Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Palladium-catalyzed 1,1-alkynylbromination of alkenes with alkynyl bromides

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1. General Information

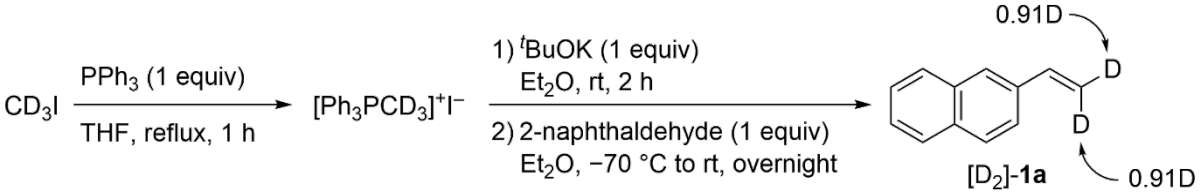
^{1}H, ^{2}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL ECS-400 or ECZ-400 spectrometer. The chemical shifts in ^{1}H NMR spectra were recorded relative to tetramethylsilane (δ: 0.0). The chemical shifts in ^{2}H NMR spectra were recorded relative to $CDCl_3$ (δ: 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ: 77.0). The chemical shifts in ^{11}B NMR spectra were recorded relative to $BF_3{\cdot}OEt_2$ (δ: 0.0). The chemical shifts in ^{19}F NMR spectra were recorded relative to $CFCl_3$ (δ: 0.0). Data are recorded as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad singlet, sep = septet, m = multiplet, c = complex), coupling constant (Hz), and integration. Infrared spectra (IR) were recorded on a JASCO FT/IR-4000 spectrometer using the ATR method. Absorption data are reported in reciprocal centimeters from 800 to 3500 cm^{-1} with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a SHIMDZU QP-2020NX spectrometer or a JEOL JMS-700 spectrometer with a quadrupole mass analyzer at 70 eV. Data were recorded as follows: mass/charge ratio (*m*/*z*) and relative intensity to the base peak at 100 %. High-resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer with a time-of-flight mass analyzer. Melting points were determined on a Stanford Research Systems MPA100 apparatus equipped with a digital thermometer and are uncorrected. Preparative gel permeation chromatography (GPC) were carried out on a JAI LC-5060 equipped with two JAIGEL-2HR columns connected in series or two JAIGEL-2HR-40 columns connected in series. Medium-pressure liquid chromatography (MPLC) was performed with a Biotage Isolera® equipped with Biotage® Sfär Silica HC chromatography cartridges connected in series. High-pressure liquid chromatography (HPLC) was performed with a SHIMADZU LC-20AR equipped with a SHIMADZU SPD-20A (UV Detector, λ = 254 nm) and Phenomenex Luna® Silica (5 μm, 210 × 21.2 mm).

2. Materials

All commercially available alkenes (**1a**-**1p**, **1r**, **1z**, **1aa**, **1ac**, **1ad**) were purchased from Sigma-Aldrich, TCI, Combi-Blocks, FUJIFILM Wako, Alfa Aesar, or BLD pharma. Alkenes **1q**,[1], **1s**,[2] **1t**,[3] **1u**,[2] **1v**,[4] **1w**,[5] **1x**,[6] **1y**,[7] **1ab**,[8] **1ae**,[9] [D_1]-**1a**,[10] and α-[D_1]-**1s**[10] were prepared according to the previously reported procedures. All of the alkenes were distilled over CaH_2 or recrystallized prior to use. The alkynyl bromide **2** was prepared according to a previously reported procedure and purified by distillation over CaH_2.[11] Toluene (super dehydrated) was purchased from Kanto Chemicals and was used as received. $Pd(OAc)_2$ were purchased from FUJIFILM Wako and used as received.

3. Preparation of the Deuterated Substrates

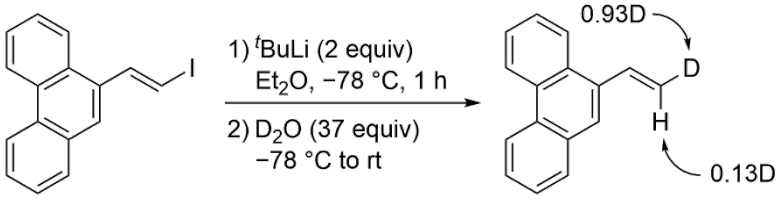
Preparation of [D_2]-1a.



The deuterated 2-vinylnaphthalene-d_2 ([D_2]-**1a,** CASRN: 1308650-67-0) was prepared from 2-naphthaldehyde (937.1 mg, 6.0 mmol) by referring to the reported procedure for the synthesis of 4-*tert*-butylstyrene-d_2.[12] The crude material was purified by column chromatography on silica gel (eluent: hexane, R_f = 0.40) to afford [D_2]-**1a** as a white powder (834.5 mg, 89%). Spectral data are consistent with those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.78 (c, 3H), 7.75 (s, 1H), 7.65 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.49–7.42 (c, 2H), 6.88 (br, 1H), 5.87 (d, *J* = 17.6 Hz, 0.09H), 5.33 (d, *J* = 10.9 Hz, 0.09H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.7, 134.9, 133.5, 133.1, 128.1, 128.0, 127.6, 126.4, 126.2, 125.9, 123.1, 114.1–113.6 (m). MS (EI, relative intensity, %) *m*/*z*: 157 (12, $[M + 1]^+$), 156 (100, M^+), 155 (86), 154 (53), 153 (30), 152 (13), 129 (11), 128 (10), 77 (20).

Preparation of (*E*)-[D_1]-1s.



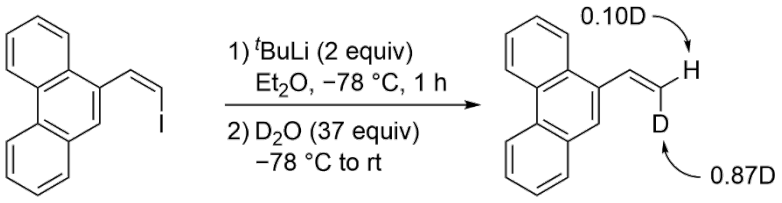
(*E*)-[D_1]-**1s**

To a solution of (*E*)-9-(2-iodovinyl)phenanthrene[14] (1 mmol) in Et_2O (20 mL), a solution of *t*BuLi (1.6 M in pentane, 1.25 mL, 2 mmol)

was slowly added via a syringe at −78 °C, and the reaction mixture was stirred at the same temperature. After 1 h, D_2O (99.8% D, 0.75 mL, 37 mmol) was slowly added to the mixture via a syringe, and the stirring was continued with the temperature being allowed to warm to room temperature. The resulting mixture was extracted with Et_2O (3 × 10 mL), and the combined organic layers were washed with sat. aq. $Na_2S_2O_3$ (10 mL) and brine (10 mL) and dried over Na_2SO_4. After concentration under the reduced pressure, the resulting crude mixture was purified by silica gel column chromatography (eluent: hexane, R_f = 0.51) and subsequent preparative GPC (eluent: $CHCl_3$) to give (*E*)-[D1]-**1s** as a colorless solid (184.9 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74–8.71 (m, 1H), 8.67–8.64 (m, 1H), 8.17–8.14 (m, 1H), 7.90–7.87 (m, 1H), 7.84 (s, 1H), 7.69–7.56 (c, 4H), 7.47 (d, *J* = 16.9 Hz, 1H), 5.85 (d, *J* = 17.2 Hz, 0.87H), 5.51 (d, *J* = 10.8 Hz, 0.07H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.1, 134.8, 131.9, 130.7, 130.5, 130.4, 128.8, 126.9, 126.8, 126.7, 126.6, 124.8, 123.2, 122.7, 117.4 (t, *J* = 24.6 Hz) (one signal is obscured by overlap with another signal). MS (EI, relative intensity, %) *m*/*z*: 206 (15, $[M + 1]^+$), 205 (95, M^+), 204 (100), 203 (64), 202 (20), 201 (13). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{12}D$ 206.10745; Found 206.10796.

Preparation of (*Z*)-[D_1]-1s.



(*Z*)-[D_1]-**1s**

To a solution of (*Z*)-9-(2-iodovinyl)phenanthrene[15] (1 mmol) in Et_2O (20 mL), a solution of *t*BuLi (1.6 M in pentane, 1.25 mL, 2 mmol) was slowly added via a syringe at −78 °C, and the reaction mixture was stirred at the same temperature. After 1 h, D_2O (99.8% D, 0.75 mL, 37 mmol) was slowly added to the mixture via a syringe, and the stirring was continued with the temperature being allowed to warm to room temperature. The resulting mixture was extracted with Et_2O (3 × 10 mL), and the combined organic layers were washed with sat. aq. $Na_2S_2O_3$ (10 mL) and brine (10 mL) and dried over Na_2SO_4. After concentration under the reduced pressure, the resulting crude mixture was purified by silica gel column chromatography (eluent: hexane, R_f = 0.52) and subsequent preparative GPC (eluent: $CHCl_3$) to give (*Z*)-[D1]-**1s** as a pale yellow solid (89.6 mg, 43% yield).

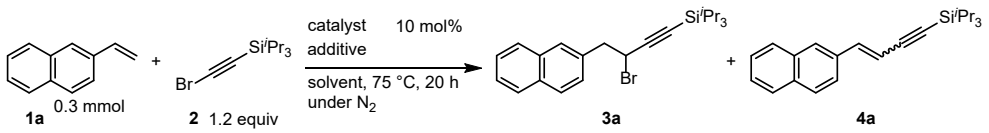
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69–8.65 (m, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.13–8.10 (m, 1H), 7.86–7.83 (m, 1H), 7.80 (s, 1H), 7.65–7.52 (c, 4H), 7.47–7.39 (m, 1H), 5.87–5.79 (c, 0.13H), 5.51–5.46 (c, 0.90H. ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.1, 134.8, 131.9, 130.7, 130.5, 130.4, 128.8, 126.9, 126.8, 126.7, 126.6, 124.8, 123.2, 122.6, 117.4 (t, *J* = 23.6 Hz) (one signal is obscured by overlap with another signal). MS (EI, relative intensity, %) *m*/*z*: 205 (83, M^+), 204 (100), 203 (70), 202 (28), 201 (13). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{12}D$ 206.10745; Found 206.10763.

4. General Procedure for the Pd-Catalyzed 1,1-Alkynylbromination of Alkenes

$Pd(OAc)_2$ (0.7 mg, 0.03 mmol, 10 mol%), (bromoethynyl)triisopropylsilane **2** (94 mg, 0.36 mmol, 1.2 equiv), alkene **1** (0.3 mmol, 1 equiv) and toluene (1 mL) were successively added to a 10 mL-sample vial equipped with a Teflon-sealed screwcap under air or N_2. After stirring the mixture at 75 °C for 20 h, the resulting solution was filtered through a pad of celite and further eluted with EtOAc. The filtrate was concentrated under reduced pressure, and the resulting mixture was purified by preparative MPLC (flow rate: 40 mL/min).

5. Screening of Reaction Conditions

Table S1. Screening of reaction conditions.



1a 0.3 mmol **2** 1.2 equiv **3a** **4a**

entry	catalyst	additive	solvent	yield of **3a** [%]	yield of **4a** [%]	recovery of **1a** [%]
1	$Pd(OAc)_2$	—	toluene	68	8	0
2	$PdBr_2$	—	toluene	40	3	42
3	$Pd(PPh_3)_4$	—	toluene	0	0	94
4	$Pd_2(dba)_3$ (5 mol%)	—	toluene	38	3	43
5	$Ni(OAc)_2$	—	toluene	0	0	96
6	$Ru(OAc)_2$(*p*-cymene)	—	toluene	0	0	78
7	$[Rh(OAc)_2]_2$ (5 mol%)	—	toluene	0	0	72
8	$Cu(OAc)_2$	—	toluene	0	0	94
9	$Ag(OAc)_2$	—	toluene	0	0	95
10	$Pd(OAc)_2$	—	CCl_4	46	8	7
11	$Pd(OAc)_2$	—	HFIP	0	0	0
12	$Pd(OAc)_2$	—	MeCN	2	0	0
13	$Pd(OAc)_2$	—	DMF	0	9	70
14[a]	$Pd(OAc)_2$	—	toluene	71 (61)	7	0
15[a]	$Pd(OAc)_2$	LiBr (2 equiv)	toluene	66	4	<5
16[a]	$Pd(OAc)_2$	AcOH (2 equiv)	toluene	59	7	0
17[a]	$Pd(OAc)_2$	PPh_3 (20 mol%)	toluene	0	0	>99
18[a]	$Pd(OAc)_2$	$P(OEt)_3$ (20 mol%)	toluene	65	6	<5
19[a]	$Pd(OAc)_2$	bpy (10 mol%)	toluene	38	3	43

Reaction conditions: **1a** (0.3 mmol), **2** (0.36 mmol), $Pd(OAc)_2$ (0.03 mmol), solvent (1 mL), 75 °C, 20 h, under N_2 unless otherwise noted. Yields and recovery were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as internal standard. Value in parenthesis is isolated yield. (a) Under air.

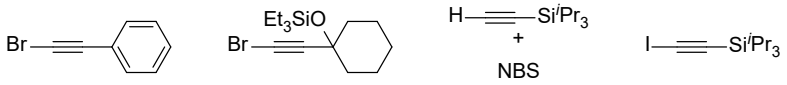
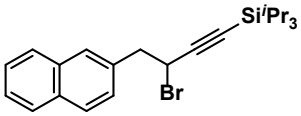


Figure S1. Ineffective reagents for Pd-catalyzed 1,1-alkynylhalogenation of **1a**.

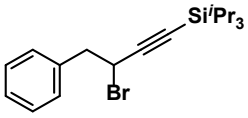
6. Characterization of Products

[3-Bromo-4-(naphthalen-2-yl)but-1-yn-1-yl]triisopropylsilane (3a).



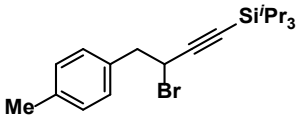
Pale yellow oil, 75.8 mg, 61% yield. R_f = 0.37 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.77 (c, 3H), 7.73 (s, 1H), 7.48–7.39 (c, 3H), 4.77 (dd, *J* = 7.5, 6.9 Hz, 1H), 3.53–3.47 (m, 2H), 1.01 (br, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.6, 133.3, 132.6, 128.4, 128.0, 127.7, 127.6, 127.5, 126.0, 125.7, 105.2, 90.1, 46.2, 36.9, 18.5, 11.1. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1463 m, 1382 w. MS (EI, relative intensity, %) *m*/*z*: 416 (37, $[M + 2]^+$), 414 (36, M^+), 291 (18), 249 (29), 221 (34), 219 (23), 207 (28), 205 (32), 195 (52), 193 (42), 179 (22), 178 (25), 167 (91), 165 (100), 141 (41), 139 (62), 137 (60), 125 (16), 123 (12), 115 (28), 111 (28), 110 (21), 83 (18), 59 (34). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{23}H_{32}BrSi$ 415.14512; Found 415.14421.

(3-Bromo-4-phenylbut-1-yn-1-yl)triisopropylsilane (3b).



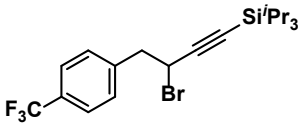
Pale yellow oil, 80.1 mg, 69% yield. R_f = 0.42 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.22 (m, 5H), 4.67 (dd, *J* = 7.8, 6.9 Hz, 1H), 3.36–3.26 (m, 2H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.1, 129.5, 128.3, 127.2, 105.1, 89.8, 46.0, 37.0, 18.5, 11.1. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1462 m. MS (EI, relative intensity, %) *m*/*z*: 323 (10), 321 (10, $[M - {}^i\text{Pr}]^+$), 241 (10), 195 (39), 193 (38), 185 (10), 183 (10), 171 (21), 169 (11), 168 (10), 167 (100), 166 (10), 165 (98), 139 (65), 137 (66). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{30}BrSi$ 365.12947; Found 365.13066.

[3-Bromo-4-(4-tolyl)but-1-yn-1-yltriisopropylsilane (3c).



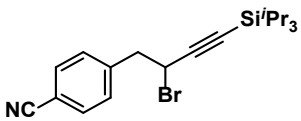
Pale yellow oil, 69.8 mg, 61% yield. R_f = 0.41 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.64 (t, *J* = 7.3 Hz, 1H), 3.27 (d, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.8, 134.1, 129.4, 129.0, 105.3, 89.7, 45.6, 37.4, 21.1, 18.5, 11.1. IR (ATR, cm^{-1}): 2942 m, 2865 m, 1463 m. MS (EI, relative intensity, %) *m*/*z*: 380 (2, $[M + 2]^+$), 378 (2, M^+), 255 (14), 213 (20), 199 (11), 197 (13), 195 (55), 193 (54), 185 (20), 183 (10), 167 (100), 165 (95), 139 (52), 137 (51). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{32}BrSi$ 379.14512; Found 379.14502.

{3-Bromo-4-[4-(trifluoromethyl)phenyl]but-1-yn-1-yl}triisopropylsilane (3d).



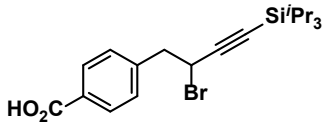
Pale yellow oil, 125.3 mg, 98% yield. R_f = 0.43 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 4.72 (dd, *J* = 7.7, 6.5 Hz, 1H), 3.40 (dd, *J* = 13.9, 6.5 Hz, 1H), 3.35 (dd, *J* = 13.7, 7.8 Hz, 1H), 1.02 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.9, 129.9, 129.5 (q, *J* = 32.4 Hz), 125.2 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 272.0 Hz), 104.4, 90.6, 45.4, 35.9, 18.4, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.0. IR (ATR, cm^{-1}): 2945 w, 2867 w, 1323 s, 1166 m, 1127 s. MS (EI, relative intensity, %) *m*/*z*: 392 (17), 391 (80), 390 (18), 389 (79, $[M - {}^i\text{Pr}]^+$), 309 (18), 267 (25), 239 (34), 177 (34), 159 (34), 141 (34), 140 (42), 139 (15), 122 (100). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{29}BrF_3Si$ 433.11685; Found 433.11544.

4-[2-Bromo-4-(triisopropylsilyl)but-3-yn-1-yl]benzonitrile (3e).



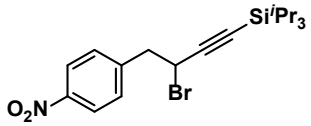
Pale yellow oil, 94.8 mg, 72% yield. R_f = 0.45 (hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.72 (dd, *J* = 7.6, 6.4 Hz, 1H), 3.39 (dd, *J* = 13.7, 6.4 Hz, 1H), 3.35 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1, 132.0, 130.4, 118.7, 111.1, 104.1, 90.8, 45.4, 35.4, 18.4, 11.0. IR (ATR, cm^{-1}): 2943 m, 2865 m, 2229 w, 1463 m. MS (EI, relative intensity, %) *m*/*z*: 348 (55), 346 (53, $[M - {}^i\text{Pr}]^+$), 268 (59), 266 (45), 224 (28), 212 (32), 210 (27), 198 (36), 196 (61), 167 (100), 165 (94), 139 (58), 137 (59). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{29}BrNSi$ 390.12472; Found 390.12611.

4-[2-Bromo-4-(triisopropylsilyl)but-3-yn-1-yl]benzoic acid (3f).



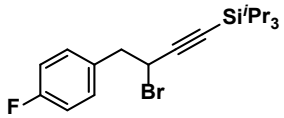
White powder, 114.1 mg, 91% yield. R_f = 0.05 (hexane/EtOAc = 4/1). Mp = 108.5–110.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.21 (br, 1H), 8.08–8.05 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.73 (dd, *J* = 7.5, 6.7 Hz, 1H), 3.45–3.35 (m, 2H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 143.2, 130.3, 129.8, 128.2, 104.6, 90.5, 45.7, 35.9, 18.5, 11.1. IR (ATR, cm^{-1}): 3075 w, 2943 m, 2865 m, 1692 s, 1423 m. MS (EI, relative intensity, %) *m*/*z*: 368 (24), 367 (99), 366 (24), 365 (100, [M − ^{i}Pr]$^+$), 287 (11), 286 (10), 285 (24), 155 (13). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{20}H_{30}BrO_2Si$ 409.11930; Found 409.11972.

[3-Bromo-4-(4-nitrophenyl)but-1-yn-1-yl]triisopropylsilane (3g).



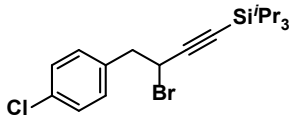
Pale yellow oil, 99.9 mg, 82% yield. R_f = 0.51 (hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (dt, *J* = 9.0, 2.2 Hz, 2H), 7.48 (dt, *J* = 9.1, 2.2 Hz, 2H), 4.75 (dd, *J* = 7.3, 6.5 Hz, 1H), 3.44 (dd, *J* = 13.9, 6.5 Hz, 1H), 3.40 (dd, *J* = 13.9, 7.3 Hz, 1H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.2, 144.2, 130.5, 123.4, 104.1, 91.0, 45.1, 35.3, 18.4, 11.0. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1522 s, 1463 m, 1345 s. MS (EI, relative intensity, %) *m*/*z*: 369 (23), 368 (100), 367 (23), 366 (97, [M − ^{i}Pr]$^+$), 288 (23), 286 (31), 279 (68), 277 (63), 216 (32), 167 (58), 165 (50), 139 (50), 137 (47), 128 (39). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{19}H_{29}BrNO_2Si$ 410.11454; Found 410.11413.

[3-Bromo-4-(4-fluorophenyl)but-1-yn-1-yl]triisopropylsilane (3h).



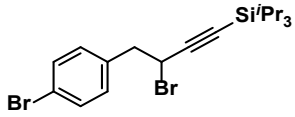
Pale yellow oil, 84.4 mg, 72% yield. R_f = 0.42 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.22 (m, 2H), 6.99 (tt, *J* = 9.0, 2.4 Hz, 2H), 4.65 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.30 (dd, *J* = 13.8, 6.5 Hz, 1H), 3.26 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.1 (d, *J* = 245.6 Hz), 132.8 (d, *J* = 3.9 Hz), 131.1 (d, *J* = 7.7 Hz), 115.1 (d, *J* = 22.2 Hz), 104.8, 90.2, 45.0, 36.9, 18.5, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.9. IR (ATR, cm^{-1}): 2943 m, 2866 m, 1510 s, 1463 m, 1227 s. MS (EI, relative intensity, %) *m*/*z*: 341 (10), 339 (10, [M − ^{i}Pr]$^+$), 261 (10), 259 (11), 195 (31), 193 (31), 189 (29), 167 (100), 165 (99), 139 (69), 137 (65), 127 (32), 95 (15). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{19}H_{29}BrFSi$ 383.12004; Found 383.12014.

[3-Bromo-4-(4-chlorophenyl)but-1-yn-1-yl]triisopropylsilane (3i).



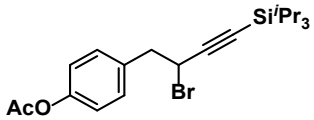
Pale yellow oil, 100.0 mg, 83% yield. R_f = 0.46 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (dt, *J* = 8.6, 2.1 Hz, 2H), 7.22 (dt, *J* = 8.5, 2.1 Hz, 2H), 4.65 (dd, *J* = 7.5, 6.6 Hz, 1H), 3.30 (dd, *J* = 14.0, 6.6 Hz, 1H), 3.26 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.4, 133.1, 130.9, 128.4, 104.7, 90.3, 45.1, 36.5, 18.5, 11.1. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1686 w, 1493 m, 1463 m, 1092 m. MS (EI, relative intensity, %) *m*/*z*: 357 (13), 355 (10, [M − ^{i}Pr]$^+$), 207 (12), 205 (16), 195 (37), 193 (40), 167 (100), 165 (100), 139 (60), 137 (58), 125 (25), 111 (10). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{19}H_{29}BrClSi$ 399.09049; Found 399.08878.

[3-Bromo-4-(4-bromophenyl)but-1-yn-1-yl]triisopropylsilane (3j).



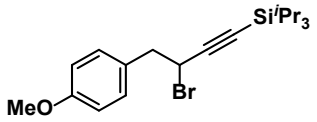
Pale yellow oil, 80.7 mg, 64% yield. R_f = 0.43 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dt, *J* = 8.8, 2.2 Hz, 2H), 7.16 (dt, *J* = 8.5, 2.2 Hz, 2H), 4.65 (dd, *J* = 7.6, 6.6 Hz, 1H), 3.28 (dd, *J* = 14.0, 6.6 Hz, 1H), 3.24 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.0, 131.4, 131.2, 121.3, 104.7, 90.3, 45.1, 36.4, 18.5, 11.1. IR (ATR, cm^{-1}): 2942 m, 2865 m, 1489 m, 1463 m, 1072 m. MS (EI, relative intensity, %) *m*/*z*: 403 (10), 401 (20), 399 (10, [M − ^{i}Pr]$^+$), 322 (36), 321 (25), 320 (33), 280 (52), 279 (93), 278 (52), 277 (84), 265 (11), 251 (34), 249 (31), 197 (35), 195 (40), 193 (36), 183 (13), 169 (32), 167 (100), 165 (95), 155 (20). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{19}H_{29}Br_2Si$ 443.03998; Found 443.03681.

4-[2-Bromo-4-(triisopropylsilyl)but-3-yn-1-yl]phenyl acetate (3k).



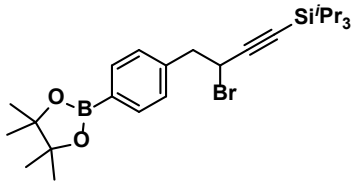
Pale yellow oil, 109.1 mg, 83% yield. R_f = 0.33 (hexane/Et_2O = 6/1). The analytically pure sample was obtained by GPC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dt, *J* = 9.0, 2.3 Hz, 2H), 7.03 (dt, *J* = 8.9, 2.4 Hz, 2H), 4.65 (dd, *J* = 7.5, 6.9 Hz, 1H), 3.35–3.26 (m, 2H), 2.30 (s, 3H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.4, 149.8, 134.6, 130.5, 121.4, 104.9, 90.1, 45.2, 36.7, 21.1, 18.5, 11.1. IR (ATR, cm^{-1}): 2943 w, 2865 w, 1765 m, 1508 w, 1463 w, 1368 w, 1194 s. MS (EI, relative intensity, %) *m*/*z*: 382 (25), 381 (100), 380 (25), 379 (96, [M − ^{i}Pr]$^+$), 301 (35), 299 (34), 257 (33), 229 (32), 215 (25), 201 (22), 187 (25), 167 (45), 165 (44), 139 (26), 137 (29). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{21}H_{32}BrO_2Si$ 423.13495; Found 423.13541.

[3-Bromo-4-(4-methoxyphenyl)but-1-yn-1-yl]triisopropylsilane (3l).



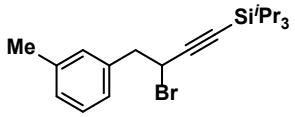
Pale yellow oil, 27.0 mg, 21% yield. R_f = 0.22 (hexane/toluene = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.62 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.30–3.20 (m, 2H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 130.6, 129.3, 113.7, 105.3, 89.7, 55.2, 45.1, 37.5, 18.5, 11.1. IR (ATR, cm^{-1}): 2942 m, 2865 m,1612 w, 1513 s, 1463 m, 1249 s. MS (EI, relative intensity, %) *m*/*z*: 396 (5, [M + 2]$^+$), 394 (5, M$^+$), 351 (4), 314 (15), 271 (36), 229 (18), 215 (13), 201 (20), 167 (29), 165 (30), 139 (21), 137 (21), 121 (100). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{20}H_{32}BrOSi$ 395.14003; Found 395.14184.

{3-Bromo-4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]but-1-yn-1-yl}triisopropylsilane (3m).



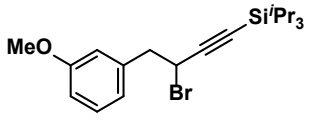
Pale yellow oil, 87.2 mg, 59% yield. R_f = 0.50 (hexane/Et_2O = 6/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 3.38–3.29 (c, 2H), 1.34 (s, 12H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.3, 134.9, 128.8, 105.2, 89.9, 83.7, 46.1, 36.8, 24.8, 18.5, 11.1 (one signal is missing). ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.3. IR (ATR, cm^{-1}): 2943 m, 2866 m, 1464 w, 1399 m, 1360 s. MS (EI, relative intensity, %) *m*/*z*: 492 (3, [M + 2]$^+$), 490 (3, M$^+$), 449 (18), 447 (17), 410 (17), 368 (10), 367 (30), 211 (19), 197 (14), 169 (15), 155 (12), 83 (100). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{25}H_{41}BBrO_2Si$ 491.21468; Found 491.21273.

[3-Bromo-4-(3-tolyl)but-1-yn-1-yl]triisopropylsilane (3n).



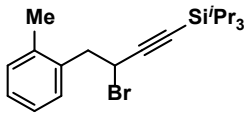
Pale yellow oil, 93.2 mg, 77% yield. R_f = 0.40 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.11–7.04 (c, 3H), 4.66 (dd, *J* = 8.1, 6.7 Hz, 1H), 3.30 (dd, *J* = 13.7, 6.7 Hz, 1H), 3.26 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.33 (s, 3H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.9, 137.1, 130.2, 128.2, 127.9, 126.5, 105.3, 89.7, 46.0, 37.1, 21.3, 18.5, 11.1. IR (ATR, cm^{-1}): 2942 m, 2865 m, 1463 m. MS (EI, relative intensity, %) *m*/*z*: 337 (10), 335 (10, [M − ^{i}Pr]$^+$), 257 (14), 255 (14), 213 (15), 195 (41), 193 (38), 185 (22), 171 (16), 169 (18), 167 (100), 165 (92), 139 (59), 137 (59). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{20}H_{32}BrSi$ 379.14512; Found 379.14530.

[3-Bromo-4-(3-methoxyphenyl)but-1-yn-1-yl]triisopropylsilane (3o).



Pale yellow oil, 76.9 mg, 65% yield. R_f = 0.56 (hexane/Et_2O = 6/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.19 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.81–6.79 (c, 2H), 4.67 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.34–3.25 (c, 2H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 138.6, 129.3, 121.8, 115.3, 112.4, 105.2, 89.8, 55.1, 46.1, 36.9, 18.5, 11.1. IR (ATR, cm^{-1}): 2942 m, 2865 m,1601 m, 1587 m, 1491 m, 1462 m, 1261 s, 1153 m. MS (EI, relative intensity, %) *m*/*z*: 396 (12, [M + 2]$^+$), 394 (12, M$^+$), 353 (53), 351 (52), 273 (22), 271 (28), 201 (34), 195 (22), 193 (21), 187 (27), 185 (16), 167 (100), 165 (99), 139 (67), 137 (67), 121 (13). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{20}H_{31}BrOSi$ 395.14003; Found 395.14026.

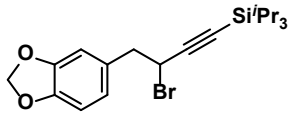
[3-Bromo-4-(2-tolyl)but-1-yn-1-yl]triisopropylsilane (3p).



Pale yellow oil, 84.3 mg, 72% yield. R_f = 0.45 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.22 (m, 1H), 7.16–7.12 (c, 3H), 4.67 (dd, *J* = 8.7, 6.6 Hz, 1H), 3.38 (dd, *J* = 13.8, 6.8 Hz, 1H), 3.33 (dd, *J* = 13.8, 8.6 Hz, 1H), 2.35 (s, 3H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.3, 135.6, 130.4, 130.3, 127.3, 125.9, 105.3, 89.6, 43.3, 36.0, 19.6, 18.5, 11.1. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1462 m. MS (EI, relative intensity, %) *m*/*z*: 337 (8), 335 (8, [M − ^{i}Pr]$^+$), 257 (12), 255 (15), 213 (20), 195 (40), 193 (39), 185 (23), 183 (18), 171

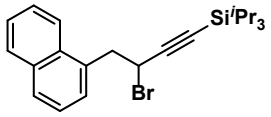
(16), 169 (15), 167 (100), 165 (94), 141 (20), 139 (66), 137 (65), 105 (24). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{32}BrSi$ 379.14512; Found 379.14443.

[4-(1,3-Benzodioxol-5-yl)-3-bromobut-1-yn-1-yl]triisopropylsilane (3q).



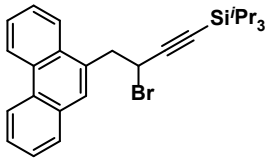
Pale yellow oil, 57.8 mg, 43% yield. R_f = 0.28 (hexane/toluene = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79–6.71 (c, 3H), 5.94–5.92 (m, 2H), 4.61 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.24 (dd, *J* = 13.7, 6.6 Hz, 1H), 3.20 (dd, *J* = 13.7, 8.0 Hz, 1H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.4, 146.7, 130.9, 122.8, 109.9, 108.1, 105.1, 100.9, 90.0, 45.6, 37.3, 18.5, 11.1. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1491 m, 1444 m, 1249 s. MS (EI, relative intensity, %) *m*/*z*: 410 (32, $[M + 2]^+$), 408 (31, M^+), 310 (16), 308 (16), 285 (38), 272 (62), 243 (26), 229 (20), 227 (15), 215 (30), 213 (23), 201 (24), 185 (32), 167 (40), 165 (44), 139 (34), 137 (34), 135 (100). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{30}BrO_2Si$ 409.11930; Found 409.11813.

[3-Bromo-4-(naphthalen-1-yl)but-1-yn-1-yl]triisopropylsilane (3r).



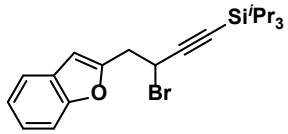
Pale yellow oil, 96.5 mg, 80% yield. R_f = 0.36 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.56–7.37 (c, 4H), 4.87–4.82 (m, 1H), 3.88 (dd, *J* = 14.1, 6.1 Hz, 1H), 3.73 (dd, *J* = 14.0, 9.0 Hz, 1H), 1.05–0.99 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 133.8, 133.1, 131.6, 129.0, 128.4, 128.1, 126.3, 125.6, 125.3, 123.1, 105.2, 90.1, 43.4, 36.1, 18.5, 11.1. IR (ATR, cm^{-1}): 2942 m, 2864 m, 1462 m. MS (EI, relative intensity, %) *m*/*z*: 373 (29), 371 (28, $[M - {}^i\text{Pr}]^+$), 293 (30), 292 (31), 291 (100), 263 (24), 249 (31), 221 (31), 219 (37), 207 (31), 205 (39), 167 (31), 165 (27), 141 (25). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{23}H_{32}BrSi$ 415.14512; Found 415.14627.

[3-Bromo-4-(phenanthren-9-yl)but-1-yn-1-yl]triisopropylsilane (3s).



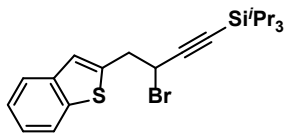
The reaction was performed for 48 h. Pale yellow oil, 82.7 mg, 59% yield. R_f = 0.30 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76–8.73 (m, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.04–8.00 (m, 1H), 7.82 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.74 (s, 1H), 7.69–7.55 (c, 4H), 4.94 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.95 (dd, *J* = 14.1, 5.8 Hz, 1H), 3.77 (dd, *J* = 14.2, 9.1 Hz, 1H), 0.97 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.32, 131.26, 130.8, 130.47, 130.1, 129.2, 128.5, 126.9, 126.7, 126.6, 126.4, 123.6, 123.4, 122.4, 105.2, 90.1, 44.1, 35.7, 18.4, 11.0. IR (ATR, cm^{-1}): 2942 s, 2864 s, 1462 s. MS (EI, relative intensity, %) *m*/*z*: 466 (6, $[M + 2]^+$), 464 (6, M^+), 386 (27), 385 (30), 384 (87), 344 (15), 343 (49), 342 (33), 341 (100), 285 (59), 271 (65), 269 (67), 191 (39). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{27}H_{34}BrSi$ 465.16077; Found 465.15953.

[4-(Benzofuran-2-yl)-3-bromobut-1-yn-1-yl]triisopropylsilane (3t).



The reaction was performed for 48 h. Pale yellow oil, 48.0 mg, 39% yield. R_f = 0.39 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.26–7.17 (c, 2H), 6.61 (s, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 3.53 (dd, *J* = 15.1, 7.3 Hz, 1H), 3.49 (dd, *J* = 15.2, 7.2 Hz, 1H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.8, 153.7, 128.4, 123.9, 122.7, 120.7, 110.9, 105.1, 104.6, 89.8, 39.3, 33.4, 18.4, 11.0. IR (ATR, cm^{-1}): 2943 s, 2865 s, 1454 s, 1254 m. MS (EI, relative intensity, %) *m*/*z*: 406 (36, $[M + 2]^+$), 404 (35, M^+), 363 (77), 361 (75), 321 (35), 319 (34), 239 (62), 225 (24), 211 (100), 197 (47), 195 (33), 193 (25), 167 (61), 165 (70), 131 (79). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{30}BrOSi$ 405.12438; Found 405.12392.

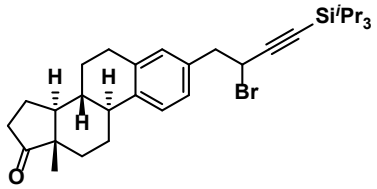
[4-(Benzo[*b*]thiophen-2-yl)-3-bromobut-1-yn-1-yl]triisopropylsilane (3u).



The reaction was performed for 48 h. Pale yellow oil, 54.8 mg, 43% yield. R_f = 0.37 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.75 (m, 1H), 7.70–7.67 (m, 1H), 7.34–7.26 (c, 2H), 7.20 (d, *J* = 0.7 Hz, 1H), 4.76 (t, *J* = 7.0 Hz, 1H), 3.66–3.56 (m, 2H), 1.04–1.01 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.7, 139.6, 124.2, 124.0, 123.7, 123.2, 122.1, 104.6, 90.5, 41.0, 35.8, 18.5, 11.1 (one signal is obscured by overlap with another signal). IR (ATR, cm^{-1}): 2942 s, 2865 s, 1461 s. MS (EI, relative intensity, %) *m*/*z*: 422 (16, $[M + 2]^+$), 420 (14, M^+), 379 (81), 377 (74), 287 (39), 285 (46), 255 (50), 227 (53), 215 (41), 195 (29), 193 (26), 167 (89), 165 (100), 147 (60), 139

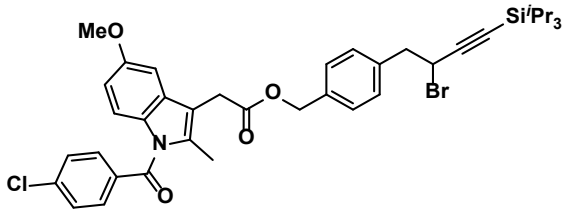
(54), 137 (60). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{21}H_{30}BrSSi$ 421.10154; Found 421.10050.

3-[2-Bromo-4-(triisopropylsilyl)but-3-yn-1-yl]estra-1,3,5(10)-trien-17-one (3v).



