Electronic supplementary materials

Cp_2ZrCl_2 – Et_3Al Reagent in the Homo-Coupling of Silyl-Substituted Alkynes

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General information

The reagents were obtained from Sigma-Aldrich or Acros. Toluene was distilled over Na. Silyl-substituted alkynes were prepared by the reaction of terminal acetylenes with EtMgBr and trialkylchlorosilanes [1]. IR spectra were recorded on Bruker VE Vertex 70v spectrometer as liquid films or in Nujol and are reported in wavenumbers (cm^{-1}). Nuclear magnetic resonance spectroscopy was performed on a Brucker Avance 500. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C-{^{1}H} NMR spectra at 125 MHz in $CDCl_3$. The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard. The numbering of atoms in the ^{13}C and ^{1}H NMR spectra of the compounds **2a-e, 3b, 4a, 4b, 4d, 6, 7** is shown in Figure 1. Mass spectra were obtained on a Finnigan 4021 instrument. All quantum-chemical calculations were performed using B3LYP/6-31G(d)/LanL2DZ basis set as implemented in Gaussian 09 software [2].

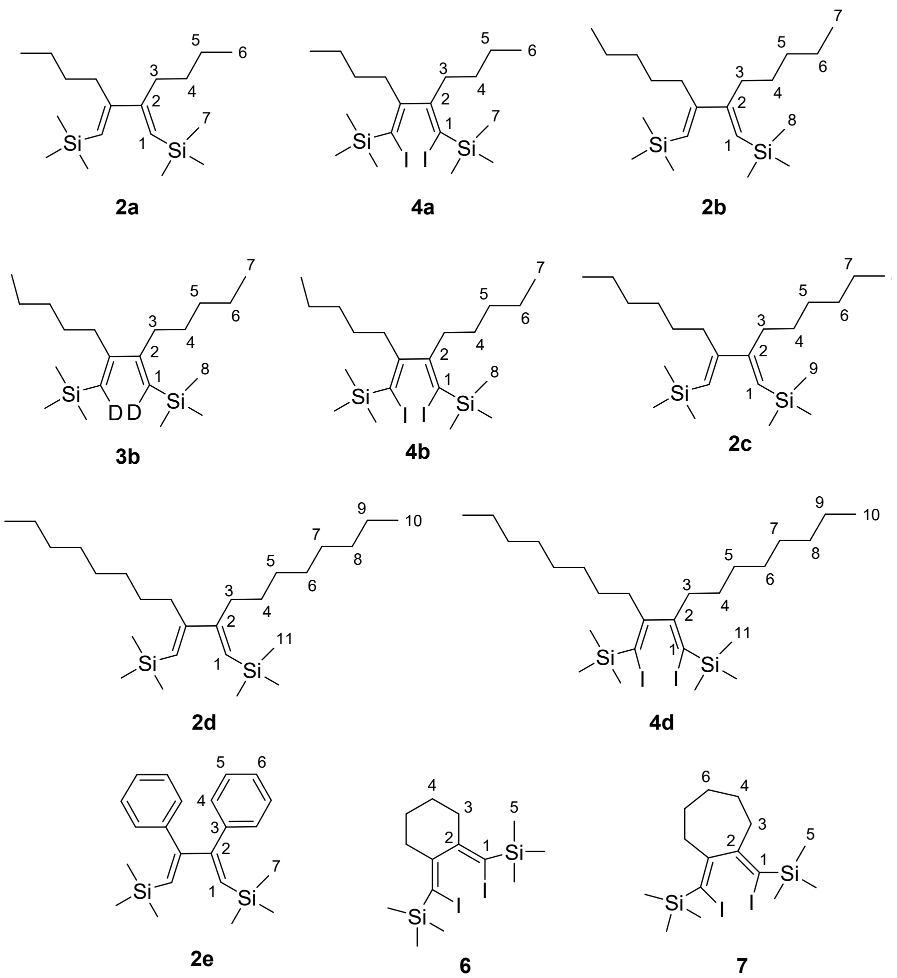

Figure 1. The numbering of atoms in the reported ^{13}C- and ^{1}H-NMR spectral data of the compounds **2a-e, 3b, 4a, 4b, 4d, 6, 7**.

4.2. Homo-Coupling of Trimethylsilyl-Substituted Alkynes by Cp_2ZrCl_2 – Et_3Al Reagent.
A suspension of Cp_2ZrCl_2 (292 mg, 1.00 mmol) in toluene (3 mL) in a 25 mL round bottom flask was cooled with an ice-bath and then Et_3Al (0.3 mL, 2.00 mmol) was added. After stirring the mixture at 0 °C for 30 minutes, 1 mmol of trimethylsilyl-substituted alkyne or 0.5 mmol of trimethylsilyl-substituted α,ω-diyne was added. The mixture was stirred at 23 °C for 18 h. Then the mixture was diluted with hexane (5 mL) and H_2O (3 mL) (to prepare **2a-e**) or D_2O (3 mL) (to prepare **3b**) was added dropwise while cooling the reactor flask with an ice-bath. The precipitate was filtered on a filter paper. To prepare the compounds **4a, 4b, 4d**, a solution of I_2 (787.5 mg, 6.25 mmol) in THF (5 mL) was added to the reaction mixture while cooling the reactor flask with an ice-bath and stirred at 23 °C for 1 h. To prepare the compounds **6, 7**, a solution of I_2 (787.5 mg, 6.25 mmol) in THF (5 mL) was used. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$. Evaporation of solvent and purification of the residue by column chromatography (hexane) gave a colourless oil.
*4.2.1. ((1E,3E)-2,3-dibutylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**2a**)* [3]. Yield: 133 mg (86%); R_f= 0.8 (hexane). IR (liquid film): 2956, 2873, 2861, 1593, 1561, 1465, 1248, 839, 769, 689, 619 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, C(7)H_3), 0.92 (t, J = 7.0 Hz, 3H, C(6)H_3), 1.28–1.36 (m, 4H, C(4, 5)H_2), 2.29 (t, J = 6.4 Hz, 2H, C(3)H_2), 5.48 (s, 1H, C(1)H). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 0.36 (C(7)), 14.06 (C(6)), 22.93 (C(5)), 31.69 (C(4)), 33.74 (C(3)), 125.07 (C(1)), 160.67 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): -10.79. MS (EI): *m/z*, % = 311 (3) [M+], 295 (5), 268 (9), 237 (15), 207 (10), 165 (7), 138 (6), 73 (100), 45 (9).

*4.2.2. ((1Z,3Z)-2,3-dibutyl-1,4-diiodobuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**4a**)* [4]. Yield: 247 mg (88%); Rf = 0.6 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.36 (s, 9H, C(7)H_3), 0.94 (t, J = 7.3 Hz, 1H, C(6)H_3), 1.34 (q, J = 7.3 Hz, J = 14.5 Hz, 2H, C(5)H_2), 1.46–1.55 (m, 1H(A), 1H(B), C(4)H_2), 2.21 (t, J = 13.7 Hz, 1H(A), C(3)H_2), 2.52 (t, J = 13.7 Hz, 1H(B), C(3)H_3). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 1.89 (C(7)), 13.83 (C(6)), 23.26 (C(5)), 30.84 (C(4)), 36.25 (C(3)), 108.67 (C(1)), 163.54 (C(2)). MS (EI): *m/z*, % = 562 (<1) [M+], 435 (84), 185 (14), 161 (26), 139 (7), 73 (100), 45 (13).

*4.2.3. ((1E,3E)-2,3-dipentylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**2b**)*. Yield: 141 mg (83%); Rf = 0.8 (hexane). IR (liquid film): 2956, 2926, 2856, 1593, 1560, 1466, 1248, 839, 772, 689, 620 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, C(8)H_3), 0.91 (t, J = 7.0 Hz, 3H, C(7)H_3), 1.28–1.35 (m, 6H, C(4, 5, 6)H_2), 2.29 (t, J = 6.0 Hz, 2H, C(3)H_2), 5.48 (s, 1H, C(1)H). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 0.35 (C(8)), 14.03 (C(7)), 22.54 (C(6)), 29.13 (C(4)), 32.03 (C(5)), 33.95 (C(3)), 125.10 (C(1)), 160.69 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): -10.82. MS (EI): *m/z*, % = 339 (4) [M$^+$], 338 (11), 282 (15), 265 (30), 209 (8), 191 (10), 73 (100), 45 (8). $C_{20}H_{40}D_2Si_2$ Calc. C 70.92, H 12.50; CHN analysis, C 70.4, H 12.8.

*4.2.4. ((1E,3E)-2,3-dipentylbuta-1,3-diene-1,4-diyl-1,4-d2)bis(trimethylsilane) (**3b**)*. Yield: 145 mg (85%); Rf = 0.8 (hexane). IR (liquid film): 2956, 2928, 2859, 1589, 1556, 1466, 1379, 1248, 1097, 1042, 837, 761, 689, 616 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, C(8)H_3), 0.91 (t, J = 6.7 Hz, 3H, C(7)H_3), 1.28–1.33 (m, 6H, C(4, 5, 6)H_2), 2.28 (t, J = 7.4 Hz, 2H, C(3)H_2), 5.48 (s, 1H, C(1)H). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 0.35 (C(8)), 14.04 (C(7)), 22.54 (C(6)), 29.14 (C(4)), 32.03 (C(5)), 32.95 (C(3)), 125.09 (C(1)), 160.60 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): -10.84. MS (EI): *m/z*, % = 341 (<1) [M$^+$], 339 (4), 283 (5), 266 (10), 210 (4), 192 (5), 73 (100), 45 (6). $C_{20}H_{42}Si_2$ Calc. C 70.50; CHN analysis, C 70.1.

*4.2.5. ((1Z,3Z)-1,4-diiodo-2,3-dipentylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**4b**)*. Yield: 204 mg (69%); Rf = 0.7 (hexane). IR (liquid film): 2956, 2930, 2873, 1970, 1462, 1249, 1116, 841, 759, 693, 588 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.36 (s, 9H, C(8)H_3), 0.92 (t, J = 7.1 Hz, 3H, C(7)H_3), 1.28–1.31 (m, 2H, C(5)H_2), 1.33–1.37 (m, 2H, C(6)H_2), 1.50–1.56 (m, 1H(A), C(4)H2), 1.62–1.67 (m, 1H(B),

$C(4)H_2$), 2.22 (t, J = 13.2 Hz, 1H(A), $C(3)H_2$), 2.50 (t, J = 13.3 Hz, 1H(B), $C(3)H_2$). ^{13}C-{^1H} NMR (500 MHz, $CDCl_3$): δ = 1.88 (C(8)), 14.04 (C(7)), 22.38 (C(6)), 28.50 (C(4)), 32.35 (C(5)), 36.49 (C(3)), 108.58 (C(1)), 163.68 (C(2)). ^{29}Si-{^1H} (500 MHz, $CDCl_3$): 0.93. MS (EI): *m/z*, % = 591 (<1) [M^+], 463 (13), 189 (10), 95 (3), 73 (100), 45 (4). $C_{20}H_{40}I_2Si_2$ Calc. C 40.68, H 6.83; CHN analysis, C 40.5, H 6.6.

*4.2.6. ((1E,3E)-2,3-dihexylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**2c**)* [5]. Yield: 143 mg (78%); Rf = 0.7 (hexane). IR (liquid film): 2956, 2927, 2857, 1592, 1561, 1466, 839, 771, 749, 689, 619 cm^{-1}. ^1H NMR (50 0MHz, $CDCl_3$): δ = 0.14 (s, 9H, $C(9)H_3$), 0.91 (t, J = 6.9 Hz, 3H, $C(8)H_3$), 1.28–1.33 (m, 8H, $C(4, 5, 6, 7)H_2$), 2.29 (t, J = 7.3 Hz, 2H, $C(3)H_2$), 5.48 (s, 1H, C(1)H). ^{13}C-{^1H} NMR (500 MHz, $CDCl_3$): δ = 0.35 (C(9)), 14.06 (C(8)), 22.59 (C(7)), 29.40 (C(4)), 29.47 (C(5)), 31.73 (C(6)), 34.00 (C(3)), 125.10 (C(1)), 160.71 (C(2)). ^{29}Si-{^1H} (500 MHz, $CDCl_3$): -10.84. MS (EI): *m/z*, % = 367 (2) [M^+], 293 (14), 263 (5), 219 (6), 138 (4), 73 (100), 45 (6).

*4.2.7. ((1E,3E)-2,3-dioctylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**2d**)*. Yield: 186 mg (84%); Rf = 0.7 (hexane). IR (liquid film): 2955, 2926, 2855, 1736, 1465, 1378, 1248, 840, 722, 690, 620 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, $C(11)H_3$), 0.91 (t, J = 7.2 Hz, 3H, $C(10)H_3$), 1.29 (s, 12H, $C(4\text{-}9)H_2$), 2.29 (t, J = 7.8 Hz, 2H, $C(3)H_2$), 5.48 (s, 1H, C(1)H). ^{13}C-{^1H} NMR (500 MHz, $CDCl_3$): δ = 0.36 (C(11)), 14.12 (C(10)), 22.69 (C(9)), 29.26 (C(4)), 29.44 (C(5)), 29.49 (C(7)), 29.80 (C(6)), 31.89 (C(8)), 33.99 (C(3)), 125.08 (C(1)), 160.71 (C(2)). ^{29}Si-{^1H} (500 MHz, $CDCl_3$): -10.82. MS (EI): *m/z*, % = 423 (6) [M^+], 422 (<1), 349 (15), 324 (9), 275 (6), 251 (7), 226 (5), 73 (100), 45 (3). $C_{26}H_{54}Si_2$ Calc. C 73.85, H 12.87; CHN analysis, C 74.3, H 12.5.

