Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Dehalogenation of Vicinal Dihalo Compounds by 1,1'-Bis(trimethylsilyl)-1*H*,1'*H*-4,4'-bipyridinylidene for Giving Alkenes and Alkynes in a Salt-free Manner

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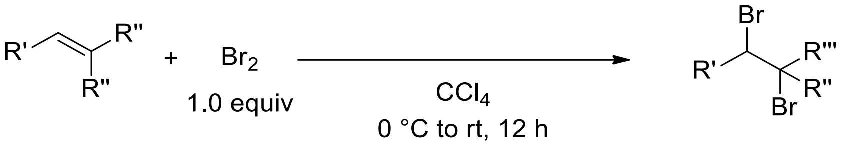
1. General information.

All reactions and manipulations involving air- and moisture-sensitive organosilicon compounds were operated using the standard Schlenk or glovebox techniques under argon atmosphere. Organosilicon reductants **1**, **2a**—**c**, and **3** are prepared according to the modified procedure of the literature by replacing potassium metal by sodium metal except for the synthesis of **2c** that needed the use of potassium.[1] Anhydrous acetonitrile was purchased from Kanto Chemical, and further purified by pass through activated alumina under positive argon pressure as described by Grubbs *et al.*[2] Deuterated solvents ($CDCl_3$, toluene-d_8, THF-d_8, CD_2Cl_2) were distilled over CaH_2, degassed, and stored under Ar-filled glovebox. Other solid chemicals were purchased and used without further purification, whereas liquid compounds are purified through freeze-pump-thaw. ^1H NMR (400 MHz), and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All ^1H NMR chemical shifts were recorded in ppm (δ) and referenced to the residual internal solvent. All $^{13}C\{^1H\}$ NMR chemical shifts were recorded in ppm (δ) relative to carbon resonances in $CDCl_3$ at δ 77.16. Flash column chromatography was performed using silica gel 60 (0.040–0.0663 nm, 230–400 mesh ASTM). For UV-irradiation MAX-303 (Asahi Spectra) was used with compact Xenon light source.

2. General procedure for the preparation of vicinal dibromo substrates[3]

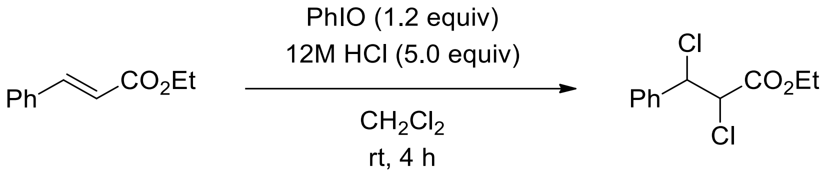
To a solution of olefin (1.0 equiv, 1.00 mmol) in 10 mL of CCl_4, a mixture of Br_2 (1.1 equiv, 1.00 mmol) and CCl_4 (10 mL) was added dropwise at 0 °C temperature for 10 minutes time period while stirring. The reaction was stirred overnight at room temperature. The reaction progress was monitored by thin layer chromatography (TLC) and after completion of the reaction, the excess Br_2 was quenched with $NaHSO_3$ by vigorous stirring. After quenching the reaction mixture, saturated $NaHCO_3$ and brine solution were added and the resulting mixture was extracted with DCM (3 × 15 mL). The solvent was evaporated and the crude mixture was purified by flash column chromatography on silica gel using EtOAc and hexane as eluent.



(1)

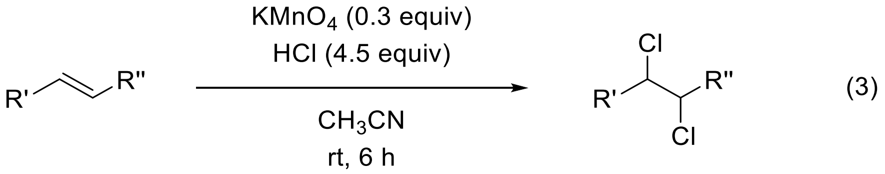
3. General procedure for the preparation of vicinal dichloro substrates[4a,b]

Procedure A:[4a] In a round bottom flask PhIO (1.2 equiv, 1.20 mmol) and conc. HCl (12 M, 5.00 mmol) was mixed in DCM (8 mL) for 15 minutes time period. To the resultant reaction mixture *E*-ethyl cinnamate (1.0 equiv, 1.00 mmol) was added and the reaction mixture was stirred for 4 hours. After completion of the reaction, the mixture was neutralized with saturated solution of $NaHCO_3$ and it was extracted with DCM (3 × 15 mL). The organic layer was evaporated and the crude mixture was purified by column chromatography on silica gel using EtOAc and hexane as eluent. Only *erythro*-isomer was isolate.



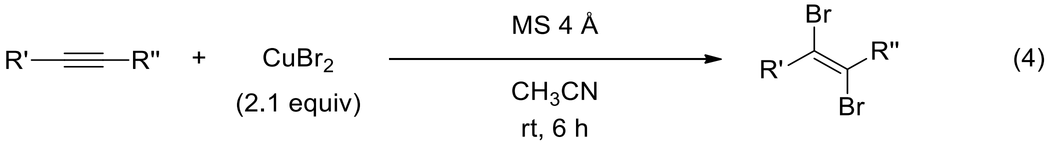
(2)

Procedure B:[4b] In a round bottom flask $KMnO_4$ (0.3 equiv, 1.20 mmol) and CH_3CN (20 mL) were mixed, followed by addition of HCl (4.5 equiv, 37%, 1.50 mL, 18.0 mmol) and the reaction mixture stirred for 10 min. After addition of the proper substrate (styrene or (*E*)-stilbene) (1.0 equiv, 4.00 mmol) into the reaction mixture, stirring was continued for 6 h. After completion, the solvent was removed under vacuum and crude was extracted with $CHCl_3$ (3 × 25 mL). The organic layer was evaporated and the crude mixture was purified by column chromatography on silica gel using EtOAc and hexane as eluent. In the case of, (*E*)-stilbene only *meso*-isomer of 1,2-dibromo-1,2-diphenylethane was isolated.



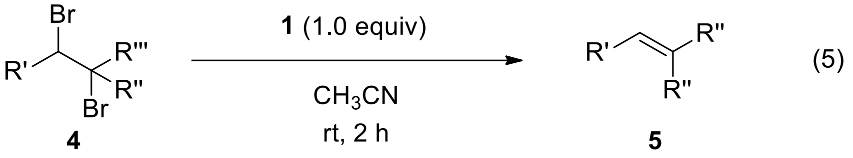
4. General procedure for the preparation of vicinal dibromo alkene substrates[5]

In a Schlenk tube, $CuBr_2$ (2.1 equiv, 6.00 mmol) and molecular sieves 4 Å (120 mg) were taken in acetonitrile (10 mL) and the appropriate alkyne (1.0 equiv, 2.90 mmol) was added into the mixture. The reaction mixture was stirred at room temperature for 6 h. After completion, the residue was concentrated and the residue was purified by column chromatography on silica gel using hexane as eluent.



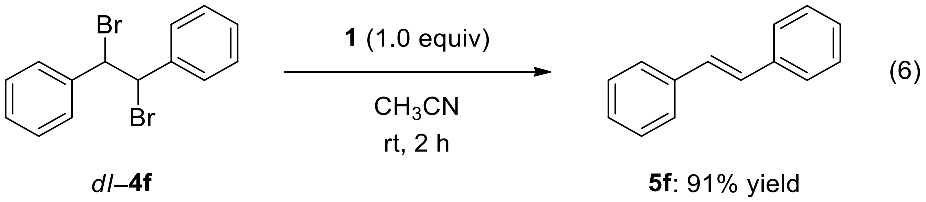
5. General procedure for the organosilicon reductant-mediated debromination reaction of vicinal dibromo alkanes

To a solution of reductant **1** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL) at room temperature, corresponding dibromo compound (1.0 equiv, 0.40 mmol) was added under argon atmosphere. The reaction was stirred at room temperature for 2 h. After completion of the reaction, the solvent was directly evaporated and the crude mixture was purified by flash column chromatography on silica gel using EtOAc and hexane as eluent.



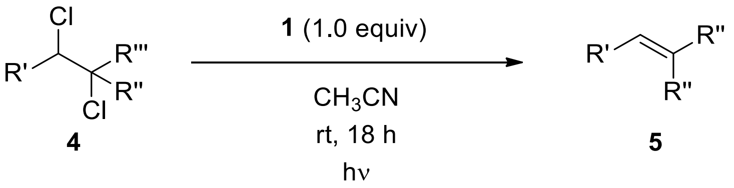
6. Stereoselective formation of (*E*)-alkene from *dl*-1,2-dibromo-1,2-diphenylethane

In a similar method as mentioned above, when *dl*-1,2-dibromo-1,2-diphenylethane was treated with organosilicon reductant **1**, selectively (*E*)-stilbene formed in 91% yield.



7. Procedure for organosilicon reductant-mediated dechlorination reaction

To a solution of reductant **1** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL) at room temperature, vicinal dichloro compounds (1.0 equiv, 0.40 mmol) was added under argon atmosphere. The reaction was stirred at room temperature for 18 h under the UV-irradiation (385 nm). After completion of the reaction, the solvent was evaporated and the crude mixture was purified by flash column chromatography on silica gel using EtOAc and hexane as eluent.



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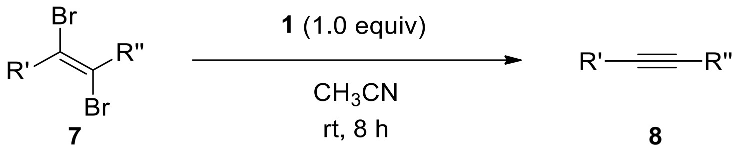
8. General procedure for the organosilicon reductant-mediated debromination reaction of vicinal dibromo alkenes

To a solution of reductant **1** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL) at room temperature, corresponding dibromo alkenes (1.0 equiv, 0.40 mmol) was added under argon atmosphere. The reaction was stirred at room temperature for 8 h. After completion of the reaction, the solvent was directly evaporated and the crude mixture was purified by flash column chromatography on silica gel using hexane as eluent.

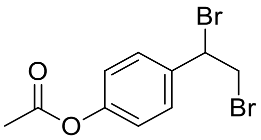


(8)

9. Spectral data of Starting Materials

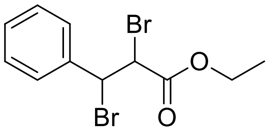
9.1. Vicinal dibromo alkanes

4-(1,2-dibromoethyl)phenyl acetate (4d) [CAS: 360068–17–3]



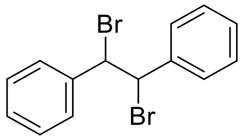
Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); White solid; IR (neat KBr, ν/cm^{-1}) 2918, 2850, 1685, 1655, 1637, 1073, 670, 645; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 7.42 (d, *J* = 8.4 Hz, 2H, Ar), 7.12 (d, *J* = 8.4 Hz, 2H, Ar), 5.14 (dd, *J* = 10.6 Hz, *J* = 5.2 Hz 1H, CHBr), 4.08–3.95 (m, 2H, CH$_2$Br), 2.30 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C) δ 169.2, 151.2, 136.2, 129.0, 122.1, 50.2, 35.1, 21.3; HRMS (FAB$^+$, *m/z*): [M+H]$^+$ calculated for $C_{10}H_{11}Br_2O_2$: 320.9120, found 320.9125.

***meso*-ethyl 2,3-dibromo-3-phenylpropanoate (4e)**[6a] [CAS: 5464–70–0]



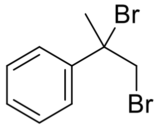
Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); Colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 7.41–7.26 (m, 5H, Ph), 5.34 (d, *J* = 11.6 Hz, 1H, CHBr), 4.83 (d, *J* = 11.6 Hz, 1H, CHBr), 4.37 (q, *J* = 7.2 Hz, 2H, $CO_2C\mathit{H_2}CH_3$), 1.38 (t, *J* = 7.2 Hz, 3H, $OCH_2C\mathit{H_3}$); ^{13}C NMR (100 MHz, CDCl$_3$): 168.0, 137.8, 129.5, 129.0, 128.2, 62.8, 50.9, 47.2, 14.0.

***dl*-1,2-dibromo-1,2-diphenylethane[6b] (4f)** [CAS: 5789–30–0]



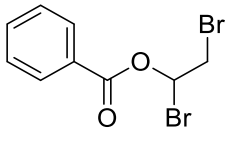
Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/5); White solid; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 7.20–7.16 (m, 10H, Ph), 5.48 (s, 2H, CHBr); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C) δ 138.0, 128.9, 128.7, 128.3, 59.3.

(1,2-dibromopropan-2-yl)benzene (4g)[7] [CAS: 36043–44–4]



Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless liquid; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 7.58 (d, J = 7.6 Hz, 2H, Ph), 7.41–7.31 (m, 3H, Ph), 4.44–4.31 (m, 1H, C*H*HBr), 4.16 (d, J = 10.4 Hz, 1H, CH*H*Br), 2.34 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C) δ 142.4, 128.64, 128.59, 126.7, 63.9, 43.6, 30.1.

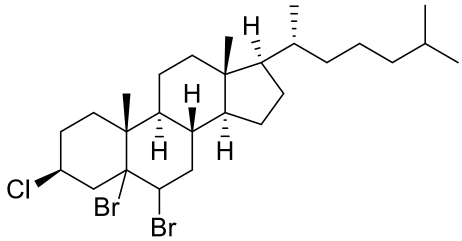
1,2-dibromoethyl benzoate (4h)



Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); Colorless liquid; IR (neat KBr, ν/cm^{-1}) 3066, 3034, 2918, 2849, 1685, 1655, 1637, 1097, 1060, 670, 610; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 8.10 (d, J = 7.6 Hz, 2H, Ph), 7.64 (t, J = 7.6 Hz, 1H, Ph), 7.49 (t, J = 7.6 Hz, 2H, Ph), 6.97 (dd, J = 10.0 Hz, J = 2.6 Hz, 1H, C*H*BrCH$_2$Br), 4.10 (dd, J = 11.0 Hz, J = 10.0 Hz, 1H, CHBrCH*H*Br), 3.98 (dd, J = 11.0 Hz, J = 2.6 Hz, 1H, CHBrC*H*HBr);

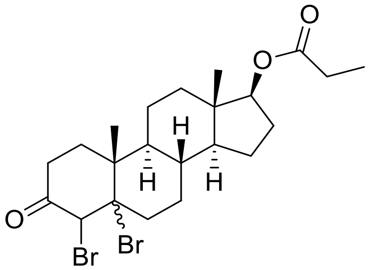
^{13}C NMR (100 MHz, $CDCl_3$): 163.9, 134.3, 130.3, 128.8, 128.3, 71.4, 33.4; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_9H_9Br_2O_2$: 306.8964, found 306.8971.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-5,6-dibromo-3-chloro-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene[3] (4j) [CAS: 5337–45–1]



Purified by crystallization in DCM/hexane; White solid; Only one isomer isolated. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 4.81–4.80 (m, 1H, CHBr), 4.69–4.61 (m, 1H, CHCl), 2.82 (dd, J = 14.4 Hz, J = 11.2 Hz, 1H), 2.69–2.61 (m, 1H), 2.38 (dd, J = 14.4 Hz, J = 4.4 Hz, 1H), 2.13-0.86 (m, 37H), 0.71 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 89.6, 57.5, 56.2, 55.6, 55.3, 47.5, 46.9, 42.8, 41.9, 39.7, 39.6, 38.1, 37.4, 36.3, 35.9, 31.9, 30.9, 28.3, 28.1, 24.2, 23.9, 22.9, 22.7, 21.3, 20.4, 18.8, 12.3.

