Supporting Information

Cobalt-catalysed Csp^3-Cps^3 Cross-Coupling of Benzyl Katritzky Pyridinium Salts and C_{allyl}-O Electrophiles

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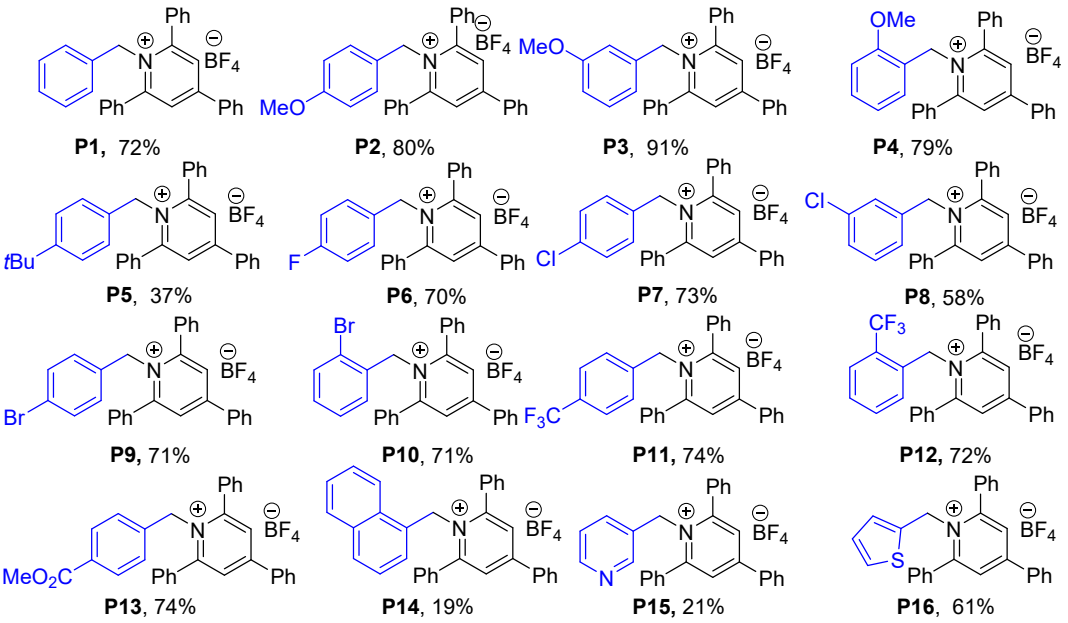
1. General Procedure for Benzyl Katritzky Pyridinium Salts Derivatives

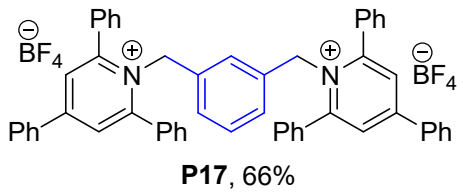
GP-A[1]: The amine (1.2 - 1.4 equiv) was added to a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate in EtOH (1 M), which led to an immediate color change to deep red, and dissolving of the material. Then, the solution was refluxed for the indicated time and cooled to rt. Then, Et_2O was added. If a precipitate formed, the suspension was stirred for 1 h, the material was collected by filtration, and washed with Et_2O. After drying under vacuum, the product was obtained. In cases no precipitate, sticky material had formed, all solvents were removed under vacuum, and the crude material was dissolved in DCM. was purified by column chromatography (0 – 10% MeOH /DCM).

GP-B[2]: 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv.) was added to a stirred solution of the primary amine (1.2 - 1.4 equiv.) in CH_2Cl_2 (0.5 M) in a round bottom flask. And then AcOH (2.0 equiv) was added after 15 min. The reaction mixture was stirred at room temperature overnight. If product precipitation occurred, the solid was collected by filtration, washed with Et_2O, and dried under high vacuum. If product precipitation did not occur, the solvent was removed in vacuo, it was subjected to flash column chromatography, eluting with 0 – 10% MeOH /DCM.

P1[66310-10-9][1], P6[1], P8[1], P9[2], P10[3], P11[2], P12[4], P13[5], P15[3] were synthesized according to *GP-A*, their spectroscopic data match the reported one in the literature.

P2[71017-75-9][3], P3[2], P4[4], P5[6], P7[71017-85-1][2], P14[6], P16[2] were synthesized according to *GP-B*, their spectroscopic data match the reported one in the literature.





P17, 66%

Characterization data of P17

Following ***GP-A,*** 2,4,6-triphenylpyrylium tetrafluoroborate (5 mmol, 2 g) with 1,3-di(aminomethyl)benzene (1 g, 7.5 mmol) was used, affording the corresponding benzyl Katritzky pyridinium salt **P17** as a light-yellow solid (4.4 g, 66%).

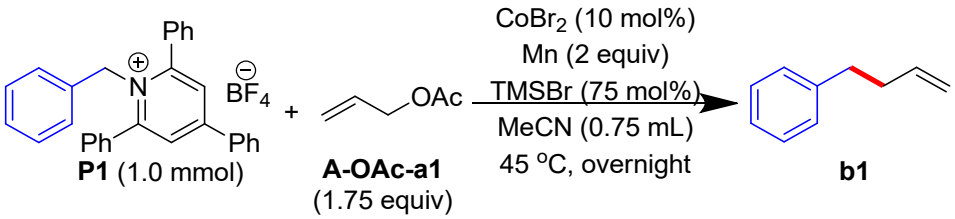
^{1}H NMR (300 MHz, Chloroform-d) δ 7.83 (s, 4H), 7.81 – 7.74 (m, 4H), 7.52 (dt, J = 5.9, 2.0 Hz, 14H), 7.43 – 7.32 (m, 12H), 6.83 (t, J = 7.8 Hz, 1H), 6.22 (dd, J = 7.9, 1.7 Hz, 2H), 5.81 (d, J = 1.7 Hz, 1H), 5.63 (s, 2H).

^{13}C NMR (75 MHz, Chloroform-d) δ 157.37, 156.65, 134.55, 133.64, 132.51, 130.95, 129.76, 129.26, 129.13, 128.22, 126.73.

HRMS (ESI^{2+}) m/z: [M^{2+}] calculated for ($C_{54}H_{42}N_2$ $^{2+}$) 359.1678; Found 359.1669.

2. Optimisation of the reaction between benzyl Katritzky pyridinium salts and allyl acetate.

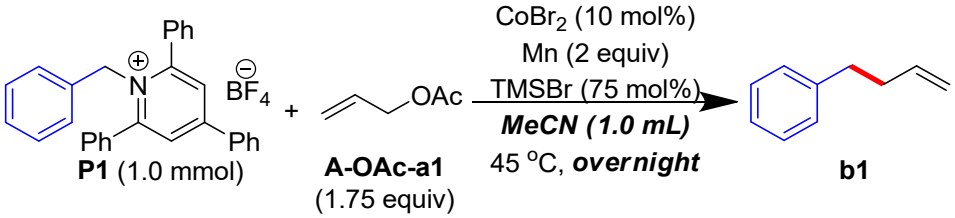
Table 2.1. Optimisation of pyridinium salt P1 with allyl acetate.

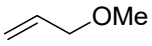
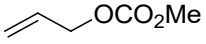
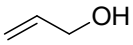


Entry	Conditions	b1 yield[a]/%	Entry	Conditions	b1 yield[a]/%
1	no	79	6	a1 (1.5 equiv)	66
2	Zn instead of Mn	21	7	a1 (2.0 equiv)	76
3	TFA instead of TMSBr	37	8	MeCN (1.0 mL)	90
4	rt	47	9	MeCN (1.5 mL)	88
5	60 °C	57	10	$CoBr_2$ (5 mol%)	34

[a]GC yields using dodecane as internal standard.

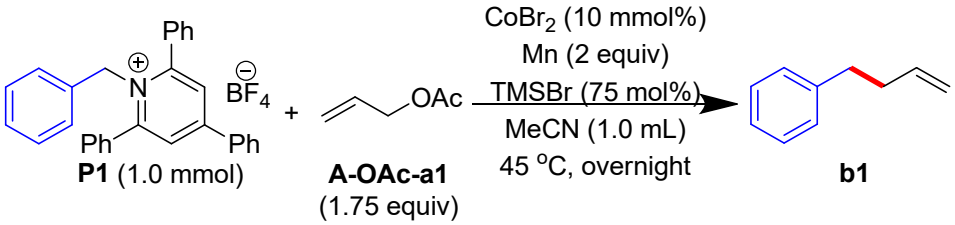
Table 2.2. Optimization of pyridinium salt P1 with allyl acetate.



Entry	Conditions	b1 yield[a]/%	Entry	Conditions	b1 yield[a]/%
1	no	92	10	Mn (3.0 equiv)	85
2	Bipy	86	11	THF	Trace
3	4-Mebipy	82	12	Dioxane	Trace
4	4-tbubipy	84	13	Toluene	Trace
5	TMSBr (50 mol%)	85	14	DMA	Trace
6	TMSBr (100 mol%)	83	15	DMF	Trace
7	TMSCl (75 mol%)	75	16		75
8	Mn (1.5 equiv)	60	17		88
9	Mn (2.5 equiv)	75	18		8

[a]GC yields using dodecane as internal standard.

Table 2.3. Control experiments.



Entry	Variations	b1[a] /%
1	w/o $CoBr_2$	ND
2	w/o Mn	ND
3	w/o TMSBr	Trace

[a]GC yields using dodecane as internal standard.

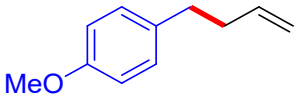
3. The Cross-Coupling of Benzyl Katritzky Pyridinium Salts and Allyl Derivatives

1) General procedure of allylation products (GP-C)

In an oven-dried, 20-mL reaction tube sealed with a septum, benzyl Katritzky pyridinium salt (**P**) (1.0 mmol, 1.0 equiv), Mn powder (110 mg, 2.0 mmol, 2.0 equiv) and $CoBr_2$ (21.8 mg, 0.1 mmol, 10 mol%) were added. The tube was filled with N_2 three times and added the MeCN (1.0 mL), allyl derivatives (**A-OR**) (1.75 equiv, if it is liquid) under N_2. The mixture was stirred at rt and then TMSBr (100 µL, 0.75 mmol, 75 mol%) was added. After the reaction mixture was allowed to stir overnight (around 15 h) at 45 °C., the mixture was poured into a solution of 2N HCl and extracted with DCM. The organic layer was washed with a saturated solution of NaCl and dried over $MgSO_4$. Evaporation of solvent and purification by column chromatography on silica gel (pentane/diethyl ether) afforded the corresponding product characterized by NMR (^{1}H, ^{13}C, ^{19}F).

2) Characterisation data of products

4-(p-Methoxyphenyl)but-1-ene (b2) [20574-98-5]



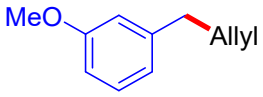
Following ***GP-C***, **P2** (515 mg, 1.0 mmol) and **A-OAc-1a** (189 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (66 mg, 41% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane), **Rf** (pentane/Et_2O 95:5) = 0.75.

^{1}H NMR (300 MHz, Chloroform-d) δ 7.12 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 5.87 (m, 1H), 5.18 – 4.88 (m, 2H), 3.80 (s, 3H), 2.66 (dd, *J* = 8.9, 6.7 Hz, 2H), 2.35 (q, *J* = 7.2 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-d) δ 157.78, 145.42, 134.30, 129.19, 113.74, 110.20, 55.21 (d, *J* = 4.2 Hz), 39.88, 33.37, 22.62 (d, *J* = 3.3 Hz).

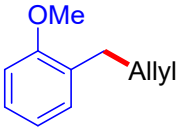
The spectroscopic data match the reported one in the literature.[6]

4-(3-Methoxyphenyl)-1-butene (b3) [1199-90-2]



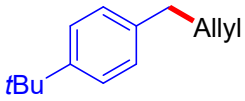
Following ***GP-C***, **P3** (515 mg, 1.0 mmol) and **A-OMe-1a** (187 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (110 mg, 68% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane), **R**$_f$ (pentane/Et_2O 95:5)= 0.75.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 (tt, *J* = 8.4, 1.2 Hz, 1H), 6.94 – 6.71 (m, 3H), 5.92 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.29 – 4.82 (m, 2H), 3.84 (s, 3H), 2.74 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.57 – 2.31 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 160.41, 144.31, 138.83, 130.07, 130.05, 121.66, 115.74, 115.03, 111.87, 55.91, 36.25.
The spectroscopic data match the reported one in the literature.[7]

4-(2-Methoxyphenyl)-1-butene (b4) [63667-83-4]



Following ***GP-C***, **P4** (515 mg, 1.0 mmol) and **A-OMe-1a** (187 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (141 mg, 87% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane), **R**$_f$ (pentane/Et_2O 95:5) = 0.77.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 – 7.12 (m, 2H), 7.08 – 6.75 (m, 2H), 5.94 (ddtd, *J* = 16.8, 10.2, 6.6, 0.8 Hz, 1H), 5.35 – 4.81 (m, 2H), 3.86 (d, *J* = 0.9 Hz, 3H), 2.77 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.55 – 2.25 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 157.48, 138.77, 130.28, 129.87, 127.09, 120.34, 114.51, 110.22, 55.25, 33.96, 29.85.
The spectroscopic data match the reported one in the literature. [7]

1-(But-3-en-1-yl)-4-(tert-butyl)benzene (b5) [27798-45-4]



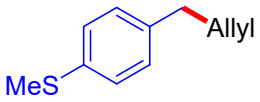
Following ***GP-C***, **P5** (515 mg, 1.0 mmol) and **A-OAc-1a** (189 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (141 mg, 75% yield) after purification by column chromatography (SiO_2: pure pentane), **R**$_f$ (pentane) = 0.80.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.98 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.48 – 4.86 (m, 2H), 2.79 (dd, *J* = 9.3, 6.5 Hz, 2H), 2.49 (td, *J* = 6.9, 3.1 Hz, 2H), 1.42 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.63, 138.91, 138.40, 128.15, 125.28, 114.87, 35.63, 34.95, 34.46, 31.54.

The spectroscopic data match the reported one in the literature.[8]

4-(p-Thiomethylyphenyl)but-1-ene (b6) [59209-69-7]



Following ***GP-C***, 1-(4-(methylthio)benzy pyridinium salt (531 mg, 1.0 mmol) and **A-OMe-1a** (187 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (126 mg, 71% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane).