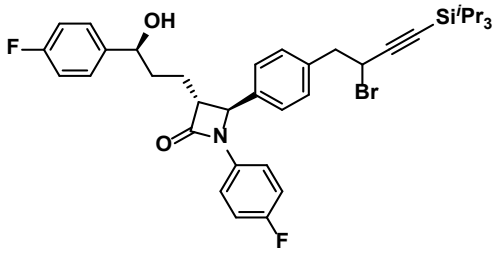
Pale yellow oil, 95.1 mg, 59% yield. R_f = 0.15 (hexane/Et_2O = 6/1). The analytically pure sample was obtained by preparative HPLC (eluent: hexane/Et_2O = 87/13, flow rate: 8 mL/min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.02–6.99 (m, 1H), 4.68–4.64 (m, 1H), 3.31–3.21 (m, 2H), 2.93–2.85 (m, 2H), 2.54–2.36 (c, 2H), 2.33–2.22 (m, 1H), 2.20–1.90 (c, 4H), 1.68–1.37 (m, 6H), 1.08–1.00 (m, 21H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 221.0, [138.63, 138.61], 136.4, [134.67, 134.63], [130.1, 130.0], [126.83, 126.79], 125.3, [105.35, 105.30], [89.66, 89.62], 50.4, 48.0, 45.5, 44.3, 38.1, [37.12, 37.09], 35.8, 31.5, 29.3, 26.4, 25.6, 21.5, 18.5, 13.8, 11.1. IR (ATR, cm^{-1}): 2940 s, 2864 m, 1740 s, 1462 m. MS (EI, relative intensity, %) *m*/*z*: 540 (3, M$^+$), 461 (14), 460 (32), 458 (10), 420 (21), 419 (69), 418 (36), 417 (100), 267 (5). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{31}H_{46}BrOSi$ 541.24958; Found 541.24986.

4-[2-Bromo-4-(triisopropylsilyl)but-3-yn-1-yl]benzyl 2-[1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]acetate (3w).



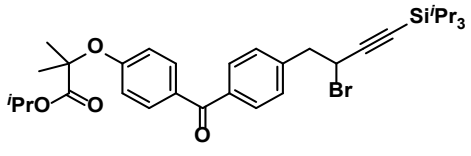
Pale yellow sticky solid, 173.0 mg, 79% yield. R_f = 0.13 (hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dt, *J* = 8.8, 2.1 Hz, 2H), 7.45 (dt, *J* = 8.8, 2.2 Hz, 2H), 7.29–7.21 (m, 4H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.67 (dd, *J* = 9.2, 2.5 Hz, 1H), 5.11 (s, 2H), 4.67 (t, *J* = 7.1 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 2H), 3.36–3.24 (m, 2H), 2.37 (s, 3H), 1.03 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 168.2, 156.0, 139.2, 137.2, 135.9, 134.6, 133.8, 131.1, 130.7, 130.5, 129.7, 129.1, 128.2, 114.9, 112.4, 111.7, 105.0, 101.1, 90.0, 66.5, 55.6, 45.5, 36.8, 30.3, 18.5, 13.4, 11.1. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1737 m, 1684 s, 1593 w, 1477 m, 1459 m, 1357 m, 1316 s, 1259 m, 1222 s, 1142 s, 1089 m, 1067 s. MS (EI, relative intensity, %) *m*/*z*: 653 (24, [M − HBr]$^+$), 610 (16), 312 (16), 141 (32), 139 (100). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{39}H_{46}BrClNO_4Si$ 734.20625; Found 734.20403.

(3*R*,4*S*)-4-{4-[2-Bromo-4-(triisopropylsilyl)but-3-yn-1-yl]phenyl}-1-(4-fluorophenyl)-3-[(*S*)-3-(4-fluorophenyl)-3-hydroxypropyl]azetidin-2-one (3x).



Pale yellow sticky solid, 70.2 mg, 35% yield. R_f = 0.10 (hexane/EtOAc = 4/1). The analytically pure sample was obtained by preparative HPLC (eluent: hexane/EtOAc = 75/25, flow rate: 8 mL/min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.19 (c, 8H), 7.05–6.98 (m, 2H), 6.95–6.88 (m, 2H), 4.75–4.64 (c, 2H), 4.62–4.57 (m, 1H), 3.37–3.24 (m, 2H), 3.12–3.04 (m, 1H), 2.30 (br, 1H), 2.07–1.82 (m, 4H), 1.05–0.94 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.4, 162.2 (d, *J* = 245.6 Hz), 159.0 (d, *J* = 243.7 Hz), 140.0, 137.6, 136.4, 133.7, 130.5, 127.3 (d, *J* = 7.7 Hz), 125.8, 118.3 (d, *J* = 7.7 Hz), 115.8 (d, *J* = 23.1 Hz), 115.3 (d, *J* = 21.2 Hz), [104.74, 104.72], [90.20, 90.15], 73.1, 61.1, 60.3, 45.4, [36.64, 36.62], 36.4, 25.0, [18.48, 18.43], [11.04, 11.02]. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.3, −118.5. IR (ATR, cm^{-1}): 3461 w, 2943 m, 2865 m, 1745 m, 1510 s, 1462 w, 1224 m. MS (EI, relative intensity, %) *m*/*z*: 681 (4, [M + 2]$^+$), 679 (4, M$^+$), 599 (11), 558 (18), 557 (15), 556 (31), 421 (11), 419 (29), 417 (12), 406 (15), 365 (18), 364 (53), 363 (16), 362 (49), 209 (11), 167 (16), 165 (10), 154 (18), 153 (16), 147 (18), 146 (16), 145 (13), 136 (12), 135 (100). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{37}H_{45}BrF_2NO_2Si$ 680.23655; Found 680.23360.

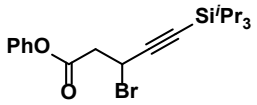
Isopropyl 2-(4-{4-[2-bromo-4-(triisopropylsilyl)but-3-yn-1-yl]benzoyl}phenoxy)-2-methylpropanoate (3y).



Pale yellow sticky solid, 151.0 mg, 81% yield. R_f = 0.28 (hexane/EtOAc = 9/1). The analytically pure sample was obtained by preparative HPLC (eluent: hexane/EtOAc = 94/6, flow rate: 8 mL/min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.68 (c, 4H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.86 (dt, *J* = 9.3, 2.5 Hz, 2H), 5.09 (sept, *J* = 6.3 Hz, 1H), 4.74 (dd, *J* = 7.8, 6.4 Hz, 1H), 3.42 (dd, *J* = 13.7, 6.4 Hz, 1H), 3.37 (dd, *J* =

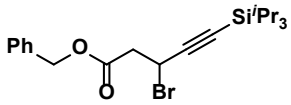
13.7, 7.8 Hz, 1H), 1.66 (s, 6H), 1.21 (d, *J* = 6.2 Hz, 6H), 1.04 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.0, 173.1, 159.5, 141.1, 137.0, 132.0, 130.5, 129.8, 129.4, 117.0, 104.7, 90.3, 79.3, 69.2, 45.6, 36.0, 25.3, 21.5, 18.5, 11.1. IR (ATR, cm^{-1}): 2942 m, 2865 m, 1731 m, 1655 m, 1599 s, 1464 m, 1281 s, 1250 s, 1175 s, 1146 s, 1102 s. MS (EI, relative intensity, %) *m*/*z*: 614 (1, $[M + 2]^+$), 612 (1, M^+), 572 (11), 571 (27), 570 (10), 569 (25), 534 (10), 533 (21), 532 (24), 492 (25), 491 (73), 490 (46), 489 (100), 363 (62), 361 (70), 121 (90). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{33}H_{46}BrO_4Si$ 613.23433; Found 613.23299.

Phenyl 3-bromo-5-(triisopropylsilyl)pent-4-ynoate (3z).



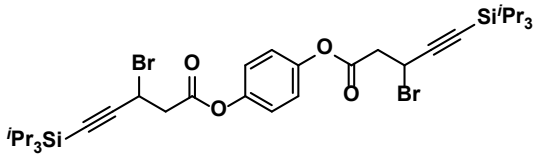
Pale yellow oil, 96.6 mg, 79% yield. R_f = 0.52 (hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.35 (m, 2H), 7.27–7.22 (m, 1H), 7.11–7.08 (m, 2H), 5.00 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.39 (dd, *J* = 16.3, 6.2 Hz, 1H), 3.32 (dd, *J* = 16.2, 8.5 Hz, 1H), 1.08 (br, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.4, 150.3, 129.5, 126.1, 121.4, 104.1, 90.1, 45.1, 30.1, 18.5, 11.1. IR (ATR, cm^{-1}): 2943 m, 2866 m, 1764 m, 1492 m, 1462 m, 1233 m, 1193 s, 1165 s. MS (EI, relative intensity, %) *m*/*z*: 367 (20), 365 (20, $[M - {}^iPr]^+$), 287 (20), 286 (28), 285 (100), 257 (26), 215 (28), 151 (23). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{30}BrO_2Si$ 409.11930; Found 409.11900.

Benzyl 3-bromo-5-(triisopropylsilyl)pent-4-ynoate (3aa).



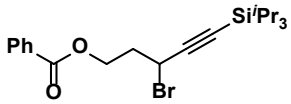
Pale yellow oil, 92.6 mg, 76% yield. R_f = 0.47 (hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.33 (c, 5H), 5.16 (s, 2H), 4.91 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.22–3.10 (c, 2H), 1.05 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 135.3, 128.6, 128.4, 128.3, 104.3, 89.6, 67.0, 45.0, 30.2, 18.5, 11.0. IR (ATR, cm^{-1}): 2943 m, 2866 m, 1742 s, 1461 m, 1176 s. MS (EI, relative intensity, %) *m*/*z*: 381 (4), 379 (4, $[M - {}^iPr]^+$), 300 (12), 299 (49), 229 (13), 91 (100). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{32}BrO_2Si$ 423.13495; Found 423.13381.

1,4-Phenylene bis(3-bromo-5-(triisopropylsilyl)pent-4-ynoate) (3ab).



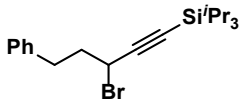
Pale yellow sticky solid, 153.8 mg, 69% yield. R_f = 0.43 (hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (s, 4H), 4.99 (dd, *J* = 8.5, 6.3 Hz, 2H), 3.39 (dd, *J* = 16.2, 6.3 Hz, 2H), 3.32 (dd, *J* = 16.2, 8.5 Hz, 2H), 1.08 (s, 42H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 147.9, 122.4, 103.9, 90.2, 45.0, 29.9, 18.5, 11.0. IR (ATR, cm^{-1}): 2943 m, 2866 m, 1764 m, 1500 m, 1463 m, 1174 s, 1124 s. MS (EI, relative intensity, %) *m*/*z*: 699 (11), 697 (15) 695 (7, $[M - {}^iPr]^+$), 618 (10), 617 (18), 615 (13), 538 (10), 537 (29), 536 (54), 535 (100), 249 (21), 248 (27), 209 (36), 167 (13), 153 (10), 139 (19). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{34}H_{53}Br_2O_4Si_2$ 739.18436; Found 739.18293.

3-Bromo-5-(triisopropylsilyl)pent-4-yn-1-yl benzoate (3ac).



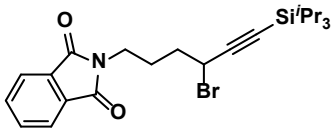
Pale yellow oil, 88.4 mg, 72% yield. R_f = 0.56 (hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.02 (m, 2H), 7.59–7.54 (m, 1H), 7.47–7.42 (m, 2H), 4.73 (t, *J* = 7.0 Hz, 1H), 4.58-4.47 (m, 2H), 2.52–2.45 (m, 2H), 1.07 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 133.1, 129.8, 129.6, 128.4, 104.7, 89.7, 62.2, 38.8, 33.2, 18.5, 11.0. IR (ATR, cm^{-1}): 2943 m, 2865 m, 1724 s, 1463 w, 1269 s. MS (EI, relative intensity, %) *m*/*z*: 381 (29), 379 (31, $[M - {}^iPr]^+$), 301 (27), 299 (20), 273 (11), 271 (10), 257 (10), 236 (16), 235 (79), 193 (15), 177 (17), 135 (10), 105 (100). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{32}BrO_2Si$ 423.13495; Found 423.13500.

(3-Bromo-5-phenylpent-1-yn-1-yl)triisopropylsilane (3ad).



Pale yellow oil, 45.6 mg, 41% yield. R_f = 0.51 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.28 (m, 2H), 7.25–7.18 (c, 3H), 4.49 (t, *J* = 6.7 Hz, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.38–2.24 (m, 2H), 1.12–1.06 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.2, 128.6, 126.3, 105.6, 89.3, 41.5, 36.6, 33.5, 18.6, 11.2 (one signal is obscured by overlap with another signal). IR (ATR, cm^{-1}): 2943 m, 2865 m, 1461 m. MS (EI, relative intensity, %) *m*/*z*: 337 (17), 335 (17, $[M - {}^iPr]^+$), 255 (18), 227 (10), 213 (11), 109 (14) , 95 (16) , 91 (100). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{32}BrSi$ 379.14512; Found 379.14656.

2-[4-Bromo-6-(triisopropylsilyl)hex-5-yn-1-yl]isoindoline-1,3-dione (3ae).



Pale yellow oil, 61.5 mg, 44% yield. R_f = 0.51 (pentane/$CHCl_3$ = 3/2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.83 (m, 2H), 7.75–7.70 (m, 2H), 4.62 (t, *J* = 6.3 Hz, 1H), 3.75 (t, *J* = 6.7 Hz, 2H), 2.10–2.02 (m, 2H), 2.01–1.93 (m, 2H), 1.05 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 134.0, 132.0, 123.3, 105.2, 89.3, 36.9, 36.3, 26.5, 18.5, 11.1 (one signal is obscured by overlap with another signal). IR (ATR, cm^{-1}): 2943 w, 2865 w, 1773 w, 1714 s, 1394 m. MS (EI, relative intensity, %) *m*/*z*: 420 (27), 418 (27, [M − ^{i}Pr]$^+$), 341 (18), 340 (67), 339 (29), 338 (100), 160 (10), 130 (15). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{23}H_{33}BrNO_2Si$ 462.14584; Found 462.14528.

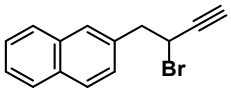
7. Large-Scale Preparation of 3a

$Pd(OAc)_2$ (168 mg, 0.75 mmol, 10 mol%), (2-bromoethynyl)triisopropylsilane (2.352 g, 9.0 mmol, 1.2 equiv), alkene (7.5 mmol, 1.157 g, 1 equiv) and toluene (25 mL) were added to a 100 mL of round-bottomed flask under air. After stirring the mixture at 75 °C for 20 h, the resulting solution was filtered through a pad of celite and further eluted with EtOAc. The crude mixture was concentrated under reduced pressure, and the resulting mixture was purified by preparative MPLC with Biotage® Sfär Silica HC chromatography cartridges (3 × 25 g) connected in series (eluent: hexane, flow rate: 80 mL/min) to give **3a** as a pale yellow oil (1.677 g, 54% yield).

8. Removal of Triisopropyisilyl Group

To a solution of **3a** (135 mg, 0.325 mmol) in THF (5 mL) at 0 °C, a mixture of TBAF (1 M in THF, 1 mL, 1 mmol) and AcOH (60.1 mg, 1 mmol) in THF (5 mL) added and the resulting mixture was stirred for 1.5 h. The reaction was quenched by adding water (10 mL), followed by Et_2O (10 mL). After separating the organic layer, the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude mixture was purified by silica-gel column chromatography (eluent: hexane/Et_2O = 100/0 to 50/1) to obtain **5a** as a pale yellow oil (67.8 mg, 81% yield).

2-(2-Bromobut-3-yn-1-yl)naphthalene (5a).



R_f = 0.07 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.77 (c, 3H), 7.72 (s, 1H), 7.50–7.43 (c, 2H), 7.38 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.70 (td, *J* = 7.3, 2.3 Hz, 1H), 3.52–3.43 (m, 2H), 2.65 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.2, 133.3, 132.6, 128.4, 128.1, 127.73, 127.67, 127.3, 126.2, 125.9, 82.0, 76.0, 45.6, 35.5. IR (ATR, cm^{-1}): 3289 w, 3054 w, 2359 w, 1509 w. MS (EI, relative intensity, %) *m*/*z*: 260 (14, [M + 2]$^+$), 258 (14, M$^+$), 179 (40), 178 (29), 142 (12), 141 (100), 115 (15), 89 (10). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{14}H_{12}Br$ 259.01169; Found 259.01008.

9. Mechanistic Studies

Monitoring Reaction Progress

$Pd(OAc)_2$ (33.7 mg, 0.15 mmol) or $Pd_2(dba)_3{\cdot}CHCl_3$[16] (77.7 mg, 0.075 mmol) was added to a 5 mL of volumetric flask, followed by the successive addition of **2** (472 mg, 1.8 mmol), **1a** (232 mg, 1.5 mmol), 1,1,2,2-tetrachloroethane (internal standard, 125 mg). Toluene-d_8 was added to the mixture up to a total volume of 5 mL and the resulting mixture was sonicated, after which 0.50 mL of the solution was transferred via a micro syringe to a NMR tube equipped with a J. Young valve. Each reaction mixture was heated at 75 °C and cooled on an ice bath every 5 minutes. Concentrations of **3a** were determined by ^{1}H NMR analysis. Each reaction was repeated three times, and the average values of the concentrations of **3a** versus time were respectively plotted (Figure S2).

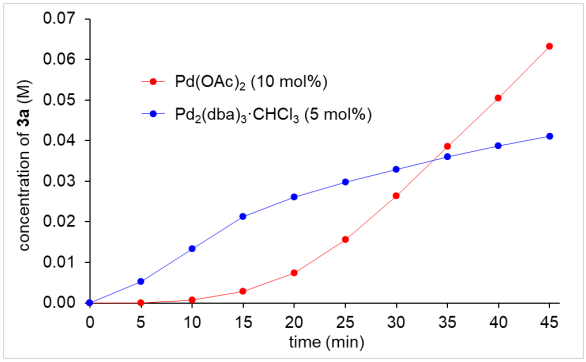
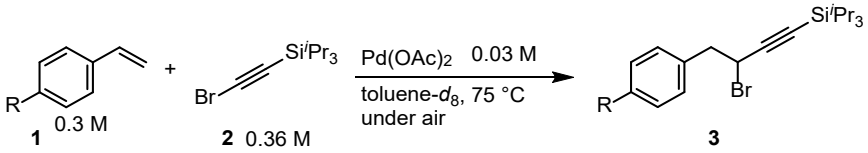


Figure S2. Monitoring the initial progress of Pd-catalyzed 1,1-alkynylbromination of **1a**.

Hammett Plot



R	σ_p	k_R 1	k_R 2	k_R 3	Average k_R	Average $\log(k_R/k_H)$
Me	**−0.17**	**0.00846**	**0.00804**	**0.00862**	**0.00837**	**0.0767**
H	**0**	**0.00727**	**0.00712**	**0.00666**	**0.00702**	**0**
F	**0.06**	**0.00685**	**0.00651**	**0.00632**	**0.00656**	**−0.0292**
OAc	**0.31**	**0.00539**	**0.00555**	**0.00535**	**0.00543**	**−0.111**
CF_3	**0.54**	**0.00371**	**0.00395**	**0.00403**	**0.00390**	**−0.256**

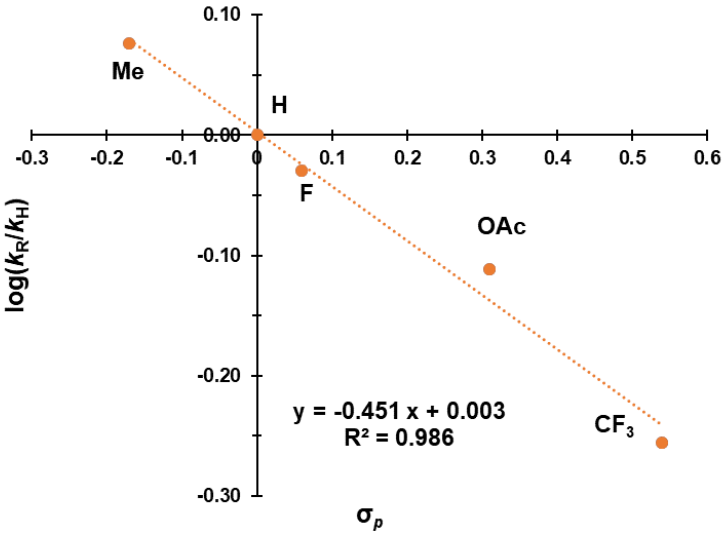


Figure S3. Hammett plot.

Deuterium-Labeling Experiments

^{1}H NMR spectra of 1a and deuterated starting materials ([D_1]-1a and [D_2]-1a).

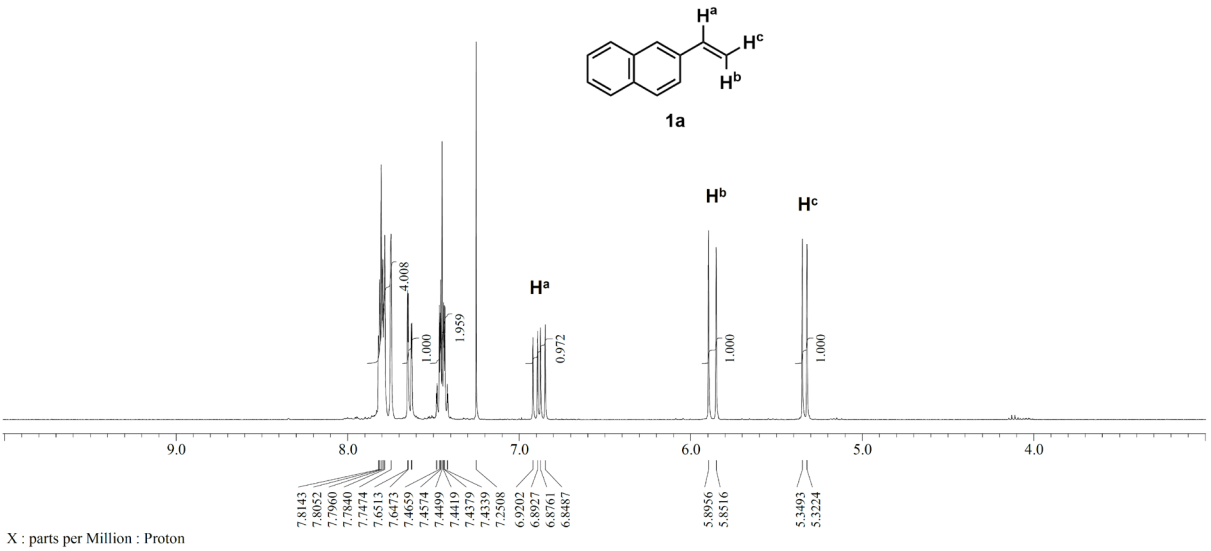


Figure S4. ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$).

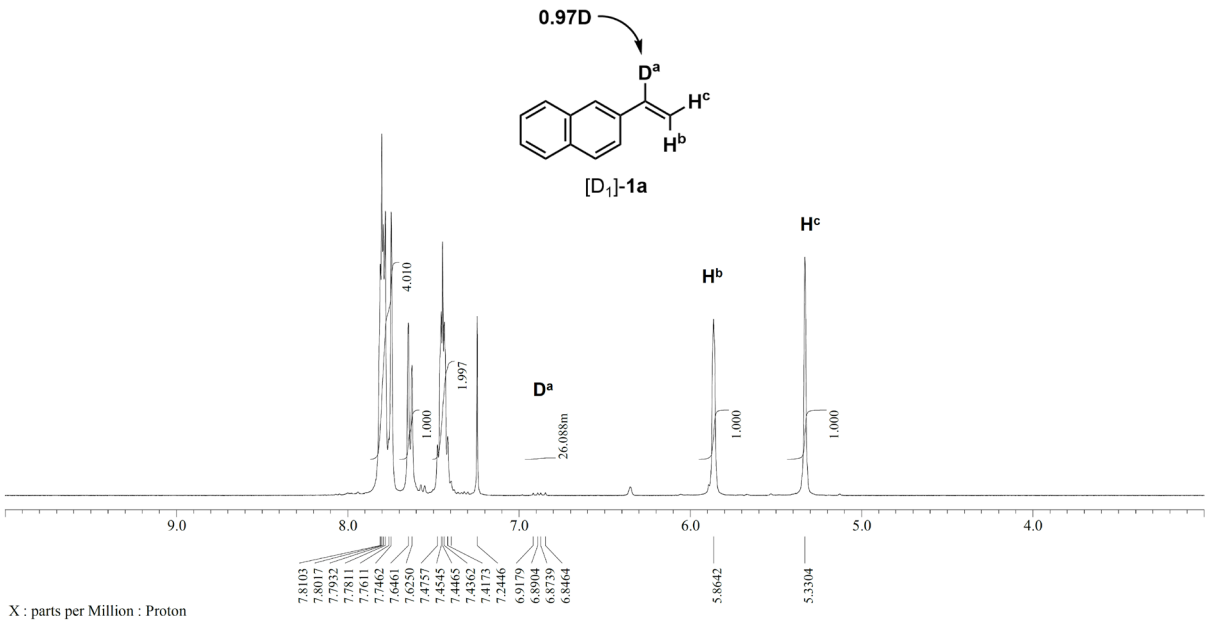


Figure S5. ^{1}H NMR spectrum of [D_1]-**1a** (400 MHz, $CDCl_3$).

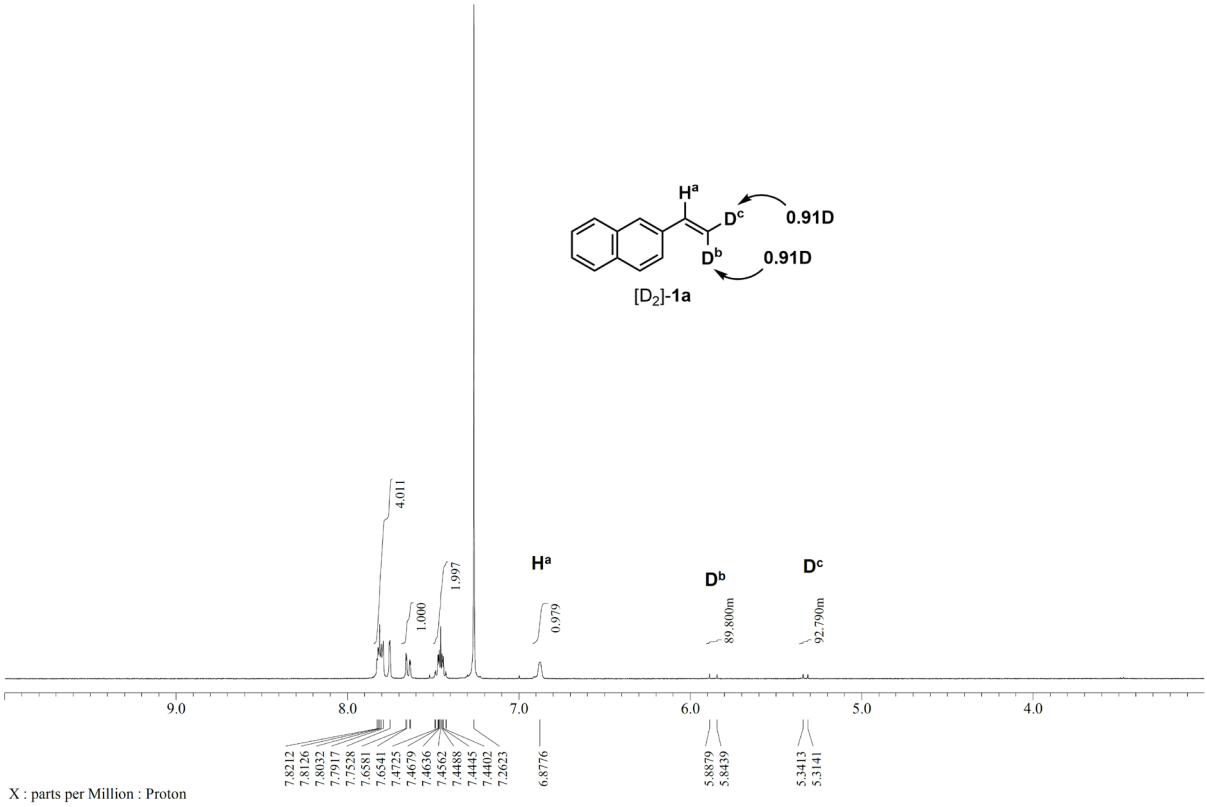


Figure S6. ^{1}H NMR spectrum of [D_2]-**1a** (400 MHz, $CDCl_3$).

Reaction of the deuterated substrate [D_1]-1a.

The reaction of [D_1]-**1a** (46.9 mg, 0.3 mmol) with **2** was performed by following the General Procedure for the Pd-Catalyzed 1,1-Alkynylbromination of Alkenes under air, giving the corresponding 1,1-alkynylbromination product [D_1]-**3a** as a pale yellow oil (73.3 mg, 58% yield). The obtained [D_1]-**3a** was analyzed by ^{1}H and ^{2}H NMR spectroscopies to confirm the incorporation of deuterium atoms (Figure S7 and S8). According to the ^{1}H NMR spectrum for **3a**, the integral of the aromatic proton's singlet at 7.73 ppm was set to 1.00.

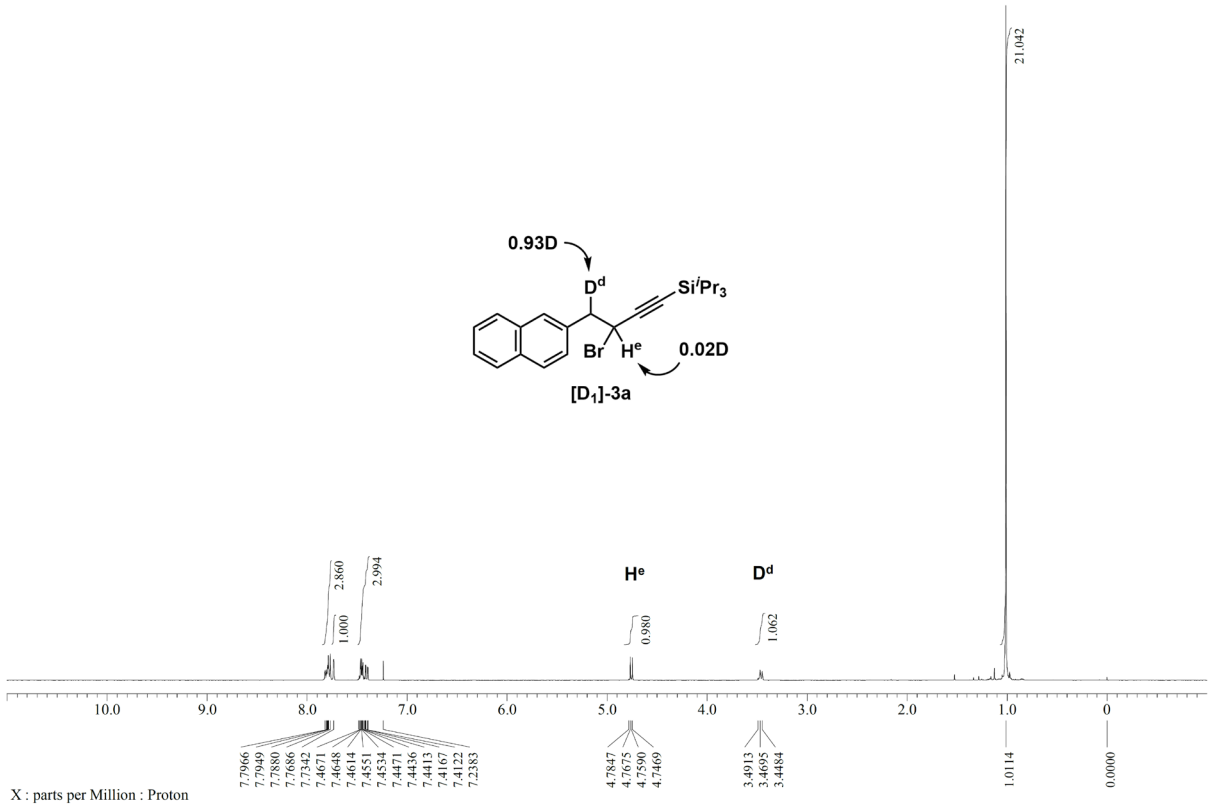


Figure S7. ^{1}H NMR spectrum of [D_1]-**3a** (400 MHz, $CDCl_3$).

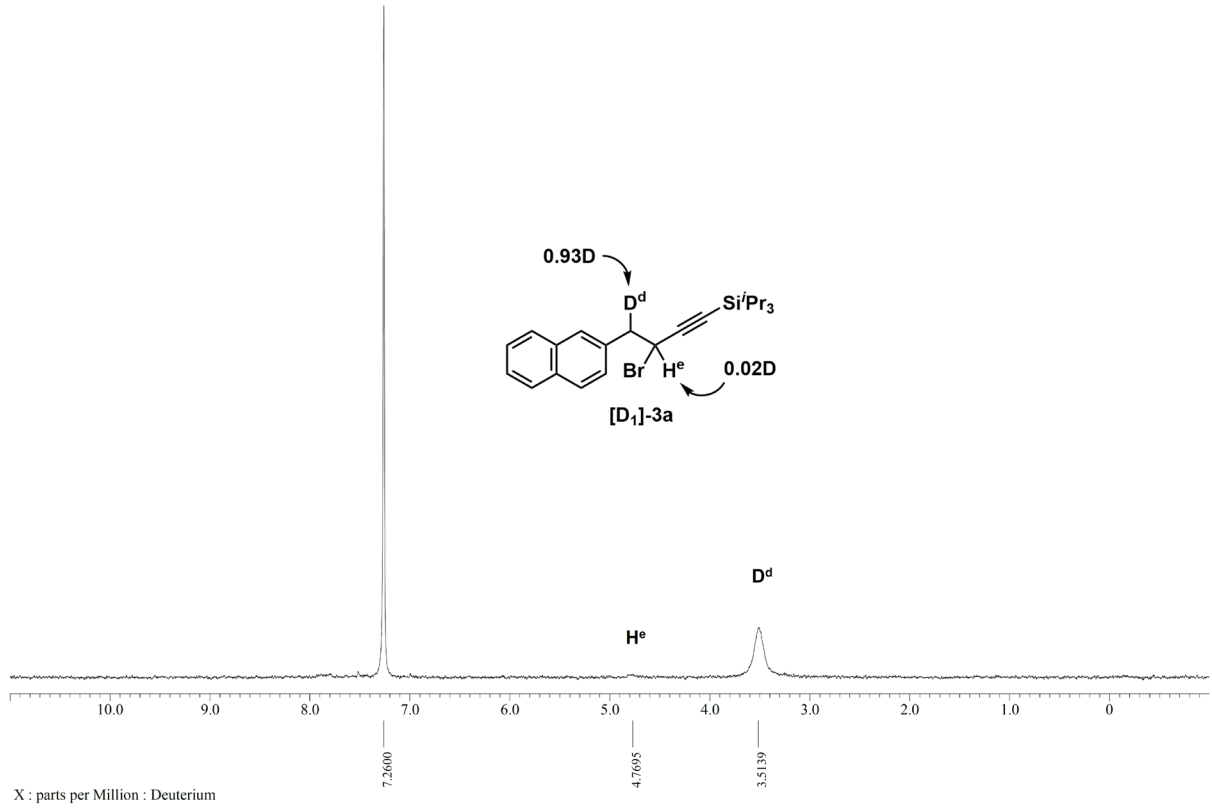


Figure S8. ^{2}H NMR spectrum of [D_1]-**3a** (61 MHz, $CHCl_3$/$CDCl_3$).

Reaction of the deuterated substrate [D_2]-1a.
The reaction of [D_2]-**1a** (46.9 mg, 0.3 mmol) with **2** was performed by following the General Procedure for the Pd-Catalyzed 1,1-Alkynylbromination of Alkenes under air, giving the corresponding 1,1-alkynylbromination product [D_2]-**3a** as a pale yellow oil (80.0 mg, 64% yield). The obtained [D_2]-**3a** was analyzed by ^{1}H and ^{2}H NMR spectroscopies to confirm the incorporation of deuterium atoms (Figure S9 and S10). According to the ^{1}H NMR spectrum for **3a**, the integral of the aromatic proton's singlet at 7.73 ppm was set to 1.00.

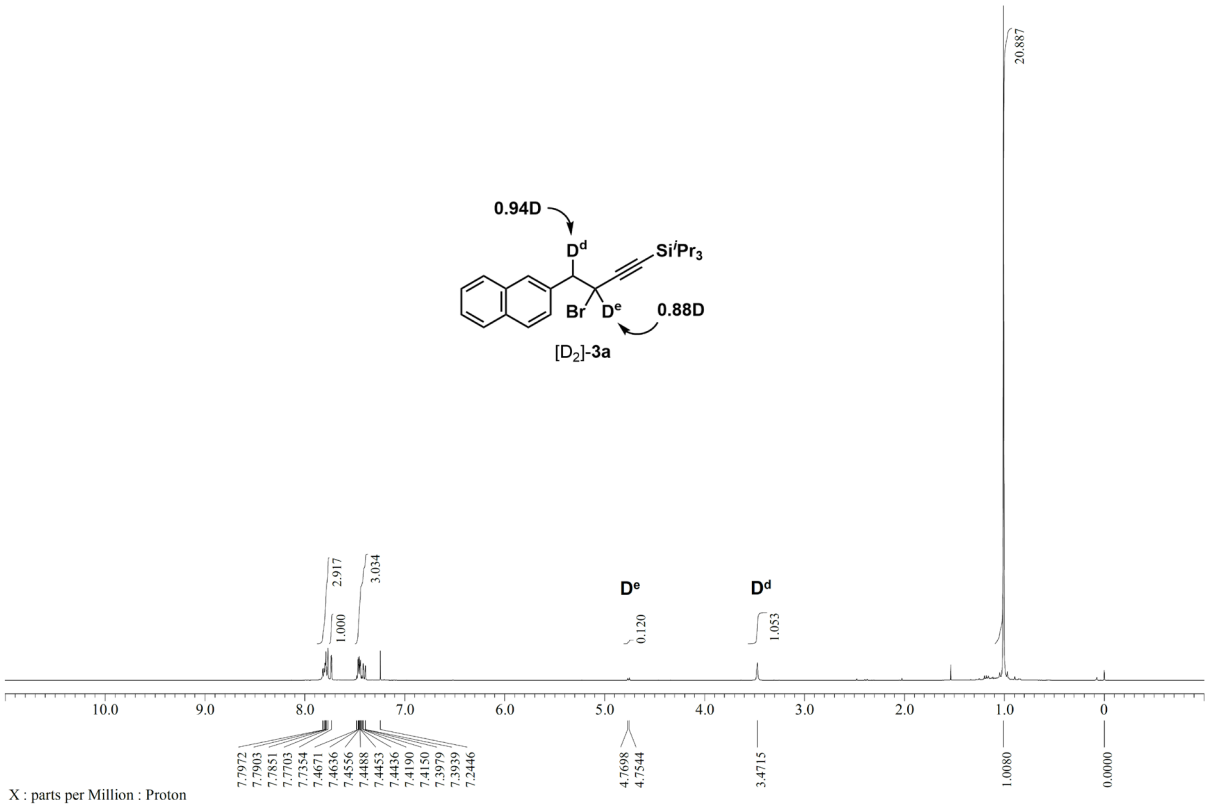


Figure S9. ^{1}H NMR spectrum of [D_2]-**3a** (400 MHz, $CDCl_3$).