*4.2.8. ((1Z,3Z)-1,4-diiodo-2,3-dioctylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**4d**)*. Yield: 233 mg (69%); Rf = 0.7 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.36 (s, 9H, $C(11)H_3$), 0.91 (t, J = 6.9 Hz, 3H, $C(10)H_3$), 1.29 (s, 8H, $C(5,7\text{-}9)H_2$), 1.51–1.56 (m, 2H, $C(6)H_2$), 1.51–1.56 (m, 1H(A), $C(4)H_2$), 1.61–1.66 (m, 1H(B), $C(4)H_2$), 2.22 (t, J = 13.0 Hz, 1H(A), $C(3)H_2$), 2.47–2.54 (m, 1H(B), $C(3)H_2$). ^{13}C-{^1H} NMR (500 MHz, $CDCl_3$): δ = 1.88 (C(11)), 14.12 (C(10)), 22.68 (C(9)), 28.83 (C(4)), 29.26 (C(5)), 29.28 (C(7)), 30.18 (C(6)), 31.84 (C(8)), 36.54 (C(3)), 100.56 (C(1)), 163.72 (C(2)). MS (EI): *m/z*, % = 675 (<1) [M^+], 547 (7), 273 (11), 207 (100), 191 (11), 133 (9), 96 (16), 73 (88), 40 (13). $C_{26}H_{52}I_2Si_2$ Calc. C 46.29, H 7.77; CHN analysis, C 46.5, H 7.7.

*4.2.9. ((1E,3E)-2,3-diphenylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (**2e**)* [5]. Yield: 106 mg (61%); Rf = 0.7 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ = -0.28 (s, 9H, $C(7)H_3$), 5.48 (s, 1H, C(1)H), 7.22 (d, J = 6.9 Hz, 1H, C(4)H), 7.31–7.38 (m, 2H, C(5,6)H). ^{13}C-{^1H} NMR (500 MHz, $CDCl_3$): δ = -0.28 (C(7)), 126.88 (C(6)), 127.57 (C(5)), 129.91 (C(4)), 133.90 (C(1)), 142.16 (C(3)), 159.87 (C(2)). MS (EI): *m/z*, % = 351 (7) [M+], 350 (20), 335 (7), 276 (13), 262 (21), 247 (28), 135 (18), 73 (100), 45 (12).

*4.2.9. (1Z,2Z)-1,2-bis(iodo(trimethylsilyl)methylene)cyclohexane (**6**)* [6]. Yield: 199 mg (79%); Rf = 0.6 (hexane). IR (liquid film): 2953, 2930, 2896, 2854, 1567, 1460, 1442, 1421, 1406, 1250, 1075, 963, 936, 842, 758, 692, 627, 499 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.33 (s, 9H, $C(5)H_3$), 1.52 (t, J = 9.2 Hz, 1H(A), $C(4)H_3$), 1.92 (s, 1H(B), $C(4)H_2$), 2.21 (t, J = 12.0 Hz, 1H(A), $C(3)H_2$), 2.88 (d, J = 12.0 Hz, 1H(B), $C(3)H_2$). ^{13}C-{^1H} NMR (500 MHz, $CDCl_3$): δ = 1.74 (C(5)), 29.13 (C(4)), 36.42 (C(3)), 101.65 (C(1)), 165.99 (C(2)). ^{29}Si-{^1H} (500 MHz, $CDCl_3$): 0.95. MS (EI): *m/z*, % = 504 (<1) [M^+], 377 (59), 289 (16), 161 (20), 97 (13), 73 (100), 45 (12).

*4.2.10. (1Z,2Z)-1,2-bis(iodo(trimethylsilyl)methylene)cycloheptane (**7**)*. Yield: 279 mg (82%); Rf = 0.6 (hexane). IR (liquid film): 2952, 2926, 2852, 1557, 1442, 1408, 1249, 1182, 1038, 899, 865, 839, 758, 693, 627, 480 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.34 (s, 9H, $C(5)H_3$), 1.47–1.52 (m, 2H(A), $C(4,6)H_3$), 1.56–1.63 (m, 2H(B), $C(4,6)H_2$), 2.39–2.47 (m, 1H(A), $C(3)H_2$), 2.62 – 2.68 (m, 1H(B), $C(3)H_2$). ^{13}C-{^1H}

NMR (500 MHz, $CDCl_3$): δ = 1.64 (C(5)), 26.91 (C(6)), 28.31 (C(4)), 34.26 (C(3)), 104.51 (C(1)), 165.88 (C(2)). MS (EI): *m/z*, % = 518 (1). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): 0.96. [M^+], 391 (54), 358 (4), 303 (8), 175 (17), 131 (17), 97 (20), 73 (100), 40 (55). $C_{15}H_{28}I_2Si_2$ Calc. C 34.76, H 5.44; CHN analysis, C 35.1, H 5.7.

References

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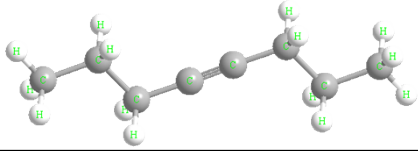
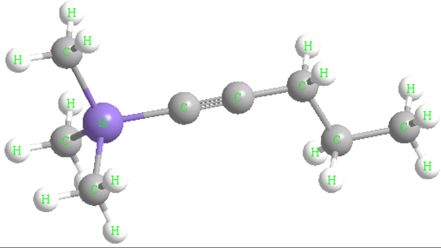
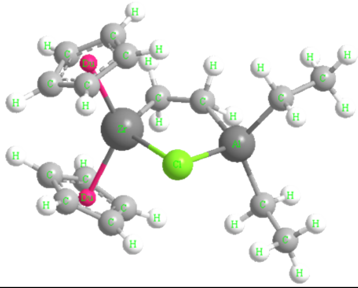
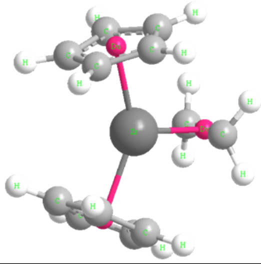
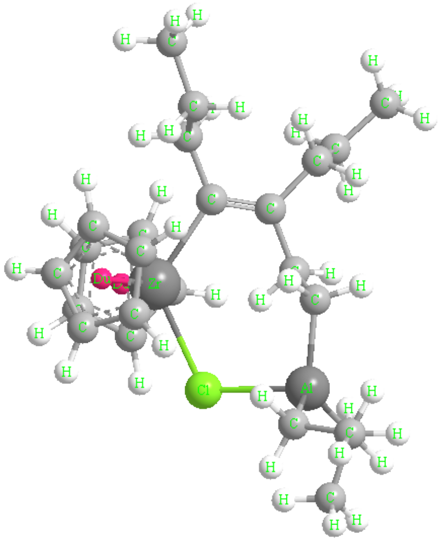
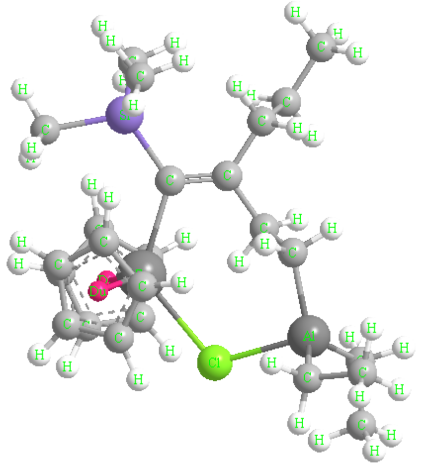
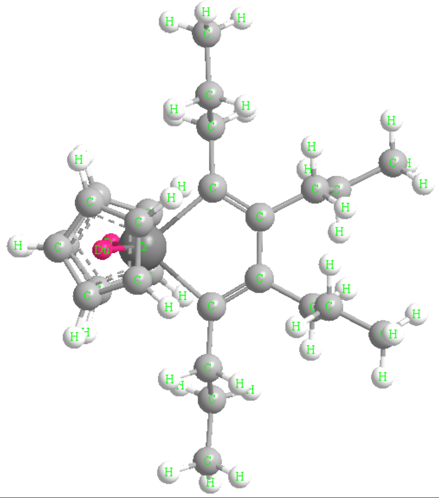
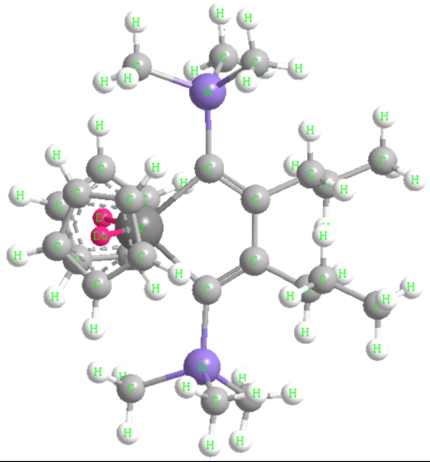
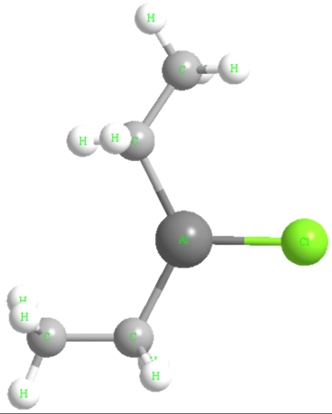
Table 1. The calculated free Gibbs energies and imaginary frequencies at B3LYP/6-31G*/LANL2DZ level of theory in gas phase.

Structure	$\Delta_f G^o$ at 298.15 K, Hartree	MDL Mol Format File
	-313.067115	4-octyne.mol
	-603.799991	trimethyl(pent-1-yn-1-yl)silane.mol
	-1373.192070	intermediate_A.mol
	-512.114157	intermediate_B.mol
	-1686.255530	C1.mol

	-1976.969971	C2.mol
	-1059.721081	D1.mol
	-1641.157660	D2.mol
	-861.063077	Et2AlCl.mol

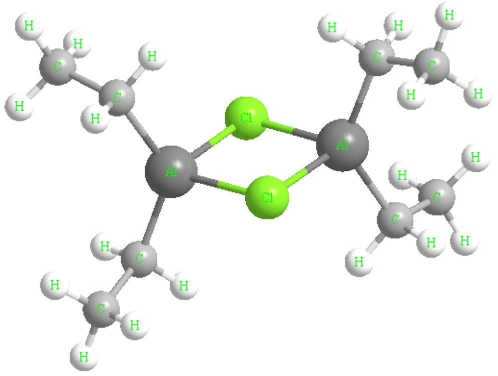
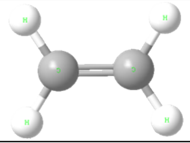
	-1722.137502	(Et2AlCl)2.mol
	-7.557119	ethylene.mol

Table 2. Quantum chemical calculations at B3LYP/6-31G*/LANL2DZ level of theory in gas phase. The standard Gibbs energy is given at 298.15 K.

r1: (Intermediate A) + alkyne = (Product of alkyne insertion) (**A**→**C**)

r2: Cp_2Zr(ethylene) + 2 alkyne = Zirconacyclopentadiene + ethylene (**B**→**D**)

r3: (Intermediate A) = Cp_2Zr(ethylene) + Et_2AlCl (**A**→**B**)

r4: (Intermediate A) +2 alkyne = Zirconacyclopentadiene + ethylene + Et_2AlCl (**A**→**D**)

r5: (Intermediate A) = Cp_2Zr(ethylene) + 0.5*$(Et_2AlCl)_2$ (**A**→**B**)

r6: (Intermediate A) +2 alkyne = Zirconacyclopentadiene + ethylene + 0.5*$(Et_2AlCl)_2$ (**A**→**D**)

