Supporting Information

Cu^{I}-Amido(bisphosphine) catalyzed C(sp^3)—C(sp^3) direct homo- and hetero-coupling of unactivated alkanes *via* C(sp^3)-H activation

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1. General Information

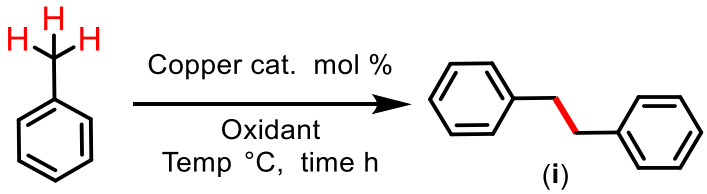
All air-sensitive compounds were handled and stored in the MBRAUN Glove box. All manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All solvents were dried using conventional methods and distilled before use. Amidobisphosphine,[1] and $[PNP\text{-}Cu]_2$ were synthesized published procedures.[2] Aryl alkanes, cyclohexane, cyclopentane, cyclooctane, and oxidants such as DTBP, TBHP, DCP and TBPB were purchased from Aldrich Chemicals.

Instrumentation. NMR spectra were recorded on Bruker FT spectrometers (Avance-400 or 500 MHz) at ambient probe temperatures. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were acquired using broadband decoupling method. The spectra were recorded in $CDCl_3$ solutions with TMS as an internal standard; chemical shifts of ^1H and $^{13}C\{^1H\}$ NMR spectra are reported in ppm downfield from TMS. The chemical shifts of $^{31}P\{^1H\}$ NMR spectra are referred to 85% H_3PO_4 as an external standard. Positive values indicate downfield shifts. GC-MS analyses were performed on an Agilent 7890A GC system with an FID detector using a J & amp; WDB-1 column (10 m, 0.1 mm ID). Catalytic reactions were magnetically stirred, and monitored by thin-layer chromatography (TLC) using Merck Silica Gel 60 F254 plates.

Precaution notes: Due to the low boiling points of alkanes such as toluene and its derivatives, cyclohexane, cyclopentane, cyclooctane, and oxidants (such as DTBP, TBHP, TBPB, DCP), the reactions were conducted in 20 mL sealed Teflon capped reaction tubes. This approach was necessary because, at elevated temperatures in an open system, there is a possibility of significant loss of reactants. Additionally, special precautions were taken when handling oxidants. This included wearing a lab coat, hand gloves, mask, safety goggles and performing the reactions in a well-ventilated fume hood.

2. Optimization of Reaction Condition

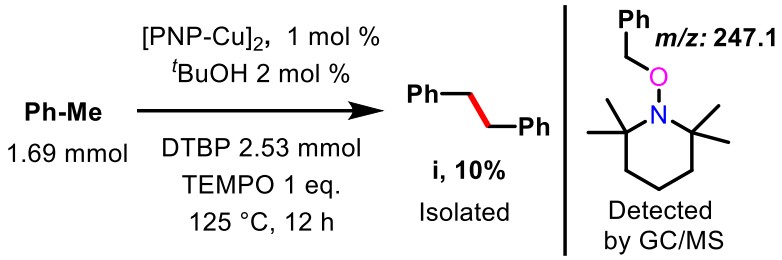
Table S1. Optimization of reaction conditions for homocoupling of toluene[a]



Entries	Catalyst (mol%)	Base (1 eq.)	Yield in %[a]
1)	No	No	N. R
2)	(1)	-	80
3)	(1)	-	90[b]
4)	(0.5)	-	63
5)	(1)	-	51[c]
6)	(1)	-	26[d]
7)	(1)	-	70[e]
8)	(1)	LiOH	38
9)	(1)	K_2CO_3	N. R
10)	(1)	KOAc	70
11)	(1)	^{t}BuOK	62
12)	PPh_3 (4) + CuI (2)	No	29
13)	XanthPhos (2) + CuI (2)	-	38
14)	(S)-BINAP (2) + CuI (2)	-	45
15)	[CuCl] (2)	-	28
16)	[CuBr] (2)	-	32
17)	[CuI] (2)	-	34
18)	$[CuCl_2]$ (2)	-	30
19)	$[Cu(OAc)_2]$ (2)	-	29

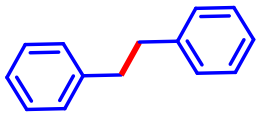
[a]Catalytic reaction conditions: 1.69 mmol toluene, Copper(I) catalysts (0.5-1 mol %) (Entries 2-11 $[PNP\text{-}Cu]_2$), [b]tert-butanol 2 mol % was added (Entry 3). 2.5 mmol Oxidants were used such as (DTBP= Di-*tert*-butyl peroxide (Entries 1-4 and 8-19), [c]TBPB = *tert*-Butyl perbenzoate, [d]TBHP = *tert*-Butyl hydrogenperoxide, [e]DCP = Dicumyl peroxide. All reactions performed at 125 °C for 12 h, isolated yields. N. R = No reaction.

3. Radical Trapping Experiment



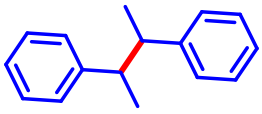
The radical pathway was validated with the addition of a radical quencher (TEMPO) to the reaction medium, which resulted in a decrease of the product yield to merely 10%. The proposed catalytic pathway is based on the calculations and experimental observations as summarized in Scheme 4, in the manuscript.