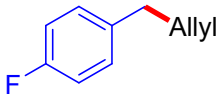
R$_f$ (pentane/Et_2O 95:5) = 0.6

^{1}H NMR (300 MHz, Chloroform-d) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.07 – 5.69 (m, 1H), 5.08 (t, *J* = 15.3 Hz, 2H), 2.73 (t, *J* = 7.8 Hz, 2H), 2.51 (s, 3H), 2.41 (q, *J* = 9.5, 8.5 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-d) δ 138.98 , 137.98 , 135.41 , 129.05 , 127.12 , 115.14 , 35.56 , 34.90 , 16.34 .

The spectroscopic data match the reported one in the literature.[9]

1-(But-3-en-1-yl)-4-fluorobenzene (b7)[2248-13-7]



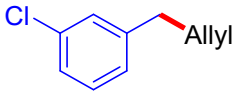
Following ***GP-C***, **P6** (503 mg, 1.0 mmol) and **A-OAc-1a** (189 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (68 mg, 45% yield) after purification by column chromatography (SiO_2: pure pentane), **R**$_f$ (pentane) = 0.82.

^{1}H NMR (300 MHz, Chloroform-d) δ 7.14 (dd, *J* = 8.3, 5.4 Hz, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 5.85 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.02 (t, *J* = 13.9 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.36 (q, *J* = 7.4 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.85, 159.63, 137.79, 137.42 (d, *J* = 3.2 Hz), 129.75 (d, *J* = 7.7 Hz), 116.02 – 113.65 (m), 35.65, 34.55.

The spectroscopic data match the reported one in the literature.[6]

1-(But-3-en-1-yl)-3-chlorobenzene (b8) [91426-46-9]



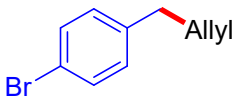
Following ***GP-C***, **P6** (519 mg, 1.0 mmol) and **A-OAc-1a** (189 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (100 mg, 60% yield) after purification by column chromatography (SiO_2: pure pentane). **R**$_f$ (pentane) = 0.82

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 7.1 Hz, 3H), 7.09 (dt, *J* = 6.5, 1.8 Hz, 1H), 5.86 (ddt, *J* = 16.7, 9.9, 6.6 Hz, 1H), 5.31 – 4.73 (m, 2H), 2.71 (dd, *J* = 9.0, 6.5 Hz, 2H), 2.52 – 2.28 (m, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 144.62, 138.25, 134.80, 130.28, 129.34, 127.41, 126.77 (d, *J* = 3.1 Hz), 35.96 (d, *J* = 2.4 Hz), 35.77.

The spectroscopic data match the reported one in the literature.[10]

1-(3-Butenyl)-4-bromobenzene (b9) [15451-32-8]

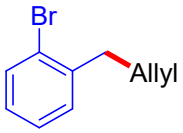


Following ***GP-C***, **P9** (563 mg, 1.0 mmol) and **A-CO_2Me** (251 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (105 mg, 50% yield) after purification by column chromatography (SiO_2: pure pentane). **R_f** (pentane) = 0.82

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.30 – 4.75 (m, 2H), 2.68 (dd, *J* = 8.9, 6.7 Hz, 2H), 2.49 – 2.24 (m, 2H).

The spectroscopic data match the reported one in the literature.[6]

1-Bromo-2-(but-3-en-1-yl)benzene (b10) [71813-50-8]



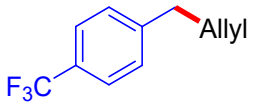
Following ***GP-C***, **P10** (563 mg, 1.0 mmol) and **A-OAc-1a** (189 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (152 mg, 72% yield) after purification by column chromatography (SiO_2: pure pentane). **R_f** (pentane) = 0.82

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.22 (m, 2H), 7.11 (ddd, *J* = 7.1, 4.3, 1.5 Hz, 1H), 6.06 – 5.83 (m, 1H), 5.22 – 4.95 (m, 2H), 2.89 (dd, *J* = 9.2, 6.6 Hz, 2H), 2.44 (dtd, *J* = 7.9, 6.5, 1.4 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.07, 137.66, 132.81, 130.42, 127.61, 127.36, 124.49, 115.23, 35.68, 33.88.

The spectroscopic data match the reported one in the literature.[7]

4-(4-TrifluoromethyPhenyl)-1-butene (b11)



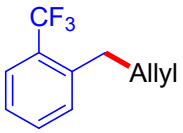
Following ***GP-C***, **P10** (552 mg, 1.0 mmol) and **A-CO_2Me** (251 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (86 mg, 43% yield) after purification by column chromatography (SiO_2: pure pentane). **R_f** (pentane) = 0.82

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.84 (ddt, *J* = 16.8, 10.3, 6.6 Hz, 1H), 5.03 (t, *J* = 13.1 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.40 (q, *J* = 7.4 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 145.90, 137.36, 128.75, 125.21 (q, *J* = 3.7 Hz), 115.47, 35.14 (d, *J* = 1.9 Hz).

The spectroscopic data match the reported one in the literature.[7]

1-(But-3-en-1-yl)-2-(trifluoromethyl)benzene (b12) [1417514-27-2]



Following ***GP-C***, **P10** (552 mg, 1.0 mmol) and **A-CO_2Me** (251 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (92 mg, 46% yield) after purification by column chromatography (SiO_2: pure pentane). **R_f** (pentane) = 0.83

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 – 7.21 (m, 2H), 5.91 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.15 – 4.98 (m, 2H), 3.03 – 2.82 (m, 2H), 2.52 – 2.23 (m, 2H).

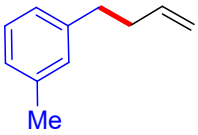
^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.38, 138.34, 132.37, 131.79, 129.23 (d, *J* = 29.5 Hz), 126.68, 123.59, 115.99, 100.73, 36.33, 32.85.

The spectroscopic data match the reported one in the literature.[7]

4-(3-Methylphenyl)-1-butene (b13) and 1,3-Bis(but-3-enyl)benzene (b14)

Following ***GP-C***, **P17** (892 mg, 1.0 mmol) and A-OMe-1a (374 µL, 3.5 mmol) were used, affording the title compound as a colorless oil 4-(3-Methylphenyl)-1-butene（b13) (21mg, 14% yield) and 1,3-Bis(but-3-enyl)benzene (b14) (57 mg, 31% yield) after purification by column chromatography (SiO_2: pure pentane). For b13; **R_f** (pentane) = 0.81 and for b14: **R_f** (pentane) = 0.77

4-(3-Methylphenyl)-1-butene (b13) [20574-99-6]

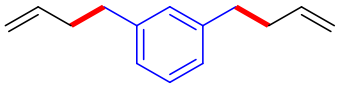


^{1}H NMR (300 MHz, Chloroform-d) δ 7.16 (s, 4H), 5.94 (m, 1H), 5.17 – 4.78 (m, 0H), 2.75 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.50 – 2.17 (m, 5H).

^{13}C NMR (75 MHz, Chloroform-d) δ 139.61, 139.01, 136.02, 129.81, 129.13, 115.65, 36.51, 35.78, 21.84.

The spectroscopic data match the reported one in the literature.[11]

1,3-Bis(but-3-enyl)benzene (b14):

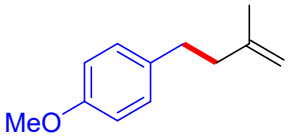


^{1}H NMR (300 MHz, Chloroform-d) δ 7.42 – 7.12 (m, 1H), 7.17 – 6.92 (m, 3H), 6.07 – 5.65 (m, 1H), 5.39 – 4.79 (m, 4H), 2.71 (dd, *J* = 9.3, 6.3 Hz, 4H), 2.44 – 2.17 (m, 4H).

^{13}C NMR (75 MHz, Chloroform-d) δ 142.61 (d, *J* = 1.2 Hz), 129.39, 128.99, 126.67 (d, *J* = 1.2 Hz), 115.59, 36.34, 36.15 (d, *J* = 1.3 Hz).

HRMS (APCI-P): $[MH]^+$ calculated for ($C_{14}H_{19}^+$) 187.1478; Found 187.1481.

4-(4-Methoxyphenyl)-2-methyl-1-butene (b18) [18491-21-9]



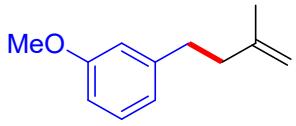
Following ***GP-C***, **P2** (515 mg, 1.0 mmol) with methallyl acetate (186 µL, 1.5 mmol) were used, affording the title compound as a colorless oil (97 mg, 55% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane). **R**f (pentane/Et_2O 95:5) = 0.75

H NMR (300 MHz, Chloroform-d) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.88 – 4.68 (m, 2H), 3.83 (s, 3H), 2.87 – 2.60 (m, 2H), 2.35 (dd, *J* = 9.6, 6.6 Hz, 2H), 1.82 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 157.78, 145.42, 134.30, 129.19, 113.74, 110.20, 55.21 (d, *J* = 4.2 Hz), 39.88, 33.37, 22.62 (d, *J* = 3.3 Hz).

The spectroscopic data match the reported one in the literature.[12]

5-(3-methoxyphenyl)-2-pentene (b19) [162707-40-6]



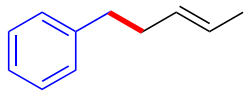
Following ***GP-C***, **P3** (515 mg, 1.0 mmol) with methallyl acetate (186 µL, 1.5 mmol) were used, affording the title compound as a colorless oil (107 mg, 61% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane). **R**$_f$ (pentane/Et_2O 95:5) = 0.75

^{1}H NMR (300 MHz, Chloroform-d) δ 7.29 – 7.15 (m, 1H), 6.94 – 6.70 (m, 3H), 4.84 – 4.66 (m, 2H), 3.82 (s, 3H), 2.90 – 2.66 (m, 2H), 2.47 – 2.23 (m, 2H), 1.80 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 160.36, 146.1, 144.65, 130.00, 121.52, 114.89, 111.77, 110.97, 55.88, 40.25, 35.07, 23.40.

HRMS (APCI-P): $[MH]^+$ calculated for ($C_{12}H_{17}O^+$) 177.1270; Found 177.1274.

(*E*)-3-Pentenylbenzene (b20) [1745-16-0]



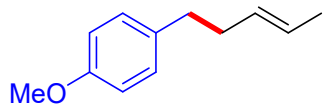
Following ***GP-C***, **P1** (484 mg, 1.0 mmol) and trans-2-butenyl acetate (134 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (106 mg, 72% yield) after purification by column chromatography (SiO_2: pure pentane). **R**$_f$ (pentane) = 0.85

^{1}H NMR (300 MHz, Chloroform-d) δ 7.42 – 7.34 (m, 2H), 7.33 – 7.24 (m, 3H), 5.58 (td, J = 3.6, 1.9 Hz, 2H), 2.77 (dd, J = 9.1, 6.6 Hz, 2H), 2.61 – 2.29 (m, 2H), 1.76 (dq, J = 2.7, 1.4 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 142.98, 131.39, 129.25, 129.03, 126.48, 126.18, 36.93, 35.30, 18.73.

The spectroscopic data match the reported one in the literature.[13]

5-(4-Methoxyphenyl)-2-pentene (b21) [140836-82-4]



Following ***GP-C***, **P2** (515 mg, 1.0 mmol) with trans-2-butenyl acetate (134 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (106 mg, 60% yield) after

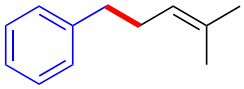
purification by column chromatography (SiO_2: 5% diethyl ether in pentane). **R_f** (pentane/Et_2O 95:5) = 0.75

^{1}H NMR (300 MHz, Chloroform-d) δ 7.18 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.56 (td, *J* = 3.6, 1.8 Hz, 2H), 5.13 – 4.96 (m, 3H), 3.85 (s, 2H), 2.70 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.43 – 2.07 (m, 2H), 1.93 – 1.55 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 157.80, 134.31, 130.76, 129.33, 125.32, 113.72, 55.18 (d, *J* = 4.1 Hz), 35.26, 34.78, 17.96 (d, *J* = 3.2 Hz).

The spectroscopic data match the reported one in the literature.[14]

(4-methylpent-3-en-1-yl)benzene (b22) [33501-90-5]



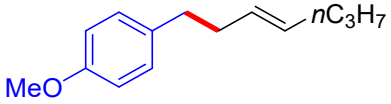
Following ***GP-C***, **P1** (484 mg, 1.0 mmol) and 3-methylbut-2-enyl acetate (246 µL, 1.75 mmol) were use, affording the title compound as a colorless oil (77 mg, 48% yield) after purification by column chromatography (SiO_2: pure pentane). **R_f** (pentane) = 0.85

^{1}H NMR (300 MHz, Chloroform-d) δ 7.39 – 7.31 (m, 2H), 7.29 – 7.22 (m, 3H), 5.26 (m, 1H), 2.72 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.38 (q, *J* = 7.9 Hz, 3H), 1.78 (s, 3H), 1.65 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 142.43, 132.10, 128.47, 128.24, 125.68, 123.79 (d, *J* = 1.6 Hz), 36.20, 30.11, 25.70 (d, *J* = 3.3 Hz), 17.66 (d, *J* = 3.1 Hz).

The spectroscopic data match the reported one in the literature. [15]

(4*E*)-7-(4-Methoxybenzyl)-4-heptene (b23)



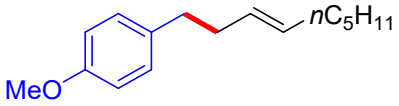
Following ***GP-C***, **P2** (515 mg, 1.0 mmol) (515 mg, 1.0 mmol) with (E)-2-hexen-1-yl acetate (190 µL, 1.5 mmol) were used, affording the title compound as a colorless oil (127 mg, 62% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane). **R_f** (pentane/Et_2O 95:5) = 0.75

^{1}H NMR (300 MHz, Chloroform-d) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.65 – 5.24 (m, 2H), 3.80 (s, 3H), 2.62 (dd, *J* = 8.9, 6.6 Hz, 2H), 2.43 – 2.16 (m, 2H), 2.03 – 1.81 (m, 2H), 1.37 (q, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 157.66, 134.31, 130.83, 129.56, 129.29, 113.62, 55.20, 35.24, 34.66, 22.65, 13.61.