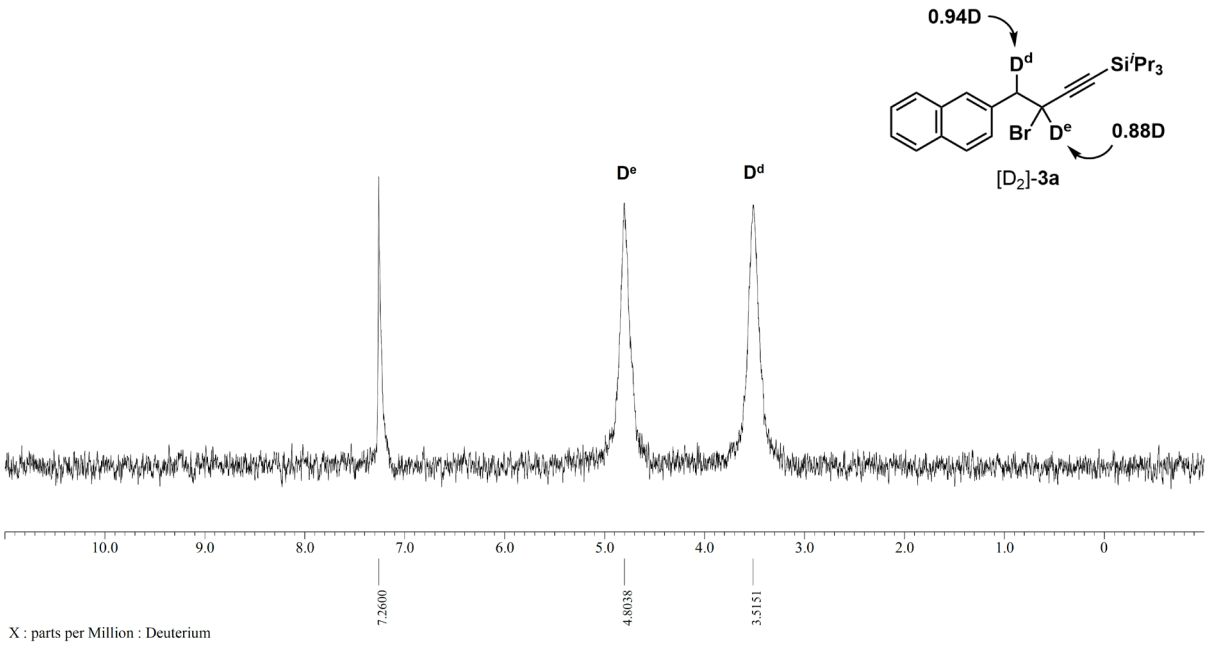


Figure S10. ^{2}H NMR spectrum of [D_2]-**3a** (61 MHz, $CHCl_3$/$CDCl_3$).

Reaction of the deuterated substrate [D_2]-1a in the absence of 2.

The reaction of [D_2]-**1a** (47.2 mg, 0.3 mmol) was performed by following the General Procedure for the Pd-Catalyzed 1,1-Alkynylbromination of Alkenes in the absence of **2** under air. The resulting crude mixture (54.5 mg) was analyzed by ^{1}H NMR to determine the 86% recovery of [D_2]-**1a**. The incorporation of deuterium atoms in the recovered [D_2]-**1a** was confirmed by ^{1}H and ^{2}H NMR analysis (Figure S11 and S12). According to the ^{1}H NMR spectrum for **1a** (Figure S4), the integral of the aromatic proton's multiplet at 7.65–7.62 ppm was set to 1.00.

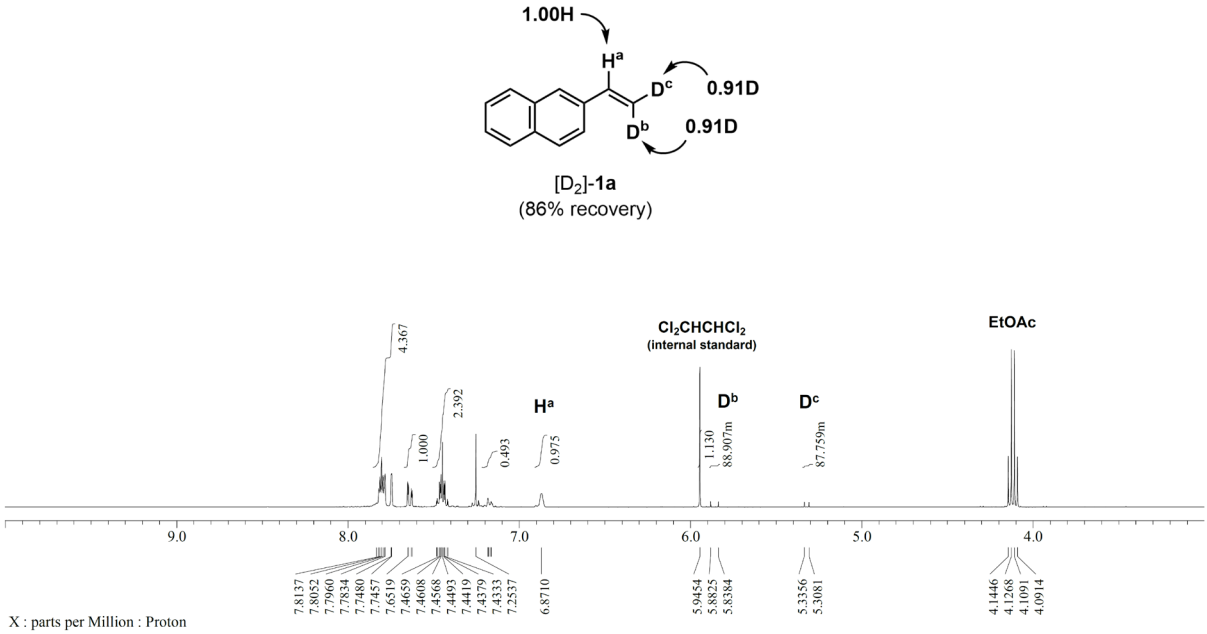


Figure S11. ^{1}H NMR spectrum of the crude mixture obtained from the reaction of [D_2]-**1a** in the absence of **2** (400 MHz, $CDCl_3$).

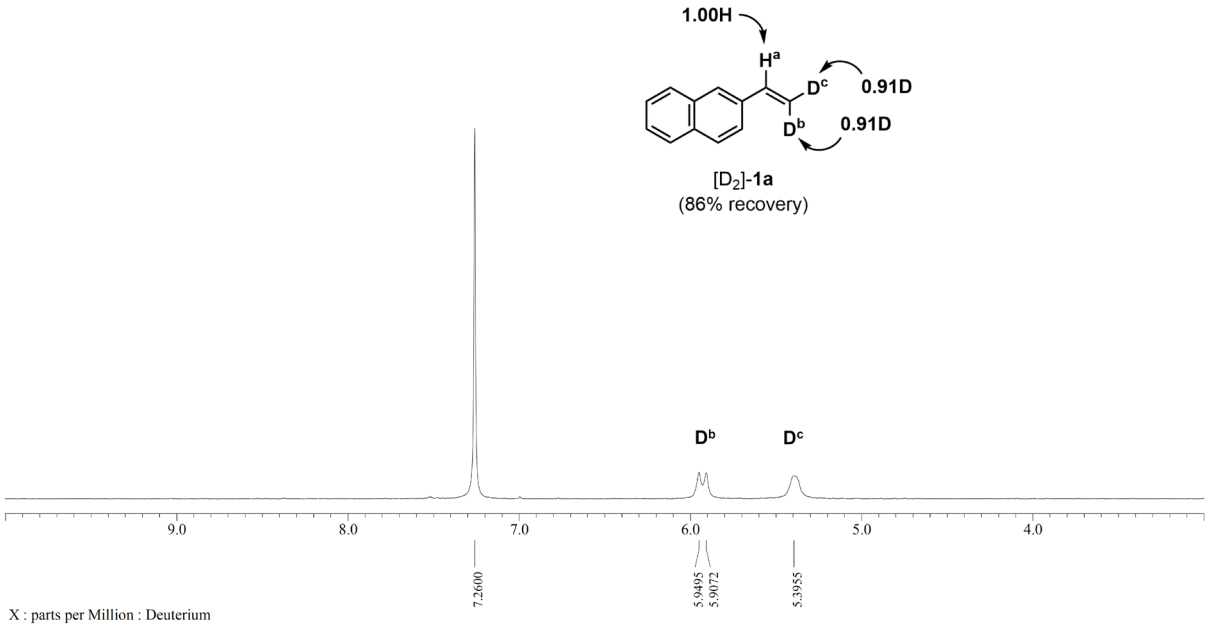


Figure S12. ^{2}H NMR spectrum of the crude mixture obtained from the reaction of [D_2]-**1a** in the absence of **2** (61 MHz, $CHCl_3$/$CDCl_3$).

^{1}H NMR spectra of 1s and deuterated starting materials (α-[D_1]-1s, (*E*)-[D_1]-1s, and (*Z*)-[D_1]-1s).

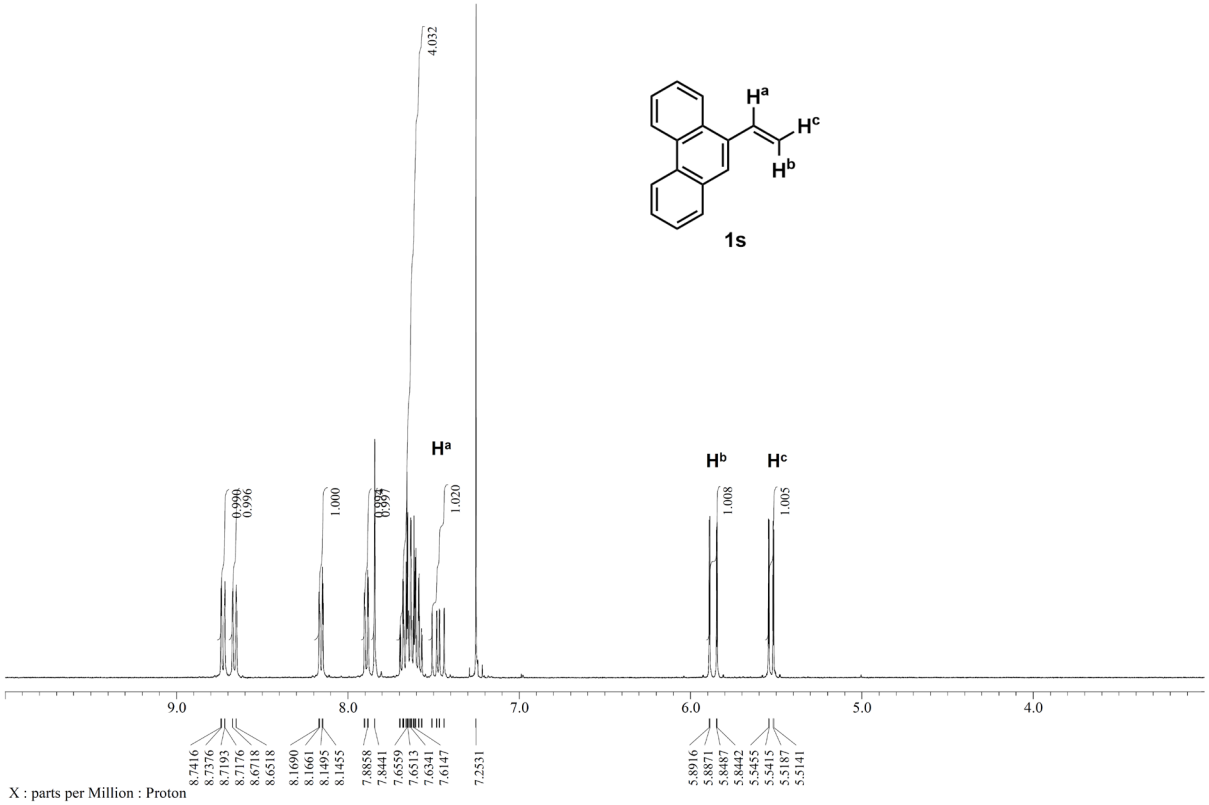


Figure S13. ^{1}H NMR spectrum of **1s** (400 MHz, $CDCl_3$).

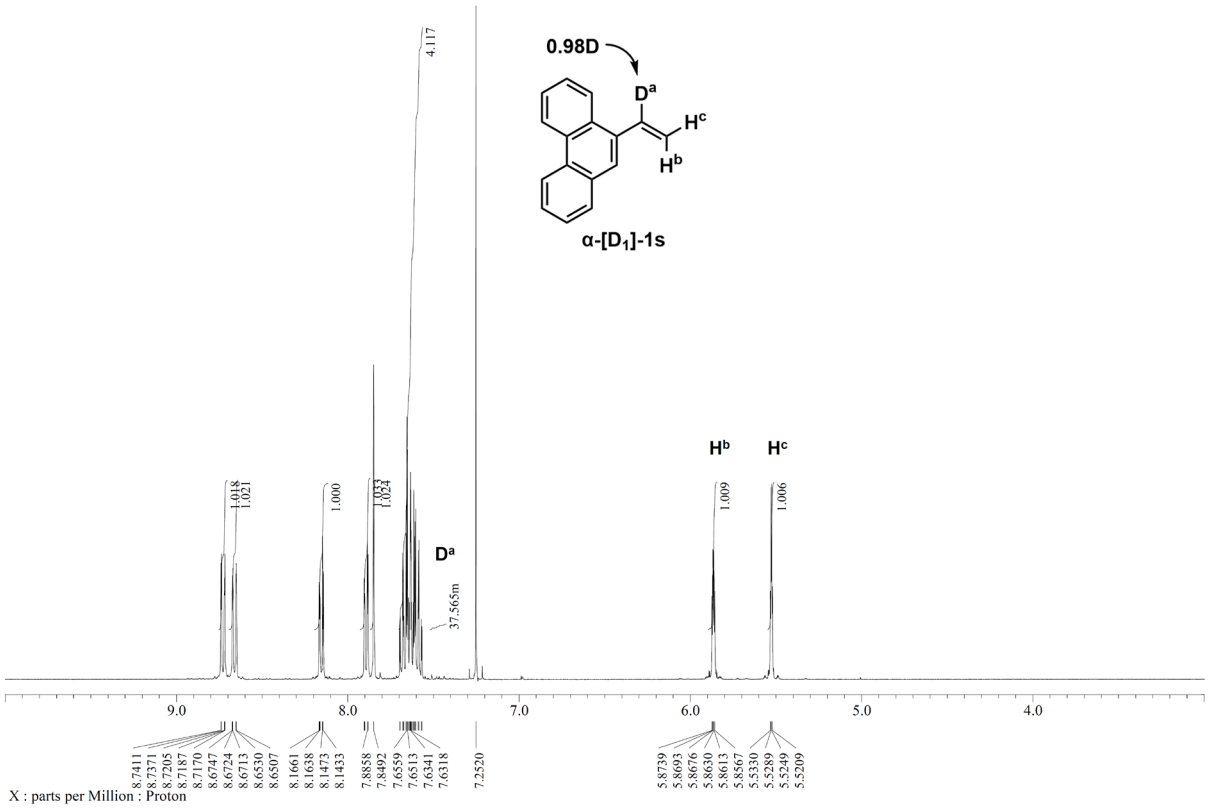


Figure S14. ^{1}H NMR spectrum of α-[D_1]-**1s** (400 MHz, $CDCl_3$).

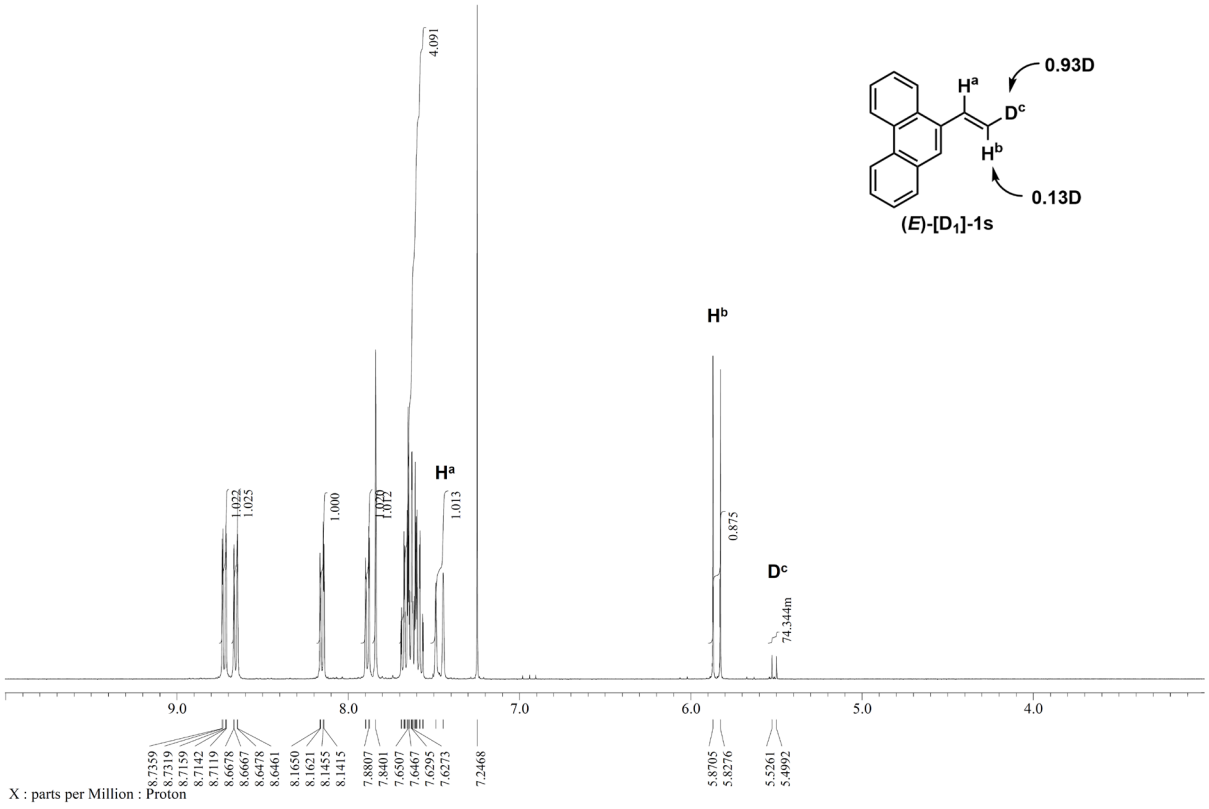


Figure S15. ^{1}H NMR spectrum of (*E*)-[D_1]-**1s** (400 MHz, $CDCl_3$).

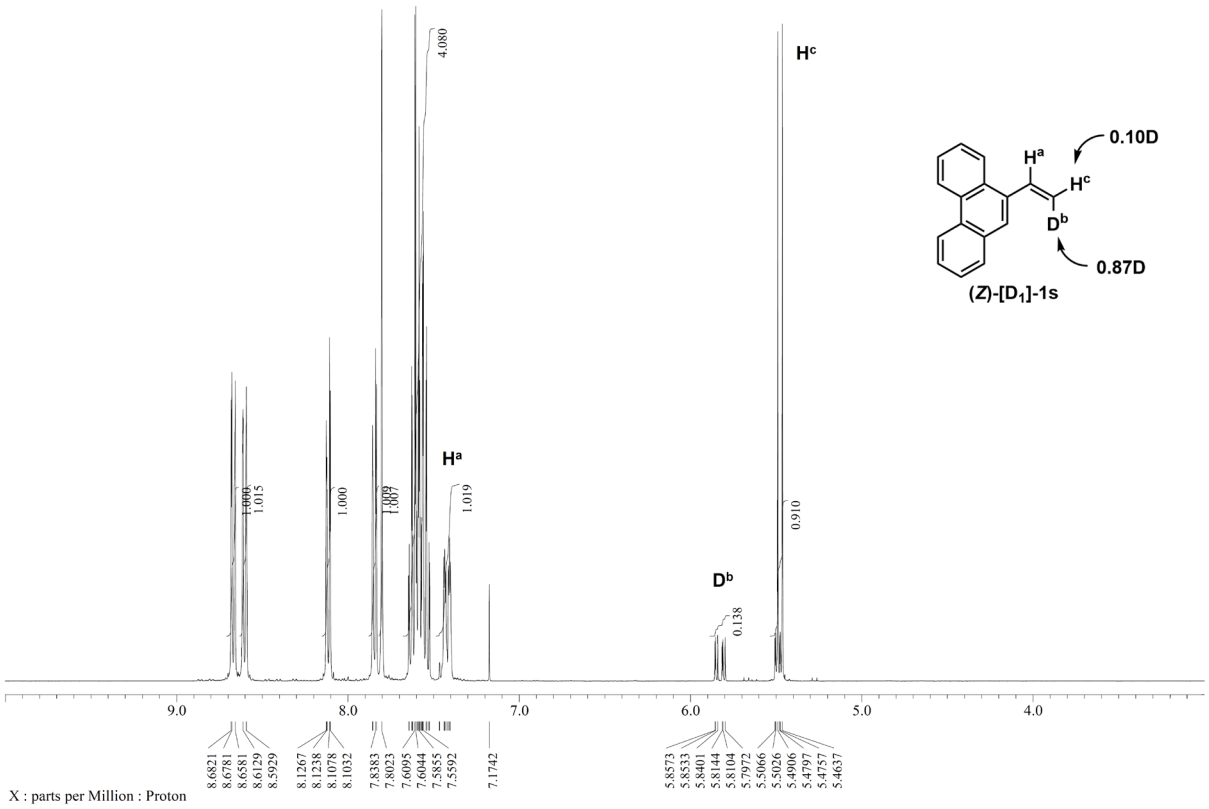


Figure S16. ^{1}H NMR spectrum of (*Z*)-[D_1]-**1s** (400 MHz, $CDCl_3$).

Reaction of the deuterated substrate α-[D_1]-1s.

The reaction of α-[D_1]-**1s** (61.6 mg, 0.3 mmol) with **2** was performed by following the General Procedure for the Pd-Catalyzed 1,1-Alkynylbromination of Alkenes under air for 48 h, giving the corresponding 1,1-alkynylbromination product [D_1]-**3s** as a pale yellow oil (84.6 mg, 60% yield). The obtained [D_1]-**3s** was analyzed by ^1H and ^2H NMR spectroscopies to confirm the incorporation of deuterium atoms (Figure S17 and S18). According to the ^1H NMR spectrum for **3s**, the integral of the aromatic proton's multiplet at 8.04–8.00 ppm was set to 1.00.

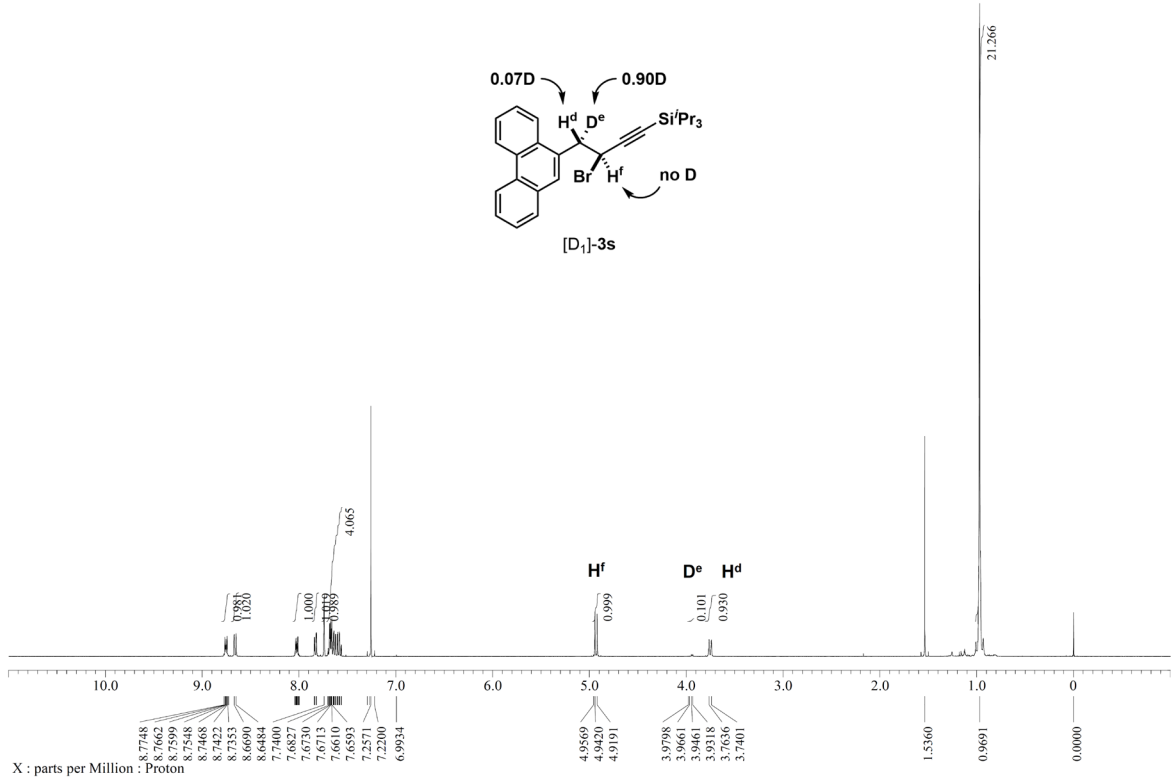


Figure S17. ^1H NMR spectrum of [D_1]-**3s** (400 MHz, $CDCl_3$).

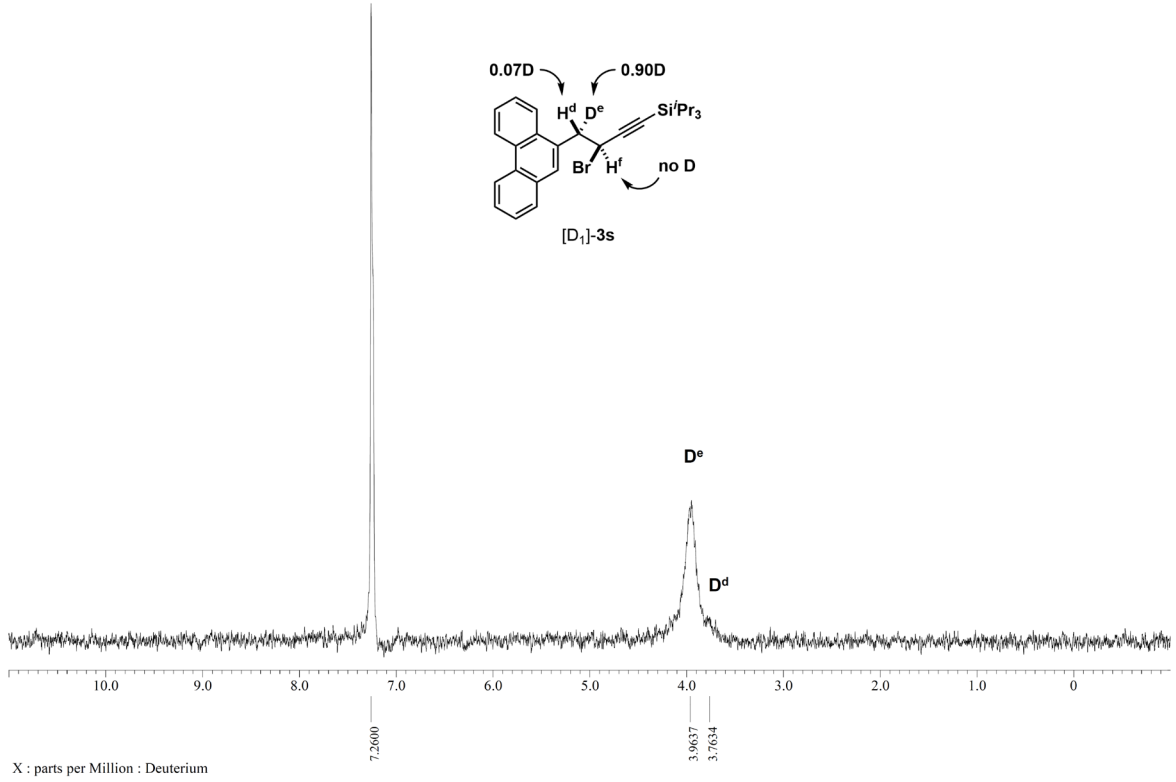


Figure S18. ^2H NMR spectrum of [D_1]-**3s** (61 MHz, $CHCl_3/CDCl_3$).

Reaction of the deuterated substrate (*E*)-[D_1]-1s.

The reaction of (*E*)-[D_1]-**1s** (61.6 mg, 0.3 mmol) with **2** was performed by following the General Procedure for the Pd-Catalyzed 1,1-Alkynylbromination of Alkenes under air for 48 h, giving the corresponding 1,1-alkynylbromination product [D_1]-**3s'** as a pale yellow oil (52.9 mg, 38% yield). The obtained [D_1]-**3s'** was analyzed by ^{1}H and ^{2}H NMR spectroscopies to confirm the incorporation of deuterium atoms (Figure S19 and S20). According to the ^{1}H NMR spectrum for **3s**, the integral of the aromatic proton's multiplet at 8.04–8.00 was set to 1.00.

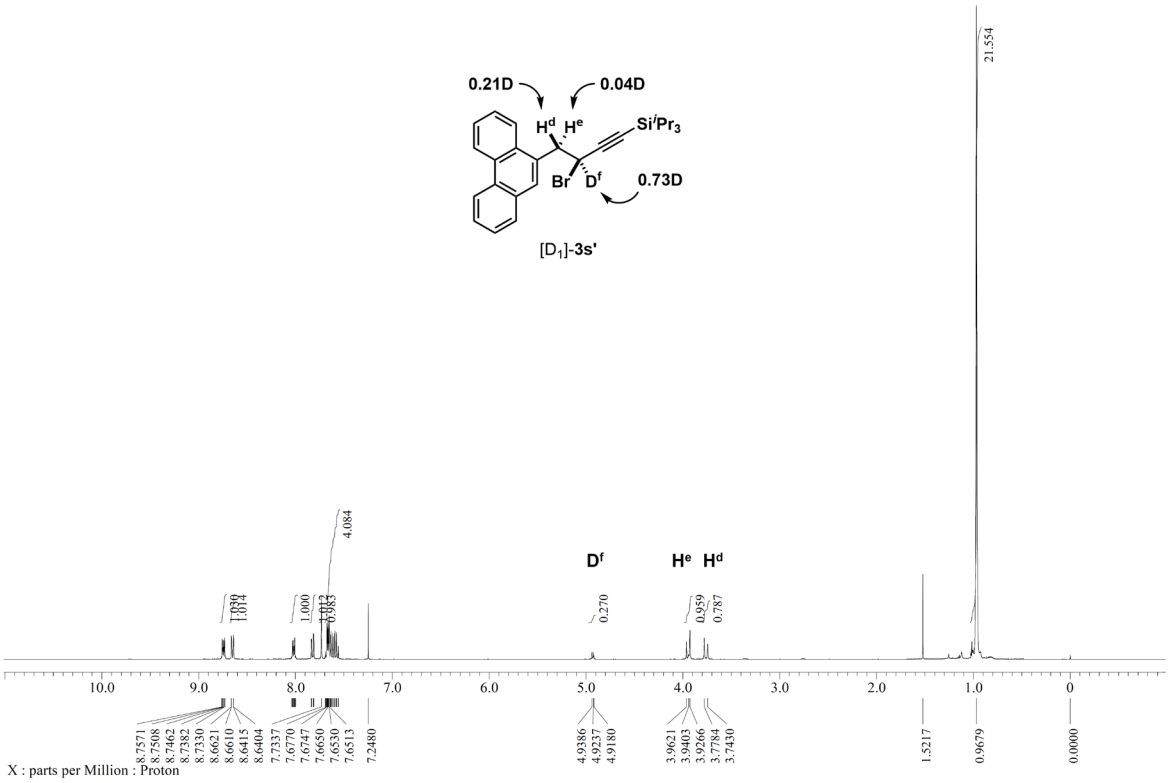


Figure S19. ^{1}H NMR spectrum of [D_1]-**3s'** (400 MHz, $CDCl_3$).

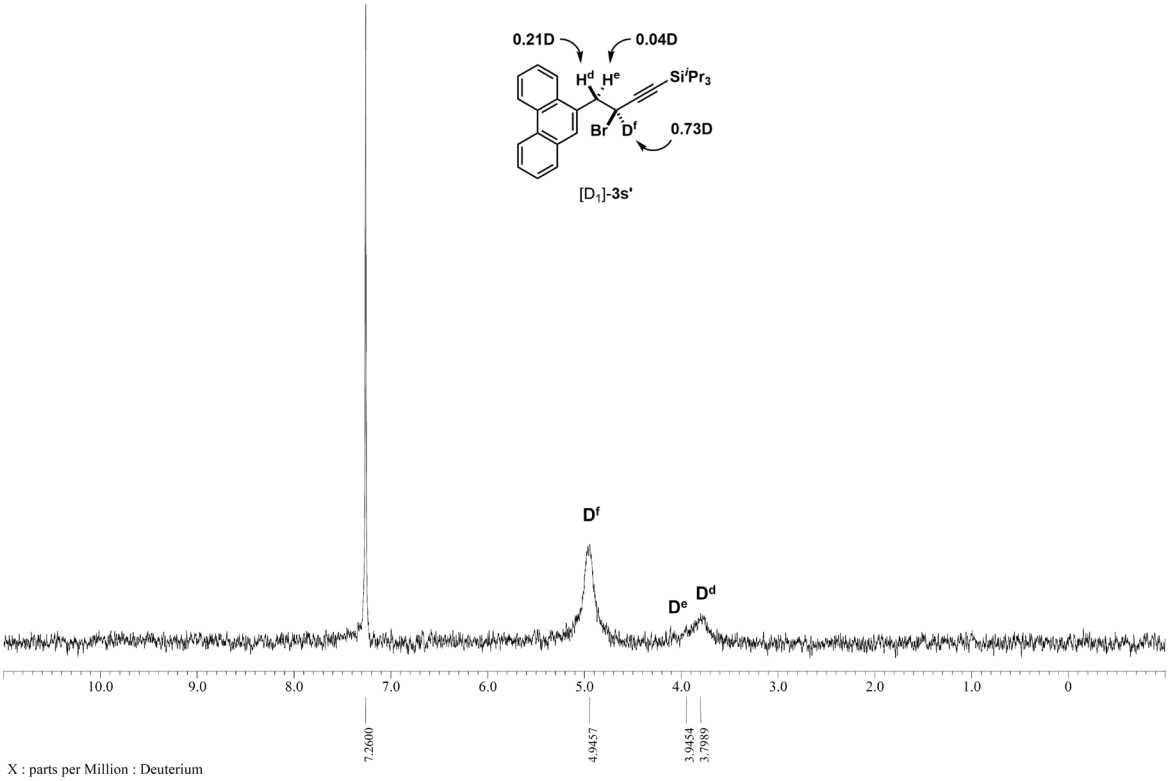


Figure S20. ^{2}H NMR spectrum of [D_1]-**3s'** (61 MHz, $CHCl_3/CDCl_3$).

Reaction of the deuterated substrate (*Z*)-[D_1]-1s.

The reaction of (*Z*)-[D_1]-**1s** (61.6 mg, 0.3 mmol) with **2** was performed by following the General Procedure for the Pd-Catalyzed 1,1-Alkynylbromination of Alkenes under air for 48 h, giving the corresponding 1,1-alkynylbromination product [D_1]-**3s''** as a colorless oil (59.4 mg, 42% yield). The obtained [D_1]-**3s''** was analyzed by ^1H and ^2H NMR spectroscopies to confirm the incorporation of deuterium atoms (Figure S21 and S22). According to the ^1H NMR spectrum for **3s**, the integral of the aromatic proton's multiplet at 8.04–8.00 ppm was set to 1.00.

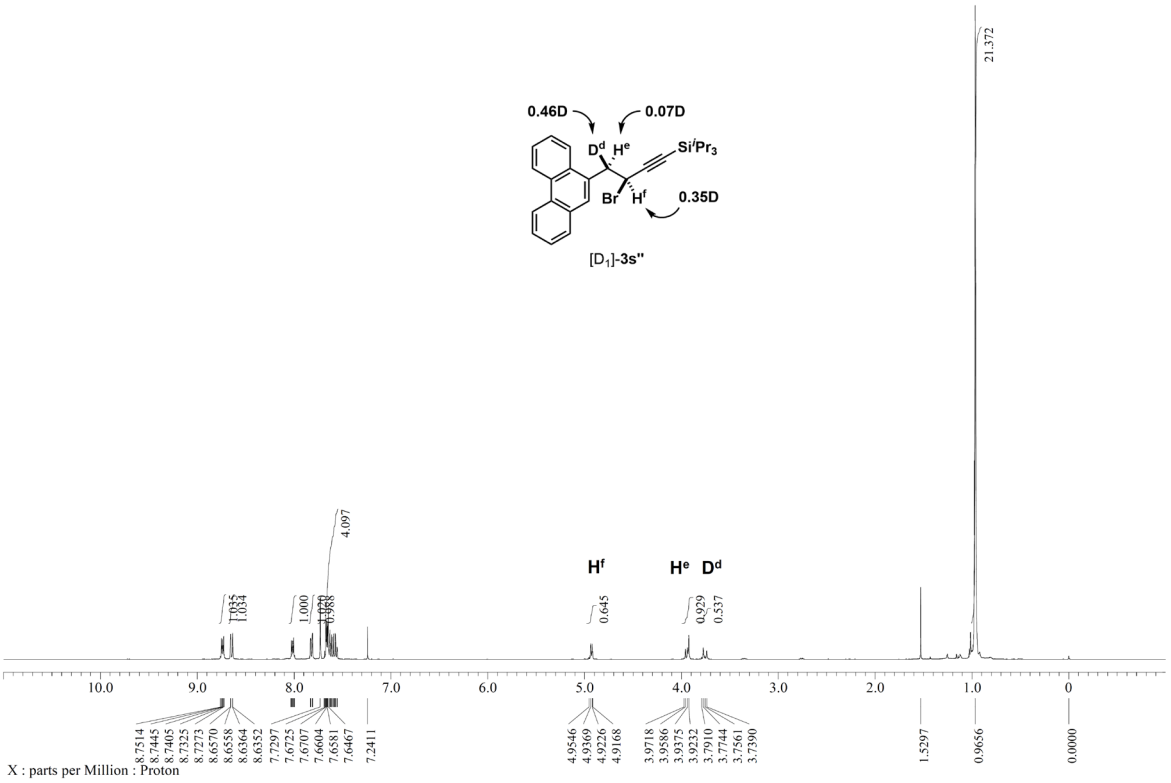


Figure S21. ^1H NMR spectrum of [D_1]-**3s''** (400 MHz, $CDCl_3$).

