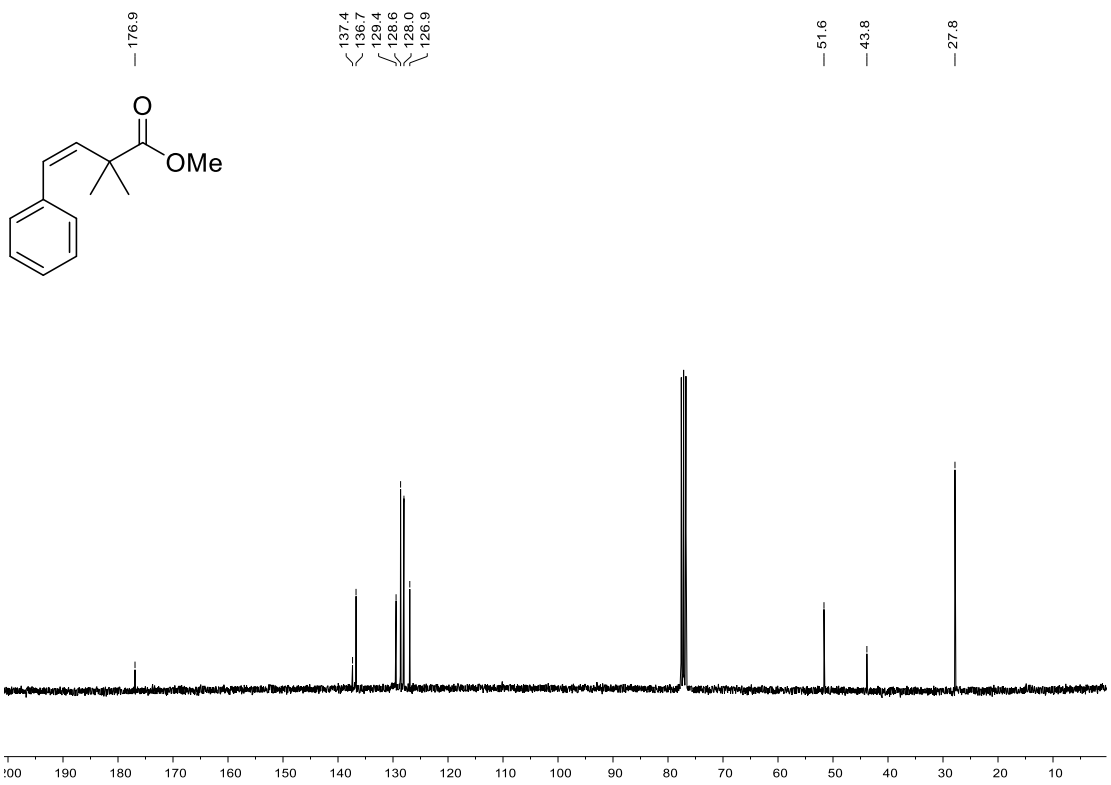
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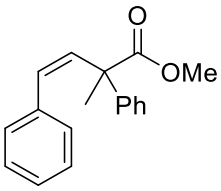
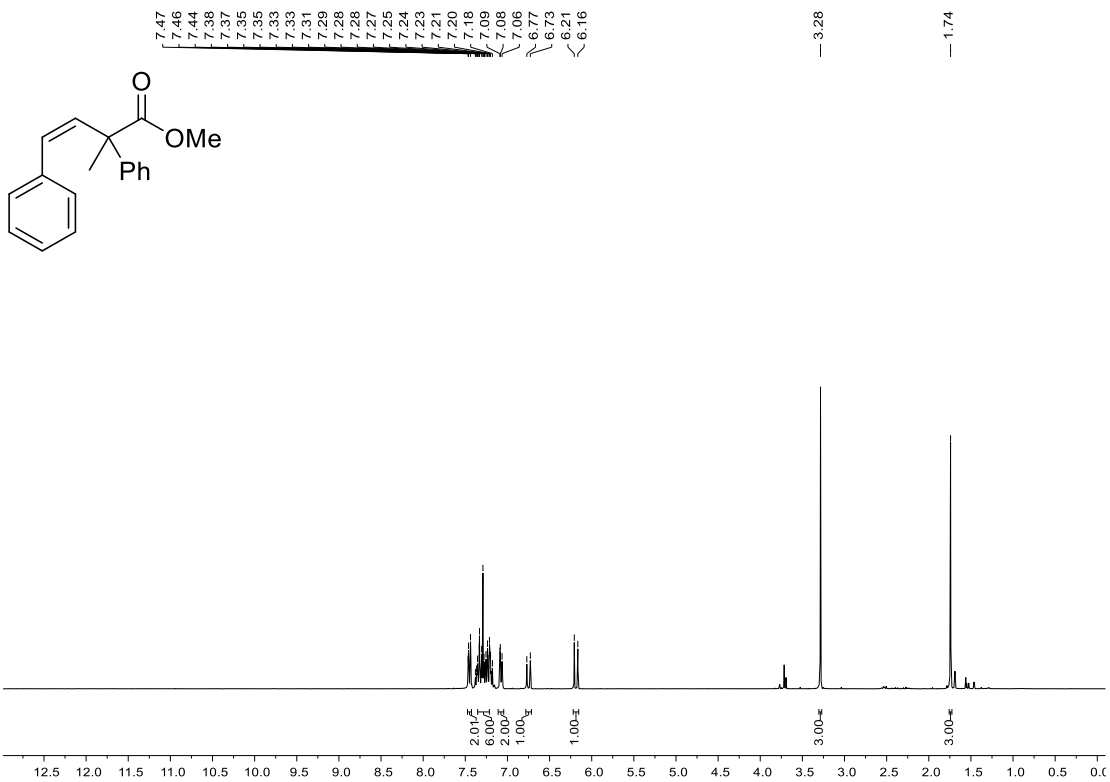
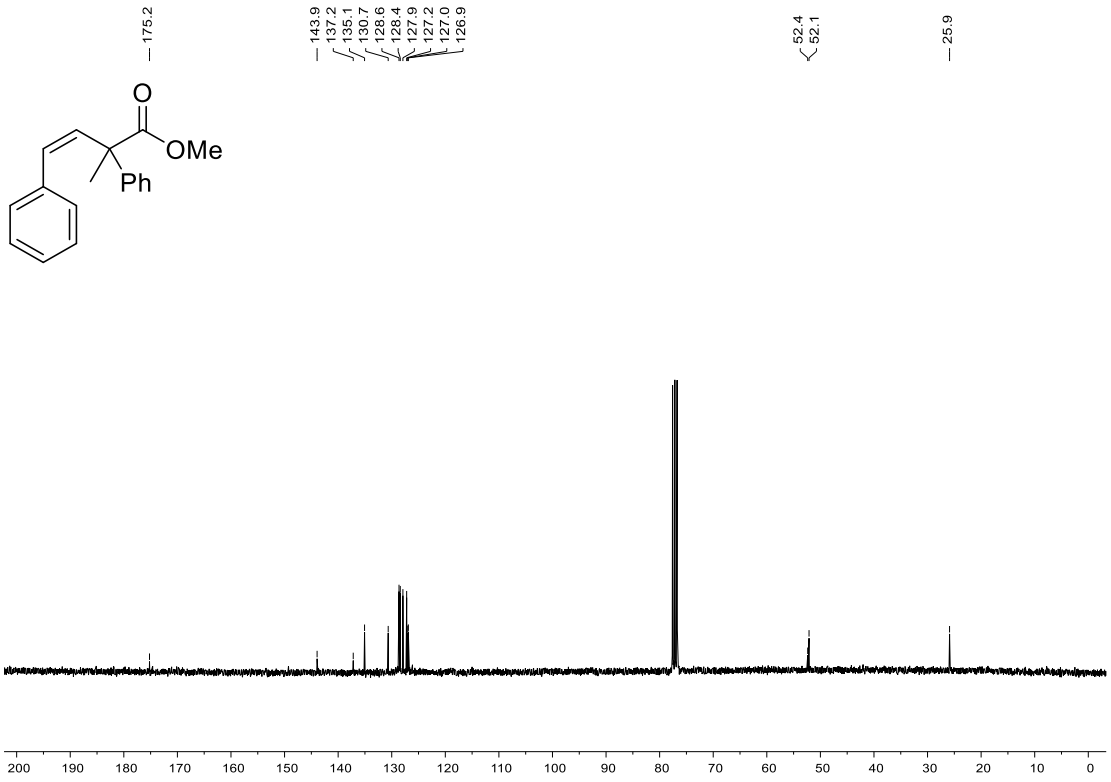
Methyl (*Z*)-2-methyl-2,4-diphenylbut-3-enoate



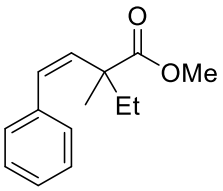
Methyl 2,2-dimethyl-4-phenylbut-3-ynoate (500 mg, 1.89 mmol, 1.0 equiv.) was added to a mixture of DIPA/quinoline (3/1, 2.0 equiv.) and *Lindlar* catalyst (206 mg, 0.208 mmol, 11 mol%) in MeOH (19 mL). The reaction mixture was stirred under H_2-atmosphere (atmospheric pressure) for 2 h. The reaction mixture was filtered through a short pad of Celite and purification by column chromatography (SiO_2, P/DEE = 100/1) afforded the desired product (468 mg, 1.76 mmol, 93%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.48 – 7.42 (m, 2H, CH_{arom}), 7.38 – 7.17 (m, 6H, CH_{arom}), 7.11 – 7.05 (m, 2H, CH_{arom}), 6.75 (d, *J* = 12.6 Hz, 1H, CH_{olefin}), 6.19 (d, *J* = 12.6 Hz, 1H, CH_{olefin}), 3.28 (s, 3H, OCH_3), 1.74 (s, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 175.2 (C), 143.9 (C), 137.2 (C), 135.1 (CH), 130.7 (CH), 128.6 (2 x CH), 128.4 (2 x CH), 127.9 (2 x CH), 127.2 (2 x CH), 127.0 (CH), 126.9 (CH), 52.4 (C), 52.1 (CH_3), 25.9 (CH_3). **IR** (neat): 3024*w*, 2987*w*, 2950*w*, 2184*w*, 1957*w*, 1778*w*, 1730*s*, 1599*w*, 1494*m*, 1445*m*, 1373*w*, 1234*m*, 1136*w*, 1104*w*, 1073*w*, 1029*w*, 981*w*, 934*w*, 757*w*, 729*w*, 698*s*, 574*w*. **HRMS** (ESI) *m*/*z* = 289.1204 calcd. for $C_{18}H_{18}O_2Na$ $[M+Na]^+$, found: 289.1198.



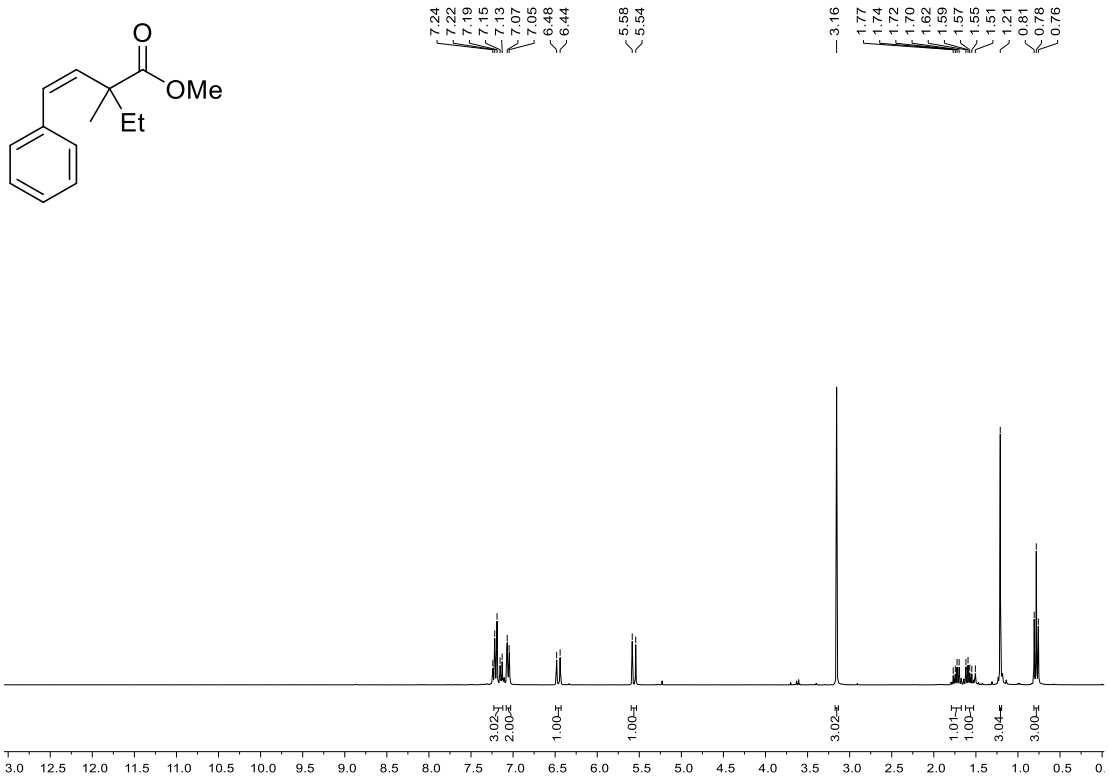


Methyl (*Z*)-2-ethyl-2-methyl-4-phenylbut-3-enoate



Methyl 2-ethyl-2-methyl-4-phenylbut-3-ynoate (71 mg, 0.33 mmol, 1.0 equiv.) was added to quinoline (0.10 mL, 0.82 mmol, 2.5 equiv.) and *Lindlar* catalyst (33 mg, 30 µmol, 10 mol%) in EtOAc (2.0 mL). The reaction mixture was stirred under H_2-atmosphere (atmospheric pressure) for 2 h. The reaction mixture was filtered through a short pad of Celite and purification by column chromatography (SiO_2, P/DEE = 100/1) afforded the desired product (70 mg, 32 µmol, 97%) as colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.24 – 7.13 (m, 3H, CH_{arom}), 7.07 – 7.05 (m, 2H, CH_{arom}), 6.46 (d, *J* = 12.4 Hz, 1H, CH_{olefin}), 5.56 (d, *J* = 12.5 Hz, 1H, CH_{olefin}), 3.16 (s, 3H, OCH_3), 1.77 – 1.70 (m, 1H, CH_2), 1.62 – 1.51 (m, 1H, CH_2), 1.21 (s, 3H, CH_3), 0.78 (t, *J* = 7.5 Hz, 3H, $CH_2C\mathit{H}_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 176.2 (C), 137.4 (C), 135.8 (CH), 129.5 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 126.8 (CH), 51.4 (CH_3), 47.6 (C), 34.2 (CH_2), 23.1 (CH_3), 8.9 (CH_3). **IR** (neat): 2973*w*, 2939*w*, 1732*s*, 1494*w*, 1458*w*, 1232*m*, 1202*w*, 1139*m*, 1028*w*, 981*w*, 782*w*, 731*w*, 700*m*. **HRMS** (ESI) *m*/*z* = 241.1204 calcd. for $C_{14}H_{18}O_2Na$ $[M+Na]^+$, found: 241.1208.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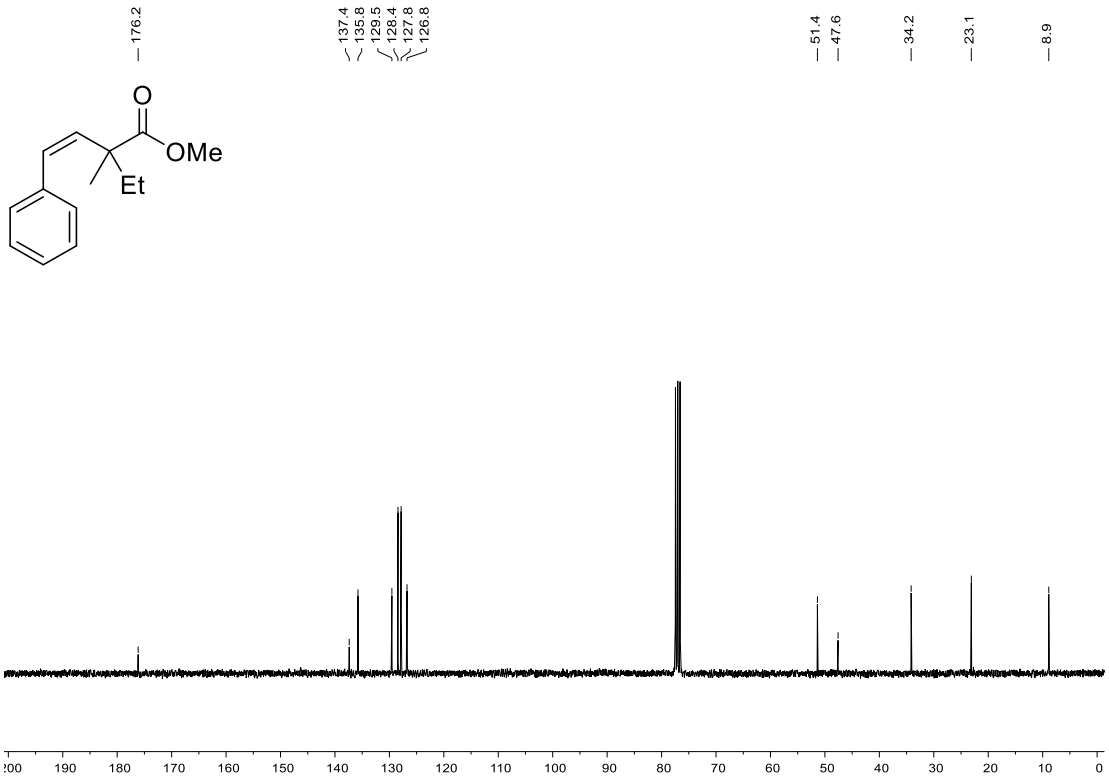
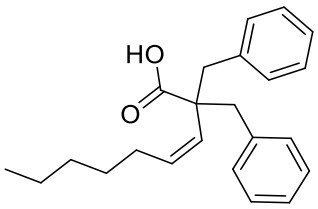
OMe
Et
7.24
7.22
7.19
7.15
7.13
7.07
7.05
6.48
6.44
5.58
5.54
3.16
1.77
1.74
1.72
1.70
1.62
1.59
1.57
1.55
1.51
1.21
0.81
0.78
0.76
3.02
2.00
1.00
1.00
3.02
1.01
1.00
3.04
3.00

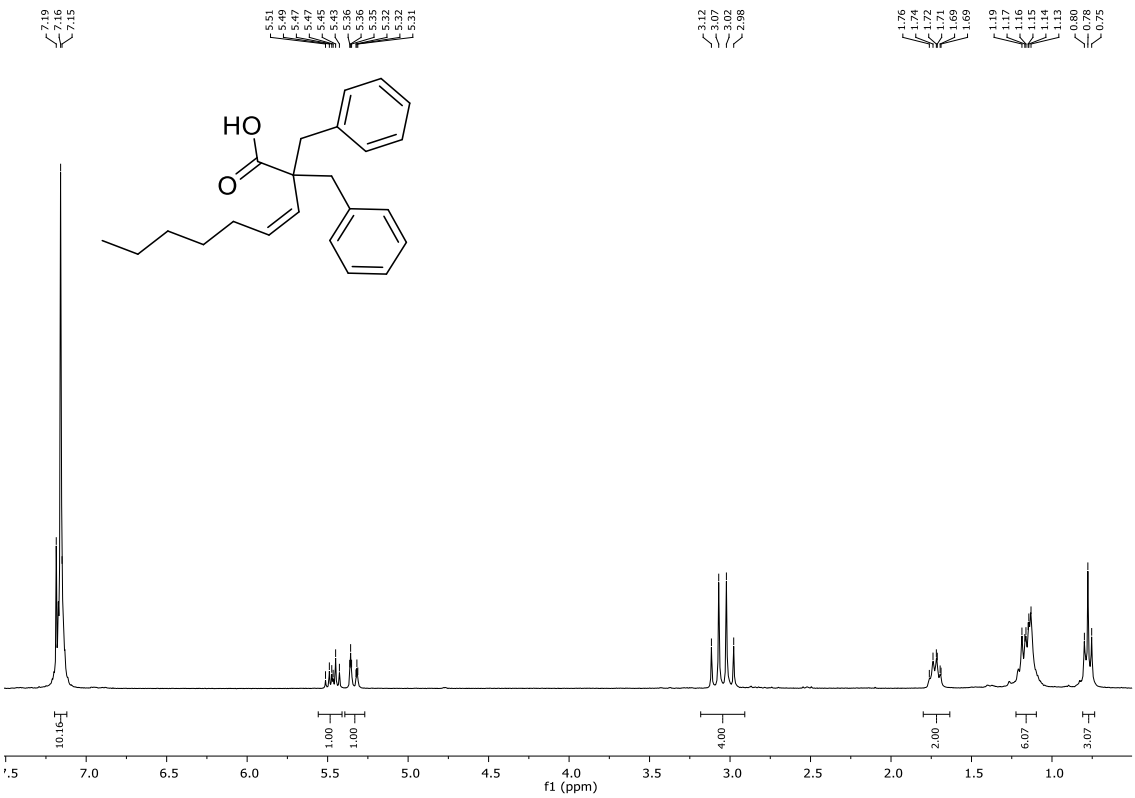

O
OMe
Et
176.2
137.4
135.8
129.5
128.4
127.8
126.8
51.4
47.6
34.2
23.1
8.9

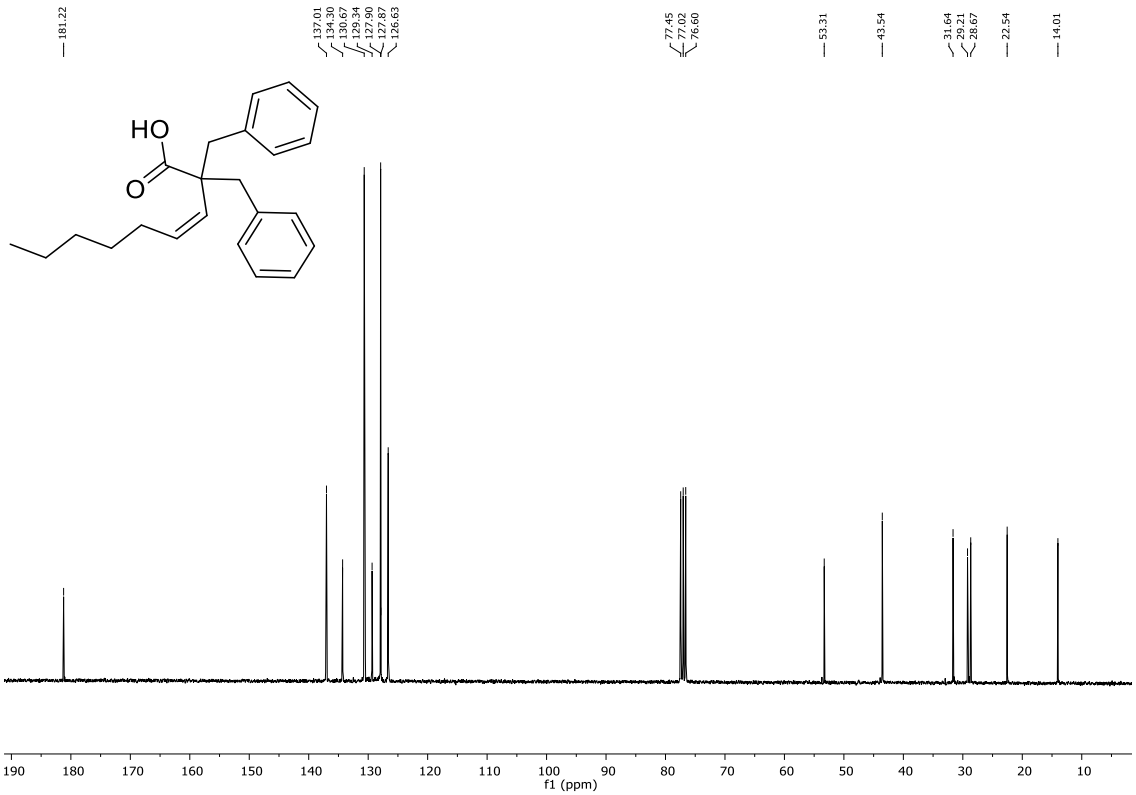
(*Z*)-2,2-Dibenzylnon-3-enoic acid (1e)



According to a literature procedure by *Lindlar*[6] and *Granja*[7] 2,2-dibenzylnon-3-ynoic acid (2.5 g, 7.5 mmol, 1.0 equiv.) and *Lindlar* catalyst (377 mg, 37.7 mmol, 5 mol%) in EtOAc (45 mL) were stirred under H_2-atmosphere (atmospheric pressure) for 19 h. The reaction mixture was filtered through a short pad of Celite and purification by column chromatography (SiO_2, P/DEE = 40/1 → 5/1) afforded the desired product (2.22 g, 6.58 mmol, 87%) as yellow oil.

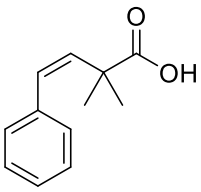
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.12 – 7.20 (m, 10H, CH_{arom}), 5.47 (dt, *J* = 11.5, 7.0 Hz, 1H, CH_{olefin}), 5.34 (dt, *J* = 11.5, 1.5 Hz, 1H, CH_{olefin}), 3.05 (q, *J* = 13.5 Hz, 4H, 2 x CH_2), 1.80 – 1.63 (m, 2H, CH_2), 1.22 – 1.10 (m, 6H, 3 x CH_2), 0.78 (t, *J* = 7.0 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 181.2 (C), 137.0 (C), 134.3 (CH), 130.7 (CH), 129.3 (CH), 127.9 (CH), 127.9 (CH), 126.6 (CH), 53.3 (C), 43.5 (CH_2), 31.6 (CH_2), 29.2 (CH_2), 28.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3). **IR** (neat): 2926*w*, 1696*m*, 1496*w*, 1454*w*, 1273*w*, 1222*w*, 1084*w*, 1032*w*, 909*w*, 730*m*, 697*s*. **HRMS** (ESI) *m*/*z* = 359.1982 calcd. for $C_{23}H_{28}O_2Na$ $[M+Na]^+$, found: 359.1976.