The spectroscopic data match the reported one in the literature.[15]

(E)-1-(4′-methoxyphenyl)non-3-ene (b24) [1510836-86-8]



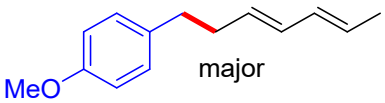
Following ***GP-C***, **P2** (515 mg, 1.0 mmol) with (*E*)-2-octen-1-yl acetate (256 mg, 1.5 mmol) were used, affording the title compound as a colorless oil (125 mg, 51% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane). **Rf** (pentane/Et_2O 95:5) = 0.73

^{1}H NMR (300 MHz, Chloroform-d) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.48 (q, *J* = 4.1, 3.2 Hz, 2H), 3.82 (s, 3H), 2.66 (dd, *J* = 9.0, 6.6 Hz, 2H), 2.45 – 2.26 (m, 2H), 2.12 – 1.95 (m, 2H), 1.57 – 1.17 (m, 6H), 0.95 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 158.45, 135.07, 131.89, 130.12 (d, *J* = 4.0 Hz), 114.39, 55.96, 36.04, 35.51, 33.34, 32.15, 30.04, 23.35, 14.86.

The spectroscopic data match the reported one in the literature.[16]

((2*E*,4*E*)-7-(4-Methoxyphenyl) hepta-2,4-diene (b25)



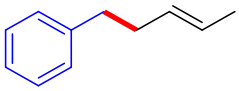
Following ***GP-C***, **P2** (515 mg, 1.0 mmol) with (*E*)-2-hexen-1-yl acetate (190 µL, 1.5 mmol) were used, affording the title compound as a colorless oil (89 mg, 44% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane). **Rf** (pentane/Et_2O 95:5) = 0.75

^{1}H NMR (300 MHz, Chloroform-d) δ 7.22 – 7.04 (m, 2H), 6.88 (dd, *J* = 8.6, 2.2 Hz, 2H), 6.15 – 5.94 (m, 2H), 5.85 – 5.51 (m, 2H), 3.82 (s, 3H), 2.69 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.42 (dd, *J* = 16.3, 9.1 Hz, 2H), 1.78 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 158.53, 134.79, 132.38, 131.75, 131.56, 130.06, 127.95, 114.48, 55.99, 35.79, 35.48 (d, *J* = 1.9 Hz), 18.81.

HRMS (APCI-P): $[MH]^+$ calculated for ($C_{14}H_{19}O^+$) 203.1427; Found 203.1430.

(*E*)-3-Pentenylbenzene (b26)



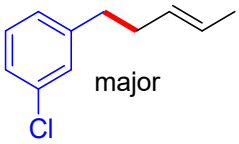
Following ***GP-C***, P1 (480 mg, 1.0 mmol) with 2-acetoxy-3-butene (224 µL, 1.5 mmol)were used, affording the title compound as a colorless oil (88 mg, 60% yield) after purification by by column chromatography (SiO_2: pure pentane). **R**$_f$ (pentane) = 0.85

1H NMR (300 MHz, Chloroform-d) δ 7.42 – 7.34 (m, 2H), 7.33 – 7.24 (m, 3H), 5.58 (td, J = 3.6, 1.9 Hz, 2H), 2.77 (dd, J = 9.1, 6.6 Hz, 2H), 2.61 – 2.29 (m, 2H), 1.76 (dq, J = 2.7, 1.4 Hz, 3H).

13C NMR (75 MHz, Chloroform-d) δ 142.98, 131.39, 129.25, 129.03, 126.48, 126.18, 36.93, 35.30, 18.73.

The spectroscopic data match the reported one in the literature.[13]

1-Chloro-3-[(Z)-pent-3-enyl]benzene (b27)



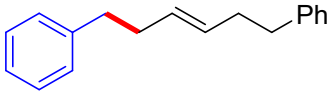
Following ***GP-C***, **P8** (519 mg, 1.0 mmol) with 2-acetoxy-3-butene (224 µL, 1.5 mmol) were used, affording the title compound as a colorless oil (110 mg, 61% yield) after purification by column chromatography SiO_2: pure pentane). **R**$_f$ (pentane) = 0.85

^{1}H NMR (300 MHz, Chloroform-d) δ 7.31 – 7.13 (m, 3H), 7.08 (dt, *J* = 6.7, 1.8 Hz, 1H), 5.48 (td, *J* = 3.7, 1.9 Hz, 2H), 2.66 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.43 – 2.18 (m, 2H), 1.68 (dd, *J* = 3.4, 1.3 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 144.95, 134.74, 130.80, 130.23, 129.35, 127.42, 126.67, 126.61, 36.51, 34.93, 18.69.

HRMS (APCI-P): $[M-H]^+$ calculated for ($C_{11}H_{12}Cl^+$) 179.0619; Found 179.0622.

(*E*)-1,6-Diphenyl-3-hexene (b28) [52772-46-0]



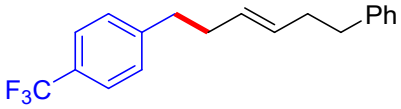
Following ***GP-C***, **P1** (480 mg, 1.0 mmol) with 5-phenylpenten-3-yl acetate (306 µL, 1.5 mmol) were used, affording the title compound as a colorless oil (117 mg, 49% yield) after purification by column chromatography (SiO_2: pure pentane). **R**$_f$ (pentane) = 0.7

^{1}H NMR (300 MHz, Chloroform-d) δ 7.39 (t, *J* = 7.2 Hz, 4H), 7.28 (td, *J* = 6.5, 1.7 Hz, 6H), 5.65 – 5.39 (m, 2H), 2.77 (td, *J* = 8.6, 7.9, 4.1 Hz, 4H), 2.54 – 2.34 (m, 4H).

^{13}C NMR (75 MHz, Chloroform-d) δ 142.91, 130.93, 129.32, 129.08, 126.57, 36.92, 35.27.

The spectroscopic data match the reported one in the literature.[17]

(E)-1-(4-TrifluoromethyPhenyl)-6-phenyl-3-hexene (b29)

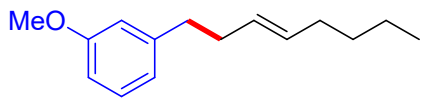


Following ***GP-C***, **P11** (553 mg, 1.0 mmol) with 5-phenylpenten-3-yl acetate (357 µL, 1.75 mmol) were used, affording the title compound as a colorless oil (192 mg, 63% yield) after purification by column chromatography (SiO_2: pure pentane). **R**$_f$ (pentane) = 0.7

^{1}H NMR (300 MHz, Chloroform-d) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.05 (m, 3H), 5.53 (td, *J* = 5.3, 3.8 Hz, 1H), 2.98 – 2.61 (m, 2H), 2.38 (dt, *J* = 11.3, 5.7 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-d) δ 146.15, 141.96, 130.69, 129.44, 128.82, 128.49, 128.28, 125.80, 125.17 (d, *J* = 3.6 Hz), 35.93 (d, *J* = 11.3 Hz), 34.16 (d, *J* = 24.2 Hz).

(*E*)-1-(3′-Methoxyphenyl) oct-3-ene (b30)



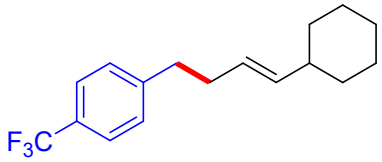
Following ***GP-C***, **P3** (515 mg, 1.0 mmol) with 3-Acetoxy-1-heptene (273 mg, 1.75 mmol) were used, affording the title compound as a colorless oil (132 mg, 61% yield) after purification by column chromatography (SiO_2: 5% diethyl ether in pentane). **Rf** (pentane/Et_2O 95:5) = 0.73

^{1}H NMR (300 MHz, Chloroform-d) δ 7.24 (tt, *J* = 7.2, 1.8 Hz, 1H), 6.92 – 6.67 (m, 3H), 5.69 – 5.30 (m, 2H), 3.84 (s, 3H), 2.70 (td, *J* = 7.8, 2.0 Hz, 2H), 2.44 – 2.23 (m, 2H), 2.16 – 1.78 (m, 2H), 1.47 – 1.24 (m, 4H), 0.94 (dt, *J* = 8.4, 4.0 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 159.59, 143.85, 131.15, 129.28, 129.15, 120.91, 114.24, 111.00, 55.08 (d, *J* = 4.6 Hz), 36.25, 34.37, 32.26, 31.75, 22.18, 13.97.

HRMS (APCI-P): $[MH]^+$ calculated for ($C_{14}H_{19}O^+$) 203.1427; Found 203.1430.

4-(*E*-4-cyclohexylbut-3-en-1-yl)- trifluoromethyl-benzene (b31)



Following ***GP-C***, **P11** (553 mg, 1.0 mmol) with 1-acetoxy-1-cyclohexyl-2-propene (319 mg, 1.75 mmol) were used, affording the title compound as a colorless oil (132 mg, 47% yield) after purification by column chromatography (SiO_2: pure pentane). **Rf** (pentane) = 0.7

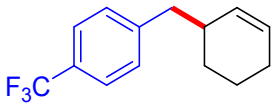
^{1}H NMR (300 MHz, Chloroform-d) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.40 (s, 2H), 2.74 (t, *J* = 7.7 Hz, 3H), 2.40 – 2.27 (m, 2H), 1.92 (tt, *J* = 11.6, 4.8 Hz, 1H), 1.79 – 1.58 (m, 5H), 1.46 – 1.18 (m, 3H), 1.13 – 0.94 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 146.23, 137.74, 136.67, 128.79, 127.10, 125.97, 125.07 (d, *J* = 3.8 Hz), 40.65, 35.99, 34.11, 33.27, 33.13, 26.36 – 25.89 (m).

^{19}F NMR (282 MHz, Chloroform-d) δ -62.26.

HRMS (APCI-P): $[MH-H_2]^+$ calculated for ($C_{17}H_{20}F_3^+$) 281.1506; Found 281.1512.

4-(Cyclohex-2-en-1-ylmethyl)-trifluoromethyl-benzene (b32)



Following ***GP-C***, P11 (553 mg, 1.0 mmol) with cyclohex-2-enyl acetate (196 mg, 1.75 mmol) were used, affording the title compound as a colorless oil (79 mg, 33% yield) after purification by column chromatography (SiO_2: pure pentane). **R**f (pentane) = 0.75

^{1}H NMR (300 MHz, Chloroform-d) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.75 (dt, *J* = 6.4, 2.8 Hz, 1H), 5.58 (tt, *J* = 7.8, 3.8 Hz, 1H), 2.68 (qd, *J* = 13.3, 7.6 Hz, 2H), 2.43 (m, 1H), 2.11 – 1.93 (m, 2H), 1.74 (dq, *J* = 6.9, 3.9, 3.4 Hz, 2H), 1.54 (m, 1H), 1.42 – 1.22 (m, 1H).

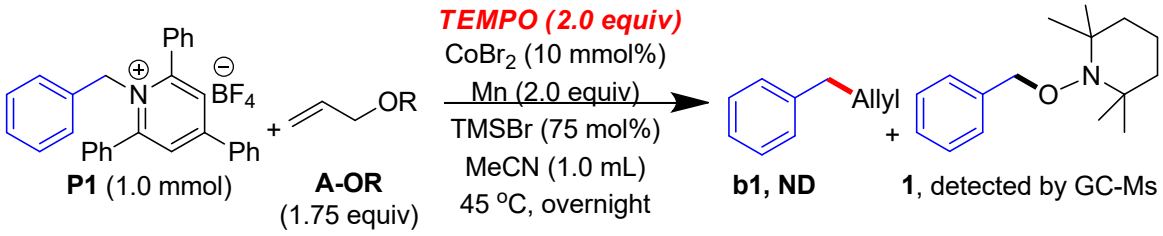
^{13}C NMR (75 MHz, Chloroform-d) δ 145.00, 130.60, 129.37, 128.04 – 127.20 (m), 125.05 (d, *J* = 3.8 Hz), 42.50, 36.99, 28.82, 25.29, 21.18.

^{19}F NMR (282 MHz, Chloroform-d) δ -62.37 (d, *J* = 66.4 Hz).

The spectroscopic data match the reported one in the literature. [18]

4. Mechanistic experiments

1) Radical trapping experiments of P1 with allyl acetate (A-OAc-a1) with TEMPO

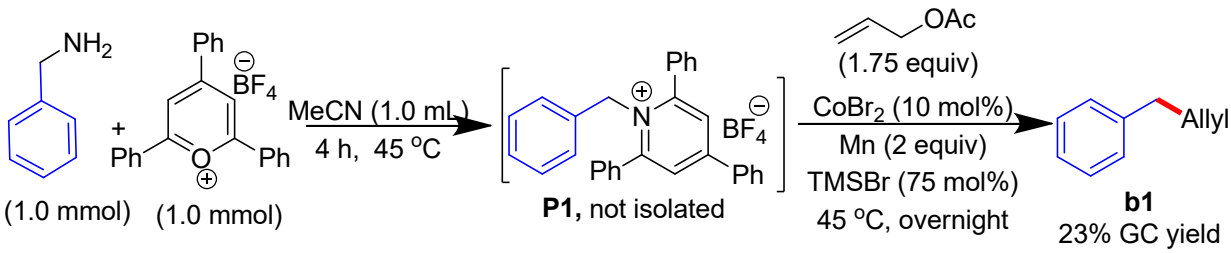


Entry	R	1[a]/ %	b1[b]/ %
1	Ac	Trace	ND
2	Me		

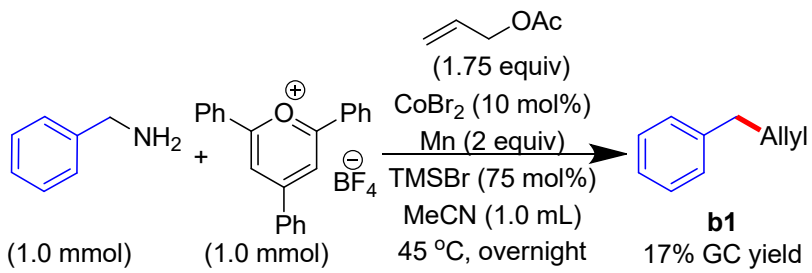
[a]detected by GC-Ms. [b]GC yield with 250 μL dodecane as reference.

In an oven-dried, 20-mL reaction tube sealed with a septum, **P1** (480 mg, 1.0 mmol, 1.0 equiv), Mn powder (110 mg, 2.0 mmol, 2.0 equiv) and $CoBr_2$ (21.8 mg, 0.1 mmol, 10 mol%) were added. The tube was filled with N_2 three times and added the MeCN (1.0 mL), A-OAc-1a (189 µL, 1.75mmol)/ A-OMe-1a (164 µL, 1.75mmol) under N_2. The mixture was stirred at rt and then TMSBr (100 µL, 0.75 mmol, 75 mol%) was added. After the reaction mixture was allowed to stir overnight (around 15 h) at 45 °C. After completion, the reaction mixture was added 250 µL dodecane as reference and filtered by flash chromatography. The filtrate was analysed by GC and GC-Ms. And results with different allyl derivatives showed that no target product was observed when TEMPO was added in the reaction.