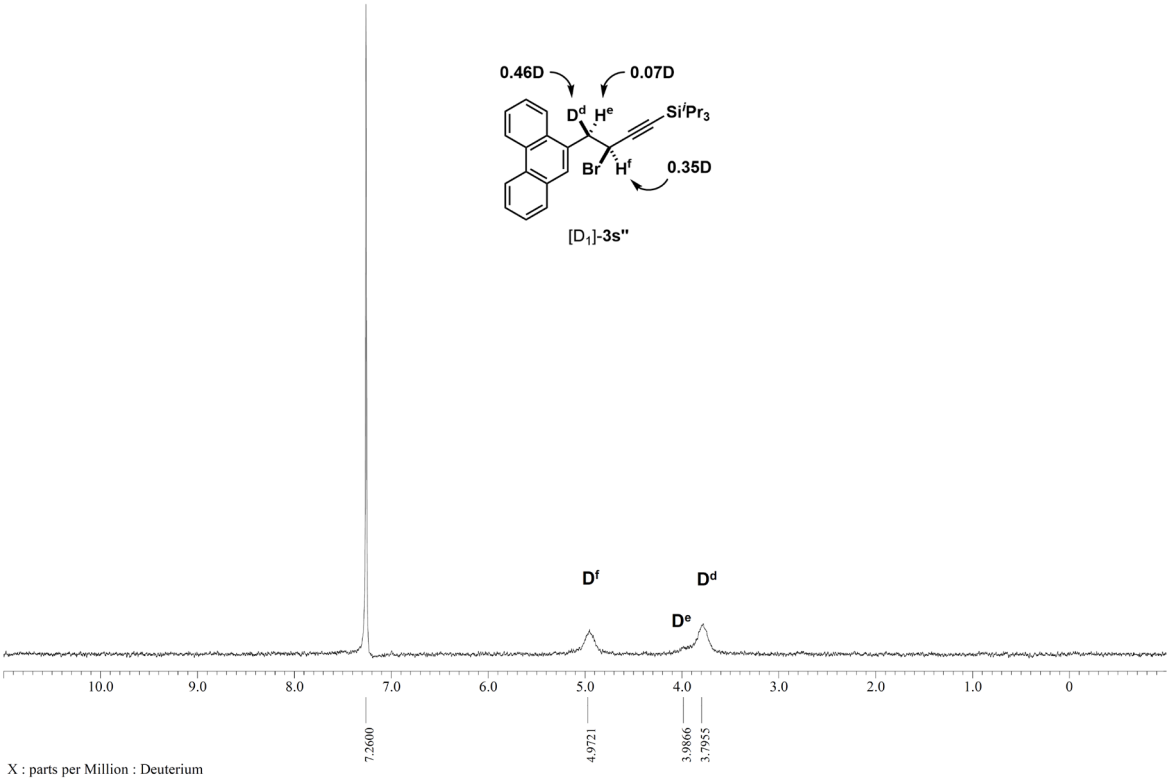
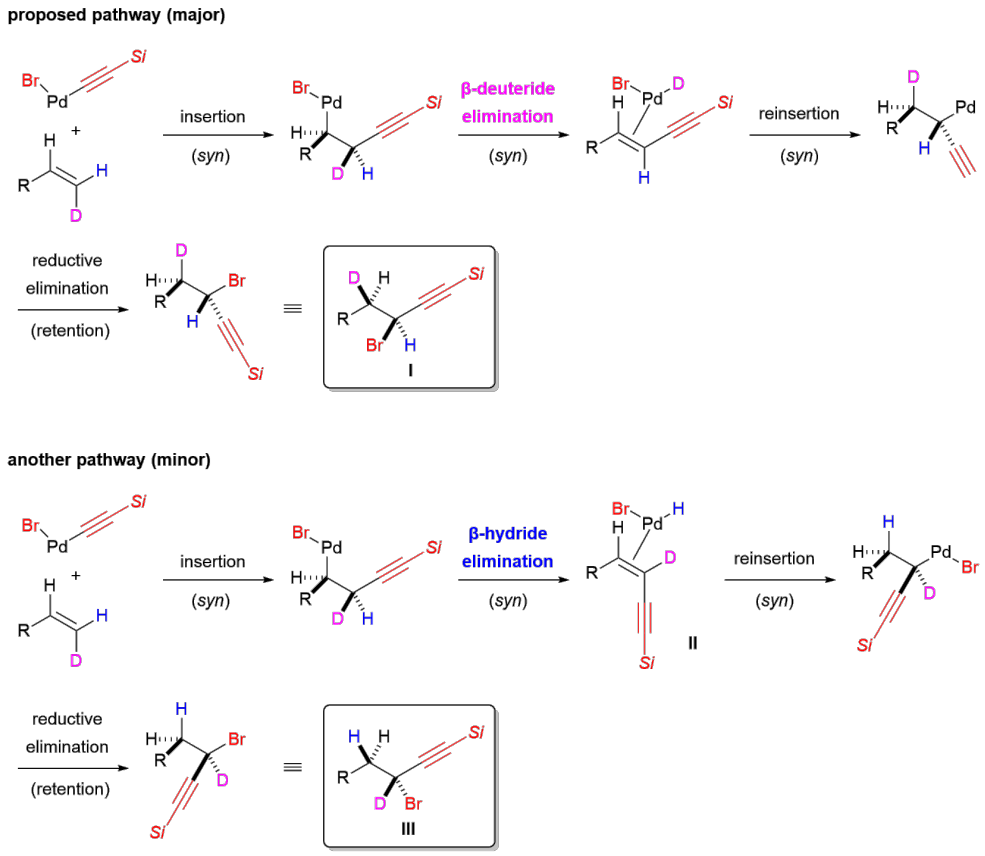


Figure S22. ^2H NMR spectrum of [D_1]-**3s''** (61 MHz, $CHCl_3/CDCl_3$).

Deuterium scrambling in the reaction of (Z)-[D_1]-1s.

The reaction of (*Z*)-[D_1]-**1s** with **2** gave [D_1]-**3s**" with deuterium scrambling (Scheme 6f), indicating that another reaction pathway appears to be involved as a minor pathway in this reaction. When the reaction proceeds through the "proposed pathway", the 1,1-alkynylbromination product **I** is formed via the migration of the deuterium atom at the β-carbon to the α-carbon. On the other hand, the "another pathway" proceeds via the β-hydride elimination to give *cis*-intermediate **II**, which gives 1,1-alkynylbromination product **III** with the deuterium at the β-carbon being retained. Although the formation of *cis*-alkene is a less favorable process, the cleavage of C–H bond may be preferable to that of C–D bond in the β-hydride elimination,[17] which supports the involvement of "another pathway". Therefore, we propose that the progress of both pathways in parallel should provide the deuterium scrambling.



Scheme S1. Plausible reaction pathways for the reaction of (*Z*)-[D1]-**1s** (*Si* = Si^iPr_3).

Crossover Experiments

Reaction of 1a in the presence of 4z.
$Pd(OAc)_2$ (0.7 mg, 0.03 mmol), (bromoethynyl)triisopropylsilane **2** (94.6 mg, 0.362 mmol), alkene **1a** (24.0 mg, 0.155 mmol), alkynylalkene **4z** (49.5 mg, 0.151 mmol) and toluene (1 mL) were successively added to a 10 mL-sample vial equipped with a Teflon-sealed screwcap under air. After stirring the mixture at 75 °C for 20 h, the resulting solution was filtered through a pad of celite and further eluted with EtOAc. The filtrate was concentrated under reduced pressure, and the resulting mixture was purified by preparative MPLC (flow rate: 40 mL/min) to obtain **3a** (33.6 mg, 52% yield) along with the 97% recovery of **4z** (48.1 mg).

Reaction of 1z in the presence of 4a.
$Pd(OAc)_2$ (0.7 mg, 0.03 mmol), (bromoethynyl)triisopropylsilane **2** (96.8 mg, 0.370 mmol), alkene **1z** (23.2 mg, 0.157 mmol), alkynylalkene **4a** (51.5 mg, 0.153 mmol) and toluene (1 mL) were successively added to a 10 mL-sample vial equipped with a Teflon-sealed screwcap under air. After stirring the mixture at 75 °C for 20 h, the resulting solution was filtered through a pad of celite and further eluted with EtOAc. The filtrate was concentrated under reduced pressure, and the resulting mixture was purified by preparative MPLC (flow rate: 40 mL/min) to obtain **3z** (39.2 mg, 61% yield) along with the 81% recovery of **4a** (41.8 mg).

10. Computational Studies

Computational Methods

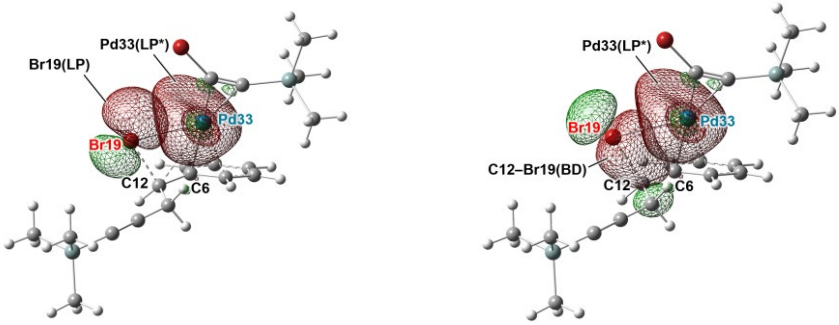
All calculations were performed with the Gaussian 16[18] or the Gaussian 09[19] program. All geometry optimizations and normal coordinate analyses at stationary points were performed using B3LYP functional[20] with the LANL2DZ effective core potential for Pd and Br[21] and the 6-31G(d) basis set for the others.[22] Each reported minimum has no imaginary frequency and each transition state structure has one imaginary frequency. Intrinsic reaction coordinate (IRC) analyses[23] from transition states to minima were used for confirming the reaction pathways. For single-point energy calculations, the M06L functional[24] was conducted using def2-TZVP[25] as a basis set on all atoms. For both optimization and single-point energy calculation, the solvation effects of toluene (ε = 2.3741) were added using the integral equation formalism model (IEFPCM) calculation with radii and non-electrostatic terms for Truhlar and coworkers' solvation model based on density (SMD).[26] Energy values were shown by the used of Gibbs' free energies (T = 298.15 K and p = 1 atm).

Table S2. Calculated energies and imaginary frequencies for the reaction pathways in Figure 1.

geometry	$E_{SMD/B3LYP}$ [Hartree][a]	$H_{corr\text{-}SMD/B3LYP}$ [Hartree][b]	$G_{corr\text{-}SMD/B3LYP}$ [Hartree][c]	$E_{SMD/M06L}$ [Hartree][d]	Im. Freq. [cm^{-1}][e]
INT0	-1622.52412578	0.407435	0.286280	-9306.69512925	—
2'	-498.572671591	0.133942	0.084157	-3059.53882788	—
INT1	-1123.96186835	0.272179	0.183227	-6247.15922244	—
TS_{1-2}	-1123.93118543	0.270889	0.181768	-6247.11731235	-128.1859
INT2	-1123.95146610	0.272260	0.180872	-6247.13463498	—
1b	-309.657014718	0.141487	0.102676	-309.717365858	—
INT3	-1433.62865388	0.416468	0.309376	-6556.89015178	—
TS_{3-4}	-1433.61020571	0.415116	0.307819	-6556.86867063	-384.7426
INT4	-1433.65456992	0.417380	0.312559	-6556.91284719	—
INT5	-1433.65964283	0.417758	0.312749	-6556.91463525	—
TS_{5-6}	-1433.62755961	0.412111	0.306879	-6556.88581901	-626.6273
INT6	-1433.63430160	0.413985	0.307243	-6556.89490491	—
INT7	-1433.63540101	0.414190	0.306521	-6556.89442218	—
TS_{7-8}	-1433.62695620	0.412052	0.306257	-6556.88287466	-583.4155
INT8	-1433.66159020	0.417520	0.310591	-6556.91376528	—
INT9	-1433.66777419	0.417573	0.312869	-6556.92525902	—
TS_{9-10}	-1433.63416456	0.415543	0.308731	-6556.88772763	-109.9679
INT10	-1433.66061134	0.417587	0.310585	-6556.91446106	—
3b'	-808.279588560	0.279709	0.209962	-3369.29652852	—
INT11	-1433.65472398	0.417297	0.308366	-6556.90879424	—
TS_{11-12}	-1433.62272751	0.416065	0.310860	-6556.87820743	-127.2876
INT12	-1433.63913360	0.417671	0.308244	-3807.07286684	—

(a) The electronic energy calculated by B3LYP in toluene solvent. (b) The thermal correction to enthalpy calculated by B3LYP in toluene solvent. (c) The thermal correction to Gibbs free energy calculated by B3LYP in toluene solvent. (d) The electronic energy calculated by M06L in toluene solvent. (e) The B3LYP calculated imaginary frequencies for the transition states.

Natural Bond Orbital (NBO) Analysis[27] of $TS_{11\text{-}12}$



Br19(LP) → Pd33(LP*)
E(2) = 23.18 kcal/mol

C12–Br19(BD) → Pd33(LP*)
E(2) = 16.43 kcal/mol

Figure S23. Representative donor-acceptor interactions among Pd, Br, and C(benzyl) atoms in **$TS_{11\text{-}12}$** based on NBO analysis.

We evaluated the transition state for the reductive elimination of C(benzyl)–Br bond (**$TS_{11\text{-}12}$**) using an NBO analysis. The NBO analysis revealed a donor-acceptor interaction from the lone pair of the Br19 atom to the *s*-orbital of the Pd33 atom. In addition, an interaction from the *σ*-orbital of C12–Br19 to *s*-orbital of Pd33 atom was also involved in **$TS_{11\text{-}12}$**. These results indicate that Pd, Br, and C12 (e.g. C(benzyl)) atoms interact with each other to produce a three-membered transition state.

DFT Studies on the Reaction Pathway Catalyzed by a Pd-Alkene Complex

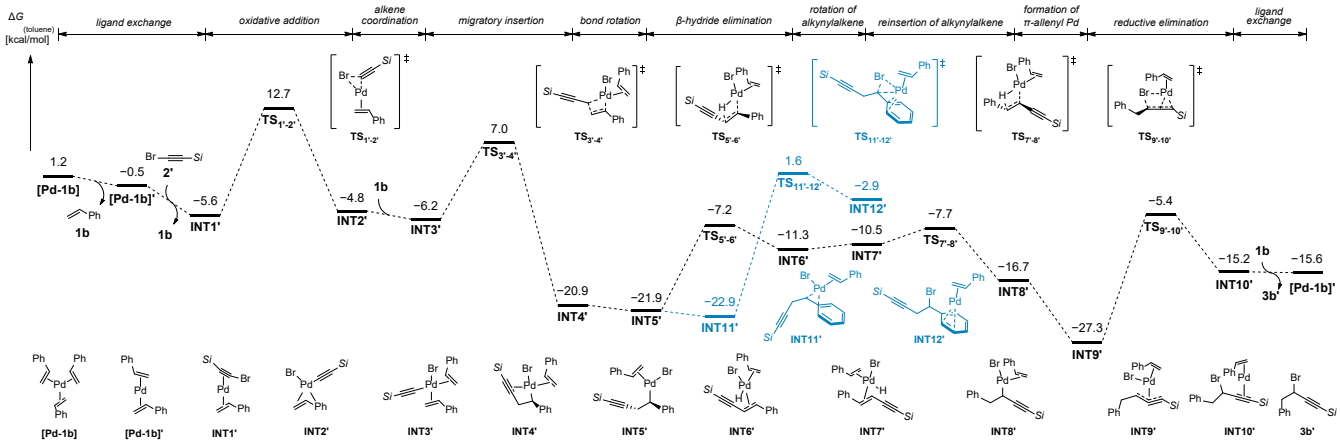


Figure S24. Gibbs free energy profiles for the Pd-catalyzed 1,1-alkynylbromination of **1b** with **2'** involving Pd(0)-alkene complexes (*Si* = $SiMe_3$).

Table S3. Calculated energies and imaginary frequencies for the reaction pathways in Figure S14.

geometry	$E_{SMD/B3LYP}$ [Hartree][a]	$H_{corr\text{-}SMD/B3LYP}$ [Hartree][b]	$G_{corr\text{-}SMD/B3LYP}$ [Hartree][c]	$E_{SMD/M06L}$ [Hartree][d]	Im. Freq. [cm^{-1}][e]
[Pd-1b]	-1055.75336742	0.430777	0.345447	-1057.23257239	—
[Pd-1b]'	-746.097414421	0.287447	0.220504	-747.496113004	—
INT1'	-935.028559303	0.279685	0.200615	-3497.32586218	—
$TS_{1'\text{-}2'}$	-935.009911185	0.278819	0.201949	-3497.29613802	-89.5467
INT2'	-935.038102328	0.280424	0.203132	-3497.32448122	—
INT3'	-1244.70822141	0.425121	0.329717	-3807.06824904	—
$TS_{3'\text{-}4'}$	-1244.68980276	0.423569	0.327127	-3807.04579097	-385.5448
INT4'	-1244.73540964	0.425688	0.332742	-3807.09260150	—
INT5'	-1244.73839087	0.425787	0.330954	-3807.09302914	—

$TS_{5'-6'}$	-1244.70946938	0.420297	0.325035	-3807.06492100	-599.8996
INT6'	-1244.71690750	0.422075	0.326327	-3807.07286684	—
INT7'	-1244.71670483	0.422147	0.326039	-3807.07234863	—
$TS_{7'-8'}$	-1244.71184001	0.420393	0.325001	-3807.06537363	-575.2267
INT8'	-1244.73188258	0.424768	0.327556	-3807.08482427	—
INT9'	-1244.74722898	0.425808	0.331543	-3807.10339096	—
$TS_{9'-10'}$	-1244.71070872	0.423281	0.329331	-3807.06722230	-127.3847
INT10'	-1244.72871178	0.425121	0.328418	-3807.08428659	—
INT11'	-1244.74208352	0.425800	0.331663	-3807.09522091	—
$TS_{11'-12'}$	-1244.69810978	0.423553	0.330969	-3807.05566665	-128.3470
INT12'	-1244.71095956	0.425069	0.327109	-3807.06290649	—

(a) The electronic energy calculated by B3LYP in toluene solvent. (b) The thermal correction to enthalpy calculated by B3LYP in toluene solvent. (c) The thermal correction to Gibbs y calculated by B3LYP in toluene solvent. (d) The electronic energy calculated by M06L in toluene solvent. (e) The B3LYP calculated imaginary frequencies for the transition states.

Optimized Geometries for All Intermediates and Transition States

INT0

Pd	-0.18362100	-0.13533200	0.01318700
C	0.32001500	1.95185100	0.70813900
C	0.82439100	2.12660600	-0.41060400
C	1.49946900	-1.38521000	-0.73812200
C	2.05181500	-1.18452700	0.35520400
C	-1.75412800	-1.42106200	0.11945200
C	-2.37256200	-0.31400500	0.01108100
Br	1.37422900	-2.18366800	-2.43622200
Br	-0.18116700	2.49529500	2.43585300
Br	-1.99323900	-3.32003100	0.28053100
Si	-3.82720100	0.83060700	-0.14061000
Si	3.00494300	-1.11671300	1.94992500
Si	1.57925400	2.64860400	-2.02880700
C	0.43300600	2.14028500	-3.43496500
H	-0.55301300	2.60797300	-3.32799100
H	0.84877600	2.45320500	-4.40175300
H	0.28526500	1.05511000	-3.46801400
C	3.28403000	1.86094000	-2.19227500
H	3.74370900	2.14219700	-3.14889800
H	3.95319100	2.19616600	-1.39074000
H	3.23570300	0.76743600	-2.15154300
C	1.73027000	4.53066400	-1.94784800
H	2.36728600	4.84922600	-1.11396200
H	2.17503000	4.91866900	-2.87385600
H	0.75113300	5.00848300	-1.82352800
C	4.32746700	-2.46115300	1.82868600
H	4.93488700	-2.48394900	2.74331000
H	3.88007300	-3.45413800	1.70105600
H	5.00445500	-2.28698900	0.98367200
C	3.81139800	0.57926800	2.11812800
H	3.07327800	1.38831800	2.09901200
H	4.36054900	0.64799700	3.06640300
H	4.52668900	0.75963300	1.30661200
C	1.82552100	-1.47910000	3.37414100
H	1.34766500	-2.45827900	3.24903800
H	2.36552400	-1.48899100	4.33007400
H	1.02990900	-0.72900800	3.44474700
C	-4.37220300	1.35637600	1.59099400
H	-5.24845100	2.01607000	1.53712200
H	-4.64547900	0.48832500	2.20331100
H	-3.57884100	1.89861900	2.11821000
C	-5.22320900	-0.11478500	-0.99924900
H	-6.11128600	0.52070600	-1.11603500
H	-4.92204900	-0.45268000	-1.99846800
H	-5.52089600	-1.00050000	-0.42487100
C	-3.34004200	2.33567600	-1.16942500
H	-3.04243400	2.03852000	-2.18261900
H	-4.17943400	3.03752800	-1.26077400
H	-2.49788200	2.87385300	-0.71895500

2'

C	-0.97267200	0.00011800	-0.00019400
C	0.24515200	-0.00004400	-0.00015700
Si	2.09712300	-0.00001500	-0.00000700
C	2.68409000	1.17592400	-1.35357200
H	3.78101900	1.20636000	-1.38925000
H	2.32769900	0.86173300	-2.34199000
H	2.32836000	2.19868400	-1.18004500
C	2.68392300	-1.76029500	-0.34145700
H	3.78084700	-1.80665400	-0.35004500
H	2.32744400	-2.45897900	0.42500500
H	2.32807700	-2.12152700	-1.31387400
C	2.68371500	0.58436300	1.69523900
H	3.78063400	0.59959000	1.73986000
H	2.32766100	1.59767900	1.91680000
H	2.32741400	-0.07687500	2.49431000
Br	-2.81754600	-0.00000600	0.00000500

INT1

Pd	0.00034200	-0.00692600	-0.15579200
C	-1.84767500	0.72353100	-0.65695200
C	-2.13063800	-0.09833300	0.25845500
Br	-2.40608000	2.00323600	-1.94004400
Si	-2.96571100	-1.19669400	1.51180900
C	-4.82426700	-0.87607100	1.40473100
H	-5.36694000	-1.50329800	2.12432000
H	-5.06548900	0.17040400	1.62730700

H	-5.21380900	-1.10371700	0.40508800
C	-2.30371100	-0.74762700	3.21972500
H	-2.78519900	-1.35820600	3.99476500
H	-1.22225900	-0.91689500	3.28449900
H	-2.49350100	0.30565300	3.45986100
C	-2.56293700	-2.98637700	1.07654500
H	-1.48255700	-3.17082100	1.11201700
H	-3.04527400	-3.67623600	1.78134700
H	-2.91172300	-3.24110900	0.06837700
C	2.13083800	0.11708900	0.25195100
C	1.84958100	-0.77189900	-0.59902700
Br	2.40979300	-2.14477400	-1.78076300
Si	2.96266300	1.30915300	1.41891800
C	2.59365100	3.05886400	0.82130200
H	2.96296600	3.21938300	-0.19888600
H	1.51563700	3.25979600	0.82114100
H	3.07412900	3.80162700	1.47150700
C	4.81751300	0.95457000	1.37201100
H	5.03883000	-0.07173000	1.68917500
H	5.22634600	1.08833200	0.36314600
H	5.35837900	1.63464300	2.04333400
C	2.26716600	1.02108600	3.14806700
H	2.74682500	1.68942800	3.87509000
H	1.18780300	1.21178100	3.17958500
H	2.43566300	-0.01003600	3.48196100

TS_{1-2}

Pd	-0.25867500	-0.24461700	-0.00123900
C	1.64162500	-0.68763300	-0.00050700
C	2.76126600	-0.15603600	-0.00217500
Br	0.77165600	-2.73776000	0.00671200
Si	4.41613600	0.66211200	-0.00403300
C	5.70992600	-0.66255100	0.37237200
H	6.71681600	-0.22444600	0.38348500
H	5.53624700	-1.12623300	1.35077000
H	5.70051000	-1.45913400	-0.38112800
C	4.43448100	1.99937200	1.32929600
H	5.41335600	2.49520300	1.36893900
H	3.67878400	2.77056500	1.13621700
H	4.23417500	1.57682000	2.32132200
C	4.71794600	1.41776700	-1.70766300
H	3.96693000	2.17990800	-1.94874700
H	5.70483900	1.89704000	-1.75142500
H	4.68264800	0.65486000	-2.49475100
C	-2.17841100	0.98027000	-0.00084000
C	-2.46805400	-0.23123900	-0.00281200
Br	-3.60460300	-1.71470400	-0.00549500
Si	-2.06683900	2.84695300	0.00305300
C	-1.14320600	3.37100000	1.55939300
H	-1.64847300	3.01381600	2.46477600
H	-0.11900300	2.97912400	1.57106500
H	-1.08261300	4.46546800	1.62041500
C	-3.84179000	3.48682000	0.00929900
H	-4.39373900	3.15080900	-0.87656100
H	-4.38916700	3.14594500	0.89614000
H	-3.85214200	4.58478400	0.01233700
C	-1.15158000	3.37788300	-1.55593600
H	-1.09057600	4.47258500	-1.61205900
H	-0.12772200	2.98539000	-1.57500400
H	-1.66203700	3.02532400	-2.46022000

INT2

Pd	0.12507300	-0.09404300	-0.14859200
C	-1.79665500	0.03386100	-0.16297800
C	-3.01786000	0.12459700	-0.28126000
Br	-0.06814100	-0.48659600	2.30106800
Si	-4.83736300	0.27429900	-0.53715900
C	-5.31982400	2.09609200	-0.39857000
H	-6.40108300	2.22557600	-0.53956500
H	-5.06084100	2.50382400	0.58611900
H	-4.81018400	2.70500000	-1.15534600
C	-5.71413800	-0.74010100	0.79345900
H	-6.80433700	-0.67446400	0.67917500
H	-5.43512900	-1.79925800	0.73732300
H	-5.46068500	-0.38332900	1.79899900
C	-5.26899700	-0.38600900	-2.25466800
H	-4.97926200	-1.43839700	-2.36266000
H	-6.34914000	-0.31721800	-2.43989500
H	-4.75947400	0.18192400	-3.04276800
C	2.41591500	0.36807600	-0.45083100
C	2.22494000	-0.84936100	-0.58094300
Br	2.50794900	-2.66752300	-0.81953300
Si	2.94267100	2.16845500	-0.30773200
C	1.57580800	3.22782200	-1.05169800
H	1.38633900	2.96802700	-2.10035000
H	0.63387500	3.12247900	-0.49988000
H	1.85924200	4.28806000	-1.01997100
C	4.54116500	2.30062700	-1.29779600
H	5.31906500	1.63897400	-0.89884300
H	4.38670700	2.04372800	-2.35242400
H	4.92493000	3.32849600	-1.25772100
C	3.21210200	2.53593600	1.51633700
H	3.54875800	3.57271200	1.64689500
H	2.29022600	2.40705100	2.09445100
H	3.97529200	1.87915400	1.95014000

1b

C	1.95532100	-0.53031200	-0.00023500
H	2.18735200	-1.59562500	-0.00075400
C	2.97692400	0.33558400	0.00032100
H	2.84054400	1.41424300	0.00095900
H	4.00457900	-0.01682800	0.00019300
C	0.51524000	-0.22110700	-0.00015200
C	0.00958300	1.09269300	-0.00021100
C	-0.40699200	-1.28226600	0.00000000
C	-1.36180900	1.33019700	-0.00006400
C	-1.78156800	-1.04604500	0.00014500
C	-2.26548300	0.26251000	0.00012700
H	0.69512600	1.93530100	-0.00041600
H	-0.03638500	-2.30500200	0.00002900
H	-1.72966000	2.35313100	-0.00011400
H	-2.47323700	-1.88458400	0.00027700
H	-3.33561700	0.45184000	0.00024200

INT3

C	-2.51173600	4.36970300	-0.07486200
C	-1.36712000	3.65512000	0.26952400
C	-3.76384300	3.92673300	0.35686200
H	-0.39318400	4.00610700	-0.06144500
H	-4.65899000	4.48367700	0.09390000
C	-1.45303100	2.48108900	1.04177500
C	-3.86362000	2.76896900	1.13627800
H	-4.83566000	2.42863000	1.48208200
C	-2.72195100	2.05057400	1.47608400
H	-2.81220700	1.15710900	2.08332100
H	-2.42726000	5.27114300	-0.67501200
C	-0.21316400	1.79532100	1.41091700
C	-0.06664400	0.61532000	2.11360700

H	0.88948200	0.38952700	2.57393800
H	0.69386900	2.36291600	1.21212300
H	-0.91988300	0.05663800	2.48149200
C	-1.42542300	-0.86435000	-0.01393900
C	-2.57416400	-1.30065900	-0.01044200
Br	0.87247500	-1.73028800	-1.94208300
Si	-4.26906200	-1.99898600	-0.09386200
C	-5.05691600	-1.96237400	1.62859200
H	-6.06254800	-2.40324800	1.60754100
H	-4.46200700	-2.53146400	2.35390300
H	-5.15481100	-0.93796600	2.00952600
C	-4.17528500	-3.78637700	-0.70222100
H	-5.17585600	-4.23357800	-0.77354300
H	-3.71091800	-3.84221600	-1.69415200
H	-3.57851200	-4.40846700	-0.02385200
C	-5.30681300	-0.96297400	-1.28843100
H	-4.87996100	-0.97998400	-2.29863700
H	-6.33445900	-1.34502400	-1.35262700
H	-5.35767000	0.08548600	-0.97016000
Pd	0.40318500	-0.19928400	0.04047000
C	2.45749700	0.91207700	-0.33454600
C	2.78727700	0.02925700	0.46281600
Si	3.64599500	-1.28785600	1.49671500
C	4.83443500	-0.35535400	2.62713500
H	5.40809600	-1.06374500	3.23910200
H	5.55123700	0.24417100	2.05344100
H	4.30343000	0.31828200	3.31064600
C	2.38264600	-2.26211800	2.49437600
H	1.61112900	-2.70342800	1.85347900
H	2.89019800	-3.08368300	3.01739100
H	1.88493000	-1.64944900	3.25492000
C	4.55970200	-2.38744600	0.27439200
H	3.86129700	-2.86181000	-0.42391900
H	5.28787900	-1.81686400	-0.31402500
H	5.10267900	-3.18024000	0.80549100
Br	2.50824100	2.27558000	-1.58803100

TS_{3-4}

C	-2.99155900	3.87100300	-0.95228700
C	-2.38675300	2.70679100	-1.42220400
C	-2.25470100	4.78882200	-0.20036400
H	-2.96420800	1.99668900	-2.00908700
H	-2.72547900	5.69545200	0.16969000
C	-1.02916400	2.44219600	-1.16124200
C	-0.90874600	4.53178100	0.07902600
H	-0.33185300	5.23628300	0.67199500
C	-0.29998600	3.37212400	-0.39354600
H	0.74124500	3.17851800	-0.15121900
H	-4.03862600	4.06097500	-1.17248400
C	-0.42067300	1.22273700	-1.72095600
C	0.96062100	1.09131100	-1.99161400
H	1.26893600	0.37139300	-2.74081800
H	-1.08868500	0.57759800	-2.28701200
H	1.60111400	1.95697300	-1.88538300
C	1.98279200	0.17201800	-0.46238900
C	3.21332300	0.21101500	-0.38678400
Br	0.72675800	-1.83447100	1.83645000
Si	5.04886500	0.20972900	-0.21702700
C	5.78923100	1.13060900	-1.69615400
H	6.88519300	1.14886900	-1.63005400
H	5.52395000	0.64957900	-2.64578200
H	5.44415300	2.17110400	-1.74017300
C	5.65488600	-1.57812800	-0.19688500
H	6.74658200	-1.62130700	-0.08669400
H	5.21029500	-2.13626000	0.63558000
H	5.39150400	-2.10100600	-1.12445400
C	5.50775500	1.08880500	1.39005100
H	5.05842800	0.58886100	2.25638500
H	6.59626600	1.09732500	1.53434900
H	5.16267600	2.13005100	1.39140500
Pd	0.05820500	-0.24077700	-0.08826300
C	-2.09839800	-0.31152500	0.65471000
C	-2.11785600	-1.17637500	-0.23154400
Si	-2.41953900	-2.61881500	-1.38861100
C	-4.27984000	-2.62623900	-1.70922100
H	-4.54894300	-3.46753900	-2.36136900
H	-4.84715600	-2.73419900	-0.77713800
H	-4.61294000	-1.70425300	-2.20083900
C	-1.46627100	-2.34766900	-2.99232800
H	-0.38510900	-2.29879700	-2.81733800
H	-1.64997300	-3.18663500	-3.67656200
H	-1.77511800	-1.43193000	-3.51099700
C	-1.85818500	-4.18387100	-0.51236800
H	-0.79678000	-4.13184200	-0.24689700
H	-2.42236600	-4.34555300	0.41361400
H	-2.01002400	-5.05912700	-1.15775500
Br	-2.63818600	0.74102300	2.08139700

INT4

C	2.71592100	3.94738700	0.66307700
C	2.34576500	2.69207600	1.13540200
C	1.73796800	4.89533300	0.34520900
H	3.11046000	1.96168500	1.38772300
H	2.02671400	5.87453800	-0.02661800
C	0.98740000	2.35263400	1.31456500
C	0.38802100	4.57688500	0.51140500
H	-0.37808000	5.30795400	0.26772700
C	0.01356400	3.32330300	0.99150800
H	-1.04091000	3.09398000	1.11210400
H	3.76860900	4.18951800	0.54378500
C	0.63370500	1.01370200	1.82866500
C	-0.62481000	0.87671200	2.68938200
H	-0.51023800	0.05364300	3.40409300
H	1.48917800	0.46663000	2.22037100
H	-0.84951700	1.78330100	3.26781000
C	-1.72218600	0.56392000	1.75703400
C	-2.59895600	0.32254100	0.93142200
Br	-0.97778200	-0.77540200	-2.29135100
Si	-4.20838100	0.05450700	0.01498300
C	-5.54434300	0.49262800	1.28236600
H	-6.54179700	0.36809600	0.84017200
H	-5.49183900	-0.15331500	2.16725700
H	-5.45978500	1.53271800	1.62007200
C	-4.34477500	-1.75395500	-0.48241000
H	-5.29955500	-1.93964400	-0.99192900
H	-3.53295100	-2.02683200	-1.16469400
H	-4.29984400	-2.41509500	0.39202100
C	-4.28366900	1.22677500	-1.45349400
H	-3.47262600	1.01313300	-2.15757400
H	-5.23828700	1.11486600	-1.98432900
H	-4.19964700	2.27378400	-1.13647100
Pd	-0.02479800	0.00340200	0.08378600
C	1.91493500	-0.56347100	-0.52393300
C	1.66062400	-1.48951300	0.28412000
Si	1.57484000	-3.06311100	1.28708600
C	3.01562000	-4.12250400	0.68318300
H	3.03810800	-5.07808600	1.22354900
H	2.92465900	-4.34555300	-0.38637000

H	3.98012400	-3.62585500	0.84314000
C	1.77770100	-2.63172100	3.11324200
H	0.94562400	-2.02184500	3.48501200
H	1.80104200	-3.55023200	3.71442000
H	2.71129000	-2.08912900	3.30480800
C	-0.08202800	-3.89178900	0.96172200
H	-0.91489900	-3.28174800	1.33067100
H	-0.24088200	-4.04958000	-0.11119200
H	-0.13076300	-4.86830000	1.46121300
Br	3.03130700	0.24367800	-1.79164000

INT5

C	3.86583100	-1.41703300	-2.68700600
C	2.63148700	-0.89844200	-2.30204600
C	4.34245700	-2.59211200	-2.10095900
H	2.25940100	0.01250400	-2.76439200
H	5.30756700	-2.99551000	-2.39530400
C	1.84226600	-1.55098700	-1.33393300
C	3.57614600	-3.24533800	-1.12991100
H	3.94698000	-4.15457500	-0.66496800
C	2.33979400	-2.73277300	-0.74796100
H	1.76647500	-3.23024700	0.02758800
H	4.45488100	-0.90516100	-3.44313300
C	0.49914100	-1.00708200	-1.01841100
C	-0.64580900	-2.02806800	-0.99119500
H	-0.59911300	-2.54463300	-1.96558500
H	0.25043500	-0.16194400	-1.66217600
H	-0.46600900	-2.79165400	-0.22966400
C	-1.99797600	-1.49280300	-0.83368100
C	-3.16007700	-1.13197500	-0.74647100
Br	0.33185200	-1.98361800	2.46063800
Si	-4.96991200	-0.77636900	-0.65686400
C	-5.59933800	-0.44579800	-2.40848300
H	-6.67894200	-0.24570200	-2.40262000
H	-5.10353200	0.42298400	-2.85884600
H	-5.42492300	-1.30599500	-3.06634900
C	-5.27981400	0.73163300	0.43625500
H	-6.35652700	0.93514900	0.50840800
H	-4.90368600	0.57626200	1.45434000
H	-4.80010100	1.63090400	0.03226700
C	-5.82425900	-2.29424300	0.07249100
H	-5.45692200	-2.51087700	1.08288000
H	-6.90912500	-2.13766100	0.13738400
H	-5.65228800	-3.18639100	-0.54180700
Pd	0.65606100	-0.03024300	0.83518500
C	1.70264800	1.65357500	0.15292400
C	0.52203100	2.06795500	0.04994800
Si	-1.03750600	3.09314200	-0.11171500
C	-0.45995500	4.88830400	-0.20221400
H	0.09591100	5.17873600	0.69721000
H	0.18724100	5.06302800	-1.06997900
H	-1.32416000	5.56000000	-0.29060700
C	-2.07672000	2.78273500	1.42520600
H	-2.36342700	1.72851600	1.50767700
H	-1.52288800	3.05145100	2.33329400
H	-2.99462900	3.38386900	1.40672000
C	-1.91543400	2.58445200	-1.69813200
H	-1.28104800	2.74909800	-2.57790500
H	-2.20505700	1.52792900	-1.67875000
H	-2.82718800	3.18099900	-1.83439100
Br	3.56389600	1.89485400	0.08169900