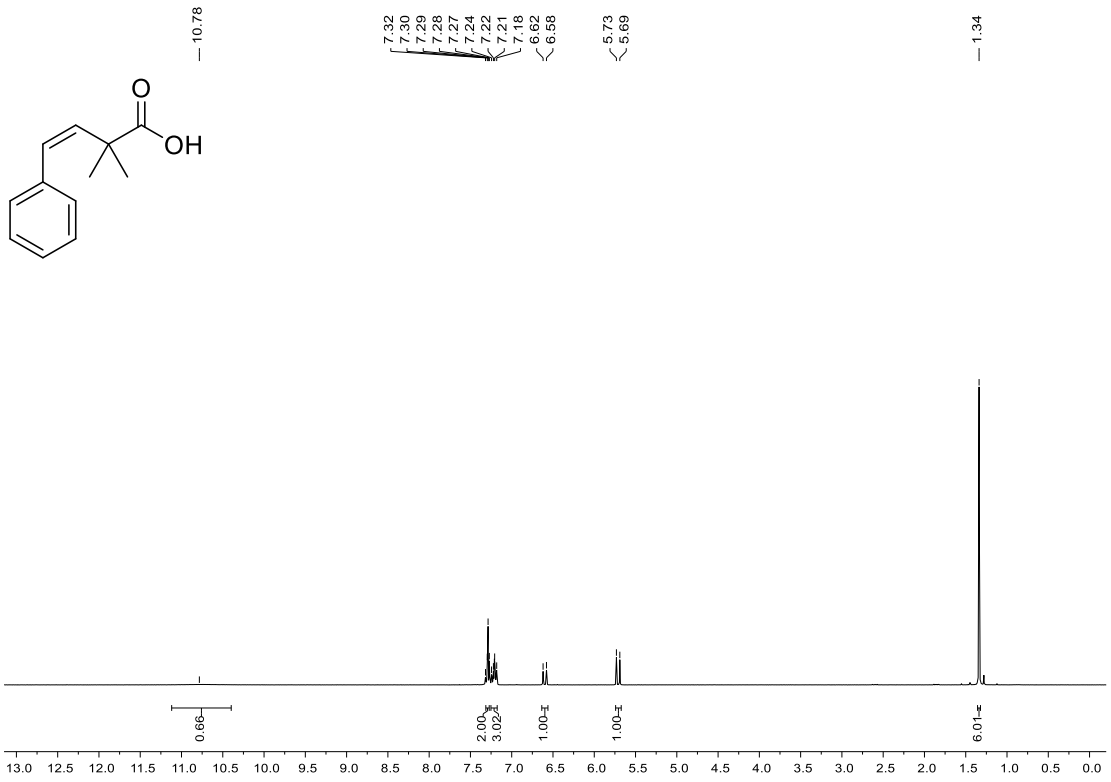
3.4 Analytical data of the ester hydrolysis products

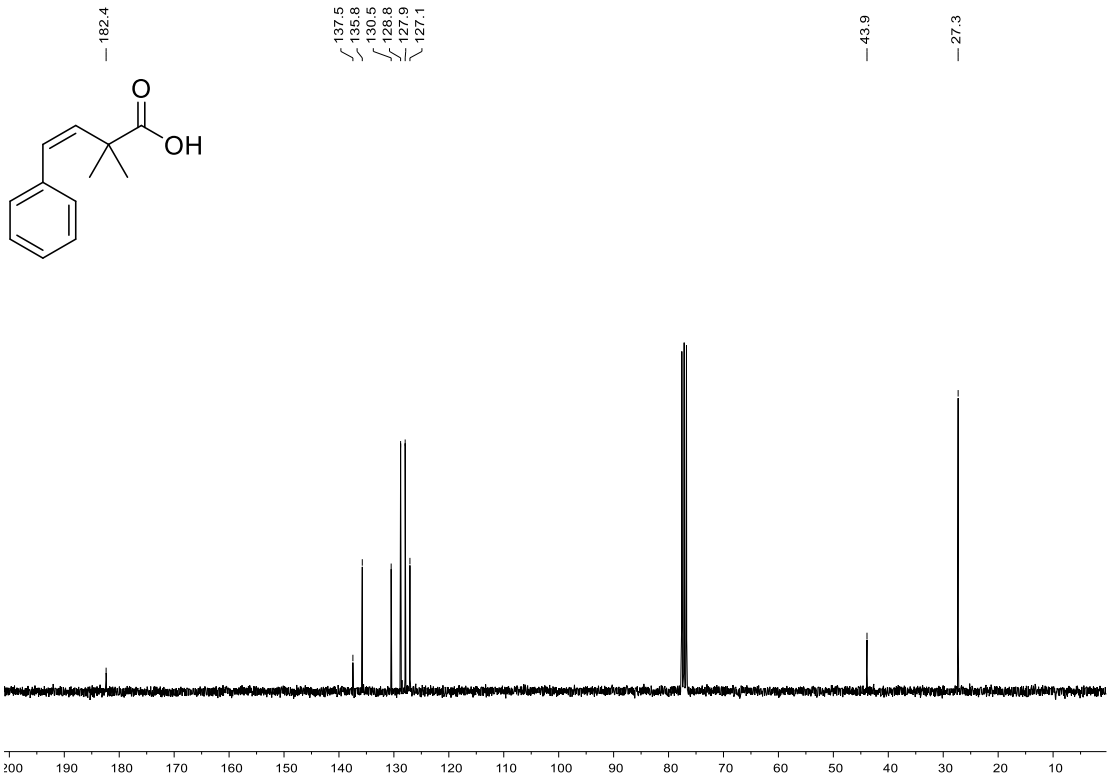
(*Z*)-2,2-Dimethyl-4-phenylbut-3-enoic acid (1a)



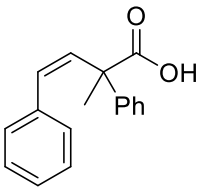
According to **GP2** with methyl (*Z*)-2,2-dimethyl-4-phenylbut-3-enoate (1.00 g, 4.95 mmol, 1.0 equiv.). The desired carboxylic acid (885 mg, 4.46 mmol, 94%) was obtained as colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 10.78 (s, 1H, COOH), 7.33 – 7.26 (m, 2H, CH_{arom}), 7.25 – 7.16 (m, 3H, CH_{arom}), 6.60 (d, *J* = 12.3 Hz, 1H, CH_{olefin}), 5.71 (d, *J* = 12.3 Hz, 1H, CH_{olefin}), 1.34 (s, 6H, 2 x CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 182.4 (C), 137.5 (C), 135.8 (CH), 130.5 (CH), 128.8 (2 x CH), 127.9 (2 x CH), 127.1 (CH), 43.9 (C), 27.3 (2 x CH_3). **IR** (neat): 2977*w*, 1701*s*, 1472*w*, 1293*w*, 1167*w*, 924*w*, 758*w*, 701*m*, 569*m*. **HRMS** (ESI) *m*/*z* = 213.0891 calcd. for $C_{12}H_{14}O_2Na$ $[M+Na]^+$, found: 213.0893.


10.78
7.32
7.30
7.29
7.28
7.27
7.24
7.22
7.21
7.18
6.62
6.58
5.73
5.69
1.34
O
OH
0.66
2.00
3.02
1.00
1.00
6.01
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

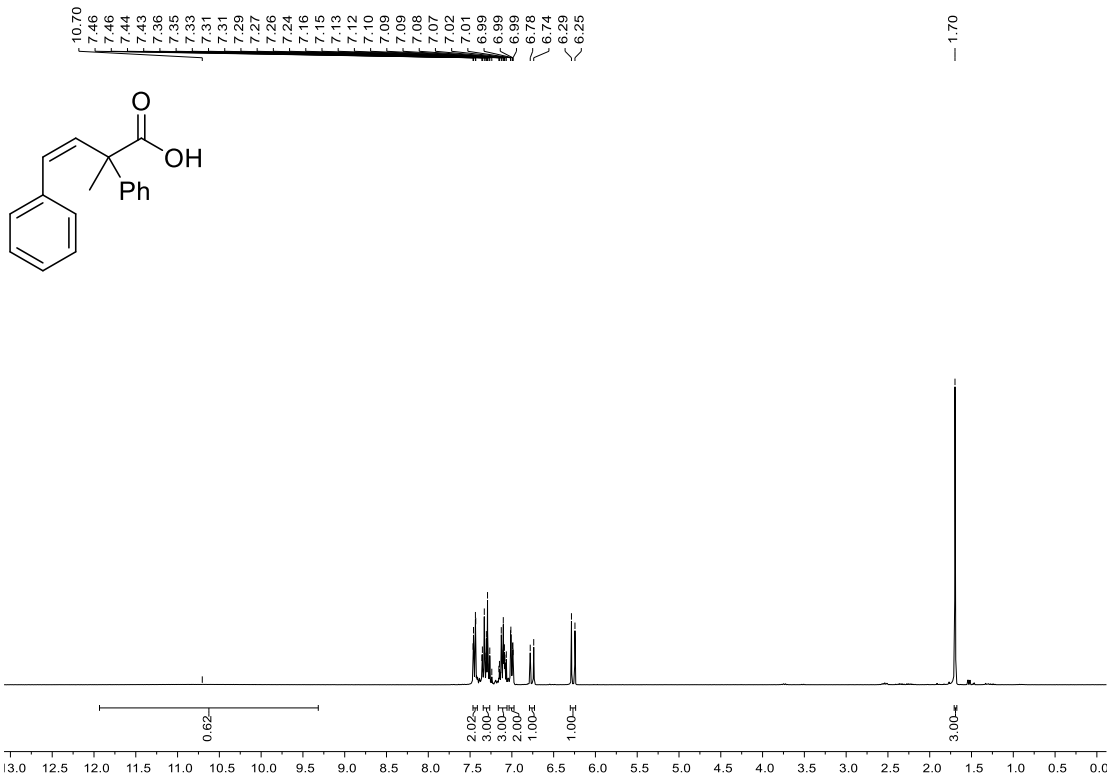

182.4
137.5
135.8
130.5
128.8
127.9
127.1
43.9
27.3
O
OH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

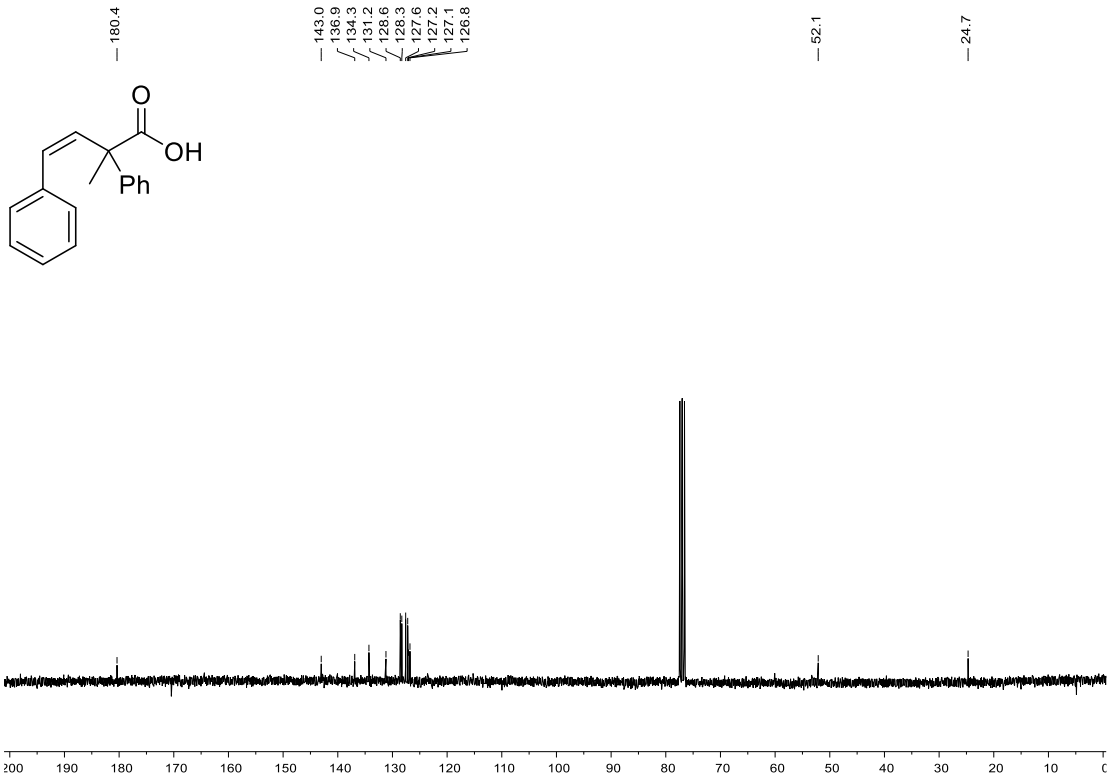
(*Z*)-2-Methyl-2,4-diphenylbut-3-enoic acid (1c)



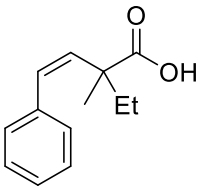
According to **GP2** with methyl (*Z*)-2-methyl-2,4-diphenylbut-3-enoate (600 mg, 2.25 mmol, 1.0 equiv.). The desired carboxylic acid (542 mg, 2.15 mmol, 96%) was obtained as white solid. Separating the enantiomers was performed *via* Preparative High-Performance Liquid Chromatography (Agilent 1100 series HPLC with auto sampler and diode-array UV detector) analysis using a Chiralpak IC column, with cyclohexane: isopropanol = 98:2 at a flow rate of 0.3 mL/min at 7 °C detected at 230 nm and 250 nm wavelength.

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 10.70 (s, 1H, COOH), 7.47 – 7.41 (m, 2H, CH_{arom}), 7.37 – 7.23 (m, 3H, CH_{arom}), 7.16 – 7.06 (m, 3H, CH_{arom}), 7.04 – 6.97 (m, 2H, CH_{arom}), 6.76 (d, *J* = 12.6 Hz, 1H, CH_{olefin}), 6.27 (d, *J* = 12.6 Hz, 1H, CH_{olefin}), 1.70 (s, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 180.4 (C), 143.0 (C), 136.9 (C), 134.3 (CH), 131.2 (CH), 128.6 (2 x CH), 128.3 (2 x CH), 127.6 (2 x CH), 127.2 (2 x CH), 127.1 (CH), 126.8 (CH), 52.1 (C), 24.7 (CH_3). **IR** (neat): 3024*w*, 1700*s*, 1599*w*, 1494*w*, 1446*w*, 1279*m*, 1073*w*, 1029*w*, 939*w*, 771*w*, 721*w*, 696*s*, 625*w*. **HRMS** (ESI) *m*/*z* = 275.1048 calcd. for $C_{17}H_{16}O_2Na$ $[M+Na]^+$, found: 275.1044. **MP**: 127-132 °C.



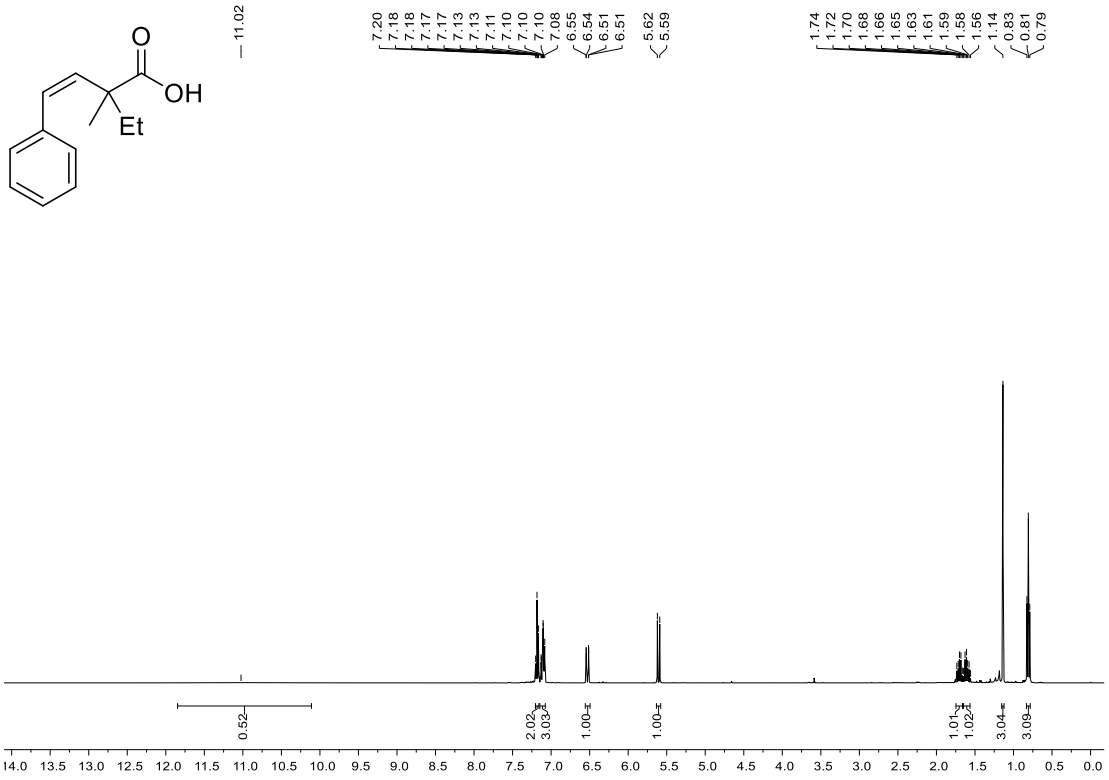


(*Z*)-2-Ethyl-2-methyl-4-phenylbut-3-enoic acid (1b)



According to **GP2** with methyl (*Z*)-2-ethyl-2-methyl-4-phenylbut-3-enoate (70 mg, 0.32 mmol, 1.0 equiv.). The desired carboxylic acid (65 mg, 0.32 mmol, 99%) was obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 11.02 (s, 1H, COOH), 7.20 – 7.17 (m, 2H, CH_{arom}), 7.13 – 7.08 (m, 3H, CH_{arom}), 6.55 (dd, *J* = 12.4 Hz, 0.8 Hz, 1H, CH_{olefin}), 5.61 (d, *J*= 12.4 Hz, 1H, CH_{olefin}), 1.74 – 1.66 (m, 1H, CH_2), 1.65 – 1.58 (m, 1H, CH_2), 1.14 (s, 3H, CH_3), 0.81 (t, *J* = 7.5 Hz, 3H, $CH_2C\mathit{H}_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ = 182.5 (C), 137.6 (C), 134.9 (CH), 130.8 (CH), 128.7 (2 x CH), 127.9 (2 x CH), 127.0 (CH), 47.9 (C), 33.8 (CH_2), 22.6 (CH_3), 9.0 (CH_3). **IR** (neat): 2974*m*, 2938*w*, 2881*w*, 2161*w*, 2031*w*, 1701*s*, 1493*w*, 1460*w*, 1257*m*, 1157*w*, 1072*w*, 1002*w*, 834*w*, 758*w*, 700*m*, 587*w*. **HRMS** (ESI) *m*/*z* = 227.1048 calcd. for $C_{13}H_{16}O_2Na$ $[M+Na]^+$, found: 227.1082.


O
OH
Et
11.02
7.20
7.18
7.18
7.17
7.17
7.13
7.13
7.11
7.10
7.10
7.10
7.08
6.55
6.54
6.51
6.51
5.62
5.59
1.74
1.72
1.70
1.68
1.66
1.65
1.63
1.61
1.59
1.58
1.56
1.14
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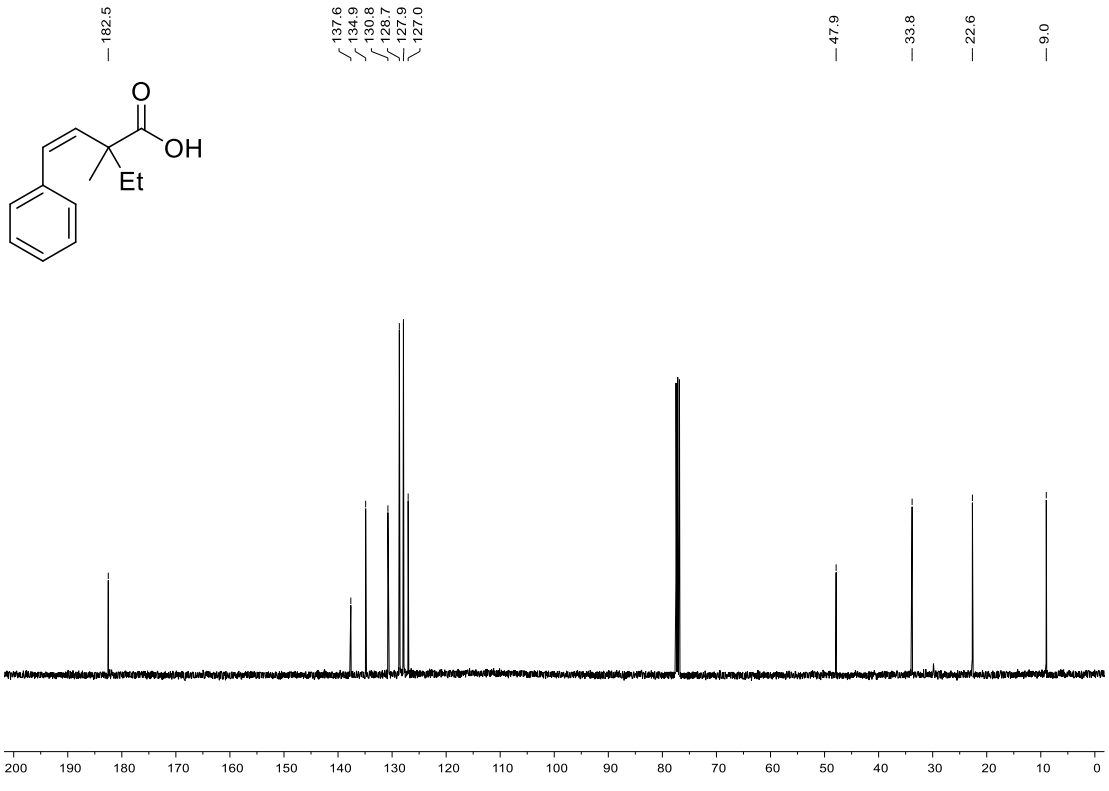
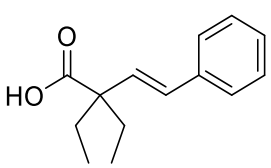
0.81
0.79
0.52
2.02
3.03
1.00
1.00
1.01
1.02
3.04
3.09


O
OH
Et
182.5
137.6
134.9
130.8
128.7
127.9
127.0
47.9
33.8
22.6
9.0

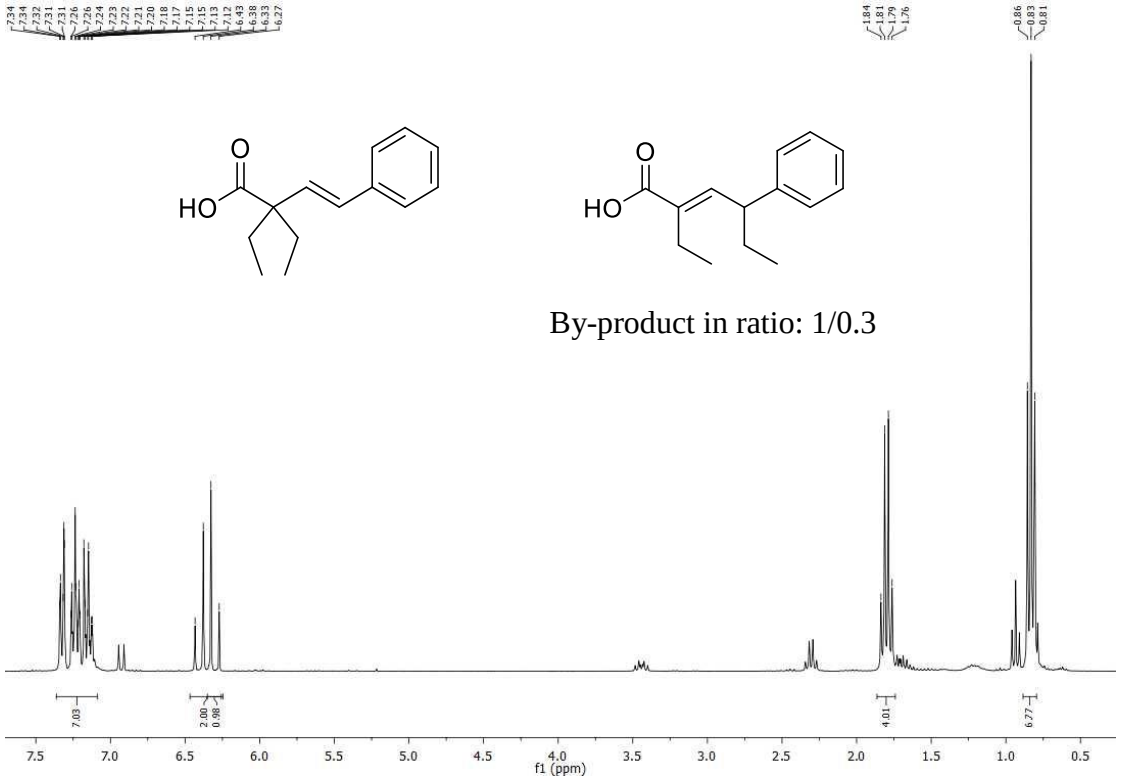
(*E*)-2,2-Diethyl-4-phenylbut-3-enoic acid (1d)



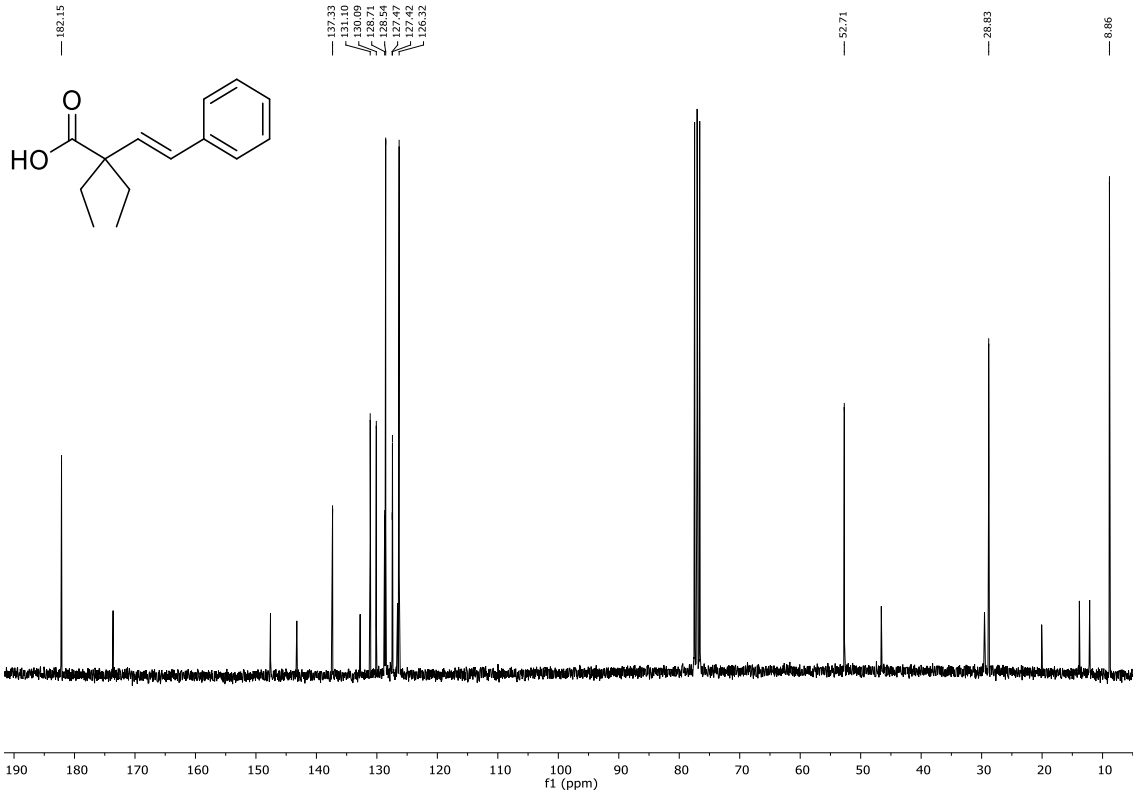
According to a literature procedure by *Fu*[8] *n*-BuLi (1.5 M solution in hexane, 13 mL, 21 mmol, 2.2 equiv.) was added to a solution of *trans*-styrene acidic acid (1.5 g, 9.4 mmol, 1.0 equiv.) in THF (25 mL) at -78 °C and stirred for 40 minutes. After adding ethyl bromide (2.1 mL, 28 mmol, 3.0 equiv.) the reaction mixture was allowed to warm up to room temperature overnight before quenching with aqueous NH_4Cl-solution (sat.). The aqueous phase was extracted with DEE (2 x). Combined organic layers were washed with aqueous NaCl-solution (sat.), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was used in the next step without further purification.