4. General procedure: Synthesis of 1, 2-diphenylethane (i)



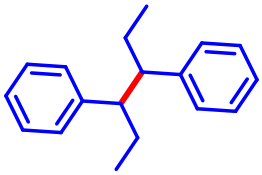
An oven-dried 20 mL pressure vessel was charged with toluene (156 mg, 1.69 mmol), $[PNP\text{-}Cu]_2$ (1 mol %), ^{t}BuOH (25 mg, 2 mol%) and di-*tert*-butyl-peroxide (2.53 mmol). The reaction mixture was degassed with nitrogen and the vessel was sealed with a Teflon cap. The reaction mixture was stirred with moderate speed for 12 h at 120 °C. The reaction mixture was washed with aq. $NaHCO_3$, after cooling at room temperature. The organic layer was extracted with ethyl acetate and dried over Na_2SO_4. The solution evaporated under reduced pressure and the crude mixture was purified by silica gel column chromatography (200-400 MESH) using petroleum ether and ethyl acetate (9:1 v/v) as an eluent to obtain **i** in 90% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (dd, J = 8.6, 6.5 Hz, 4H), 7.25 – 7.16 (m, 6H), 2.94 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.81, 128.48, 128.36, 125.94, 37.98. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{14}H_{14}$ 182.1, found 182.1.
Compounds **i -xvi** were prepared using the general procedure 4.

Butane-2, 3-diyl)dibenzene (ii)



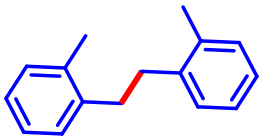
Compound **ii**: [Ethyl benzene (180 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **ii** in 91 % yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.6 Hz, 4H), 7.25 (d, *J* = 7.5 Hz, 6H), 2.84-2.80 (tt, *J* = 7.4, 3.7 Hz, 2H), 1.05-1.04 (d, *J* = 6.5 Hz, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$): δ 132.86, 128.29, 127.62, 126.05, 47.27, 21.06. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{16}H_{18}$ 210.1, found 210.0.

Hexane-3, 4-diyl)dibenzene (iii)



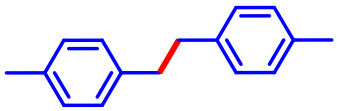
Compound **iii**: [Propyl benzene (180 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **iii** in 92 % yield as a viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.6 Hz, 4H), 7.27 – 7.13 (m, 6H), 2.61 (dt, *J* = 7.6, 2.3 Hz, 2H), 1.47 – 1.25 (m, 4H), 0.55 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 144.57, 128.43, 128.21, 125.99, 54.26, 27.46, 12.23. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{18}H_{22}$ 238.2, found 238.2.

1, 2-Di-o-tolyl-ethane (iv)



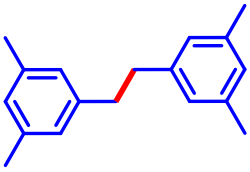
Compound **iv**: [*o*-xylene (180 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **iv** in 85 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21 – 7.17 (m, 8H), 2.89 (s, 4H), 2.36 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.20, 135.94, 130.22, 128.88, 126.14, 126.07, 34.16, 19.36. **GC/MS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{16}H_{18}$ 210.1, found 210.1.

1, 2-Di-p-tolylethane (v)



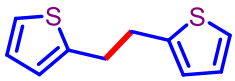
Compound **v**: [*p*-xylene (180 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **v** in 93 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12 (s, 1H), 2.89 (s, 1H), 2.36 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 138.89, 135.32, 129.03, 128.32, 37.67, 21.05. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{16}H_{18}$ 210.1, found 210.1.

1,2-Bis(3,5-dimethylphenyl)ethane (vi)



Compound **vi**: [1,3,5 trimethyl benzene (203 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **vi** in 80 % yield (190.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.89 (s, 6H), 2.84 (s, 4H), 2.34 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.10, 137.86, 125.53, 126.23, 38.13, 21.30. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{18}H_{22}$ 238.1, found 238.2.

1, 2-Di(thiophen-2-yl)ethane (vii)

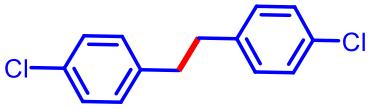


Compound **vii**: [2-methyl thiophene (166 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **vii** in 78 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (dd, J = 5.1, 1.2 Hz, 2H), 6.95 (dd, J = 5.1, 3.4 Hz, 2H), 6.87 – 6.81 (m, 2H), 3.23 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.70, 126.75, 124.65, 123.33, 32.16. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{10}H_{10}S_2$ 194.0, found 194.1.

1, 2-Bis(5-methylthiophen-2-yl)ethane (viii)

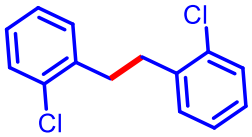
Compound **viii**: [2,4-dimethyl thiophene (190.4 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **viii** in 75 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.62 (d, J = 3.4 Hz, 2H), 6.59 (dq, J = 3.4, 1.1 Hz, 2H), 3.12 (s, 4H), 2.48 (d, J = 1.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.68, 137.66, 124.68, 124.28, 32.34, 15.35. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{12}H_{14}S_2$ 222.0, found 222.0.