TS_{5-6}

C	3.07426200	3.43531300	1.88684800
C	1.90648400	2.68694200	1.75623200
C	3.63739200	4.05517700	0.76904700
H	1.47127200	2.20563000	2.62846800
H	4.54931900	4.63736300	0.86816300
C	1.27224200	2.54928100	0.50672600
C	3.02299200	3.92073500	-0.48006400
H	3.45839300	4.39566900	-1.35489700
C	1.85408600	3.17652400	-0.61343000
H	1.39958600	3.07473400	-1.59473800
H	3.54465900	3.53439200	2.86130200
C	0.03349700	1.75835700	0.43199500
C	-0.91415200	1.85329200	-0.62681600
H	-0.74942300	2.60902200	-1.39371400
H	-0.33432100	1.36684100	1.37707300
H	-0.40805500	0.76374100	-1.82809700
C	-2.28338900	1.48542100	-0.42596300
C	-3.46599300	1.22941300	-0.26359100
Br	0.72210100	-1.78024200	-2.66792700
Si	-5.26254900	0.83900700	-0.04307700
C	-5.68537500	1.02338500	1.78778100
H	-6.74569000	0.79924100	1.96324100
H	-5.09469900	0.33980300	2.40971700
H	-5.49883700	2.04407700	2.14333900
C	-5.55617300	-0.93146300	-0.62465900
H	-6.61538200	-1.20157100	-0.52144200
H	-5.28076800	-1.05784500	-1.67852800
H	-4.97057400	-1.65103300	-0.03989800
C	-6.25685700	2.06072700	-1.08203700
H	-6.00117100	1.98418800	-2.14572000
H	-7.33259800	1.86466400	-0.98365300
H	-6.07772800	3.09633200	-0.76856300
Pd	0.42436300	-0.06955200	-0.75674100
C	2.04280500	-1.04546100	0.57173600
C	1.01204400	-1.45513600	1.11831400
Si	-0.36733300	-2.30450200	2.05407300
C	0.49906900	-3.45378600	3.27499600
H	1.12138900	-4.19216400	2.75571400
H	1.14255700	-2.89886500	3.96820600
H	-0.24100900	-4.00217900	3.87252600
C	-1.42299300	-3.26188300	0.82822800
H	-1.91390100	-2.59261800	0.11284400
H	-0.81920500	-3.97141400	0.25121600
H	-2.20197100	-3.82848200	1.35555100
C	-1.38039800	-1.00043400	2.96562400
H	-0.75701300	-0.37714200	3.61823700
H	-1.91864500	-0.34406700	2.27191100
H	-2.13029100	-1.49065600	3.60086400
Br	3.83117100	-0.78860900	0.15996100

INT6

C	3.65085800	3.34710300	1.71976900
C	2.44839200	2.64526600	1.65213300
C	4.17455300	3.94662500	0.57342700
H	2.04210600	2.18236100	2.54798800
H	5.11361500	4.49099300	0.62098100
C	1.74134600	2.53537700	0.44058100
C	3.48585700	3.84015500	-0.64010600
H	3.89115300	4.29924800	-1.53752600
C	2.28363200	3.14361400	-0.70907200
H	1.77354500	3.05932300	-1.66385900
H	4.17766300	3.42385600	2.66695000
C	0.45420700	1.82111400	0.45341300
C	-0.54367500	1.92446800	-0.51587500
H	-0.35995000	2.54516300	-1.38964400

H	0.17272600	1.38888300	1.41081500
H	0.64885600	0.69336400	-2.25196900
C	-1.91497400	1.60899700	-0.29854000
C	-3.12166800	1.45469700	-0.16557900
Br	1.23967600	-1.89357600	-2.54391400
Si	-4.96601400	1.38787300	-0.01308000
C	-5.44739900	2.17300500	1.63573600
H	-6.53845300	2.17232300	1.75858100
H	-5.01779100	1.62730400	2.48461000
H	-5.10632200	3.21331100	1.70056200
C	-5.54488300	-0.40682000	-0.08210000
H	-6.63939400	-0.45243000	-0.00528100
H	-5.25857600	-0.89025800	-1.02332000
H	-5.13041100	-0.99893000	0.74201000
C	-5.68764600	2.36868200	-1.45537400
H	-5.39363300	1.93677800	-2.41964400
H	-6.78470100	2.37067000	-1.41187200
H	-5.35189100	3.41259000	-1.44098200
Pd	0.60542800	-0.04556100	-0.91080800
C	1.48706900	-1.35021300	1.03147700
C	0.29746200	-1.65520800	1.08146900
Si	-1.38091300	-2.43584600	1.35986700
C	-1.01308700	-4.14696400	2.06545100
H	-0.43594800	-4.75315200	1.35730000
H	-0.44407700	-4.08792700	3.00091600
H	-1.94941700	-4.68037100	2.27671900
C	-2.29249900	-2.55911300	-0.27820500
H	-2.50186100	-1.57096100	-0.70117700
H	-1.70157300	-3.11706500	-1.01309700
H	-3.24786600	-3.08285000	-0.14346400
C	-2.29627200	-1.37407300	2.62134700
H	-1.73626900	-1.29946700	3.56168800
H	-2.46477400	-0.35874000	2.24519000
H	-3.27430600	-1.81459300	2.85527200
Br	3.31910100	-1.21620300	1.23061900

INT7

C	-2.86560400	4.21821800	-0.89677400
C	-1.68693100	3.51310100	-1.13218400
C	-3.44387500	4.20776900	0.37460400
H	-1.23597700	3.52535300	-2.12129500
H	-4.35862200	4.76254100	0.56386000
C	-1.06458700	2.77923700	-0.10427300
C	-2.83498000	3.48552200	1.40676400
H	-3.27276000	3.48457000	2.40127600
C	-1.66005700	2.77519200	1.17215600
H	-1.19904800	2.22808400	1.98860000
H	-3.32912400	4.77852000	-1.70388800
C	0.20871000	2.10938100	-0.40643500
C	0.99886600	1.39001000	0.49199300
H	0.63743800	1.24856900	1.50858300
H	0.67075100	2.41150900	-1.34202000
H	0.73686800	0.17310500	-1.99393600
C	2.38374600	1.12805700	0.29100700
C	3.58130400	0.91142000	0.17327100
Br	-0.58484000	-2.14809100	-2.29271700
Si	5.38135500	0.55225900	-0.04438800
C	5.60591500	-0.35293300	-1.68445300
H	6.66326300	-0.59646900	-1.85274900
H	5.03889000	-1.29142100	-1.70368200
H	5.26560000	0.25755500	-2.52963200
C	5.94520300	-0.52573000	1.39930800
H	7.01308600	-0.76471700	1.31055200
H	5.79651200	-0.02137100	2.36190300
H	5.39403800	-1.47344700	1.42929700
C	6.31935300	2.19159400	-0.05315800
H	6.18028200	2.74138300	0.88561500
H	7.39611600	2.01947400	-0.18154500
H	5.98700200	2.84028600	-0.87268700
Pd	-0.08793700	-0.17933400	-0.75671900
C	-0.81651500	-1.23322700	1.43469300
C	-1.90095600	-0.98839400	0.91202200
Si	-3.69691900	-0.95902700	0.36317800
C	-4.16047500	-2.75927200	0.05899200
H	-3.54307000	-3.19057200	-0.73676200
H	-4.02639500	-3.36956000	0.96008500
H	-5.21232400	-2.83734700	-0.24643200
C	-3.91935300	0.08056600	-1.18534100
H	-3.62064400	1.12309100	-1.03158800
H	-3.33638100	-0.32455900	-2.01934400
H	-4.97756600	0.07662600	-1.47977200
C	-4.67140200	-0.24484200	1.81397800
H	-4.50845300	-0.81903500	2.73394400
H	-4.39705600	0.79776300	2.01132100
H	-5.74680400	-0.26911400	1.59321300
Br	0.59447400	-1.84278700	2.46460400

TS_{7-8}

C	-3.78556200	4.22863700	-0.86120700
C	-2.53561700	3.64460200	-1.05720000
C	-4.50748400	3.95993900	0.30340500
H	-1.97880600	3.85085900	-1.96812200
H	-5.48279300	4.41271400	0.45849300
C	-1.98503300	2.78199600	-0.09469200
C	-3.96837000	3.10639100	1.27021200
H	-4.52183800	2.89656300	2.18130300
C	-2.71875400	2.52233400	1.07471400
H	-2.31577700	1.86638000	1.83981600
H	-4.19493200	4.89189800	-1.61791600
C	-0.63477900	2.22452300	-0.34996900
C	0.15184000	1.50579500	0.59205700
H	-0.26999700	1.28375600	1.57034400
H	-0.08029200	2.73378900	-1.13531800
H	-0.99679600	1.06776700	-1.60715000
C	1.57442500	1.52225600	0.51608300
C	2.79635800	1.57158100	0.48243100
Br	-1.55468300	-1.56651800	-2.59649200
Si	4.63600400	1.74044000	0.43476900
C	5.06491600	3.09620200	-0.80734700
H	6.15208300	3.23754400	-0.86660300
H	4.70753400	2.84510100	-1.81348000
H	4.61948200	4.05781800	-0.52493400
C	5.40426700	0.09985500	-0.09510600
H	6.49812700	0.18725800	-0.13611200
H	5.16173700	-0.70651000	0.60705600
H	5.05817800	-0.20424000	-1.09007000
C	5.22453800	2.21198000	2.16623500
H	4.96162600	1.44350300	2.90334600
H	6.31591400	2.33031600	2.18431100
H	4.78196700	3.15883400	2.49847600
Pd	-0.57608600	-0.14401600	-0.68039600
C	0.52806100	-1.93784800	0.26831600
C	-0.44454200	-1.85048600	1.02569500
Si	-1.82360800	-2.03448500	2.27401300
C	-1.69285900	-3.80867900	2.90099100
H	-1.83548700	-4.52952000	2.08736600
H	-0.71585900	-4.00560900	3.35818900
H	-2.46249100	-4.00325300	3.65946700

C	-3.47590100	-1.72389300	1.43183000
H	-3.57742700	-0.68775700	1.08916000
H	-3.60036800	-2.37185100	0.55688100
H	-4.30042300	-1.93049300	2.12708400
C	-1.50873800	-0.81051200	3.67637400
H	-0.51783100	-0.95741000	4.12265200
H	-1.57483900	0.23258600	3.34400900
H	-2.25394900	-0.94685400	4.47113000
Br	2.08694300	-2.53290700	-0.53439600

INT8

C	-3.99312600	2.93965400	0.26374500
C	-2.61247800	2.80130000	0.09519400
C	-4.57891700	2.69050400	1.50677200
H	-2.15984700	3.00051500	-0.87222300
H	-5.65149300	2.80547300	1.63949100
C	-1.79673400	2.41188700	1.16673900
C	-3.77529900	2.30493200	2.58302400
H	-4.21957800	2.12335100	3.55843200
C	-2.39571400	2.16937400	2.41225500
H	-1.77437100	1.89158900	3.26165900
H	-4.60821400	3.25089400	-0.57671700
C	-0.29431400	2.30498300	1.00596000
C	0.27257600	0.87882500	0.90944500
H	-0.17853100	0.20859300	1.64612900
H	0.18325500	2.73303500	1.90193700
H	0.05137300	2.89226600	0.15408700
C	1.69764300	0.79378800	0.89103100
C	2.92134700	0.74339500	0.89987600
Br	0.17785000	1.73965300	-2.58037400
Si	4.77050900	0.68402500	0.87675400
C	5.34218300	-0.57870000	2.15913000
H	6.43777300	-0.64873800	2.17139100
H	5.01620800	-0.30276500	3.16941400
H	4.94760900	-1.57884200	1.94276100
C	5.41812000	2.40439400	1.30477700
H	6.51595100	2.41736400	1.29521700
H	5.06951500	3.15285000	0.58314400
H	5.09093900	2.72289800	2.30199700
C	5.30831000	0.17428900	-0.85827900
H	4.95041700	0.88706100	-1.61062400
H	6.40331900	0.13255800	-0.92777400
H	4.91721600	-0.81455900	-1.12593800
Pd	-0.25615600	-0.10765200	-0.86632900
C	-0.06680700	-2.03824800	-0.06923200
C	-1.30925800	-1.87464600	0.01770600
Si	-3.15694800	-2.15381200	0.19914600
C	-3.40915200	-3.98456200	-0.18760700
H	-3.09806400	-4.22605800	-1.21090600
H	-2.84274900	-4.62655700	0.49742800
H	-4.47057400	-4.24866000	-0.09088400
C	-4.06246300	-1.06434200	-1.03585100
H	-3.91204300	-0.00009500	-0.82313900
H	-3.72486100	-1.25509300	-2.06178600
H	-5.14144800	-1.26417700	-0.99780100
C	-3.63333800	-1.76557300	1.97893200
H	-3.06719700	-2.37957100	2.68982300
H	-3.46124000	-0.71155800	2.22364600
H	-4.70000700	-1.97286100	2.13651000
Br	1.49142200	-3.06900800	0.11327700

INT9

C	6.39235500	-1.35455700	-0.82940000
C	5.06982700	-1.56873100	-0.43667300
C	7.01179700	-0.13039800	-0.56782300
H	4.59497900	-2.52709300	-0.63570700
H	8.04252100	0.03617200	-0.86955600
C	4.34650900	-0.56456100	0.22186900
C	6.30072500	0.87688100	0.08884500
H	6.77739100	1.83034400	0.30200000
C	4.97783400	0.66054300	0.47832000
H	4.43118100	1.44758100	0.99348600
H	6.93989600	-2.14624700	-1.33433900
C	2.89740000	-0.79261400	0.62387300
C	1.94044500	-0.37860800	-0.48772700
H	2.06987600	-0.91801000	-1.42656100
H	2.66232300	-0.23702000	1.53725200
H	2.72496500	-1.85394500	0.82633600
C	1.42816000	0.91741700	-0.57867500
C	0.53718700	1.79472400	-0.49494100
Br	-0.15097700	-2.99452000	0.28192000
Si	-0.22953600	3.49799300	-0.54973300
C	0.82659800	4.52881400	-1.72677100
H	0.43448200	5.55209600	-1.79604000
H	1.86643000	4.59284700	-1.38472400
H	0.83194900	4.10443100	-2.73784800
C	-0.18684800	4.21240000	1.19446000
H	-0.61473100	5.22343700	1.20385300
H	-0.76289300	3.60175700	1.89923800
H	0.83979600	4.28221400	1.57368500
C	-1.99640200	3.35336700	-1.18502800
H	-2.61356100	2.73828500	-0.52129200
H	-2.45891000	4.34701200	-1.24836700
H	-2.02481900	2.91095200	-2.18793600
Pd	-0.20222100	-0.43134300	-0.00451700
C	-2.12377300	-0.03205400	1.05297300
C	-2.56111400	-0.33501700	-0.06714400
Si	-3.46614500	-0.85507800	-1.62281200
C	-4.06344600	-2.61815400	-1.34832100
H	-3.21886200	-3.28564300	-1.14428400
H	-4.75438900	-2.68058000	-0.49908200
H	-4.58891300	-2.99047000	-2.23765100
C	-2.29584300	-0.74071500	-3.09364700
H	-1.87112700	0.26417600	-3.20253300
H	-1.46662100	-1.45043900	-2.99599300
H	-2.83252400	-0.97853100	-4.02173100
C	-4.91453200	0.34188000	-1.81242500
H	-5.57215300	0.32025900	-0.93498400
H	-4.57547400	1.37499300	-1.95373800
H	-5.51961700	0.06774500	-2.68677800
Br	-2.12961800	0.42854600	2.85854000

$TS_{9\text{-}10}$

C	6.20441400	-1.29687400	1.20059400
C	4.87634100	-0.88328700	1.32086400
C	7.12992400	-0.49932300	0.52461200
H	4.15767700	-1.51213600	1.83882000
H	8.16360600	-0.82168700	0.43137700
C	4.45671800	0.33310400	0.76957600
C	6.72175800	0.71662600	-0.02862700
H	7.43694000	1.34639600	-0.55137000
C	5.39484600	1.13004500	0.09711600
H	5.08697000	2.08550000	-0.32368400
H	6.51410700	-2.24448000	1.63321700
C	3.02322400	0.79859200	0.90328000
C	2.23732300	0.79152100	-0.39425200
H	2.78692200	0.60159100	-1.31089100
H	3.00441000	1.84025200	1.26050700

H	2.48352100	0.21761200	1.65680600
C	1.03800300	1.46704600	-0.50979200
C	-0.10886200	1.97903900	-0.63305400
Br	1.74102200	-1.84800000	-0.75030300
Si	-1.25788600	3.39537600	-1.08057500
C	-0.28437900	4.51588300	-2.24879100
H	-0.89669700	5.37331200	-2.55770800
H	0.61999600	4.90979000	-1.76943900
H	0.02133100	3.98106700	-3.15600700
C	-1.71866300	4.31644500	0.49761800
H	-2.38053400	5.16146700	0.26666900
H	-2.24137600	3.66751900	1.20880100
H	-0.82982900	4.71805700	0.99933500
C	-2.76565700	2.67106700	-1.94371700
H	-3.31260100	1.98176600	-1.29078800
H	-3.45567700	3.46947800	-2.24616100
H	-2.47832900	2.11789600	-2.84608000
Pd	-0.52716000	-0.06525700	-0.00936400
C	-2.33273100	-0.25010300	0.96132000
C	-2.35295600	-1.27053700	0.21674300
Si	-2.79886500	-2.84108200	-0.68472400
C	-1.72509300	-4.23249000	-0.00720800
H	-0.66153700	-4.01320200	-0.15743600
H	-1.89040200	-4.38007700	1.06706900
H	-1.95120800	-5.17985700	-0.51412600
C	-2.50263200	-2.57778900	-2.52747600
H	-3.08600800	-1.73194300	-2.91137400
H	-1.44437100	-2.37924100	-2.73237000
H	-2.79338600	-3.47018900	-3.09713200
C	-4.63017000	-3.16541100	-0.34222700
H	-4.82481500	-3.28370200	0.73060000
H	-5.26077000	-2.34635200	-0.70895000
H	-4.95654300	-4.08670000	-0.84298100
Br	-3.24776400	0.76109200	2.29112400

INT10

C	6.39235500	-1.35455700	-0.82940000
C	5.06982700	-1.56873100	-0.43667300
C	7.01179700	-0.13039800	-0.56782300
H	4.59497900	-2.52709300	-0.63570700
H	8.04252100	0.03617200	-0.86955600
C	4.34650900	-0.56456100	0.22186900
C	6.30072500	0.87688100	0.08884500
H	6.77739100	1.83034400	0.30200000
C	4.97783400	0.66054300	0.47832000
H	4.43118100	1.44758100	0.99348600
H	6.93989600	-2.14624700	-1.33433900
C	2.89740000	-0.79261400	0.62387300
C	1.94044500	-0.37860800	-0.48772700
H	2.06987600	-0.91801000	-1.42656100
H	2.66232300	-0.23702000	1.53725200
H	2.72496500	-1.85394500	0.82633600
C	1.42816000	0.91741700	-0.57867500
C	0.53718700	1.79472400	-0.49494100
Br	-0.15097700	-2.99452000	0.28192000
Si	-0.22953600	3.49799300	-0.54973300
C	0.82659800	4.52881400	-1.72677100
H	0.43448200	5.55209600	-1.79604000
H	1.86643000	4.59284700	-1.38472400
H	0.83194900	4.10443100	-2.73784800
C	-0.18684800	4.21240000	1.19446000
H	-0.61473100	5.22343700	1.20385300
H	-0.76289300	3.60175700	1.89923800
H	0.83979600	4.28221400	1.57368500
C	-1.99640200	3.35336700	-1.18502800
H	-2.61356100	2.73828500	-0.52129200
H	-2.45891000	4.34701200	-1.24836700
H	-2.02481900	2.91095200	-2.18793600
Pd	-0.20222100	-0.43134300	-0.00451700
C	-2.12377300	-0.03205400	1.05297300
C	-2.56111400	-0.33501700	-0.06714400
Si	-3.46614500	-0.85507800	-1.62281200
C	-4.06344600	-2.61815400	-1.34832100
H	-3.21886200	-3.28564300	-1.14428400
H	-4.75438900	-2.68058000	-0.49908200
H	-4.58891300	-2.99047000	-2.23765100
C	-2.29584300	-0.74071500	-3.09364700
H	-1.87112700	0.26417600	-3.20253300
H	-1.46662100	-1.45043900	-2.99599300
H	-2.83252400	-0.97853100	-4.02173100
C	-4.91453200	0.34188000	-1.81242500
H	-5.57215300	0.32025900	-0.93498400
H	-4.57547400	1.37499300	-1.95373800
H	-5.51961700	0.06774500	-2.68677800
Br	-2.12961800	0.42854600	2.85854000

3b'

C	-2.26366300	-3.01562600	0.71741500
C	-1.82332200	-1.72506700	1.01655400
C	-3.24995900	-3.21347200	-0.25139600
H	-1.05662200	-1.57624400	1.77263100
H	-3.59452300	-4.21785600	-0.48294000
C	-2.36414200	-0.61377300	0.35544100
C	-3.79585900	-2.11333200	-0.91689500
H	-4.56862200	-2.25778800	-1.66746800
C	-3.35538400	-0.82411600	-0.61412300
H	-3.79204700	0.02937600	-1.12885300
H	-1.83830100	-3.86609800	1.24391300
C	-1.88136400	0.79104700	0.66580500
C	-0.79428500	1.24135500	-0.32662800
H	-1.17622000	1.27496500	-1.34808100
H	-1.47830000	0.84723800	1.68101100
H	-2.71347300	1.49797800	0.59703200
C	0.45314700	0.52822100	-0.24839000
C	1.49045400	-0.10996000	-0.18063600
Br	-0.42141800	3.29015000	0.01741400
Si	3.07051600	-1.06678200	-0.08438600
C	2.92479100	-2.55788500	-1.23241500
H	3.84087300	-3.16220900	-1.19970700
H	2.08759400	-3.20587500	-0.94627900
H	2.76670300	-2.24923100	-2.27283500
C	3.32076000	-1.62283000	1.70207100
H	4.25643900	-2.18800000	1.80454900
H	3.37362000	-0.76635600	2.38512000
H	2.50311300	-2.27059100	2.04109000
C	4.47666800	0.06643000	-0.63170200
H	4.55261600	0.95126300	0.01167400
H	5.43824700	-0.46167800	-0.58781800
H	4.33426400	0.41485800	-1.66171800

INT11

C	-1.99226300	3.95627600	-0.35313300
C	-0.83006700	3.24514800	-0.59846900
C	-2.63610900	3.85902300	0.89472800
H	-0.33186500	3.31502100	-1.56156400
H	-3.54652300	4.42283800	1.07797500
C	-0.24605000	2.43310100	0.41568200
C	-2.10704900	3.04769700	1.89216800

H	-2.60049200	2.97209400	2.85670200
C	-0.91942100	2.33739200	1.66654300
H	-0.47359800	1.77187200	2.47896400
H	-2.40922100	4.59339000	-1.12806400
C	0.91081300	1.58925900	0.13389100
C	1.93306100	1.30087400	1.24431500
H	2.07700900	2.22549000	1.82570200
H	1.35979300	1.73336700	-0.84655400
H	1.54346900	0.56318200	1.95838000
C	3.23547900	0.85559400	0.75390200
C	4.33749200	0.51167200	0.36517900
Br	0.73118500	-1.48454700	-1.36678600
Si	5.96901000	-0.06772900	-0.26320700
C	7.29594000	1.18194000	0.24020200
H	8.28443300	0.86636000	-0.11902300
H	7.09281400	2.17532600	-0.17860200
H	7.35771000	1.28700200	1.33044500
C	5.87557000	-0.19761200	-2.14470000
H	6.82314500	-0.56535500	-2.56015400
H	5.08234100	-0.88839400	-2.45468700
H	5.66567300	0.77591600	-2.60457400
C	6.34548800	-1.75558800	0.49633400
H	5.57568500	-2.49033500	0.23125400
H	7.31081200	-2.13877600	0.13985100
H	6.39207200	-1.70305600	1.59106000
Pd	-0.61156200	0.16201500	0.06260900
C	-2.81912000	-0.85864100	-0.06983800
C	-2.14999000	-1.26735200	0.88748400
Br	-1.68464600	-2.25859400	2.39636500
Si	-3.99409600	-0.46098900	-1.46585100
C	-4.74516000	-2.10817800	-1.99570500
H	-5.47233400	-1.95675800	-2.80435300
H	-3.97327800	-2.79450200	-2.36357200
H	-5.26561100	-2.60155400	-1.16616200
C	-3.05566100	0.34391300	-2.88400200
H	-3.72777800	0.50537500	-3.73742700
H	-2.64188800	1.31676100	-2.59487400
H	-2.22534000	-0.28643000	-3.22116400
C	-5.31157200	0.69819000	-0.77178400
H	-4.87091500	1.63458800	-0.40962200
H	-6.04581800	0.95205700	-1.54765400
H	-5.85439200	0.23758400	0.06245500

$TS_{11\text{-}12}$

C	-1.34165500	3.65405400	-1.92537200
C	-0.26011700	2.80603000	-1.80661400
C	-2.14245700	3.94622400	-0.80201700
H	0.36982800	2.59313100	-2.66586300
H	-2.97344900	4.63928700	-0.89756500
C	0.07484500	2.21621300	-0.54791700
C	-1.86890400	3.35529600	0.42199100
H	-2.47731400	3.58743700	1.29079000
C	-0.78741900	2.46415300	0.56505300
H	-0.51093800	2.12872500	1.55871200
H	-1.56766200	4.10953100	-2.88502300
C	1.32221900	1.49010800	-0.41905700
C	1.95989400	1.24104100	0.93451700
H	1.93921400	2.20789800	1.46481000
H	2.02135000	1.65323000	-1.22868600
H	1.34269500	0.56069800	1.53395800
C	3.33967700	0.76620800	0.88118200
C	4.50147800	0.40228800	0.86493500
Br	1.28243100	-0.84337100	-1.49334100
Si	6.24903200	-0.19035500	0.81234900
C	7.36991000	1.17680500	1.47947300
H	8.42095400	0.85971200	1.46150300
H	7.28973500	2.09185800	0.87986600
H	7.11925800	1.43430700	2.51587100
C	6.68904000	-0.58474800	-0.98051200
H	7.71887700	-0.95801200	-1.05572000
H	6.02427100	-1.35241500	-1.39442500
H	6.60953800	0.30315700	-1.61958000
C	6.38999000	-1.73712800	1.88553200
H	5.72883000	-2.53432600	1.52490900
H	7.41704600	-2.12525000	1.87573900
H	6.12289600	-1.52956500	2.92893800
Pd	-0.99435100	0.13650500	-0.26474300
C	-2.96465400	-0.60934300	0.45671200
C	-2.18623500	-1.49265800	-0.00727400
Br	-1.94748500	-3.33818600	-0.41230900
Si	-4.50741200	0.10626500	1.19778400
C	-5.68473500	-1.33001400	1.55641600
H	-6.62234300	-0.96327500	1.99532900
H	-5.93825600	-1.87901600	0.64147500
H	-5.24428700	-2.04466600	2.26226400
C	-5.29320800	1.29642000	-0.03873200
H	-6.20969900	1.74015200	0.37233300
H	-4.61073600	2.11227500	-0.30246800
H	-5.56187000	0.77717500	-0.96689600
C	-4.08132800	0.99144400	2.81189500
H	-3.38971500	1.82659100	2.65216400
H	-4.98768300	1.39518100	3.28217500
H	-3.61425900	0.30433700	3.52823000

INT12

C	-0.84163500	3.73375100	-1.53408100
C	0.34931600	2.99543100	-1.53408500
C	-1.70964200	3.65886200	-0.45054700
H	1.00685100	3.02950300	-2.39913200
H	-2.63886600	4.22130500	-0.45355200
C	0.69894900	2.21009200	-0.43404000
C	-1.37708500	2.86826600	0.66414600
H	-2.01752800	2.86400000	1.54009900
C	-0.16688100	2.15903800	0.68775600
H	0.14334800	1.65912400	1.60195800
H	-1.09157800	4.34960200	-2.39323300
C	1.95866900	1.40673900	-0.46171700
C	2.92213700	1.62752000	0.71026200
H	3.10705000	2.71253100	0.74709800
H	2.47777200	1.49781600	-1.41449000
H	2.43661500	1.36853900	1.65856300
C	4.19695000	0.92503800	0.58625200
C	5.26760600	0.35441000	0.47807600
Br	1.36081200	-0.61406200	-0.48408000
Si	6.88062100	-0.52991300	0.31838500
C	8.26983500	0.75025500	0.32982600
H	9.24847000	0.26160500	0.23483400
H	8.17110000	1.45901700	-0.50152000
H	8.27714000	1.32867800	1.26178300
C	6.87926900	-1.48416500	-1.31064800
H	7.82223100	-2.03129700	-1.44083700
H	6.06244900	-2.21509800	-1.34634800
H	6.76320600	-0.81317200	-2.17054300
C	7.06420700	-1.71261400	1.77842800
H	6.25397400	-2.45144000	1.79972300
H	8.01357200	-2.26083600	1.71765700
H	7.05089800	-1.17617700	2.73505200
Pd	-1.47478800	0.19000600	0.10773300

C	-3.53863700	-0.55299200	0.21217700
C	-2.65649200	-1.42416200	-0.06194900
Br	-2.34968700	-3.27539700	-0.46181300
Si	-5.19196800	0.21527000	0.52643200
C	-6.49519800	-1.15687300	0.52451600
H	-7.49797200	-0.74355700	0.69712500
H	-6.51542000	-1.68902700	-0.43438100
H	-6.30036100	-1.89644300	1.31079200
C	-5.56386300	1.46081500	-0.84482500
H	-6.53601300	1.94520800	-0.68330500
H	-4.79962400	2.24567500	-0.89003800
H	-5.59322200	0.97221400	-1.82647600
C	-5.17548400	1.07763900	2.20810900
H	-4.44082100	1.89124600	2.23846700
H	-6.15947100	1.50904800	2.43486100
H	-4.92616600	0.37537700	3.01300600

[Pd-1b]

Pd	-0.60651000	-0.21424600	0.02539800
C	1.73273500	2.04808000	-0.25327300
C	2.62354300	2.34507800	-1.30050300
C	2.24707000	2.01786300	1.05741400
C	3.96931700	2.61774900	-1.05201800
H	2.24776200	2.37758100	-2.32114500
C	3.59016300	2.28740500	1.30594200
H	1.59035600	1.77089600	1.88689800
C	4.46029400	2.59234100	0.25389800
H	4.63282300	2.85224600	-1.88089800
H	3.96283200	2.25572000	2.32683700
H	5.50790700	2.80284300	0.45208200
C	4.55063500	-1.57137000	-0.76353500
C	3.27094100	-1.39126000	-1.28851300
C	4.71862900	-2.16104400	0.48996900
H	3.15067400	-0.93369200	-2.26737600
H	5.71426300	-2.30195200	0.90223500
C	2.12748400	-1.79632200	-0.57764700
C	3.59161800	-2.56487800	1.21334800
H	3.70943500	-3.02112200	2.19327100
C	2.31444000	-2.38347800	0.68914600
H	1.45194300	-2.69467700	1.27161100
H	5.41660500	-1.24804100	-1.33545800
C	0.79744400	-1.63347200	-1.20185300
C	0.30348100	1.84001900	-0.56770500
H	0.06912200	1.88017800	-1.63041400
C	-0.36042700	-2.28268700	-0.80742700
H	-1.19683200	-2.35601900	-1.49866600
H	0.81029600	-1.16261500	-2.18290600
H	-0.35335300	-3.00889600	0.00198700
C	-0.75182700	1.96723900	0.32842700
H	-1.75121800	2.17866700	-0.04575300
H	-0.57255500	2.23847000	1.36638500
C	-2.72840000	-1.06157000	1.05882900
H	-2.63023700	-2.11434900	0.80612600
C	-1.86964100	-0.54555700	1.99184700
H	-2.00765500	0.43930500	2.42572100
H	-1.17043300	-1.19758300	2.50827500
C	-3.89117400	-0.39261900	0.44845600
C	-4.31564200	0.90115100	0.80946300
C	-4.63424300	-1.08284900	-0.52711700
C	-5.43011100	1.48053000	0.20777600
C	-5.74934800	-0.50267300	-1.13041600
C	-6.15171100	0.78394900	-0.76711700
H	-3.77723800	1.45472300	1.57282200
H	-4.32953000	-2.08731600	-0.81237500
H	-5.74104300	2.47908400	0.50407300
H	-6.30485100	-1.05692000	-1.88247200
H	-7.02124900	1.23903300	-1.23355600

[Pd-1b]'

Pd	-0.00034900	-1.24251300	0.00167300
C	2.77172400	0.00581400	-0.44287900
C	3.81930400	-0.14817200	0.48325300
C	2.47255200	1.30635200	-0.89294600
C	4.54014700	0.95175200	0.94764500
H	4.06899200	-1.14547600	0.83868800
C	3.19310500	2.40436700	-0.43019800
H	1.66874500	1.46029500	-1.60693400
C	4.23009800	2.23476100	0.49336300
H	5.34538100	0.80496500	1.66293800
H	2.94496000	3.39898100	-0.79198700
H	4.78975900	3.09439500	0.85212100
C	-3.46117500	2.52327300	0.20812600
C	-2.56623900	1.68447800	0.87182900
C	-4.39264700	1.98854900	-0.68355900
H	-1.84466100	2.10735000	1.56725300
H	-5.09246300	2.63862100	-1.20178700
C	-2.57780500	0.29384000	0.65999500
C	-4.41942200	0.60710500	-0.90239500
H	-5.14269100	0.18032100	-1.59265800
C	-3.52511200	-0.23032900	-0.24056700
H	-3.56136100	-1.29988600	-0.42616300
H	-3.43149900	3.59448600	0.39034300
C	-1.61745300	-0.54684100	1.40853800
C	2.05680600	-1.20059700	-0.91535100
H	2.48924800	-2.13960200	-0.57067000
C	-1.55008800	-1.93053600	1.41802000
H	-0.99642400	-2.43816200	2.20430100
H	-1.05288000	-0.00935900	2.16997000
H	-2.25034300	-2.55006800	0.86292800
C	1.09962400	-1.26488000	-1.91497500
H	0.84918100	-2.22481100	-2.36032400
H	0.79159900	-0.39006000	-2.48238800

INT1'

Pd	0.01328300	0.59910100	0.59315100
C	-4.49163700	0.69077900	-1.87068500
C	-3.44299500	1.37895600	-1.26170400
C	-5.12677300	-0.35491000	-1.19828100
H	-2.95249100	2.19314200	-1.79058700
H	-5.94455700	-0.89339900	-1.66951600
C	-3.00293000	1.03804900	0.02976100
C	-4.70354400	-0.70249600	0.08864800
H	-5.19391000	-1.51292800	0.62178500
C	-3.65582700	-0.01553600	0.69660200
H	-3.34273200	-0.30012900	1.69699900
H	-4.81259500	0.97282800	-2.87011700
C	-1.89952000	1.81722900	0.63370200
C	-1.39104400	1.69258200	1.91607100
H	-0.78057400	2.48976800	2.33457900
H	-1.61174900	2.69987600	0.06215400
H	-1.78908900	0.98046900	2.63446500
C	1.05738600	-1.08551600	0.08557100
C	1.92220200	-0.19009100	-0.11301300
Br	0.55516100	-2.91539700	0.07606100
Si	3.43582000	0.80995800	-0.51824000
C	4.78582700	-0.38539800	-1.08341800
H	5.70485300	0.15958300	-1.33676200
H	5.03439600	-1.11013500	-0.29864000

H	4.47726300	-0.94854500	-1.97251900
C	3.97164800	1.73317600	1.03747900
H	4.87602000	2.32569900	0.84641500
H	3.18851000	2.41826300	1.38391100
H	4.19381500	1.03945100	1.85746300
C	2.99386700	2.01809700	-1.89856000
H	2.19930200	2.70625000	-1.58573000
H	3.86621800	2.62039500	-2.18424800
H	2.64421300	1.49070600	-2.79439900

$TS_{1'-2'}$

Pd	0.81034600	1.13860100	-0.30736500
C	-3.78021400	0.61363600	-0.52799600
C	-2.69470200	1.30348200	-1.07646200
C	-4.03902700	0.69148700	0.84844300
H	-2.48435400	1.23042900	-2.14497200
H	-4.88298500	0.15187100	1.27975200
C	-1.84220400	2.08377500	-0.26094000
C	-3.20936900	1.47436800	1.66816200
H	-3.41017600	1.54520600	2.73800000
C	-2.12538600	2.16630100	1.12292200
H	-1.49058200	2.76934100	1.77163700
H	-4.42223800	0.01284900	-1.17351400
C	-0.66606400	2.73076800	-0.88517900
C	0.34827800	3.42131700	-0.24200300
H	1.08962500	3.96415800	-0.82846800
H	-0.66702700	2.73121100	-1.97966100
H	0.32896100	3.63015600	0.82844700
C	1.26449400	-0.73642800	0.02089000
C	0.63111800	-1.81703100	-0.00793000
Br	3.25558400	0.03200600	0.41382400
Si	-0.64663800	-3.14291700	-0.09473000
C	0.21769000	-4.82861400	-0.08517700
H	-0.52446100	-5.64153400	-0.13910000
H	0.89768300	-4.93424100	-0.94407400
H	0.80815600	-4.97133100	0.83256500
C	-1.62428000	-2.90480300	-1.69932100
H	-2.40949200	-3.67159400	-1.79933800
H	-2.10864400	-1.91685600	-1.71289400
H	-0.96832900	-2.97344200	-2.58042900
C	-1.78777600	-2.96876900	1.40530800
H	-2.27744500	-1.98338200	1.41087300
H	-2.57413600	-3.74088500	1.39070900
H	-1.22835200	-3.07392600	2.34733500

INT2'

Pd	-1.11555700	-0.42284200	-0.08190300
C	-1.21155800	3.47649200	1.19395500
C	-2.05308000	2.38060800	1.29677600
C	-0.67877700	3.84371300	-0.05153200
H	-2.45898700	2.08641900	2.26076800
H	-0.01641400	4.70138800	-0.12327300
C	-2.39837300	1.62425800	0.14661000
C	-0.99572700	3.11297400	-1.19305500
H	-0.58781100	3.39799600	-2.15779500
C	-1.85208400	2.01081800	-1.10841400
H	-2.14466800	1.49574800	-2.01776500
H	-0.95716300	4.04694500	2.08222900
C	-3.23347400	0.42224300	0.30691400
C	-3.49571600	-0.49572200	-0.66967400
H	-4.03866400	-1.40263300	-0.42587300
H	-3.57987800	0.22100400	1.31834400
H	-3.29942800	-0.32190300	-1.72356500
C	0.81187100	-0.24333900	-0.03589100
C	2.02889700	-0.07127600	-0.02618700
Br	-0.81745400	-2.89835100	0.15770800
Si	3.84618100	0.18906800	-0.00723800
C	4.21646900	2.02023000	0.29619000
H	5.29898300	2.20465100	0.31029700
H	3.78146200	2.65241400	-0.48787300
H	3.80951700	2.35590700	1.25810000
C	4.56192900	-0.33695300	-1.67709000
H	5.65099000	-0.19734600	-1.70027200
H	4.35630800	-1.39468600	-1.88175300
H	4.13299400	0.24847400	-2.49976200
C	4.60560700	-0.85079000	1.37717300
H	4.39837100	-1.91789200	1.23152900
H	5.69578300	-0.72296900	1.41396600
H	4.20269600	-0.56700700	2.35715800

INT3'