The crude product was dissolved in THF (25 mL) and *n*-BuLi (1.5 M solution in hexane, 18 mL, 21 mmol, 2.2 equiv.) was added at -78 °C. After 40 minutes ethyl bromide (2.1 mL, 28 mmol, 3.0 equiv.) was added and the reaction mixture was allowed to warm up to room temperature overnight. Quenching with aqueous NH_4Cl-solution (sat.) was follwed by separating the phases. The aqueous phase was extracted with DEE (3 x). The combined organic layers were washed with aqueous NaCl-solution (sat.), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, P/DEE/HOAc = 600/100/7) affording the desired product with less impurities as colourless oil (1.21 g, 5.53 mmol, 59%).

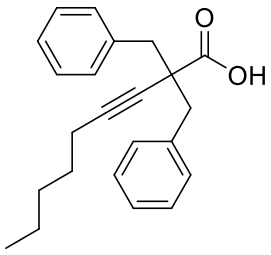
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.36 – 7.09 (m, 5H, CH_{arom}), 6.41 (d, *J* = 16.5 Hz, 1H, CH_{olefin}), 6.30 (d, *J* = 16.5 Hz, 1H, CH_{olefin}), 1.80 (q, *J* = 7.5 Hz, 4H, CH_2), 0.83 (t, *J* = 7.5 Hz, 6H, 2 x CH_3).**^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 182.1 (C), 137.3 (C), 131.1 (CH), 130.1 (CH), 128.7 (CH), 128.5 (CH), 127.5 (CH), 127.4 (CH), 126.3 (CH), 52.7 (C), 28.8 (CH_2), 8.9 (CH_3). **IR** (neat): 2967*m*, 2937*m*, 2878*w*, 2641*w*, 1690*s*, 1495*w*, 1448*m*, 1408*w*, 1295*w*, 1254*m*, 1148*w*, 969*m*, 936*w*, 743*s*, 692*s*. **HRMS** (ESI) *m*/*z* = 241.1199 calcd. for $C_{14}H_{18}O_2Na$ $[M+Na]^+$, found: 241.1203.



By-product in ratio: 1/0.3

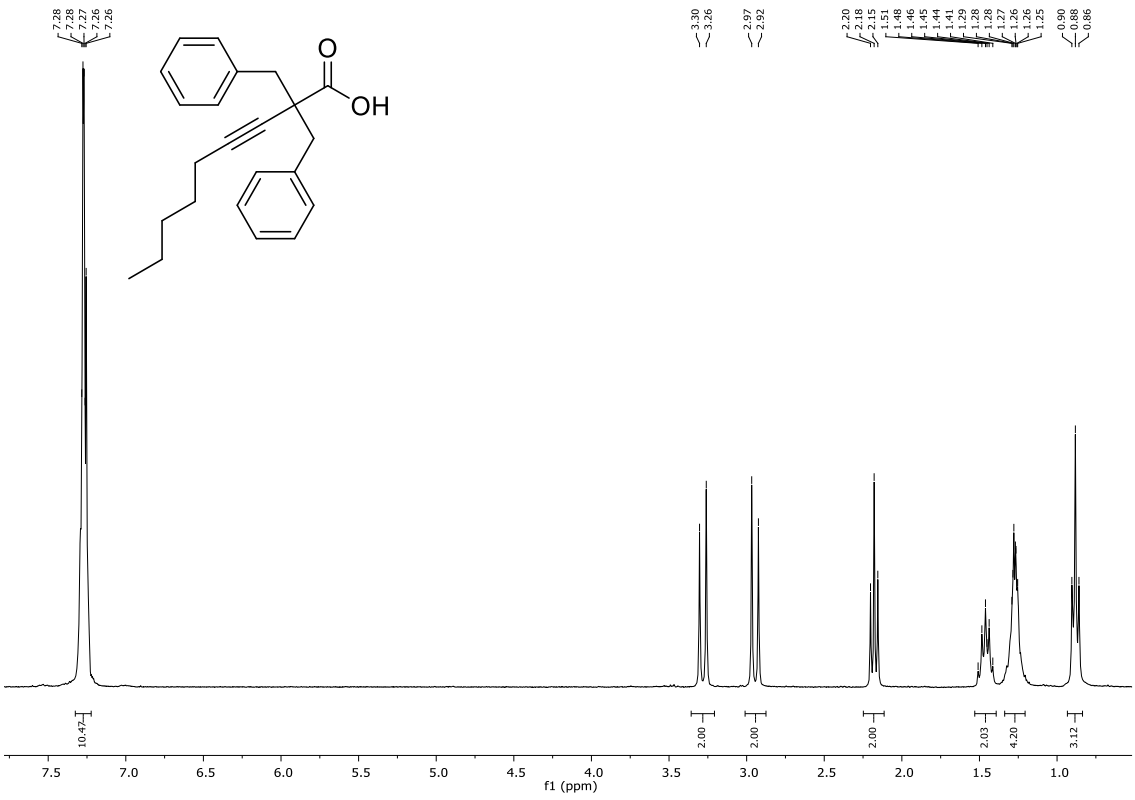


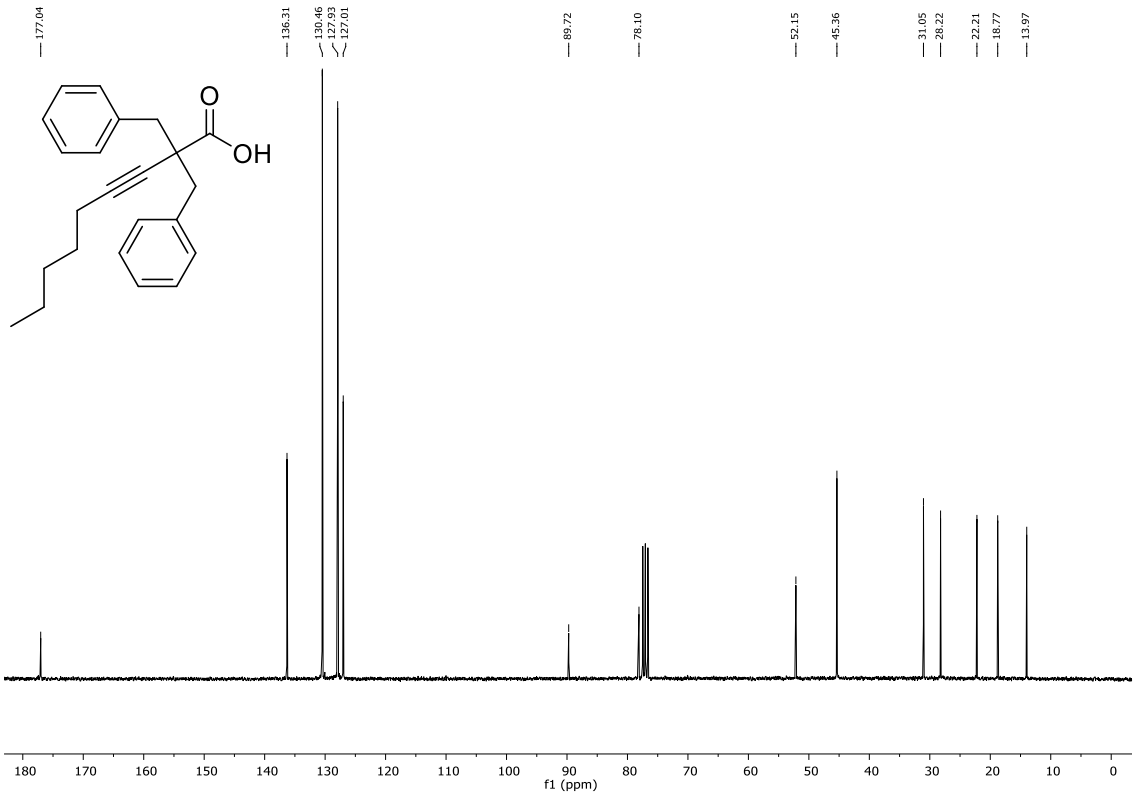
2,2-Dibenzylnon-3-ynoic acid



Methyl 2,2-dibenylon-3-ynoate (290 mg, 0.832 mmol, 1.0 equiv.) was stirred in a 1/1-mixture of THF and aqueous NaOH-solution (15 M) at 80 °C for 24 h. After cooling to room temperature the phases were separated. The aqueous phase was extracted with DEE (3 x) and after that concentrated HCl-solution (37%) was added before washing with DEE (3 x) again. The combined organic phases were washed with aqueous NaCl-solution (sat.), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, P/DEE/HOAc = 50/10/1) and afforded the analytically pure product as white crystals (261 mg, 0.780 mmol, 94%).

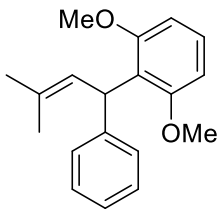
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.27 (m, 10H, CH_{arom}), 3.28 (d, *J* = 13.0 Hz, 2H, CH_2), 2.95 (d, *J* = 13.0 Hz, 2H, CH_2), 2.18 (t, *J* = 7.0 Hz, 2H, CH_2), 1.53 – 1.39 (m, 2H, CH_2), 1.27 (m, 4H, 2 x CH_2), 0.93 – 0.84 (m, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 177.0 (C), 136.3 (C), 130.5 (CH), 127.9 (CH), 127.0 (CH), 89.7 (C), 78.1 (C), 52.1 (C), 45.4 (CH_2), 31.0 (CH_2), 28.2 (CH_2), 22.2 (CH_2), 18.8 (CH_2), 14.0 (CH_3). **IR** (neat): 3031*w*, 2930*m*, 2859*w*, 1706*s*, 1496*m*, 1455*m*, 1230*w*, 1082*w*, 913*w*, 754*w*, 734*w*, 698*s*. **HRMS** (ESI) *m*/*z* = 357.1825 calcd. for $C_{23}H_{26}O_2Na$ $[M+Na]^+$, found: 357.1818. **MP**: 82-83 °C.





3.5 Analytical data of the palladium coupling products

1,3-Dimethoxy-2-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2h)

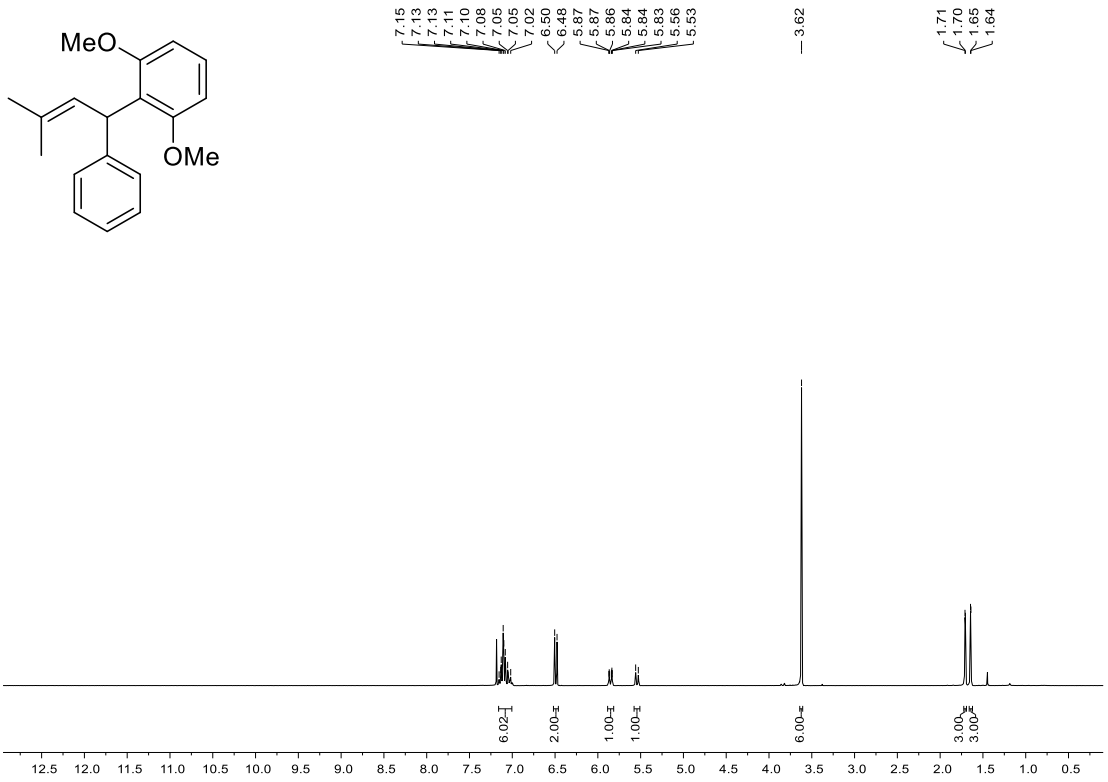


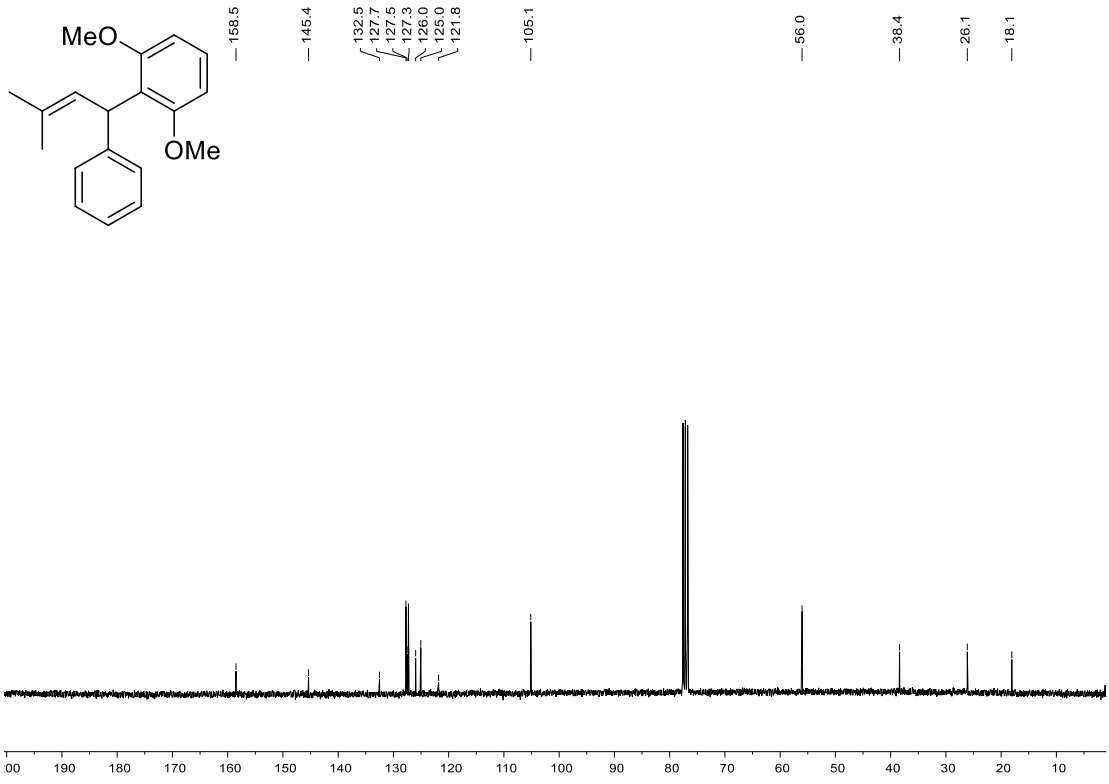
According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 2-iodo-1,3-dimethoxybenzene (84.0 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as white solid (63.0 mg, 0.223 mmol, 78%).

According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (190mg, 1.00 mmol, 1.0 equiv.) and 2-iodo-1,3-dimethoxybenzene (290 mg, 1.10 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as white solid (214 mg, 0.758 mmol, 76%) along with *trans*-β-iodo-styrene (12 mg, 5%).

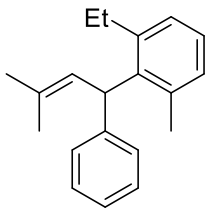
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.19 – 6.98 (m, 6H, CH_{arom}), 6.49 (d, *J* = 8.3 Hz, 2H, CH_{arom}), 5.85 (dt, *J* = 9.4 Hz, 1.4 Hz, 1H, CH_{olefin}), 5.54 (d, *J* = 9.4 Hz, 1H, CH), 3.62 (s, 6H, 2 x OCH_3), 1.71 (d, *J* = 1.4 Hz, 3H, CH_3), 1.64 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR**

(75 MHz, $CDCl_3$, 300 K): δ = 158.5 (2 x C), 145.4 (C), 132.5 (C), 127.7 (2 x CH), 127.5 (2 x CH), 127.3 (2 x CH), 126.0 (CH), 125.0 (2 x CH), 121.8 (C), 105.1 (CH), 56.0 (2 x CH_3), 38.4 (CH), 26.1 (CH_3), 18.1 (CH_3). **IR** (neat): 2976*w*, 2254*w*, 1732*w*, 1590*s*, 1473*s*, 1238*s*, 1101*s*, 773*s*. **HRMS** (ESI) *m*/*z* = 305.1517 calcd. for $C_{19}H_{22}O_2Na$ $[M+Na]^+$, found: 305.1511. **MP**: 77-78 °C.



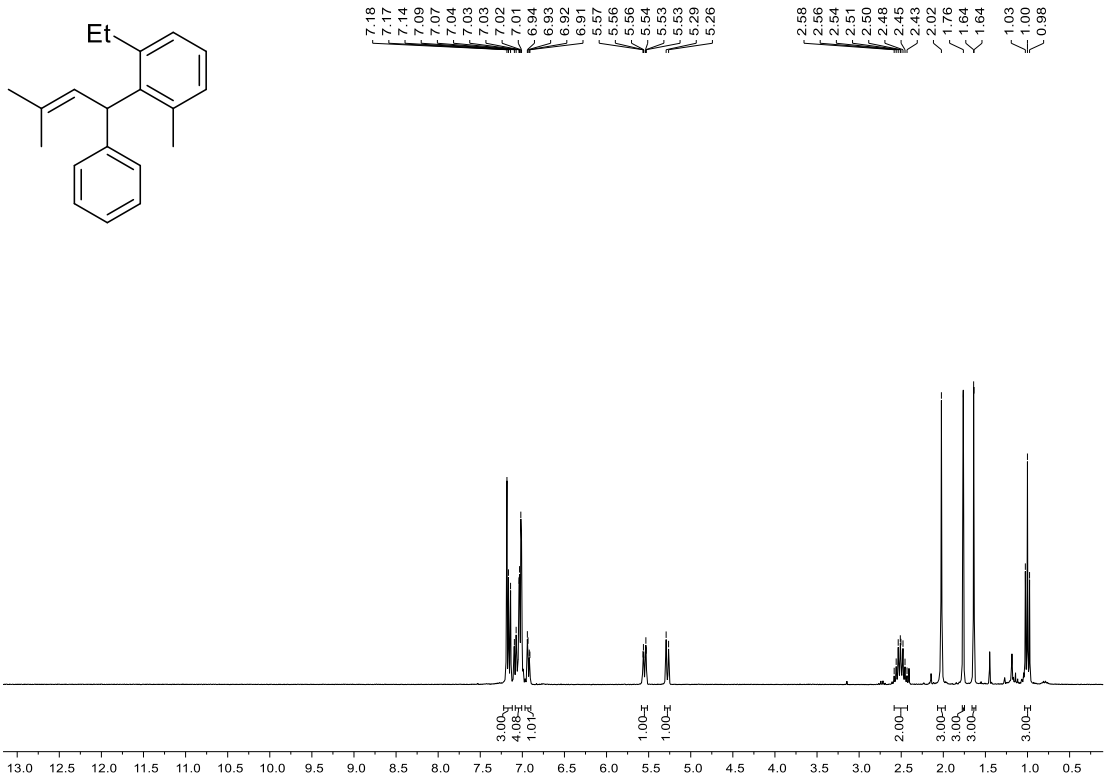


1-Ethyl-3-methyl-2-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2c)



According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 1-ethyl-2-iodo-3-methylbenzene (78.3 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as colourless oil (63.0 mg, 0.238 mmol, 83%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.20 – 7.13 (m, 3H, CH_{arom}), 7.11 – 6.98 (m, 4H, CH_{arom}), 6.93 (dd, *J* = 6.7 Hz, 2.3 Hz, 1H, CH_{arom}), 5.55 (dt, *J* = 8.7 Hz, 1.4 Hz, 1H, CH), 5.28 (d, *J* = 8.7 Hz, 1H, CH_{olefin}), 2.59 – 2.40 (m, 2H, CH_2), 2.02 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.64 (d, *J* = 1.4 Hz, 3H, CH_3), 1.00 (t, *J* = 7.5 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K) δ = 144.5 (C), 143.0 (C), 140.5 (C), 137.0 (C), 134.2 (C), 129.3 (CH), 128.1 (2 x CH), 127.3 (CH), 127.1 (2 x CH), 126.4 (CH), 125.5 (CH), 125.4 (CH), 43.6 (CH), 27.2 (CH_2), 25.9 (CH_3), 21.6 (CH_3), 18.3 (CH_3), 15.4 (CH_3). **IR** (neat) 2965*w*, 2928*w*, 2873*w*, 1600*w*, 1492*m*, 1447*m*, 1375*w*, 1030*w*, 779*m*, 743*s*, 705*s*. **HRMS** (APCI) *m*/*z* = 371.0924 calcd. for $C_{20}H_{24}Ag$ $[M+Ag]^+$, found: 371.0922.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5.57
5.56
5.56
5.54
5.53
5.53
5.29
5.26
2.58
2.56
2.54
2.51
2.50
2.48
2.45
2.43
2.02
1.76
1.64
1.64
1.03
1.00
0.98
3.00
4.08
1.01
1.00
1.00
2.00
3.00
3.00
3.00
3.00
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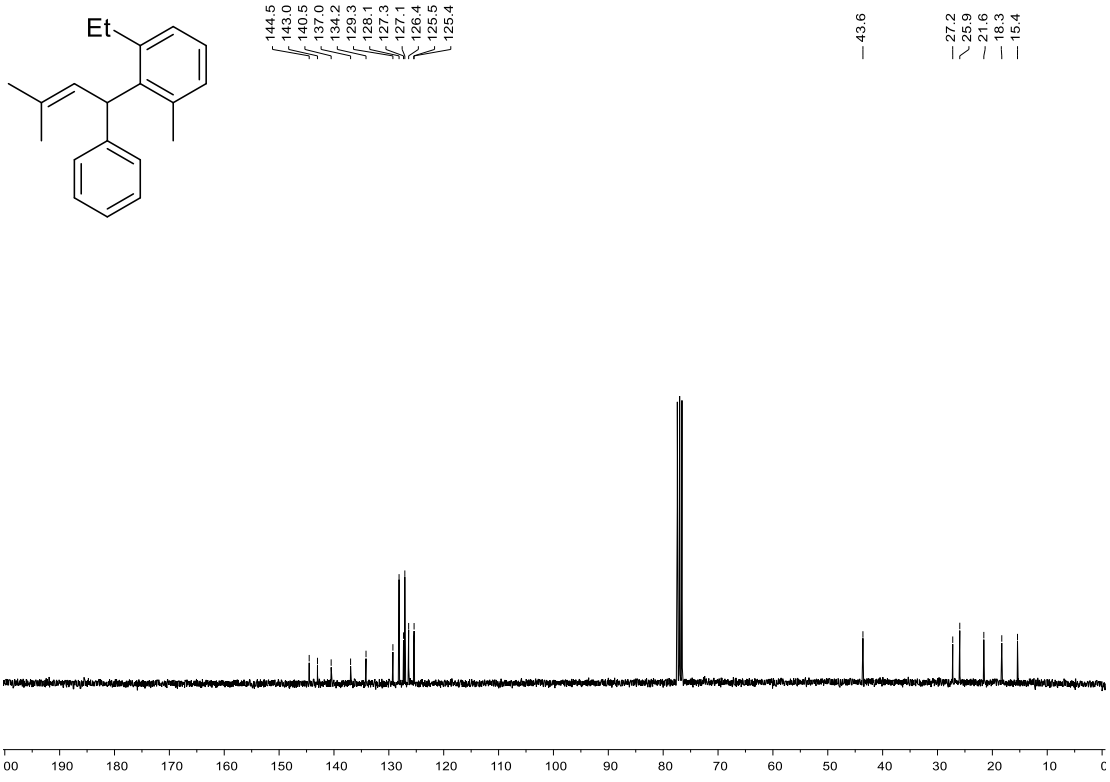
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125.4
43.6
27.2
25.9
21.6
18.3
15.4
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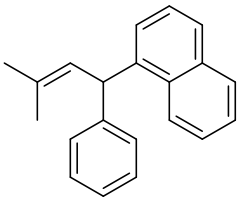
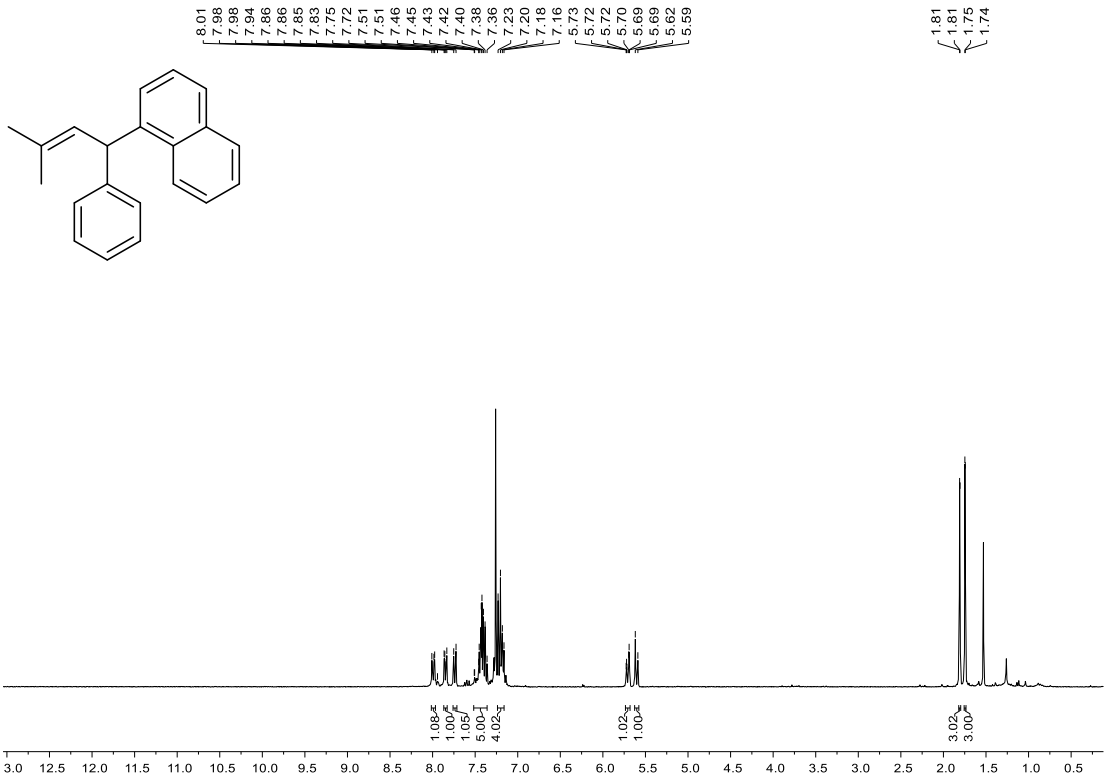
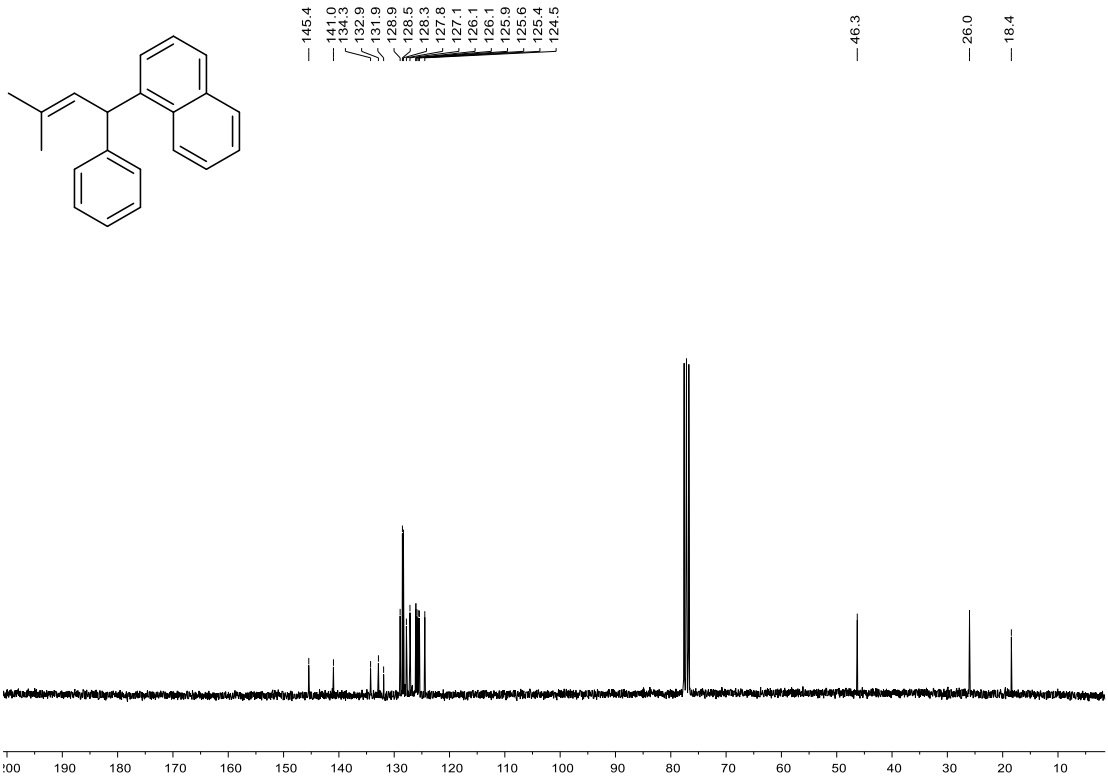
1-(3-Methyl-1-phenylbut-2-en-1-yl)naphthalene (2i)