1, 4-Bis(2-chlorophenyl)ethane (ix)



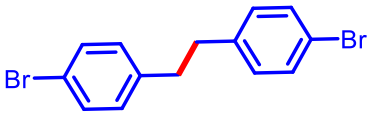
Compound **ix**: [*p*-chlorotoluene (215 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)%)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **ix** in 69 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 – 7.21 (m, 4H), 7.11 – 7.04 (m, 4H), 2.89 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.62, 131.79, 129.85, 37.04. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{14}H_{12}Cl_2$ 250.0, found 250.0.

1, 2-bis(2-chlorophenyl)ethane (x)



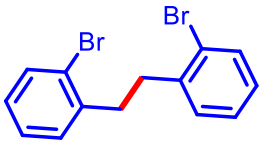
Compound **x**: [*o*-chlorotoluene (215 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **x** in 83% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 – 7.36 (m, 2H), 7.22 – 7.16 (m, 6H), 3.07 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 138.97, 134.03, 130.63, 129.49, 127.57, 126.78, 33.83. **GC/MS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{14}H_{12}Cl_2$ 250.0, found 250.0.

1, 2-Bis(4-bromophenyl)ethane (xi)



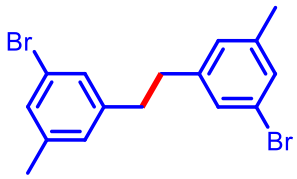
Compound **xi**: [*p*-bromotoluene (290 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **xi** in 80 % yield (187.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 4H), 7.02 (d, J = 8.3 Hz, 4H), 2.87 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.10, 131.43, 130.25, 119.84, 37.01. **GC/MS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{14}H_{12}Br_2$ 377.9, found 338.0.

1, 2-Bis(2-bromophenyl)ethane (xii)



Compound **xii**: [*o*-bromotoluene (290 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **xii** in 79 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.53 (m, 2H), 7.32 – 7.21 (m, 4H), 7.16 – 7.05 (m, 2H), 2.46 (t, J = 2.0 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.62, 137.90, 132.39, 130.89, 127.37, 127.29, 22.97. **GC/MS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{14}H_{12}Br_2$ 377.9, found 338.0.

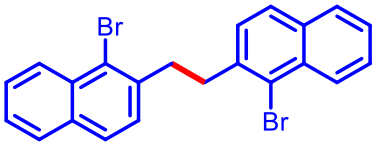
1, 2-Bis(3-bromo-5-methylphenyl)ethane (xiii)



Compound **xiii**: 1-Br-*m*-xylene (314 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **xiii** in 91 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.16 (s, 2H), 6.92 (s, 2H), 2.82 (s, 4H), 2.32 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.38, 140.10, 129.80, 128.47, 128.05, 122.21, 37.37,

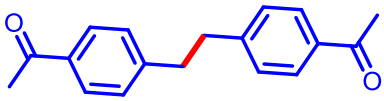
21.12. **GC/MS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{16}H_{16}Br_2$ 365.9, found 366.0.

1,2-Bis(1-bromonaphthalen-2-yl)ethane (xiv)



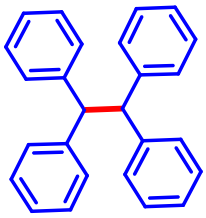
Compound **xiv**: 1-Br-2-methyl naphthalene (375 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), $[PNP\text{-}Cu]_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **xiv** in 80 % yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.63 (ddd, J = 8.3, 6.7, 1.3 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.38 (d, J = 8.3 Hz, 2H), 3.40 (s, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.84, 133.35, 132.63, 128.29, 128.07, 127.67, 127.36, 127.31, 125.97, 123.85, 37.84. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{22}H_{16}Br_2$ 437.9, found 438.0.

1, 1'-(Ethane-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) (xv)



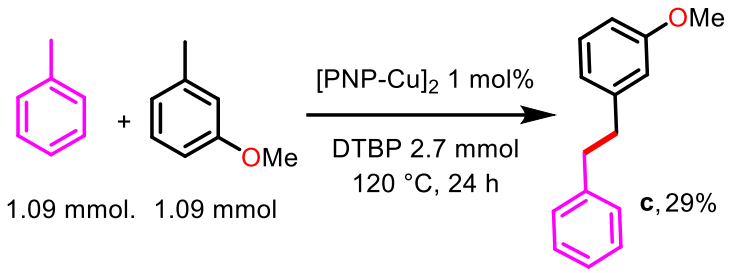
Compound **xv**: [4-methyl acetophenone (227.8 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), $[PNP\text{-}Cu]_2$ (21.2 mg, 1 mol %)] Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **xv** in 80 % yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 3.03 (s, 3H), 2.61 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.84, 146.73, 135.34, 128.72, 128.59, 37.32, 26.57. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{18}H_{18}O_2$ 266.1, found 266.1.

1,1,2,2-Tetraphenylethane (xvi)



Compound **xvi**: [diphenyl methane (285.6 mg, 1.69 mmol), DTBP (371 mg, 2.53 mmol), ^{t}BuOH (2 mol%), [PNP-Cu]$_2$ (21.2 mg, 1 mol %)]. Crude mixture purified by silica gel (200-400 MESH) column chromatography, using petroleum ether:ethyl acetate (9:1 v/v) as an eluent to afford **xvi** in 90 % yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 8H), 7.10 (dd, J = 8.4, 6.8 Hz, 8H), 7.05 – 6.96 (m, 4H), 4.77 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.47, 128.52, 128.14, 125.85, 56.33. **GC/MS** (ESI) *m/z* : $[M]^+$ Calcd for $C_{26}H_{22}$ 334.1, found 334.1.