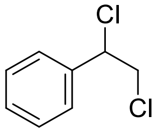
(8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-4,5-dibromo-10,13-dimethyl-3-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl propionate (4k)



Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/10); White solid; IR (neat KBr, ν/cm^{-1}) 2964, 2915, 2847, 1872, 1791, 1718, 1685, 1193, 1091, 800, 604; Two isomer formed in the ratio of 52:48. Combined ^{1}H NMR data of two diastereomers (400 MHz, $CDCl_3$, 30 °C) δ 6.55 (d, J = 2.0 Hz, 1H), 6.01 (s, 1H), 4.97–4.77 (m, 4H), 4.65–4.59 (m, 2H), 2.61 (ddd, J = 12.6 Hz, J = 5.0 Hz, J = 3.1 Hz, 2H), 2.48 (ddd, J = 12.6 Hz, J = 5.0 Hz, J = 3.1 Hz, 1H), 2.36–2.04 (m, 12H), 1.85–1.58 (m, 12H), 1.32 (s, 3H), 1.20–1.02 (m, 14H), 0.90–0.86 (m, 9H), 0.83 (s, 3H); Combined ^{13}C NMR data of two diastereomers (100 MHz, $CDCl_3$, 30 °C) δ 191.5, 190.8, 174.6, 174.5, 166.8, 165.3, 124.9, 124.7, 82.0, 81.8, 53.5, 52.7, 50.6, 50.4, 50.2, 50.0, 49.82, 49.79, 49.6, 48.3, 44.1, 43.9, 42.7, 42.6, 41.8, 40.3, 37.0, 36.4, 36.3, 31.7, 30.2, 27.8, 27.53, 27.51, 23.5, 23.4, 23.0, 22.7, 20.5, 18.6, 14.2, 12.2, 12.1, 9.3; HRMS (FAB^{+}, *m/z*): $[M–H]^{+}$ calculated for $C_{22}H_{31}Br_2O_3$: 501.0640, found 501.0638.

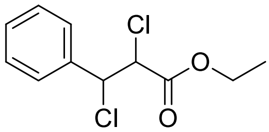
9.2. Vicinal dichloro alkanes

(1,2-dichloroethyl)benzene[4,8] (6a) [CAS: 1074–11–9]



Purified by flash column chromatography (silica gel, hexane); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.42–7.26 (m, 5H, Ph), 5.02 (t, J = 7.2 Hz, 2H, CHCl), 4.03–3.92 (m, 2H, CH_2Cl); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 138.1, 129.3, 128.9, 127.5, 61.9, 48.5.

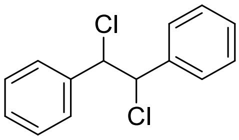
***erythro*-ethyl 2,3-dichloro-3-phenylpropanoate[4,9] (6e)** [CAS: 23482–69–1]



Purified by flash column chromatography (silica gel, hexane); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.42–7.39 (m, 5H, Ph), 5.19 (d, J = 10.8 Hz, 1H, CHCl), 4.61 (d, J =

10.8 Hz, 1H, CHCl), 4.36 (q, J = 7.2 Hz, 2H, CH_2CH_3), 1.37 (t, J = 7.2 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 167.6, 136.6, 129.6, 128.9, 128.2, 62.8, 61.2, 59.2, 14.1.

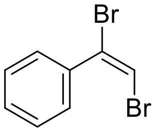
***meso*-1,2-dichloro-1,2-diphenylethane[4,9] (6f)** [CAS: 15951−99−2]



Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/10); White solid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.47−7.29 (m, 10H, Ph), 5.27 (s, 2H, CHCl); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 138.4, 129.1, 128.6, 128.1, 65.8.

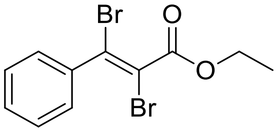
9.3. Vicinal dibromo alkenes

(*E*)-(1,2-dibromovinyl)benzene[5] (7a) [CAS: 6607−46−1]



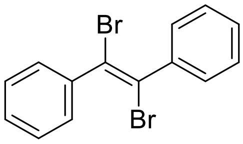
Purified by flash column chromatography (silica gel, hexane); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.55−7.53 (m, 2H, Ph), 7.43−7.41 (m, 3H, Ph), 6.83 (s, 1H, CHBr); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 137.2, 129.5, 129.3, 128.4, 121.5, 103.2.

(*E*)-ethyl 2,3-dibromo-3-phenylacrylate (7b)[10] [CAS: 176246−53−0]



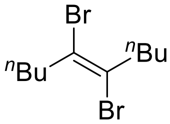
Purified by flash column chromatography (silica gel, hexane); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.46−7.35 (m, 5H, Ph), 4.39 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 1.41 (t, *J* = 7.0 Hz, 1H, $CO_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 164.1, 138.3, 133.1, 129.8, 128.9, 128.7, 128.5, 121.7, 107.8, 63.0, 14.1.

(*E*)-1,2-dibromo-1,2-diphenylethene (7c)[11] [CAS: 20432–10–4]



Purified by flash column chromatography (silica gel, hexane); White Solid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.55–7.36 (m, 6H, Ph), 7.21–7.14 (m, 4H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 140.9, 139.6, 129.9, 129.2, 129.1, 128.53, 128.5, 128.2, 125.8, 118.2.

(*E*)-5,6-dibromodec-5-ene[5] **(7d)**

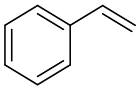


Purified by flash column chromatography (silica gel, hexane); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 2.67 (t, *J* = 7.2 Hz, 4H, CH_2CBr), 1.59–1.52 (m, 4H, CH_2CH_2CBr), 1.38–1.31 (m, 4H, CH_3CH_2), 0.94 (t, *J* = 7.2 Hz, 6H, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 121.8, 40.7, 29.7, 21.8, 14.1.

10. Spectral data of Products

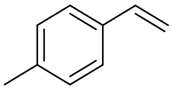
10.1. Spectral data of alkenes

styrene (5a)[3] [CAS: 100–42–5]



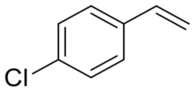
Purified by flash column chromatography (silica gel, pentane); Colorless liquid; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 7.50 (dd, *J* = 7.2 Hz, *J* = 0.8 Hz, 2H, Ph), 7.41 (t, *J* = 7.2 Hz, 2H, Ph), 7.33 (t, *J* = 7.2 Hz, 1H, Ph), 6.81 (d, *J* = 17.6 Hz, *J* = 10.8 Hz, 1H, C*H*CH$_2$), 5.84 (d, *J* = 17.6 Hz, 1H, CHCH*H*), 5.33 (d, *J* = 10.8 Hz, 1H, CHC*H*H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 30 °C) δ 137.7, 137.0, 128.6, 127.9, 126.3, 113.9.

1-methyl-4-vinylbenzene (5b)[3] [CAS: 622–97–9]



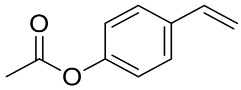
Purified by flash column chromatography (silica gel, pentane); Colorless liquid; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 7.36 (d, *J* = 7.6 Hz, 2H, Ar), 7.20 (d, *J* = 7.6 Hz, 2H, Ar), 6.74 (dd, *J* = 17.6 Hz, *J* = 11.0 Hz 1H, C*H*CH$_2$), 5.75 (d, *J* = 17.6 Hz, 1H, CHC*H*H), 5.23 (d, *J* = 11.0 Hz, 1H, CHC*H*H), 2.39 (s, 3H, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 30 °C) δ 137.7, 136.9, 135.0, 129.3, 126.3, 112.9, 21.3.

1-chloro-4-vinylbenzene (5c)[12] [CAS: 1037–67–2]



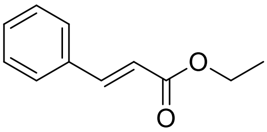
Purified by flash column chromatography (silica gel, pentane); Colorless liquid; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 7.35–7.28 (m, 4H, Ar), 6.67 (d, *J* = 17.6 Hz, *J* = 10.8 Hz, 1H, C*H*CH$_2$), 5.72 (d, J = 17.6 Hz, 1H, CHCHH), 5.27 (d, J = 10.8 Hz, 1H, CHCHH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 136.2, 135.8, 133.6, 128.8, 127.6, 114.6.

4-vinylphenyl acetate (5d)[13] [CAS: 2628–16–2]



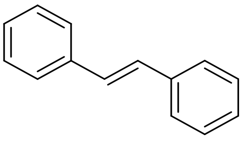
Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); Yellow liquid; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.45 (d, J = 8.4 Hz, 2H, Ar), 7.09 (d, J = 8.4 Hz, 2H, Ar), 6.74 (dd, J = 17.6 Hz, J = 10.8 Hz, 1H, CHCH$_2$), 5.74 (d, J = 17.6 Hz, 1H, CHCHH), 5.28 (d, J = 10.8 Hz, 1H, CHCHH), 2.32 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 169.4, 150.3, 136.0, 135.4, 127.2, 121.7, 114.1, 21.1.

(*E*)-ethyl cinnamate (5e)[3] [CAS: 103–36–6]



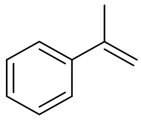
Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); Yellowish liquid; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.69 (d, J = 16.0 Hz, 1H, PhCH), 7.53–7.51 (m, 2H, Ph), 7.39–7.37 (m, 3H, Ph), 6.44 (d, J = 16.0 Hz, 1H, CHCO$_2$Et), 4.27 (q, J = 7.0 Hz, 2H, OCH_2CH$_3$), 1.34 (t, J = 7.0 Hz, 3H, OCH$_2$CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 167.1, 144.7, 134.6, 130.3, 129.0, 128.1, 118.4, 60.6, 14.4.

(*E*)-1,2-diphenylethene (5f)[3] [CAS: 103–30–0]



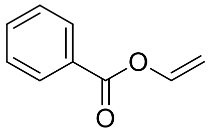
Purified by flash column chromatography (silica gel, hexane); White solid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.56 (d, *J* = 8.0 Hz, 4H, Ph), 7.40 (t, *J* = 7.2 Hz, 4H, Ph), 7.32–7.28 (m, 2H, Ph), 7.15 (s, 2H, CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 137.5, 128.85, 128.83, 127.8, 126.7.

prop-1-en-2-ylbenzene (5g)[3] [CAS: 98–83–9]



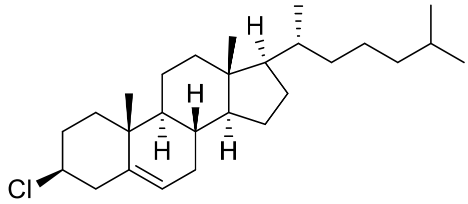
Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/5); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.56–7.54 (m, 2H, Ph), 7.42–7.34 (m, 3H, Ph), 5.46–5.45 (m, 1H, CC*H*H), 5.17–5.16 (m, 1H, CCH*H*), 2.25 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 143.5, 141.4, 128.3, 127.5, 125.6, 112.5, 21.9

vinyl benzoate (5h)[3] [CAS: 769–78–8]



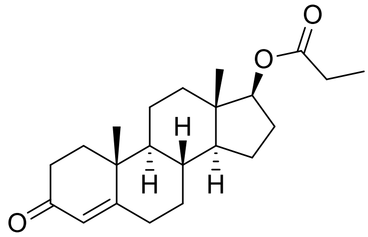
Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.11 (dd, *J* = 8.2 Hz, *J* = 1.0 Hz, 2H, Ph), 7.58 (t, *J* = 7.6 Hz, 1H, Ph), 7.53 (dd, *J* = 14.0 Hz, *J* = 6.2 Hz, 1H, OC*H*CH_2), 7.45 (t, *J* = 7.6 Hz, 2H, Ph), 5.08 (dd, *J* = 14.0 Hz, *J* = 1.6 Hz, 1H, OCHCH*H*), 4.70 (dd, *J* = 6.2 Hz, *J* = 1.6 Hz, 1H, OCHC*H*H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 163.6, 141.5, 133.6, 130.0, 129.0, 128.6, 98.2.

cholesteryl chloride (5j)[3] [CAS: 910–31–6]



Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); White solid; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 5.38–5.36 (m, 1H, CHCl), 3.81–3.72 (m, 1H), 2.60–2.47 (m, 2H), 2.08–1.81 (m, 6H), 1.56-1.33 (m, 10H), 1.16–0.85 (m, 22H), 0.68 (s, 3H, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 30 °C) δ 141.0, 122.6, 60.5, 56.9, 56.3, 50.2, 43.6, 42.5, 39.9, 39.7, 39.3, 36.5, 36.3, 35.9, 33.5, 32.0, 31.9, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.1, 19.4, 18.9, 12.0.

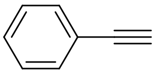
testosteron propionate (5k)[14] [CAS: 57–85–2]



Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); White solid; ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C) δ 5.72 (s, 1H, CHCOCH$_2$), 4.61 (t, *J* = 8.8 Hz, 1H, C*H*OCOCH$_2$CH$_3$), 2.41–1.02 (m, 27H), 0.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 30 °C) δ 199.5, 174.6, 171.0, 124.1, 82.4, 53.9, 50.4, 42.7, 38.8, 36.8, 35.9, 35.6, 34.0, 32.9, 31.6, 27.9, 27.7, 23.6, 20.7, 17.5, 12.2, 9.4.

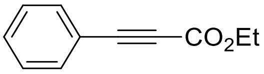
10.2. Spectral data of alkynes

phenylacetylene (8a)[15] [CAS: 536–74–3]



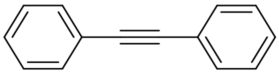
Purified by flash column chromatography (silica gel, hexane); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.57–7.55 (m, 2H, Ph), 7.42–7.35 (m, 3H, Ph), 3.13 (s, 1H, CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 132.2, 128.9, 128.4, 122.3, 83.8 (Ph*C*CH), 77.3 (PhC*C*H).

ethyl phenylpropiolate (8b)[10] [CAS: 2216–94–6]



Purified by flash column chromatography (silica gel, hexane); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.60 (d, J = 7.2 Hz, 2H, Ph), 7.46 (t, J = 7.2 Hz, 1H, Ph), 7.38 (t, J = 7.2 Hz, 2H, Ph), 4.31 (q, J = 7.2 Hz, 2H, CH_2CH_3), 1.37 (t, J = 7.2 Hz, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 154.1, 133.0, 130.7, 128.7, 119.8, 86.1, 80.8, 62.2, 14.2.