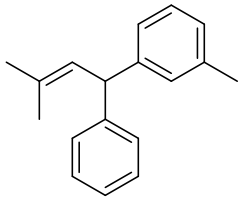
According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 1-iodonaphthalene (80.1 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as colourless oil (31 mg, 0.11 mmol, 37%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.04 – 7.91 (m, 1H, CH_{arom}), 7.90 – 7.80 (m, 1H, CH_{arom}), 7.79 – 7.69 (m, 1H, CH_{arom}), 7.54 – 7.32 (m, 5H, CH_{arom}), 7.26 – 7.12 (m, 4H, CH_{arom}), 5.71 (dt, *J* = 9.0 Hz, 1.3 Hz, 1H, CH_{olefin}), 5.60 (d, *J* = 9.0 Hz, 1H, CH), 1.81 (d, *J* = 1.3 Hz, 3H, CH_3), 1.75 (d, *J* = 1.3 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 145.4 (C), 141.0 (C), 134.3 (C), 132.9 (C), 131.9 (C), 128.9 (CH), 128.5 (2 x CH), 128.3 (2 x CH), 127.8 (CH), 127.1 (CH), 126.1 (CH), 126.1 (CH), 125.9 (CH), 125.6 (CH), 125.4 (CH), 124.5 (CH), 46.3 (CH), 26.0 (CH_3), 18.4 (CH_3). **IR** (neat): 3059*w*, 2970*w*, 2912*w*, 1733*w*, 1590*w*, 1492*m*, 1449*m*, 1395*w*, 1251*w*, 1029*w*, 889*w*, 792*s*, 776*s*, 726*m*, 699*s*, 566*m*. **HRMS** (APCI) *m*/*z* = 273.1638 calcd. for $C_{21}H_{20}Ag$ $[M+Ag]^+$, found: 273.1635.



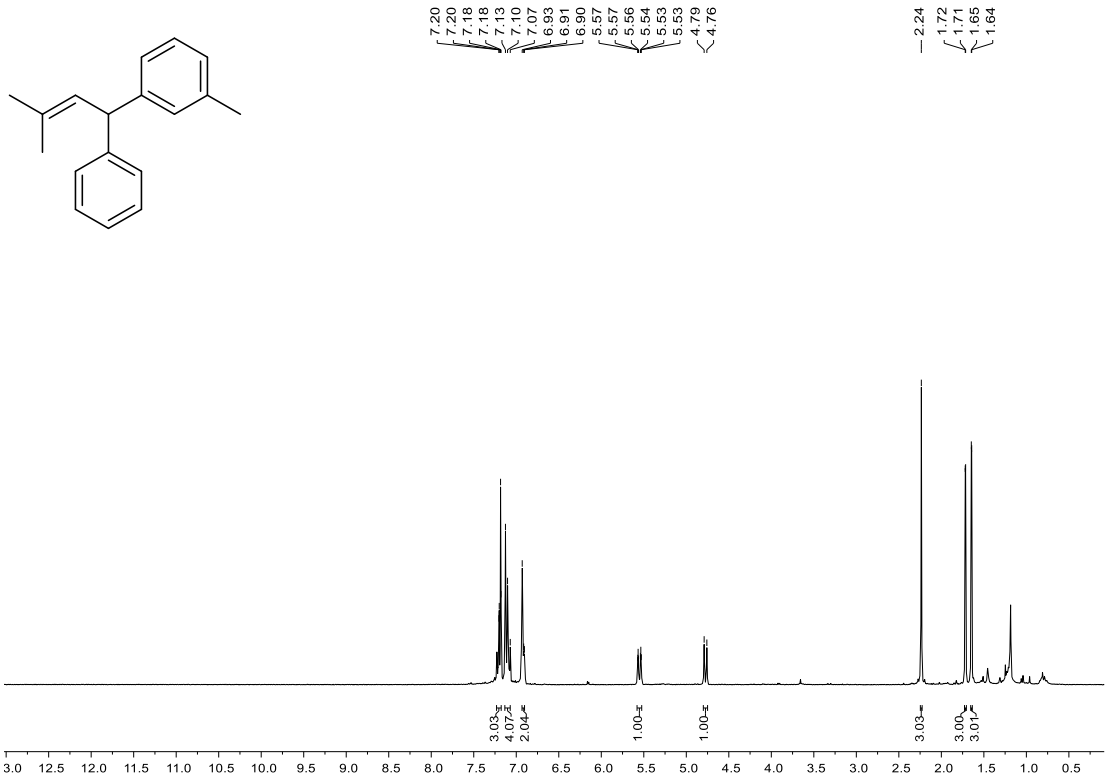


1-Methyl-3-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2a)



According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-3-methylbenzene (69.4 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as colourless oil (22.0 mg, 931 µmol, 33%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.20 – 7.18 (m, 3H, CH_{arom}), 7.13 – 7.07 (m, 4H, CH_{arom}), 6.93 – 6.90 (m, 2H, CH_{arom}), 5.55 (dt, *J* = 9.5 Hz, 1.4 Hz, 1H, CH_{olefin}), 4.76 (d, *J* = 9.5 Hz, 1H, CH), 3.70 (s, 3H, CH_3), 1.72 (d, *J* = 1.4, 3H, CH_3), 1.65 (d, *J* = 1.4, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 145.4 (C), 145.2 (C), 138.1 (C), 132.5 (C), 129.1 (CH), 128.5 (3 x CH), 128.4 (2 x CH), 127.5 (CH), 126.9 (CH), 126.1 (CH), 125.4 (CH), 49.5 (CH), 26.1 (CH_3), 21.7 (CH_3), 18.2 (CH_3). **IR** (neat): 3028*w*, 2966*w*, 2925*m*, 2856*w*, 2364*w*, 2033*w*, 1606*w*, 1492*m*, 1448*m*, 1376*m*, 1258*w*, 1073*w*, 1031*w*, 860*w*, 780*w*, 734*w*, 698*s*, 631*s*. **HRMS** (APCI) *m*/*z* = 343.0616 calcd. for $C_{18}H_{20}Ag$ $[M+Ag]^+$, found: 343.0601.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1.71
1.65
1.64
3.03
4.07
2.04
1.00
1.00
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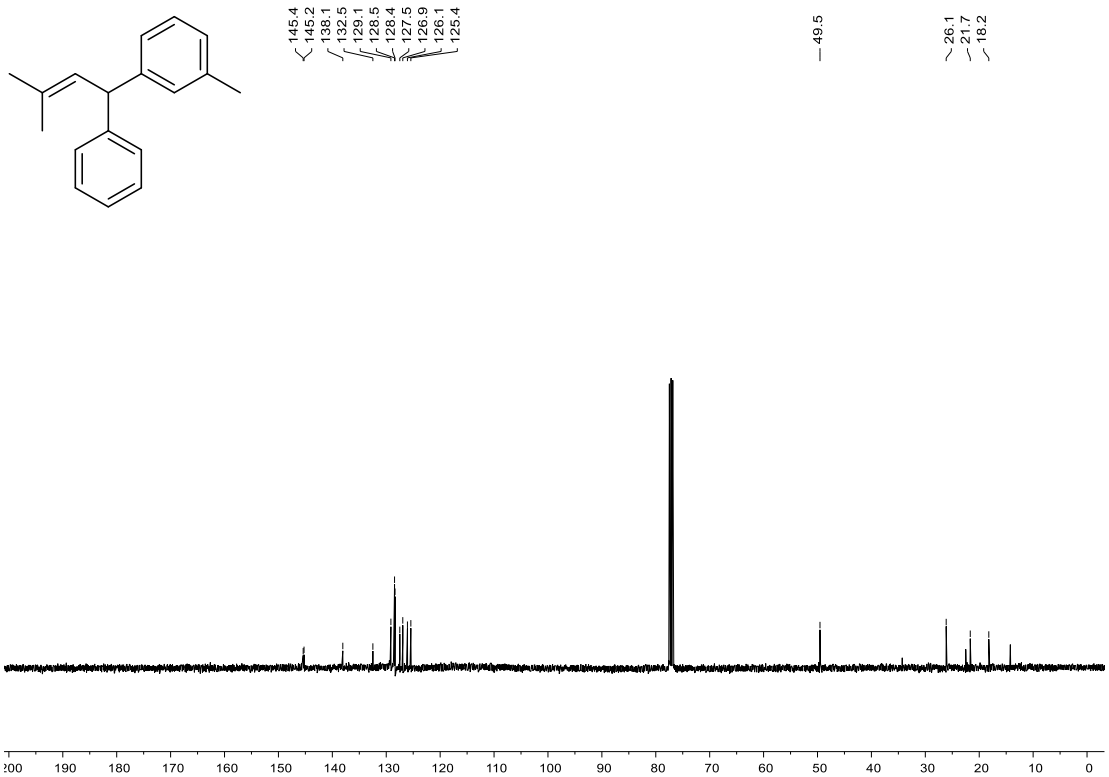
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26.1
21.7
18.2
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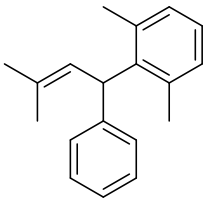
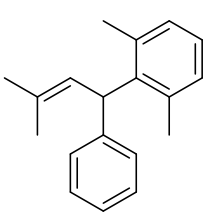
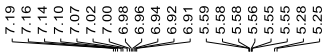
1,3-Dimethyl-2-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2b)

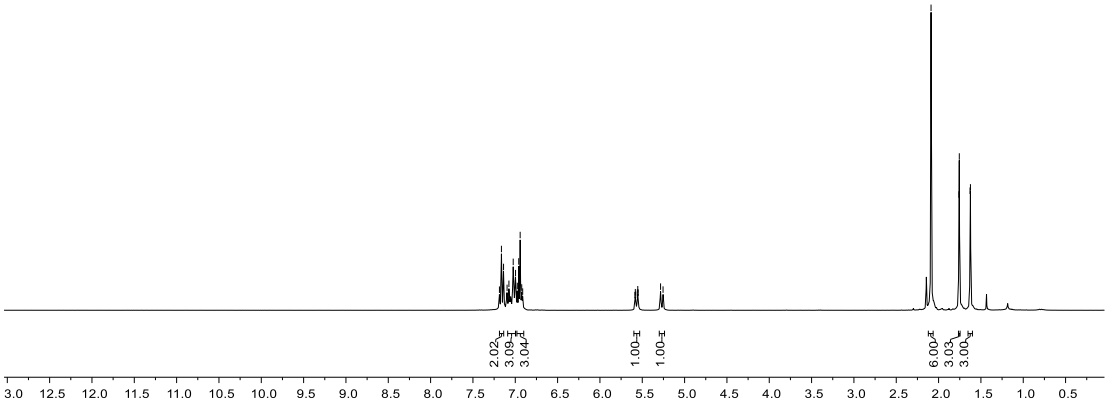


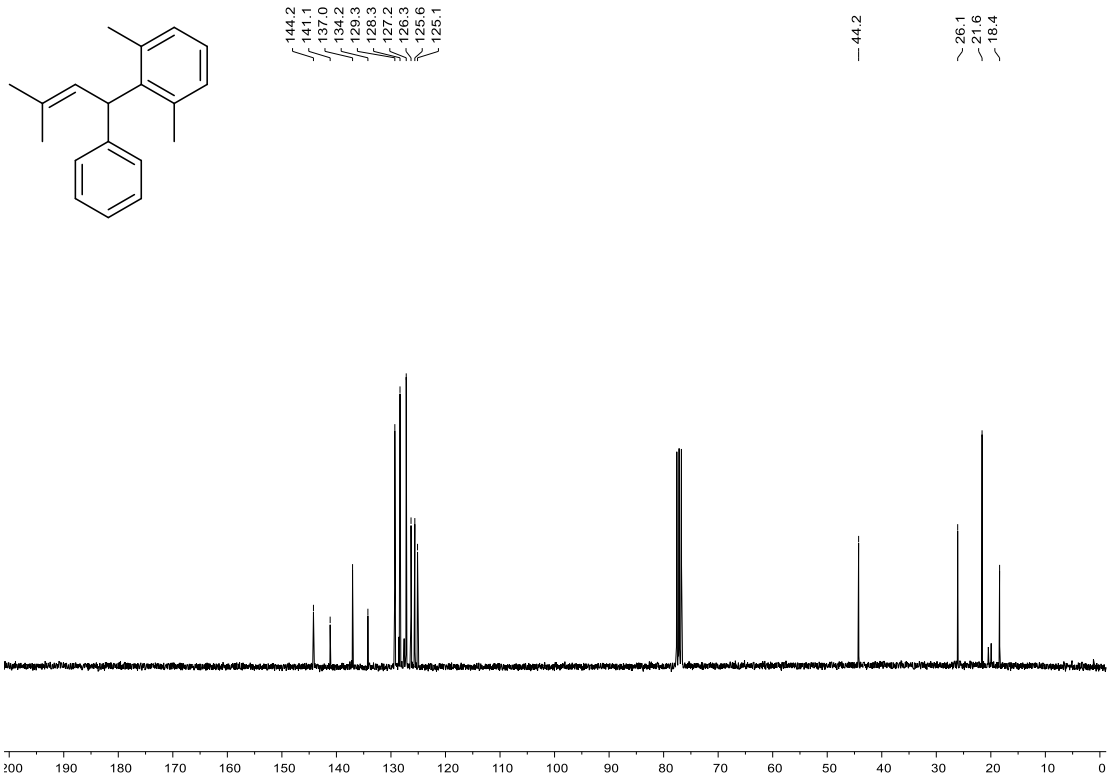
According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 2-iodo-1,3-dimethylbenzene (73.8 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as colourless oil (51.6 mg, 0.206 mmol, 72%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.16 (t, *J* = 7.3 Hz, 2H, CH_{arom}), 7.11 – 6.97 (m, 3H, CH_{arom}), 6.96 – 6.87 (m, 3H, CH_{arom}), 5.57 (dt, *J* = 8.8 Hz, 1.4 Hz, 1H, CH_{olefin}), 5.27 (d, *J* = 8.8 Hz, 1H, CH), 2.09 (s, 6H, 2 x CH_3), 1.76 (d, *J* = 1.4 Hz, 3H, CH_3), 1.63 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 144.2 (C), 141.1 (C), 137.0 (2 x C), 134.2 (C), 129.3 (2 x CH), 128.3 (2 x CH), 127.2 (2 x CH), 126.3 (CH), 125.6 (CH), 125.1 (CH), 44.2 (CH), 26.1 (CH_3), 21.6 (2 x CH_3), 18.4 (CH_3). **IR** (neat): 2926*w*, 2252*w*, 1599*w*, 1447*w*, 1378*w*, 1260*w*, 1103*w*, 1030*w*, 904*s*, 726*s*, 649*s*. **HRMS** (APCI) *m*/*z* = 357.0772 calcd. for $C_{14}H_{18}Ag$ $[M+Ag]^+$, found: 357.0769.

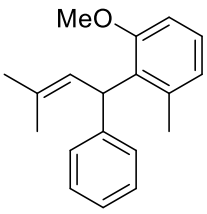






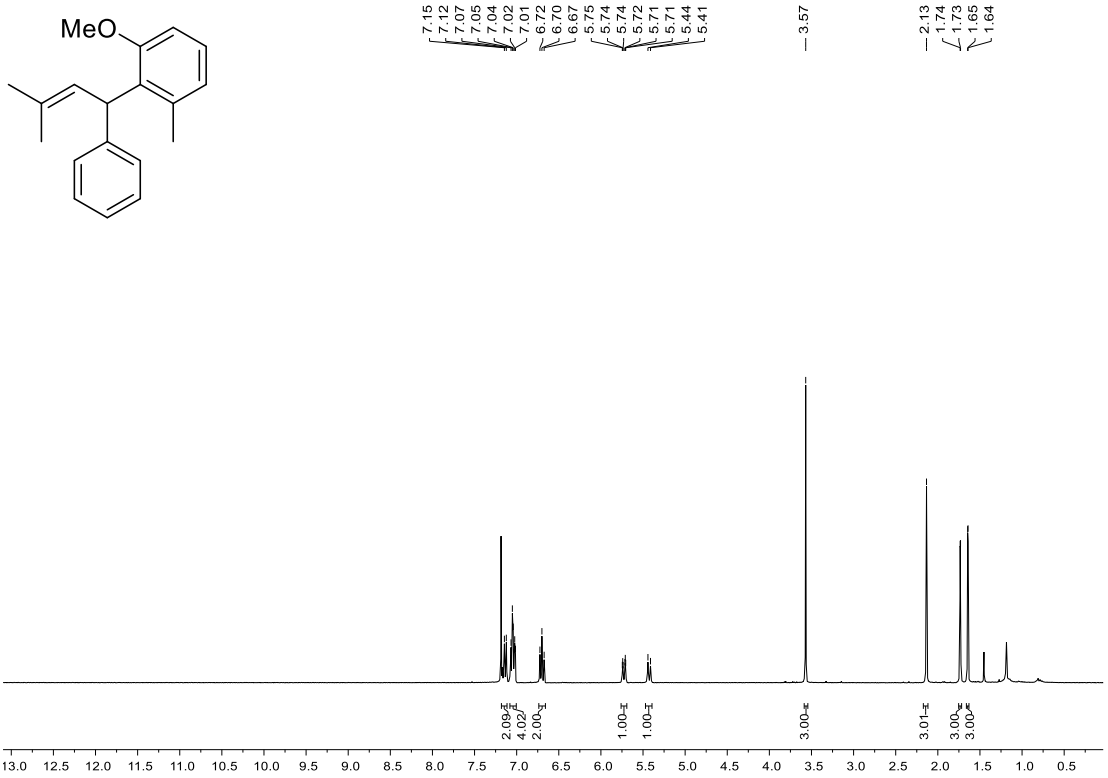


1-Methoxy-3-methyl-2-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2g)



According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 2-iodo-1-methoxy-3-methylbenzene (78.9 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as colourless oil (63.1 mg, 0.237 mmol, 83%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.18 – 7.09 (m, 2H, CH_{arom}), 7.10 – 6.98 (m, 4H, CH_{arom}), 6.70 (t, *J* = 7.5 Hz, 2H, CH_{arom}), 5.73 (dt, *J* = 9.2 Hz, 1.4 Hz, 1H, CH_{olefin}), 5.43 (d, *J* = 9.2 Hz, 1H, CH), 3.57 (s, 3H, OCH_3), 2.13 (s, 3H, CH_3), 1.73 (d, *J* = 1.4 Hz, 3H, CH_3), 1.64 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 158.0 (C), 144.9 (C), 137.9 (C), 133.3 (C), 131.8 (C), 128.0 (2 x CH), 127.1 (2 x CH), 127.1 (CH), 125.5 (CH), 125.3 (CH), 123.9 (CH), 109.8 (CH), 55.9 (CH_3), 41.2 (CH), 26.1 (CH_3), 21.0 (CH_3), 18.2 (CH_3). **IR** (neat): 2928*w*, 1581*w*, 1469*m*, 1447*w*, 1247*m*, 1077*m*, 1033*w*, 1001*w*, 908*m*, 773*m*, 733*s*, 697*s*. **HRMS** (APCI) *m*/*z* = 373.722 calcd. for $C_{19}H_{22}OAg$ $[M+Ag]^+$, found: 373.0719.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4.02
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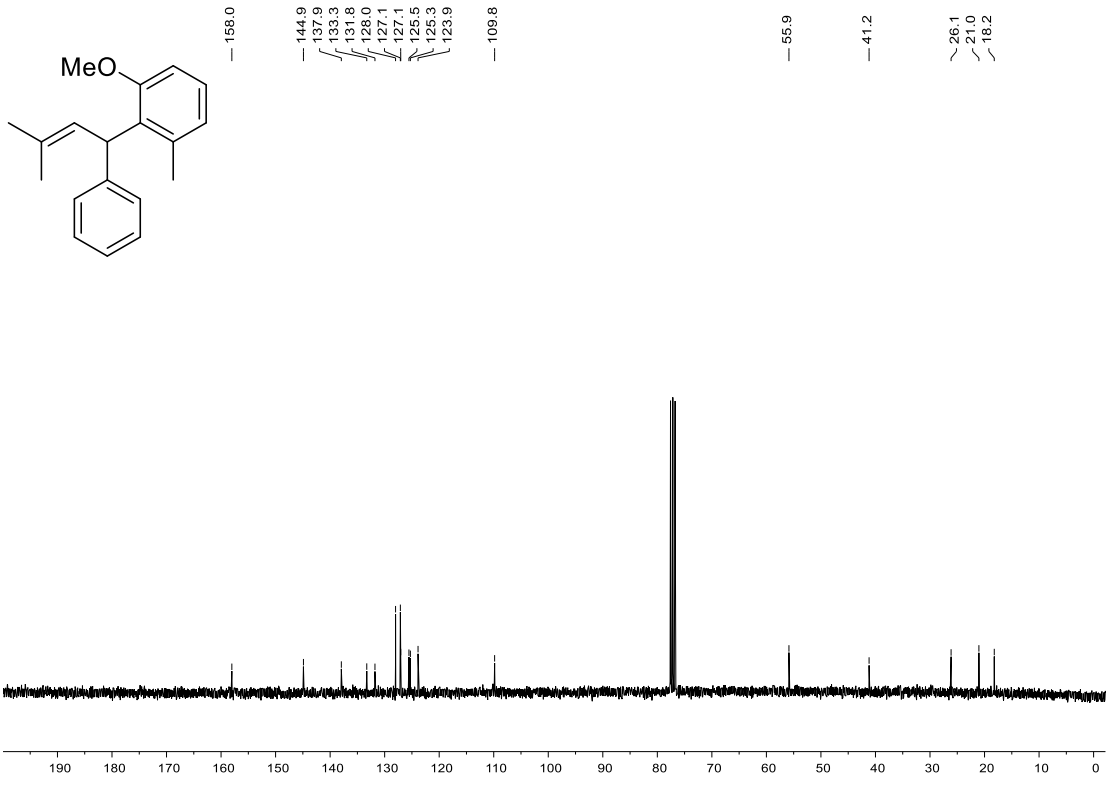
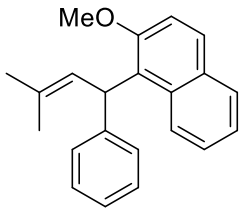
3.00
3.01
3.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