2) One-pot experiments of P1 with A-OAc-1a

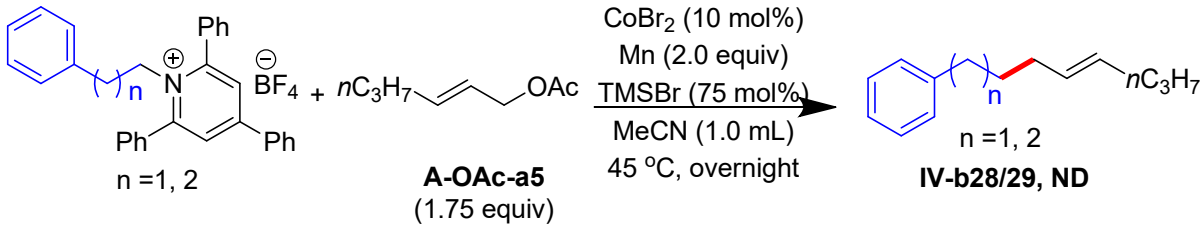


In an oven-dried, 20-mL reaction tube sealed with a septum, in the solution MeCN (1.0 mL) with benzyl amine (109 µL, 1.0 mmol, 1.0 equiv), 2,4,6-triphenylpyrylium tetrafluoroborate (396 mg, 1.0 mmol, 1.0 equiv) was added. And then mixture was allowed to stirred t at 45 °C. After reacting 4 h, the mixture was stopped and cool down to rt, Mn powder (110 mg, 2.0 mmol, 2.0 equiv), and $CoBr_2$ (21.8 mg, 0.1 mmol, 10 mol%) were added to the mixture without work-up under N_2. Then A-OAc-1a (189µL, 1.75 equiv) was injected by syringe. The mixture was stirred and TMSBr (100 µL, 75 mol%, to be sure that the reaction was triggered) was added at rt. Finally, the reaction mixture was allowed to heat to 45 °C and stirred overnight. After completion, the reaction mixture was added 250 µL dodecane as reference and filtered. It was found that 23% of **b1** was detected as well as home-coupling product of P1.

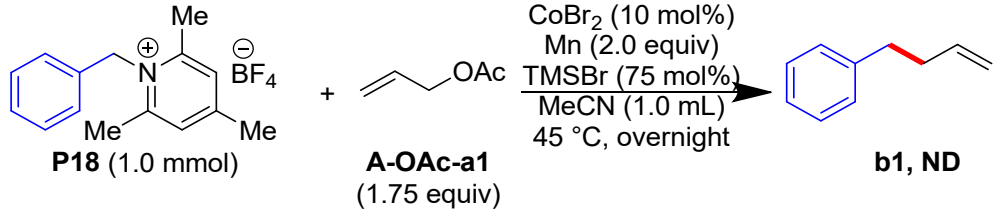


Then 2,4,6-triphenylpyrylium tetrafluoroborate (396 mg, 1.0 mmol, 1.0 equiv), Mn powder (110 mg, 2.0 mmol, 2.0 equiv), and $CoBr_2$ (21.8 mg, 0.1 mmol, 10 mol%) were added in an oven-dried 20-mL reaction tube at same time. The tube was filled with N_2 three times. And then MeCN (1.0 mL), benzyl amine (109 µL, 1.0 mmol, 1.0 equiv), A-OAc-1a (189µL, 1.75 equiv) were injected by syringe. The mixture was stirred and TMSBr (100 µL, 75 mol%, to be sure that the reaction was triggered) was added at 45 °C overnight. After completion, the reaction mixture was added 250 µL dodecane as reference and filtered. A bit lower GC yield (17 %) of **b1** was detected. However, these results still show the possibility of the cross-coupling benzylamine directly as an electrophilic partner with allyl acetate to construct Csp^3-Csp^3 bonds

3) Co-catalysed cross-coupling of Alkyl pyridinium salts with allyl acetate



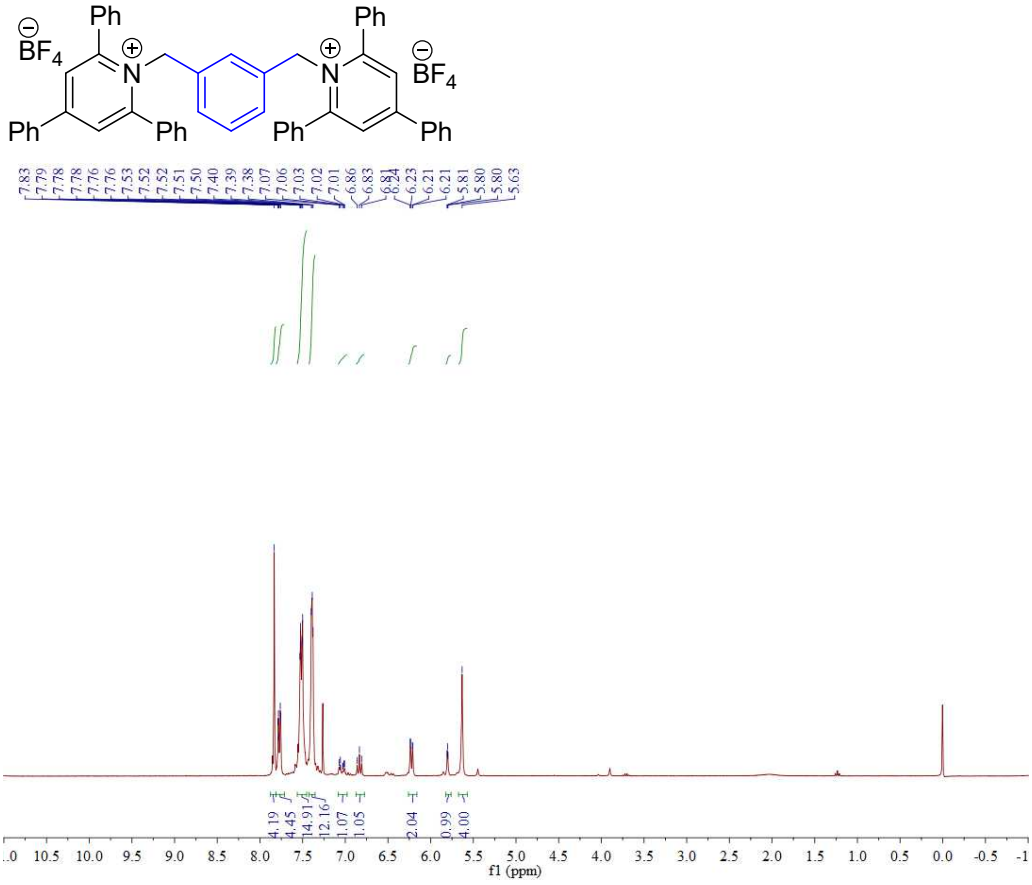
Furthermore, less reactive alkyl pyridinium salts were synthesised and used in reductive cross-coupling as the C-N electrophiles with **all-OAc-a5** under the optimised condition, as shown; no desired products were detected, and only the homocoupling product of allyl acetate was detected by GC-MS.

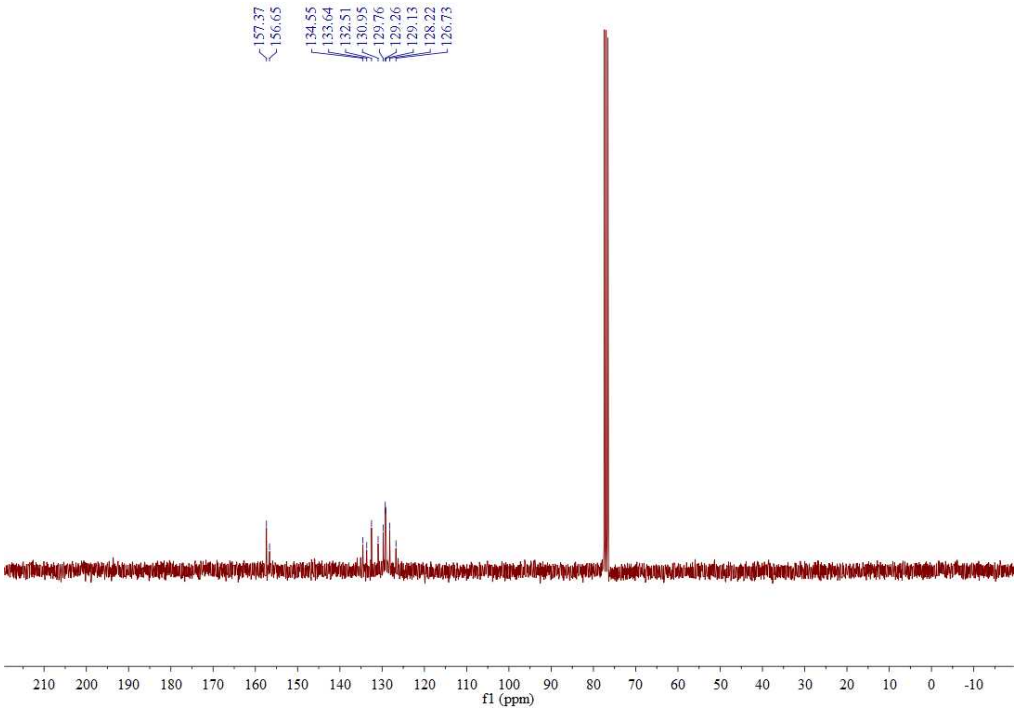


To learn deeply about this Co-catalysed Csp^3-Csp^3 cross-coupling of benzyl Katritzky pyridinium salts with C_{allyl}-O electrophiles, as well as increasing the molecular economy, benzyl pyridinium salt **P18** bearing methyl groups by instead of phenyl groups was used. However, the desired product was not detected overnight due to the lower reactivity of the C-N bond of **P18**

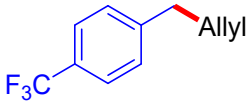
5. NMR Spectrum of Products

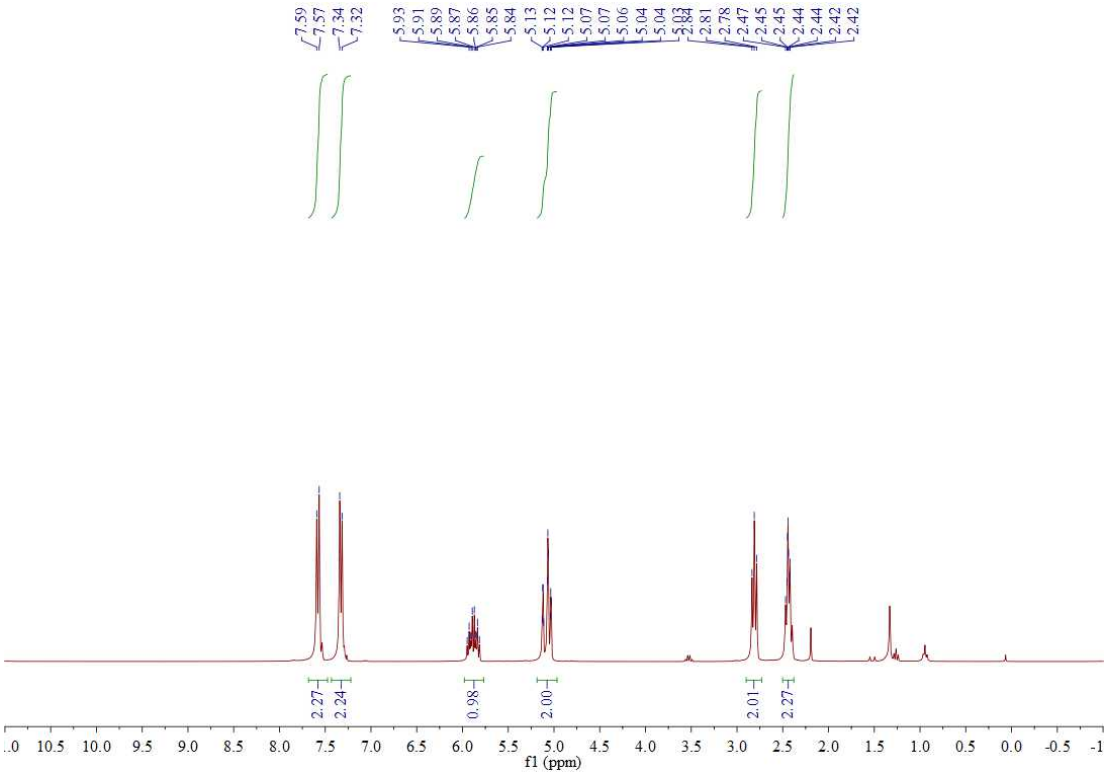
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **P17**