1,2-diphenylethyne (8c)[16] [CAS: 501–65–5]



Purified by flash column chromatography (silica gel, hexane); White solid; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.56–7.55 (m, 4H, Ph), 7.37–7.35 (m, 6H, Ph); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 131.7, 128.5, 128.4, 123.4, 89.5.

11. NMR Spectra of starting materials

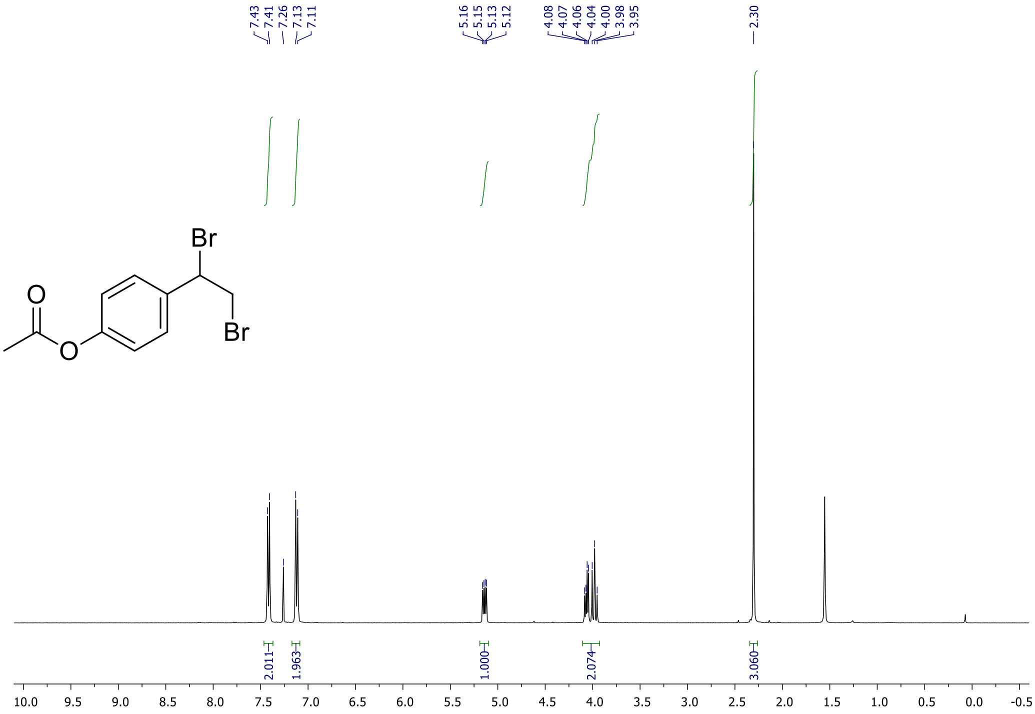


Figure S1. ^{1}H NMR Spectrum of **4d**.

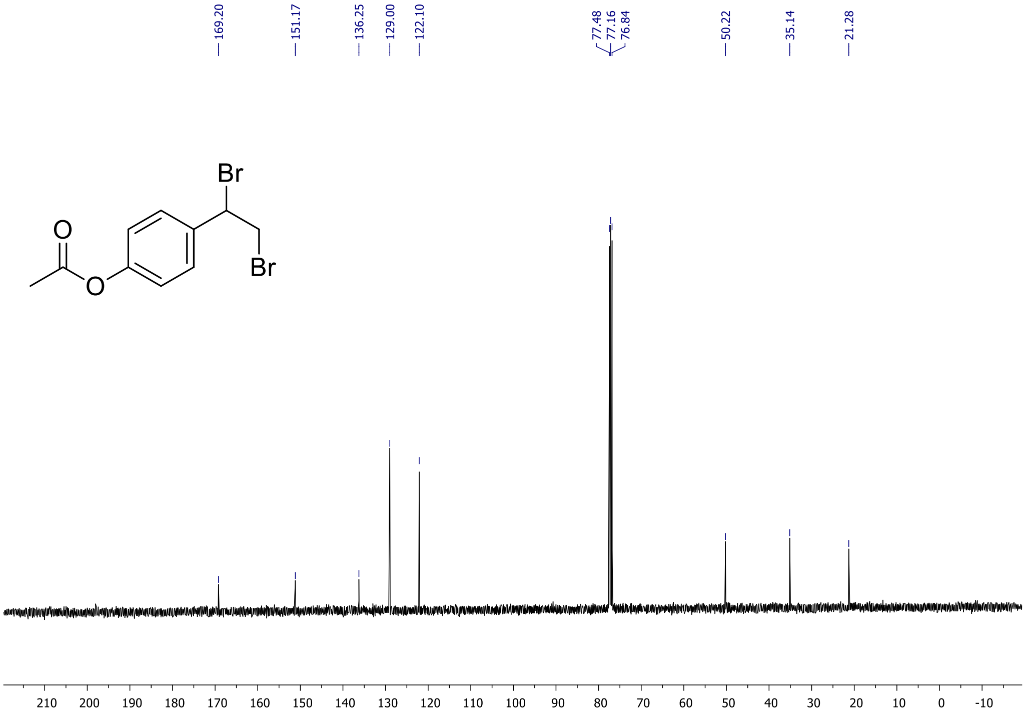


Figure S2. ^{13}C NMR Spectrum of **4d**.

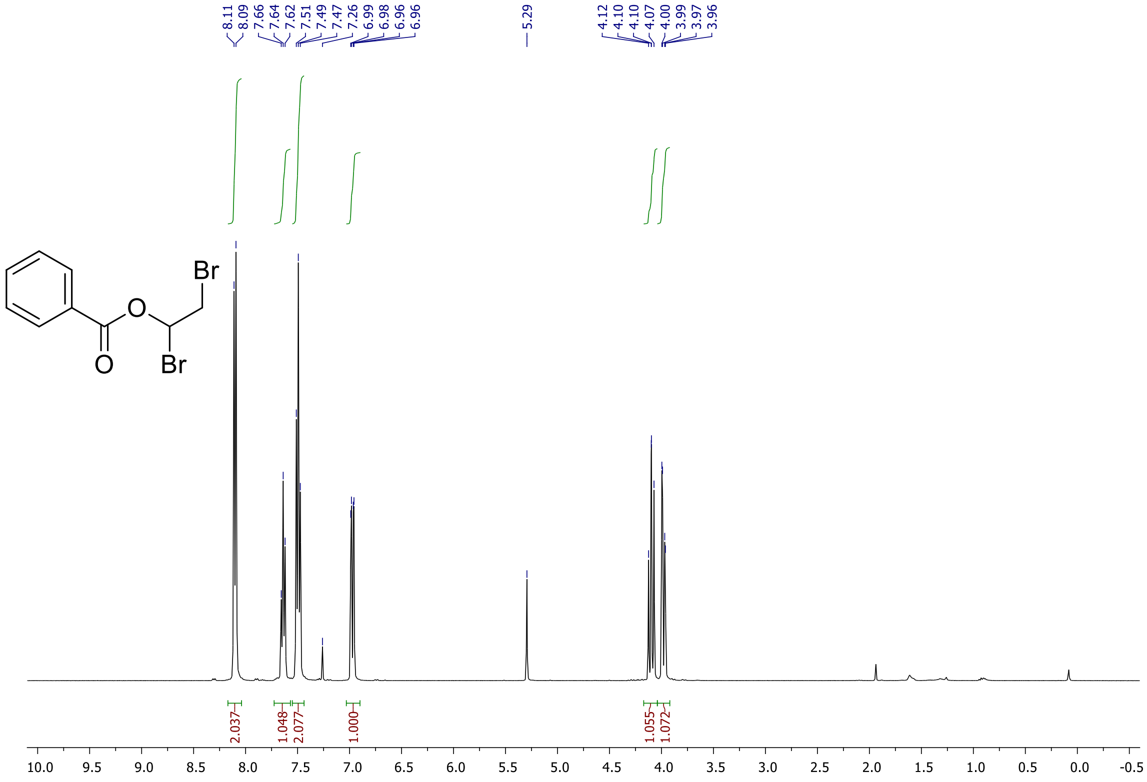


Figure S3. ^{1}H NMR Spectrum of **4h**.

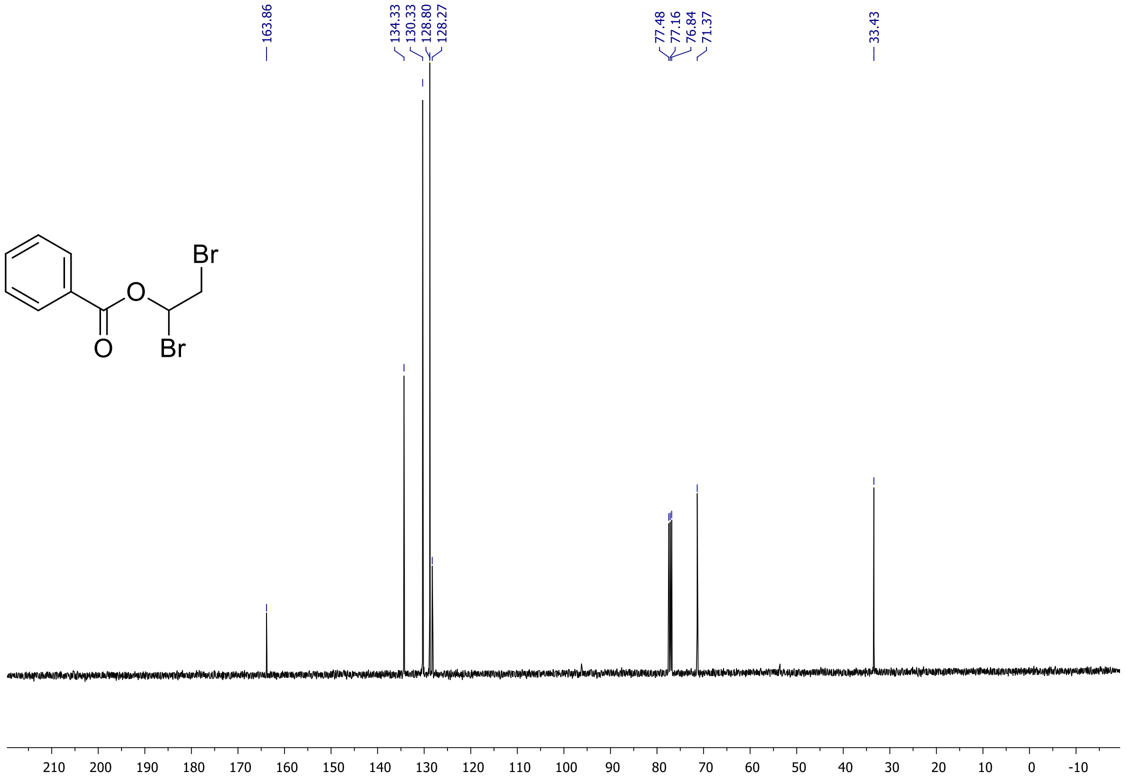


Figure S4. ^{13}C NMR Spectrum of **4h**.

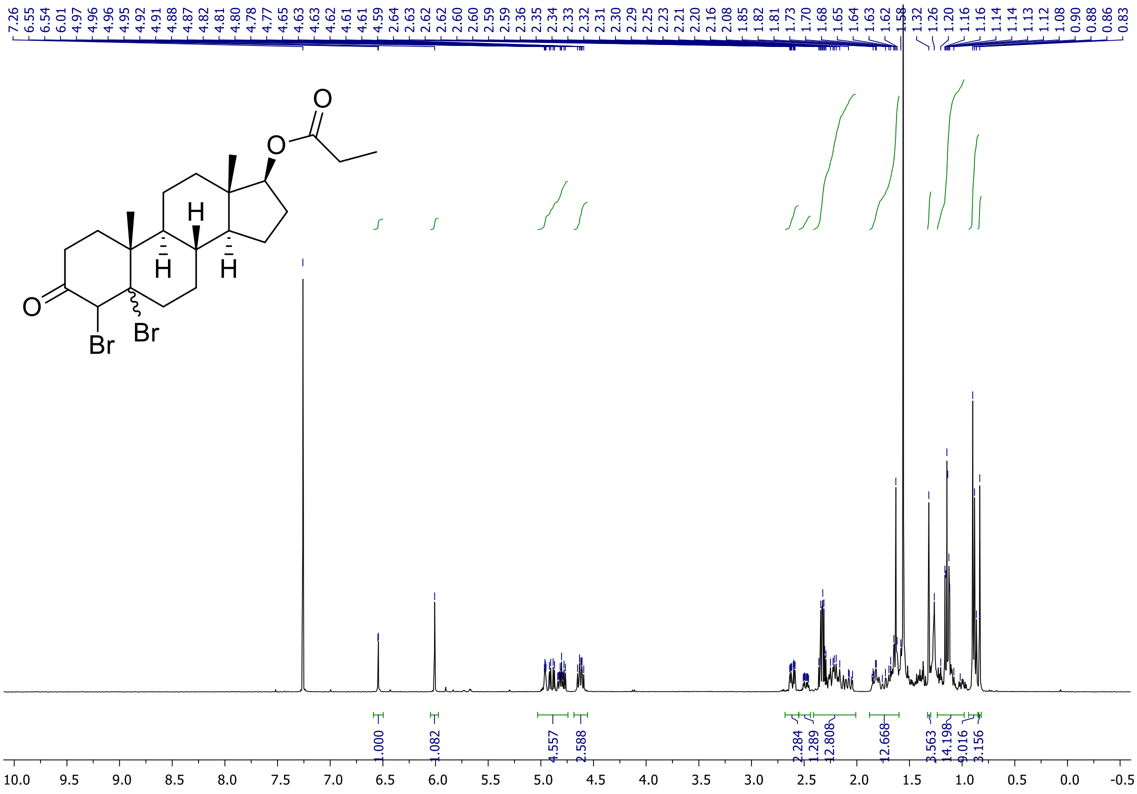


Figure S5. ^{1}H NMR Spectrum of **4k**.