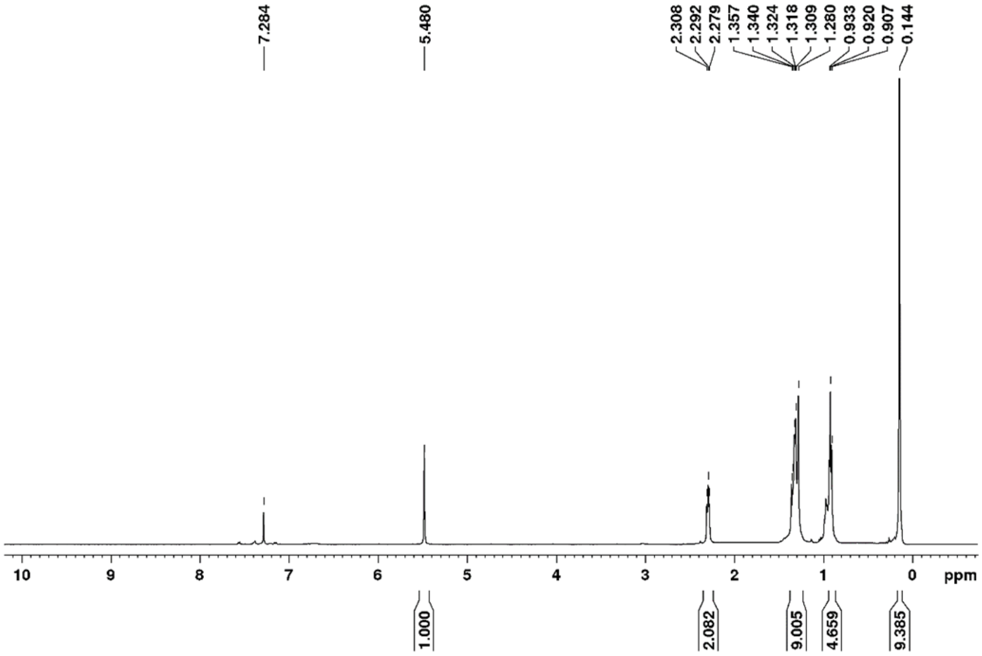
Alkyne	dG(**r1**), kcal/mol	dG(**r2**), kcal/mol	dG(**r4**), kcal/mol	dG(**r6**), kcal/mol
4-Octyne	2.293548	-18.707944	-9.398211	-12.958701
Trimethyl(pent-1-yn-1-yl)silane	13.861687	-0.401606	8.908126	5.347637

dG(**r3**) = 9.309733 kcal/mol

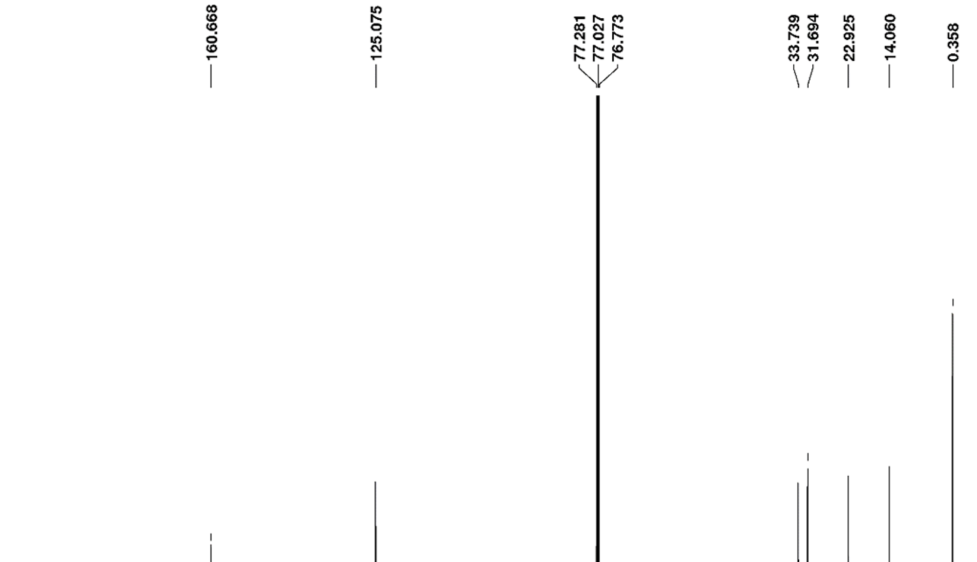
dG(**r5**) = 5.749243 kcal/mol

((1*E*,3*E*)-2,3-dibutylbuta-1,3-diene-1,4-diyl)*bis*(trimethylsilane) 2a.[2]

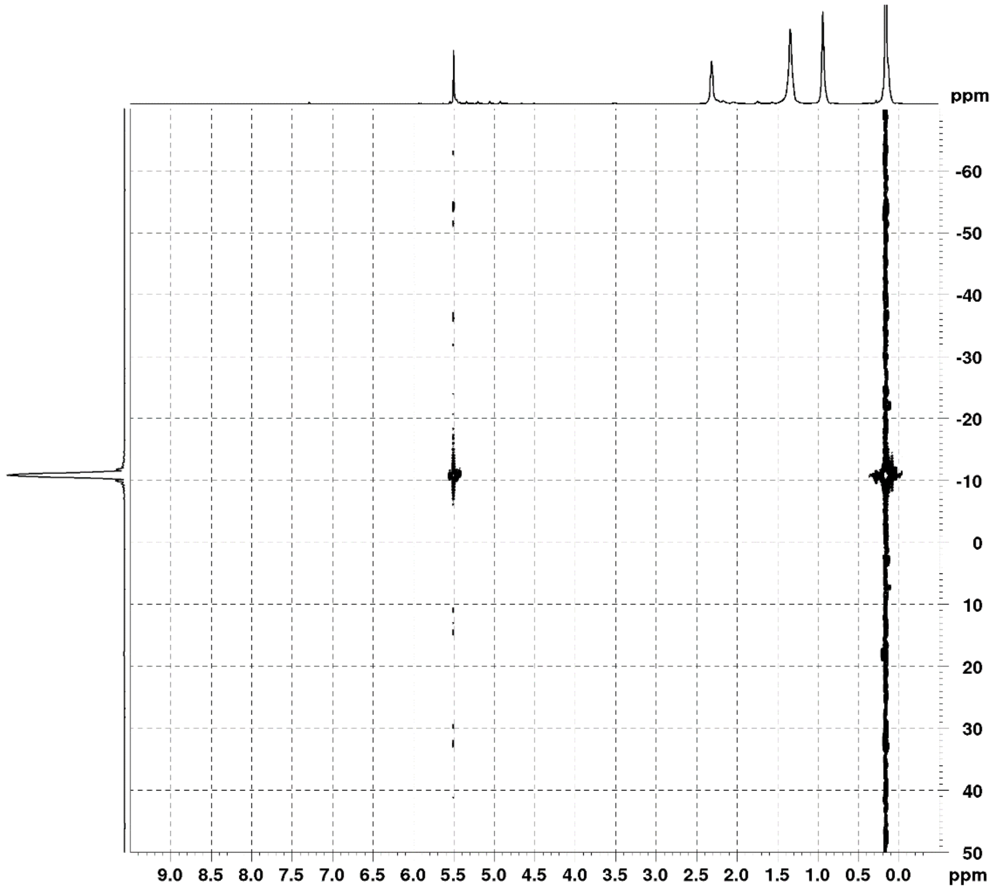
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, C(7)H_3), 0.92 (t, *J* = 7.0 Hz, 3H, C(6)H_3), 1.28–1.36 (m, 4H, C(4, 5)H_2), 2.29 (t, *J* = 6.4 Hz, 2H, C(3)H_2), 5.48 (s, 1H, C(1)H). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 0.36 (C(7)), 14.06 (C(6)), 22.93 (C(5)), 31.69 (C(4)), 33.74 (C(3)), 125.07 (C(1)), 160.67 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): -10.79.



^{1}H NMR of **2a**



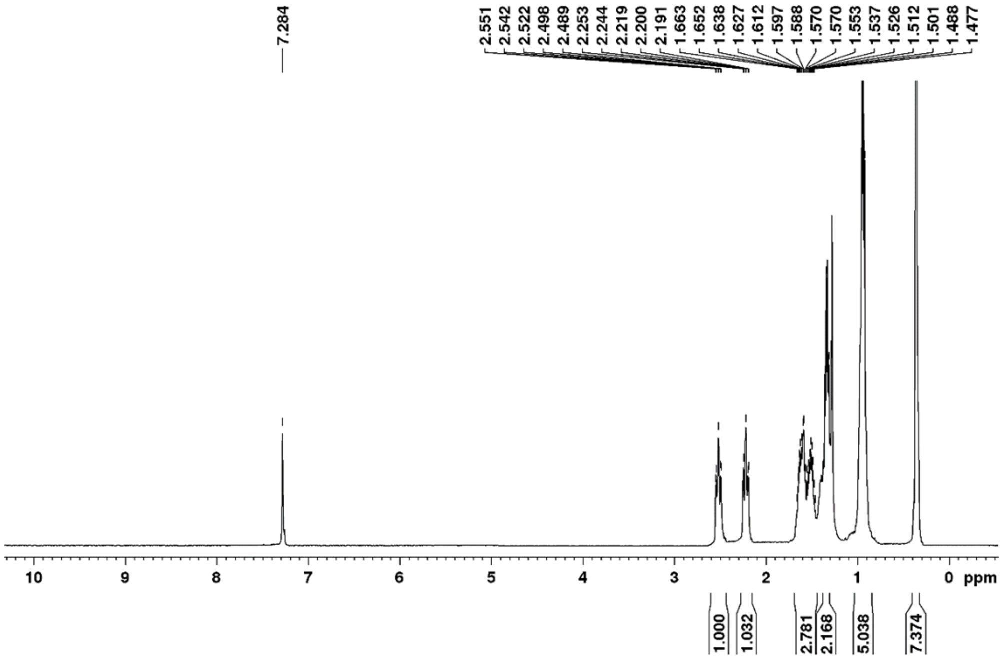
^{13}C-{^{1}H} NMR of **2a**



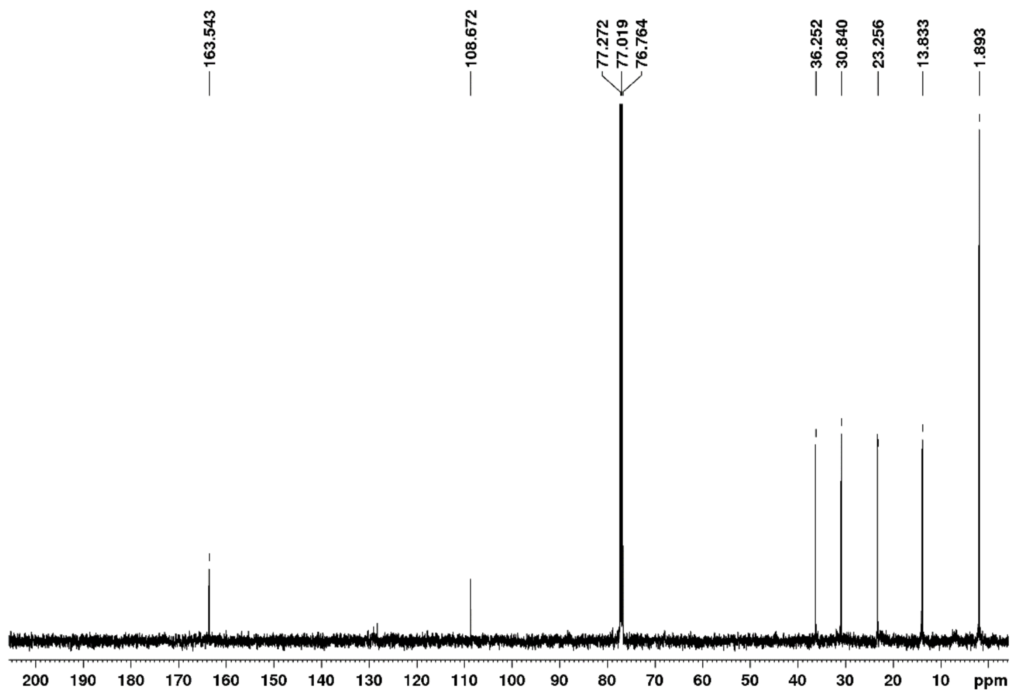
^{1}H - ^{29}Si HMBC NMR of **2a**

((1*Z*,3*Z*)-2,3-dibutyl-1,4-diiodobuta-1,3-diene-1,4-diyl)*bis*(trimethylsilane) 4a.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.36 (s, 9H, C(7)H_3), 0.94 (t, J = 7.3 Hz, 1H, C(6)H_3), 1.34 (q, J = 7.3 Hz, J = 14.5 Hz, 2H, C(5)H_2), 1.46–1.55 (m, 1H(A), 1H(B), C(4)H_2), 2.21 (t, J = 13.7 Hz, 1H(A), C(3)H_2), 2.52 (t, J = 13.7 Hz, 1H(B), C(3)H_3). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 1.89 (C(7)), 13.83 (C(6)), 23.26 (C(5)), 30.84 (C(4)), 36.25 (C(3)), 108.67 (C(1)), 163.54 (C(2)).