5. Synthesis of 1-methoxy-3-phenethylbenzene (calmodulin inhibitor)[3] (c)



In an oven dried 10 mL glass vessel, toluene (100 mg,1.09 mmol), 3-methoxy toluene (132 mg,1.09 mmol), DTBP (317 mg, 2.17 mmol) and [PNP-Cu]$_2$ (1 mol%) charged and sealed with Teflon cap. Reaction mixture stirred at 120 °C for 24 h. Reaction mixture was filtered over celite and washed with ethyl acetate, and filtrate evaporated under reduced pressure. Crude mixture purified over column chromatography over silica gel (200-400 MESH), using petroleum ether and ethyl acetate (9:1 v/v) as a eluent to afford **c** in 29 % yield, as an oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, J = 6.9 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.4 Hz, 2H), 7.24 – 7.16 (m, 4H), 7.11 (d, J = 4.8 Hz, 1H), 6.85 – 6.71 (m, 2H), 3.78 (s, 3H), 2.91 (q, J = 2.1 Hz, 4H). **HRMS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{22}$ 334.1, found 334.1. **GC/MS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{22}$ 334.1, found 334.1.

6. ^{1}H and ^{13}C Spectra of Homocoupled Products

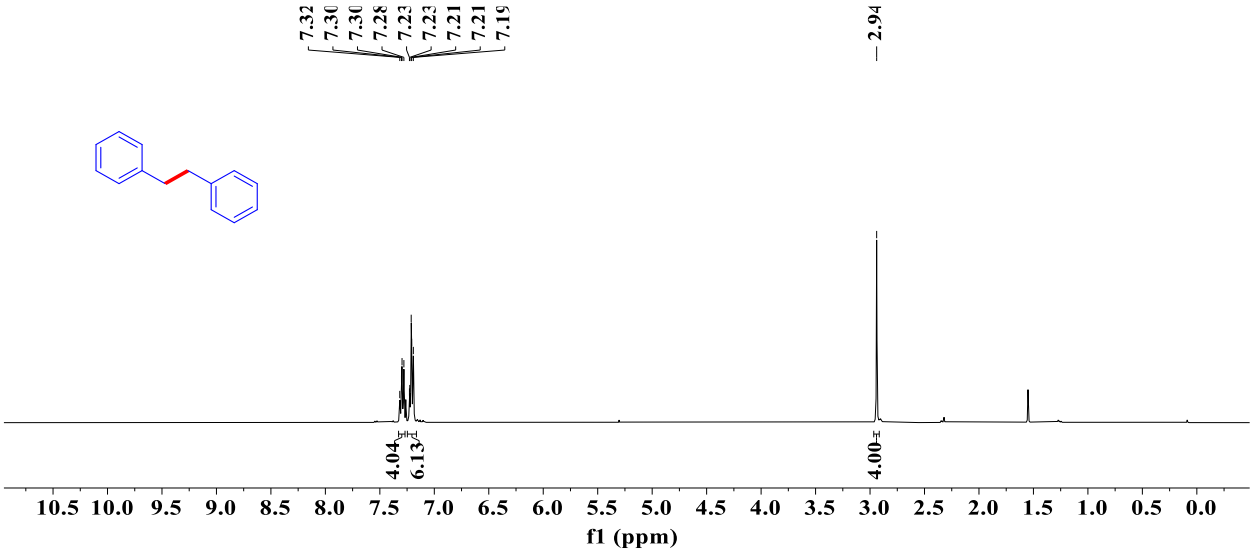


Figure S1. ^{1}H NMR spectrum of 1, 2-diphenylethane (**i**) (400 MHz, $CDCl_3$)