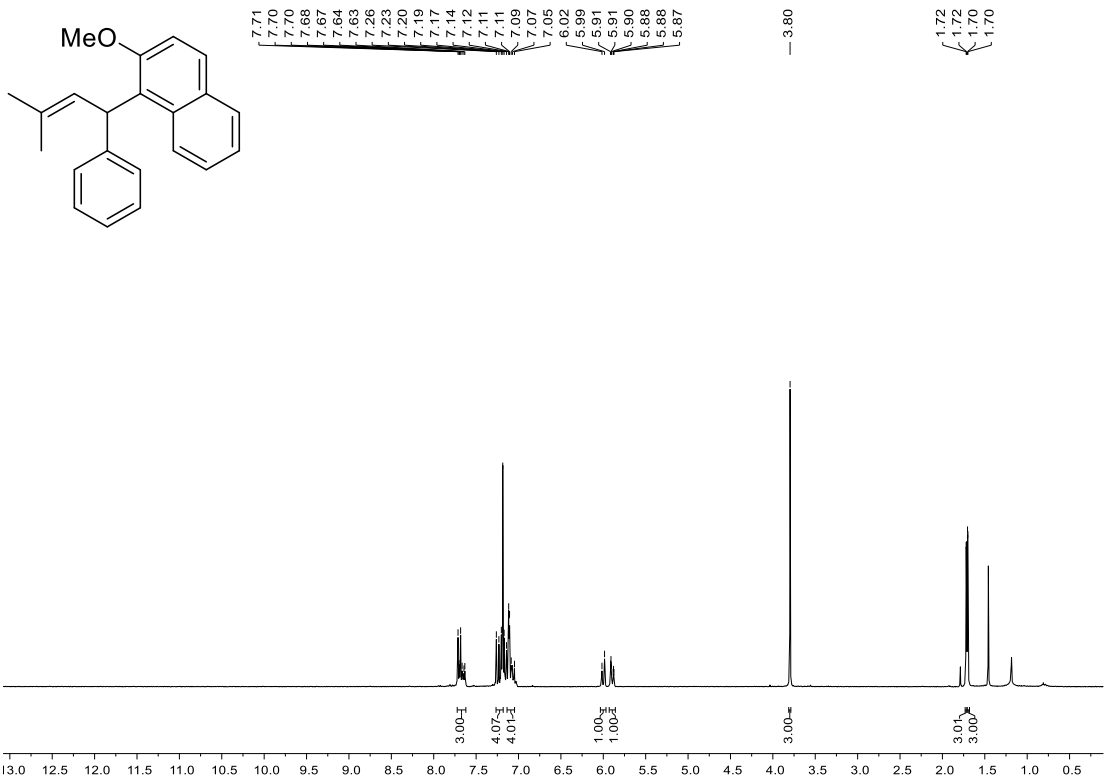

MeO
158.0
144.9
137.9
133.3
131.8
128.0
127.1
127.1
125.5
125.3
123.9
109.8
55.9
41.2
26.1
21.0
18.2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

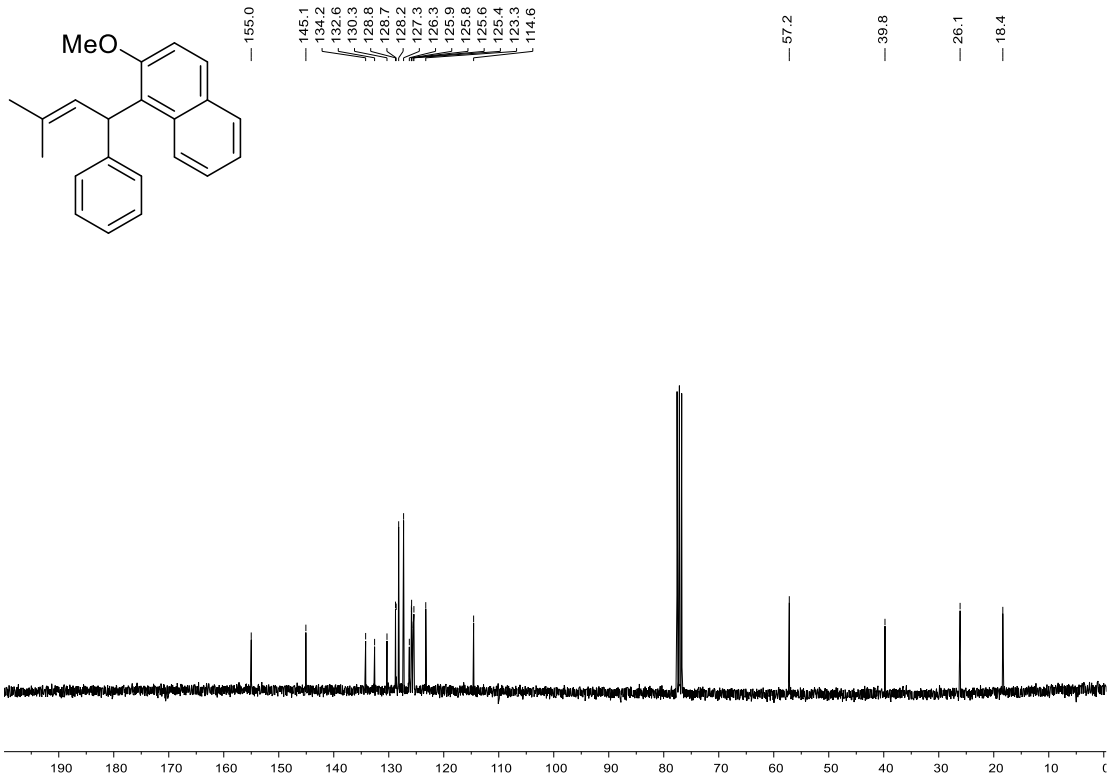
2-Methoxy-1-(3-methyl-1-phenylbut-2-en-1-yl)naphthalene (2j)



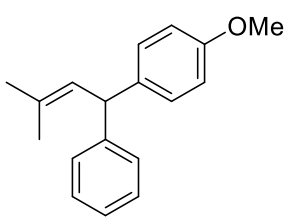
According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-2-methoxynaphthalene (90.4 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as yellow oil (50.0 mg, 0.165 mmol, 58%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.73 – 7.62 (m, 3H, CH_{arom}), 7.27 – 7.16 (m, 4H, CH_{arom}), 7.15 – 7.02 (m, 4H, CH_{arom}), 6.00 (d, *J* = 9.1 Hz, 1H, CH_{olefin}), 5.89 (dt, *J* = 9.1 Hz, 1.3 Hz, 1H, CH), 3.80 (s, 3H, OCH_3), 1.72 (d, *J* = 1.3 Hz, 3H, CH_3), 1.70 (d, *J* = 1.3 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 155.0 (C), 145.1 (C), 134.2 (C), 132.6 (C), 130.3 (C), 128.8 (C), 128.7 (CH), 128.2 (2 x CH) , 127.3 (2 x CH), 126.3 (CH), 125.9 (CH), 125.8 (CH), 125.6 (CH), 125.4 (CH), 123.3 (CH), 114.6 (CH), 57.2 (CH_3), 39.8 (CH), , 26.1 (CH_3), 18.4 (CH_3). **IR** (neat): 3050*w*, 2914*w*, 1623*w*, 1597*m*, 1549*m*, 1491*m*, 1447*w*, 1248*s*, 1179*w*, 1078*m*, 1025*w*, 887*w*, 805*m*, 748*m*, 722*w*, 697*s*. **HRMS** (ESI) *m*/*z* = 325.1568 calcd. for $C_{22}H_{22}ONa$ $[M+Na]^+$, found: 325.1564.



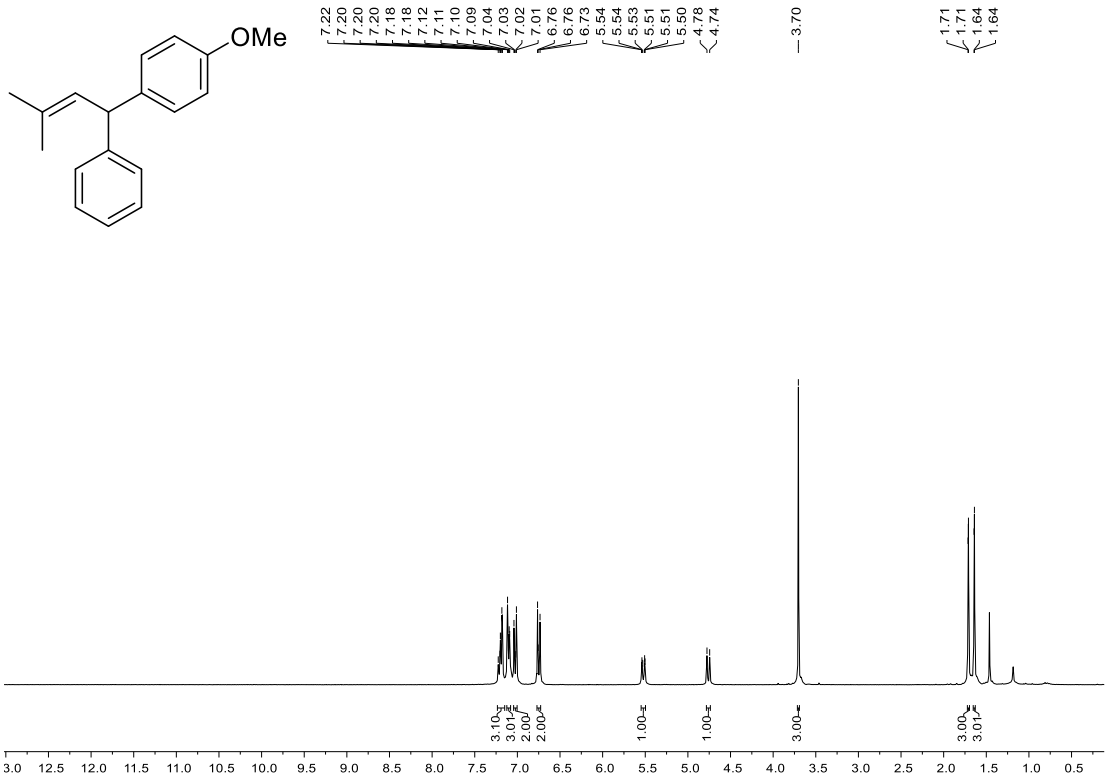


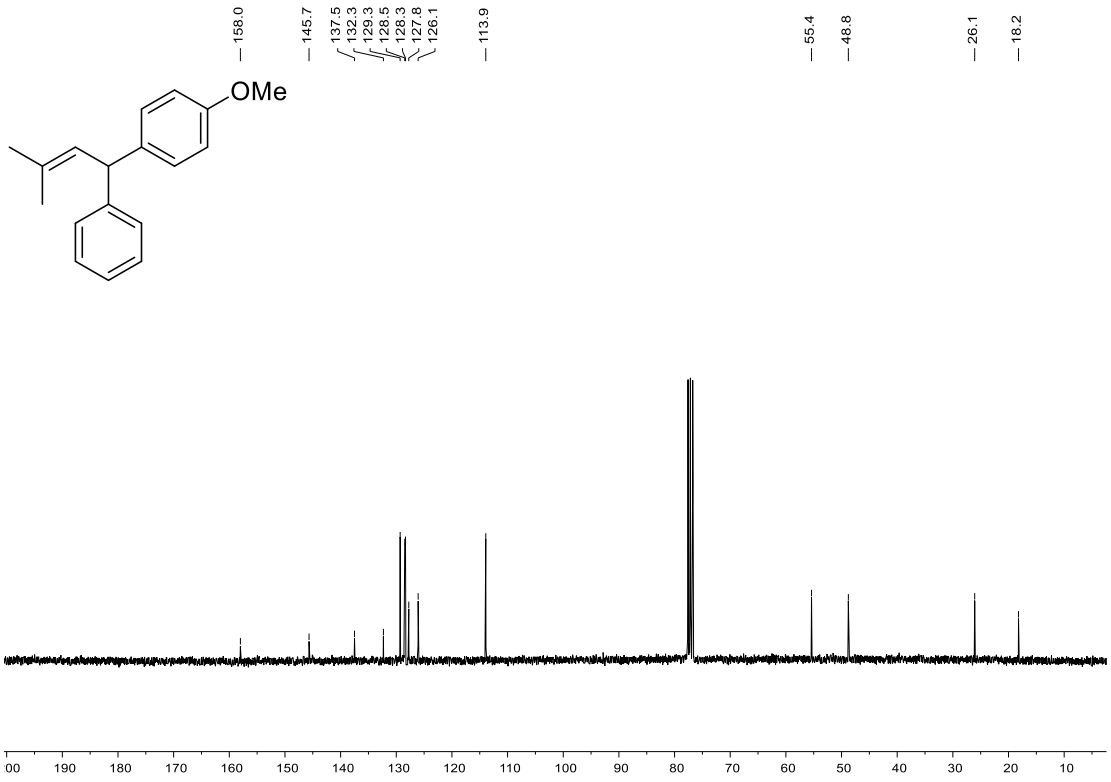
1-Methoxy-4-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2f)



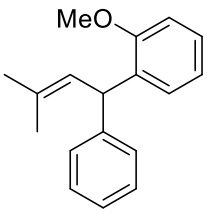
According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-4-methoxybenzene (74.4 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as colourless oil (14.4 mg, 572 µmol, 20%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.22 – 7.18 (m, 2H, CH_{arom}), 7.12 – 7.09 (m, 3H, CH_{arom}), 7.04 – 7.01 (m, 2H, CH_{arom}), 6.76 – 6.73 (m, 2H, CH_{arom}), 5.52 (dt, *J* = 9.5 Hz, 1.4 Hz, 1H, CH_{olefin}), 4.76 (d, *J* = 9.5 Hz, 1H, CH), 3.70 (s, 3H, OCH_3), 1.71 (d, *J* = 1.4 Hz, 3H, CH_3), 1.64 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 158.0 (C), 145.7 (C), 137.5 (C), 132.3 (C), 129.3 (2 x CH), 128.5 (2 x CH), 128.3 (2 x CH), 127.8 (CH), 126.1 (CH), 113.9 (2 x CH), 55.4 (CH_3), 48.8 (CH), 26.1 (CH_3), 18.2 (CH_3). **HRMS** (ESI) *m*/*z* = 275.1412 calcd. for $C_{18}H_{20}ONa$ $[M+Na]^+$, found: 275.1394.


OMe
7.22
7.20
7.20
7.20
7.18
7.18
7.12
7.11
7.10
7.09
7.04
7.03
7.02
7.01
6.76
6.76
6.73
5.54
5.54
5.53
5.51
5.51
5.50
4.78
4.74
3.70
1.71
1.71
1.64
1.64
3.10
3.01
2.00
2.00
1.00
1.00
3.00
3.00
3.01

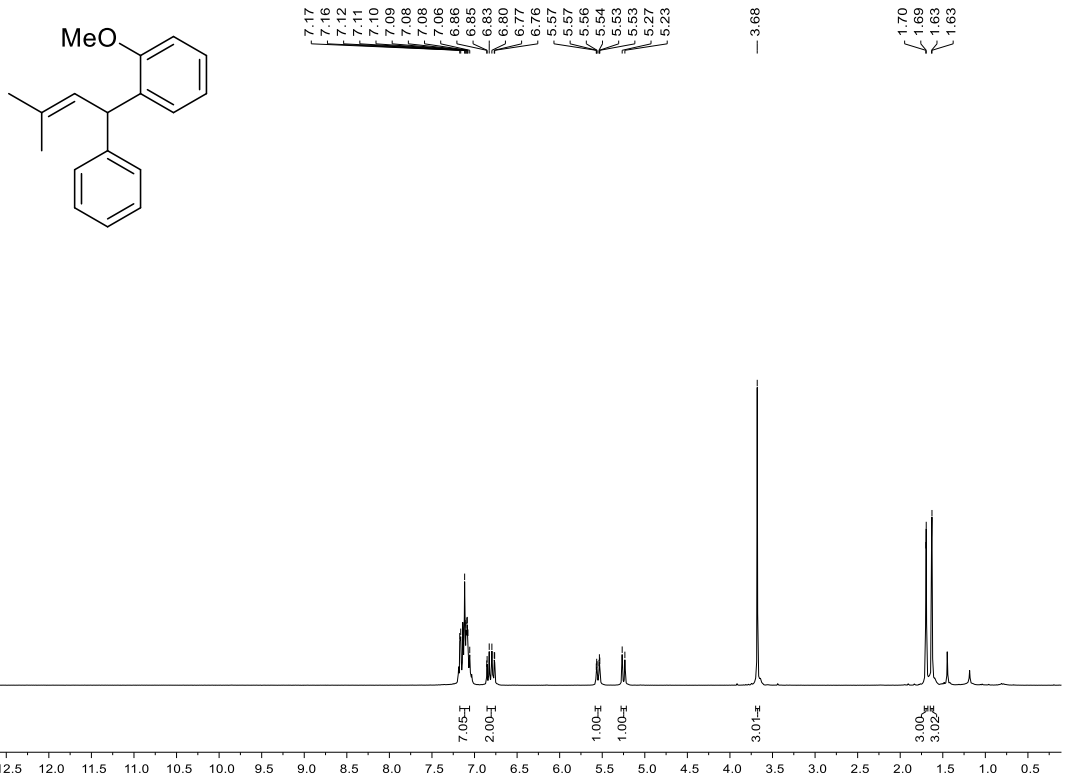

OMe
158.0
145.7
137.5
132.3
129.3
128.5
128.3
127.8
126.1
113.9
55.4
48.8
26.1
18.2

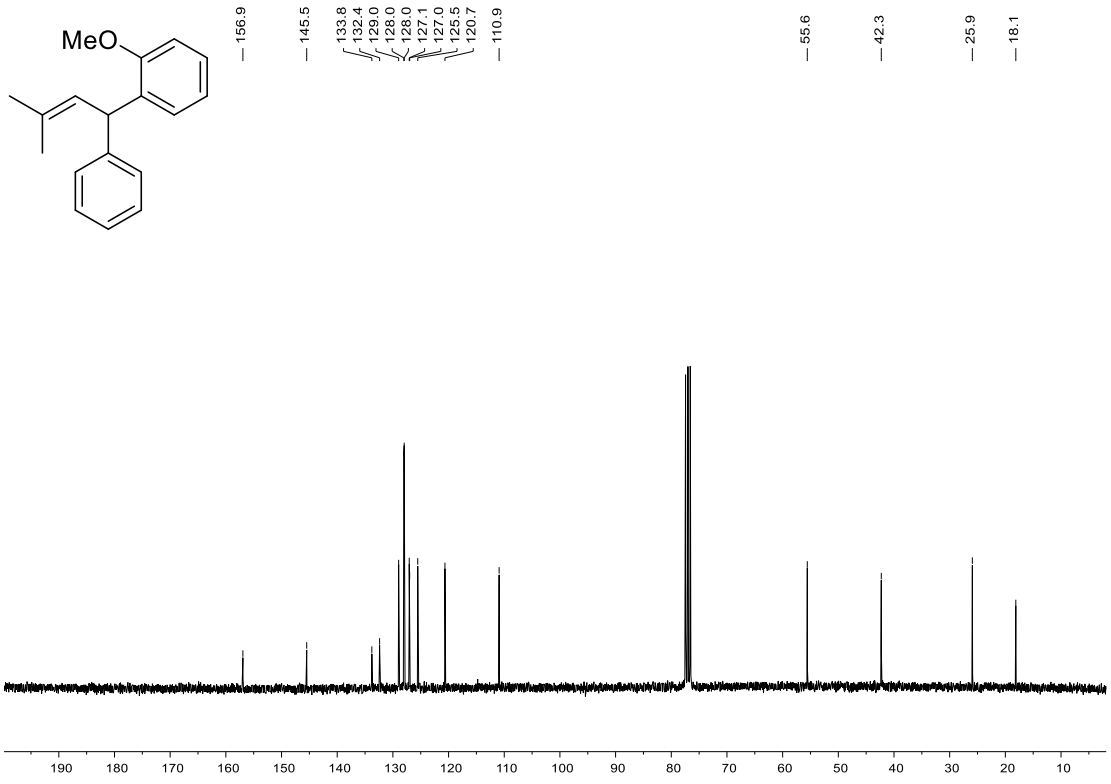
1-Methoxy-2-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2d)



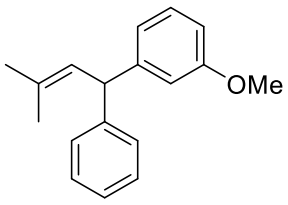
According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-2-methoxybenzene (74.4 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as colourless oil (33.3 mg, 0.132 mmol, 46%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.21 – 7.00 (m, 7H, CH_{arom}), 6.89 – 6.73 (m, 2H, CH_{arom}), 5.55 (dt, *J* = 9.5 Hz, 1.4 Hz, 1H, CH_{olefin}), 5.25 (d, *J* = 9.5 Hz, 1H, CH), 3.68 (s, 3H, OCH_3), 1.70 (d, *J* = 1.4 Hz, 3H, CH_3), 1.63 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 156.9 (C), 145.5 (C), 133.8 (C), 132.4 (C), 129.0 (CH), 128.0 (2 x CH), 128.0 (2 x CH), 127.1 (CH), 127.0 (CH), 125.5 (CH), 120.7 (CH), 110.9 (CH), 55.6 (CH_3), 42.3 (CH), 25.9 (CH_3), 18.1 (CH_3). **IR** (neat): 2966*m*, 2926*m*, 1662*w*, 1599*m*, 1447*m*, 1377*w*, 1260*w*, 1177*w*, 1109*w*, 1030*m*, 907*m*, 736*s*, 702*s*, 648*w*, 586*m*, 547*m*. **HRMS** (ESI) *m*/*z* = 275.1412 calcd. for $C_{18}H_{20}ONa$ $[M+Na]^+$, found: 275.1406.



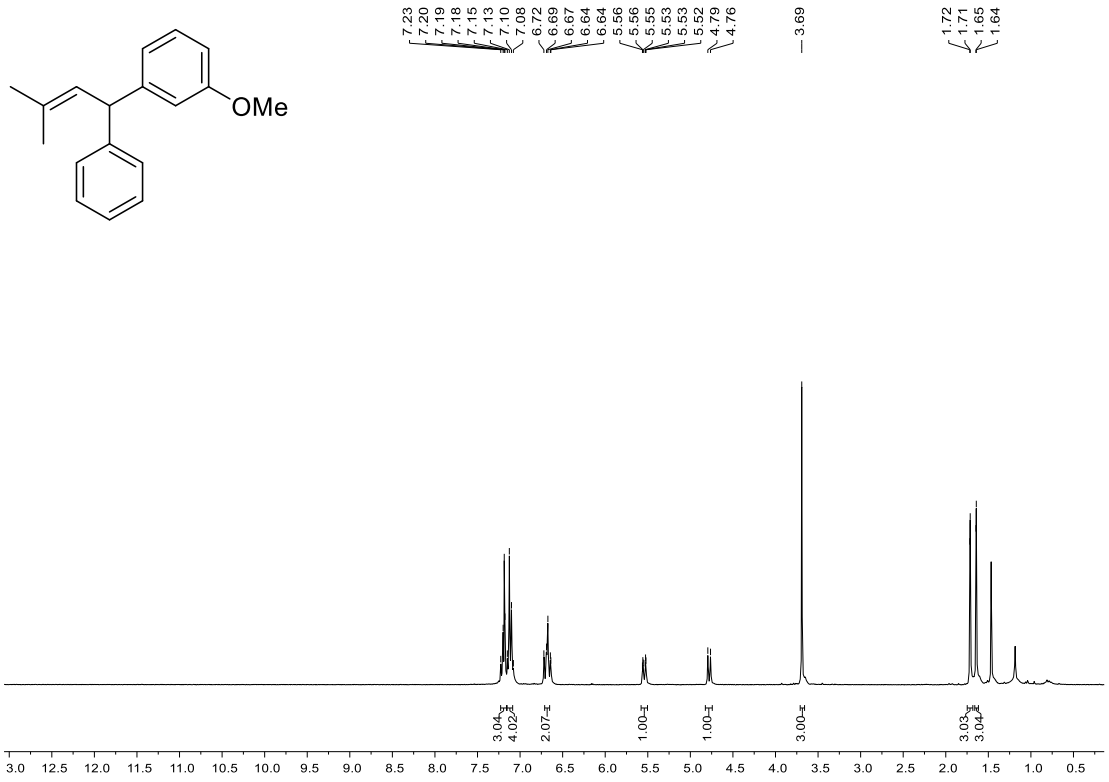


1-Methoxy-3-(3-methyl-1-phenylbut-2-en-1-yl)benzene (2e)



According to **GP3** with (*Z*)-2,2-dimethyl-4-phenylbut-3-enoic acid (55.0 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-3-methoxybenzene (74.4 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product as yellow oil (15.9 mg, 62.9 µmol, 22%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.24 – 7.17 (m, 3H, CH_{arom}), 7.16 – 7.04 (m, 4H, CH_{arom}), 6.75 – 6.60 (m, 2H, CH_{arom}), 5.54 (dt, *J* = 9.5 Hz, 1.4 Hz, 1H, CH_{olefin}), 4.78 (d, *J* = 9.5 Hz, 1H, CH), 3.69 (s, 3H, OCH_3), 1.72 (d, *J* = 1.4 Hz, 3H, CH_3), 1.64 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 159.8 (C), 147.0 (C), 145.2 (C), 132.8 (C), 129.4 (CH), 128.4 (d, *J* = 9.3 Hz, 4 x CH), 127.3 (CH), 126.2 (CH), 120.9 (CH), 114.6 (CH), 111.1 (CH), 55.3 (CH_3), 49.6 (CH), 26.1 (CH_3), 18.2 (CH_3). **IR** (neat): 2966*m*, 2926*m*, 1662*w*, 1599*m*, 1447*m*, 1377*w*, 1269*w*, 1177*w*, 1109*w*, 1030*m*, 907*m*, 736*s*, 702*s*, 648*w*, 586*m*, 547*m*. **HRMS** (ESI) *m*/*z* = 275.1412 calcd. for $C_{18}H_{20}ONa$ $[M+Na]^+$, found: 275.1406.