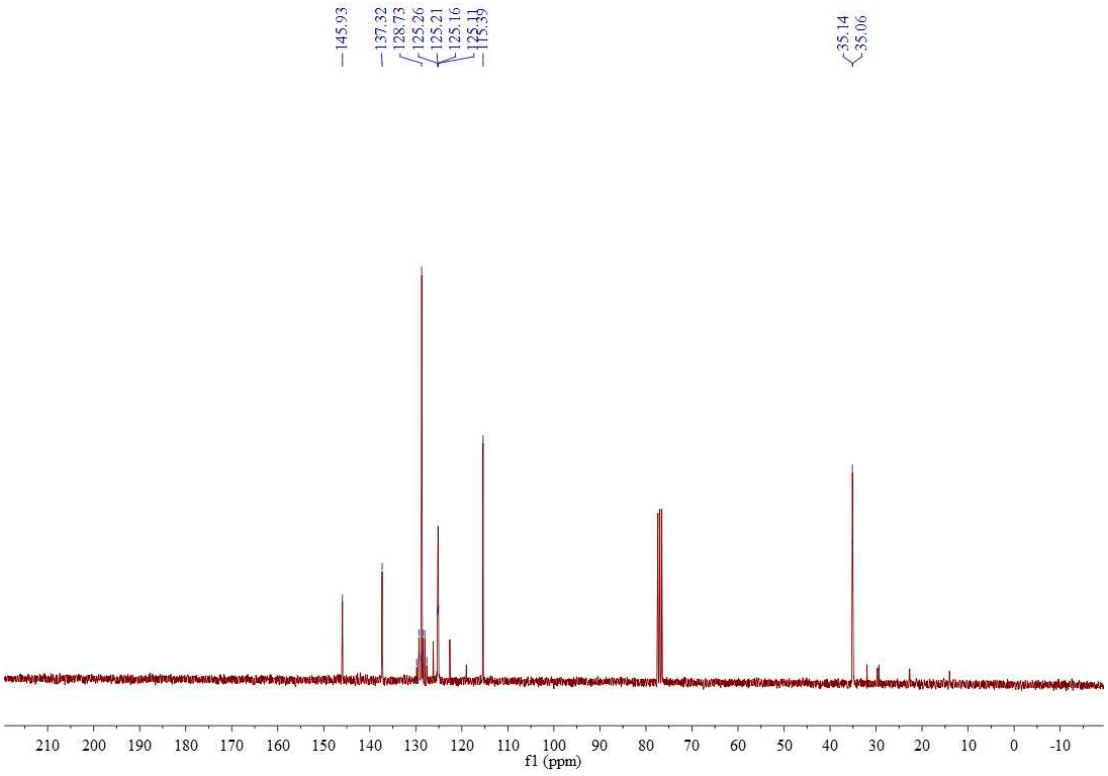


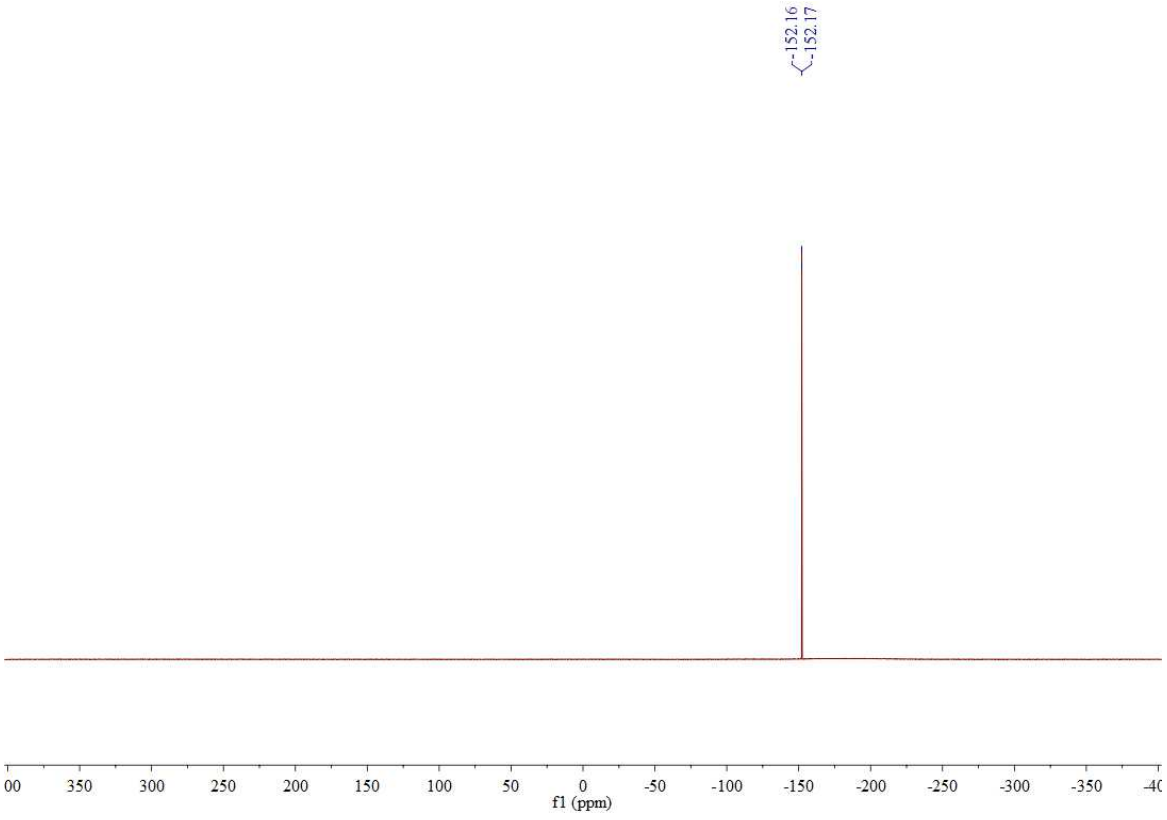


^{1}H NMR (300 MHz) and ^{13}C NMR (75 MH) of **b11**

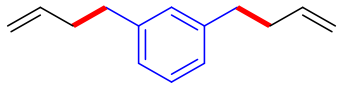


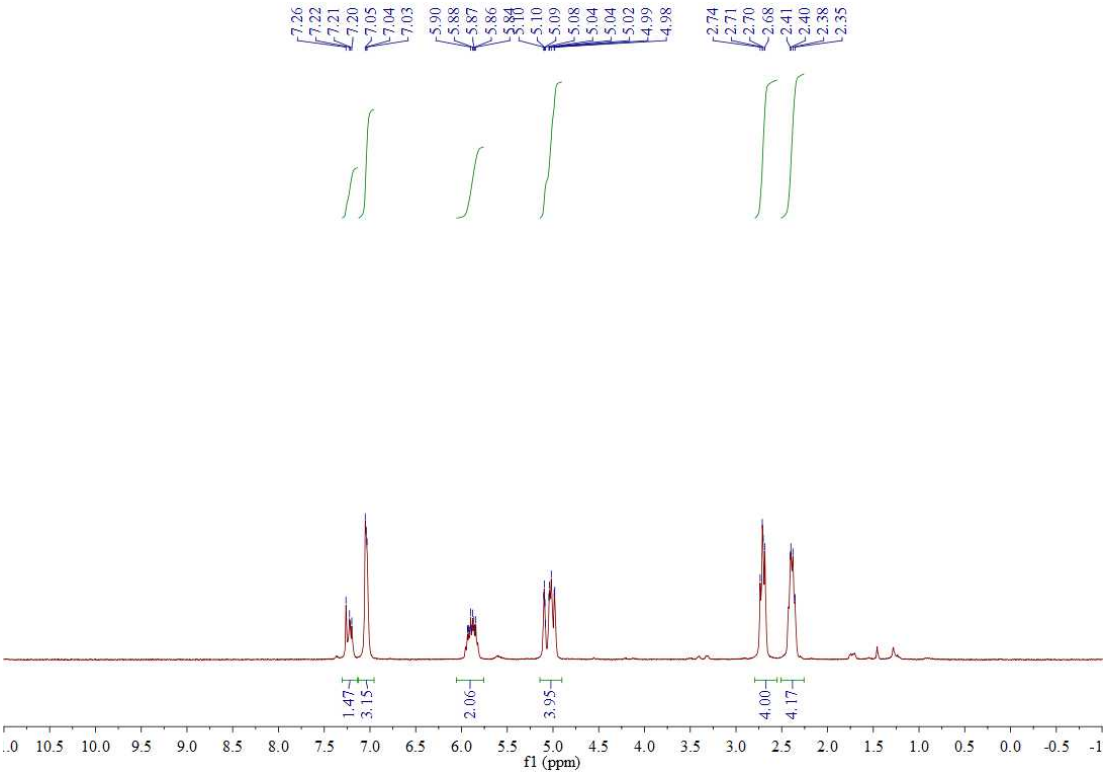


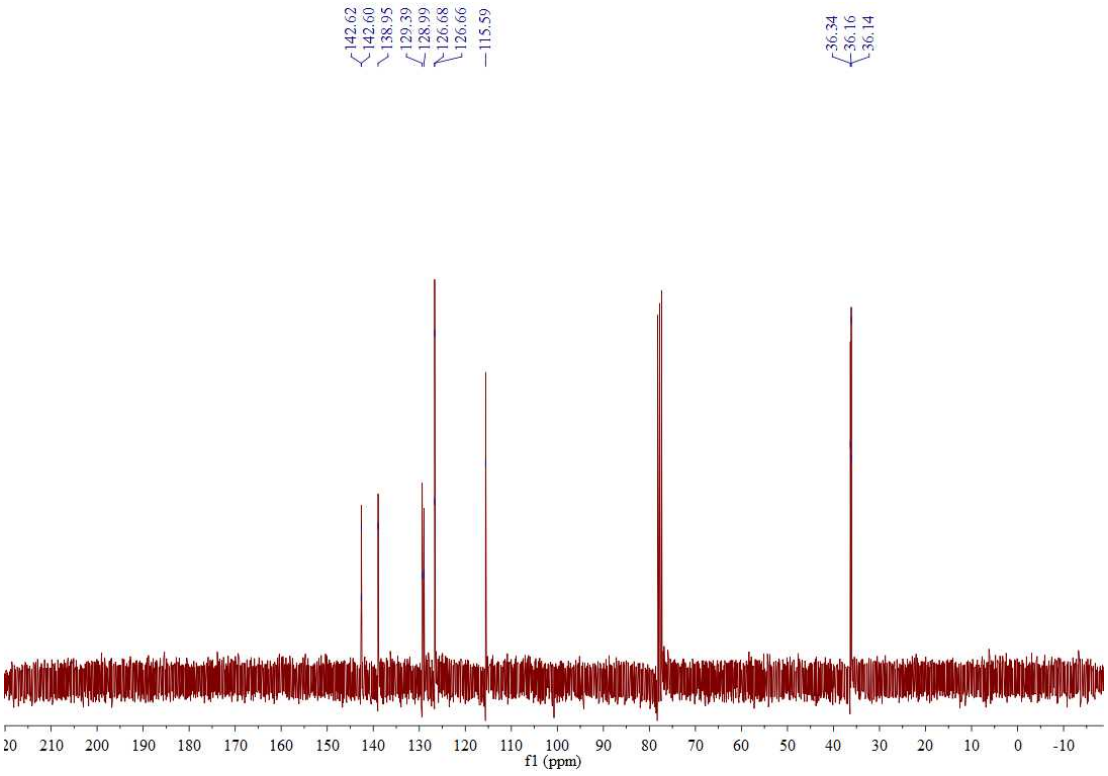

145.93
137.32
128.73
125.26
125.21
125.16
115.39
35.14
35.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-152.16
-152.17
00 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -40
f1 (ppm)

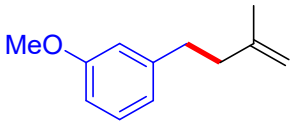
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **b14**

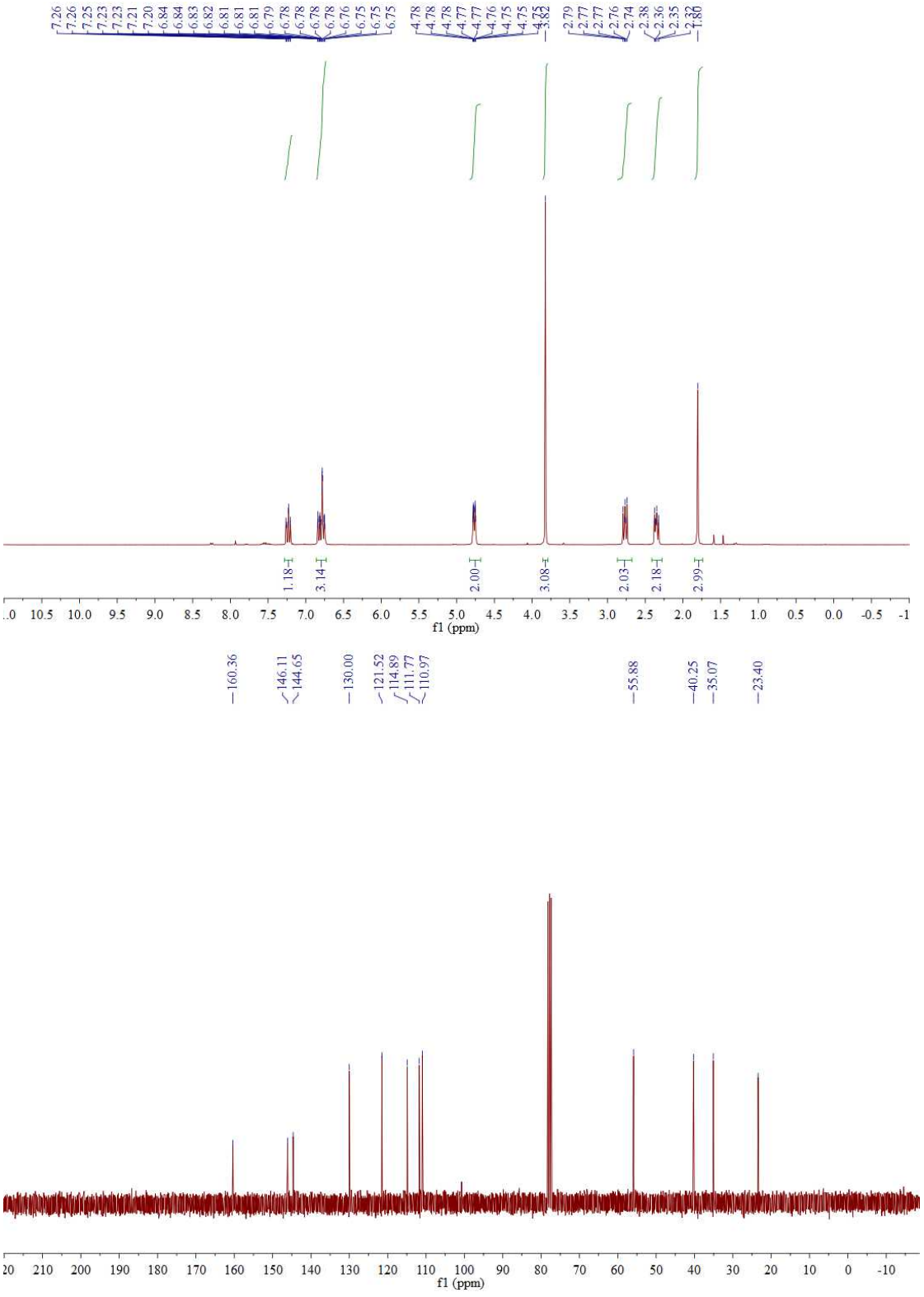




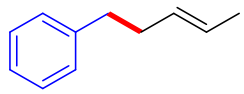


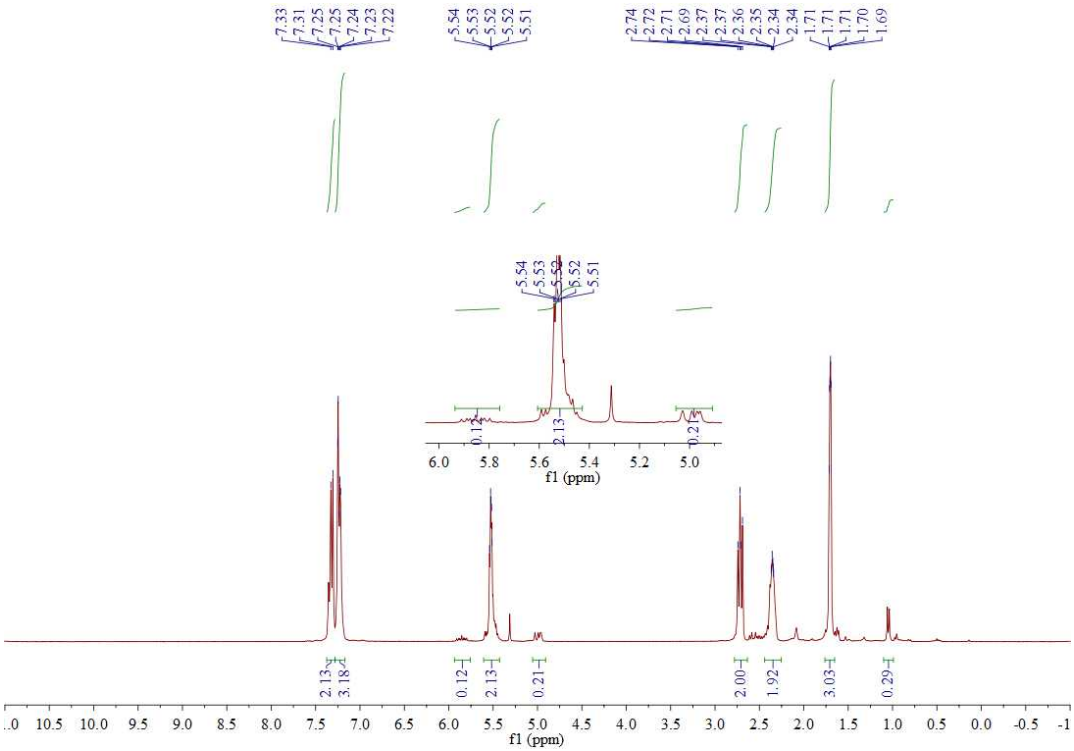
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **b18**