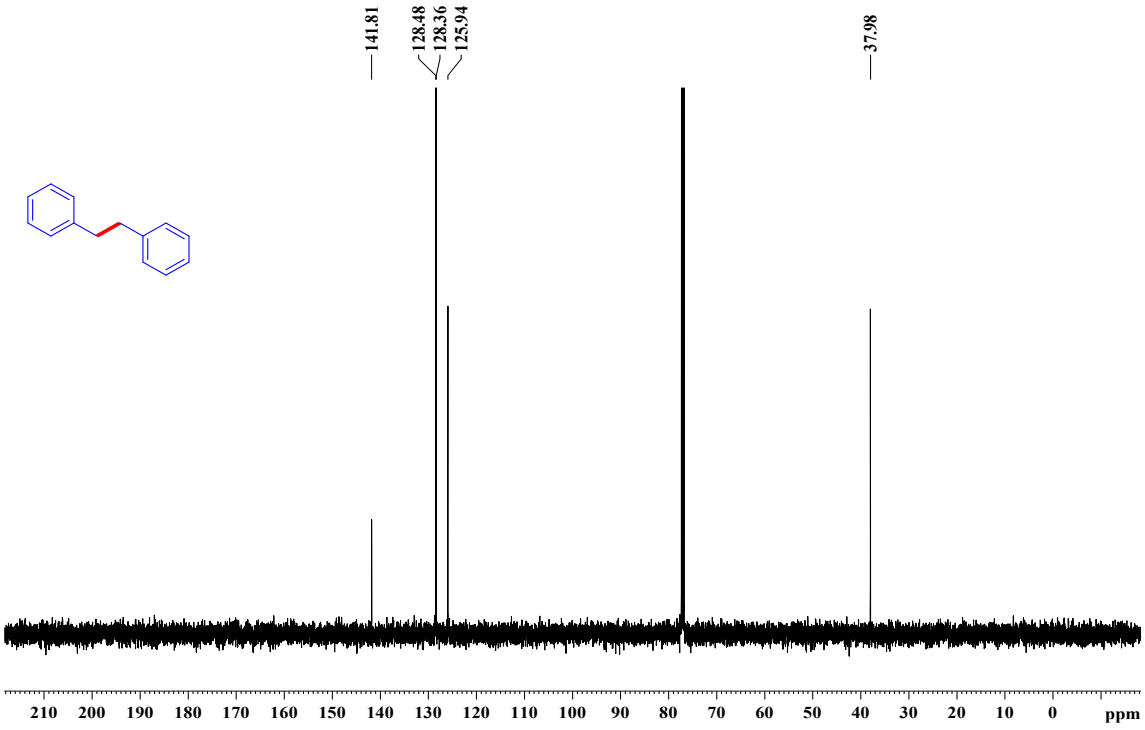


Figure S2. ^{13}C NMR spectrum of 1, 2-diphenylethane (**i**) (101 MHz, $CDCl_3$)

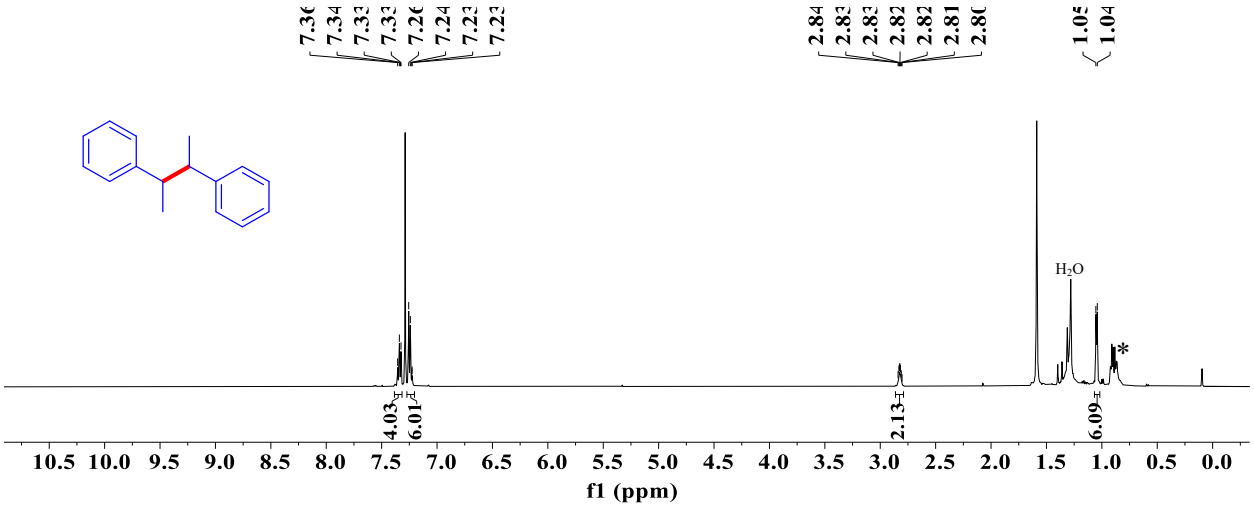


Figure S3. ^{1}H NMR spectrum of 1, 2-diphenylethane (**ii**) (500 MHz, $CDCl_3$)

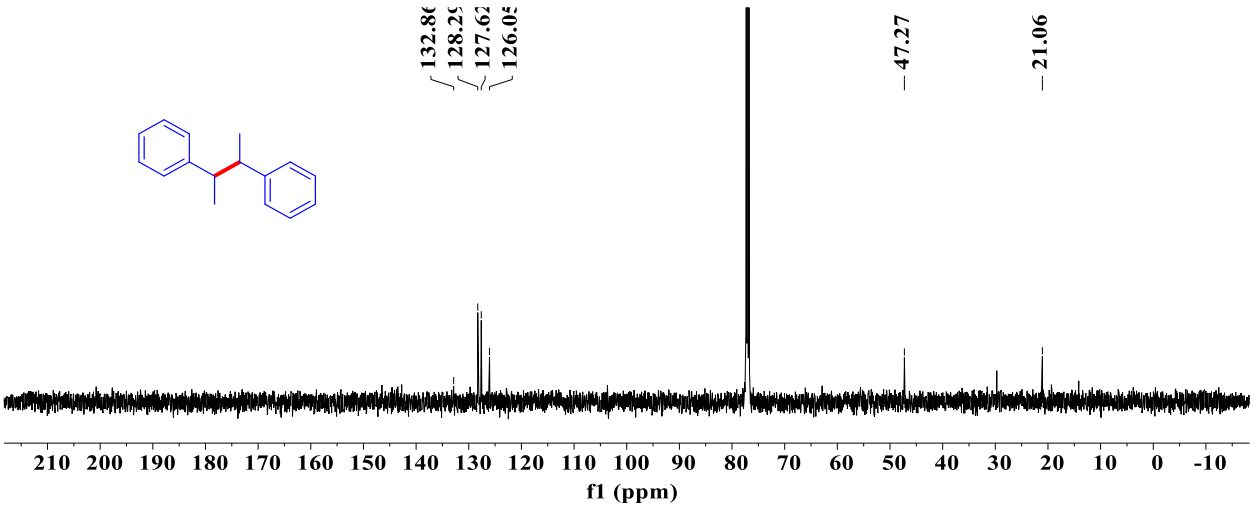


Figure S4. ^{13}C NMR spectrum of 1, 2-diphenylethane (**ii**) (126 MHz, $CDCl_3$)