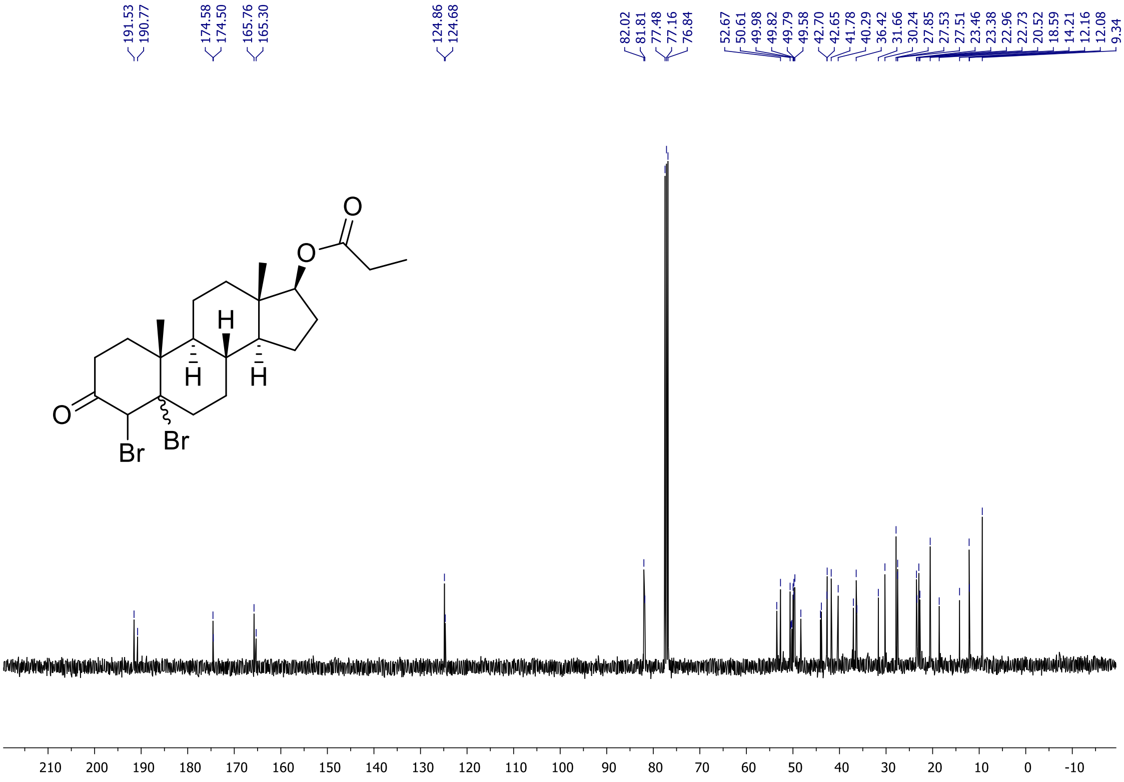


Figure S6. ^{13}C NMR Spectrum of **4k**.

12. NMR Spectra of Products

12.1. NMR Spectra of alkenes

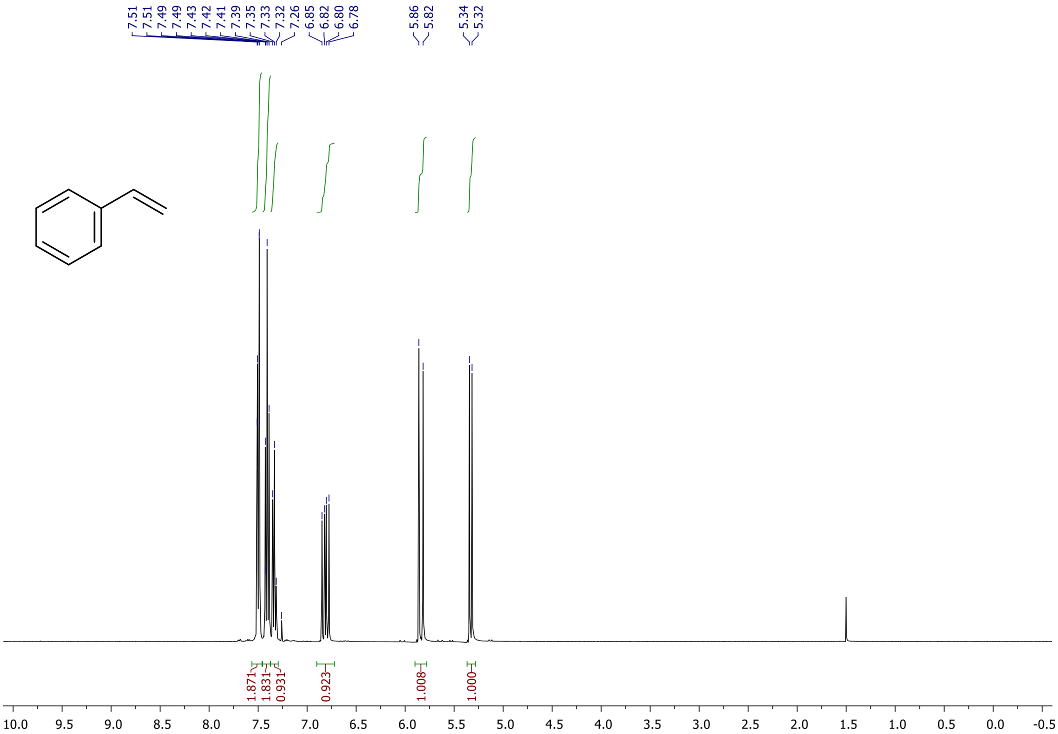


Figure S7. ^{1}H NMR Spectrum of **5a**.

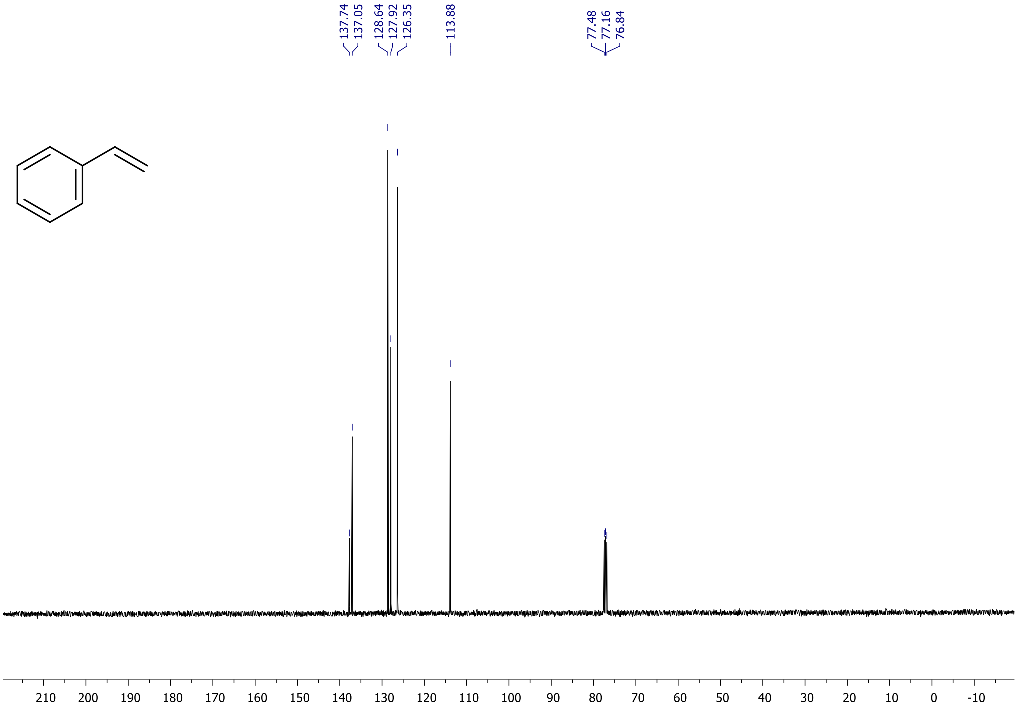


Figure S8. ^{13}C NMR Spectrum of **5a**.

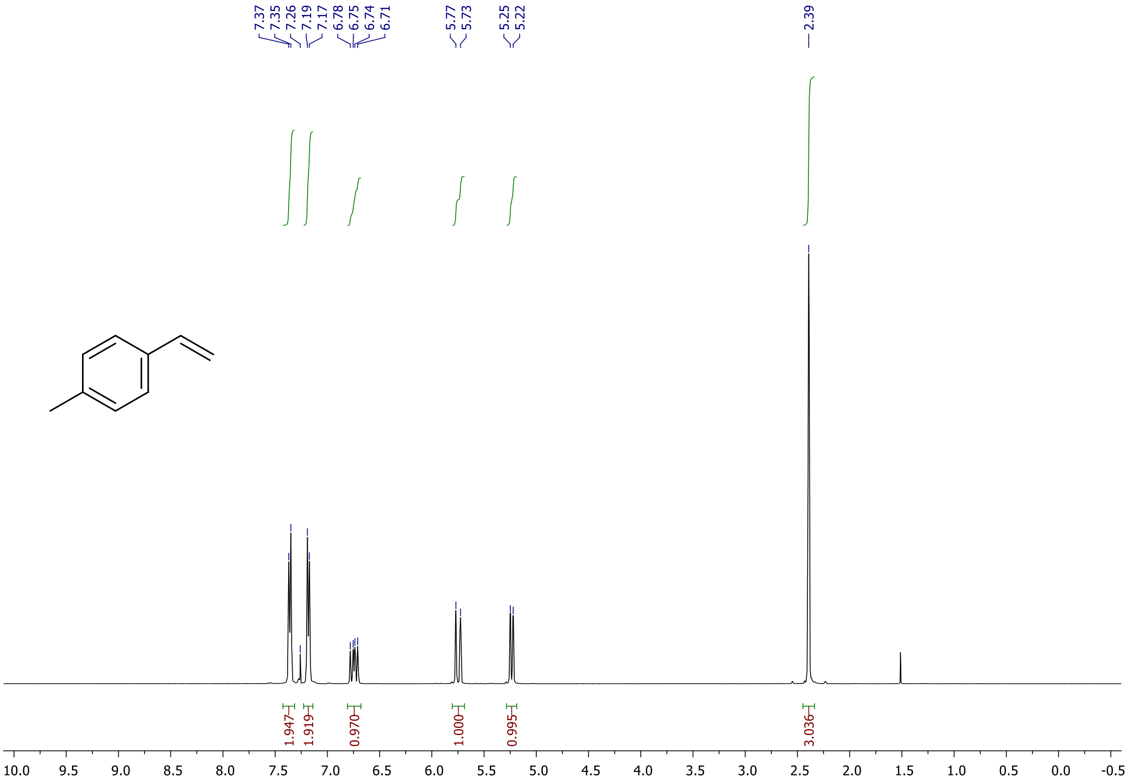


Figure S9. ^{1}H NMR Spectrum of **5b**.

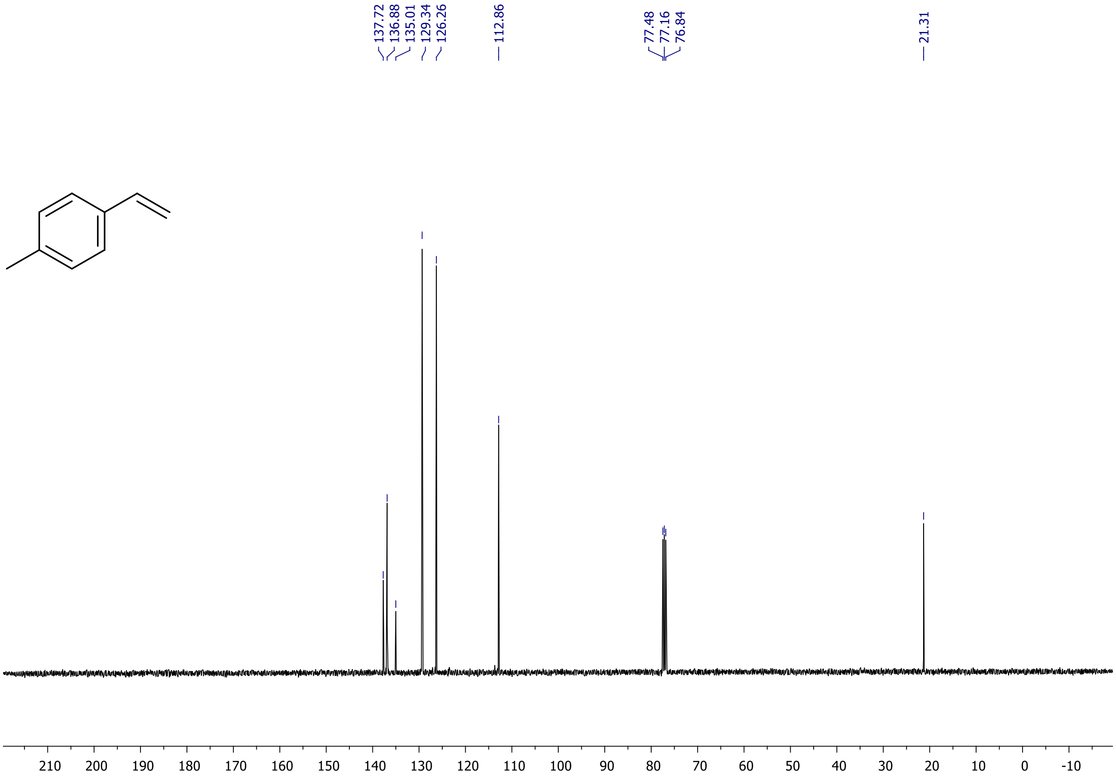


Figure S10. ^{13}C NMR Spectrum of **5b**.

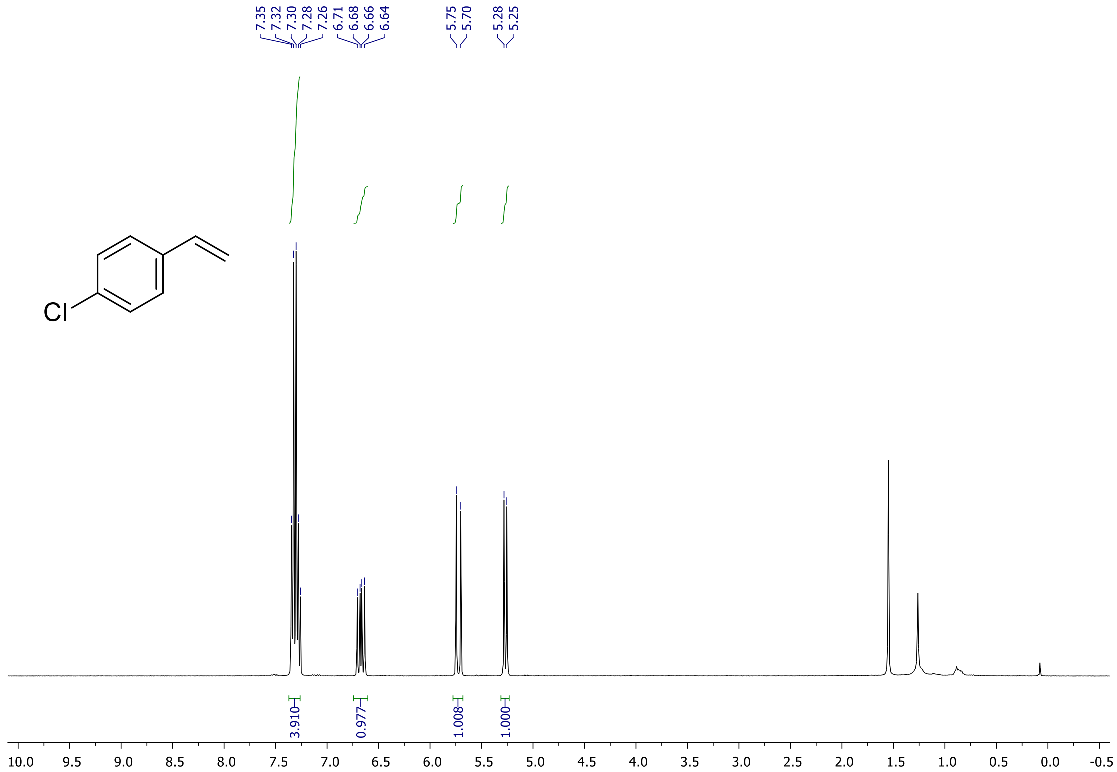


Figure S11. ^{1}H NMR Spectrum of **5c**.