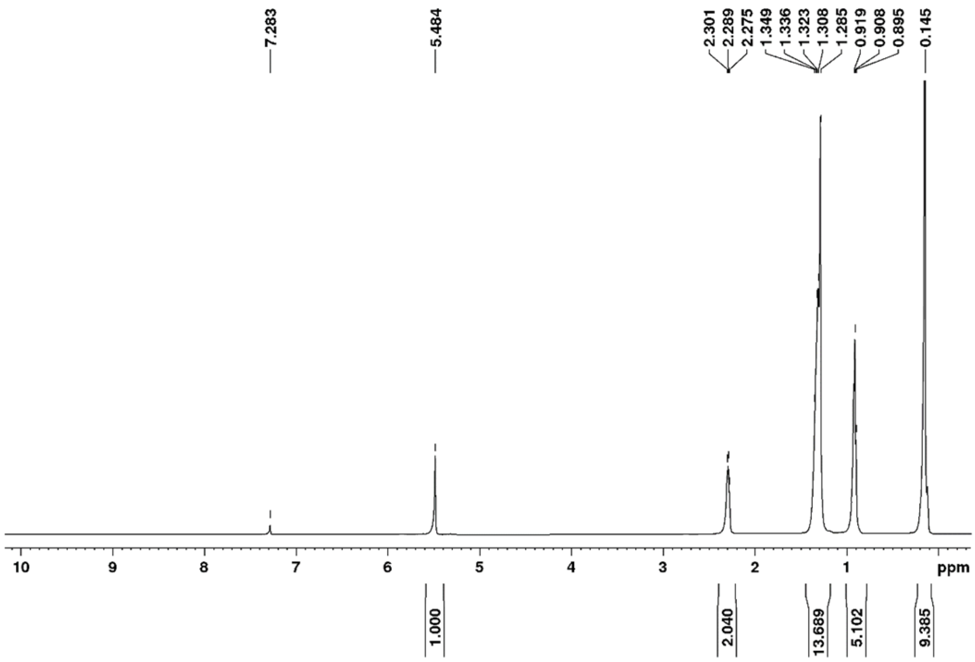
^{1}H NMR of **4a**



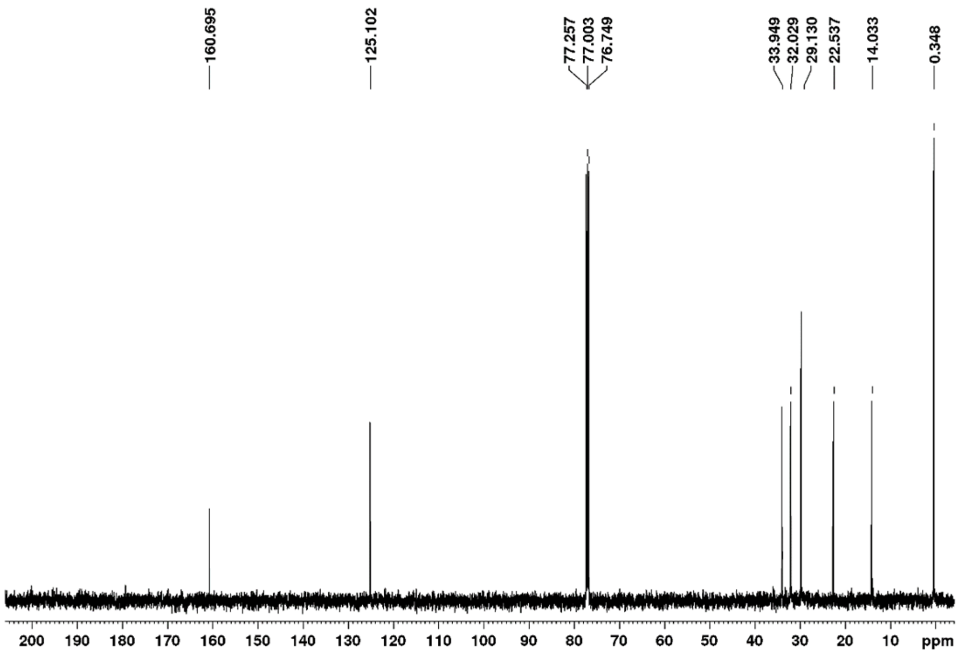
$^{13}C-\{^{1}H\}$ NMR of **4a**

((1*E*,3*E*)-2,3-dipentylbuta-1,3-diene-1,4-diyl)*bis*(trimethylsilane) 2b.

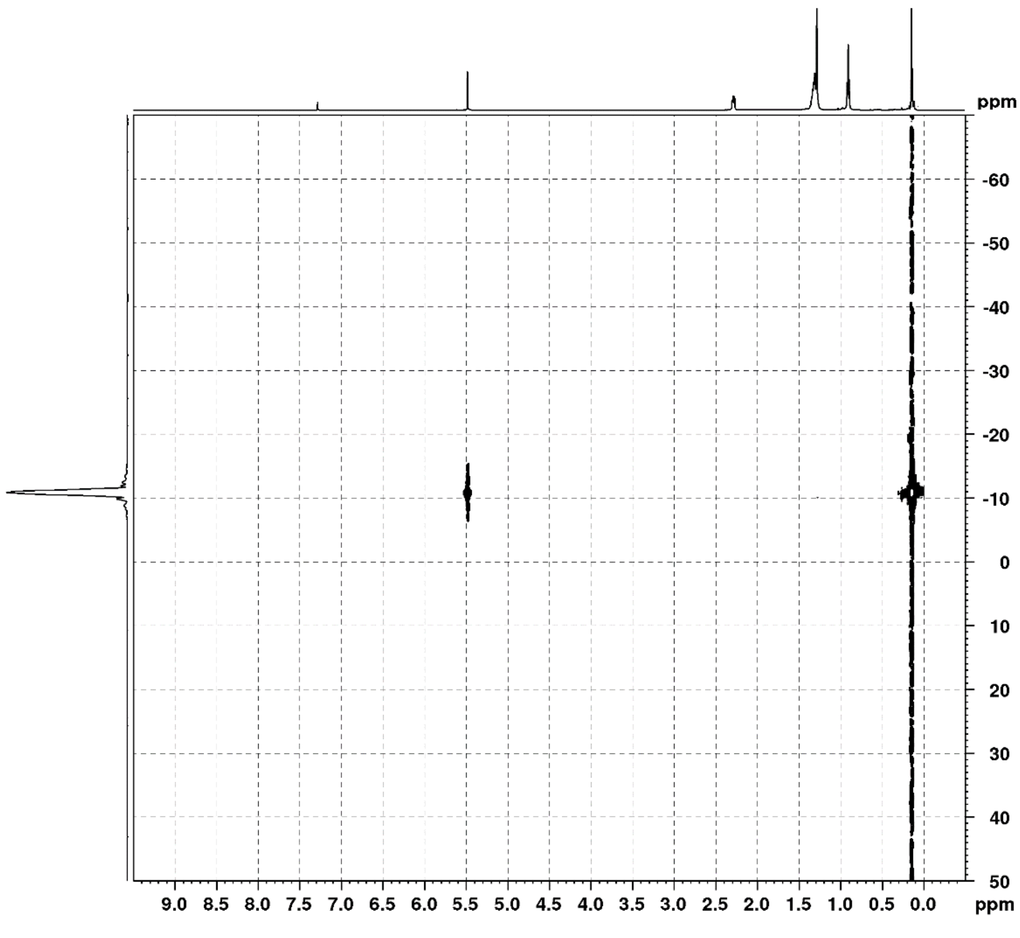
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, $C(8)H_3$), 0.91 (t, *J* = 7.0 Hz, 3H, $C(7)H_3$), 1.28–1.35 (m, 6H, C(4, 5, 6)H_2), 2.29 (t, *J* = 6.0 Hz, 2H, $C(3)H_2$), 5.48 (s, 1H, C(1)H). $^{13}C-\{^{1}H\}$ NMR (500 MHz, $CDCl_3$): δ = 0.35 (C(8)), 14.03 (C(7)), 22.54 (C(6)), 29.13 (C(4)), 32.03 (C(5)), 33.95 (C(3)), 125.10 (C(1)), 160.69 (C(2)). $^{29}Si-\{^{1}H\}$ (500 MHz, $CDCl_3$): -10.82.



^{1}H NMR of **2b**



^{13}C-{^{1}H} NMR of **2b**

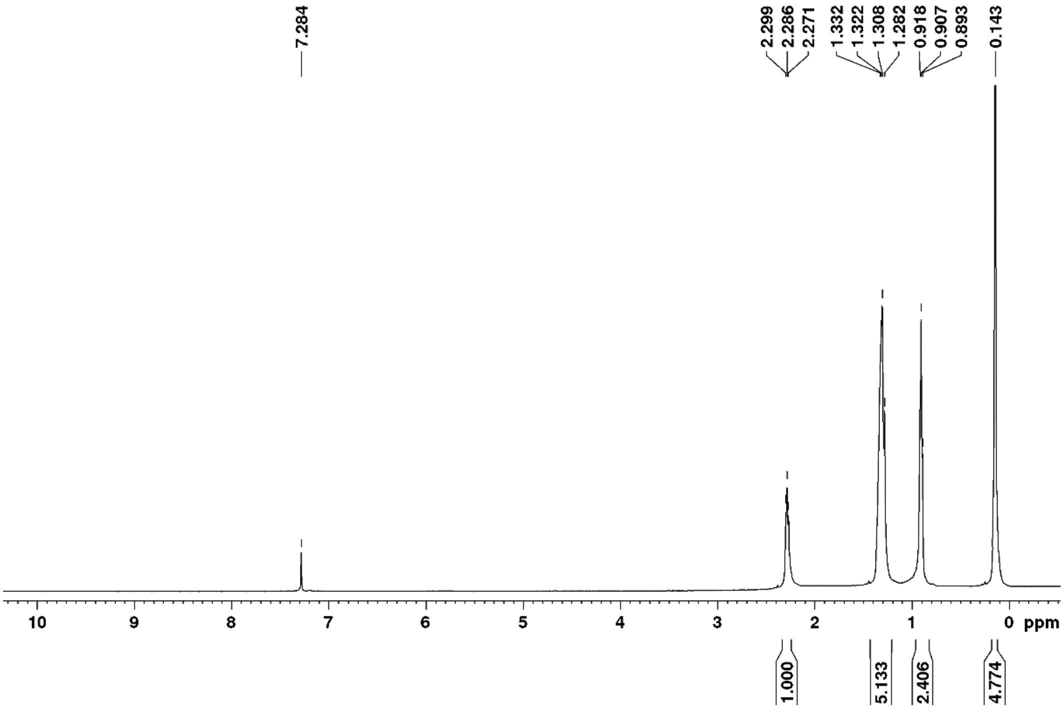


^{1}H - ^{29}Si HMBC NMR of **2b**

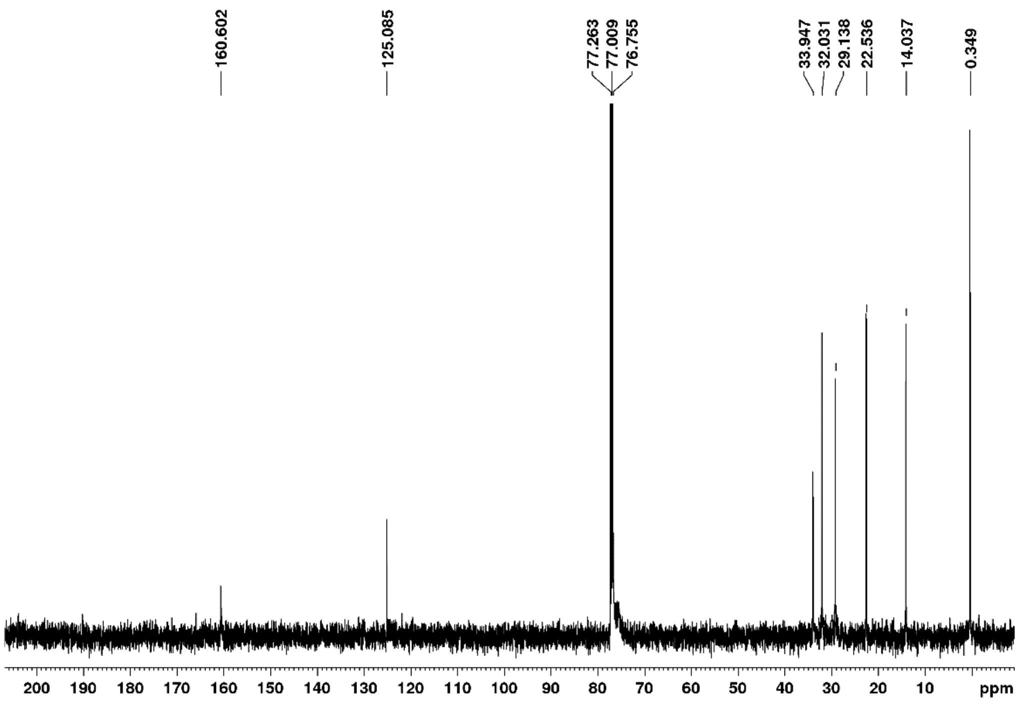
((1*E*,3*E*)-2,3-dipentylbuta-1,3-diene-1,4-diyl-1,4-d2)*bis*(trimethylsilane) 3b

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, C(8)H_3), 0.91 (t, J = 6.7 Hz, 3H, C(7)H_3), 1.28–1.33 (m, 6H, C(4, 5, 6)H_2), 2.28 (t, J = 7.4 Hz, 2H, C(3)H_2), 5.48 (s, 1H, C(1)H).^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ

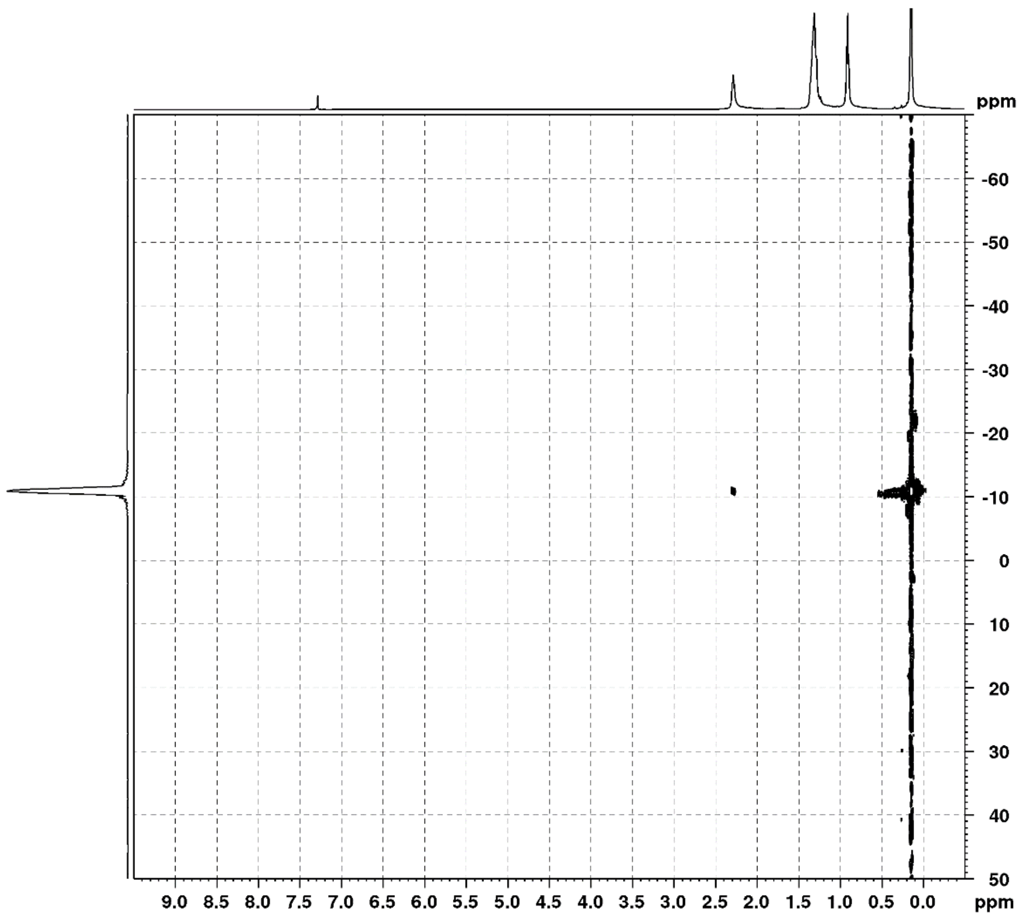
= 0.35 (C(8)), 14.04 (C(7)), 22.54 (C(6)), 29.14 (C(4)), 32.03 (C(5)), 32.95 (C(3)), 125.09 (C(1)), 160.60 (C(2)). ^{29}Si-{^1H} (500 MHz, $CDCl_3$): -10.84.