C	-3.12148800	4.16170000	-0.91851800
C	-1.88129600	3.73450000	-0.45016800
C	-4.28400200	3.51427300	-0.49510500
H	-0.97669900	4.24241200	-0.77656700
H	-5.25403900	3.84500700	-0.85594800
C	-1.77903900	2.65133100	0.44334500
C	-4.19786800	2.44104500	0.39854800
H	-5.10142300	1.93851600	0.73220400
C	-2.95994500	2.01069000	0.86489100
H	-2.90721300	1.17296600	1.55068500
H	-3.18084900	4.99765700	-1.60971200
C	-0.44467300	2.27839200	0.92564000
C	-0.09746600	1.26706400	1.80274400
H	0.87285500	1.27823700	2.28980000
H	0.33093900	2.99403300	0.65964800
H	-0.84170200	0.61782300	2.24835000
C	-1.04089800	-0.82096000	0.11107900
C	-2.01250200	-1.54076600	0.32787600
Br	1.14084400	-1.34700200	-2.00100700
Si	-3.42618400	-2.68230300	0.57585900
C	-4.45698600	-2.11063400	2.05959000
H	-5.28717800	-2.80443000	2.24838900
H	-3.85377900	-2.06178400	2.97489600
H	-4.89182800	-1.11699700	1.89295100
C	-2.76682600	-4.42319700	0.90782700
H	-3.58898000	-5.13677200	1.05300100
H	-2.15587100	-4.78102500	0.07030500
H	-2.13981900	-4.44854900	1.80768400
C	-4.50551100	-2.68348800	-0.97689200
H	-3.93599400	-3.01508600	-1.85351600
H	-5.36502100	-3.35722500	-0.86061000
H	-4.89333900	-1.68095000	-1.19577100
Pd	0.50237900	0.32992500	-0.17839400
C	2.80950200	1.56373100	0.10717900
H	2.52400800	2.24994500	0.90371900
C	3.86183400	0.61393400	0.49218400
C	4.33114800	0.64325500	1.81885200
C	4.44373400	-0.29905800	-0.40813600
C	5.34638200	-0.21371600	2.23890400
H	3.89780800	1.35081800	2.52240000
C	5.45526100	-1.15601700	0.01381900
H	4.09216800	-0.34921800	-1.43247500
C	5.91026400	-1.11748700	1.33630900
H	5.69626200	-0.17607100	3.26674600
H	5.89034400	-1.85923900	-0.69072000
H	6.70127000	-1.78880000	1.65925100
C	2.24658700	1.75370800	-1.12092400

H	2.55131500	1.18793700	-1.99327200
H	1.60707100	2.61174000	-1.30635800

$TS_{3'-4'}$

C	2.19890500	4.88418600	0.06055300
C	1.91952600	3.69710900	0.73705200
C	1.24190300	5.45071300	-0.78376800
H	2.66430000	3.26915100	1.40426800
H	1.45864100	6.37327600	-1.31502000
C	0.67509500	3.05596700	0.58960200
C	0.00309800	4.82108100	-0.94465400
H	-0.74383700	5.25172200	-1.60595000
C	-0.28019000	3.63722300	-0.26868300
H	-1.23862000	3.14985200	-0.42362100
H	3.16334500	5.36649500	0.19487200
C	0.41735700	1.81308800	1.34049800
C	-0.86984300	1.37402900	1.71793000
H	-0.95289800	0.72024800	2.57790300
H	1.24071200	1.44726500	1.94994100
H	-1.72244000	2.01245500	1.52687700
C	-1.67728900	-0.03831100	0.44018200
C	-2.86409600	-0.36347600	0.51645100
Br	-0.19296200	-1.74904900	-1.87710300
Si	-4.62155800	-0.90905300	0.56594700
C	-5.56481500	0.19561400	1.78091800
H	-6.62030900	-0.10255700	1.83497300
H	-5.15087300	0.12839700	2.79473800
H	-5.53506000	1.24933100	1.47673200
C	-4.68906700	-2.70560600	1.14488000
H	-5.72495900	-3.06838600	1.17885700
H	-4.12618600	-3.36018800	0.46881000
H	-4.26224700	-2.82019200	2.14887400
C	-5.35974800	-0.74049300	-1.16427300
H	-4.80515700	-1.34595100	-1.89097300
H	-6.40651600	-1.07209800	-1.17835100
H	-5.33383900	0.29967100	-1.51156200
Pd	0.23613300	0.11053500	-0.11568800
C	2.76735400	0.06829000	-0.04133600
H	2.93864500	0.84513000	0.70044600
C	3.26420900	-1.25728000	0.35699400
C	3.79321500	-1.40542700	1.65271900
C	3.27144700	-2.37100500	-0.50388400
C	4.31062900	-2.62616000	2.08147000
H	3.80049100	-0.55047200	2.32555400
C	3.78717100	-3.58990200	-0.07372000
H	2.85513600	-2.28665300	-1.50134000
C	4.30784000	-3.72335000	1.21783700
H	4.71493900	-2.72052500	3.08560000
H	3.78122600	-4.44169900	-0.74814500
H	4.70953100	-4.67782600	1.54713800
C	2.27250700	0.46850200	-1.25392700
H	2.19815000	-0.20282800	-2.10102600
H	2.13990200	1.52647600	-1.45967300

INT4'

C	-4.82297600	2.01640400	-0.21697000
C	-3.60986200	2.10217000	0.45601800
C	-5.38759500	0.76505800	-0.49029900
H	-3.18080500	3.07769600	0.67274600
H	-6.33388400	0.69760000	-1.01977100
C	-2.92774900	0.94045900	0.88363000
C	-4.73031900	-0.39483700	-0.07616500
H	-5.16329100	-1.36960100	-0.28336700
C	-3.51609700	-0.31330000	0.60427600
H	-3.01844900	-1.22617700	0.91542100
H	-5.33330700	2.92386800	-0.52836100
C	-1.62903900	1.07160300	1.57343300
C	-1.21554300	-0.00005300	2.58695700
H	-0.50218800	0.42267100	3.30387400
H	-1.44252800	2.08597600	1.92632500
H	-2.06918700	-0.38016800	3.16629100
C	-0.56051000	-1.09319500	1.84603700
C	-0.03134600	-1.98149000	1.18836000
Br	0.38209000	-0.34263400	-2.42054800
Si	0.77002600	-3.48019100	0.42194100
C	0.85209800	-4.77013000	1.80399200
H	1.31481900	-5.69519300	1.43517800
H	1.44983800	-4.41639700	2.65290700
H	-0.14589400	-5.02644100	2.18009700
C	2.49930000	-3.01530100	-0.15630400
H	3.00873800	-3.88554900	-0.59083900
H	2.44925600	-2.23208400	-0.92070600
H	3.11511300	-2.64620600	0.67304300
C	-0.31398400	-4.08747000	-0.99170500
H	-0.40802200	-3.31274400	-1.76078500
H	0.12359500	-4.98010900	-1.45792500
H	-1.32043900	-4.35238300	-0.64446400
Pd	-0.36700500	0.59497700	-0.03681100
C	0.92499200	2.43149700	0.47622200
H	0.57787500	2.73562300	1.46140500
C	2.36519400	2.13186000	0.42574000
C	3.09506100	2.18040900	1.62860400
C	3.05378500	1.83798800	-0.76688500
C	4.46885200	1.94802600	1.64428900
H	2.57569600	2.41009200	2.55659500
C	4.42583200	1.60554200	-0.74863000
H	2.50885700	1.76115500	-1.70148800
C	5.13932400	1.65987600	0.45362700
H	5.01455000	1.99259100	2.58295300
H	4.94152000	1.37508500	-1.67684000
H	6.21041400	1.47650100	0.46072800
C	0.05756100	2.64907800	-0.59773800
H	0.40480100	2.61575800	-1.62523700
H	-0.87027800	3.18919800	-0.43139500

INT5'

C	3.43087800	3.46760300	-0.02919900
C	2.12881200	3.10115300	0.27922700
C	4.01389000	3.04652300	-1.23191600
H	1.67032600	3.43142000	1.20744100
H	5.03505900	3.33282500	-1.46665600
C	1.35699800	2.31619900	-0.62493000
C	3.29243900	2.25104100	-2.12228500
H	3.75093600	1.91288800	-3.04667600
C	1.98048500	1.88123300	-1.82854000
H	1.42077200	1.28142900	-2.53920300
H	3.99970900	4.07701900	0.66677500
C	0.02665800	1.84854900	-0.23907000
C	-1.02613700	1.58956000	-1.32239100
H	-1.07152800	2.47311300	-1.97920500
H	-0.38740400	2.34946700	0.63678500
H	-0.73357600	0.75402800	-1.97116400
C	-2.36800300	1.34845000	-0.79035900
C	-3.48920000	1.16300700	-0.34758300
Br	3.49134400	-1.00273100	0.96567100
Si	-5.19524600	0.91578300	0.31607600
C	-5.07521600	0.61129800	2.17615300
H	-6.07248500	0.46073300	2.60988500

H	-4.47836400	-0.28105400	2.40148200
H	-4.61355100	1.46086100	2.69418300
C	-5.96747600	-0.57541900	-0.54789800
H	-6.98753200	-0.75046100	-0.18147400
H	-6.02592400	-0.42603000	-1.63297800
H	-5.38962700	-1.49020000	-0.36738400
C	-6.20428300	2.47365800	-0.03185300
H	-6.27029400	2.67886100	-1.10727000
H	-7.22822100	2.36596300	0.34944100
H	-5.76217100	3.35482100	0.44889900
Pd	1.24585600	0.25210600	0.40350200
C	-0.56121600	-1.18466400	0.77150200
H	-1.42375600	-0.57028800	0.52852100
C	-0.44394300	-2.40928000	-0.03895800
C	-1.41743200	-2.64137700	-1.02937800
C	0.56802500	-3.37049100	0.14911000
C	-1.38774300	-3.79976100	-1.80489700
H	-2.20624300	-1.90807700	-1.18096000
C	0.59536600	-4.52498100	-0.62749900
H	1.35048400	-3.19624800	0.88019400
C	-0.38084700	-4.74610300	-1.60550000
H	-2.15021300	-3.96293000	-2.56194800
H	1.38615800	-5.25426800	-0.47411100
H	-0.35324600	-5.64972200	-2.20865000
C	0.12508800	-0.86877000	1.93650900
H	0.84683800	-1.54466400	2.38314000
H	-0.26198400	-0.08632500	2.58483300

$TS_{5'-6'}$

C	4.52355400	-2.15963600	-2.16957500
C	3.17420000	-1.89712100	-1.94099700
C	5.39833200	-2.31593600	-1.09221600
H	2.49555100	-1.78547100	-2.78348200
H	6.45122700	-2.51811700	-1.26776300
C	2.66946600	-1.78989500	-0.63080700
C	4.91214200	-2.20948700	0.21498100
H	5.58779300	-2.32555200	1.05785600
C	3.56449100	-1.94870100	0.44671900
H	3.20989600	-1.85392300	1.46897900
H	4.89126700	-2.24373100	-3.18858400
C	1.23532800	-1.51275500	-0.44870300
C	0.50445000	-1.78122600	0.74234400
H	1.00725500	-2.31800900	1.54587000
H	0.64784600	-1.44098400	-1.36003000
H	0.77193600	-0.43039100	1.77313900
C	-0.91985000	-1.91482100	0.70764400
C	-2.13142100	-2.05890500	0.67887300
Br	0.99679400	2.33941100	2.32621500
Si	-3.97514900	-2.19209900	0.60915100
C	-4.46386900	-2.58843000	-1.17136300
H	-5.55470700	-2.67098600	-1.26458700
H	-4.12987700	-1.80189000	-1.85898100
H	-4.02890700	-3.53701500	-1.50900600
C	-4.69866600	-0.53465600	1.14503400
H	-5.79604200	-0.56205800	1.11639500
H	-4.39718300	-0.27759000	2.16754600
H	-4.36535100	0.27675900	0.48703100
C	-4.51716700	-3.57425700	1.77475600
H	-4.21568900	-3.36732700	2.80875100
H	-5.60947300	-3.68412600	1.76311600
H	-4.08311400	-4.53952800	1.48697700
Pd	1.03181700	0.48419500	0.50882000
C	0.74283000	1.47161200	-1.74749600
H	1.03218500	0.64380300	-2.39189900
C	-0.66856300	1.87777700	-1.87443600
C	-1.46693500	1.23043200	-2.83449600
C	-1.24919500	2.89291900	-1.09064700
C	-2.80232700	1.58828200	-3.01634100
H	-1.03043600	0.44505400	-3.44772700
C	-2.58375200	3.24593800	-1.27025300
H	-0.66186400	3.38855800	-0.32415400
C	-3.36539800	2.59821000	-2.23340300
H	-3.40045600	1.08109000	-3.76871200
H	-3.01815800	4.02791300	-0.65349300
H	-4.40595800	2.87978200	-2.37060200
C	1.73594700	2.10192000	-1.04814400
H	1.57106500	3.02758700	-0.50852100
H	2.77032600	1.79556700	-1.17832700

INT6'

C	5.07909000	1.64532100	2.04934500
C	3.69886200	1.52226900	1.89747200
C	5.89197700	1.81361500	0.92751800
H	3.06863100	1.40037300	2.77534600
H	6.96836500	1.90732000	1.04106600
C	3.10303100	1.56622100	0.62302500
C	5.31367900	1.85981600	-0.34614900
H	5.94109300	1.98814500	-1.22379100
C	3.93668100	1.73707400	-0.49963900
H	3.50919600	1.76160000	-1.49745100
H	5.51739600	1.61041700	3.04287100
C	1.63750000	1.45793900	0.54154600
C	0.83904600	1.73272800	-0.57207200
H	1.31512500	2.03349700	-1.50227800
H	1.13271100	1.39962200	1.50294300
H	1.74475900	-0.20990900	-1.81376200
C	-0.55693300	2.00264600	-0.50038100
C	-1.74190200	2.30515000	-0.50466300
Br	1.15434700	-2.80595200	-1.62945100
Si	-3.51943300	2.80904500	-0.58503700
C	-4.16456200	3.04810700	1.17381900
H	-5.21058300	3.38123100	1.15692500
H	-4.12445200	2.11635900	1.75049300
H	-3.58521000	3.80464100	1.71700400
C	-4.48738800	1.46028100	-1.47996600
H	-5.55004300	1.72838400	-1.54882600
H	-4.11401900	1.31254300	-2.50047100
H	-4.41653800	0.49886100	-0.95813300
C	-3.61096700	4.43737100	-1.53750900
H	-3.21778100	4.32972500	-2.55559800
H	-4.65127800	4.77941800	-1.61718900
H	-3.03784200	5.22908600	-1.03990000
Pd	1.09037800	-0.53553400	-0.46911600
C	-0.44993300	-1.08925200	1.80027300
H	-0.51906500	-0.07353000	2.18804000
C	-1.74872400	-1.71228500	1.50283500
C	-2.91638000	-1.05165500	1.92574700
C	-1.87741300	-2.95531000	0.85520200
C	-4.17497100	-1.61660500	1.72149600
H	-2.82940900	-0.09242100	2.43079700
C	-3.13519200	-3.51284300	0.64194700
H	-0.99409200	-3.47103800	0.49339700
C	-4.28780800	-2.84981100	1.07608100
H	-5.06443200	-1.09511500	2.06490200
H	-3.21745900	-4.46848400	0.13141500
H	-5.26654300	-3.29183900	0.90994300
C	0.77702300	-1.66738000	1.74482900
H	0.91697900	-2.70532600	1.46271200

H	1.64876200	-1.15768700	2.14564300

INT7'

C	-2.54771300	3.57859300	-1.72292700
C	-1.41377600	2.77036800	-1.72592200
C	-2.93487700	4.24009700	-0.55403300
H	-1.11633500	2.25522300	-2.63567300
H	-3.81385400	4.87877700	-0.55339800
C	-0.64991000	2.59431100	-0.55645600
C	-2.17636600	4.08914600	0.61052200
H	-2.45745900	4.61916500	1.51660600
C	-1.04422200	3.27503900	0.61134900
H	-0.44419900	3.19923100	1.51360800
H	-3.12749700	3.69576200	-2.63413900
C	0.56189300	1.75883500	-0.61946200
C	1.27921100	1.27631000	0.47772100
H	0.89592400	1.46314800	1.47978900
H	1.04754900	1.72150400	-1.59041700
H	0.86411100	-0.57813800	-1.58079400
C	2.63832500	0.85623000	0.40933800
C	3.81611400	0.52823400	0.39559400
Br	-0.63227000	-2.75615600	-1.18726900
Si	5.59571100	0.03236500	0.33015200
C	6.51444700	0.96144200	1.69415500
H	7.58026900	0.69816800	1.69368000
H	6.44052100	2.04772700	1.56161300
H	6.11371500	0.71864600	2.68597100
C	6.27507700	0.49456000	-1.36930000
H	7.33320900	0.21370700	-1.45303700
H	5.72984000	-0.01850800	-2.17074000
H	6.20201600	1.57333700	-1.55280400
C	5.70745700	-1.83189300	0.60449300
H	5.15357200	-2.38619800	-0.16264800
H	6.75316100	-2.16491300	0.56764100
H	5.30072800	-2.12169400	1.58078900
Pd	0.05391200	-0.47849600	-0.28488900
C	-1.81698800	-0.22664500	1.70934200
H	-1.70436900	0.84477200	1.86771800
C	-3.15499400	-0.62959300	1.25050100
C	-4.09138800	0.37612800	0.94859500
C	-3.55404900	-1.97434500	1.13328800
C	-5.38348200	0.05292000	0.53782100
H	-3.79619500	1.41885800	1.03297000
C	-4.84423400	-2.29587100	0.72226100
H	-2.85274500	-2.77020400	1.35829500
C	-5.76398900	-1.28545500	0.42314900
H	-6.09128200	0.84471900	0.30761300
H	-5.13467100	-3.33920700	0.63411000
H	-6.77071900	-1.54210800	0.10424400
C	-0.76589800	-1.02833400	2.02123100
H	-0.81712500	-2.11014900	1.95569400
H	0.11755600	-0.61893700	2.50292700

$TS_{7'-8'}$

C	2.13006500	5.02434200	-0.09950100
C	1.06400400	4.19219300	0.24197600
C	3.13434300	4.55882700	-0.94905700
H	0.28409900	4.55652800	0.90622400
H	3.96951800	5.20222800	-1.21165500
C	0.98127000	2.88673500	-0.26871000
C	3.06794600	3.25537100	-1.45266300
H	3.85417000	2.88233600	-2.10308300
C	2.00368500	2.42400900	-1.11511000
H	1.98087400	1.40598100	-1.49267300
H	2.17616200	6.03288300	0.30176800
C	-0.20723500	2.07703900	0.08605100
C	-0.75411500	1.05729300	-0.73532500
H	-0.24230500	0.82954500	-1.66838300
H	-0.89565600	2.55346500	0.78029100
H	0.40653900	1.22672200	1.54352500
C	-2.12914500	0.68953000	-0.66693500
C	-3.30792700	0.36133500	-0.64827600
Br	1.37203500	-0.95653200	3.00165000
Si	-5.09013000	-0.12395100	-0.59160400
C	-6.04424100	1.22806200	0.31605000
H	-7.11177700	0.97763000	0.37100700
H	-5.67975300	1.35589200	1.34252600
H	-5.95533700	2.19532700	-0.19320200
C	-5.23041900	-1.76732100	0.32744100
H	-6.27849500	-2.08858300	0.38959500
H	-4.66993400	-2.56215100	-0.17994100
H	-4.84575900	-1.68829300	1.35153600
C	-5.71203200	-0.30288800	-2.36558300
H	-5.15191100	-1.06996700	-2.91415500
H	-6.77038300	-0.59480700	-2.37544800
H	-5.62195400	0.63824400	-2.92142100
Pd	0.23590100	-0.15949300	0.82180200
C	0.22780200	-2.03172000	-0.86904700
H	-0.47330000	-1.63790400	-1.60266200
C	1.59944100	-2.22942400	-1.37100400
C	1.85234700	-1.99944000	-2.73565300
C	2.66337100	-2.65398600	-0.55208700
C	3.12448000	-2.19687700	-3.27246600
H	1.03835700	-1.67527600	-3.38062700
C	3.93311700	-2.84607300	-1.08906700
H	2.50099700	-2.81002900	0.50975100
C	4.16938000	-2.62096800	-2.44978000
H	3.29819500	-2.01963100	-4.33046900
H	4.74459700	-3.16843700	-0.44237800
H	5.16288600	-2.77279600	-2.86294600
C	-0.28069800	-2.42154200	0.33764900
H	0.30681500	-2.96156800	1.07140500
H	-1.35016200	-2.36370400	0.51980300

INT8'

C	0.87476700	5.35389700	0.24142600
C	0.00178600	4.30506500	0.53698800
C	2.24258800	5.10984500	0.10038500
H	-1.06216800	4.50145400	0.64726400
H	2.92245600	5.92675200	-0.12620500
C	0.48579100	2.99982900	0.69491400
C	2.73343300	3.81193400	0.25921000
H	3.79721600	3.61338200	0.15994600
C	1.85987900	2.76453900	0.55701200
H	2.24975500	1.75709500	0.69294800
H	0.48523800	6.36178400	0.12441000
C	-0.47241300	1.86335600	0.98116200
C	-0.82666900	1.01166800	-0.23711000
H	-0.34498500	1.33503800	-1.16076400
H	-1.38395500	2.20802200	1.48048900
H	0.00026300	1.19842100	1.76870900
C	-2.17572800	0.58399600	-0.39679900
C	-3.33429800	0.20885500	-0.53640300
Br	1.27171100	-1.98383100	2.54310500
Si	-5.08748200	-0.34310900	-0.73150700
C	-6.10214300	0.40030600	0.67539500
H	-7.15271900	0.09055300	0.60003900
H	-5.72912000	0.07465600	1.65397100

H	-6.07690100	1.49662300	0.65581100
C	-5.12604000	-2.22928000	-0.65533100
H	-6.15473100	-2.59876600	-0.75964200
H	-4.52964700	-2.67810600	-1.45911500
H	-4.73444400	-2.60052400	0.29944800
C	-5.71851500	0.26553000	-2.40395000
H	-5.12281500	-0.13921000	-3.23119400
H	-6.75929500	-0.04707900	-2.56033200
H	-5.68660100	1.35961200	-2.47333200
Pd	0.24963800	-0.56336900	0.60586500
C	0.75483500	-1.31100000	-1.52942600
H	0.19616300	-0.64992500	-2.18786500
C	2.20765400	-1.31486800	-1.76112800
C	2.72453400	-0.46779200	-2.75921300
C	3.09857500	-2.14487000	-1.05277900
C	4.08734500	-0.45365000	-3.05036100
H	2.04645400	0.17736700	-3.31316900
C	4.45908800	-2.12680400	-1.34397100
H	2.72951400	-2.78329700	-0.25668800
C	4.95906000	-1.28416000	-2.34306200
H	4.46736200	0.20445900	-3.82692900
H	5.13446200	-2.76922300	-0.78583400
H	6.02268400	-1.27456900	-2.56520000
C	0.01578900	-2.22206100	-0.77655800
H	0.48085400	-3.07650100	-0.29545500
H	-1.05944500	-2.28140800	-0.92108900

INT9'

C	5.87845300	-1.51991600	0.50192800
C	4.51259600	-1.71987800	0.29322300
C	6.31667100	-0.49017600	1.33766700
H	4.17673300	-2.52827400	-0.35266700
H	7.37960200	-0.33587600	1.50385500
C	3.56468200	-0.89529000	0.91526500
C	5.38074900	0.33723800	1.96279100
H	5.71301500	1.13737200	2.61942000
C	4.01575500	0.13611100	1.75068500
H	3.29150800	0.78118400	2.24352700
H	6.59947600	-2.17217900	0.01586500
C	2.07835400	-1.10023200	0.66518000
C	1.60300200	-0.30688300	-0.54688700
H	2.07332600	-0.58493500	-1.48986100
H	1.49936300	-0.80678400	1.54647100
H	1.87203100	-2.15604800	0.46619600
C	1.17108400	1.01702500	-0.43193400
C	0.34539500	1.95725200	-0.41684400
Br	-0.39227100	-2.74311000	-1.65143200
Si	-0.20422900	3.74175400	-0.39612600
C	1.31845500	4.75631500	0.06771900
H	1.07659700	5.82729600	0.07717400
H	1.69152200	4.48979400	1.06380000
H	2.13507500	4.60455800	-0.64793100
C	-1.56709300	3.97845500	0.88581600
H	-1.77260100	5.04902300	1.01710800
H	-2.50822000	3.50394800	0.58480600
H	-1.27953500	3.57542600	1.86413400
C	-0.81504200	4.18576700	-2.12316700
H	-1.66643700	3.56573000	-2.42800000
H	-1.13759200	5.23453600	-2.15936800
H	-0.02376100	4.05463700	-2.87098700
Pd	-0.55106300	-0.27311200	-0.87588900
C	-2.91094300	-0.60926600	-0.68709400
H	-2.98569700	-1.52719600	-1.26302100
C	-2.67514700	0.55277000	-1.37786500
H	-2.75919600	1.52722500	-0.90892000
H	-2.63267400	0.54041500	-2.46330000
C	-3.24511400	-0.75252400	0.74312100
C	-3.57887200	-2.03152100	1.22346500
C	-3.26799600	0.32790600	1.64482900
C	-3.92871800	-2.22674500	2.55882900
H	-3.55766700	-2.87616300	0.54001400
C	-3.61591200	0.13210500	2.97850100
H	-3.00793700	1.32537000	1.30438300
C	-3.94829000	-1.14548600	3.44162100
H	-4.18315000	-3.22338000	2.90904300
H	-3.62924100	0.97818300	3.66060100
H	-4.21936200	-1.29457000	4.48332400

$TS_{9'-10'}$

C	5.63535200	-1.57506900	1.01705900
C	4.33779700	-1.10578100	1.23017800
C	6.56564000	-0.78403800	0.34024800
H	3.61550100	-1.72944800	1.74987600
H	7.57546600	-1.14957300	0.17369200
C	3.95279600	0.15981100	0.77234100
C	6.19294700	0.48158800	-0.11859100
H	6.91239700	1.10702600	-0.64068200
C	4.89724800	0.95032500	0.10152700
H	4.62009100	1.94440600	-0.24477000
H	5.91714500	-2.56085600	1.37755700
C	2.55722600	0.68814600	1.02041100
C	1.71655200	0.93105400	-0.21955100
H	2.25314900	1.09366200	-1.15040600
H	2.62521200	1.67753900	1.50317300
H	2.00316300	0.05387600	1.71811200
C	0.48719500	1.58092400	-0.09442400
C	-0.61528300	2.17875200	0.04399900
Br	1.34470100	-1.44579700	-1.03786800
Si	-1.68358700	3.64953200	0.46226200
C	-0.53511500	5.07348600	0.93916800
H	-1.11633500	5.96658500	1.20415900
H	0.08888300	4.81561900	1.80352600
H	0.13235000	5.34580400	0.11252600
C	-2.78832400	3.17909800	1.91737300
H	-3.43127400	4.02187300	2.20299300
H	-3.43916400	2.33144800	1.67318800
H	-2.19444400	2.90036300	2.79636800
C	-2.70856000	4.10927500	-1.05183200
H	-3.39090000	3.30152000	-1.34000800
H	-3.31453800	5.00210400	-0.84922100
H	-2.06938500	4.33005100	-1.91539500
Pd	-1.02985700	0.15150900	-0.71840100
C	-2.73705900	-1.19017700	-1.19083100
H	-2.44594300	-1.59084100	-2.16174800
C	-3.18419100	0.12936100	-1.15022500
H	-3.74680900	0.51303000	-0.30391600
H	-3.29832500	0.68345000	-2.07810100
C	-2.90620200	-2.21081200	-0.13561000
C	-2.56067600	-3.54429200	-0.42179100
C	-3.41812000	-1.92032600	1.14419700
C	-2.71856000	-4.55083300	0.53034900
H	-2.16445200	-3.78879000	-1.40449800
C	-3.57586000	-2.92542900	2.09462800
H	-3.68989400	-0.90008500	1.39920100
C	-3.22722700	-4.24659600	1.79413300
H	-2.44352600	-5.57300200	0.28347000
H	-3.97312700	-2.67809300	3.07590900
H	-3.35162500	-5.02840700	2.53863800

INT10'

C	6.43694300	-1.15452000	-0.55373100
C	5.23967500	-0.51038800	-0.87288800
C	6.41787400	-2.37154800	0.12964700
H	5.26155000	0.43903600	-1.40176600
H	7.34898700	-2.87382700	0.37857000
C	4.00729000	-1.07173800	-0.51695000
C	5.19427100	-2.94299500	0.48800600
H	5.16944200	-3.89361600	1.01451600
C	4.00016600	-2.29864800	0.16331000
H	3.05124700	-2.75796400	0.43454500
H	7.38396600	-0.70342100	-0.83845800
C	2.70485000	-0.38639500	-0.86932300
C	1.92662500	0.17987800	0.33040100
H	1.91248900	-0.51944900	1.16593200
H	2.02326000	-1.10975200	-1.33798600
H	2.86387700	0.41347000	-1.59900600
C	0.59122000	0.65757500	0.00753300
C	-0.39853600	1.39017700	-0.22828200
Br	3.01003100	1.77682700	1.17869400
Si	-1.52922600	2.85907300	-0.42040900
C	-0.47043200	4.41717200	-0.28239700
H	-1.09388600	5.31784700	-0.35925500
H	0.05959400	4.45668700	0.67655500
H	0.28188100	4.46258100	-1.07903400
C	-2.81551800	2.79264400	0.95737500
H	-3.49546300	3.65259000	0.89584700
H	-3.42080800	1.88052900	0.89422000
H	-2.34220700	2.81204400	1.94661500
C	-2.35253700	2.75855300	-2.11529600
H	-2.96373000	1.85269700	-2.20664600
H	-3.00817200	3.62365200	-2.28032800
H	-1.60988800	2.74416100	-2.92235900
Pd	-1.04015500	-0.65659300	-0.50819300
C	-2.36932100	-2.44421600	-0.26019900
H	-1.83547900	-3.06208600	0.46115000
C	-1.88098500	-2.40008400	-1.55894500
H	-2.47509800	-2.02792000	-2.39032900
H	-1.02786300	-3.01487700	-1.83549600
C	-3.69534900	-1.97773000	0.20455100
C	-4.06560300	-2.21352000	1.54100500
C	-4.61901500	-1.32088800	-0.63152200
C	-5.30657300	-1.80600600	2.02897000
H	-3.36735700	-2.72283100	2.20142400
C	-5.85878900	-0.91370700	-0.14393900
H	-4.36752600	-1.12713100	-1.67029600
C	-6.20982600	-1.15211600	1.18877400
H	-5.56772900	-2.00093700	3.06589400
H	-6.55647000	-0.40980700	-0.80800700
H	-7.17797100	-0.83339400	1.56539400

INT11'

C	0.35862200	3.25211500	0.49101800
C	-0.07138800	1.97542800	0.80885000
C	0.37732300	3.68152700	-0.84817900
H	-0.08684100	1.63962700	1.84188200
H	0.70927700	4.68791100	-1.08799000
C	-0.53147900	1.08480800	-0.20534300
C	-0.02909600	2.82260500	-1.86431400
H	-0.01672200	3.15279900	-2.89898500
C	-0.47731900	1.53045400	-1.55779000
H	-0.86152500	0.89741100	-2.35097800
H	0.68381800	3.92406500	1.28004400
C	-0.86163600	-0.29969400	0.11486900
C	-1.91662600	-1.09119500	-0.65649900
H	-1.79515800	-0.97630400	-1.74034600
H	-0.86690200	-0.52997500	1.17960300
H	-1.76518600	-2.15524900	-0.44216700
C	-3.27367000	-0.69054200	-0.26822300
C	-4.39077600	-0.33729300	0.07031100
Br	1.17017400	-2.94736300	0.20046200
Si	-6.08582900	0.18726100	0.56683700
C	-6.10416500	0.48648000	2.43206200
H	-7.10037600	0.80223500	2.76886600
H	-5.83904600	-0.42144300	2.98749200
H	-5.39323700	1.27043700	2.72044100
C	-7.30252000	-1.18333100	0.10970600
H	-8.32825400	-0.90435600	0.38472500
H	-7.29260400	-1.38726700	-0.96803300
H	-7.06420500	-2.12103900	0.62635500
C	-6.52233300	1.77887300	-0.35455500
H	-6.50697600	1.63116300	-1.44141900
H	-7.52834400	2.12410200	-0.08166700
H	-5.82027200	2.58814800	-0.11945600
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C	3.25971600	0.36793900	-1.28419100
H	2.94672400	1.27888400	-1.79327900
C	4.03461300	0.59090300	-0.04901300
C	4.36058200	1.91091700	0.31056900
C	4.47777500	-0.45857900	0.77865300
C	5.11171900	2.17859900	1.45444900
H	4.02317800	2.73083800	-0.31936200
C	5.22420400	-0.18937200	1.92248800
H	4.21862800	-1.48474000	0.53842700
C	5.54610800	1.12824600	2.26522100
H	5.35681700	3.20555100	1.71225200
H	5.55307300	-1.01124000	2.55278000
H	6.12914700	1.33242500	3.15926800
C	3.02867400	-0.82434300	-1.91379400
H	3.43021300	-1.76442900	-1.55180400
H	2.59396400	-0.83925900	-2.90973000

$TS_{11'-12'}$

C	2.17435500	2.62185500	1.54050200
C	0.98794800	1.91790500	1.55470200
C	2.76384600	3.00582900	0.31676000
H	0.52441800	1.63983200	2.49765200
H	3.68719300	3.57759200	0.31830500
C	0.32333000	1.56937500	0.33529600
C	2.16689300	2.65343500	-0.88222300
H	2.61144400	2.95519600	-1.82644000
C	0.97051900	1.90405500	-0.90252800
H	0.44262400	1.79093800	-1.84401000
H	2.65127300	2.89213300	2.47825800
C	-1.02128800	1.02341400	0.39424700
C	-1.95945100	1.15635000	-0.79032400
H	-1.92994900	2.22123500	-1.07727900
H	-1.49935500	1.11459500	1.36203700
H	-1.57053700	0.60451800	-1.65403800
C	-3.34683400	0.78116200	-0.53124500
C	-4.51839900	0.50909400	-0.34131400
Br	-1.10575800	-1.43814300	0.86028800
Si	-6.28058500	0.03548900	-0.06652000
C	-6.92930800	0.96780400	1.44207500
H	-7.97473700	0.70102400	1.64565200
H	-6.34681200	0.73349400	2.34146700
H	-6.88890800	2.05396300	1.29364500

C	-6.36422000	-1.82800900	0.21859800
H	-7.40017800	-2.15500700	0.37868700
H	-5.97011600	-2.38108600	-0.64256200
H	-5.78074800	-2.12783900	1.09737500
C	-7.27050000	0.51012100	-1.60512200
H	-6.89892700	-0.00846400	-2.49732200
H	-8.32899500	0.24441100	-1.48440000
H	-7.22156500	1.58804800	-1.80249900
Pd	1.16875000	-0.41912200	-0.46121800
C	3.07613300	-1.11868300	-1.43260100
H	3.08845800	-0.62810600	-2.40457400
C	4.25724400	-0.82628200	-0.59105500
C	5.21647700	0.08925500	-1.06103300
C	4.49071200	-1.44309400	0.65407100
C	6.36515900	0.37769500	-0.32333800
H	5.05892800	0.57323400	-2.02259800
C	5.63681000	-1.15521100	1.39042100
H	3.76702900	-2.14831700	1.05225000
C	6.58215000	-0.24380000	0.90725700
H	7.09188000	1.08595900	-0.71364600
H	5.79482100	-1.64573500	2.34775200
H	7.47620700	-0.02333900	1.48445200
C	2.17250400	-2.16574100	-1.25295700
H	2.28082400	-2.88424900	-0.44383100
H	1.55847500	-2.49540000	-2.08822500

INT12'

C	1.47957000	2.85844700	1.12810000
C	0.22233500	2.24534100	1.24241300
C	2.26263300	2.63795200	0.00293100
H	-0.38342700	2.42423500	2.12733800
H	3.23285500	3.11658500	-0.09468700
C	-0.27514000	1.42310000	0.22989100
C	1.79033800	1.80993900	-1.03865900
H	2.34083100	1.75601100	-1.97273000
C	0.51969300	1.19603200	-0.93203000
H	0.08351100	0.71413300	-1.80312300
H	1.83552500	3.50614300	1.92418600
C	-1.65450100	0.86391800	0.36438000
C	-2.54194500	0.97923200	-0.88290100
H	-2.47487500	2.02692800	-1.21410500
H	-2.16029400	1.28039400	1.23385600
H	-2.13212600	0.37198000	-1.69822200
C	-3.94472600	0.63585600	-0.66137900
C	-5.11988300	0.36995400	-0.48211400
Br	-1.54579100	-1.16778000	0.90857700
Si	-6.89072900	-0.06658300	-0.20745700
C	-7.27046100	0.09456500	1.63561600
H	-8.31787500	-0.16317300	1.84066000
H	-6.64004400	-0.57400400	2.23435500
H	-7.10431500	1.11814100	1.99327100
C	-7.17084500	-1.84273600	-0.78395000
H	-8.21655400	-2.14169000	-0.63306000
H	-6.94200400	-1.95995900	-1.85024100
H	-6.53930900	-2.54730700	-0.22935800
C	-7.96704700	1.12406600	-1.20428800
H	-7.75100000	1.05918200	-2.27773700
H	-9.03170600	0.89417600	-1.06553800
H	-7.80924300	2.16463900	-0.89523900
Pd	1.95009700	-0.48794200	-0.35504800
C	3.84093400	-1.64220100	-0.67666500
H	3.80464000	-1.89905700	-1.73507100
C	5.03649200	-0.86089200	-0.28915500
C	5.91992800	-0.42844700	-1.29477800
C	5.35457700	-0.54720200	1.04666000
C	7.07326600	0.29255800	-0.98434900
H	5.69643500	-0.66576100	-2.33281600
C	6.50669500	0.16992700	1.35734400
H	4.68964500	-0.85984200	1.84648600
C	7.37326900	0.59618200	0.34455600
H	7.73872400	0.61353500	-1.78189700
H	6.73097600	0.39926900	2.39617000
H	8.27123900	1.15638400	0.59129100
C	2.97550600	-2.32166600	0.17811200
H	3.13293000	-2.34618000	1.25426500
H	2.34978700	-3.11851200	-0.22003100