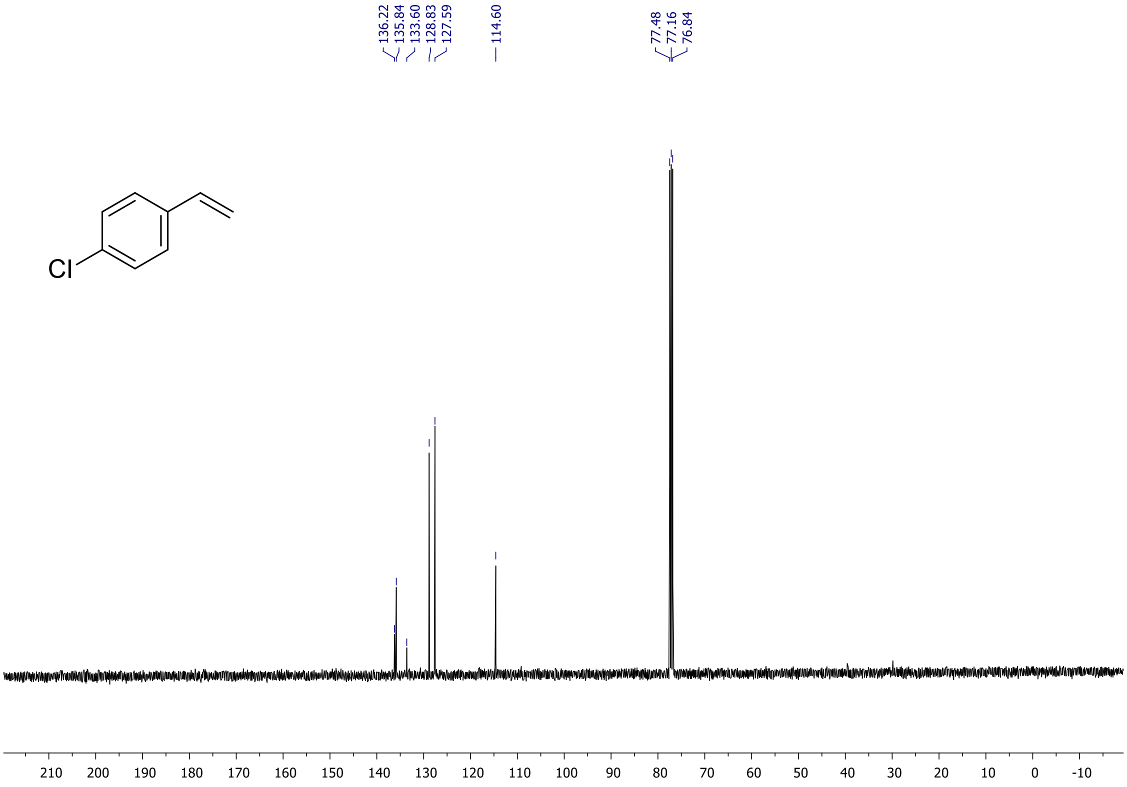


Figure S12. ^{13}C NMR Spectrum of **5c**.

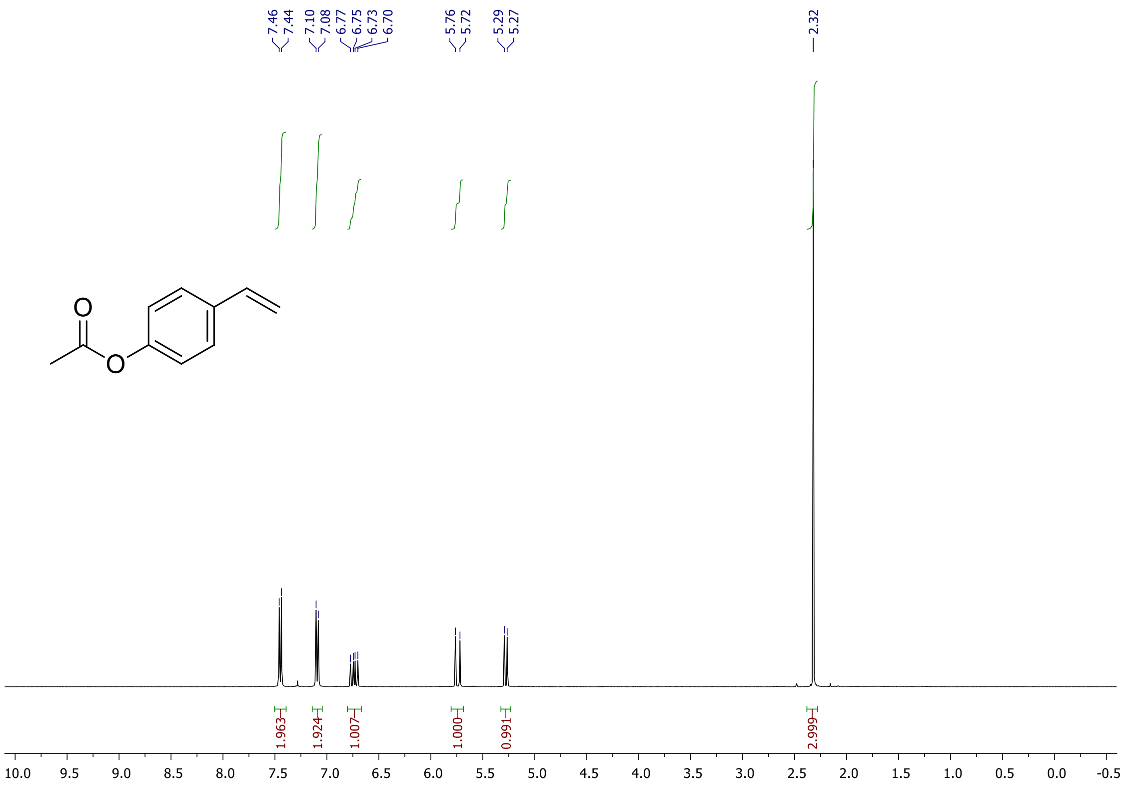


Figure S13. ^{1}H NMR Spectrum of **5d**.

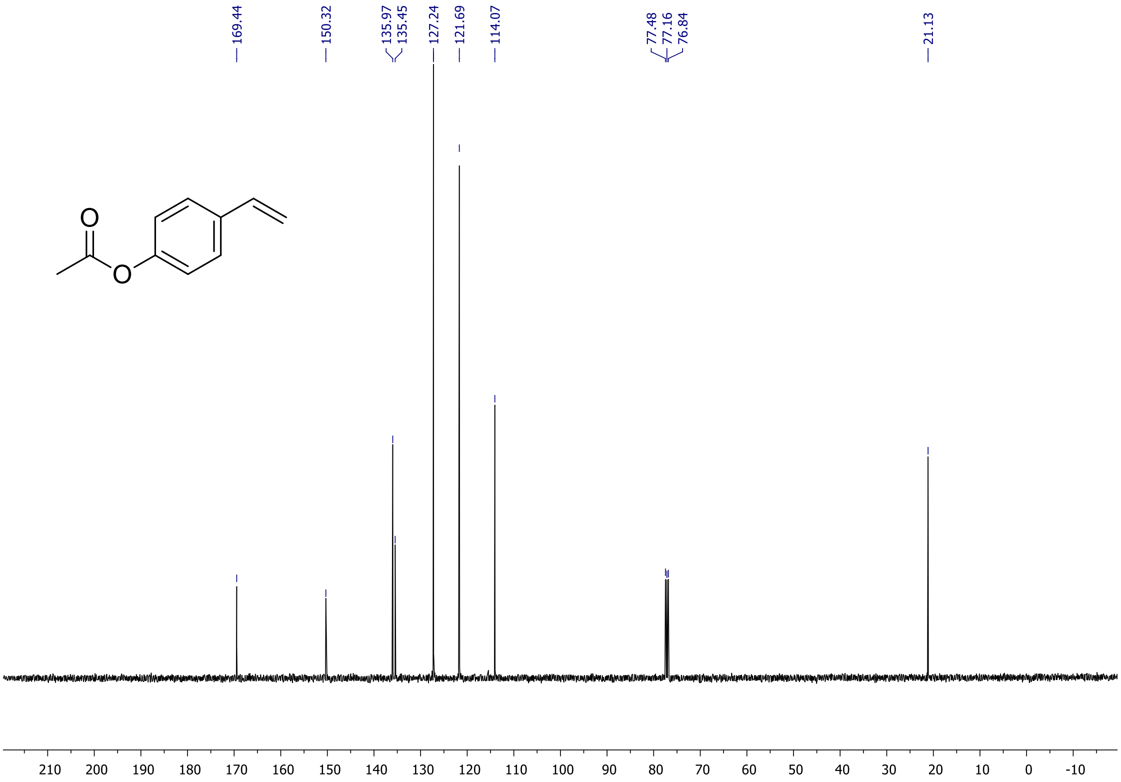


Figure S14. ^{13}C NMR Spectrum of **5d**.

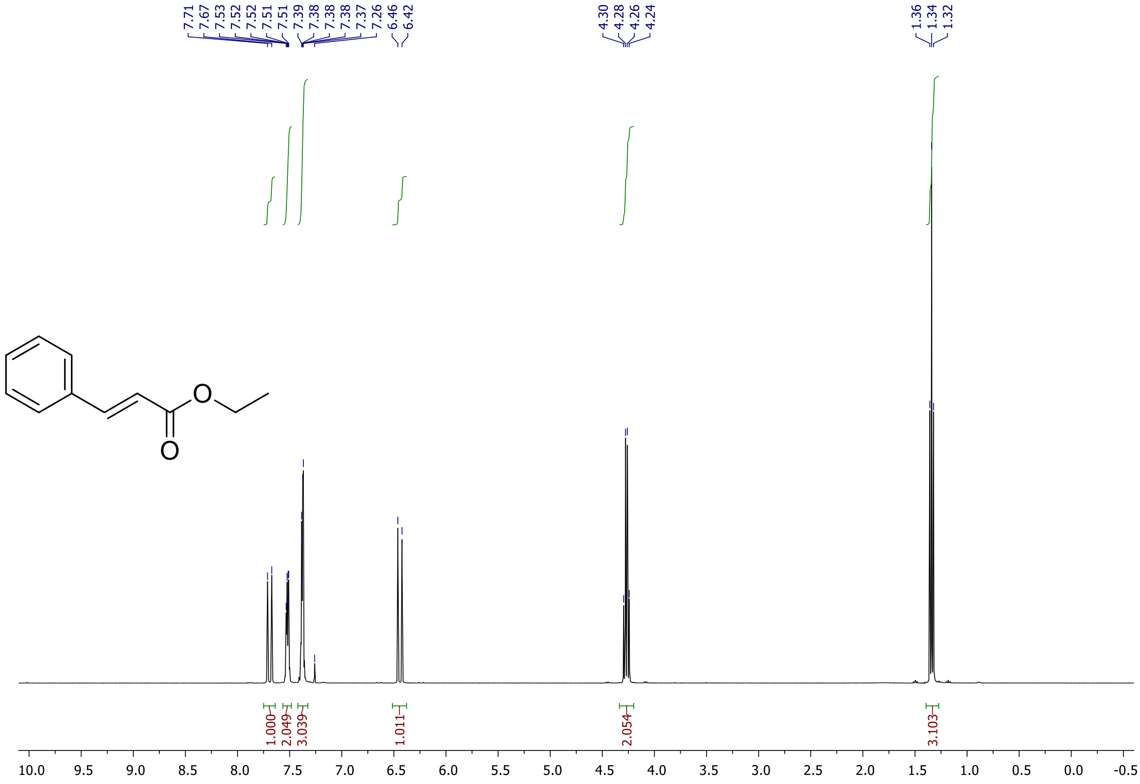


Figure S15. ^{1}H NMR Spectrum of **5e**.

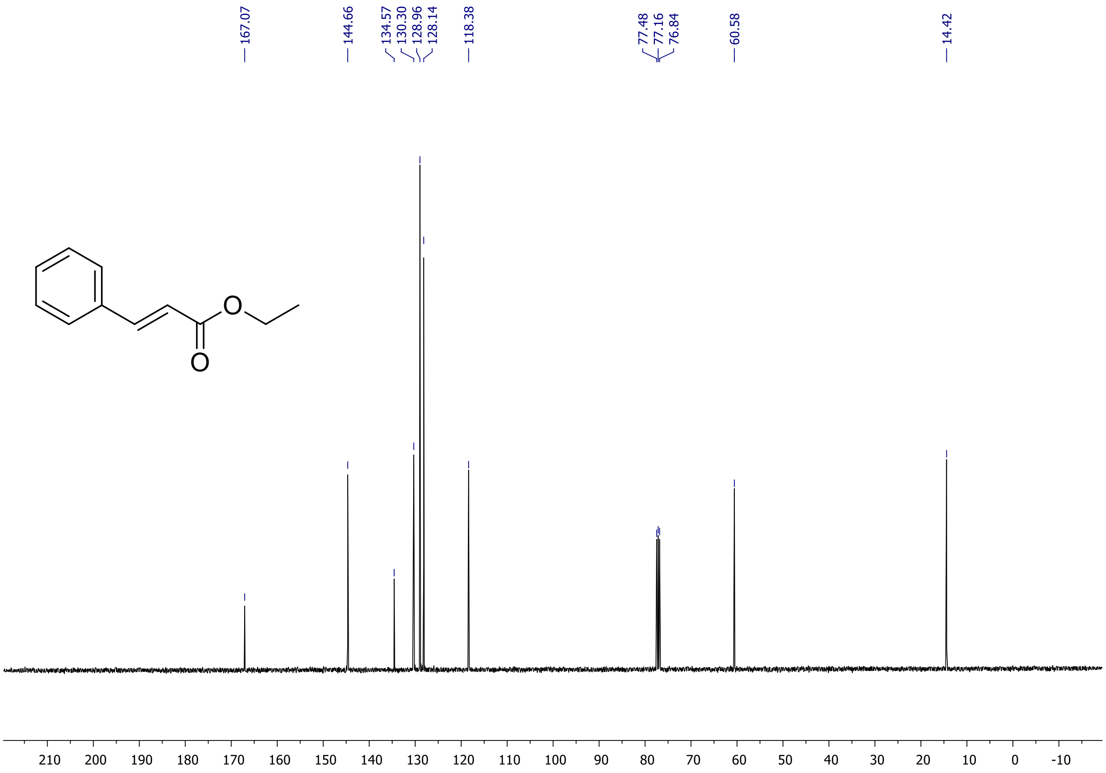


Figure S16. ^{13}C NMR Spectrum of **5e**.