^1H NMR of **3b**



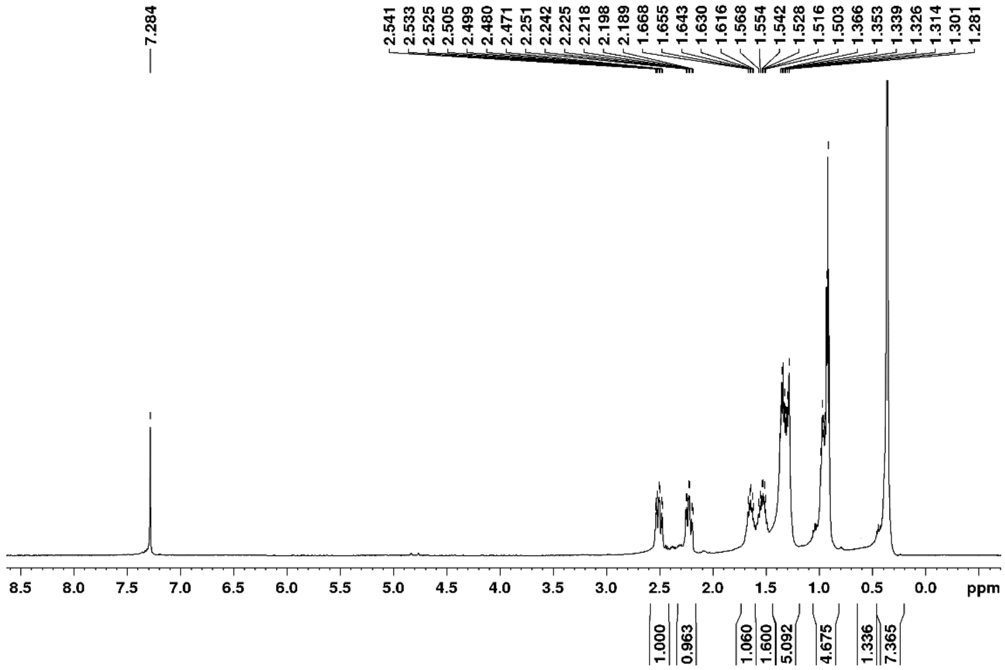
^{13}C-{^1H} NMR of **3b**



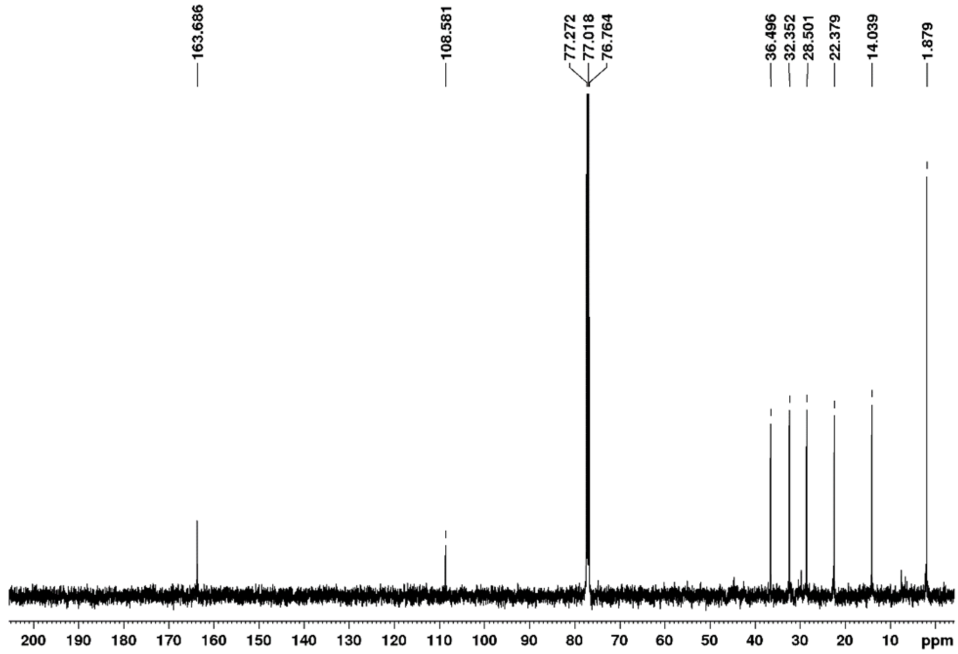
^{1}H - ^{29}Si HMBC NMR of **3b**

((1Z,3Z)-1,4-diiodo-2,3-dipentylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) 4b

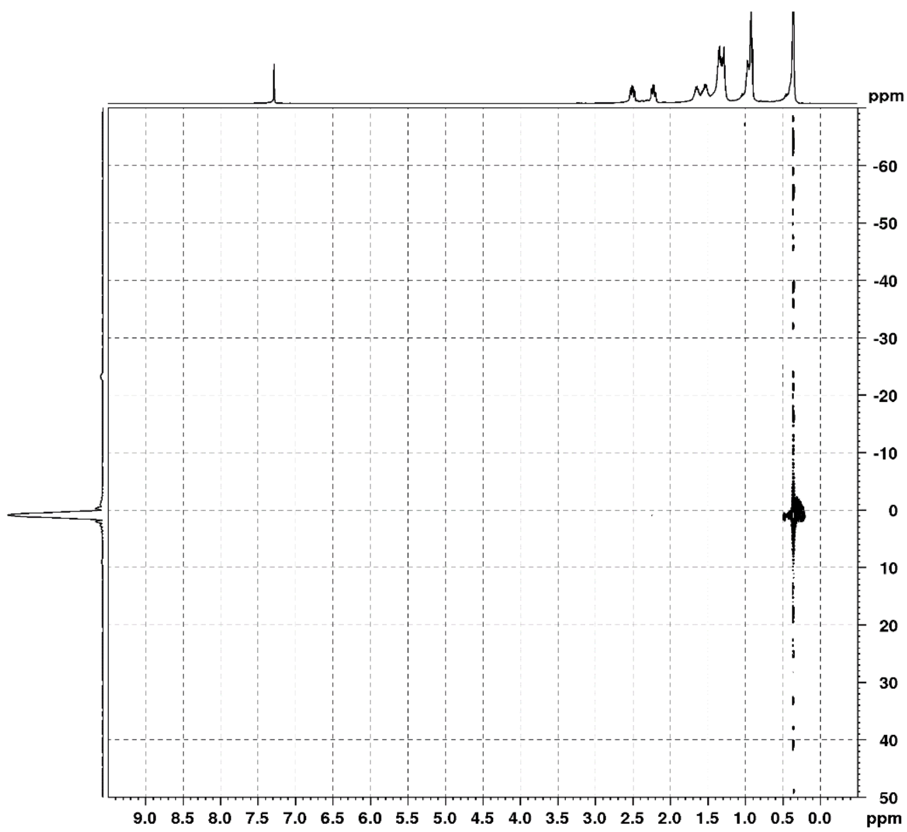
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.36 (s, 9H, C(8)H_3), 0.92 (t, *J* = 7.1 Hz, 3H, C(7)H_3), 1.28–1.31 (m, 2H, C(5)H_2), 1.33–1.37 (m, 2H, C(6)H_2), 1.50–1.56 (m, 1H(A), C(4)H2), 1.62–1.67 (m, 1H(B), C(4)H_2), 2.22 (t, *J* = 13.2 Hz, 1H(A), C(3)H_2), 2.50 (t, *J* = 13.3 Hz, 1H(B), C(3)H_2). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 1.88 (C(8)), 14.04 (C(7)), 22.38 (C(6)), 28.50 (C(4)), 32.35 (C(5)), 36.49 (C(3)), 108.58 (C(1)), 163.68 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): 0.93.



^{1}H NMR of **4b**



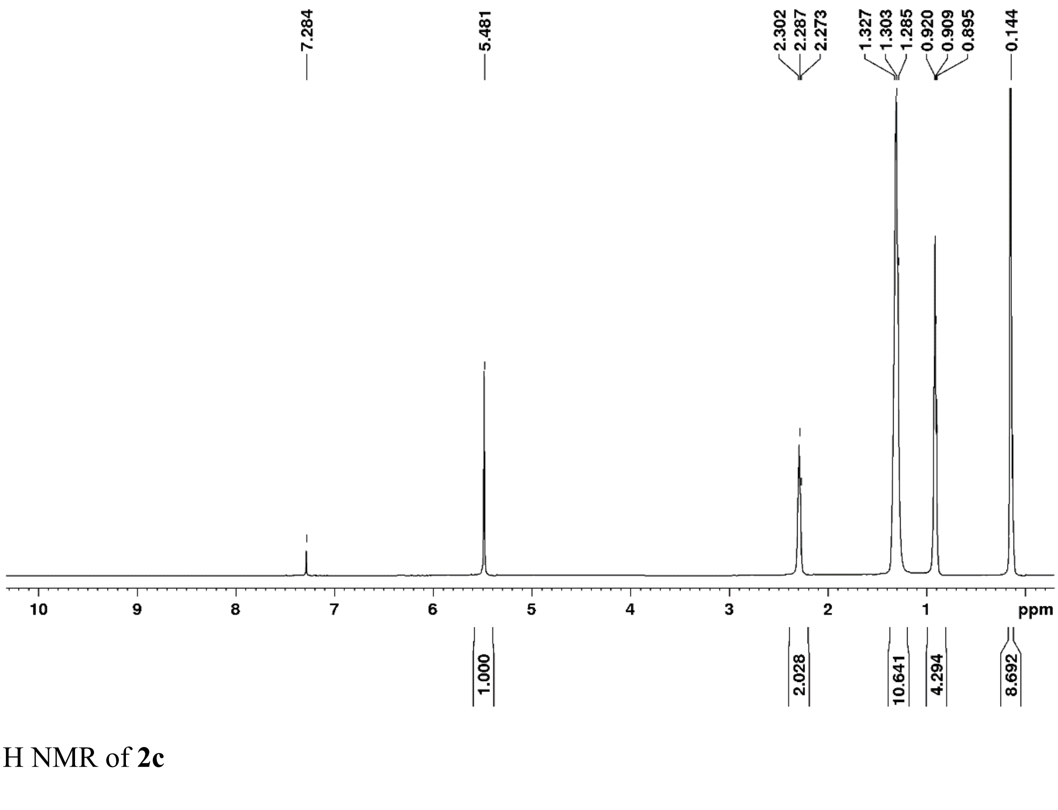
^{13}C-{^{1}H} NMR of **4b**



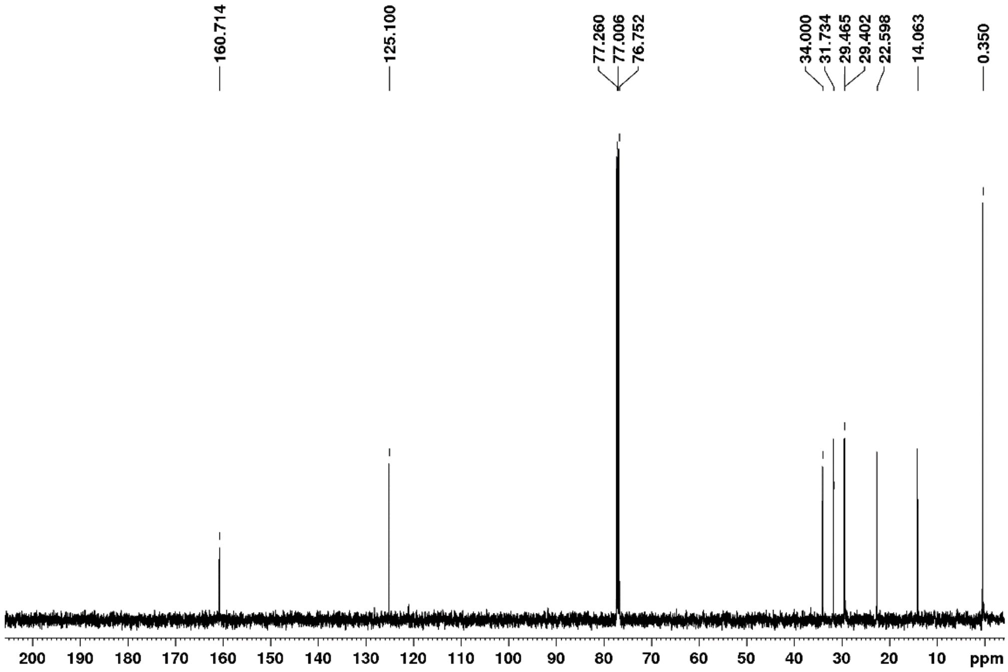
^{1}H - ^{29}Si HMBC NMR of **4b**

((1*E*,3*E*)-2,3-dihexylbuta-1,3-diene-1,4-diyl)*bis*(trimethylsilane) 2c.