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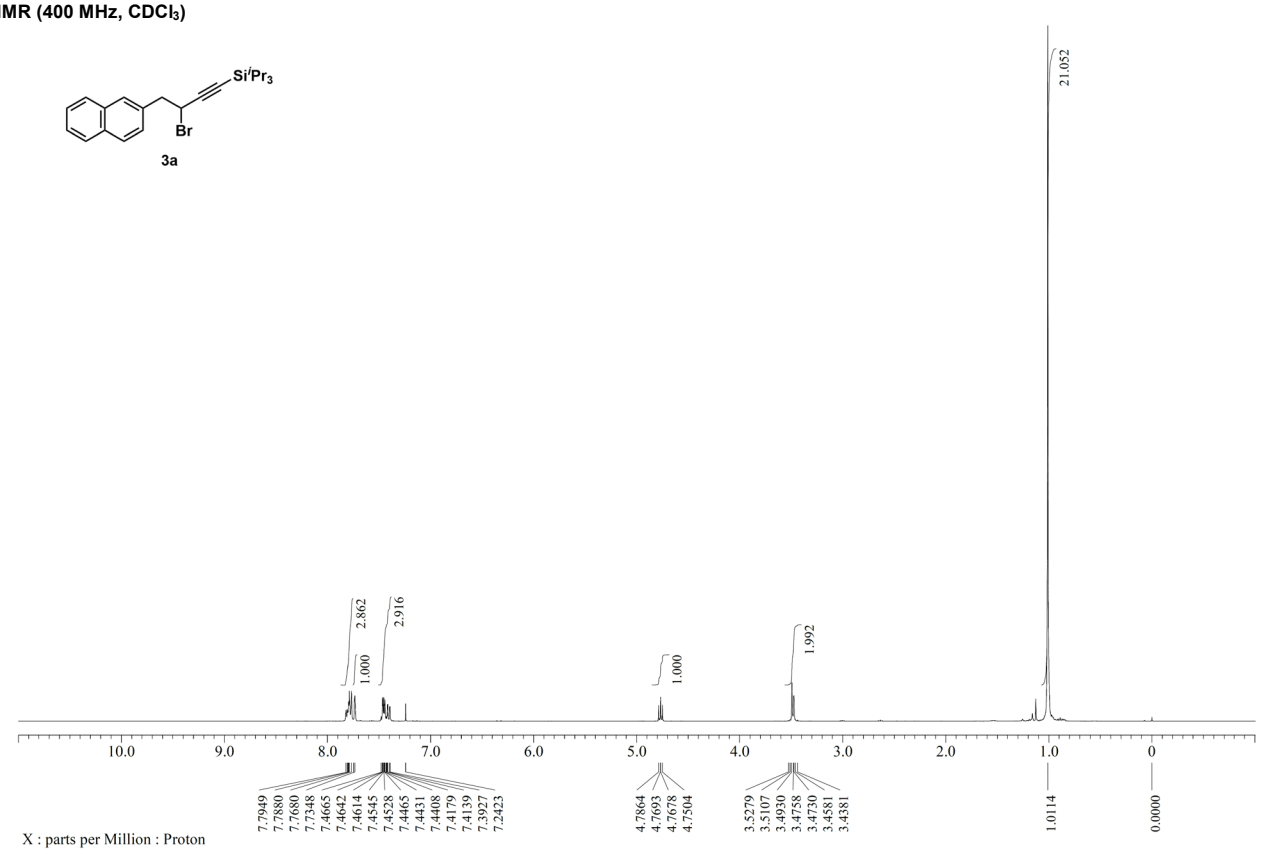
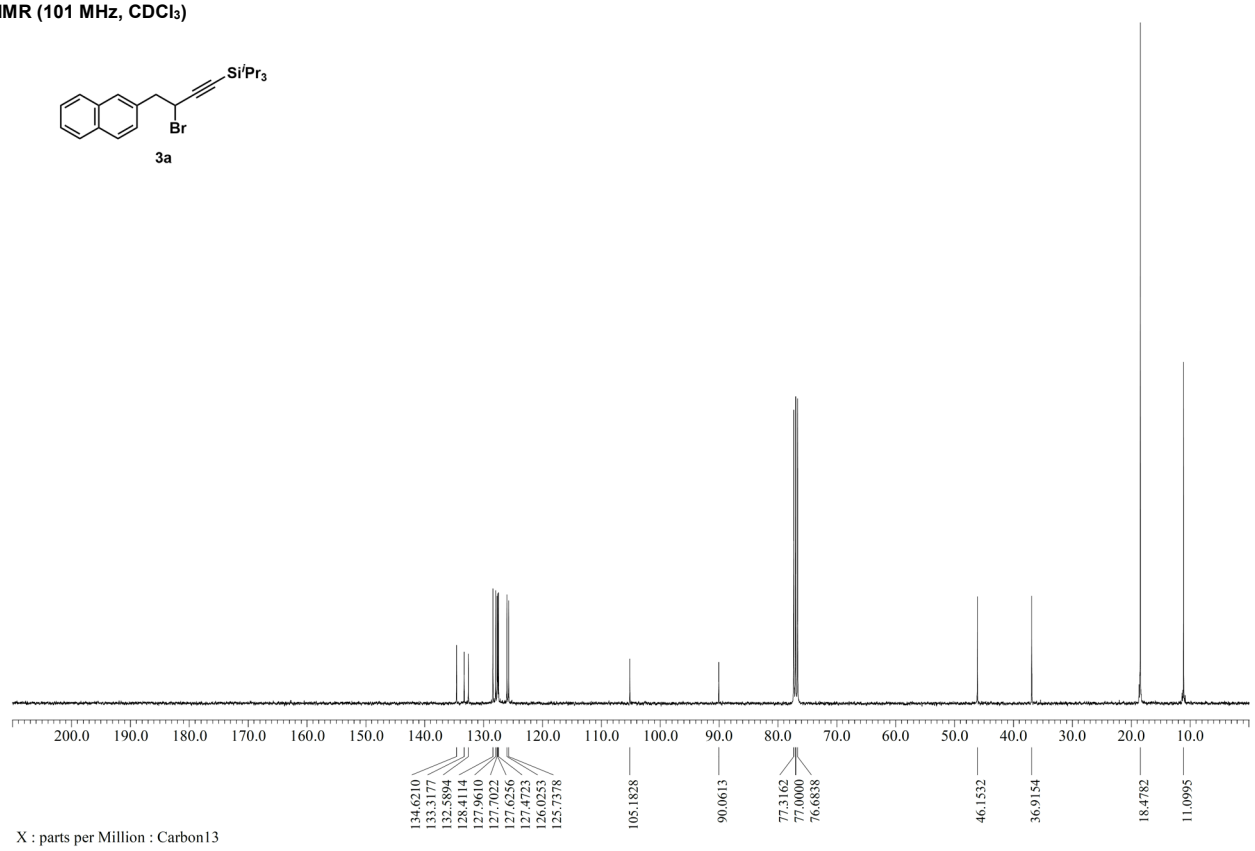
13. Copies of ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR Spectra

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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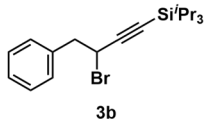
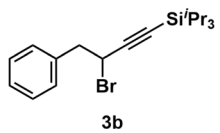


3b

X : parts per Million : Proton

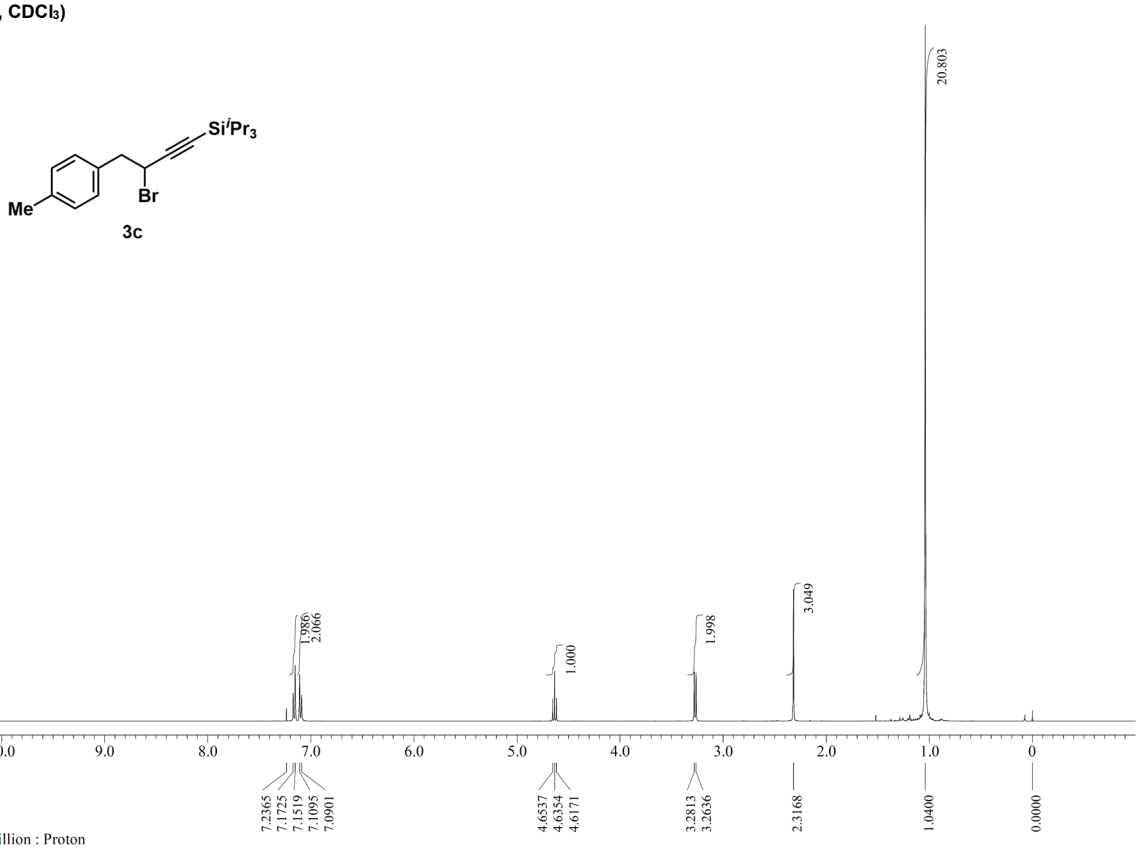
^{13}C NMR (101 MHz, $CDCl_3$)



3b

X : parts per Million : Carbon13

^{1}H NMR (400 MHz, $CDCl_3$)



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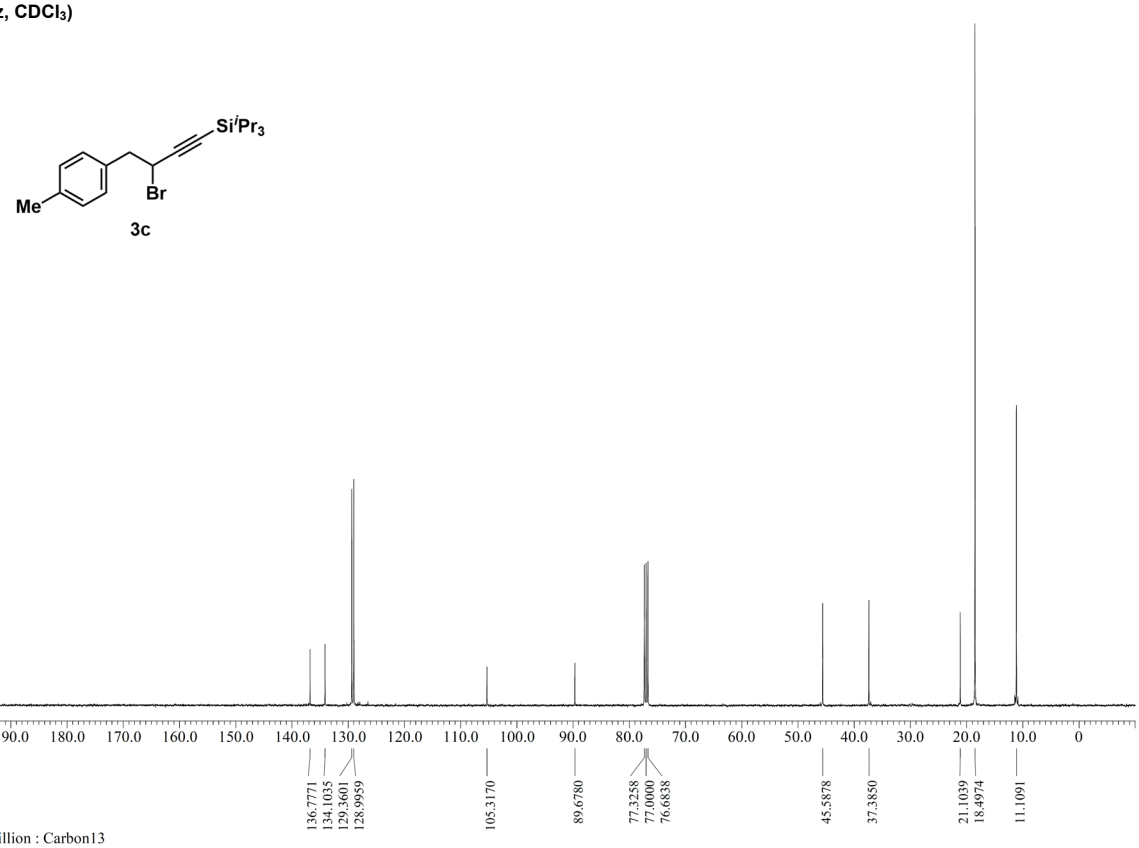

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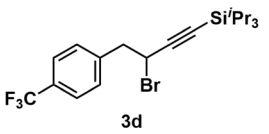

3d

X : parts per Million : Proton

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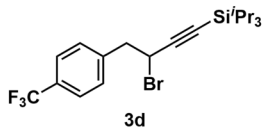
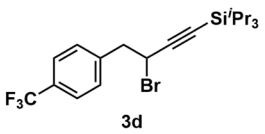


3d

X : parts per Million : Carbon13

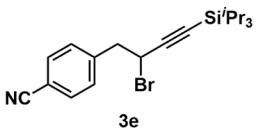
^{19}F NMR (376 MHz, $CDCl_3$)



3d

X : parts per Million : Fluorine19

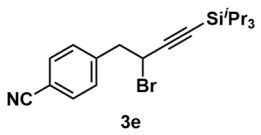
^{1}H NMR (400 MHz, $CDCl_3$)



3e

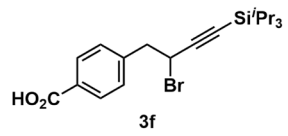
X : parts per Million : Proton

^{13}C NMR (101 MHz, $CDCl_3$)



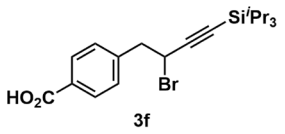
3e

^{1}H NMR (400 MHz, $CDCl_3$)



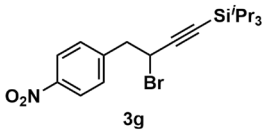
3f

^{13}C NMR (101 MHz, $CDCl_3$)



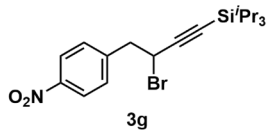
3f

^{1}H NMR (400 MHz, $CDCl_3$)



3g

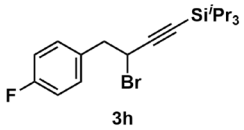
^{13}C NMR (101 MHz, $CDCl_3$)



3g

X : parts per Million : Carbon13

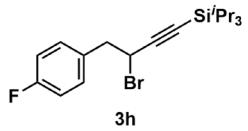
^{1}H NMR (400 MHz, $CDCl_3$)



3h

X : parts per Million : Proton

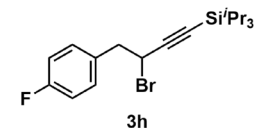
^{13}C NMR (101 MHz, $CDCl_3$)



3h

X : parts per Million : Carbon13

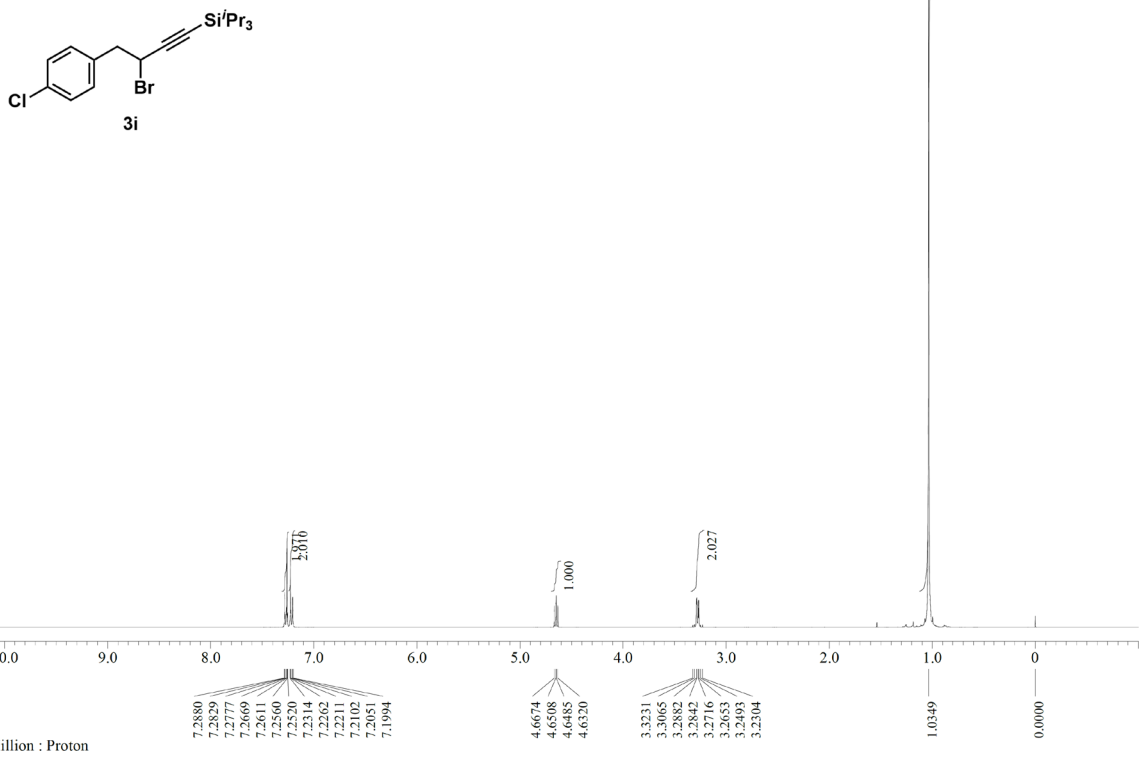
^{19}F NMR (376 MHz, $CDCl_3$)



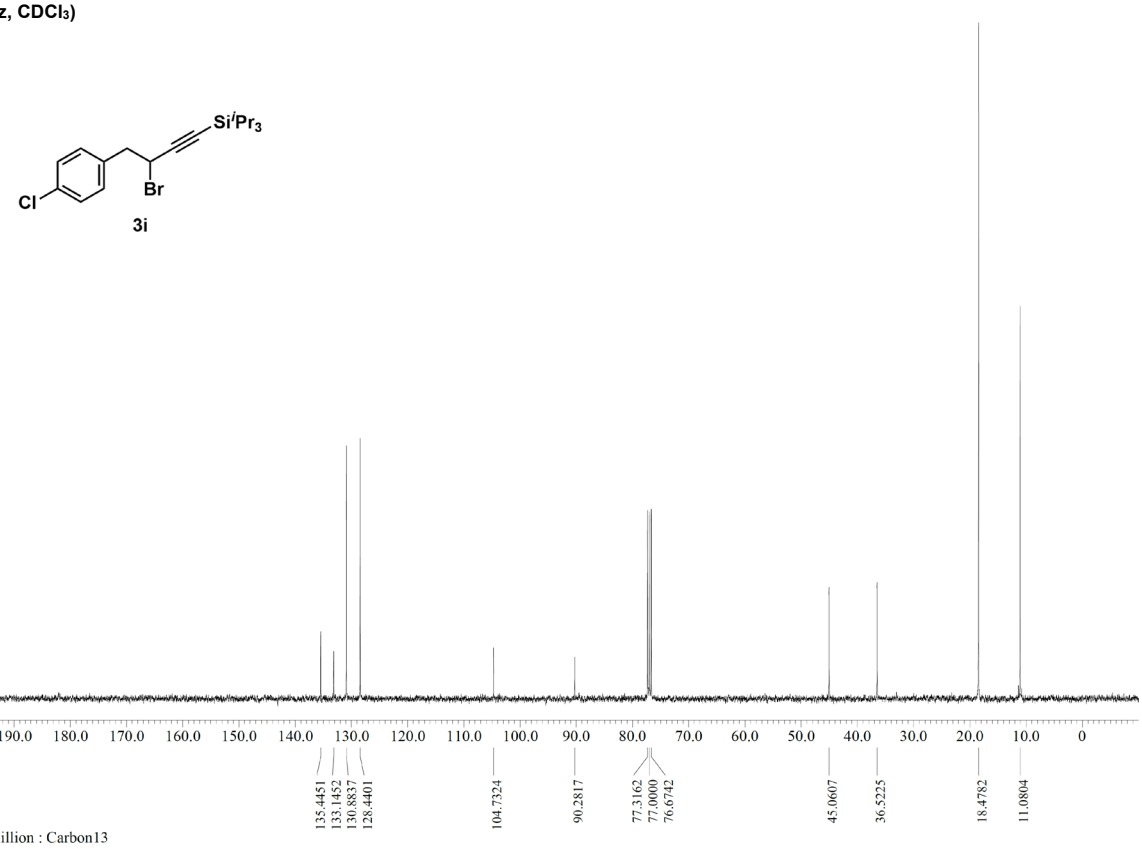
3h

X : parts per Million : Fluorine19

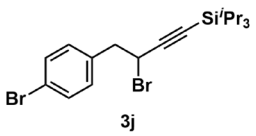
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



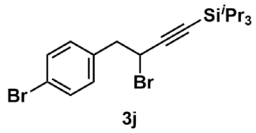
^{1}H NMR (400 MHz, $CDCl_3$)



3j

X : parts per Million : Proton

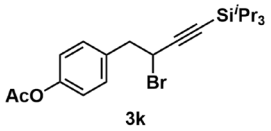
^{13}C NMR (101 MHz, $CDCl_3$)



3j

X : parts per Million : Carbon13

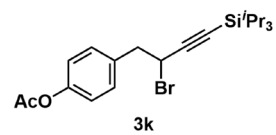
^{1}H NMR (400 MHz, $CDCl_3$)



3k

X : parts per Million : Proton

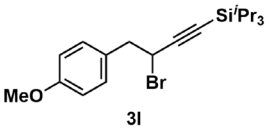
^{13}C NMR (101 MHz, $CDCl_3$)



3k

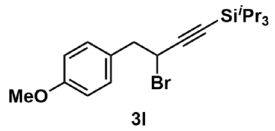
X : parts per Million : Carbon13

^{1}H NMR (400 MHz, $CDCl_3$)



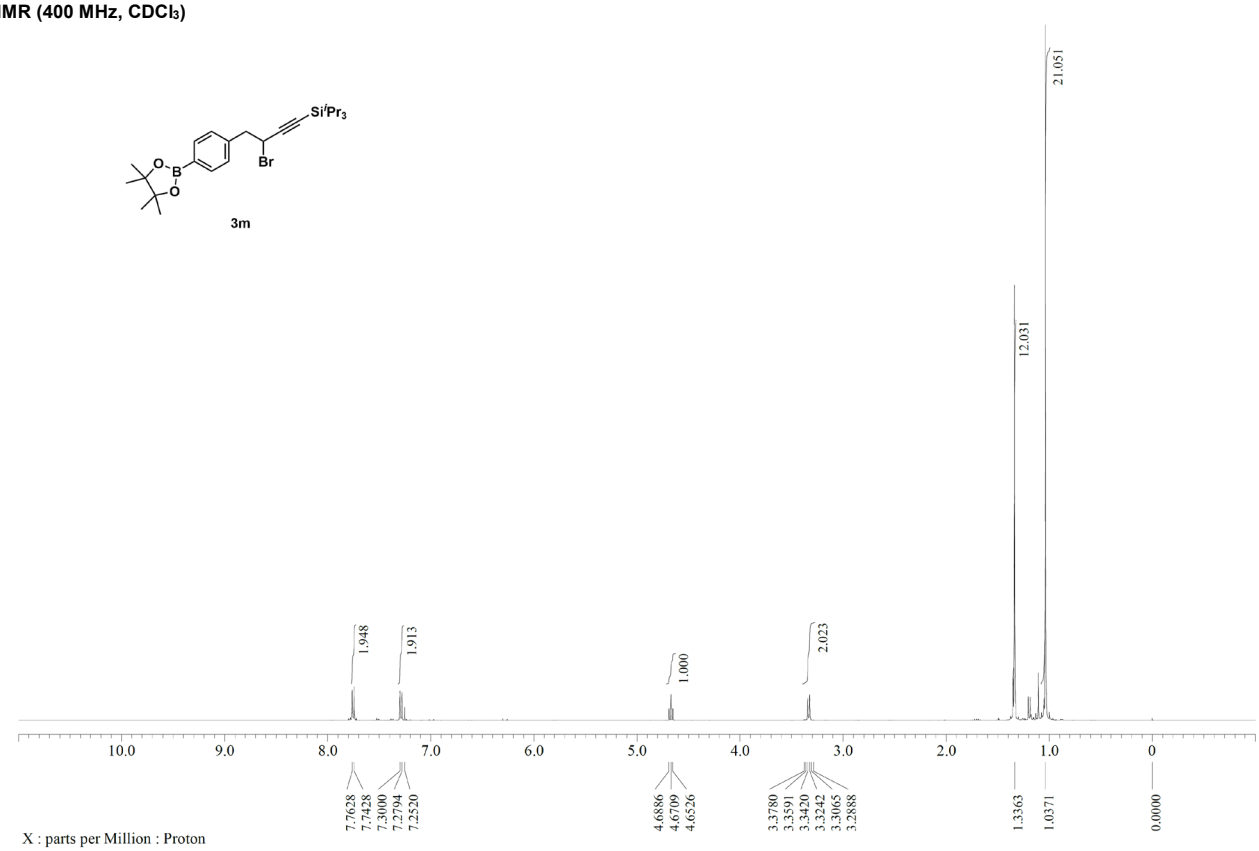
3l

^{13}C NMR (101 MHz, $CDCl_3$)

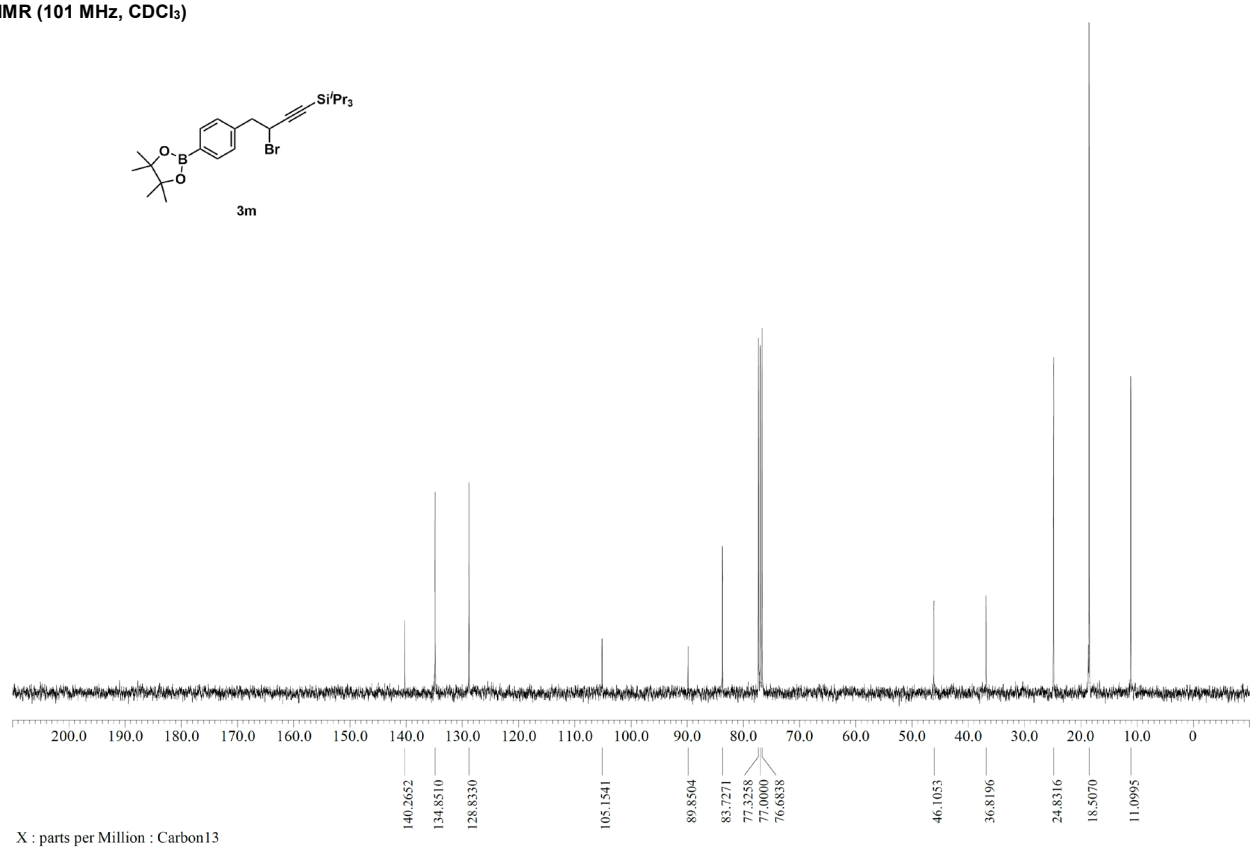


3l

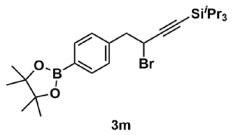
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



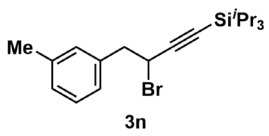
^{11}B NMR (128 MHz, $CDCl_3$)



3m

X : parts per Million : Boron11

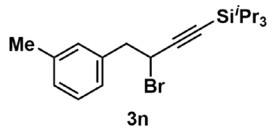
^{1}H NMR (400 MHz, $CDCl_3$)



3n

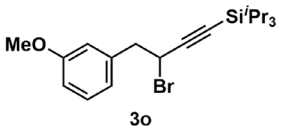
X : parts per Million : Proton

^{13}C NMR (101 MHz, $CDCl_3$)



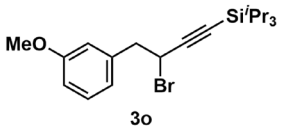
3n

^{1}H NMR (400 MHz, $CDCl_3$)



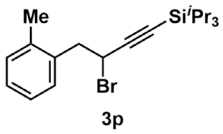
3o

^{13}C NMR (101 MHz, $CDCl_3$)



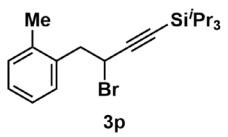
3o

^{1}H NMR (400 MHz, $CDCl_3$)



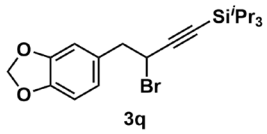
3p

^{13}C NMR (101 MHz, $CDCl_3$)



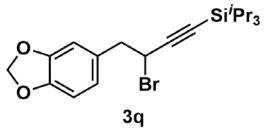
3p

^{1}H NMR (400 MHz, $CDCl_3$)



3q

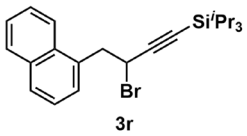
^{13}C NMR (101 MHz, $CDCl_3$)



3q

X : parts per Million : Carbon13

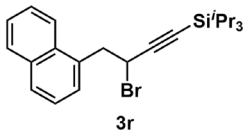
^{1}H NMR (400 MHz, $CDCl_3$)



3r

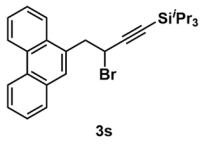
X : parts per Million : Proton

^{13}C NMR (101 MHz, $CDCl_3$)



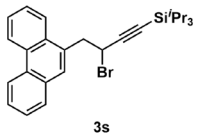
3r

^{1}H NMR (400 MHz, $CDCl_3$)



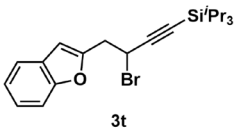
3s

^{13}C NMR (101 MHz, $CDCl_3$)



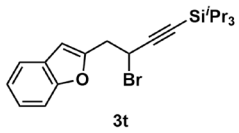
3s

^{1}H NMR (400 MHz, $CDCl_3$)



3t

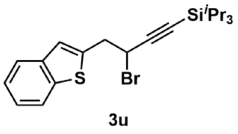
^{13}C NMR (101 MHz, $CDCl_3$)



3t

X : parts per Million : Carbon13

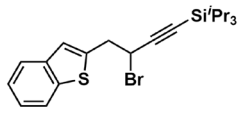
^{1}H NMR (400 MHz, $CDCl_3$)



3u

X : parts per Million : Proton

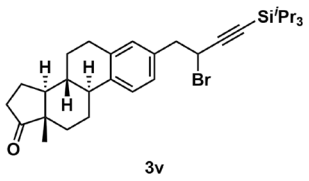
^{13}C NMR (101 MHz, $CDCl_3$)



3u

X : parts per Million : Carbon13

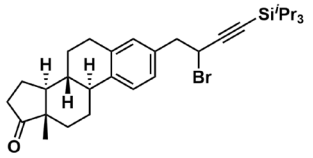
^{1}H NMR (400 MHz, $CDCl_3$)



3v

X : parts per Million : Proton

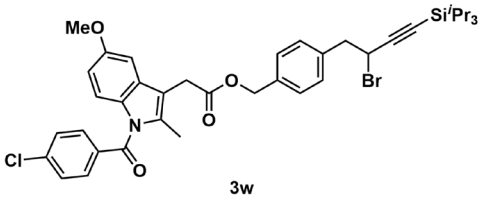
^{13}C NMR (101 MHz, $CDCl_3$)



3v

X : parts per Million : Carbon13

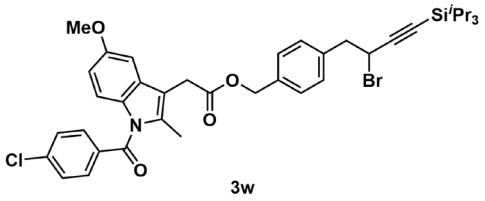
^{1}H NMR (400 MHz, $CDCl_3$)



3w

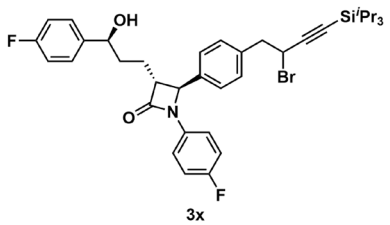
X : parts per Million : Proton

^{13}C NMR (101 MHz, $CDCl_3$)



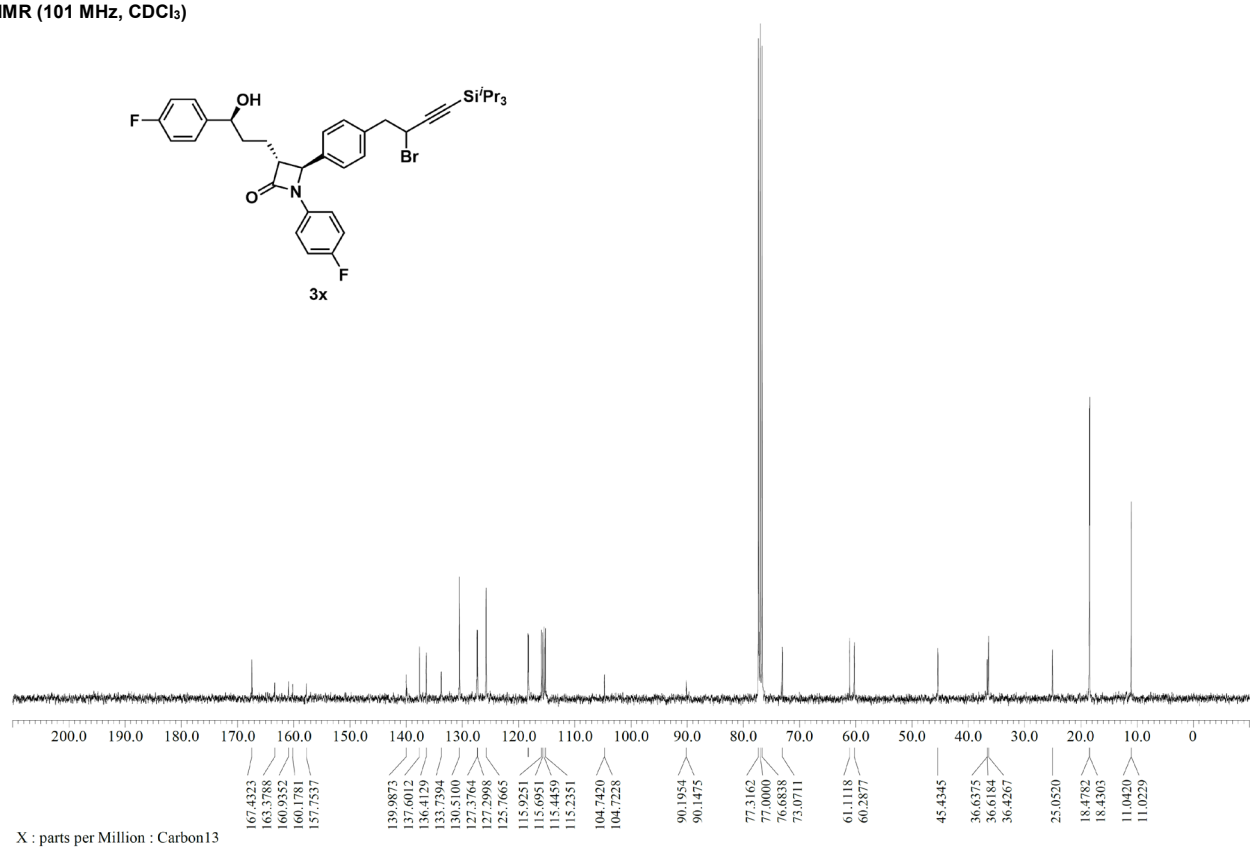
3w

^{1}H NMR (400 MHz, $CDCl_3$)