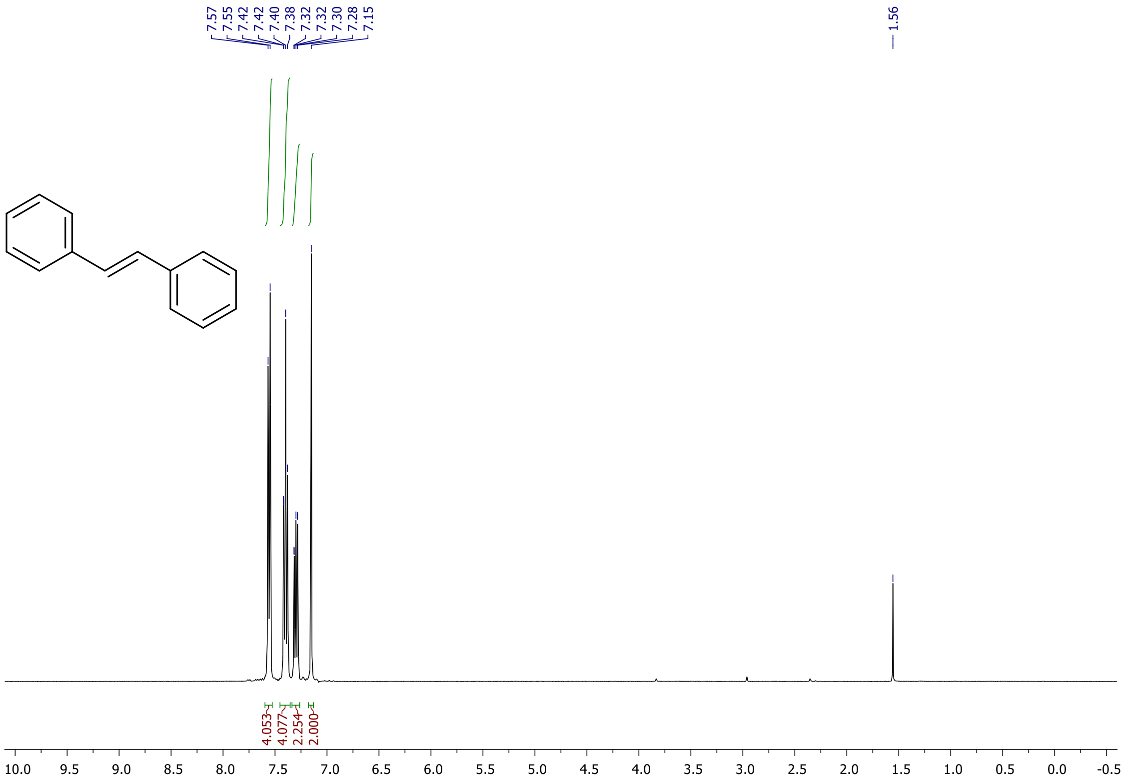


Figure S17. ^{1}H NMR Spectrum of **5f**.

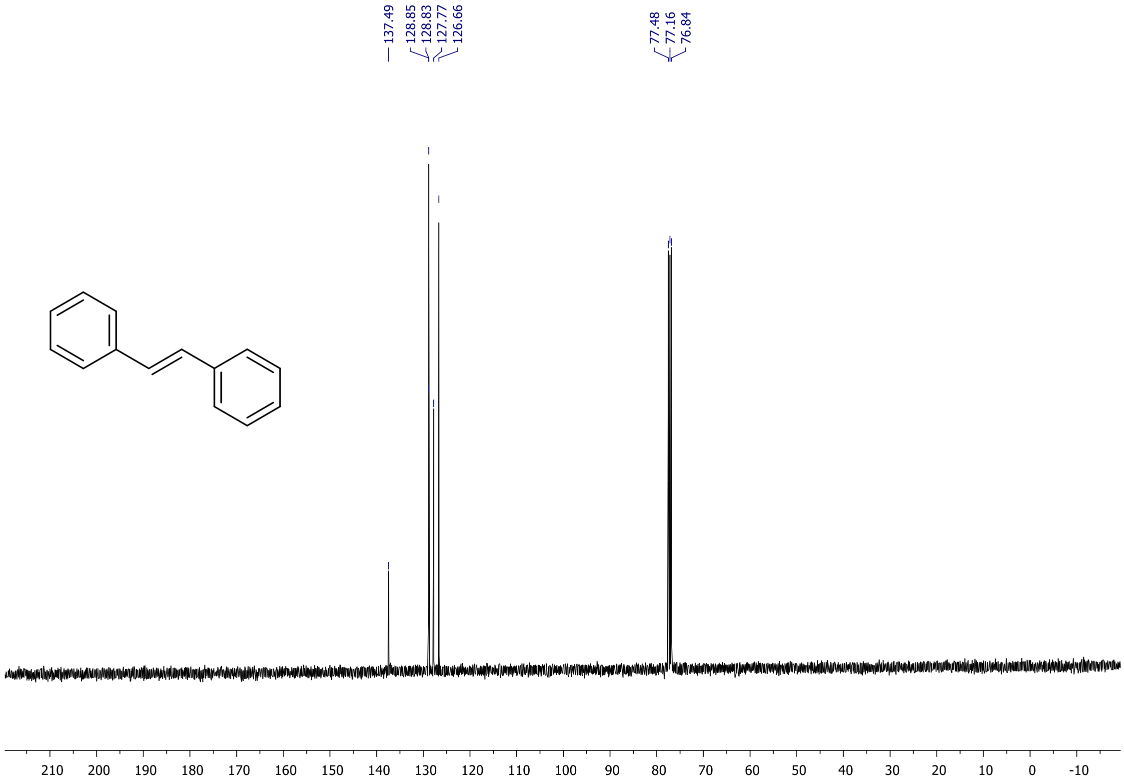


Figure S18. ^{13}C NMR Spectrum of **5f**.

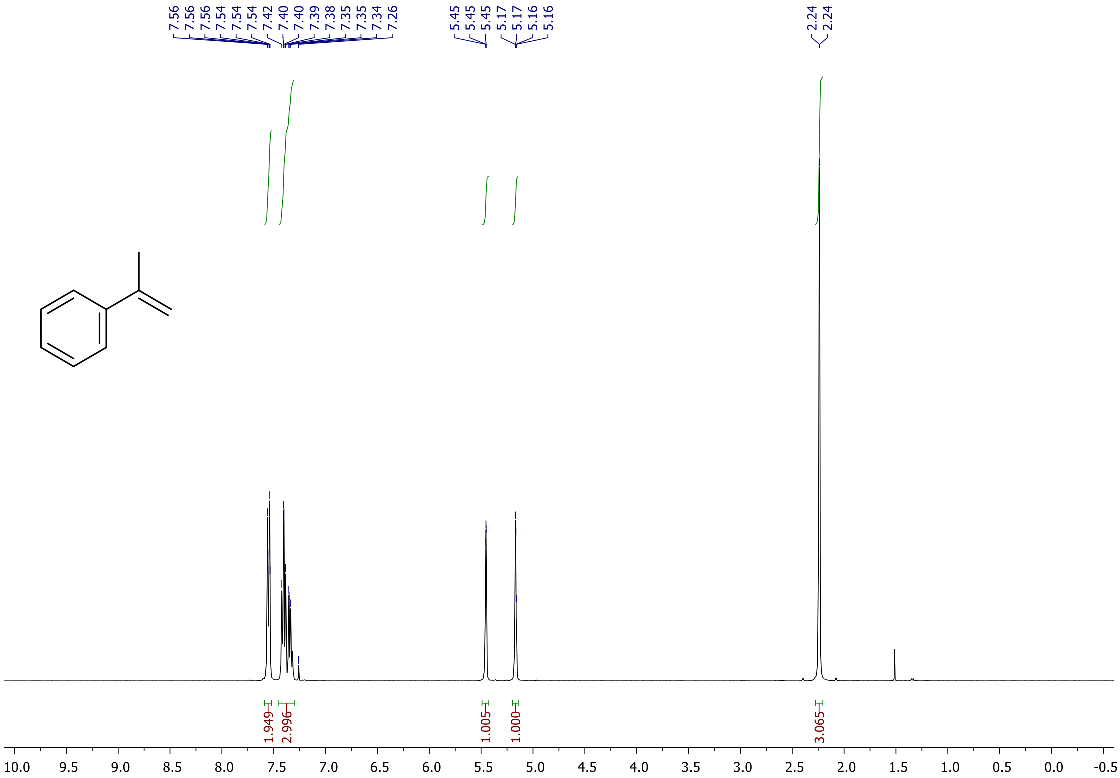


Figure S19. ^{1}H NMR Spectrum of **5g**.

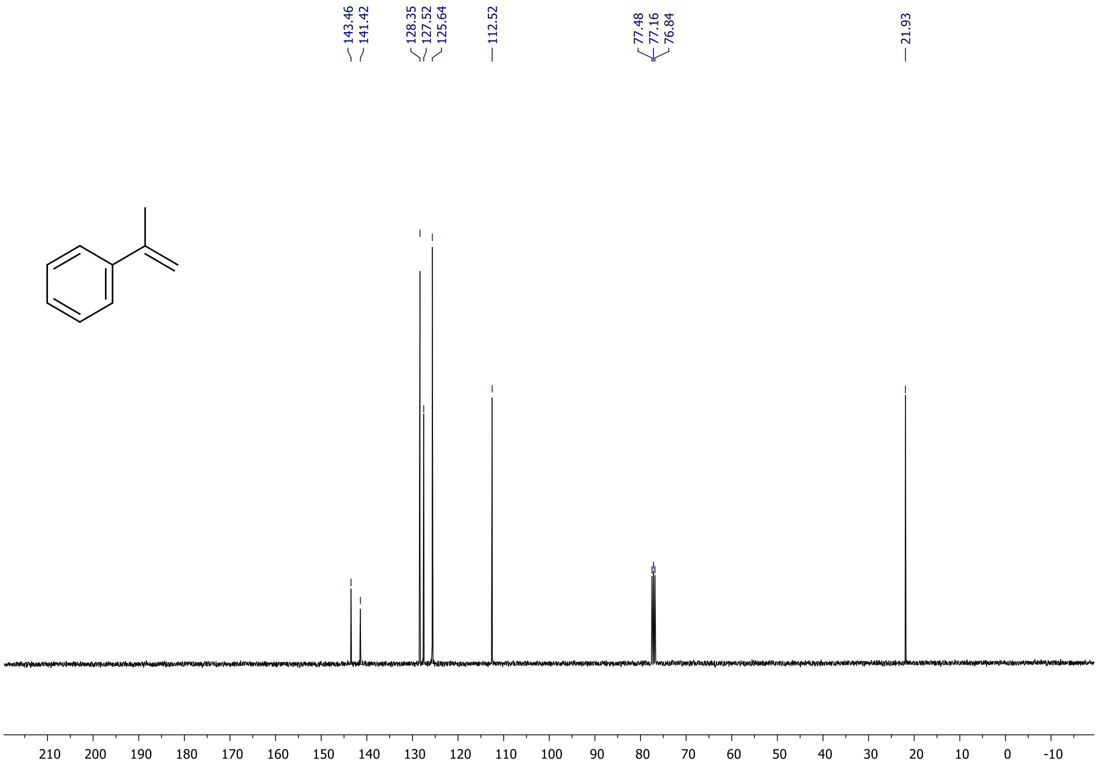


Figure S20. ^{13}C NMR Spectrum of **5g**.

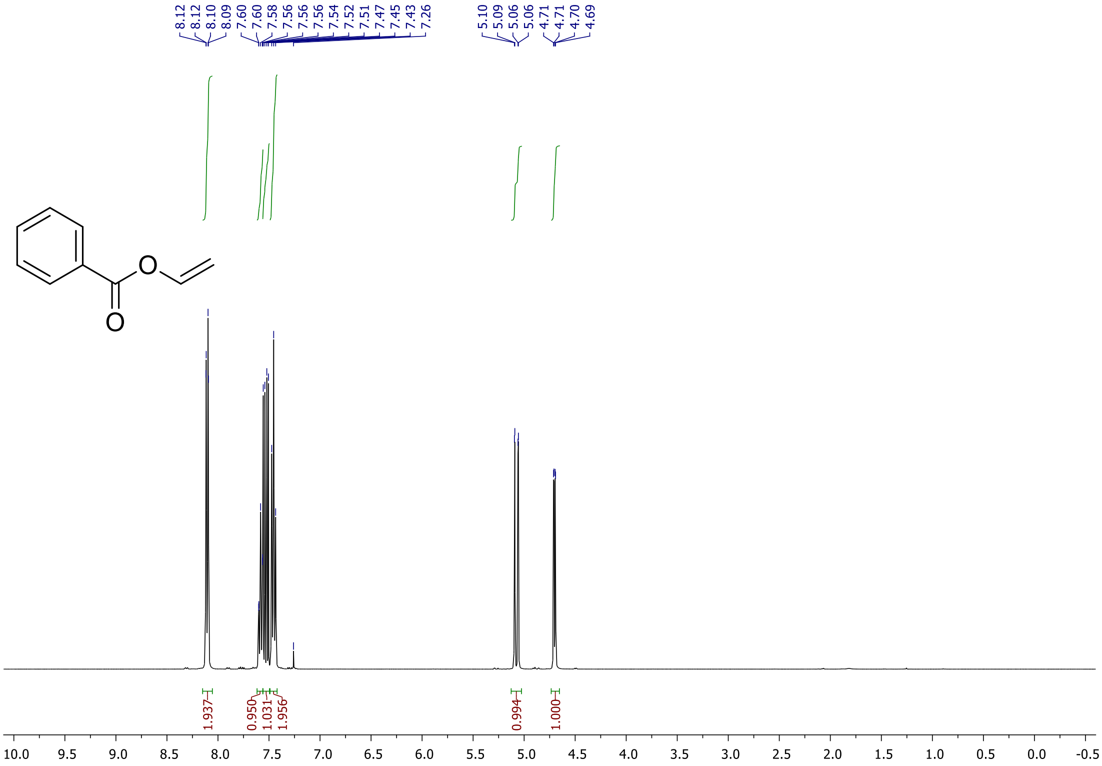


Figure S21. ^{1}H NMR Spectrum of **5h**.