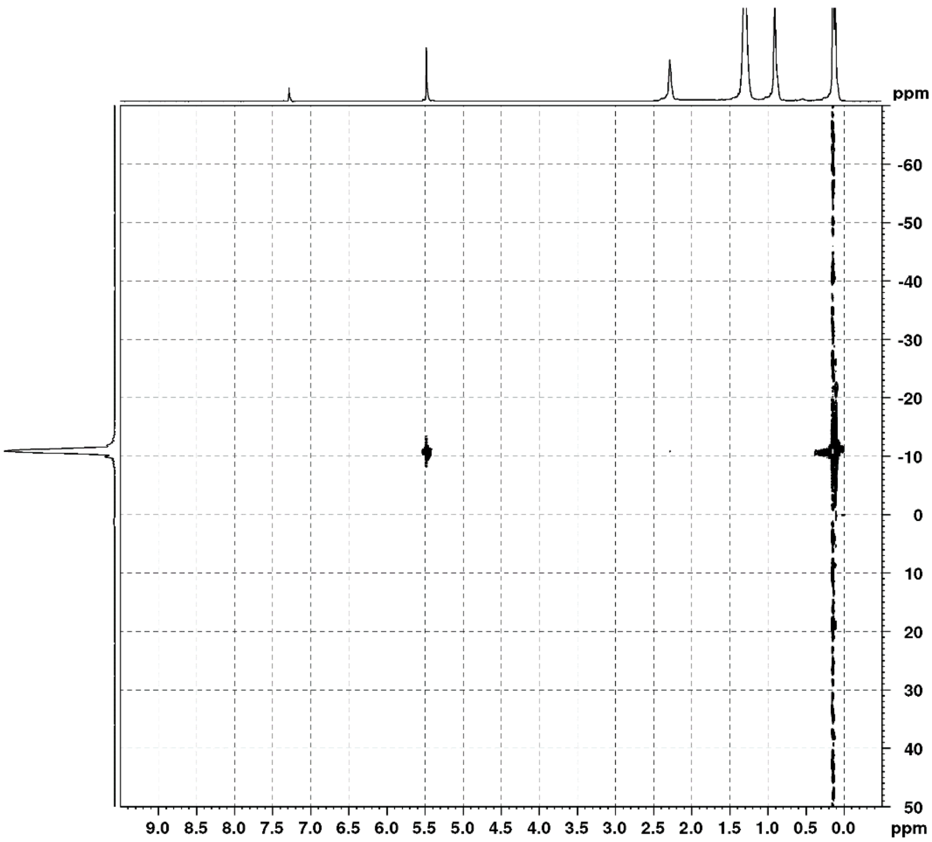
^{1}H NMR (50 0MHz, $CDCl_3$): δ = 0.14 (s, 9H, C(9)H_3), 0.91 (t, *J* = 6.9 Hz, 3H, C(8)H_3), 1.28–1.33 (m, 8H, C(4, 5, 6, 7)H_2), 2.29 (t, *J* = 7.3 Hz, 2H, C(3)H_2), 5.48 (s, 1H, C(1)H). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 0.35 (C(9)), 14.06 (C(8)), 22.59 (C(7)), 29.40 (C(4)), 29.47 (C(5)), 31.73 (C(6)), 34.00 (C(3)), 125.10 (C(1)), 160.71 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): -10.84.



^{1}H NMR of **2c**



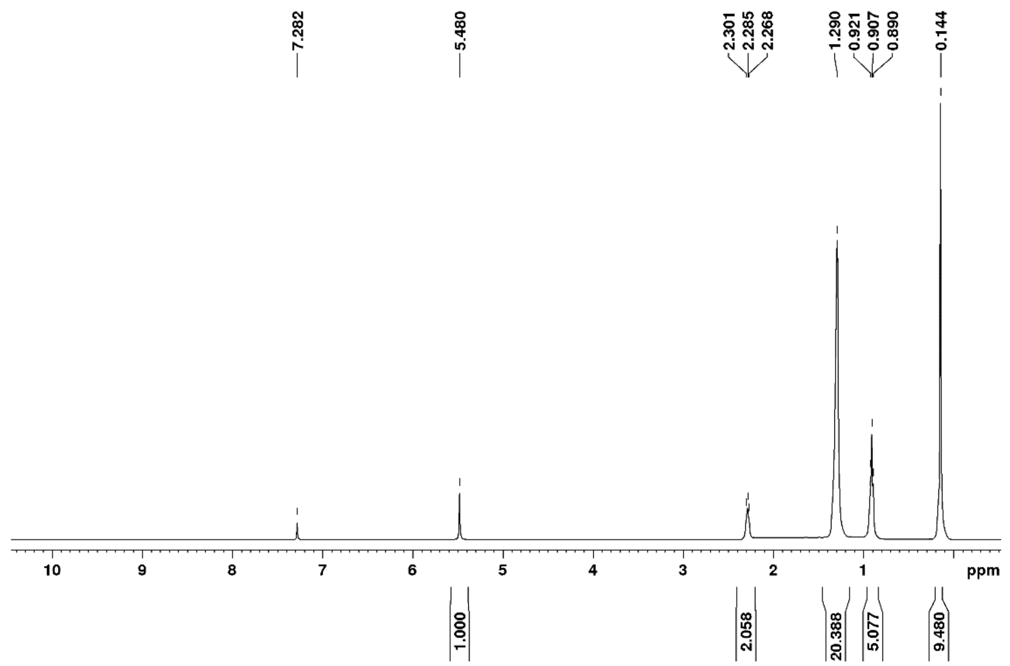
^{13}C-{^{1}H} NMR of **2c**



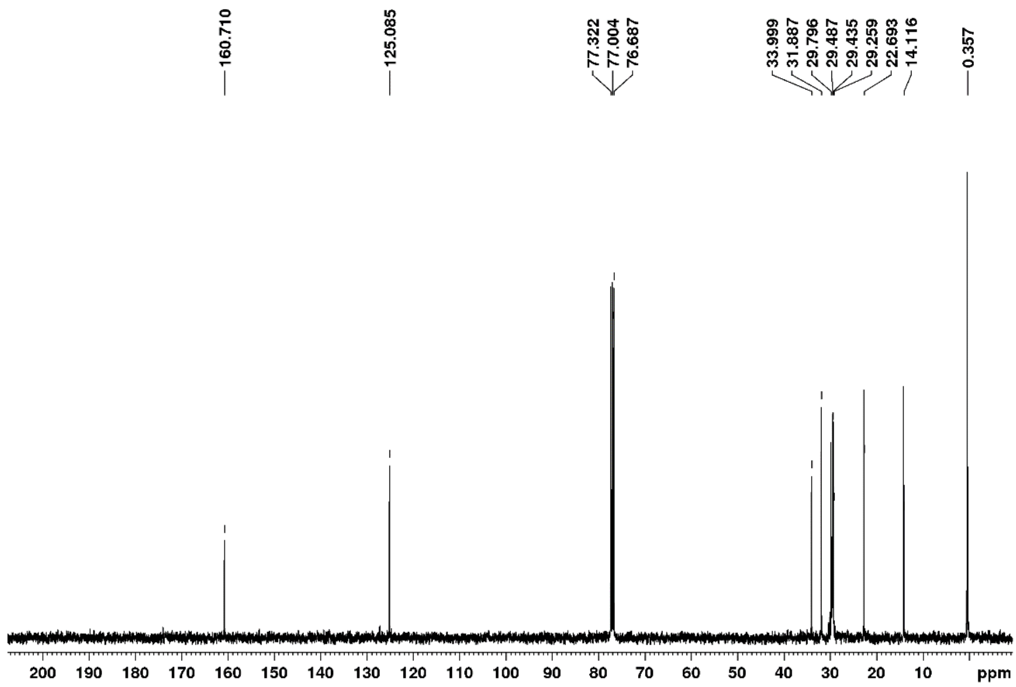
^{1}H - ^{29}Si HMBC NMR of **2c**

((1*E*,3*E*)-2,3-dioctylbuta-1,3-diene-1,4-diyl)*bis*(trimethylsilane) 2d

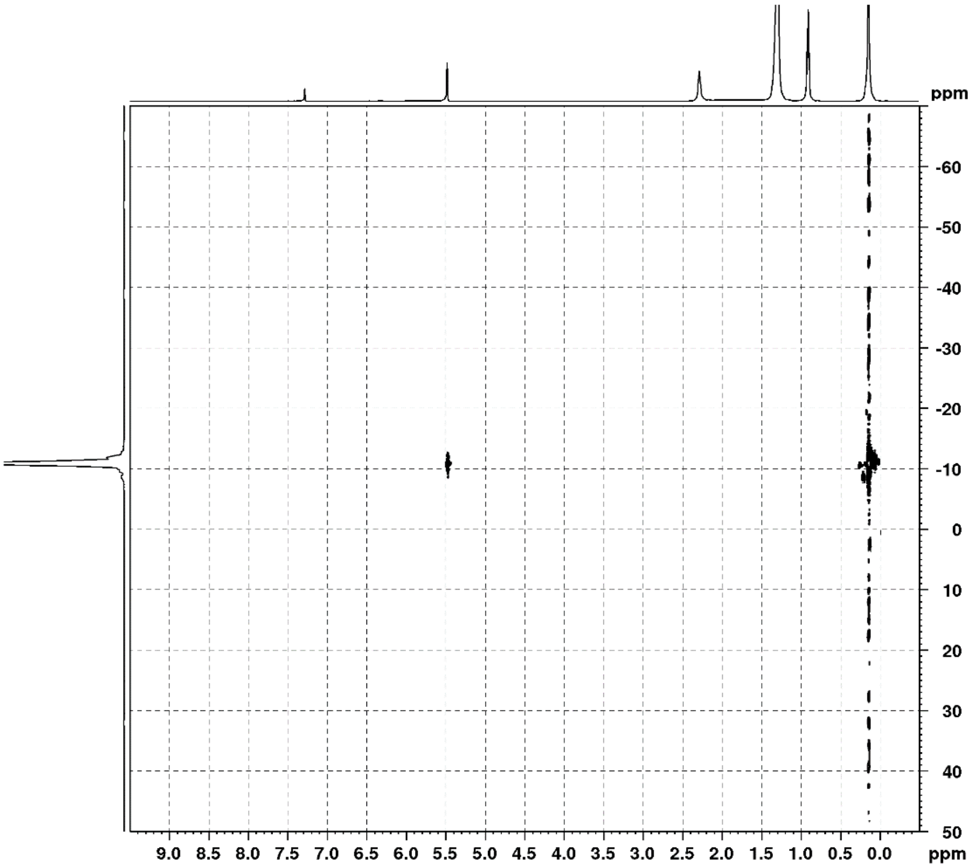
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, C(11)H_3), 0.91 (t, *J* = 7.2 Hz, 3H, C(10)H_3), 1.29 (s, 12H, C(4-9)H_2), 2.29 (t, *J* = 7.8 Hz, 2H, C(3)H_2), 5.48 (s, 1H, C(1)H). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 0.36 (C(11)), 14.12 (C(10)), 22.69 (C(9)), 29.26 (C(4)), 29.44 (C(5)), 29.49 (C(7)), 29.80 (C(6)), 31.89 (C(8)), 33.99 (C(3)), 125.08 (C(1)), 160.71 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): -10.82.