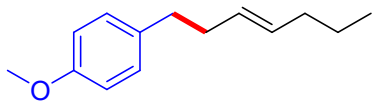


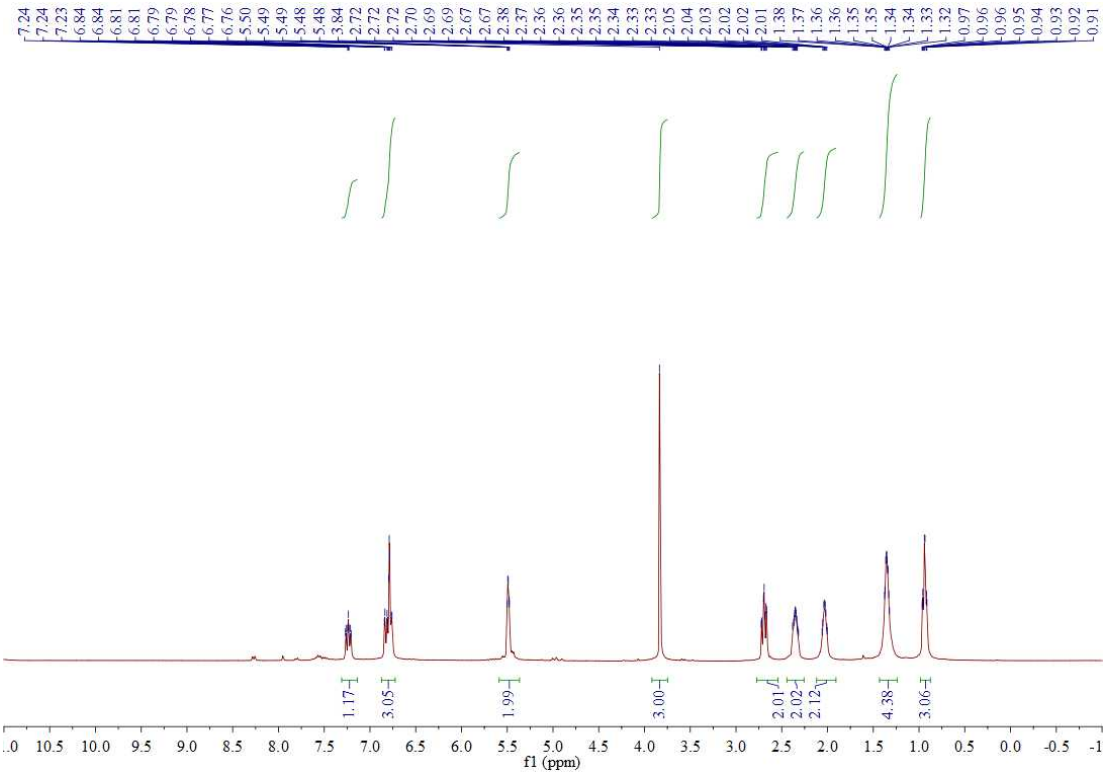
[1] H NMR (300 MHz) of **b20**

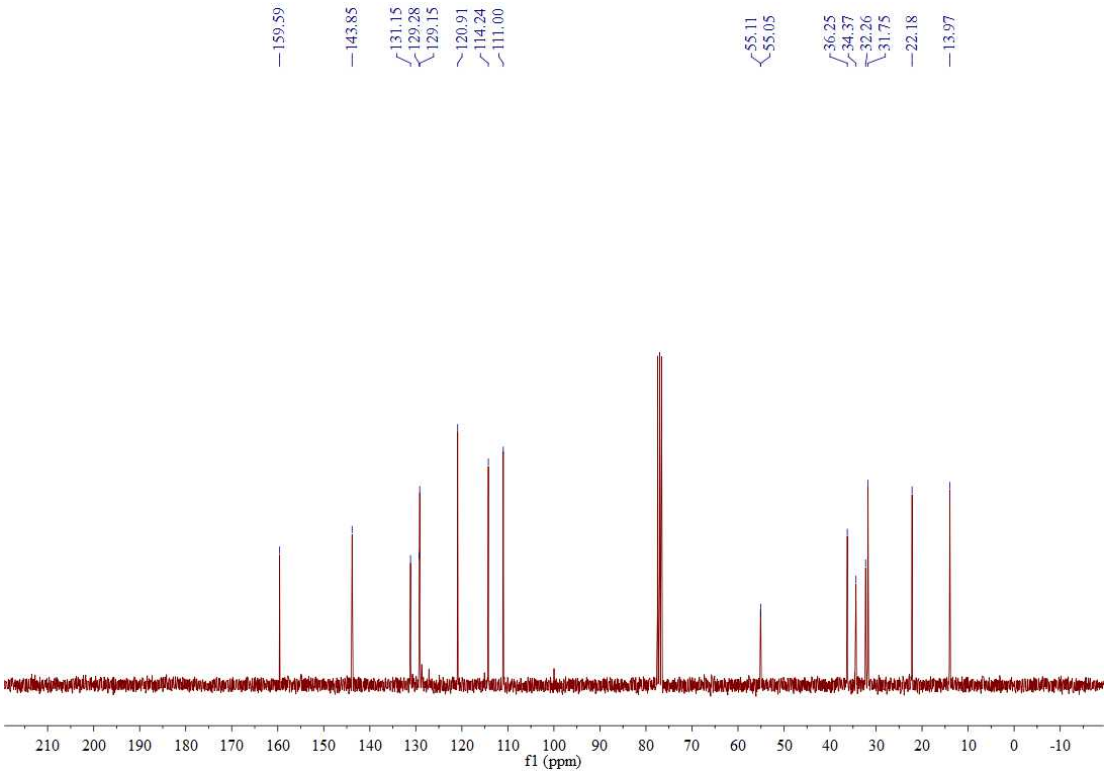



7.33
7.31
7.25
7.25
7.24
7.23
7.22
5.54
5.53
5.52
5.52
5.51
2.74
2.72
2.71
2.69
2.37
2.37
2.36
2.35
2.34
2.34
1.71
1.71
1.71
1.70
1.69
0.12
2.13
0.21
6.0
5.8
5.6
5.4
5.2
5.0
f1 (ppm)
2.13
3.18
0.12
2.13
0.21
2.00
1.92
3.03
0.29
f1 (ppm)

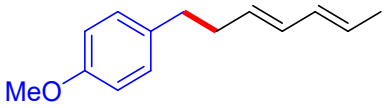
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **b23**

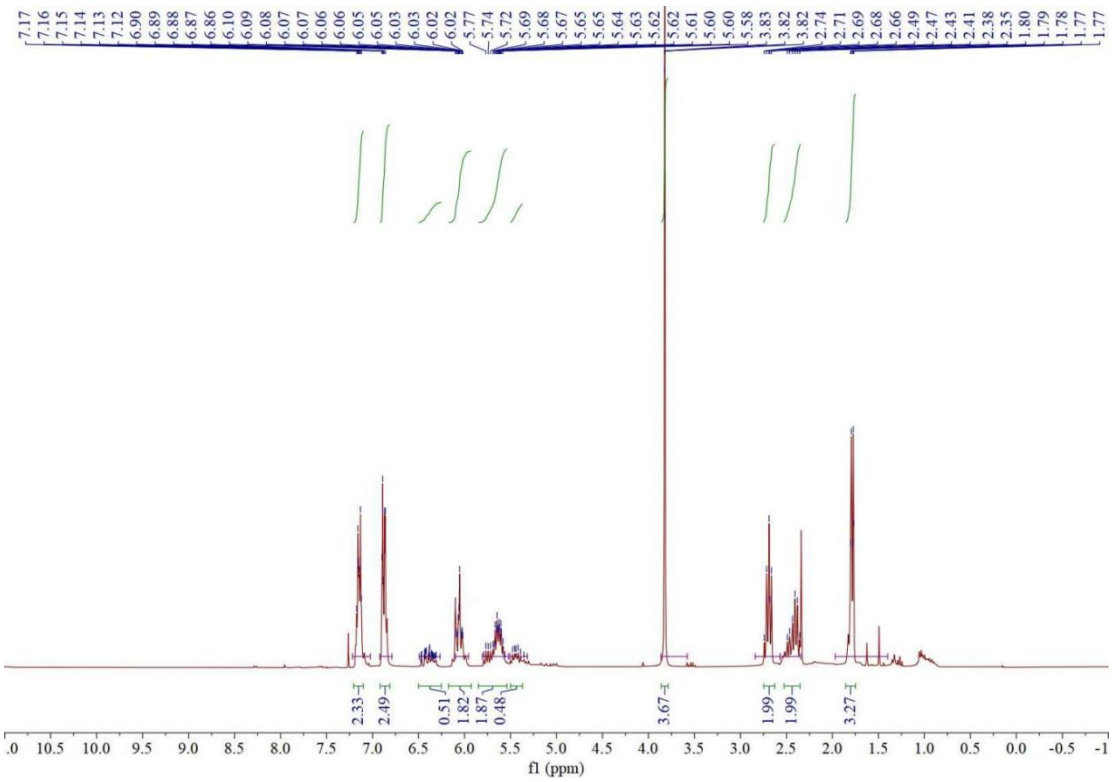


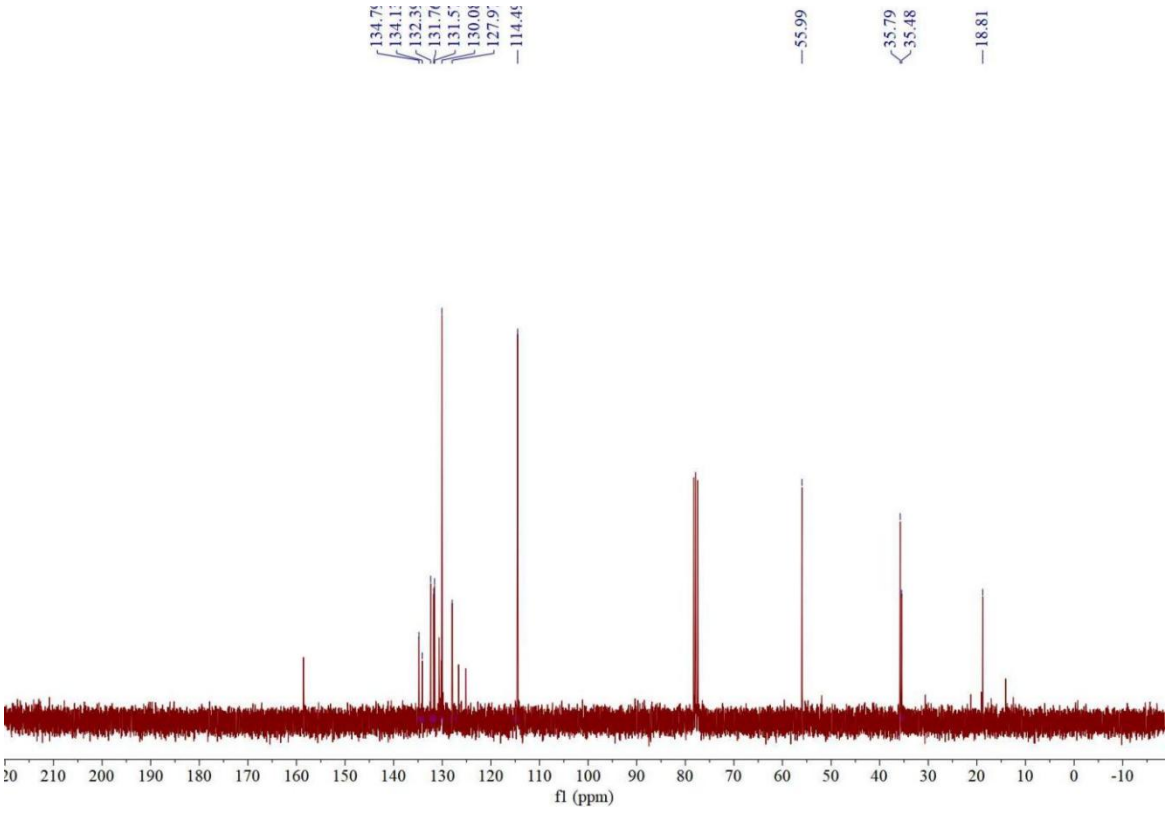




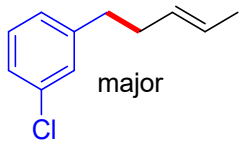
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **b25**