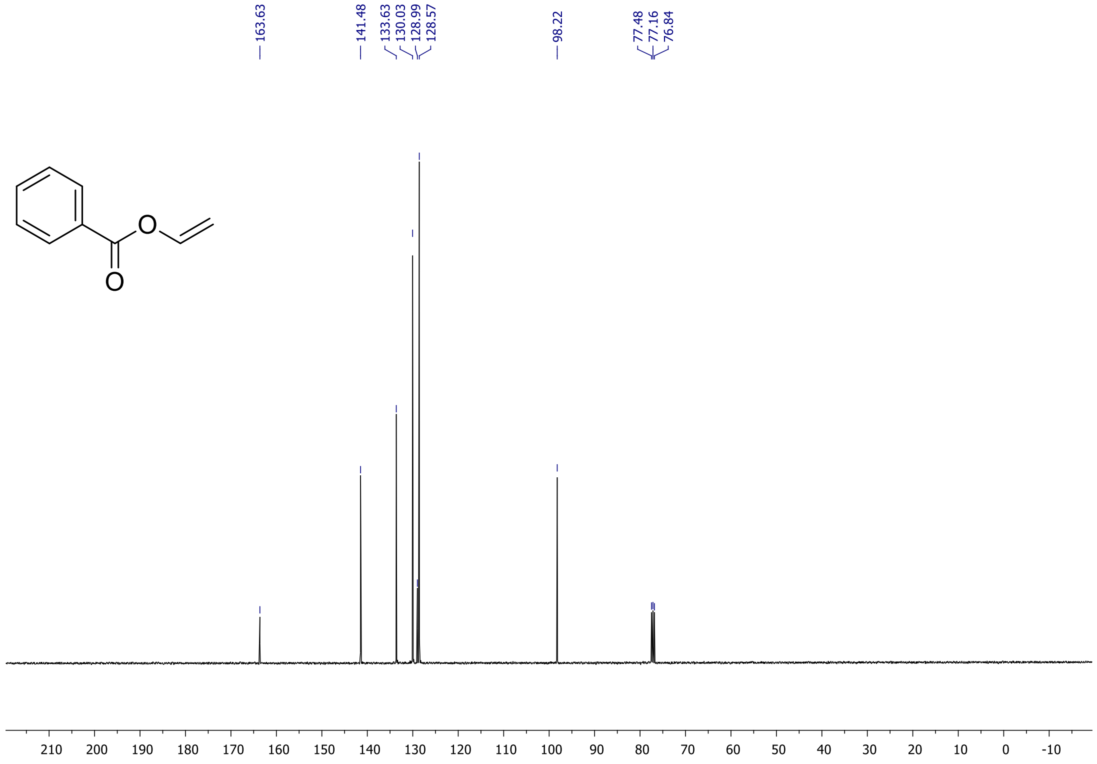
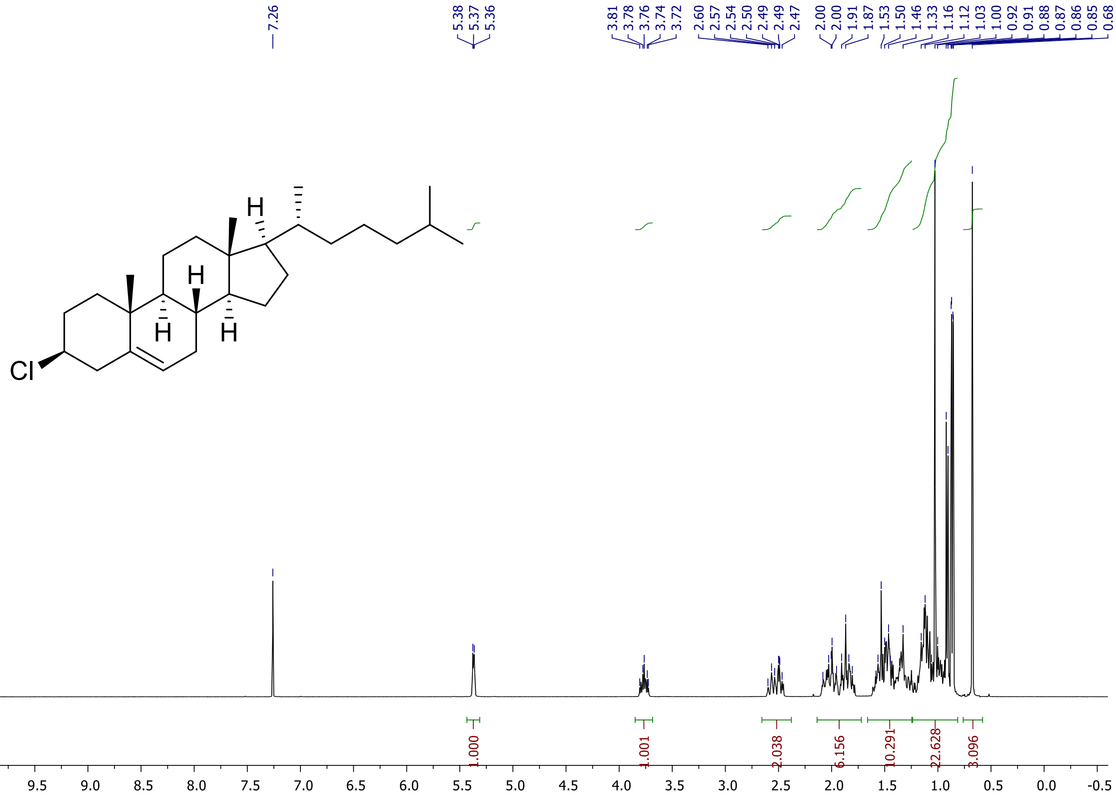


Figure S22. ^{13}C NMR Spectrum of **5h**.



FigureS23. ^{1}H NMR Spectrum of **5j**.

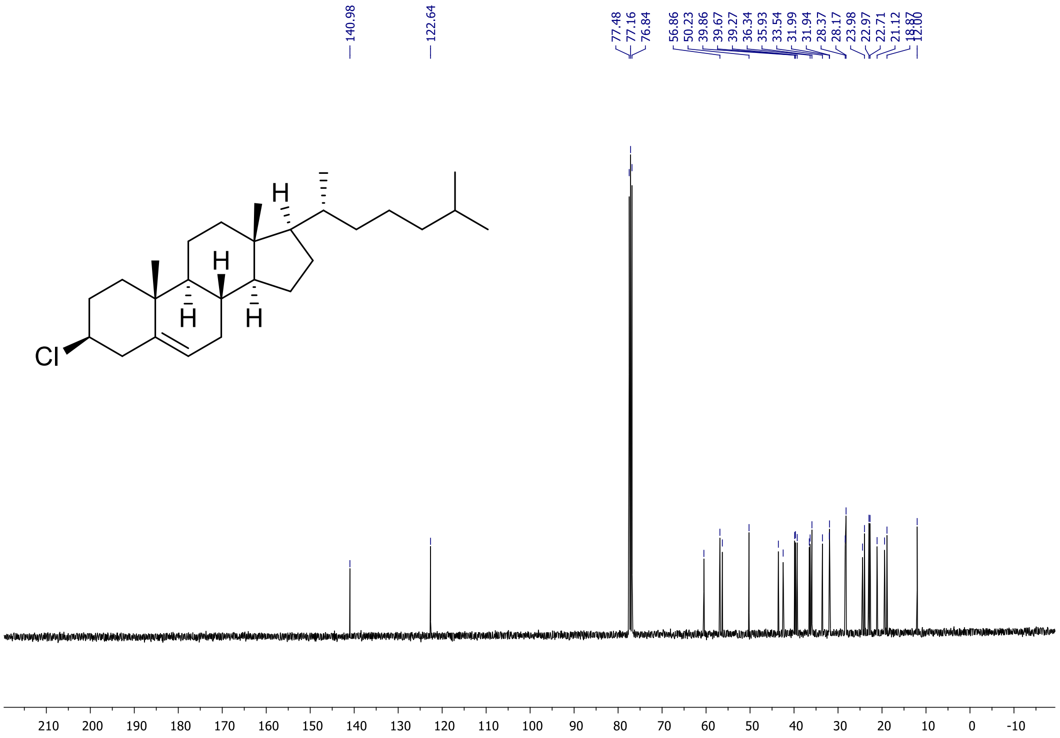


Figure S24. ^{13}C NMR Spectrum of **5j**.

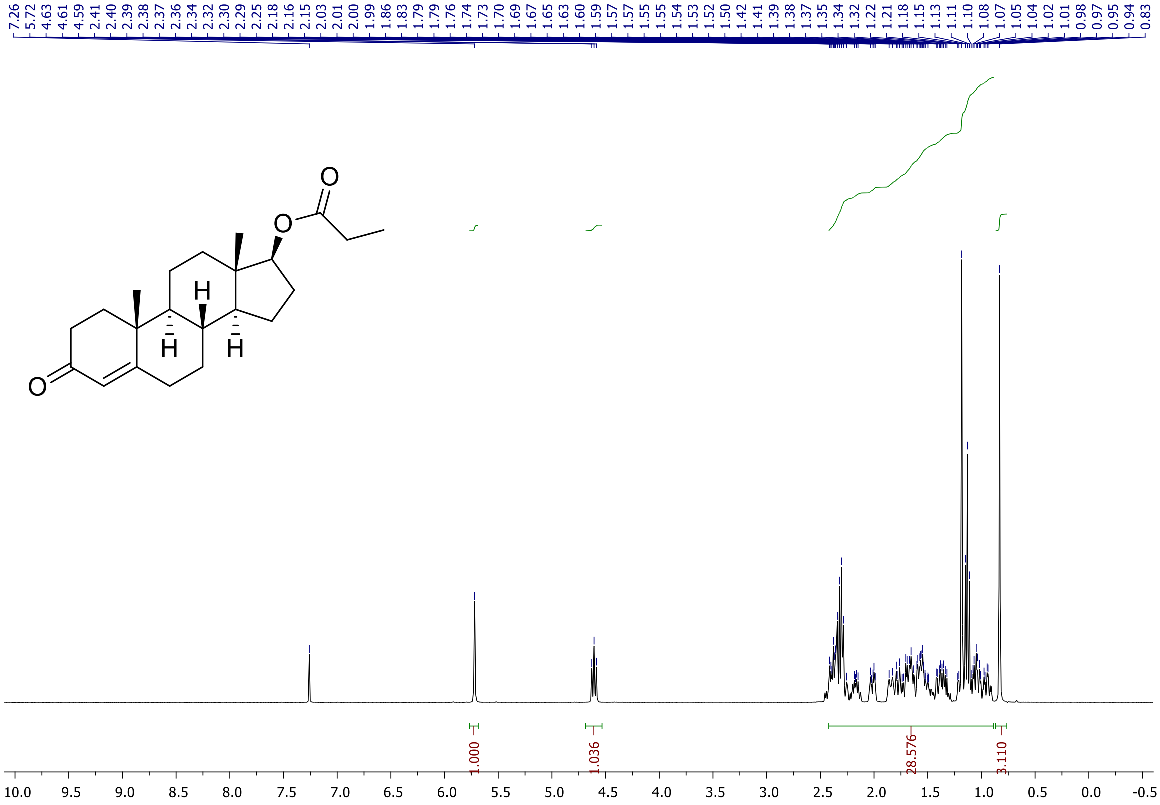


Figure S25. ^{1}H NMR Spectrum of **5k**.

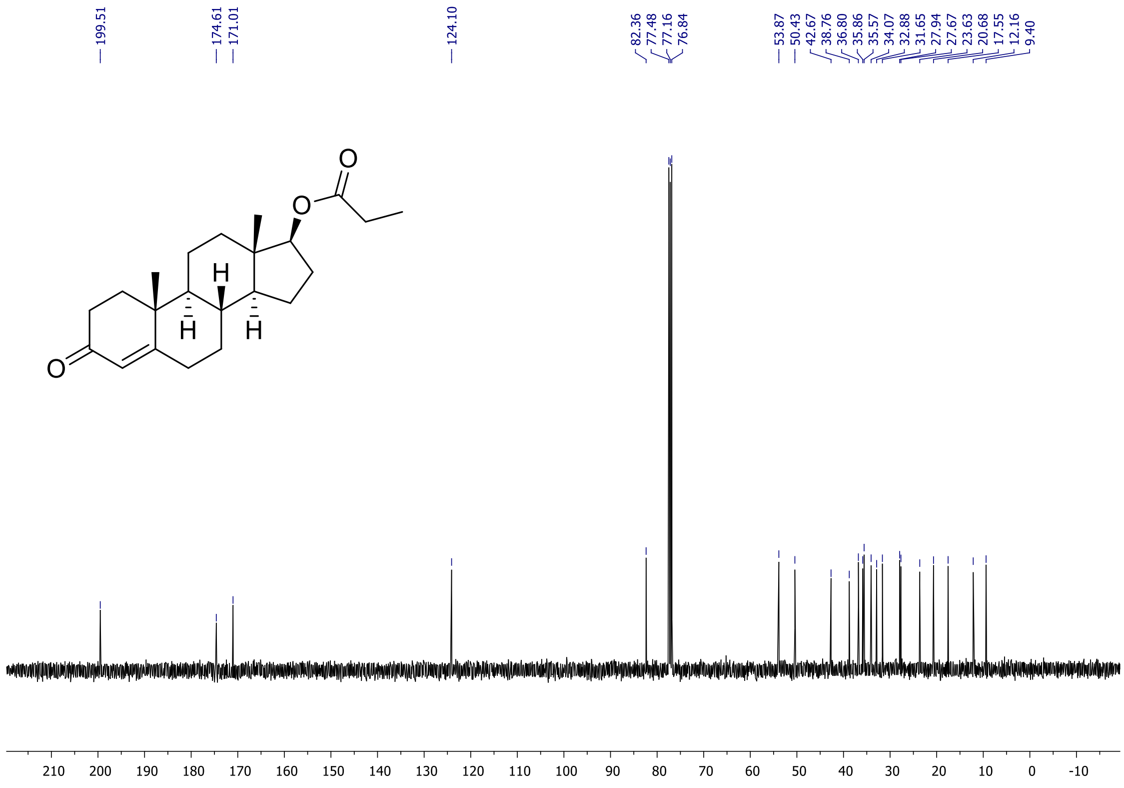


Figure S26. ^{13}C NMR Spectrum of **5k**.

12.2. NMR Spectra of alkynes

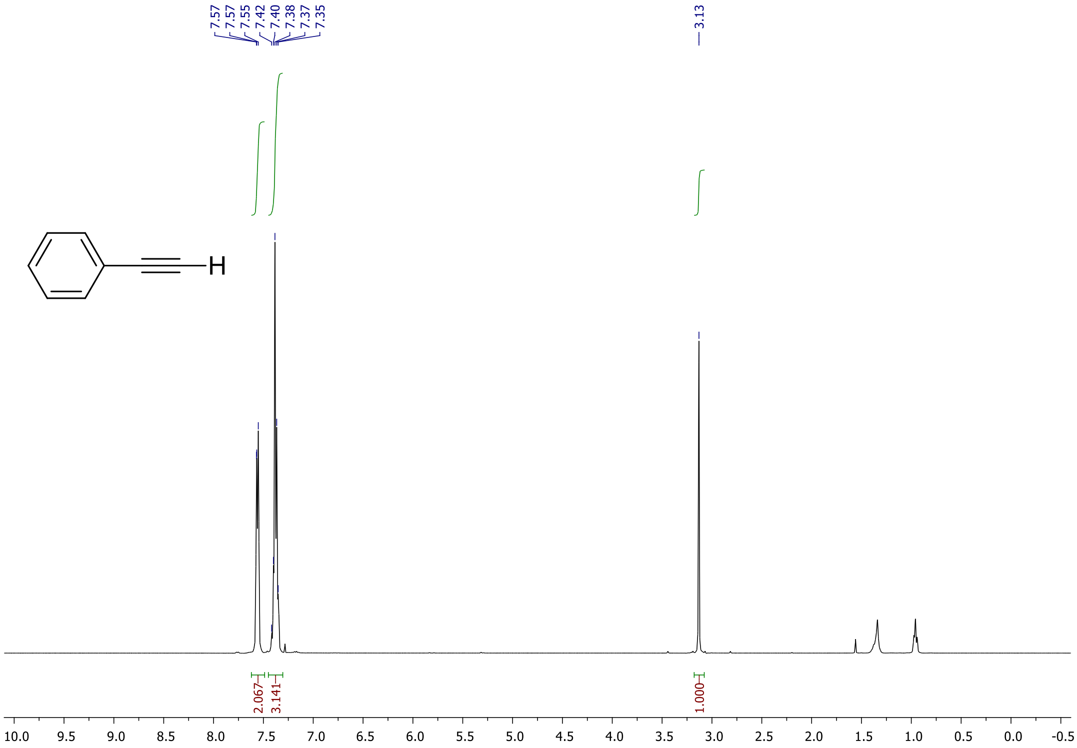


Figure S27. ^{1}H NMR Spectrum of **8a**.