[1]H NMR of **2d**



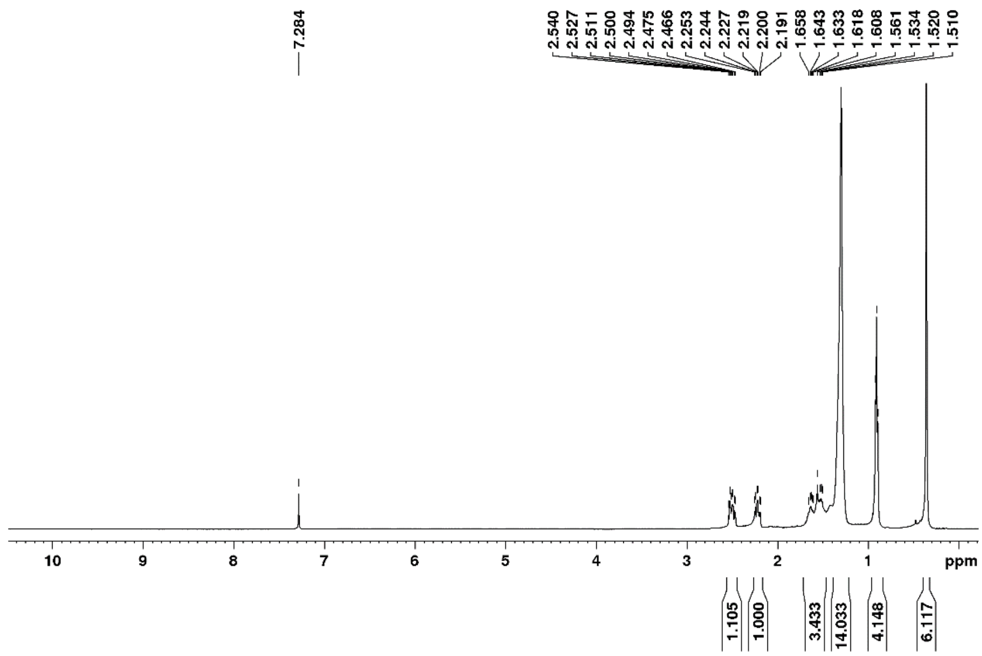
[13]C-{[1]H} NMR of **2d**



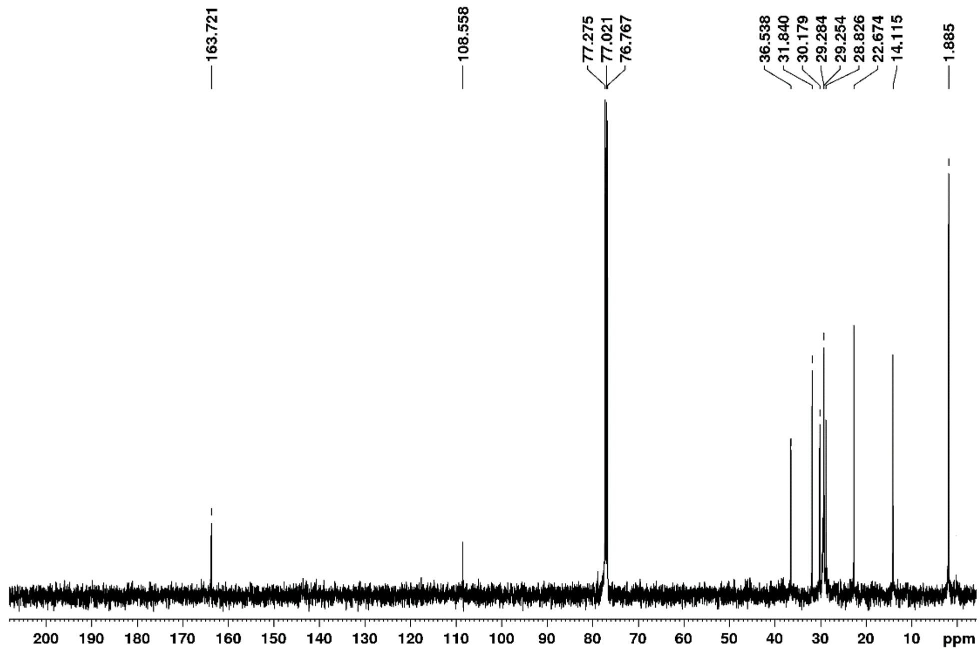
^1H - ^{29}Si HMBC NMR of **2d**

((1*Z*,3*Z*)-1,4-diiodo-2,3-dioctylbuta-1,3-diene-1,4-diyl)*bis*(trimethylsilane) 4d

^1H NMR (500 MHz, $CDCl_3$): δ = 0.36 (s, 9H, C(11)H_3), 0.91 (t, *J* = 6.9 Hz, 3H, C(10)H_3), 1.29 (s, 8H, C(5,7-9)H_2), 1.51–1.56 (m, 2H, C(6)H_2), 1.51–1.56 (m, 1H(A), C(4)H_2), 1.61–1.66 (m, 1H(B), C(4)H_2), 2.22 (t, *J* = 13.0 Hz, 1H(A), C(3)H_2), 2.47–2.54 (m, 1H(B), C(3)H_2). ^{13}C-{^1H} NMR (500 MHz, $CDCl_3$): δ = 1.88 (C(11)), 14.12 (C(10)), 22.68 (C(9)), 28.83 (C(4)), 29.26 (C(5)), 29.28 (C(7)), 30.18 (C(6)), 31.84 (C(8)), 36.54 (C(3)), 100.56 (C(1)), 163.72 (C(2)).



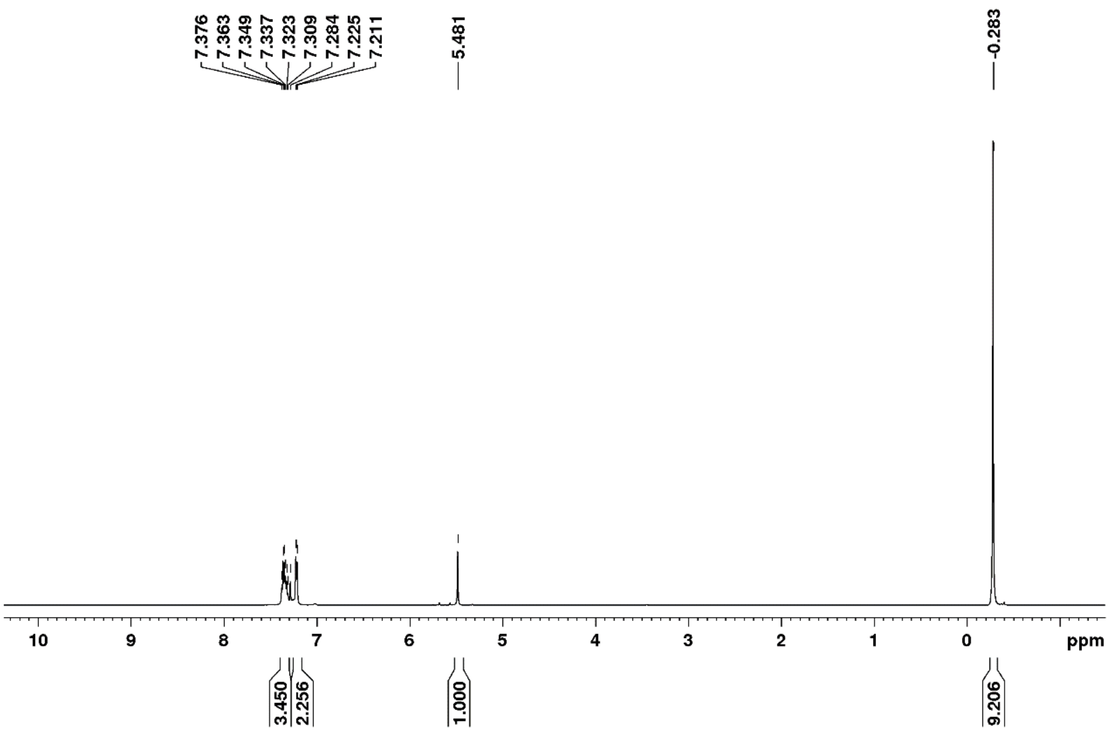
^1H NMR of **4d**



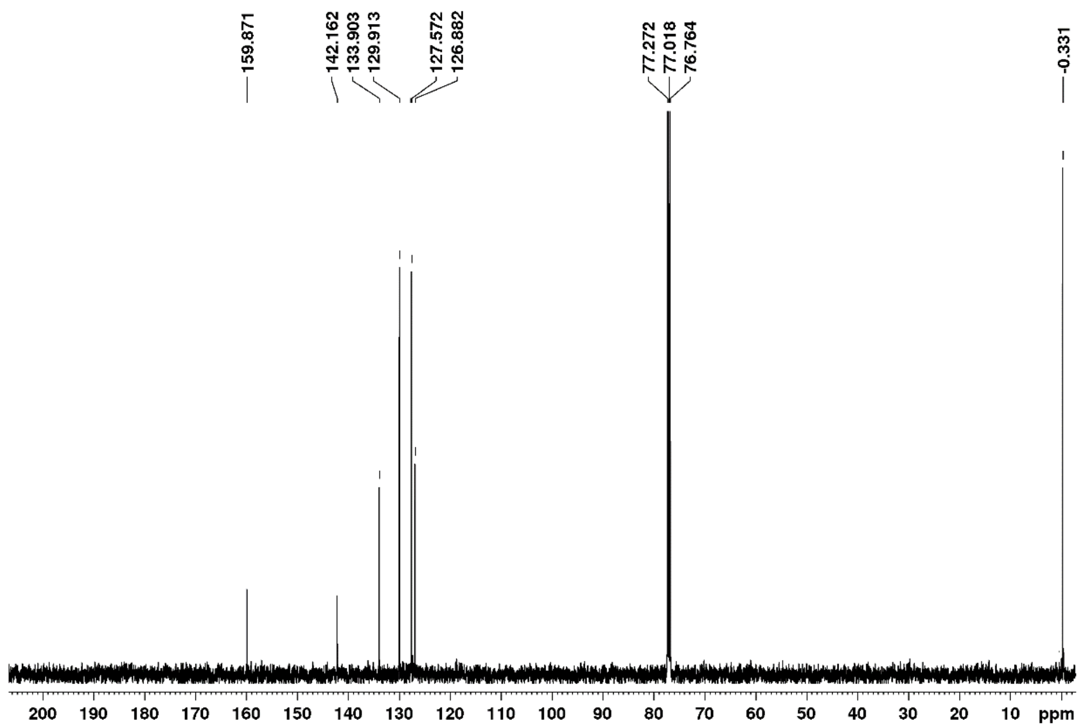
^{13}C-{^{1}H} NMR of **4d**

((1*E*,3*E*)-2,3-diphenylbuta-1,3-diene-1,4-diyl)*bis*(trimethylsilane) 2e.

^{1}H NMR (500 MHz, $CDCl_3$): δ = -0.28 (s, 9H, C(7)H_3), 5.48 (s, 1H, C(1)H), 7.22 (d, *J* = 6.9 Hz, 1H, C(4)H), 7.31–7.38 (m, 2H, C(5,6)H). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = -0.28 (C(7)), 126.88 (C(6)), 127.57 (C(5)), 129.91 (C(4)), 133.90 (C(1)), 142.16 (C(3)), 159.87 (C(2)).



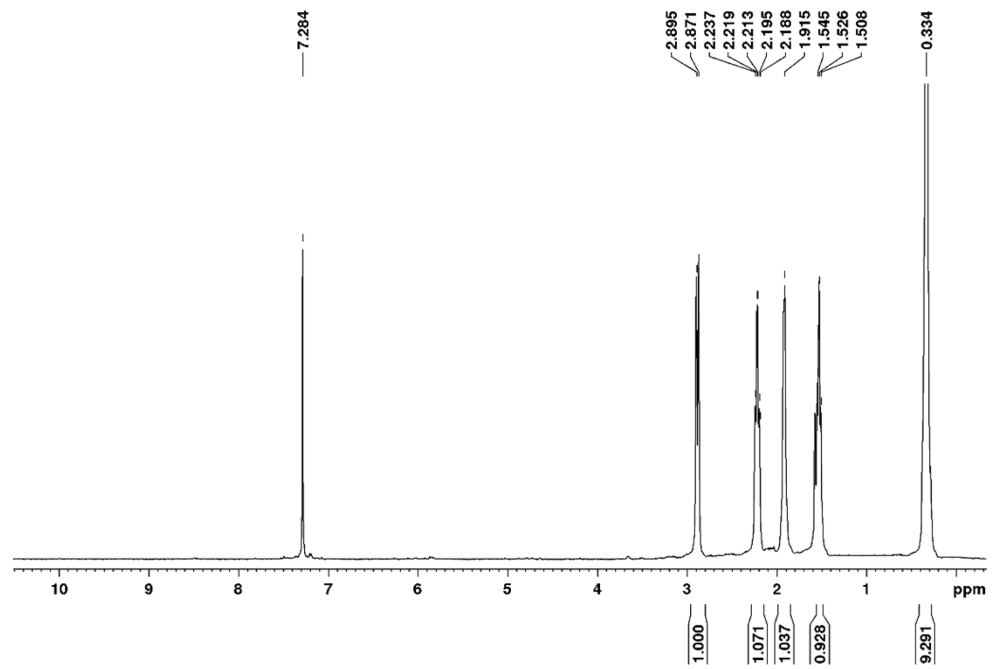
^{1}H NMR of **2e**



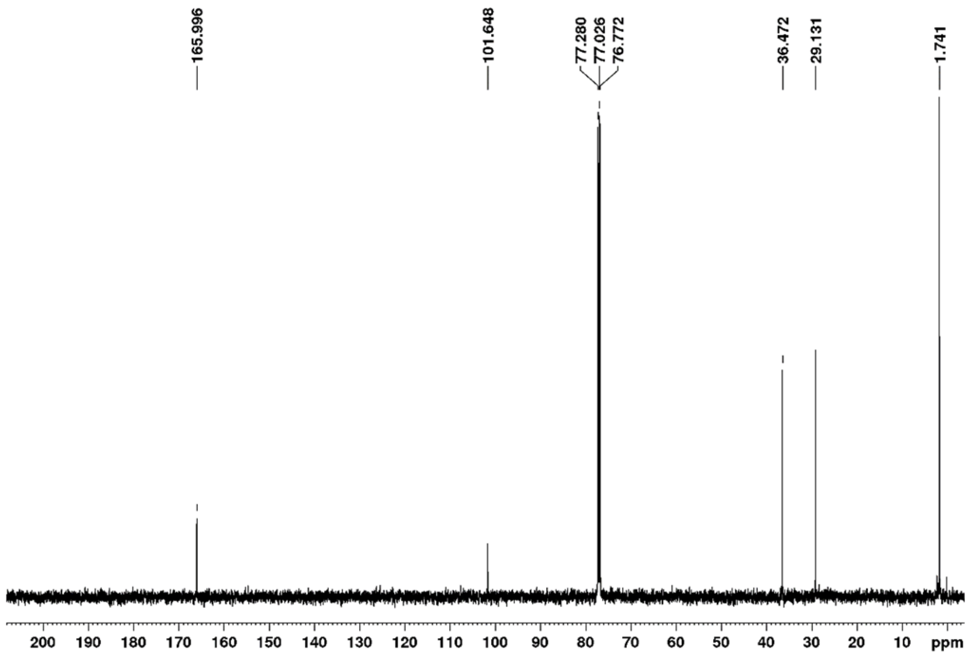
^{13}C-{^{1}H} NMR of **2e**

(1*Z*,2*Z*)-1,2-bis(iodo(trimethylsilyl)methylene)cyclohexane (6).[5]