OMe
7.23
7.20
7.19
7.18
7.15
7.13
7.10
7.08
6.72
6.69
6.67
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6.64
5.56
5.56
5.55
5.53
5.53
5.52
4.79
4.76
3.69
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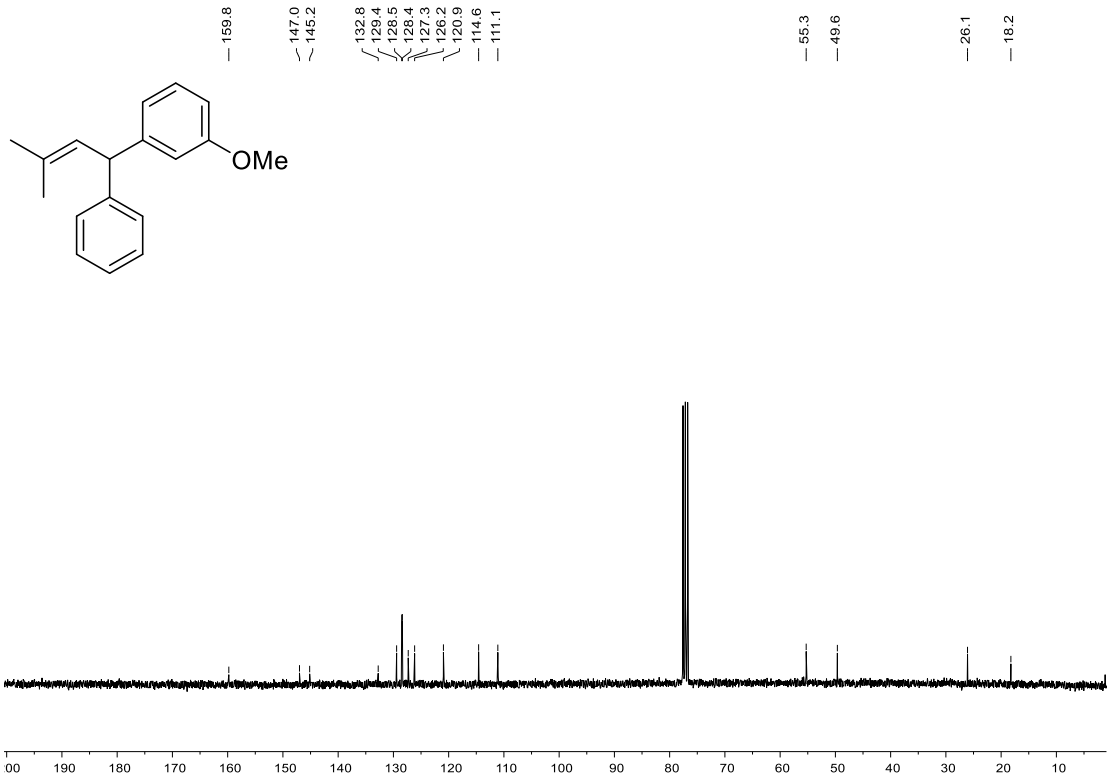
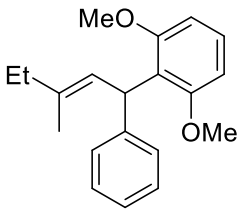
2.07
1.00
1.00
3.00
3.03
3.04

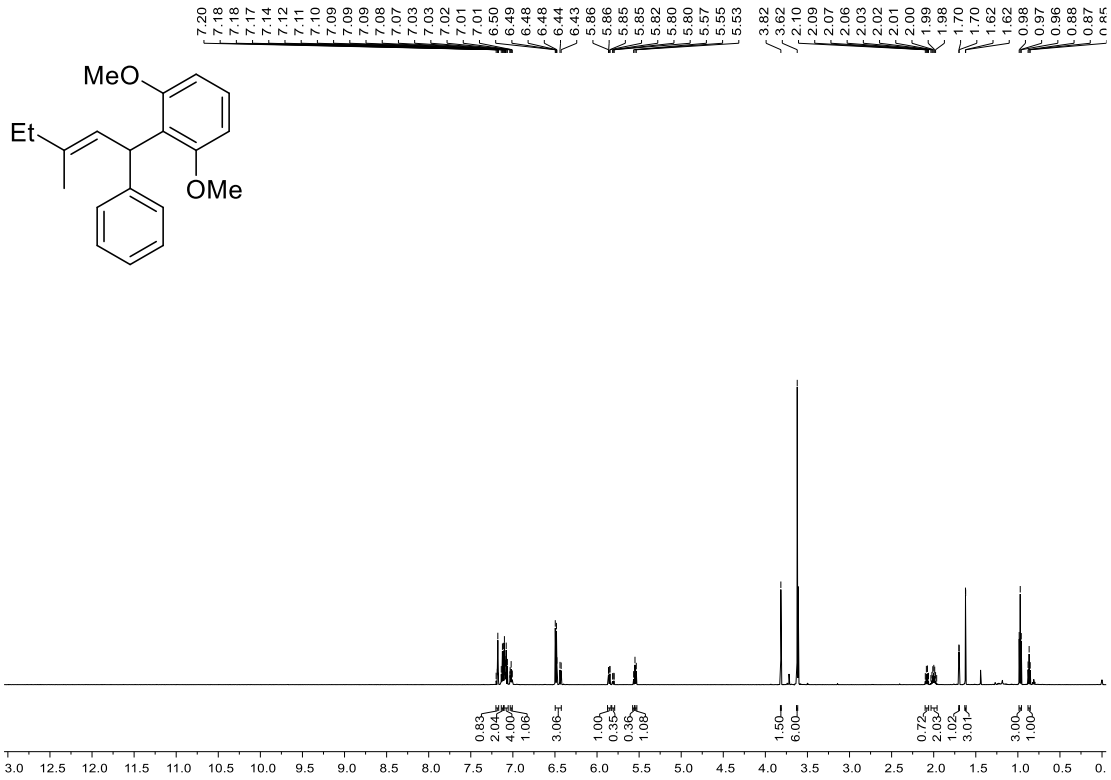

OMe
159.8
147.0
145.2
132.8
129.4
128.5
128.4
127.3
126.2
120.9
114.6
111.1
55.3
49.6
26.1
18.2

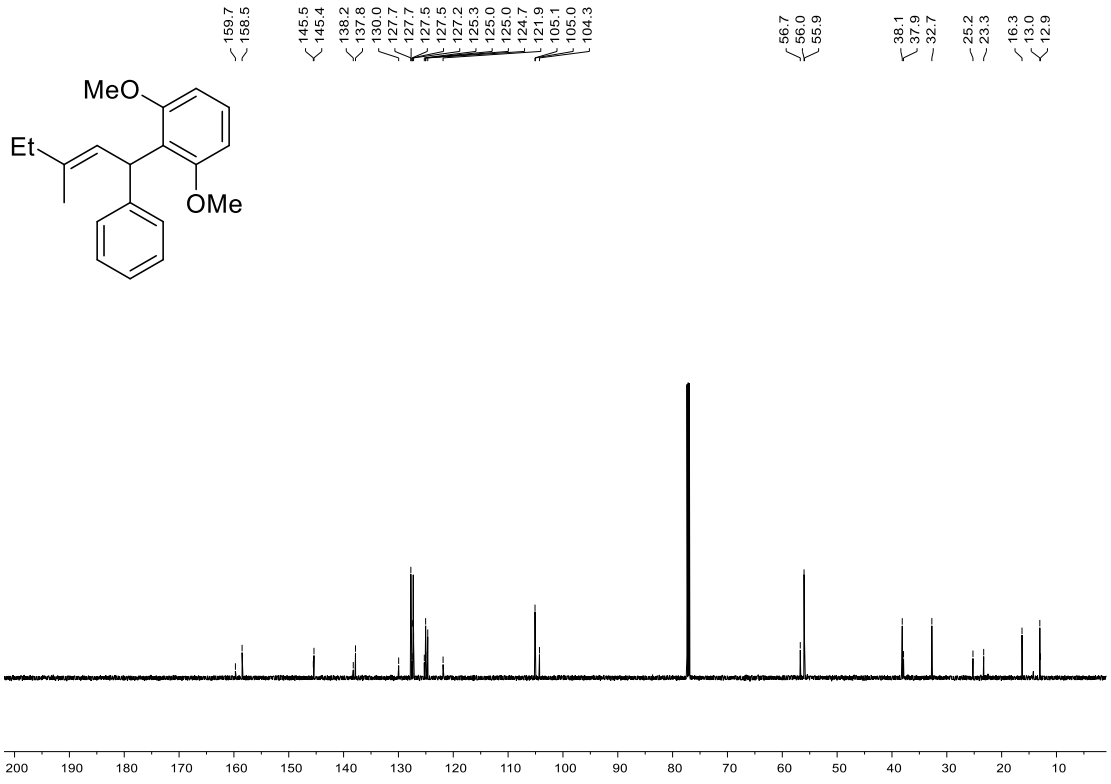
1,3-Dimethoxy-2-(3-methyl-1-phenylpent-2-en-1-yl)benzene (3a)



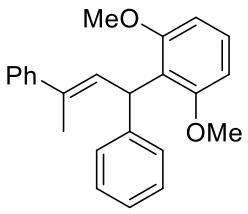
According to **GP3** with (*Z*)-2-ethyl-2-phenylbut-3-enoic acid (58.4 mg, 0.286 mmol, 1.0 equiv.) and 2-iodo-1,3-dimethoxybenzene (84.0 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide analytically pure product with an *E*/*Z*-isomer ratio of 3:1 as yellow solid (45.0 mg, 0.151 mmol, 53%).

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ = 7.20 – 7.17 (m, 1H, CH_{arom}), 7.14 – 7.10 (m, 3H, CH_{arom}), 7.10 – 7.06 (m, 3H, CH_{arom}), 7.04 – 7.00 (m, 1H, CH_{arom}), 6.49 (m, 3H, CH_{arom}), 5.86 (dd, *J* = 9.2 Hz, 1.3 Hz, 1H, (*E*)-CH_{olefin}), 5.80 (m, 1H, (*Z*)-CH_{olefin}), 5.57 (m, 1H, (*Z*)-CH), 5.54 (d, *J* = 9.3 Hz, 1H, (*E*)-CH), 3.82 (s, 2H, (*Z*)-CH_3), 3.62 (s, 6H, (*E*)-CH_3), 2.08 (q, *J* = 7.6 Hz, 2H, (*Z*)-CH_2), 2.03 – 1.96 (m, 2H, (*E*)-C*H*$_2$$CH_3$), 1.70 (d, *J* = 1.4 Hz, 1H, (*Z*)-CH_3), 1.62 (d, *J* = 1.4 Hz, 3H, (*E*)-CH_3), 0.97 (t, *J* = 7.4 Hz, 3H, (*E*)-CH_3), 0.87 (t, *J* = 7.6 Hz, 1H, (*Z*)-CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K, both isomers): δ = 159.7 (C), 158.5 (2 x C), 145.5 (C), 145.4 (C), 138.2 (C), 137.8 (C), 130.0 (CH), 127.7 (2 x CH), 127.7 (CH), 127.5 (2 x CH), 127.5 (CH), 127.2 (CH), 125.3 (CH), 125.0 (CH), 125.0 (CH), 124.7 (CH), 121.9 (C), 105.1 (CH), 105.0 (CH), 104.3 (CH), 56.7 (CH_3), 56.0 (2 x CH_3), 55.9 (CH_3), 38.1 (CH), 37.9 (CH), 32.7 (CH_2), 25.2 (CH_2), 23.3 (CH_3), 16.3 (CH_3), 13.0 (CH_3), 12.9 (CH_3). **IR** (neat): 2962*m*, 2837*w*, 2362*w*, 1591*s*, 1471*s*, 1332*w*, 1238*s*, 1172*w*, 1105*s*, 1036*w*, 905*w*, 743*w*, 699*m*, 536*m*. **HRMS** (ESI) *m*/*z* = 319.1674 calcd. for $C_{22}H_{24}O_2Na$ $[M+Na]^+$, found: 319.1685.


MeO
Et
OMe

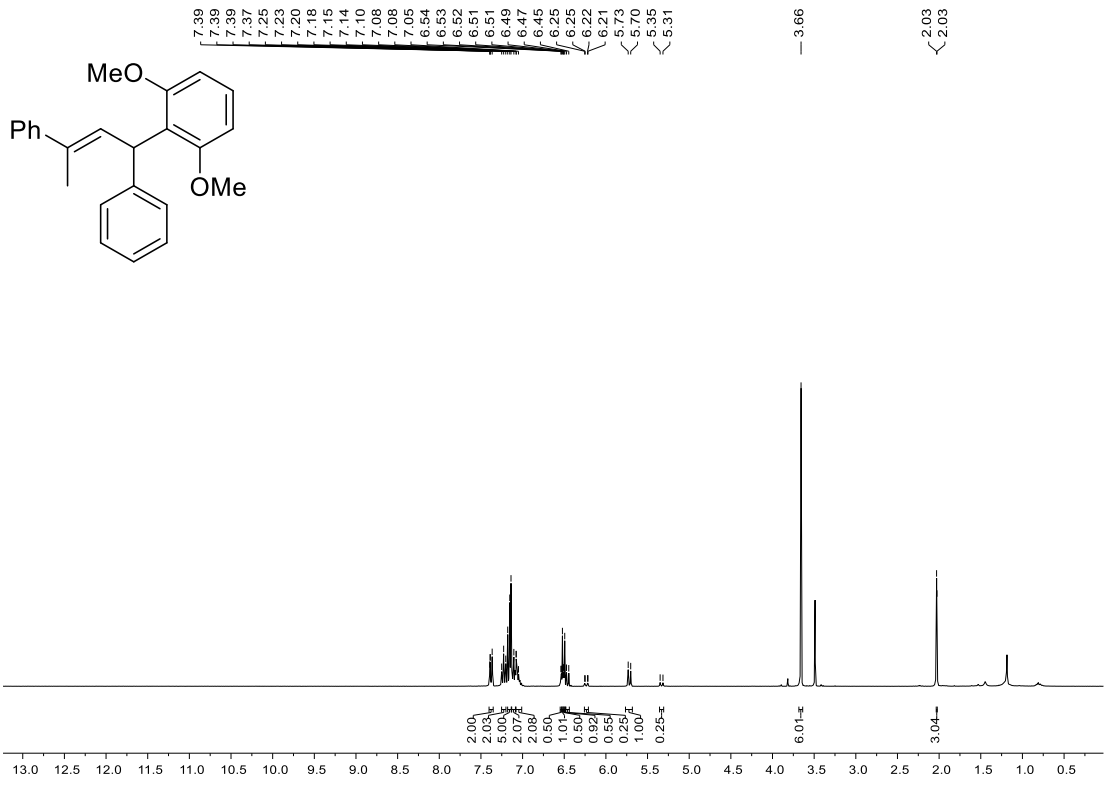

MeO
Et
OMe

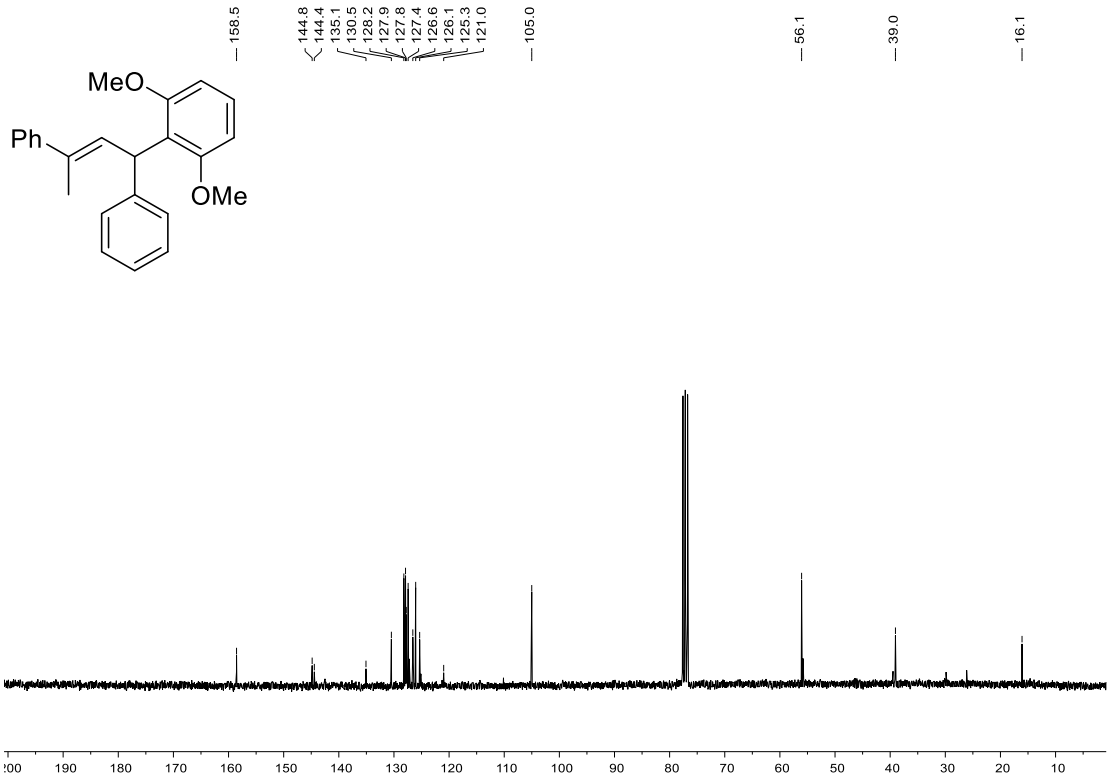
(1-(2,6-Dimethoxyphenyl)but-2-ene-1,3-diyl)dibenzene (3i)



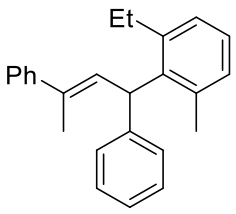
According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 2-iodo-1,3-dimethoxybenzene (84.0 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 100:1 mixture of pentane/DEE as an eluent to provide the *E*/*Z*-isomers in a ratio of 4:1 as colourless oil (55.1 mg, 0.160 mmol, 56%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.40 – 7.35 (m, 2H, CH_{arom}), 7.26 – 7.19 (m, 2H, CH_{arom}), 7.19 – 7.13 (m, 5H, CH_{arom}), 7.13 – 7.10 (m, 2H, CH_{arom}), 7.09 – 7.03 (m, 2H, CH_{arom}), 6.51 (dd, *J* = 9.0 Hz, 1.4 Hz, 1H, (*E*)-CH_{olefin}), 6.23 (dd, *J* = 10.2 Hz, 1.6 Hz, 1H, (*Z*)-CH_{olefin}), 5.72 (d, *J* = 9.0 Hz, 1H, (*E*)-CH), 5.33 (d, *J* = 10.2 Hz, 1H, (*Z*)-CH), 3.66 (s, 6H, 2 x OCH_3), 2.03 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K, both isomers): δ = 158.5 (2 x C), 144.8 (C), 144.4 (C), 135.1 (C), 130.5 (CH), 128.2 (2 x CH), 127.9 (2 x CH), 127.8 (CH), 127.4 (2 x CH), 126.6 (2 x CH), 126.1 (CH), 125.3 (C), 121.0 (CH), 105.0 (2 x CH), 56.1 (2 x CH_3), 39.0 (CH), 16.1 (CH_3). **IR** (neat): 2902*w*, 2837*w*, 2363*w*, 2191*w*, 2080*w*, 1592*m*, 1472*s*, 1241*m*, 1109*s*, 1031*w*, 905*w*, 780*w*, 760*m*, 697*m*, 668*w*, 640*w*, 588*w*. **HRMS** (ESI) *m*/*z* = 367.1674 calcd. for $C_{24}H_{24}O_2Na$ $[M+Na]^+$, found: 367.1681.



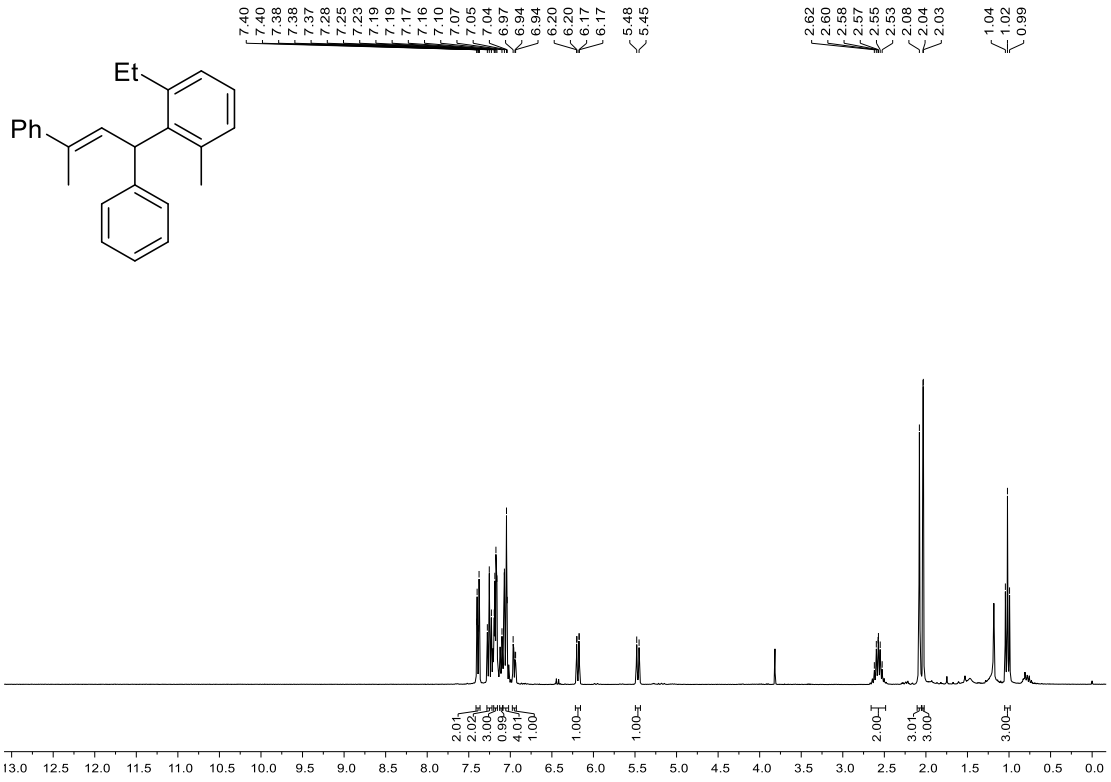


(1-(2-Ethyl-6-methylphenyl)but-2-ene-1,3-diyl)dibenzene (3h)



According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 1-ethyl-2-iodo-3-methylbenzene (78.3mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using pentane as eluent to provide the *E*-isomer as colourless oil (66.3 mg, 0.203 mmol, 71%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.41 – 7.36 (m, 2H, CH_{arom}), 7.25 (m, 2H, CH_{arom}), 7.21 – 7.14 (m, 3H, CH_{arom}), 7.13 – 7.09 (m, 1H, CH_{arom}), 7.09 – 7.02 (m, 4H, CH_{arom}), 6.98 – 6.93 (m, 1H, CH_{arom}), 6.19 (dd, *J* = 8.5 Hz, 1.4 Hz, 1H, CH_{olefin}), 5.47 (d, *J* = 8.5 Hz, 1H, CH), 2.64 – 2.52 (m, 2H, CH_2), 2.08 (s, 3H, CH_3), 2.03 (d, *J* = 1.4 Hz, 3H, C*H*$_3$), 1.02 (t, *J* = 7.5 Hz, 3H, CH_2CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 144.0 (C), 143.7 (C), 143.3 (C), 140.0 (C), 137.3 (C), 137.2 (C), 129.6 (CH), 129.5 (CH), 128.5 (2 x CH), 128.4 (2 x CH), 127.5 (CH), 127.3 (2 x CH), 127.1 (CH), 126.7 (CH), 126.0 (2 x CH), 125.8 (CH), 44.3 (CH), 27.5 (CH_2), 21.9 (CH_3), 16.6 (CH_3), 15.6 (CH_3). **IR** (neat): 3081*w*, 3059*w*, 3023*w*, 2965*m*, 2937*m*, 2876*w*, 1599*m*, 1492*s*, 1470*m*, 1446*m*, 1379*w*, 1106*w*, 1075*w*, 1029*m*, 897*w*, 783*w*, 757*s*, 742*s*, 696*s*, 566*w*. **HRMS** (APCI) *m*/*z* = 433.1085 calcd. for $C_{25}H_{26}Ag$ $[M+Ag]^+$, found: 433.1076.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Ph
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7.38
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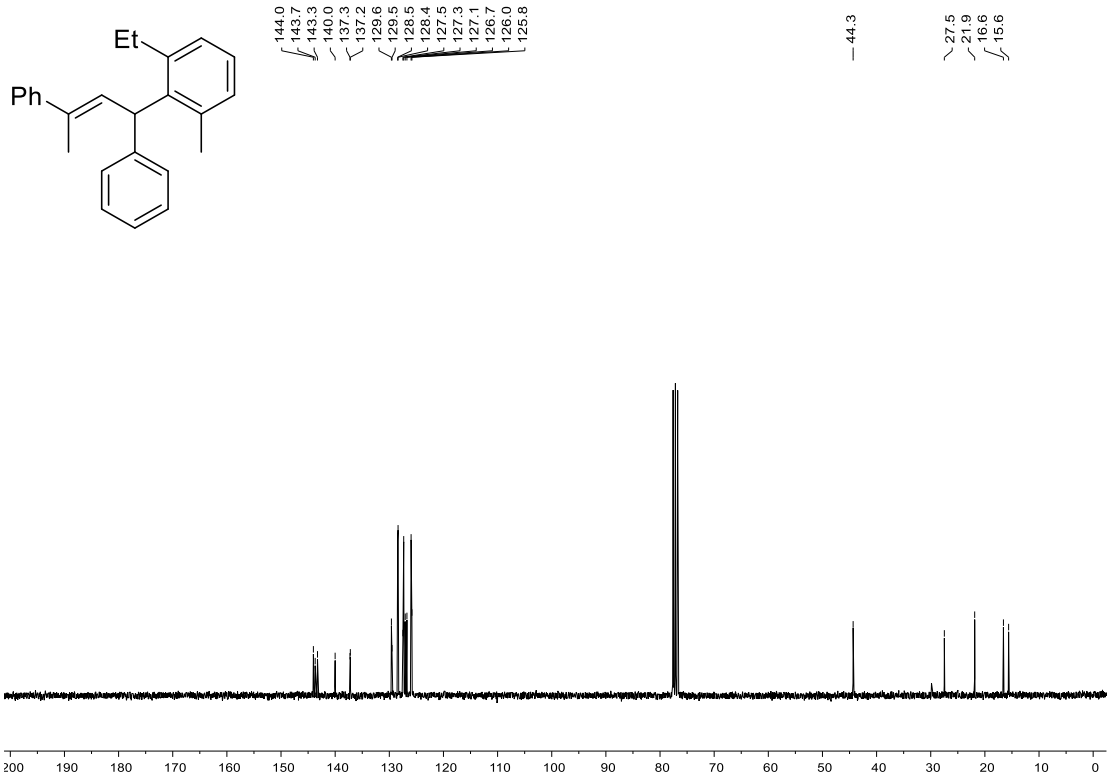
7.25
7.23
7.19
7.19
7.17
7.16
7.10
7.07
7.05
7.04
6.97
6.94
6.94
6.20
6.20
6.17
6.17
5.48
5.45
2.62
2.60
2.58
2.57
2.55
2.53
2.08
2.04
2.03
1.04
1.02
0.99
2.01
2.02
3.00
0.99
4.01
1.00
1.00
1.00
2.00
3.01
3.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


Et
Ph
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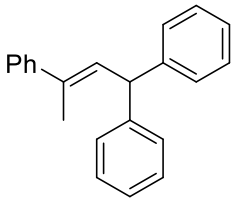
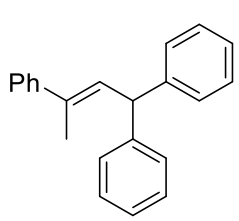
143.7
143.3
140.0
137.3
137.2
129.6
129.5
128.5
128.4
127.5
127.3
127.1
126.7
126.0
125.8
44.3
27.5
21.9
16.6
15.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

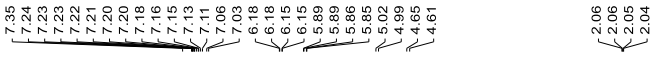
But-2-ene-1,1,3-triyltribenzene (3b)