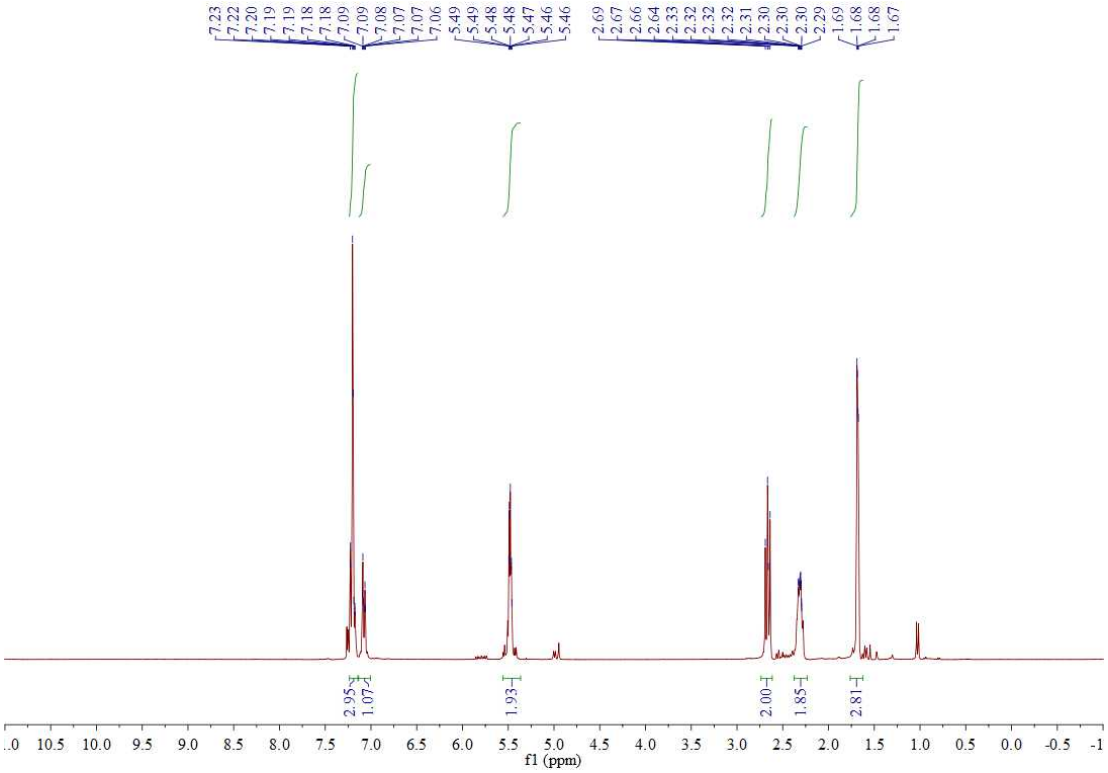


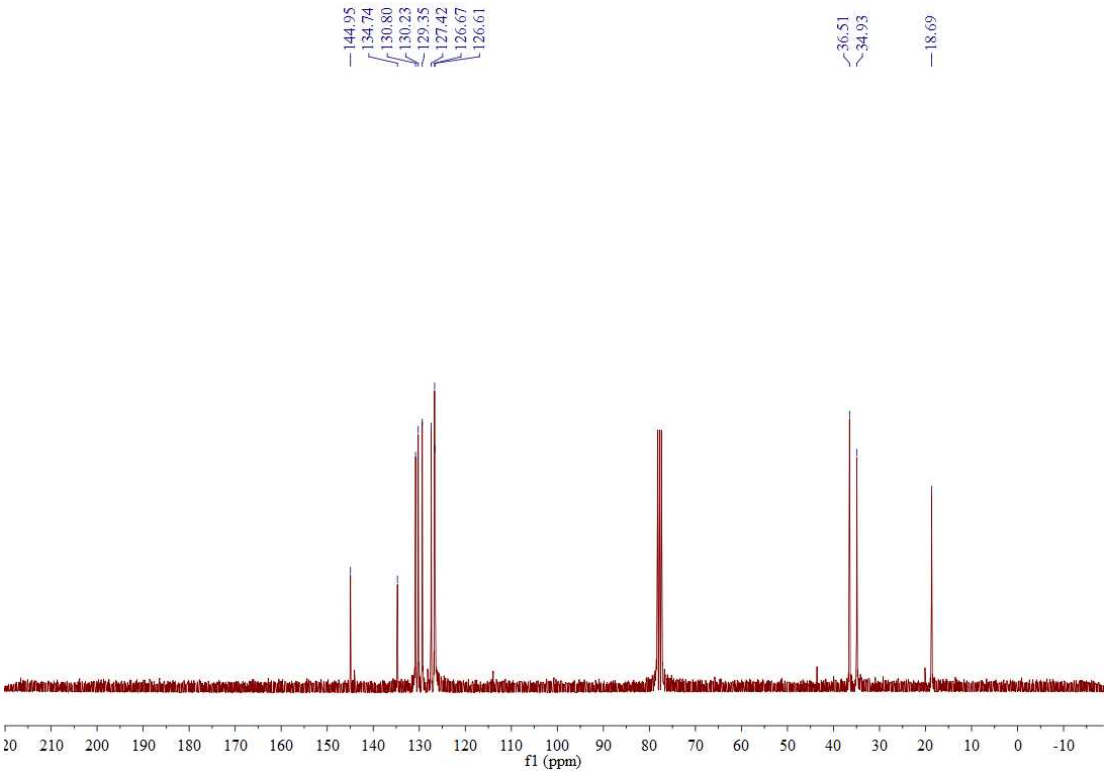

fl (ppm)


fl (ppm)

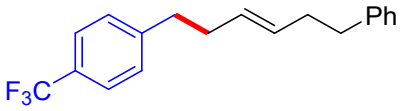
[1] H NMR (300 MHz) and [13]C NMR (75 MHZ) of **b27**

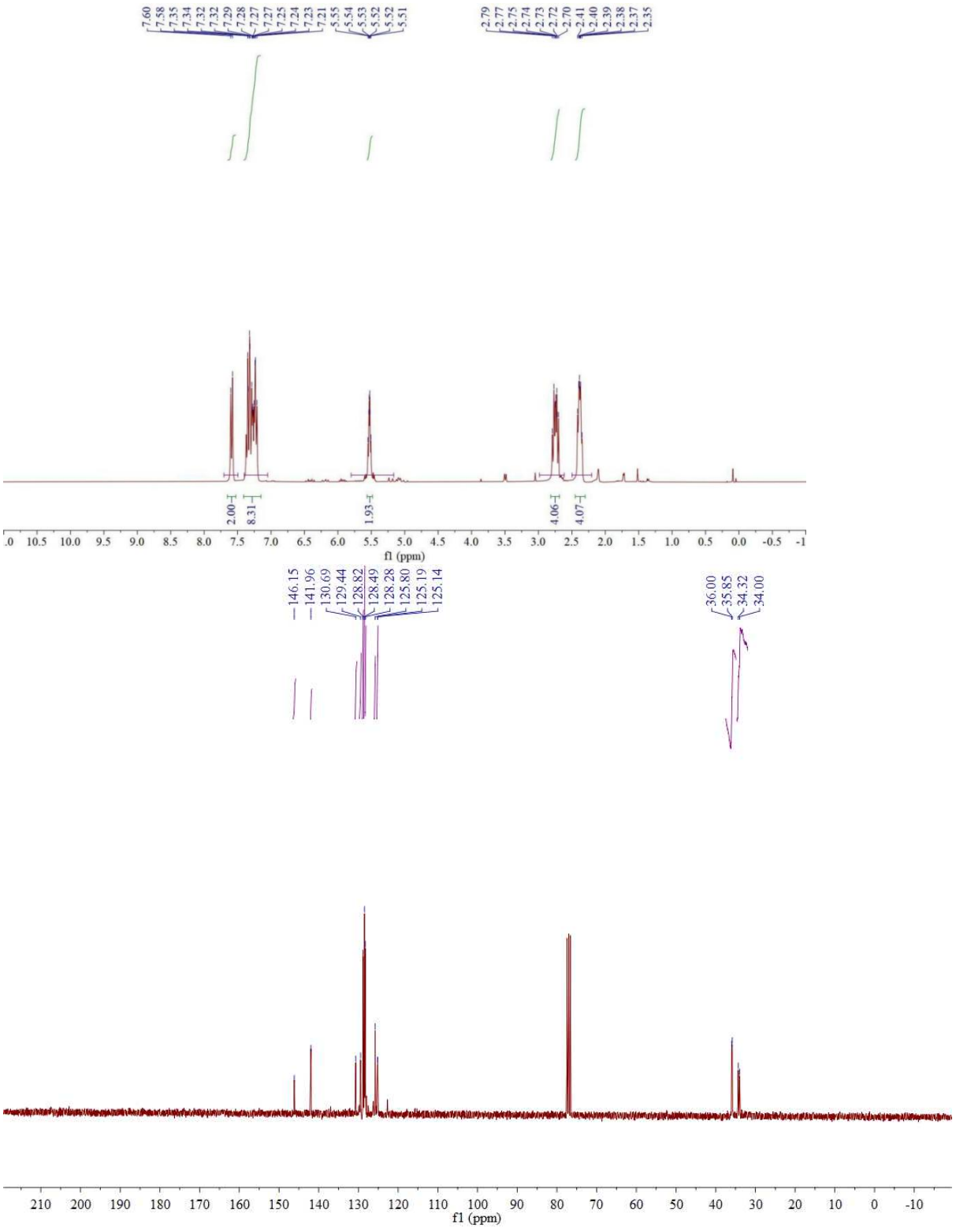




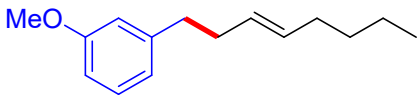


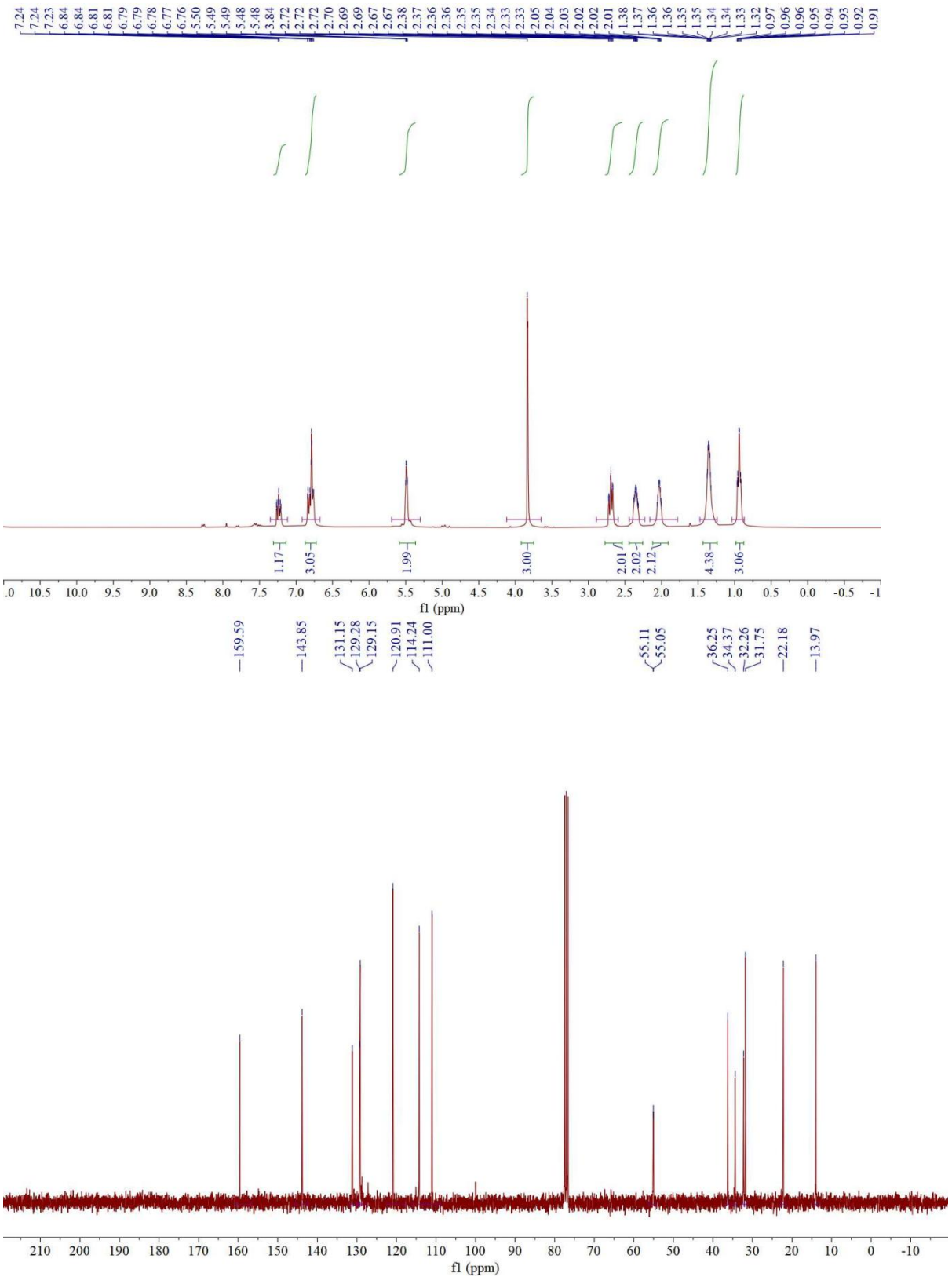
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **b29**



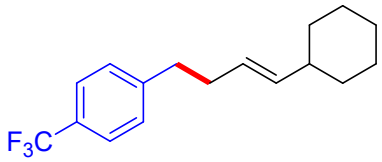

7.60
7.58
7.35
7.34
7.32
7.32
7.29
7.28
7.27
7.27
7.25
7.24
7.23
7.21
5.55
5.54
5.53
5.52
5.52
5.51
2.79
2.77
2.75
2.74
2.73
2.72
2.70
2.41
2.40
2.39
2.38
2.37
2.35
2.00
8.31
1.93
4.06
4.07
f1 (ppm)
146.15
141.96
130.69
129.44
128.82
128.49
128.28
125.80
125.19
125.14
36.00
35.85
34.32
34.00
f1 (ppm)