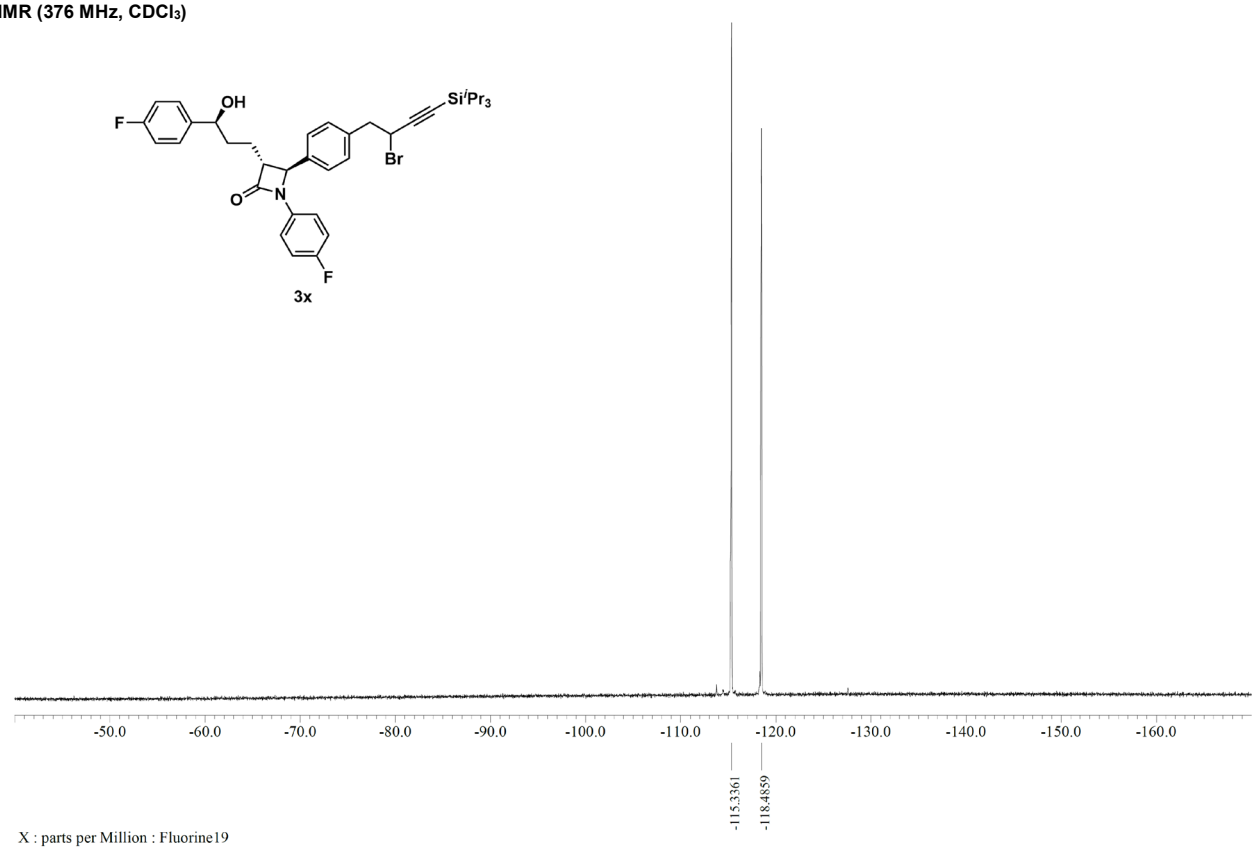


3x

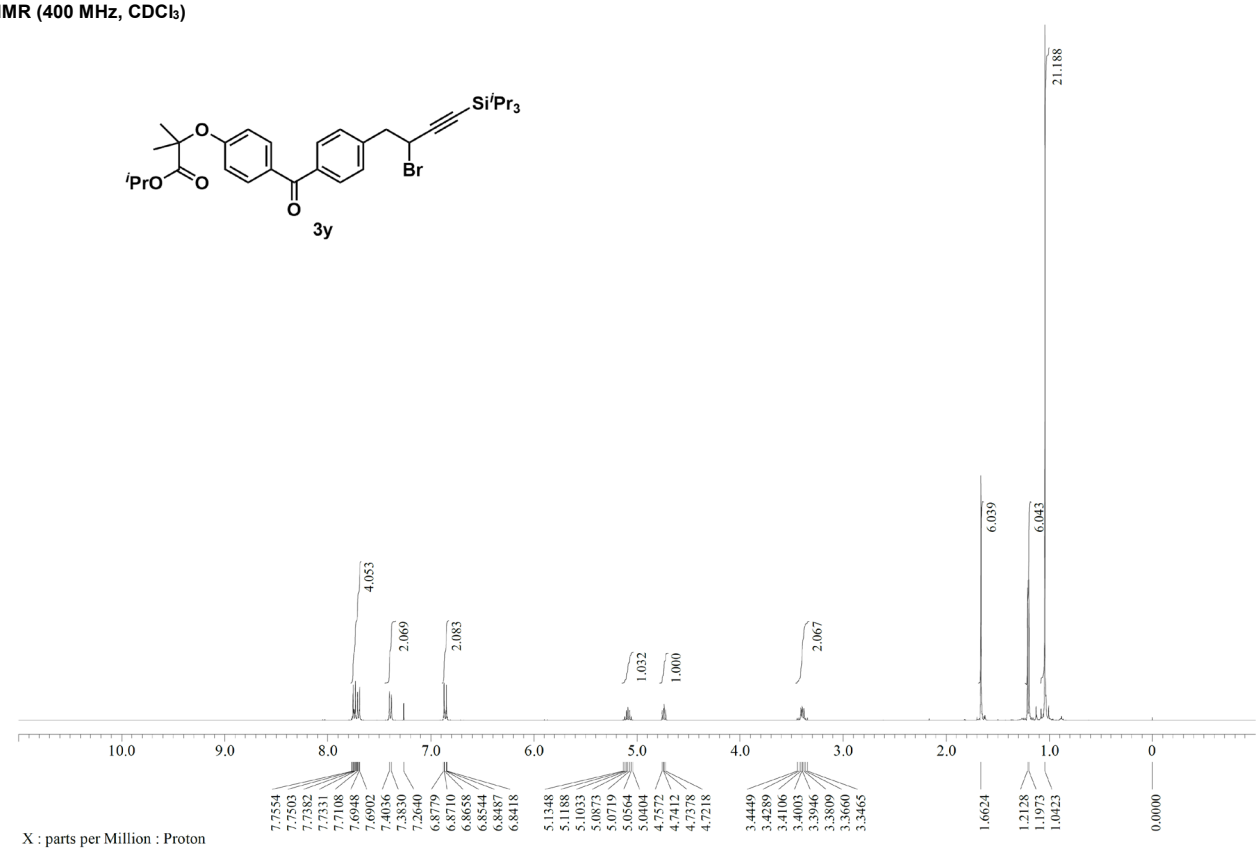
^{13}C NMR (101 MHz, $CDCl_3$)



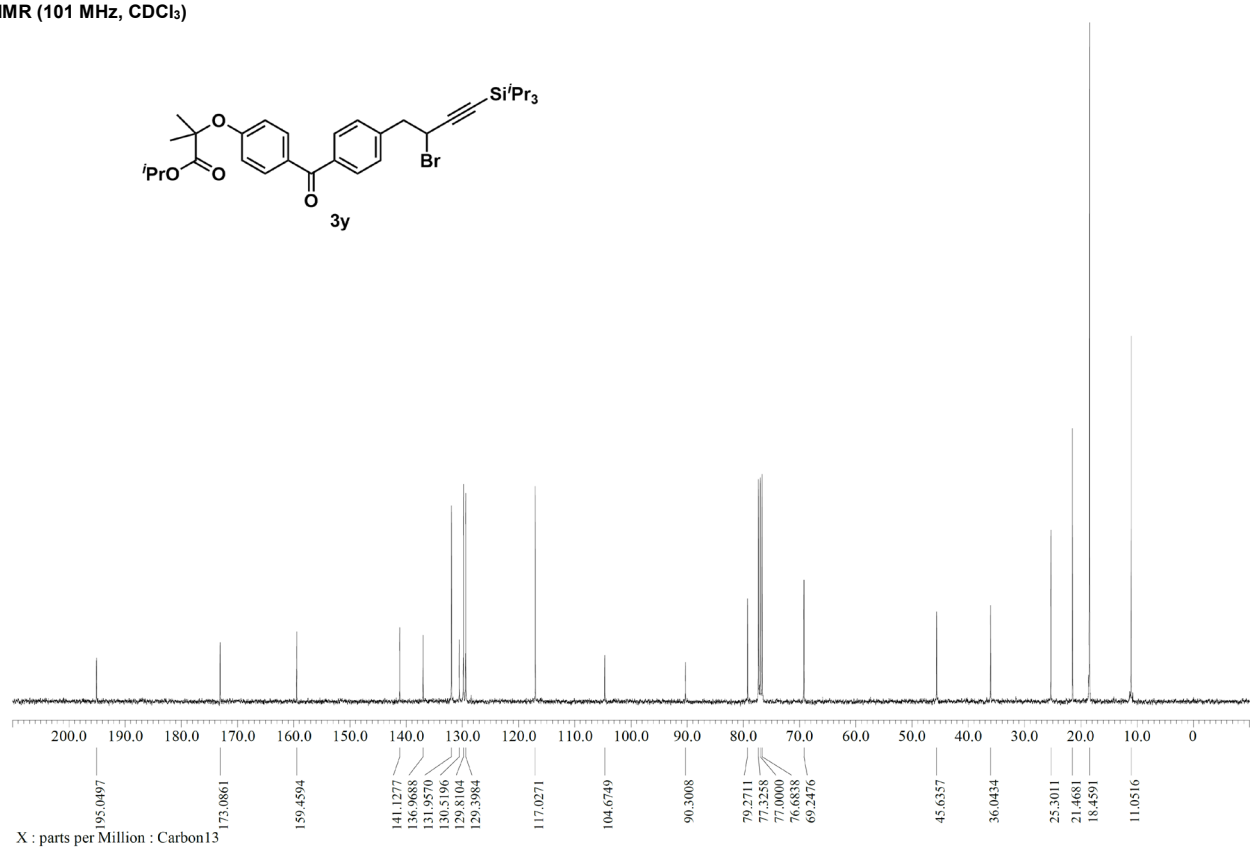
^{19}F NMR (376 MHz, $CDCl_3$)



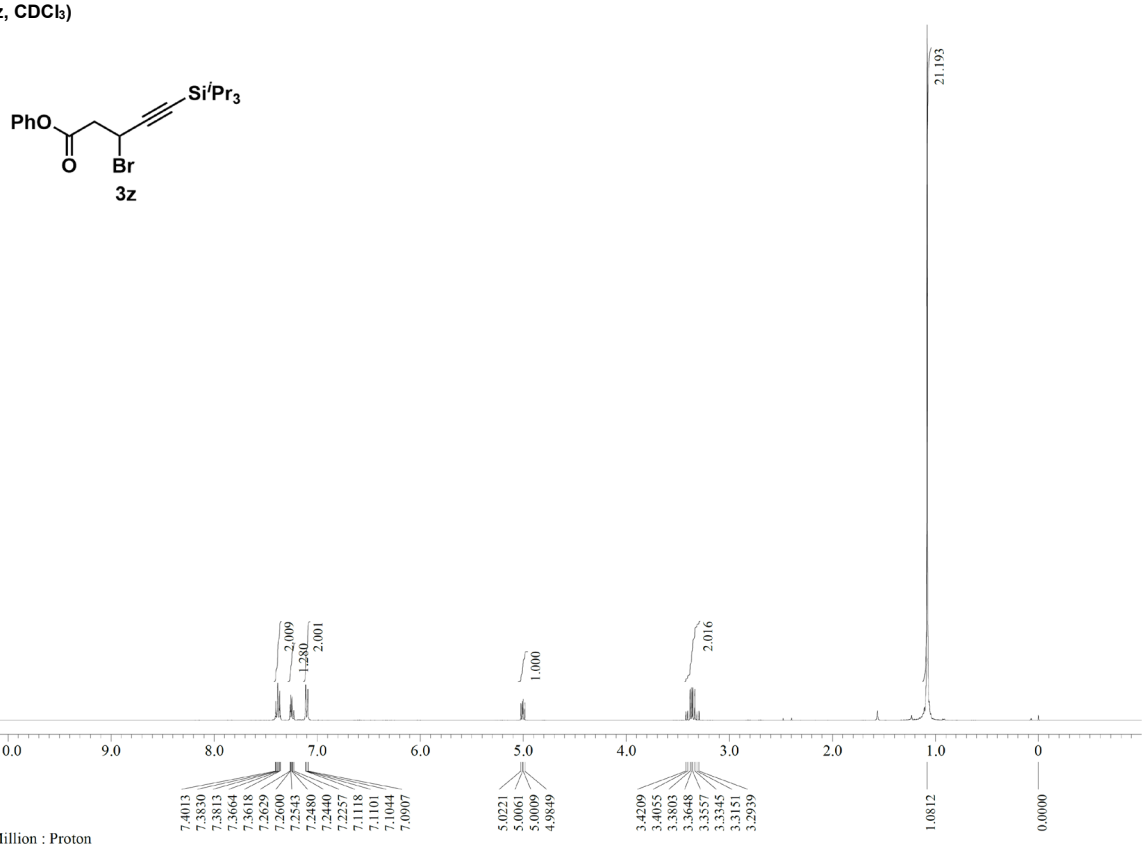
^{1}H NMR (400 MHz, $CDCl_3$)



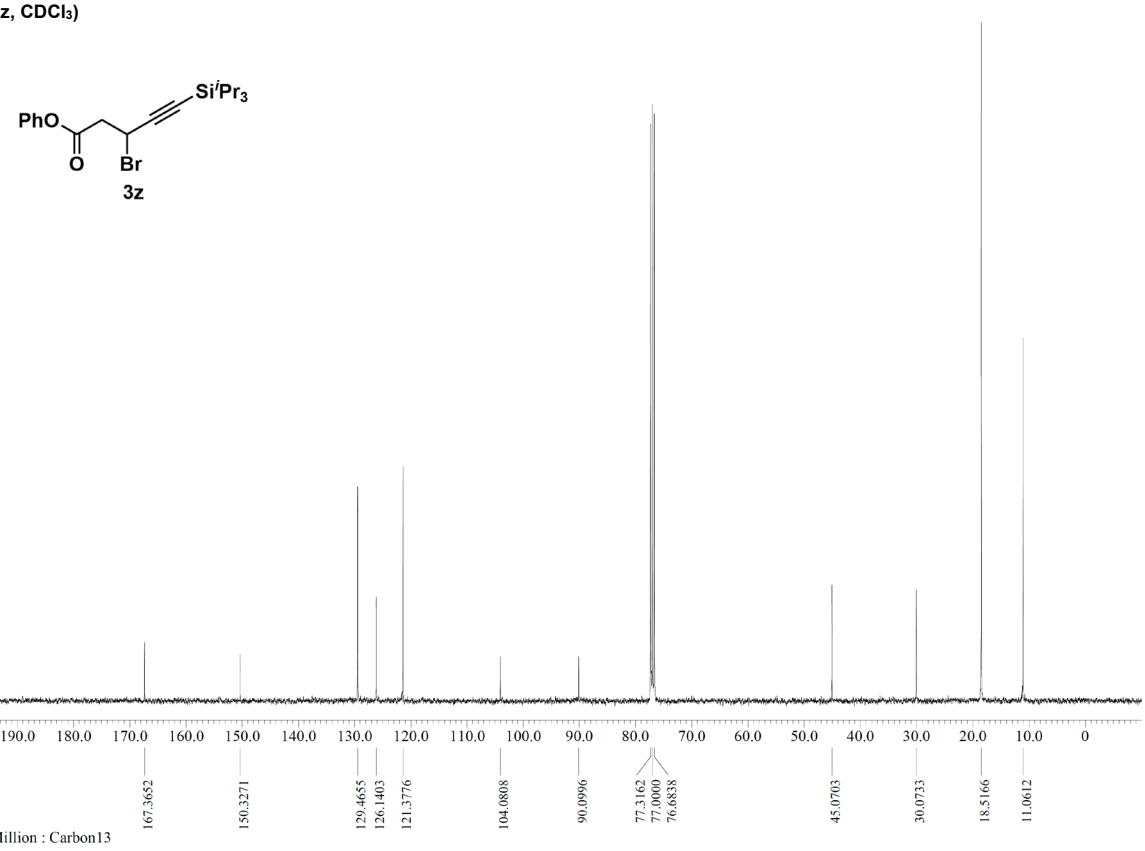
^{13}C NMR (101 MHz, $CDCl_3$)



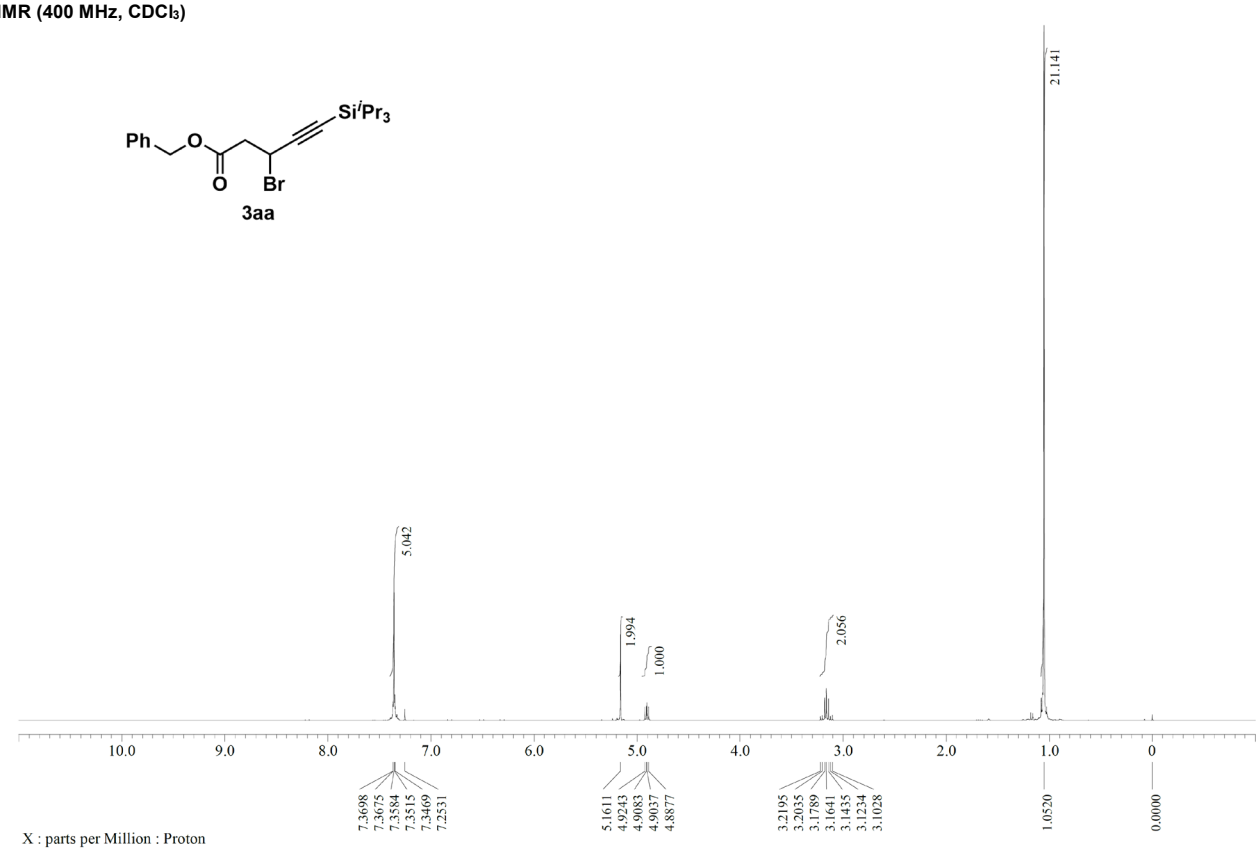
^{1}H NMR (400 MHz, $CDCl_3$)



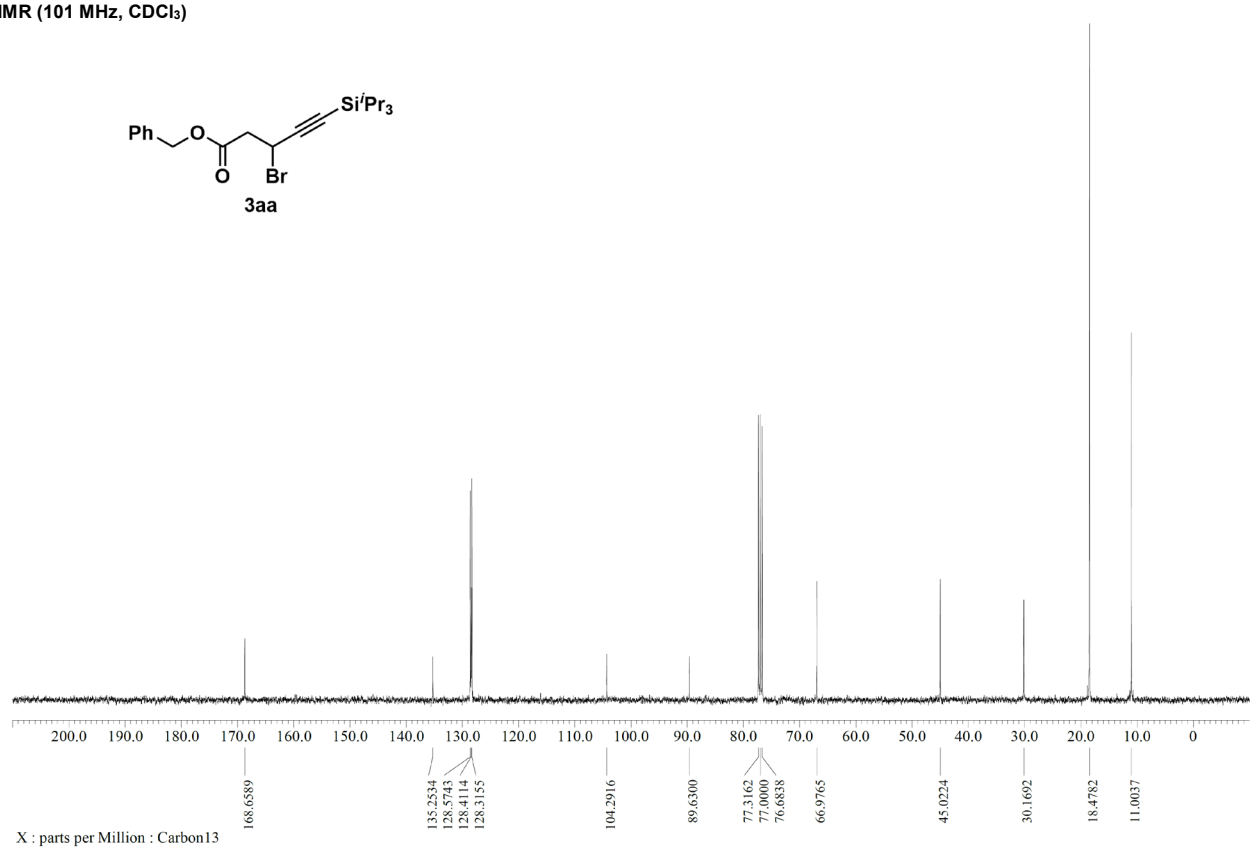
^{13}C NMR (101 MHz, $CDCl_3$)



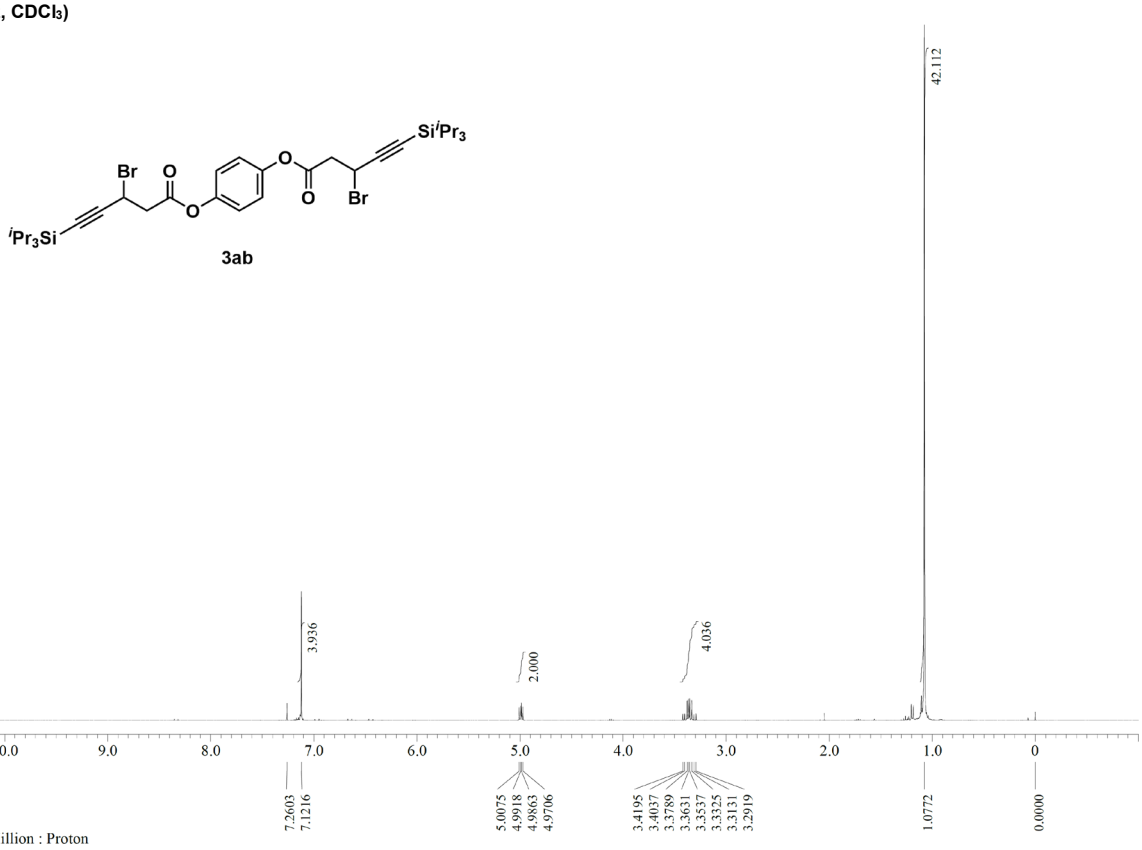
^{1}H NMR (400 MHz, $CDCl_3$)



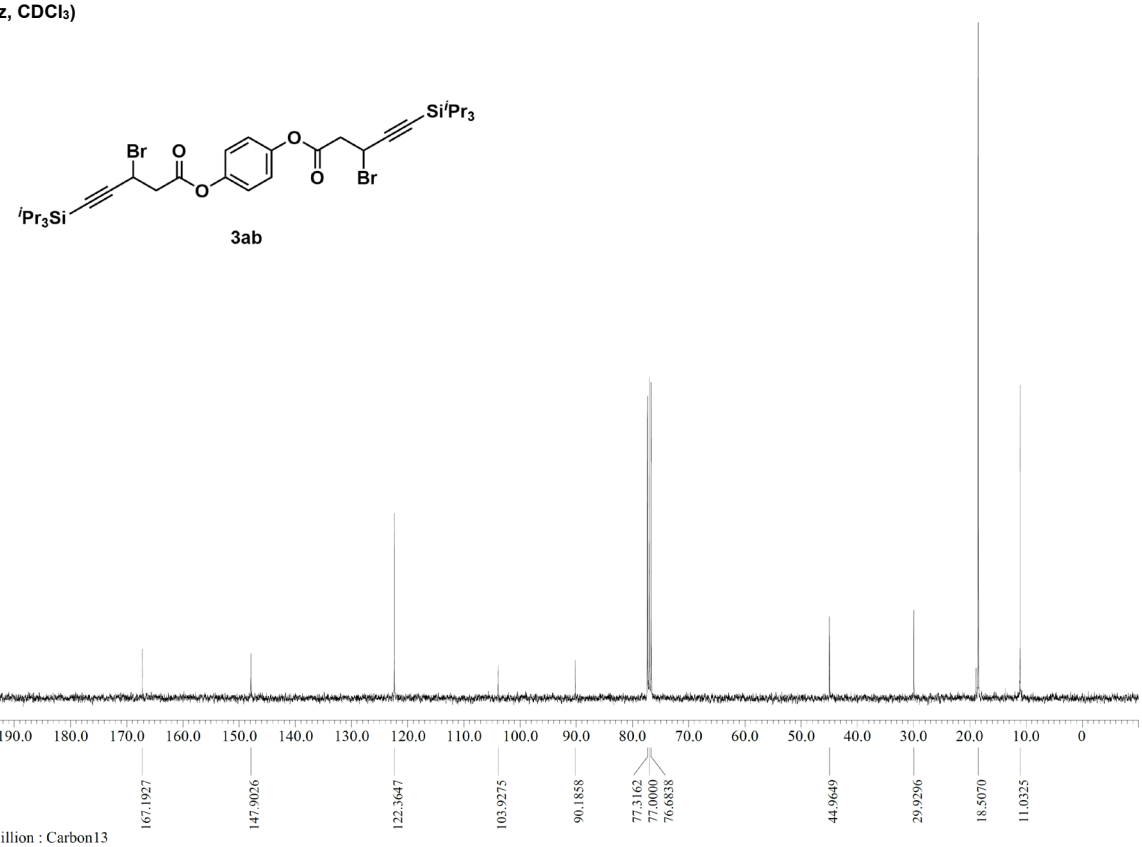
^{13}C NMR (101 MHz, $CDCl_3$)



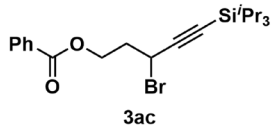
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

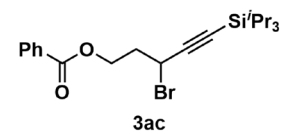


^{1}H NMR (400 MHz, $CDCl_3$)



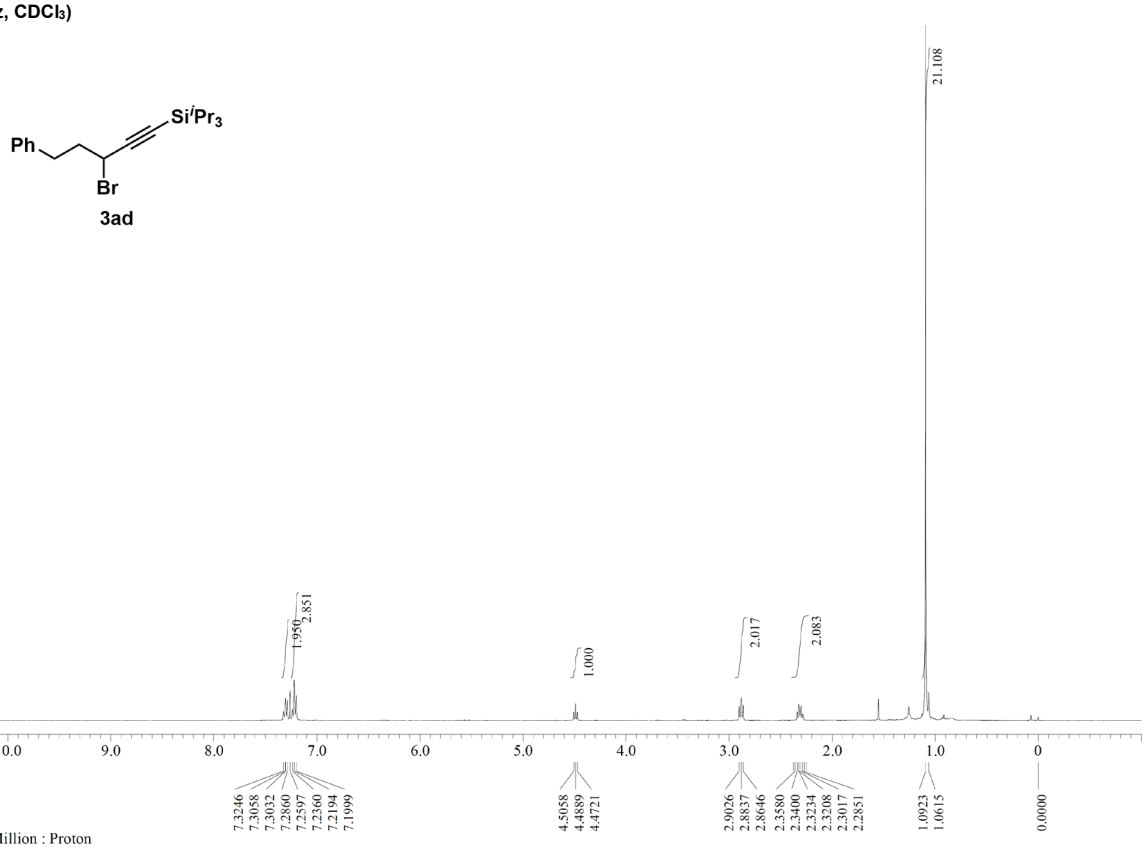
3ac

^{13}C NMR (101 MHz, $CDCl_3$)

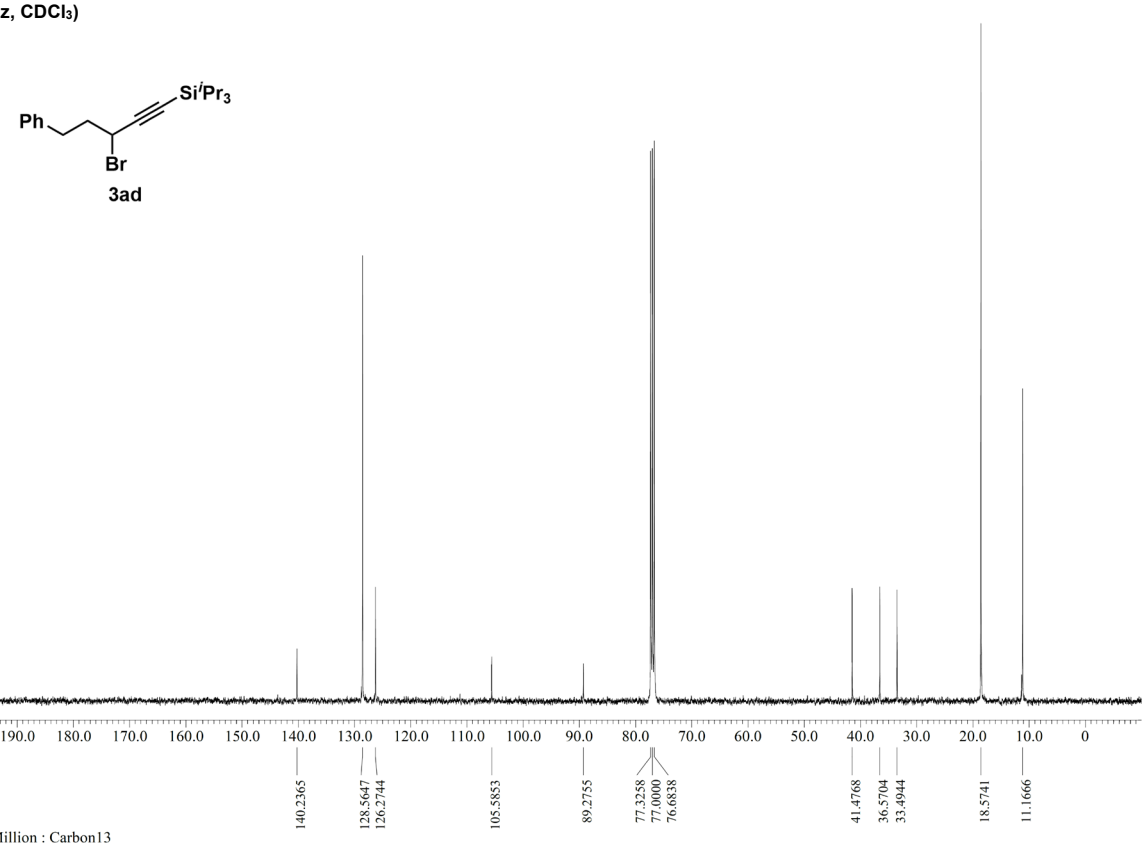


3ac

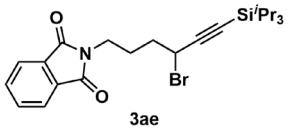
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

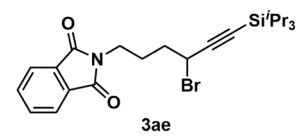


^{1}H NMR (400 MHz, $CDCl_3$)



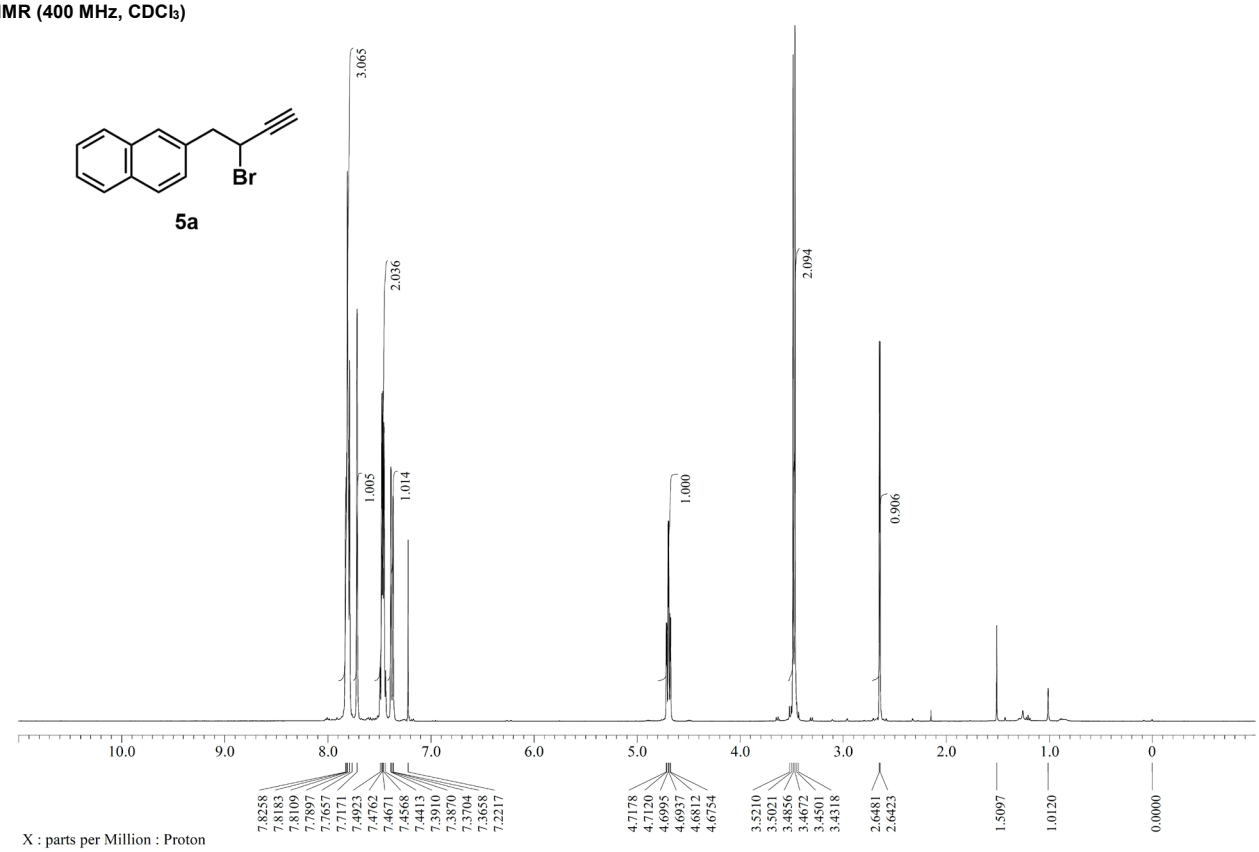
3ae

^{13}C NMR (101 MHz, $CDCl_3$)



3ae

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)