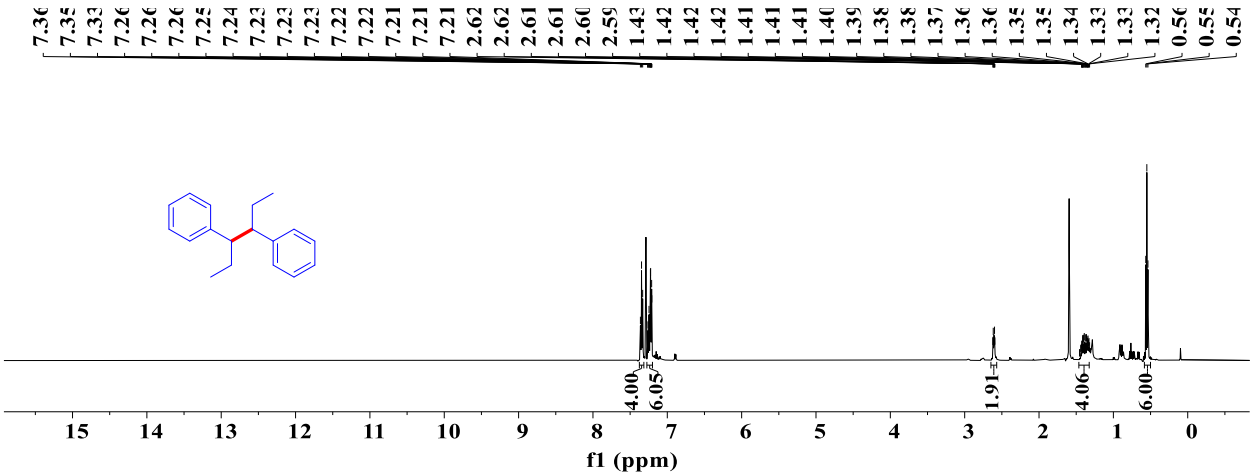


Figure S5. ^{1}H NMR spectrum of hexane-3, 4-diyl)dibenzene (**iii**) (500 MHz, $CDCl_3$)

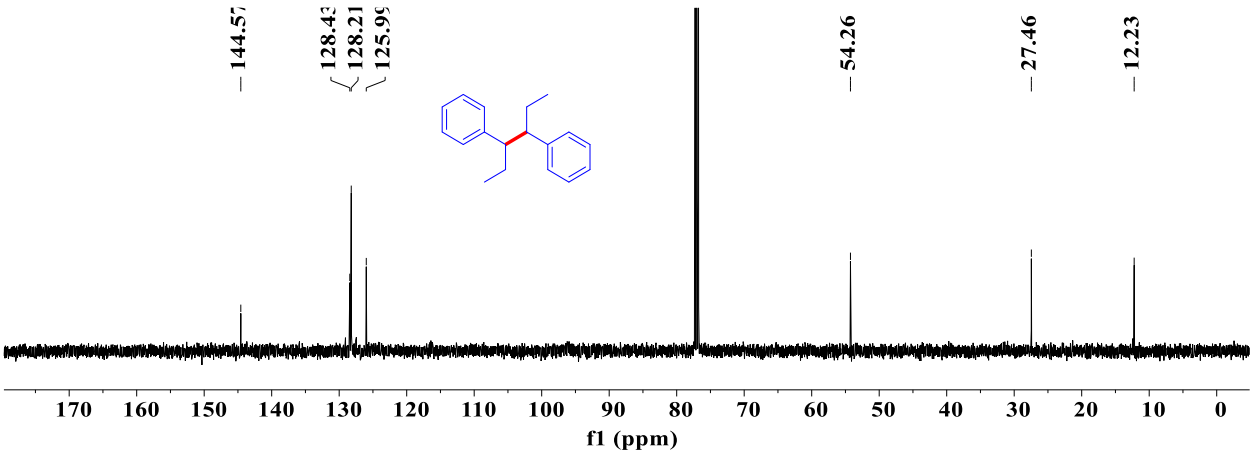


Figure S6. ^{13}C NMR spectrum of hexane-3, 4-diyl)dibenzene (**iii**) (126 MHz, $CDCl_3$)