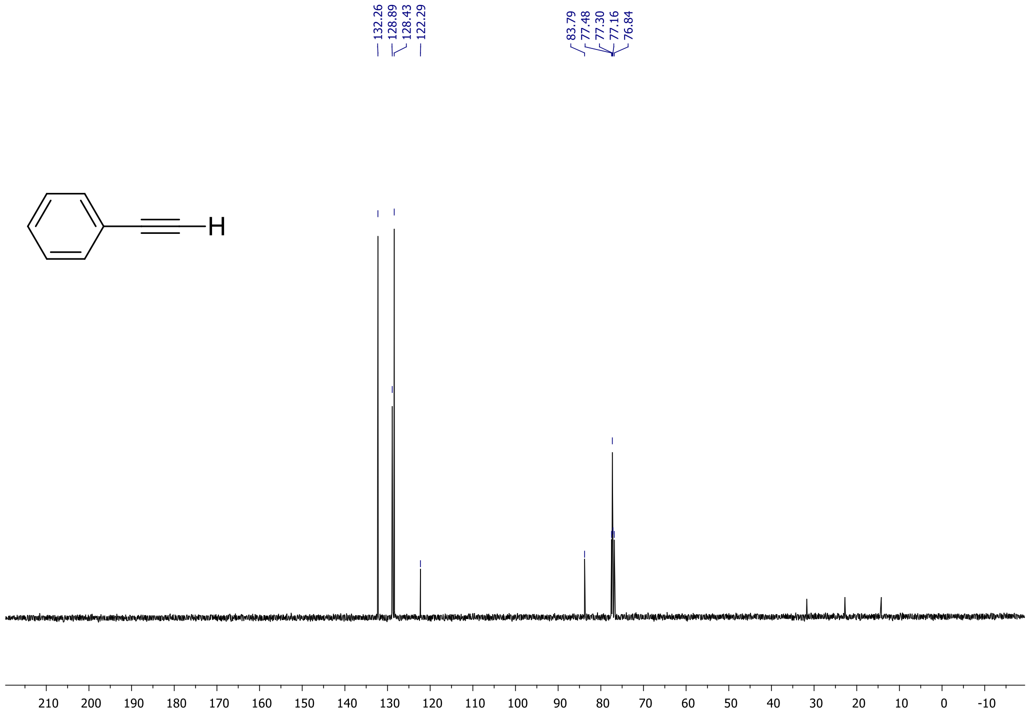


Figure S28. ^{13}C NMR Spectrum of **8a**.

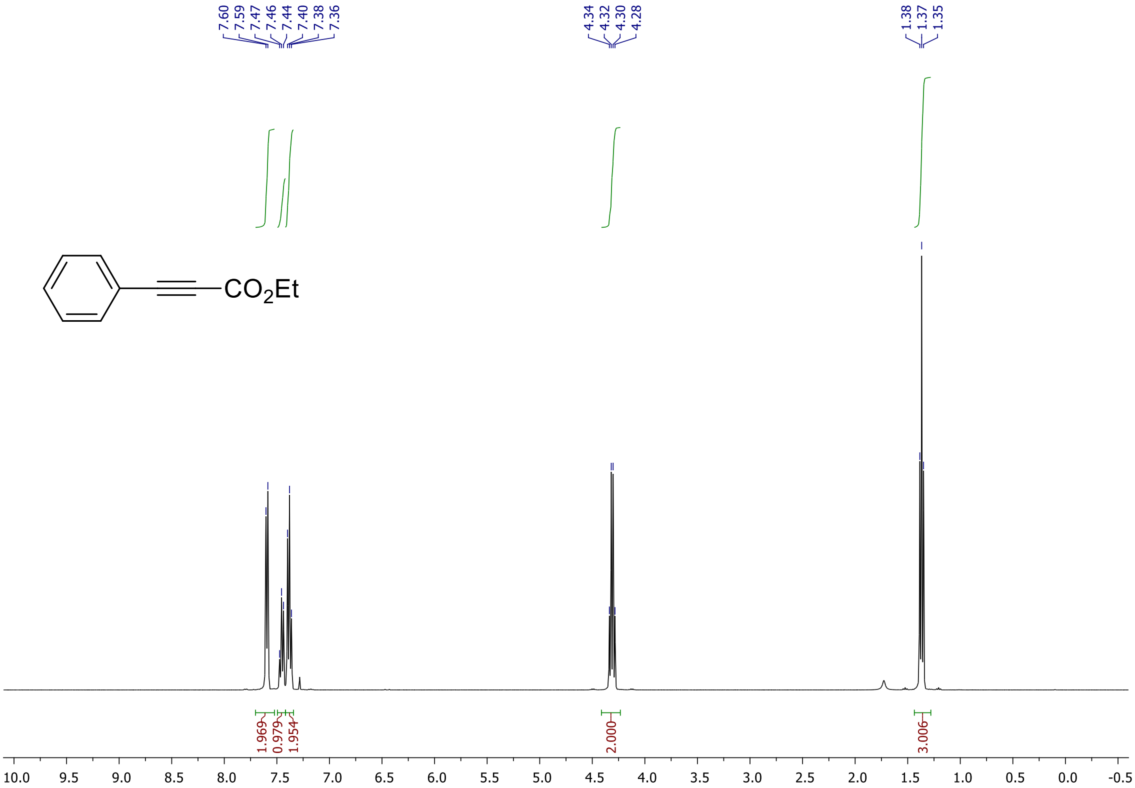


Figure S29. ^{1}H NMR Spectrum of **8b**.

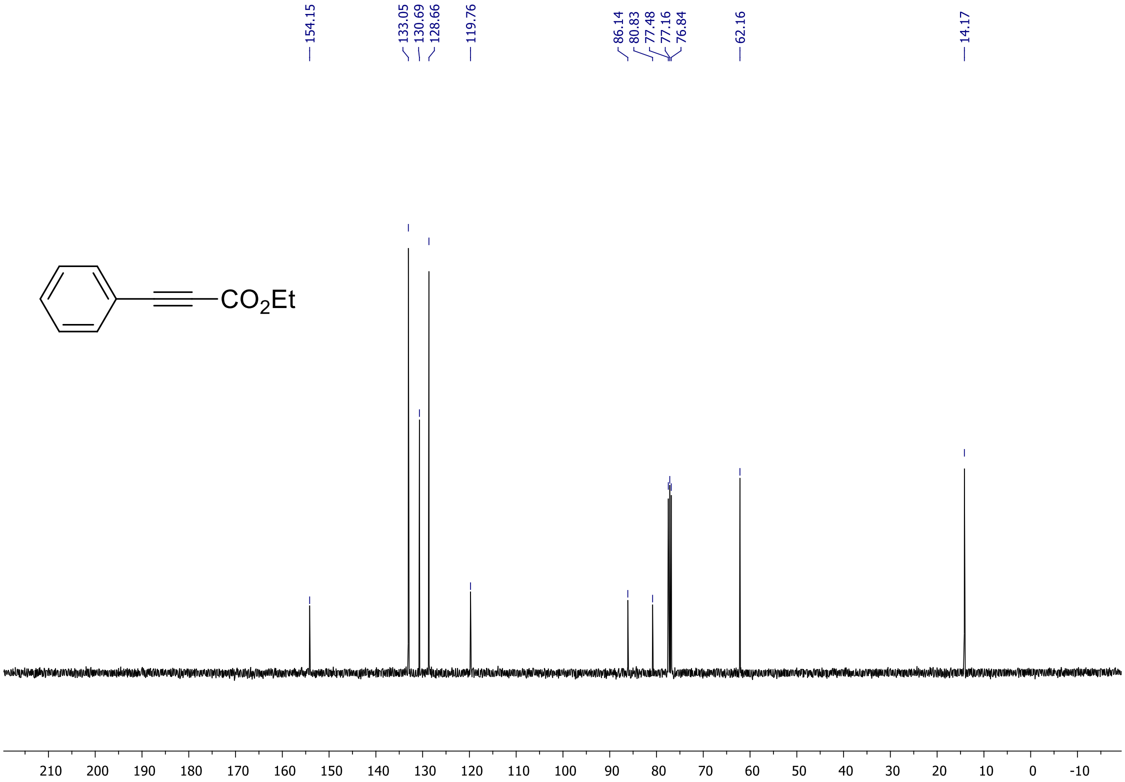


Figure S30. ^{13}C NMR Spectrum of **8b**.

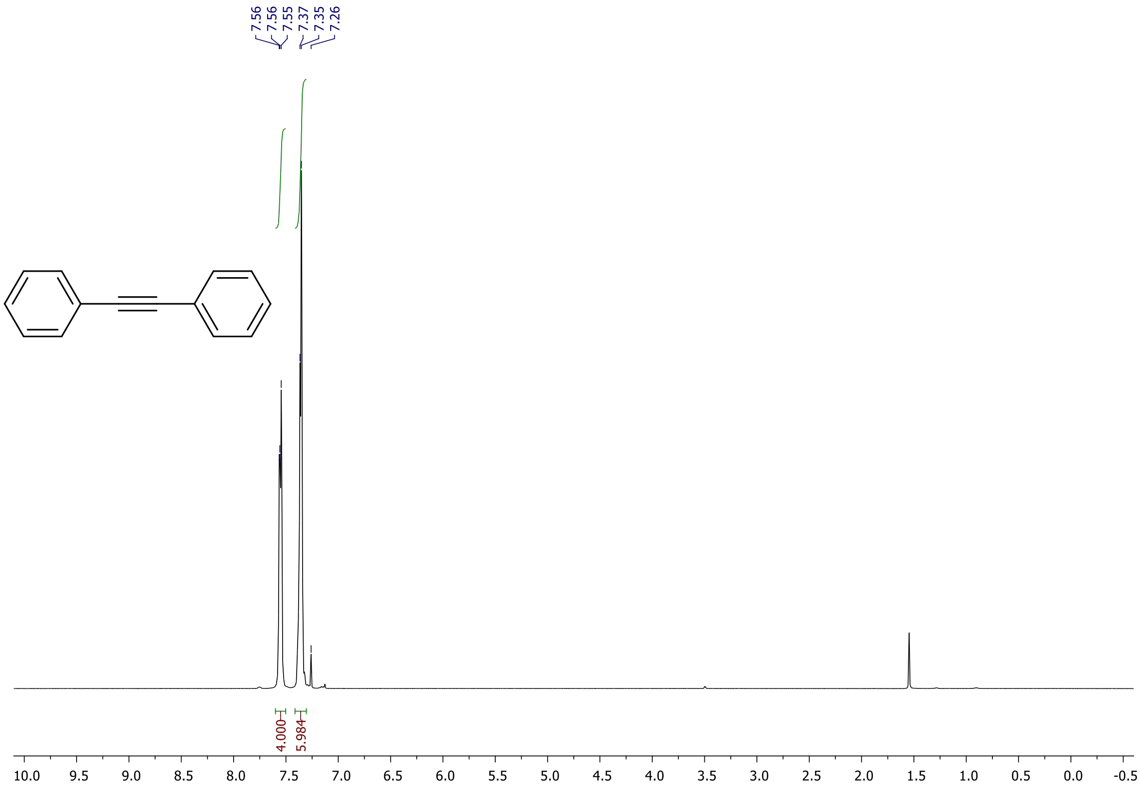


Figure S31. ^{1}H NMR Spectrum of **8c**.

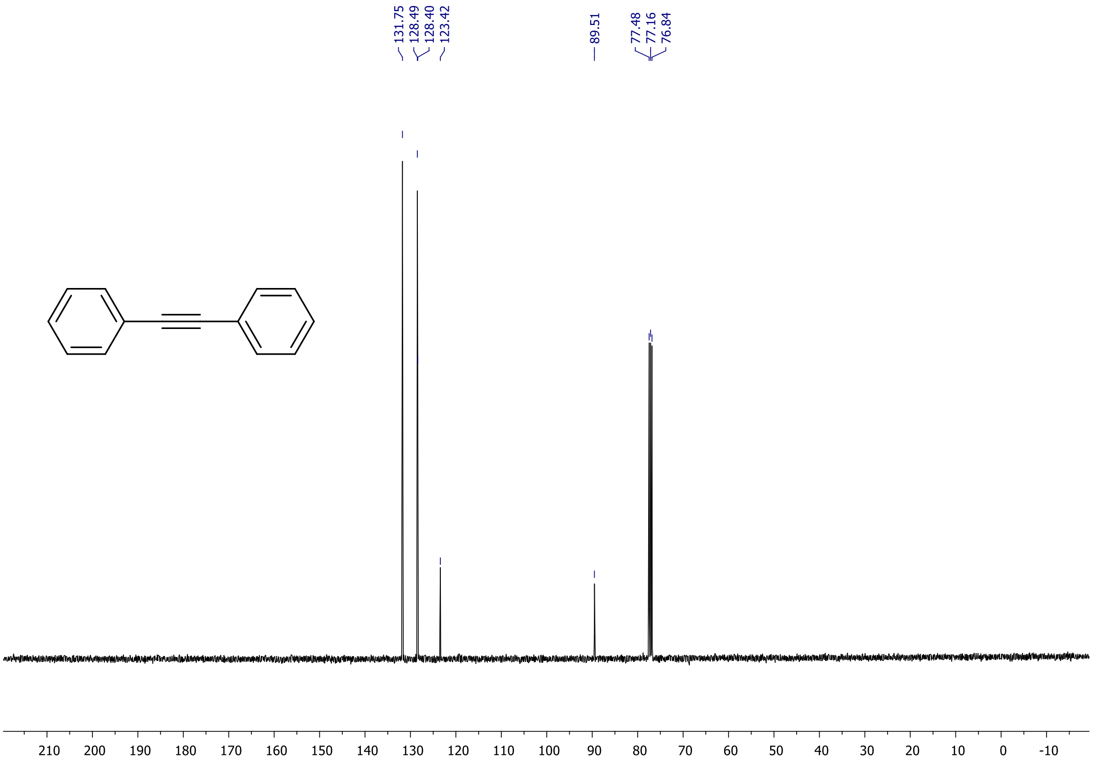


Figure S32. ^{13}C NMR Spectrum of **8c**.

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