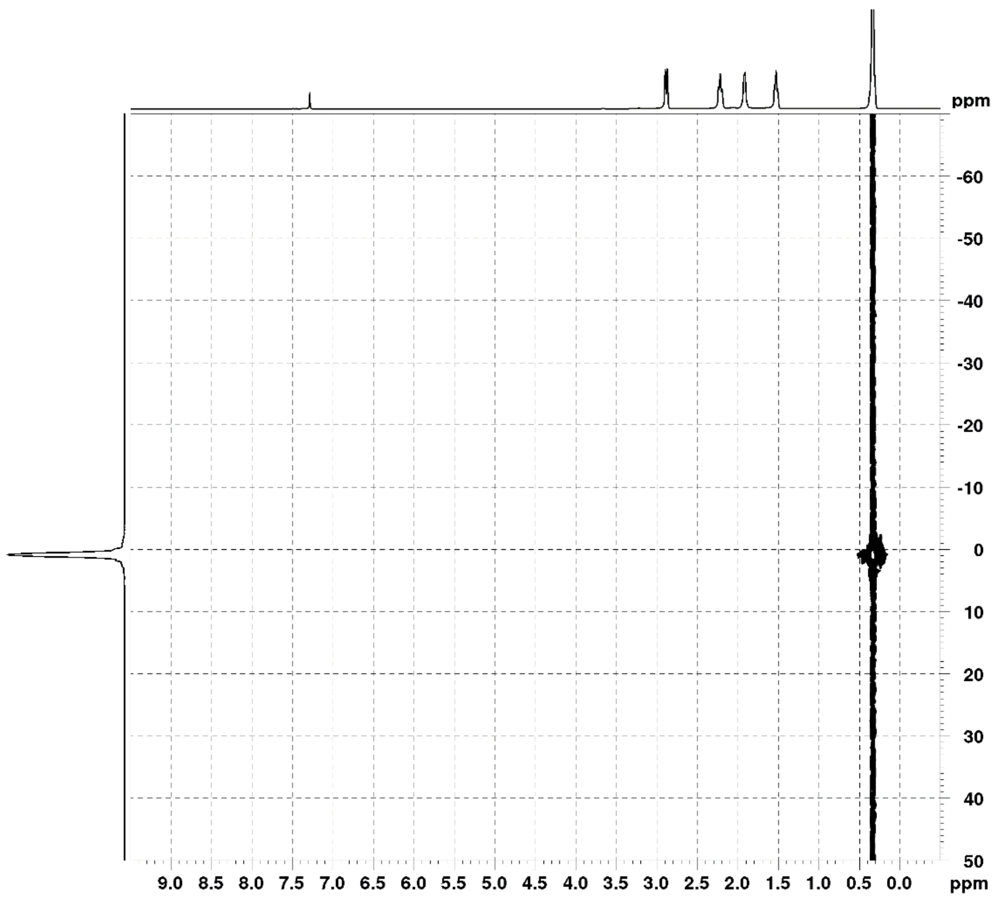
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.33 (s, 9H, C(5)H_3), 1.52 (t, *J* = 9.2 Hz, 1H(A), C(4)H_3), 1.92 (s, 1H(B), C(4)H_2), 2.21 (t, *J* = 12.0 Hz, 1H(A), C(3)H_2), 2.88 (d, *J* = 12.0 Hz, 1H(B), C(3)H_2). ^{13}C-{^{1}H} NMR (500 MHz, $CDCl_3$): δ = 1.74 (C(5)), 29.13 (C(4)), 36.42 (C(3)), 101.65 (C(1)), 165.99 (C(2)). ^{29}Si-{^{1}H} (500 MHz, $CDCl_3$): 0.95.



^{1}H NMR of **6**



^{13}C-{^{1}H} NMR of **6**

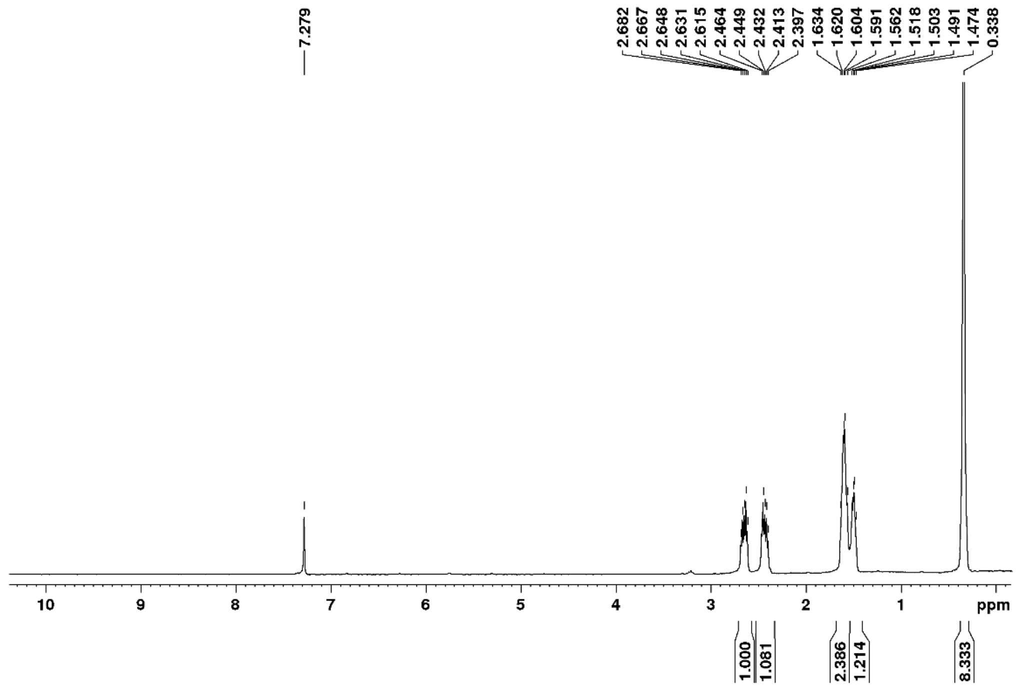


^{1}H - ^{29}Si HMBC NMR of **6**

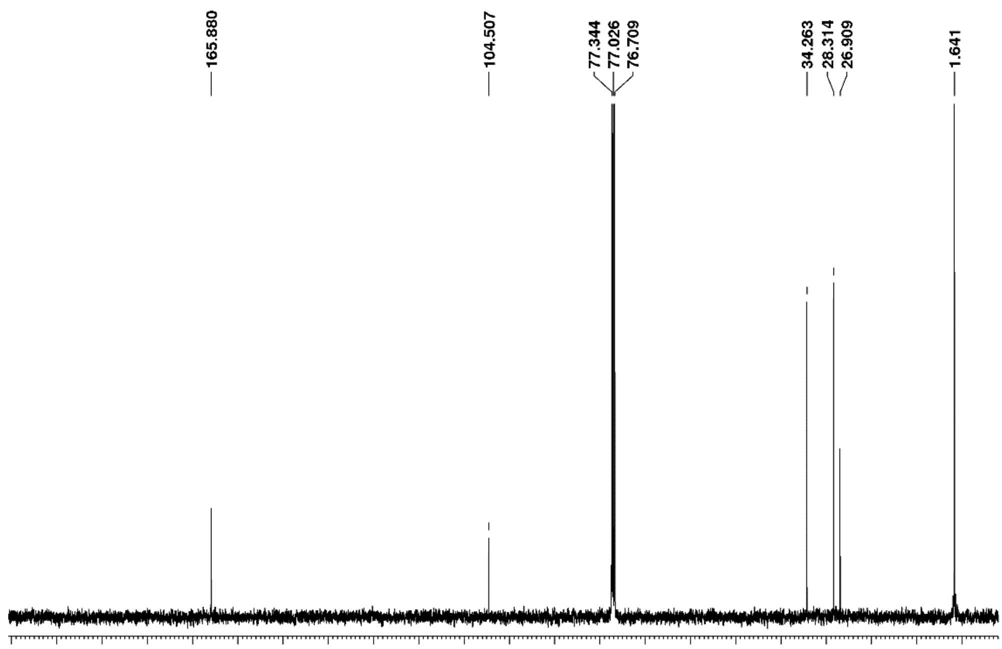
(1*Z*,2*Z*)-1,2-bis(iodo(trimethylsilyl)methylene)cycloheptane (7)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.34 (s, 9H, C(5)H_3), 1.47–1.52 (m, 2H(A), C(4,6)H_3), 1.56–1.63 (m, 2H(B), C(4,6)H_2), 2.39–2.47 (m, 1H(A), C(3)H_2), 2.62 – 2.68 (m, 1H(B), C(3)H_2). ^{13}C-{^{1}H} NMR (500

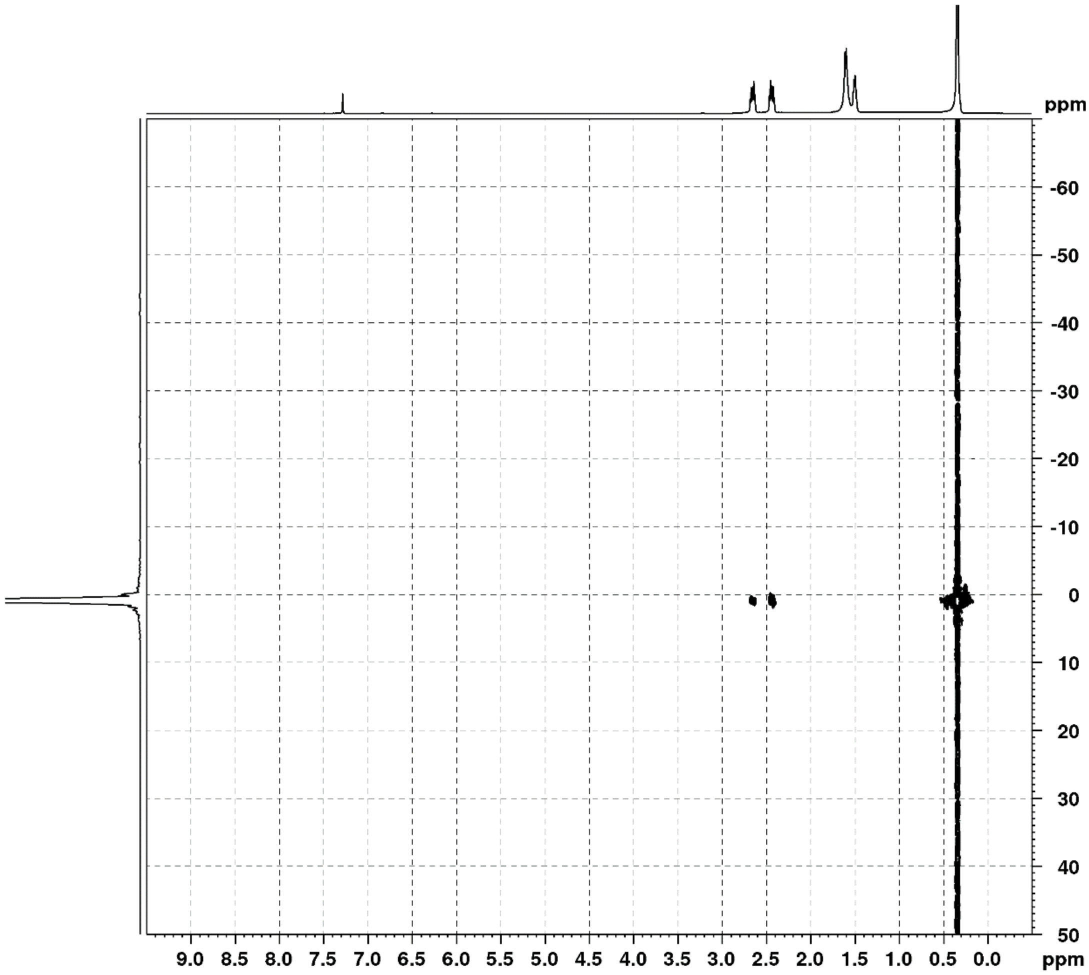
MHz, $CDCl_3$): δ = 1.64 (C(5)), 26.91 (C(6)), 28.31 (C(4)), 34.26 (C(3)), 104.51 (C(1)), 165.88 (C(2)). MS (EI): m/z, % = 518 (1). $^{29}Si-\{^1H\}$ (500 MHz, $CDCl_3$): 0.96.



^{1}H NMR of **7**



$^{13}C-\{^1H\}$ NMR of **7**



^{1}H - ^{29}Si HMBC NMR of **7**