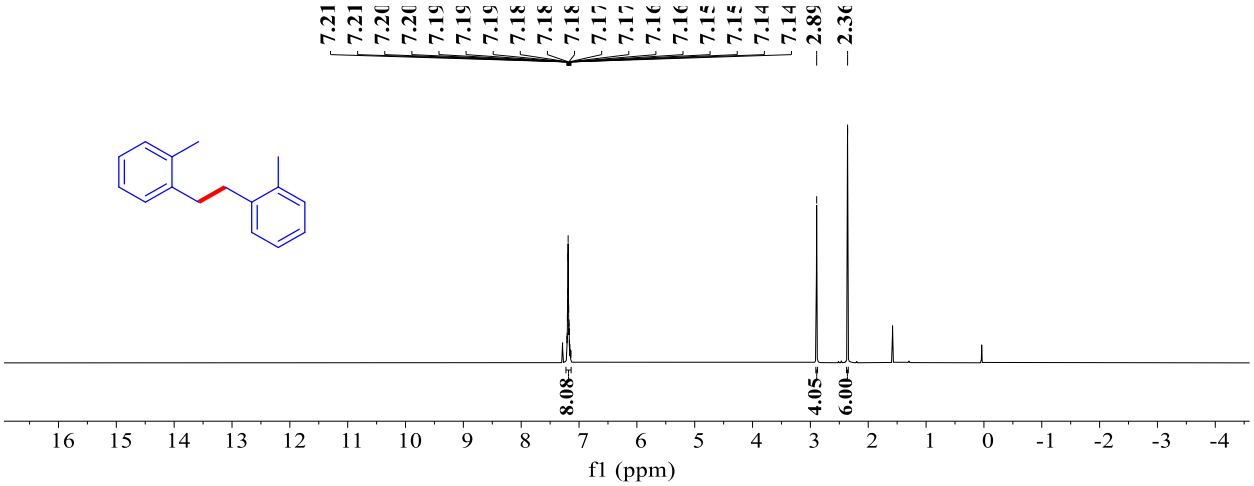


Figure S7. ^{1}H NMR spectrum of 1, 2-di-o-tolylethane (**iv**) (400 MHz, $CDCl_3$)

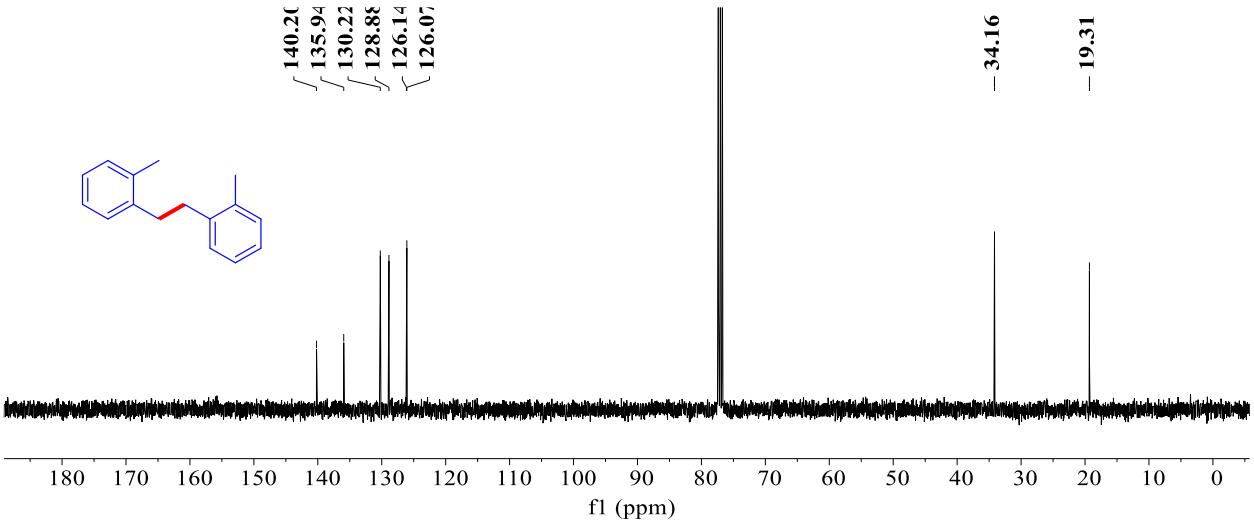


Figure S8. ^{13}C NMR spectrum of 1, 2-di-o-tolylethane (**iv**) (101 MHz, $CDCl_3$)

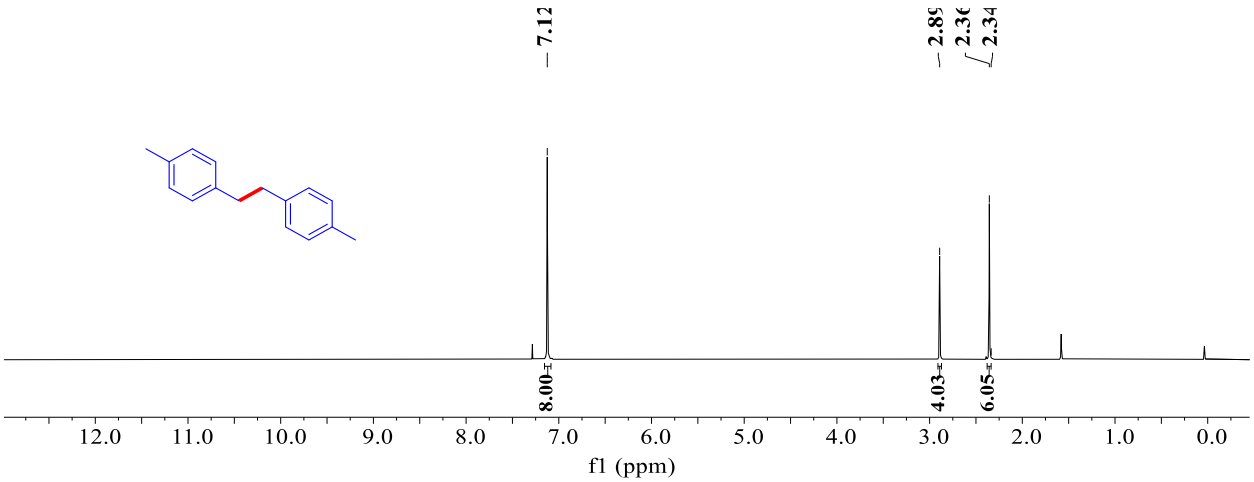


Figure S9. ^{1}H NMR spectrum of 1, 2-di-p-tolylethane (**v**) (400 MHz, $CDCl_3$)