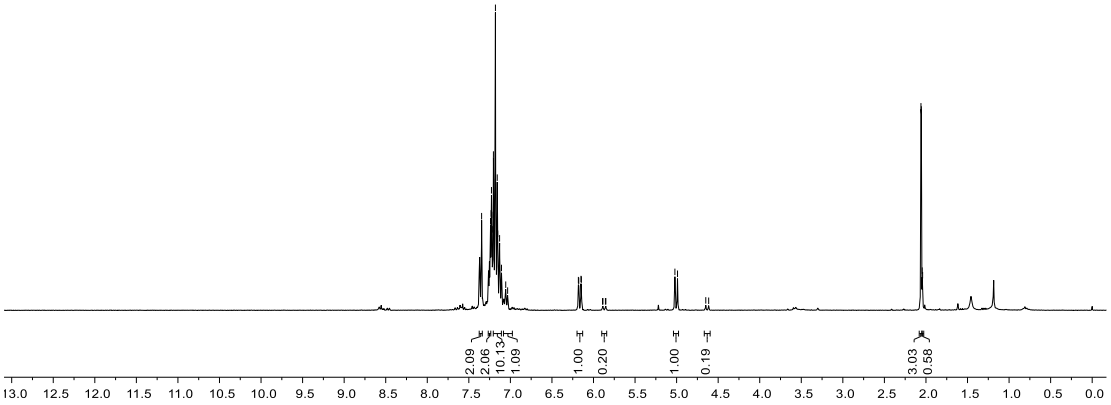


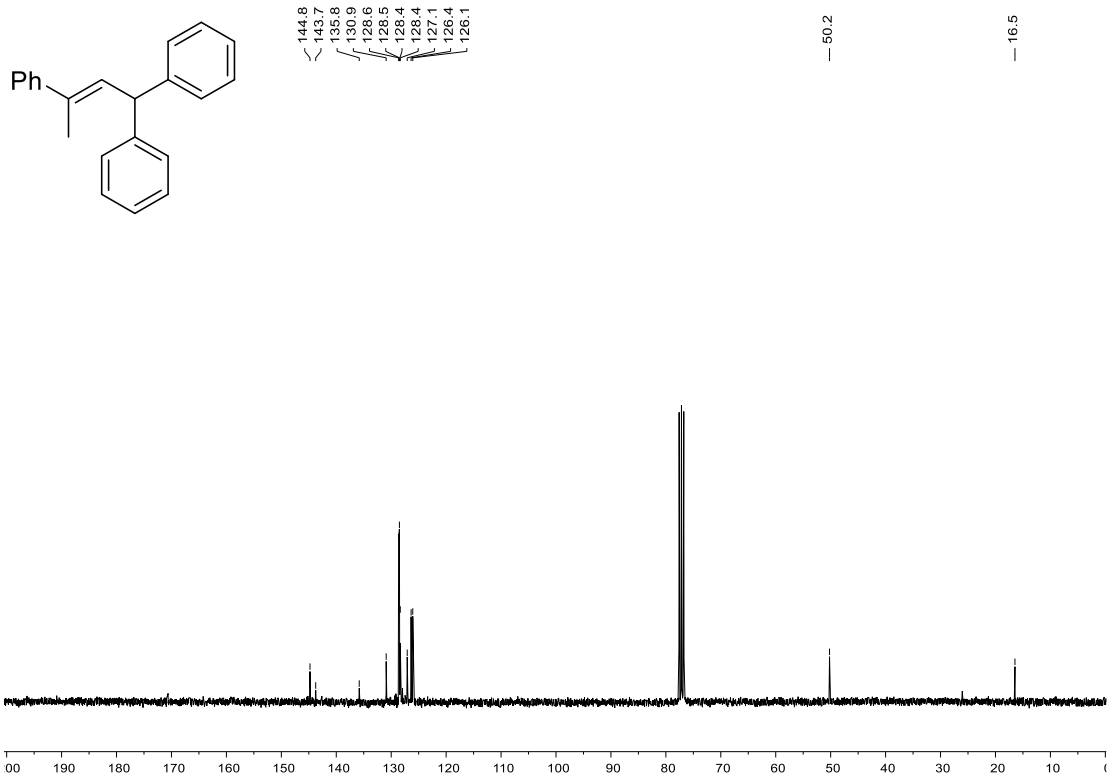
According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and iodobenzene (64.9 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using pentane as eluent to provide the *E*/*Z*-isomers in a ratio of 5:1 as colourless oil (21.9 mg, 772 µmol, 27%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.39 – 7.31 (m, 2H, CH_{arom}), 7.26 – 7.21 (m, 2H, CH_{arom}), 7.21 – 7.14 (m, 10H, CH_{arom}), 7.13 – 7.02 (m, 1H, CH_{arom}), 6.16 (dd, *J* = 9.4 Hz, 1.4 Hz, 1H, (*E*)-CH_{olefin}), 5.87 (dd, *J* = 10.5 Hz, 1.6 Hz, 1H, (*E*)-CH_{olefin}), 5.00 (d, *J* = 9.4 Hz, 1H, (*Z*)-CH), 4.63 (d, *J* = 10.5 Hz, 1H, (*E*)-CH), 2.06 (d, *J* = 1.4 Hz, 3H, (*E*)-CH_3), 2.04 (d, *J* = 1.6 Hz, 1H, (*Z*)-CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K, both isomers): δ = 144.8 (C), 143.7 (C), 135.8 (C), 130.9 (CH), 128.6 (4 x CH), 128.5 (4 x CH), 128.4 (2 x CH), 128.4 (C), 127.1 (CH), 126.4 (2 x CH), 126.1 (2 x CH), 50.2 (CH), 16.5 (CH_3). **IR** (neat): 3024*w*, 2363*w*, 2224*m*, 2208*w*, 2066*w*, 2007*w*, 1598*w*, 1493*m*, 1447*w*, 1031*w*, 757*m*, 744*m*, 696*s*, 654*w*, 585*w*. **HRMS** (APCI) *m*/*z* = 391.0616 calcd. for $C_{22}H_{20}Ag$ $[M+Ag]^+$, found: 391.0609.

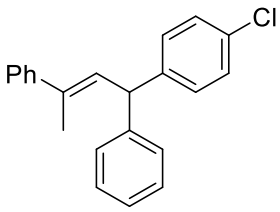






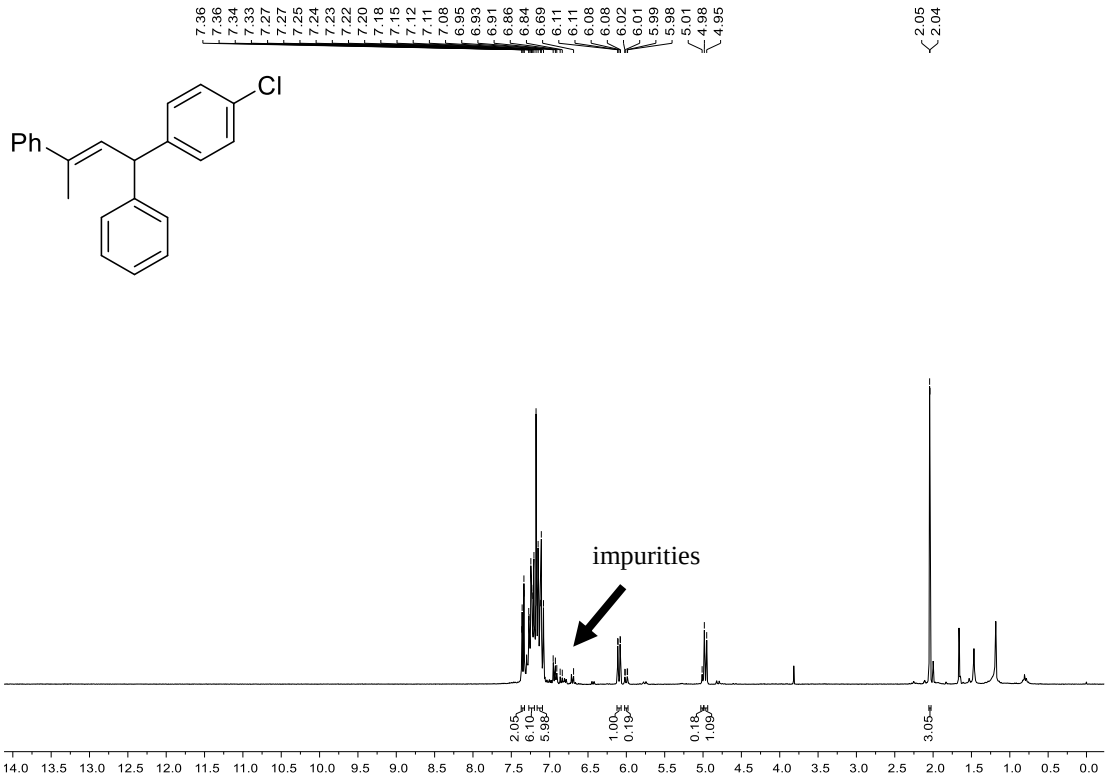


(1-(4-Chlorophenyl)but-2-ene-1,3-diyl)dibenzene (3c)



According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 1-chloro-4-iodobenzene (75.9 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using pentane as eluent to provide the *E*/*Z*-isomers in a ratio of 5:1 as colourless oil (53.9 mg, 0.169 mmol, 59%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.40 – 7.32 (m, 2H, CH_{arom}), 7.30 – 7.19 (m, 6H, CH_{arom}), 7.18 – 7.07 (m, 6H, CH_{arom}), 6.96 – 6.65 (m, 1H, CH_{arom}), 6.09 (dd, *J* = 9.2 Hz, 1.4 Hz, 1H, (*E*)-CH_{olefin}), 6.00 (dd, *J* = 9.3 Hz, 1.4 Hz, 1H, (*Z*)-CH_{olefin}), 5.01 (d, 1H, (*Z*)-CH), 4.97 (d, *J* = 9.2, 1H, (*E*)-CH), 2.04 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K, both isomers): δ = 144.3 (C), 143.4 (C), 143.2 (C), 136.3 (C), 132.1 (C), 130.3 (CH), 129.8 (2 x CH), 128.8 (2 x CH), 128.7 (CH), 128.6 (CH), 128.4 (4 x CH), 127.2 (CH), 126.6 (CH), 126.0 (2 x CH), 49.5 (CH), 16.5 (CH_3). **IR** (neat): 3059*w*, 3026*w*, 2928*m*, 2852*w*, 2065*w*, 1609*w*, 1509*s*, 1493*m*, 1463*w*, 1444*w*, 1380*w*, 1302*w*, 1249*s*, 1176*m*, 1114*w*, 1072*w*, 1036*m*, 896*w*, 834*w*, 808*w*, 755*m*, 731*w*, 697*s*, 561*m*. **HRMS** (APCI) *m*/*z* = 425.0226 calcd. for $C_{22}H_{19}ClAg$ $[M+Ag]^+$, found: 425.0225.


7.36
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7.27
7.25
7.24
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7.22
7.20
7.18
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7.12
7.11
7.08
6.95
6.93
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6.84
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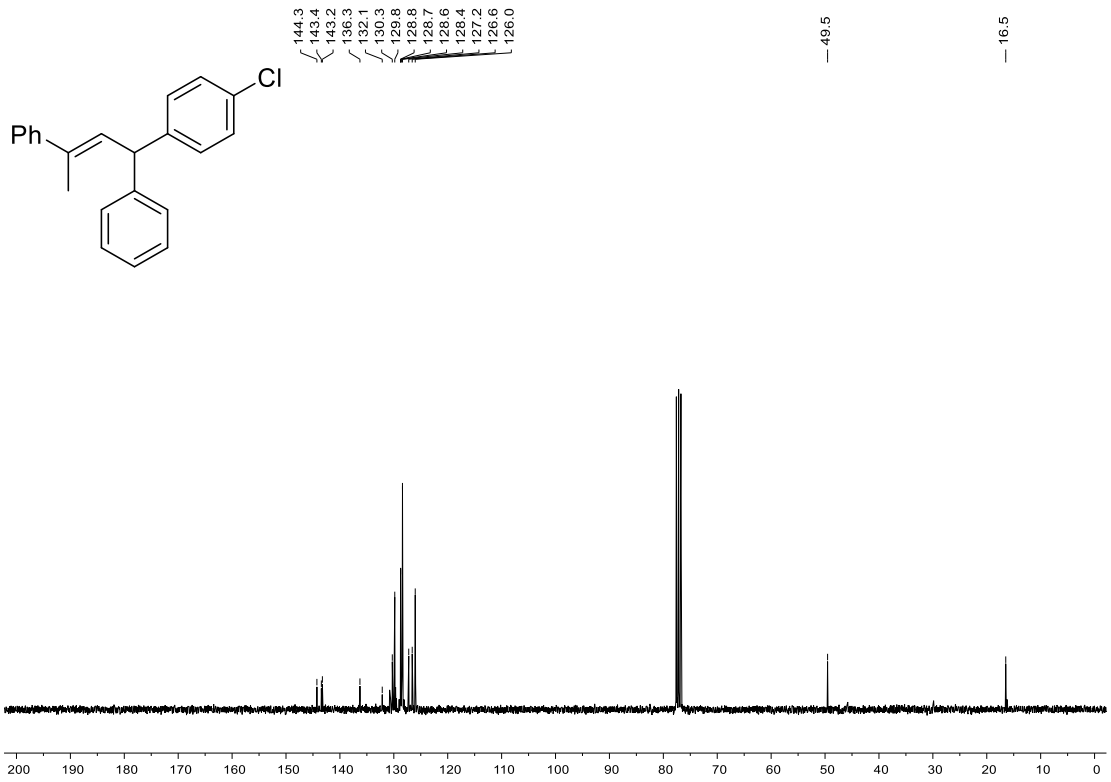
6.11
6.08
6.08
6.02
6.01
5.99
5.98
5.01
4.98
4.95
2.05
2.04
Cl
Ph
impurities
2.05
6.10
5.98
1.00
0.19
0.18
1.09
3.05
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


144.3
143.4
143.2
136.3
132.1
130.3
129.8
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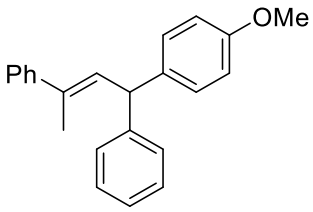
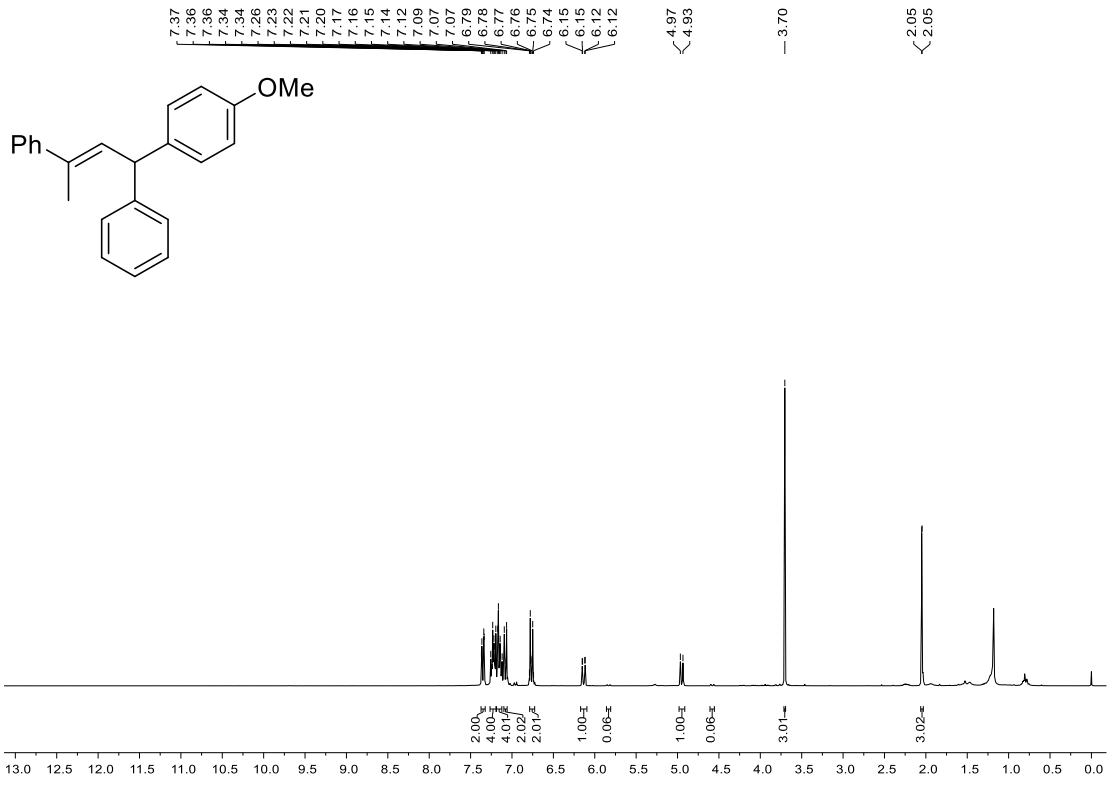
128.7
128.6
128.4
127.2
126.6
126.0
49.5
16.5
Cl
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

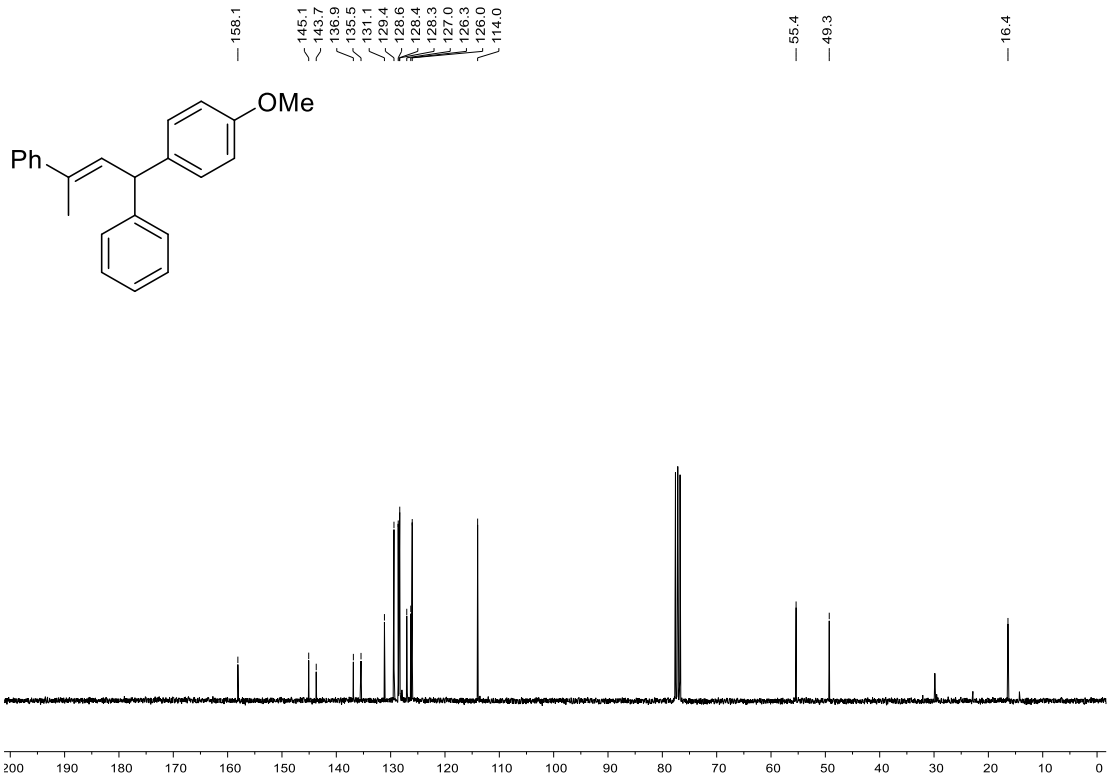
(1-(4-Methoxyphenyl)but-2-ene-1,3-diyl)dibenzene (3d)



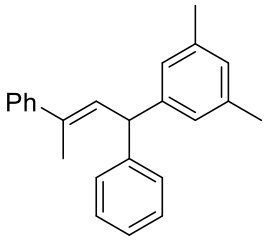
According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-4-methoxybenzene (74.5 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using a 500:1 mixture of pentane/DEE as an eluent to provide the *E*/*Z*-isomers in a ratio of 17:1 as colourless oil (54.1 mg, 0.172 mmol, 60%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.40 – 7.30 (m, 2H, CH_{arom}), 7.29 – 7.16 (m, 4H, CH_{arom}), 7.20 – 7.09 (m, 4H, CH_{arom}), 7.13 – 7.03 (m, 2H, CH_{arom}), 6.79 – 6.73 (m, 2H, CH_{arom}), 6.13 (dd, *J* = 9.4 Hz, 1.4 Hz, 1H, CH_{olefin}), 4.95 (d, *J* = 9.4 Hz, 1H, CH), 3.70 (s, 3H, OCH_3), 2.05 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 158.1 (C), 145.1 (C), 143.7 (C), 136.9 (C), 135.5 (C), 131.1 (CH), 129.4 (2 x CH), 128.6 (2 x CH), 128.4 (2 x CH), 128.3 (2 x CH), 127.0 (CH), 126.3 (CH), 126.0 (2 x CH), 114.0 (2 x CH), 55.4 (CH_3), 49.3 (CH), 16.4 (CH_3). **IR** (neat): 3026*w*, 2952*w*, 2066*w*, 2007*w*, 1618*w*, 1509*w*, 1494*w*, 1445*w*, 1414*w*, 1325*s*, 1249*w*, 1165*m*, 1124*m*, 1068*m*, 1031*w*, 1018*w*, 897*w*, 815*w*, 757*w*, 740*w*, 698*m*, 566*w*. **HRMS** (ESI) *m*/*z* = 337.1168 calcd. for $C_{23}H_{22}ONa$ $[M+Na]^+$, found: 337.1158.





(1-(3,5-Dimethylphenyl)but-2-ene-1,3-diyl)dibenzene (3j)

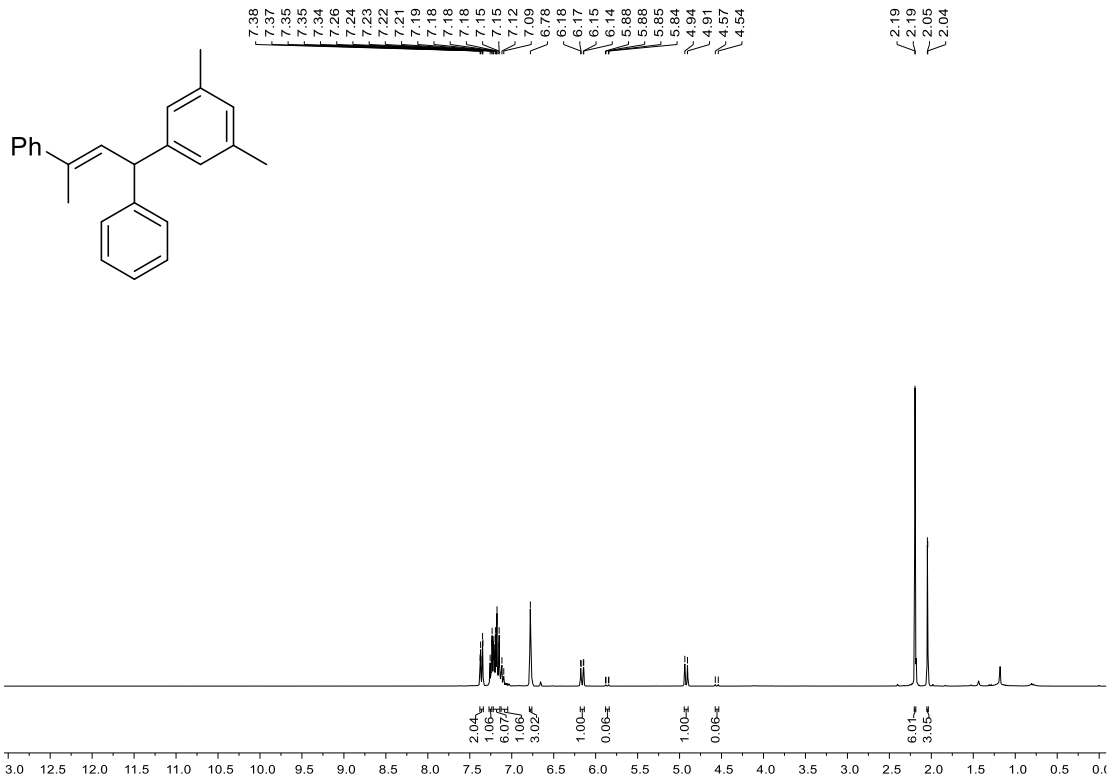


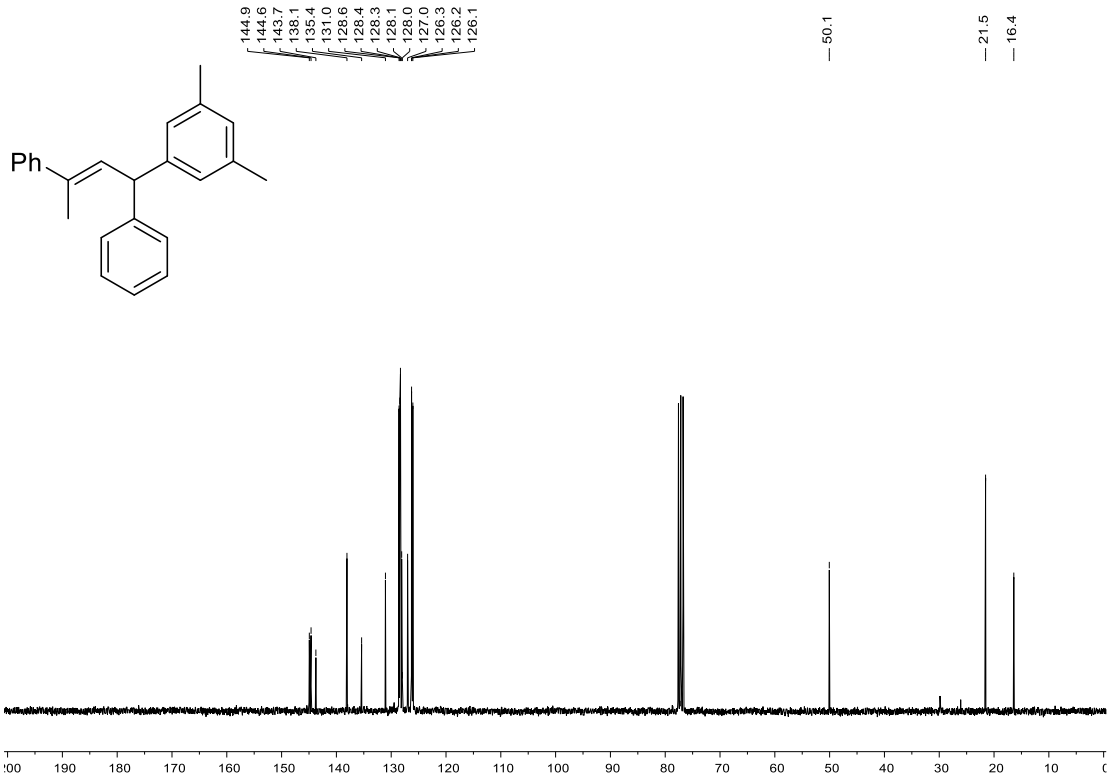
According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-3,5-dimethylbenzene (73.8 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using pentane as eluent to provide the *E*/*Z*-isomers in a ratio of 17:1 as colourless oil (77.8 mg, 0.249 mmol, 87%).

For enantioselective test reaction: According to **GP3** with enantioenriched (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (2.2 mg, 8,7 µmol, 1.0 equiv., 93% ee) and 1-iodo-3,5-dimethylbenzene (2.2 mg, 9.6 µmol, 1.1 equiv.). Enantiomeric excess of product **3j** (86% ee) was determined by HPLC analysis using a Chiralcel DJ-RH column (Agilent 1200 Series HPLC with auto sampler and UV DAD), with ACN:H_2O = 65:35 (isocratic) at a flow rate of 1.0 mL/min at 10 °C detected at 230 nm and 354 nm wavelength.