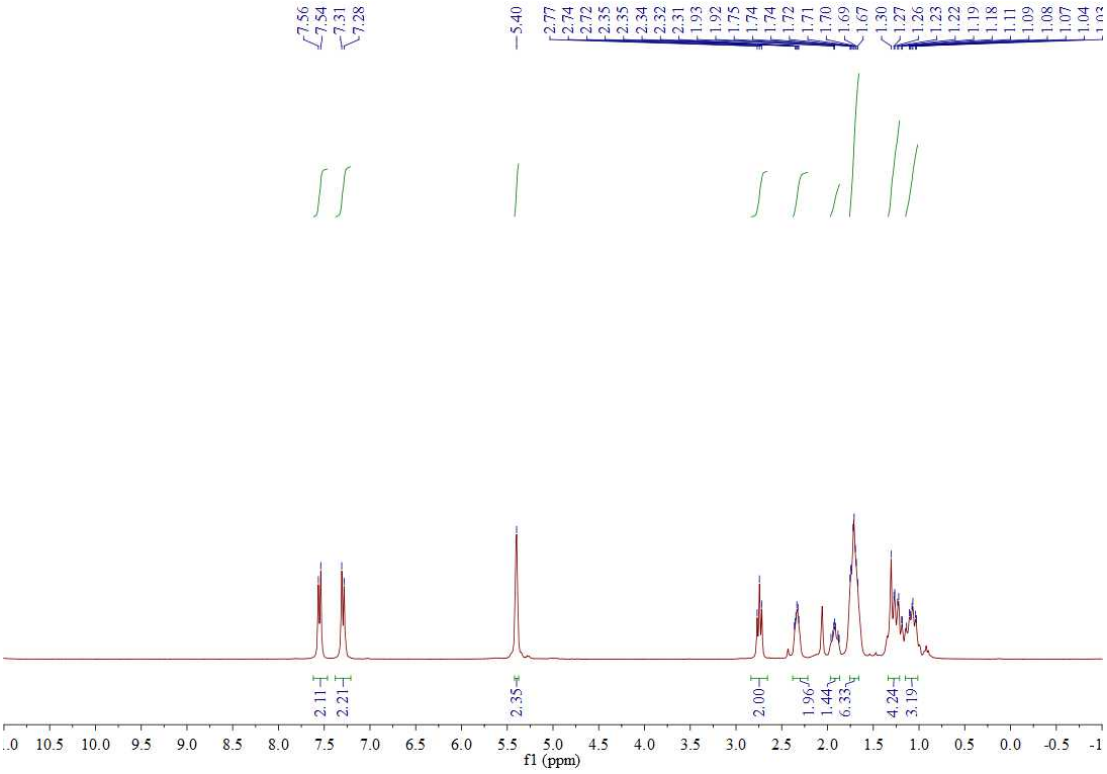
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **b30**

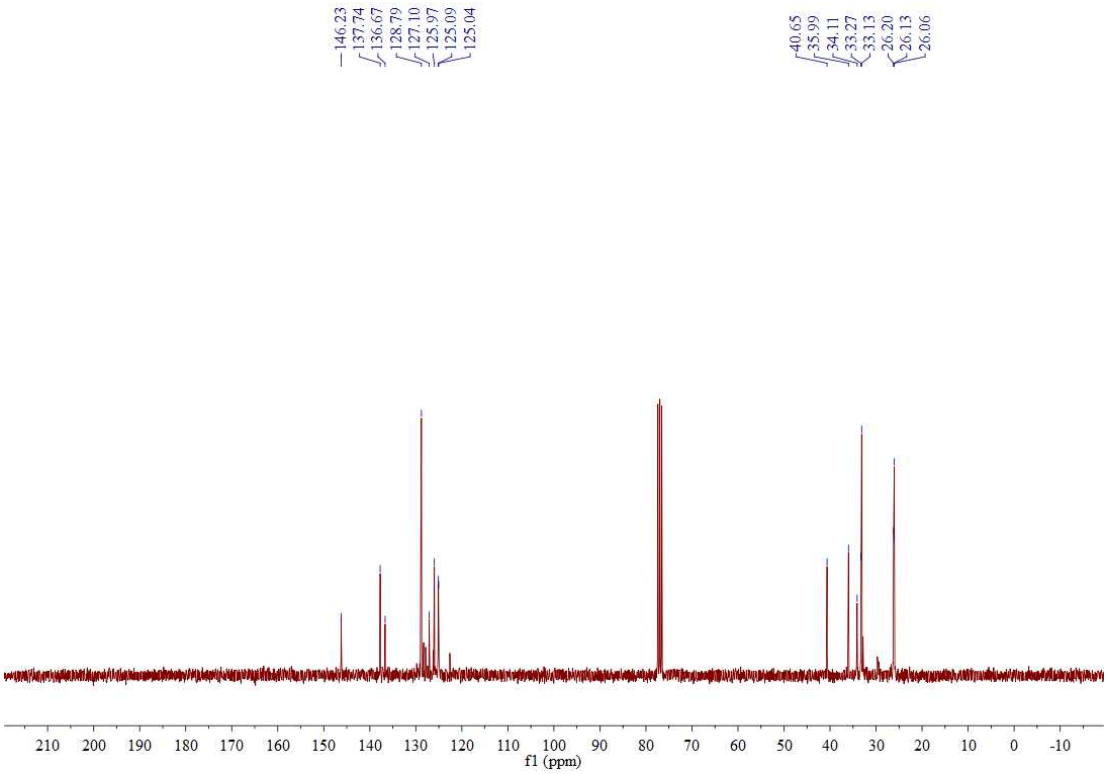


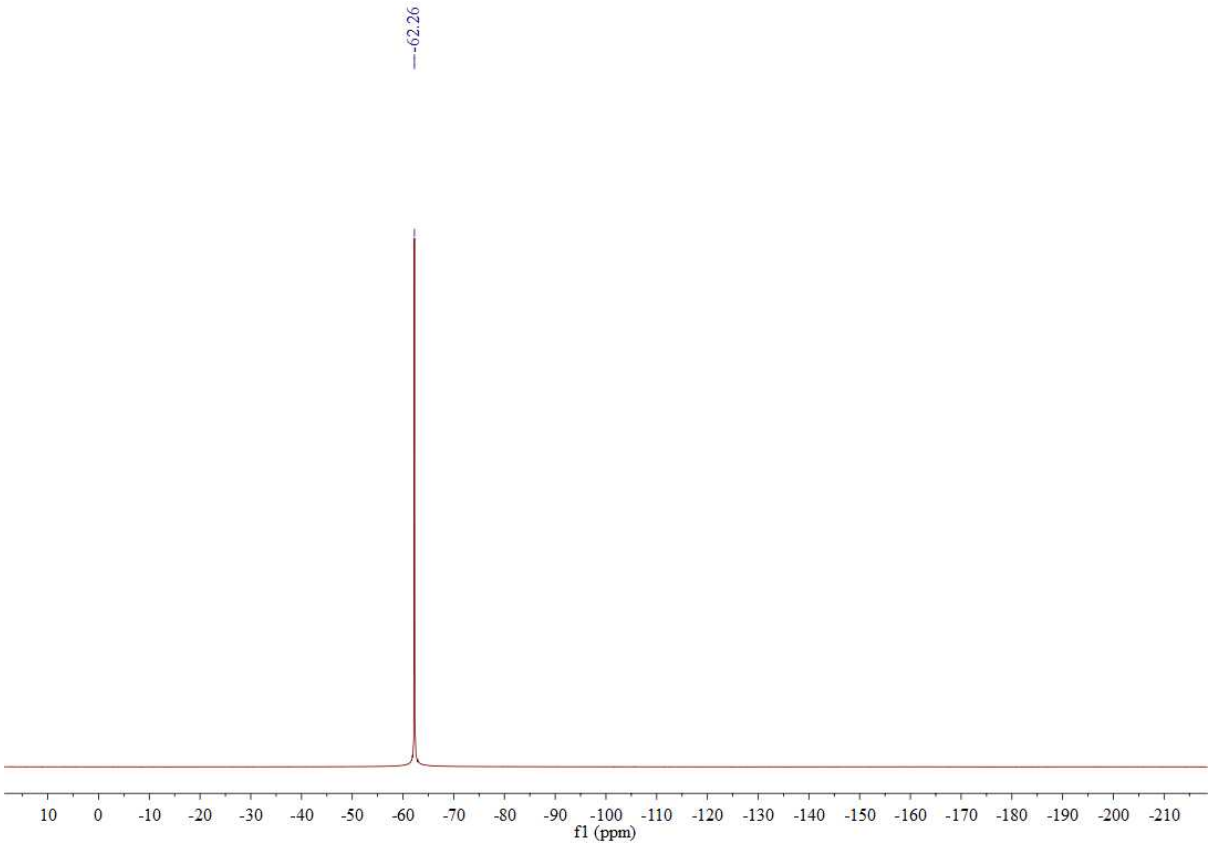

7.24 7.24 7.23 6.84 6.84 6.81 6.81 6.79 6.79 6.78 6.77 6.76 5.50 5.49 5.49 5.48 5.48 3.84 2.72 2.72 2.72 2.70 2.69 2.69 2.67 2.67 2.38 2.37 2.36 2.36 2.35 2.35 2.34 2.33 2.33 2.05 2.04 2.03 2.02 2.02 2.01 1.38 1.37 1.36 1.36 1.35 1.35 1.34 1.34 1.33 1.32 0.97 0.96 0.96 0.95 0.94 0.93 0.92 0.91
1.17 3.05 1.99 3.00 2.01 2.02 2.12 4.38 3.06
fl (ppm)
159.59 143.85 131.15 129.28 129.15 120.91 114.24 111.00 55.11 55.05 36.25 34.37 32.26 31.75 22.18 13.97
fl (ppm)

[1] H NMR (300 MHz) and [13]C NMR (75 MHZ) of **b31**

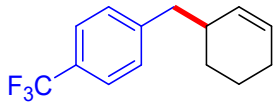


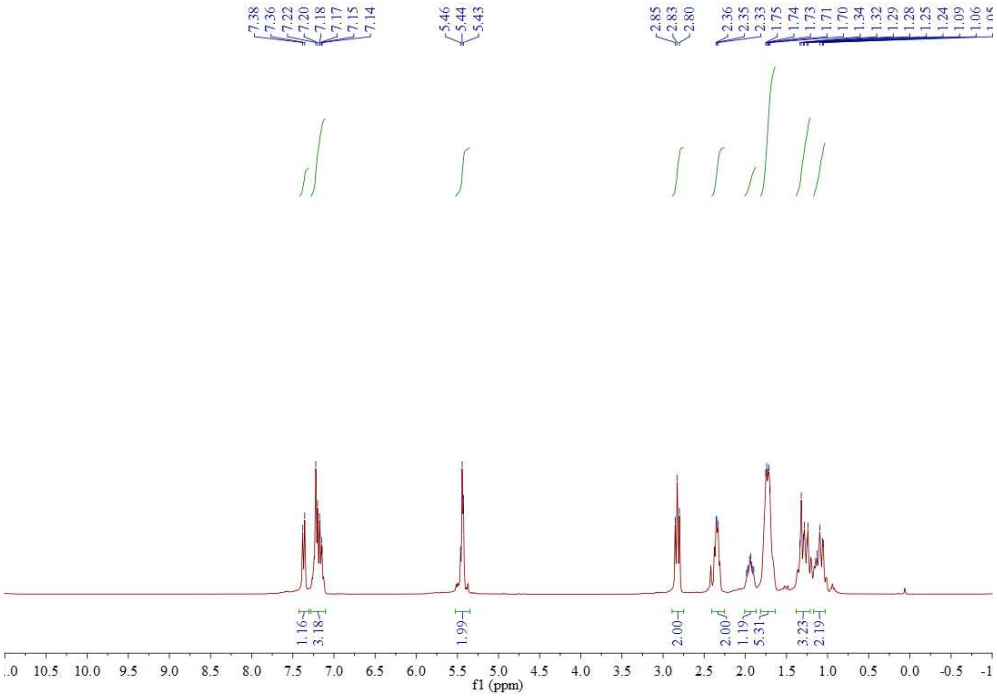


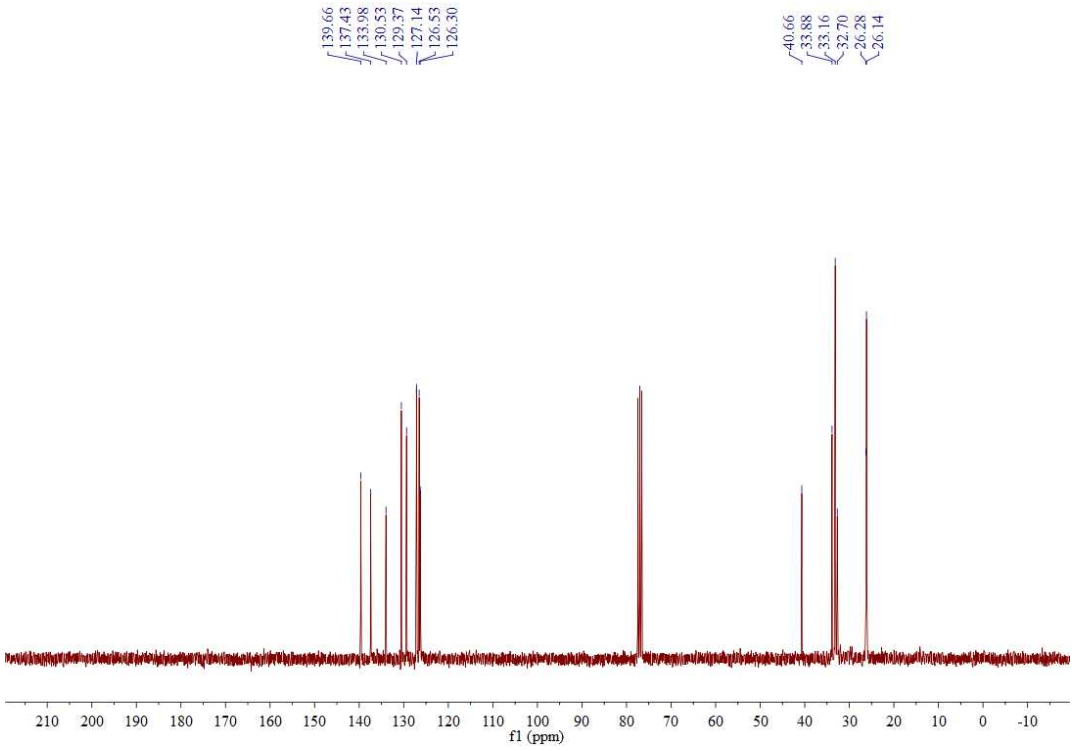

146.23
137.74
136.67
128.79
127.10
125.97
125.09
125.04
40.65
35.99
34.11
33.27
33.13
26.20
26.13
26.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.26
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHZ) of **b32**






139.66
137.43
133.98
130.53
129.37
127.14
126.53
126.30
40.66
33.88
33.16
32.70
26.28
26.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

References

[1] D. Schönbauer, C. Sambiagio, T. Noël, B. M. Schnürch. *J. Org. Chem*. **2020**, *16*, 809–817.

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