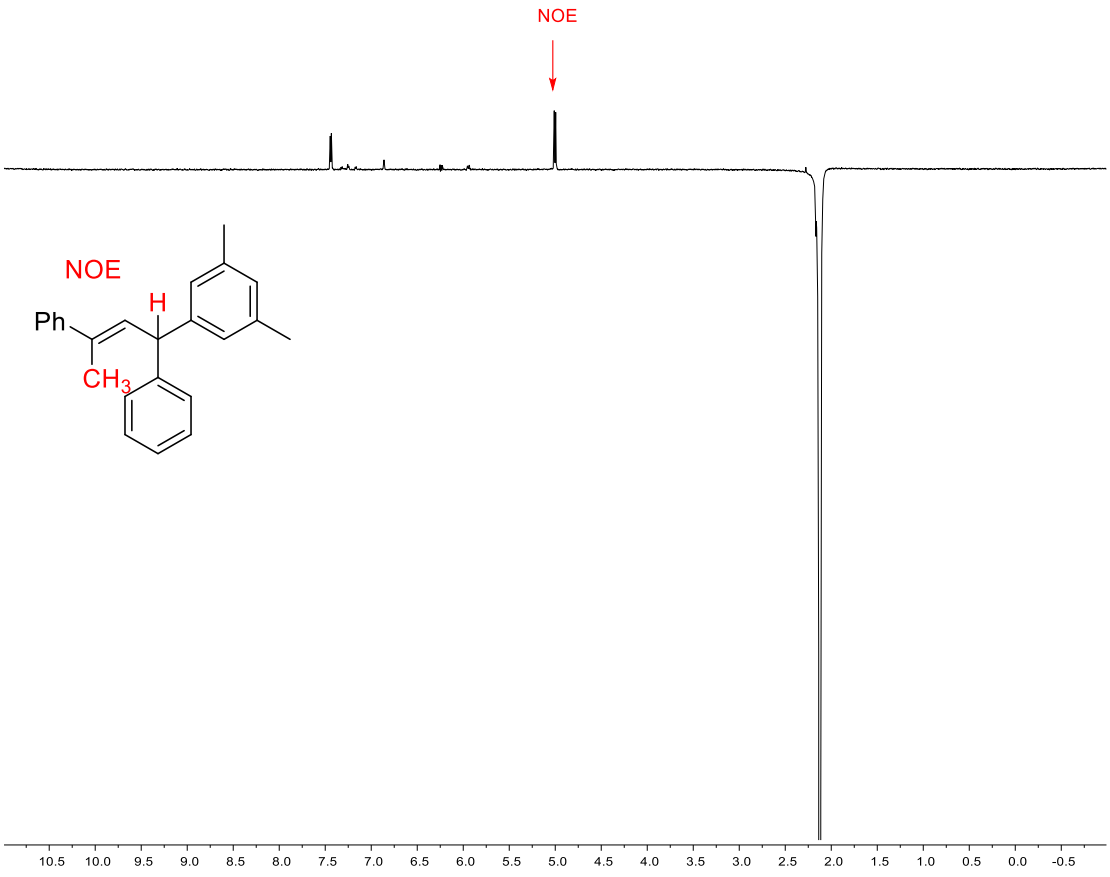
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.40 – 7.32 (m, 2H, CH_{arom}), 7.29 – 7.23 (m, 1H, CH_{arom}), 7.22 – 7.14 (m, 6H, CH_{arom}), 7.12 – 7.04 (m, 1H, CH_{arom}), 6.78 (s, 3H, CH_{arom}), 6.16 (dd, *J* = 9.5 Hz, 1.4 Hz, 1H, (*E*)-CH_{olefin}), 5.86 (dd, *J* = 10.6 Hz, 1.6 Hz, 1H, (*Z*)-CH_{olefin}), 4.92 (d, *J* = 9.5 Hz, 1H, (*E*)-CH), 4.56 (d, *J* = 10.6 Hz, 1H, (*Z*)-CH), 2.19 (d, *J* = 0.7 Hz, 6H,

2 x CH_3), 2.04 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 144.9 (C), 144.6 (C), 143.7 (C), 138.1 (2 x C), 135.4 (C), 131.0 (CH), 128.6 (2 x CH), 128.4 (2 x CH), 128.3 (2 x CH), 128.1 (CH), 128.0 (CH), 127.0 (CH), 126.3 (CH), 126.2 (CH), 126.1 (2 x CH), 50.1 (CH), 21.5 (2 x CH_3), 16.4 (CH_3). **IR** (neat): 3082*w*, 3095*w*, 3024*m*, 2921*m*, 2855*w*, 2221*w*, 2160*w*, 2121*w*, 2066*w*, 2008*w*, 1599*m*, 1492*s*, 1469*m*, 1446*m*, 1380*w*, 1253*w*, 1077*w*, 1029*m*, 896*w*, 757*s*, 744*m*, 696*s*, 636*w*, 566*m*. **HRMS** (APCI) *m*/*z* = 312.1878 calcd. for $C_{24}H_{24}$ $[M]^+$, found: 312.1872.

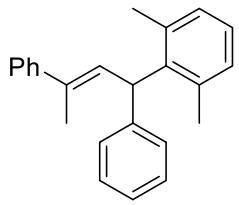




As an example to show the determination of the stereoselectivity of the double bond: 1D-NOESY spectra:

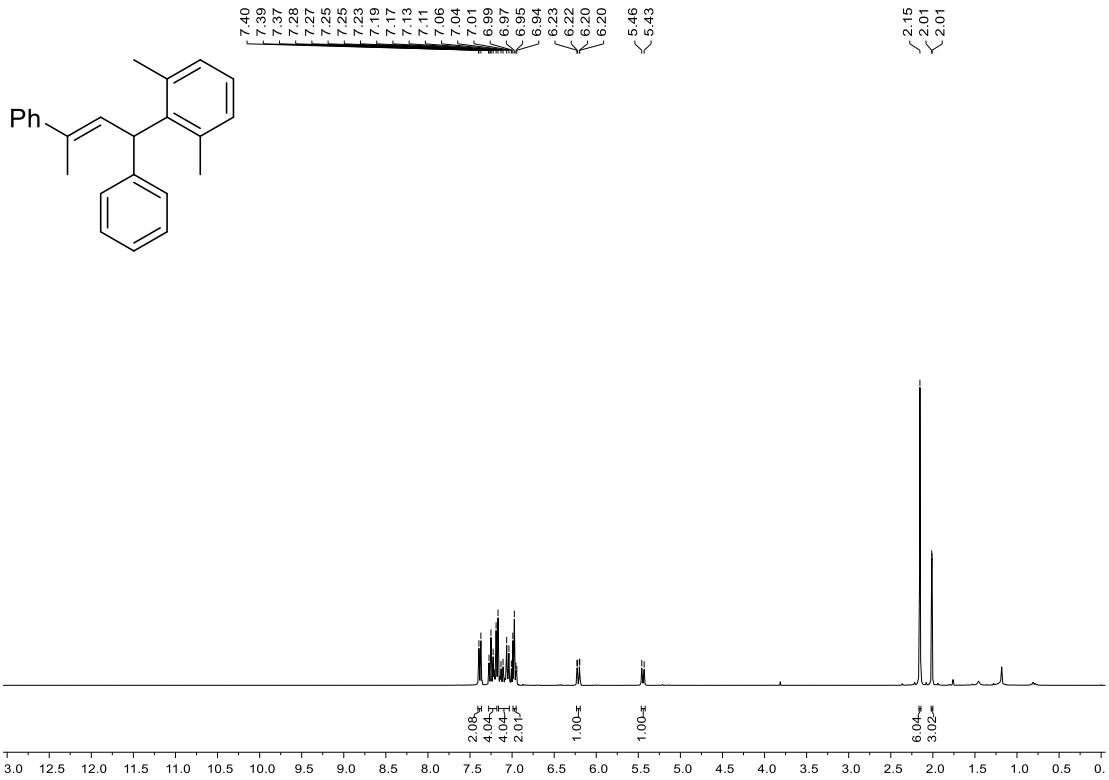


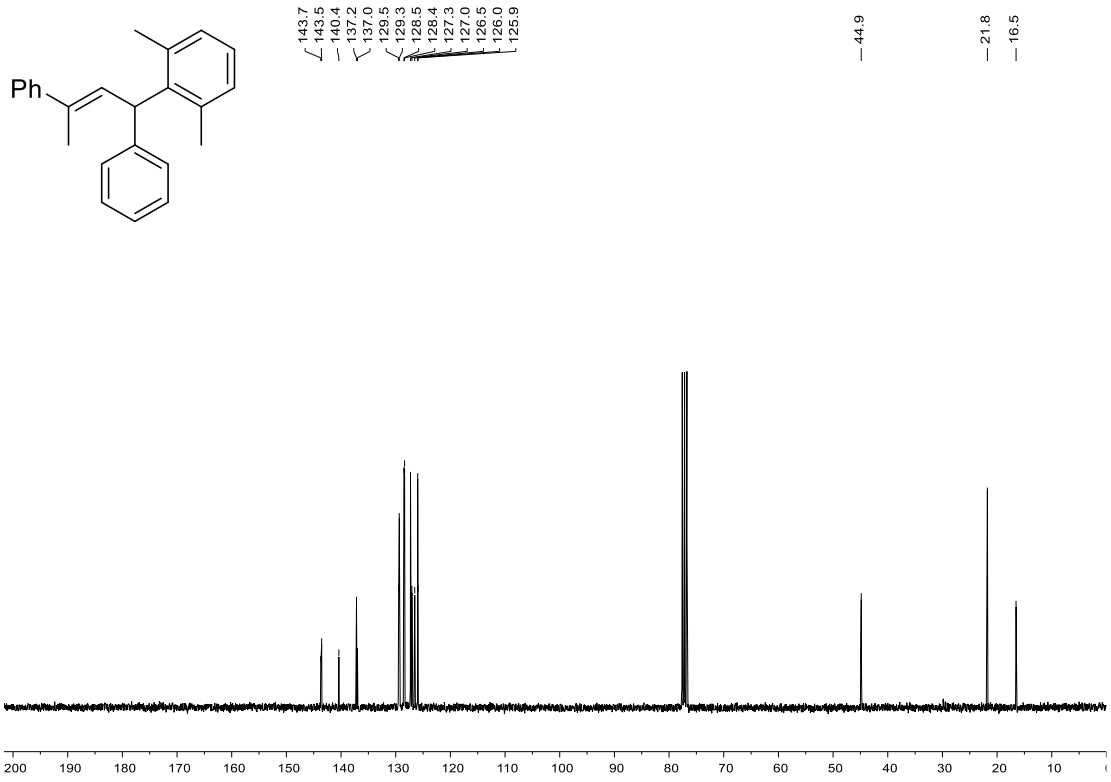
(1-(2,6-Dimethylphenyl)but-2-ene-1,3-diyl)dibenzene (3g)



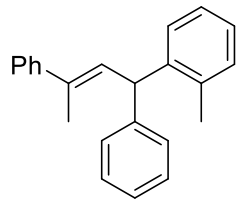
According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 2-iodo-1,3-dimethylbenzene (73.8 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using pentane as eluent to provide the *E*-isomer as colourless oil (50.0 mg, 0.160 mmol, 56%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.41 – 7.35 (m, 2H, CH_{arom}), 7.31 – 7.18 (m, 4H, CH_{arom}), 7.17 – 7.02 (m, 4H, CH_{arom}), 7.02 – 6.94 (m, 3H, CH_{arom}), 6.21 (dd, *J* = 8.4 Hz, 1.4 Hz, 1H, CH_{olefin}), 5.44 (d, *J* = 8.4 Hz, 1H, CH), 2.15 (s, 6H, 2 x CH_3), 2.01 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 143.7 (C), 143.5 (C), 140.4 (C), 137.2 (2 x C), 137.0 (C), 129.5 (CH), 129.3 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 127.3 (2 x CH), 127.0 (CH), 126.5 (CH), 126.0 (2 x CH), 125.9 (CH), 44.9 (CH), 21.8 (2 x CH_3), 16.5 (CH_3). **IR** (neat): 3024*w*, 2922*m*, 2363*w*, 2224*w*, 2066*w*, 2008*w*, 1600*w*, 1493*m*, 1445*w*, 1380*w*, 1031*w*, 756*m*, 731*w*, 696*s*, 650*w*, 566*m*. **HRMS** (APCI) *m*/*z* = 419.0929 calcd. for $C_{24}H_{24}Ag$ $[M+Ag]^+$, found: 419.0921.



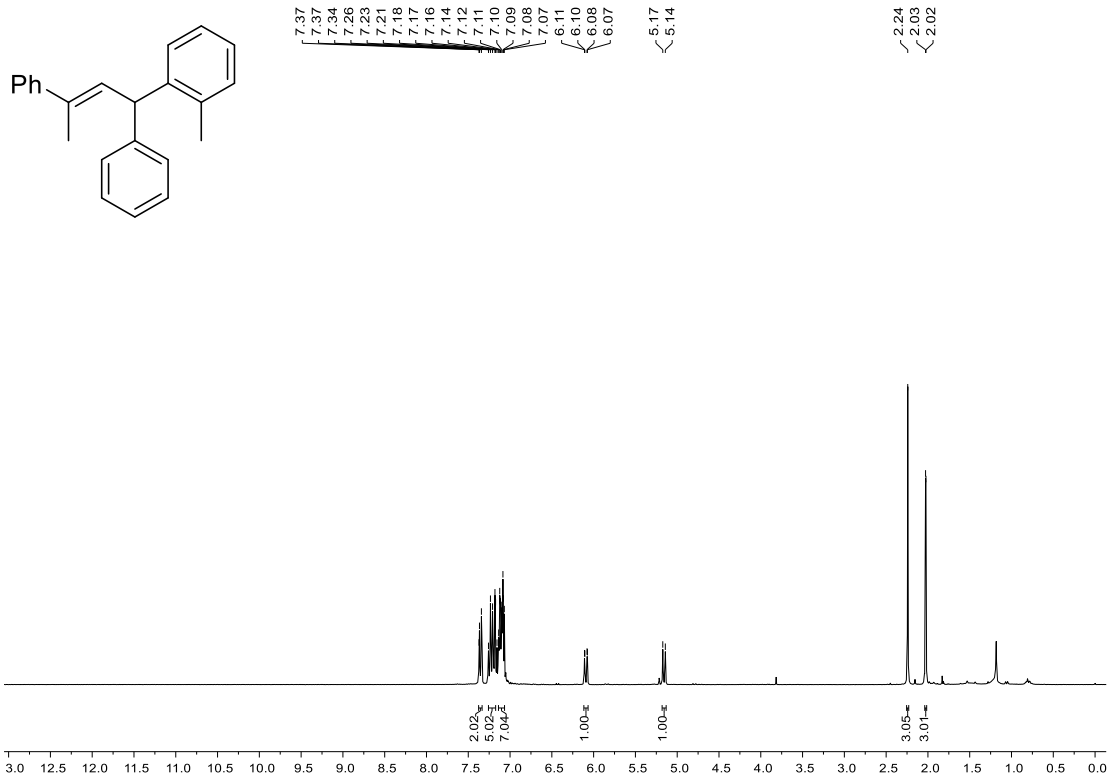


(1-(*o*-Tolyl)-but-2-ene-1,3-diyl)dibenzene (3e)



According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-2-methylbenzene (69.4 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using pentane as eluent to provide the *E*-isomer as colourless oil (62.4 mg, 0.209 mmol, 73%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.40 – 7.30 (m, 2H, CH_{arom}), 7.29 – 7.12 (m, 5H, CH_{arom}), 7.17 – 7.02 (m, 7H, CH_{arom}), 6.09 (dd, *J* = 9.1 Hz, 1.4 Hz, 1H, CH_{olefin}), 5.16 (d, *J* = 9.1 Hz, 1H, CH), 2.24 (s, 3H, CH_3), 2.03 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 144.4 (C), 143.6 (C), 142.9 (C), 136.4 (C), 135.7 (C), 130.9 (CH), 130.6 (CH), 128.6 (2 x CH), 128.4 (2 x CH), 128.4 (CH), 128.3 (2 x CH), 127.1 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 126.0 (2 x CH), 46.8 (CH), 20.1 (CH_3), 16.5 (CH_3). **IR** (neat): 3024*w*, 2363*w*, 2224*m*, 2208*w*, 2066*w*, 1598*w*, 1493*m*, 1447*w*, 1031*w*, 757*m*, 744*m*, 696*s*, 654*w*, 585*w*. **HRMS** (APCI) *m*/*z* = 298.1722 calcd. for $C_{23}H_{22}$ $[M]^+$, found: 298.1716.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7.26
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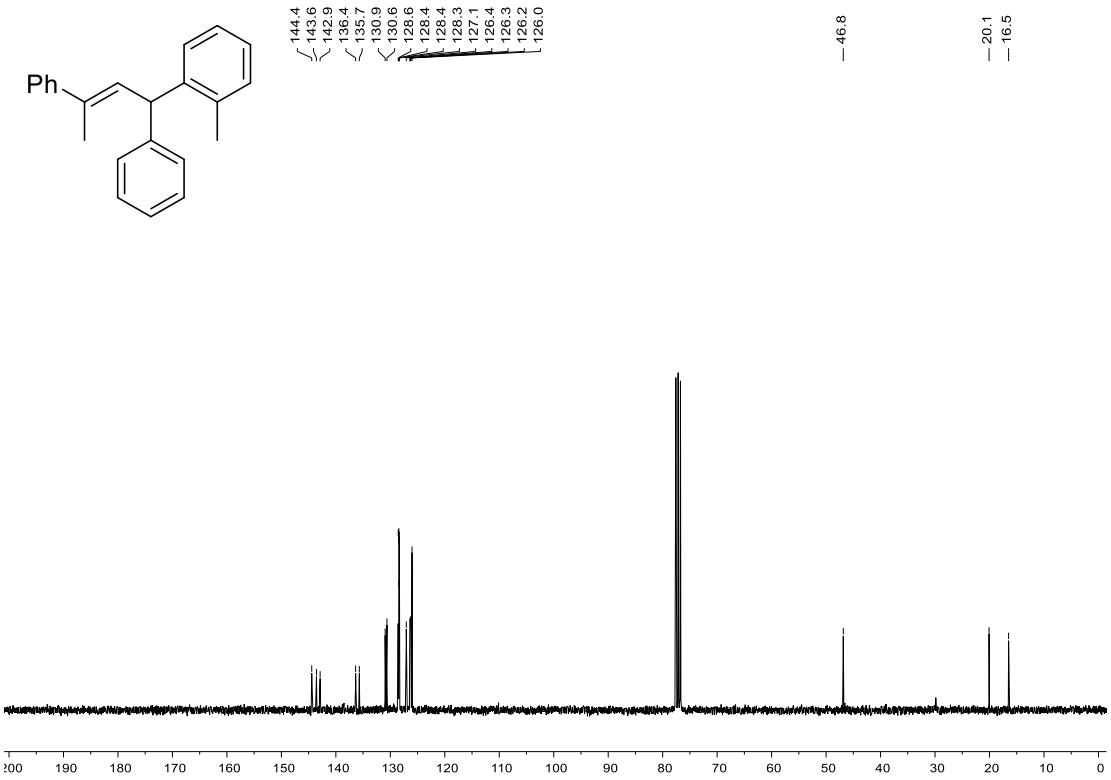
7.17
7.16
7.14
7.12
7.11
7.10
7.09
7.08
7.07
6.11
6.10
6.08
6.07
5.17
5.14
2.24
2.03
2.02
2.02
5.02
7.04
1.00
1.00
3.05
3.01


Ph
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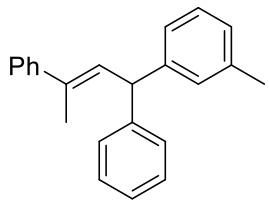
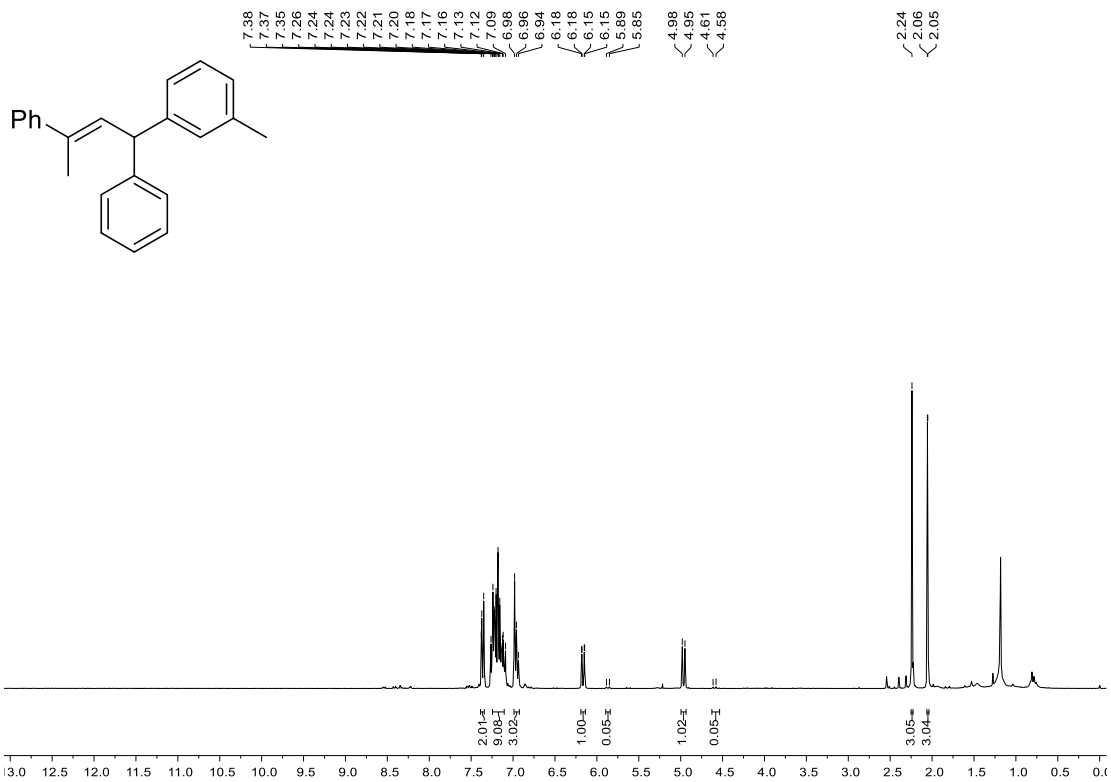
143.6
142.9
136.4
135.7
130.9
130.6
128.6
128.4
128.4
128.3
127.1
126.4
126.3
126.2
126.0
46.8
20.1
16.5

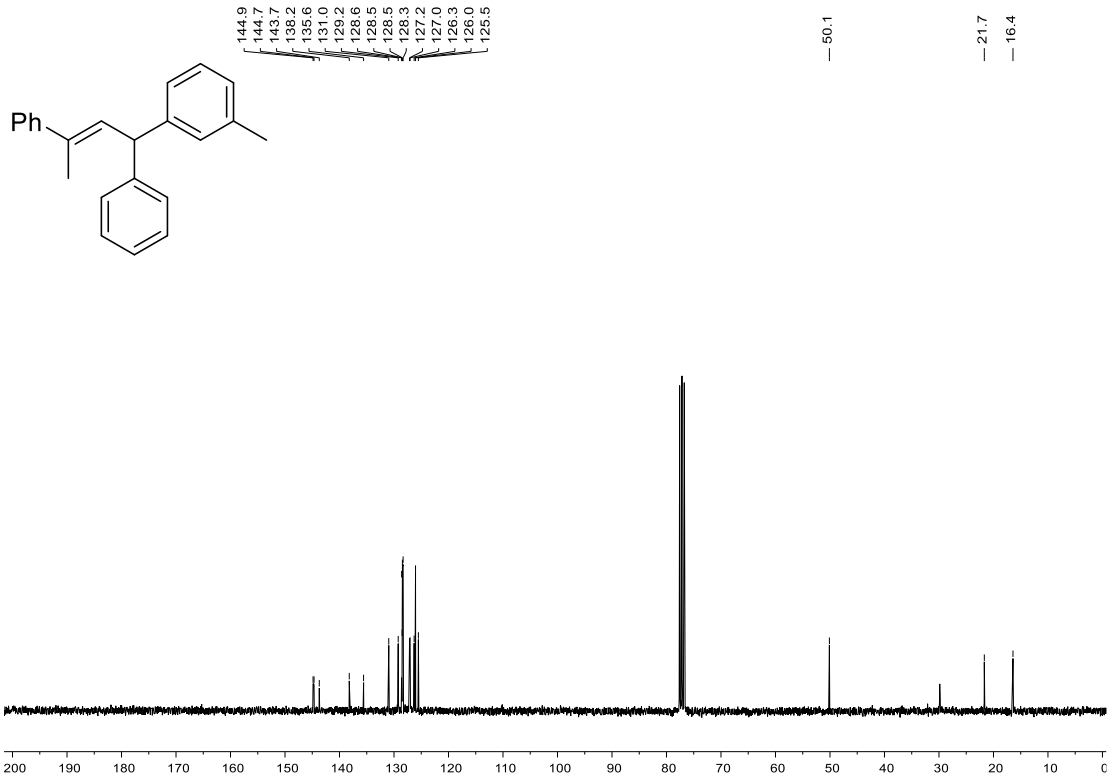
(1-(*m*-Tolyl)but-2-ene-1,3-diyl)dibenzene (3f)



According to **GP3** with (*Z*)-2-methyl-2,4-diphenylbut-3-enoic acid (72.1 mg, 0.286 mmol, 1.0 equiv.) and 1-iodo-3-methylbenzene (69.4 mg, 0.318 mmol, 1.1 equiv.). The crude product was purified by column chromatography on silica gel by using pentane as eluent to provide the *E*/*Z*-isomers in a ratio of 20:1 as colourless oil (46.9 mg, 0.157 mmol, 55%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.41 – 7.31 (m, 2H, CH_{arom}), 7.30 – 7.06 (m, 9H, CH_{arom}), 7.01 – 6.91 (m, 3H, CH_{arom}), 6.16 (dd, *J* = 9.4 Hz, 1.4 Hz, 1H, (*E*)-CH_{olefin}), 5.87 (d, *J* = 10.8 Hz, 1H, (*Z*)-CH_{olefin}), 4.96 (d, *J* = 9.5 Hz, 1H, (*E*)-CH), 4.60 (d, *J* = 10.8 Hz, 1H, (*Z*)-CH), 2.24 (s, 3H, CH_3), 2.05 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 144.9 (C), 144.7 (C), 143.7 (C), 138.2 (C), 135.6 (C), 131.0 (CH), 129.2 (CH), 128.6 (2 x CH), 128.5 (CH), 128.5 (2 x CH), 128.3 (2 x CH), 127.2 (CH), 127.0 (CH), 126.3 (CH), 126.0 (2 x CH), 125.5 (CH), 50.1 (CH), 21.7 (CH_3), 16.4 (CH_3). **IR** (neat): 3059*w*, 3024*m*, 2922*m*, 2856*w*, 2363*w*, 2208*m*, 2198*m*, 2121*w*, 2066*w*, 2008*w*, 1699*w*, 1493*m*, 1445*w*, 1380*w*, 1031*w*, 897*w*, 845*w*, 747*m*, 696*s*, 655*w*, 585*w*, 566*s*. **HRMS** (APCI) *m*/*z* = 298.1722 calcd. for $C_{23}H_{22}[M]^+$, found: 298.1716.




144.9
144.7
143.7
138.2
135.6
131.0
129.2
128.6
128.5
128.5
128.3
127.2
127.0
126.3
126.0
125.5
50.1
21.7
16.4
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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