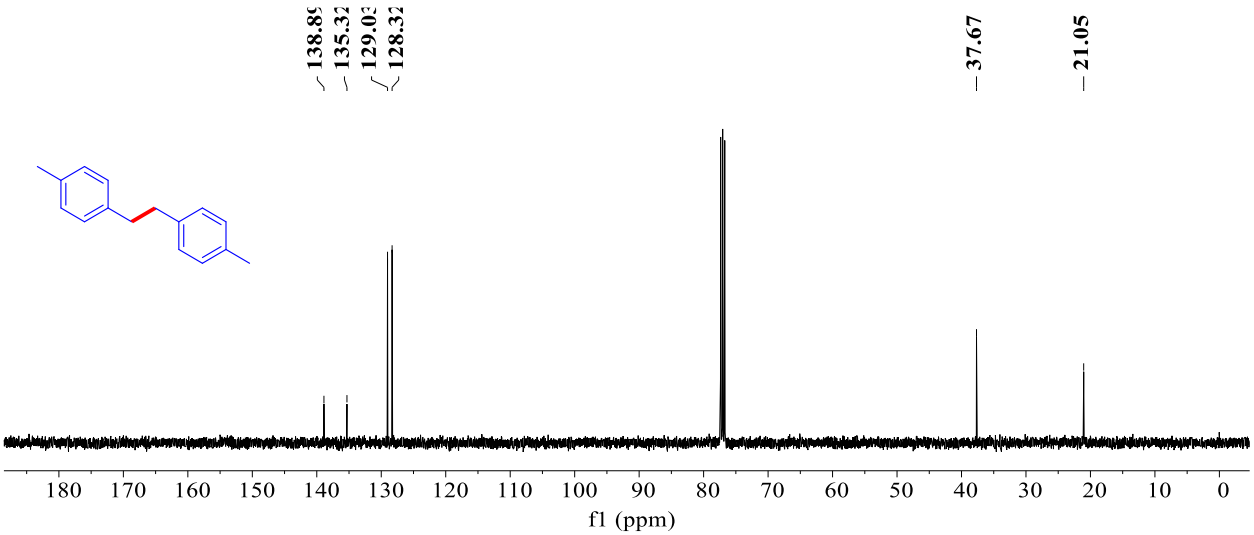


Figure S10. ^{13}C NMR spectrum of 1, 2-di-p-tolylethane (**v**) (101 MHz, $CDCl_3$)

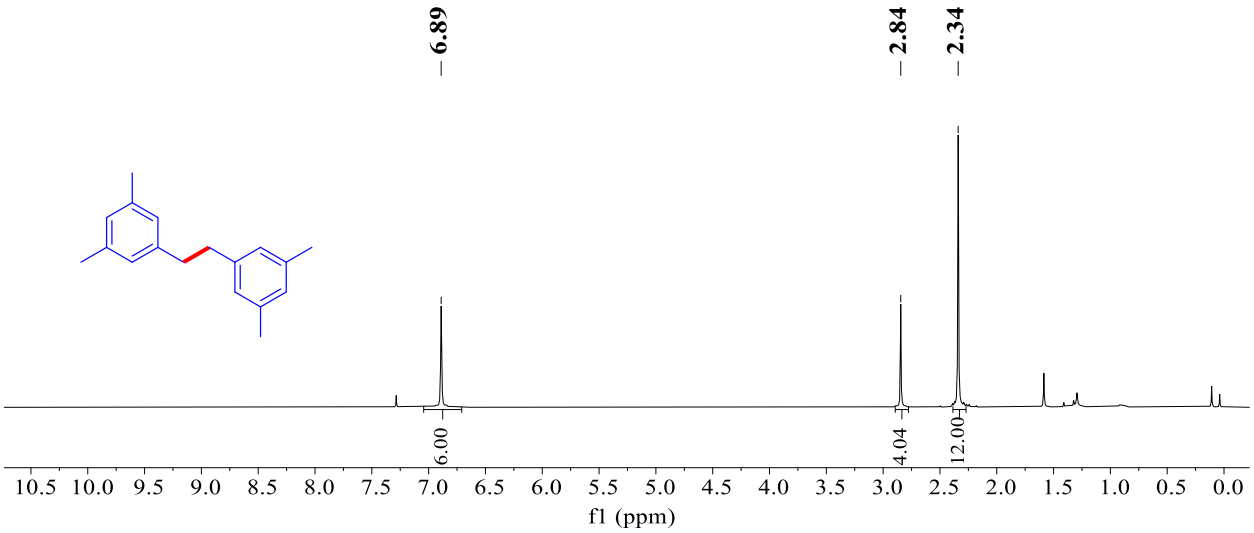


Figure S11. ^{13}C NMR spectrum of 1, 2-di-p-tolylethane (**vi**) (400 MHz, $CDCl_3$)

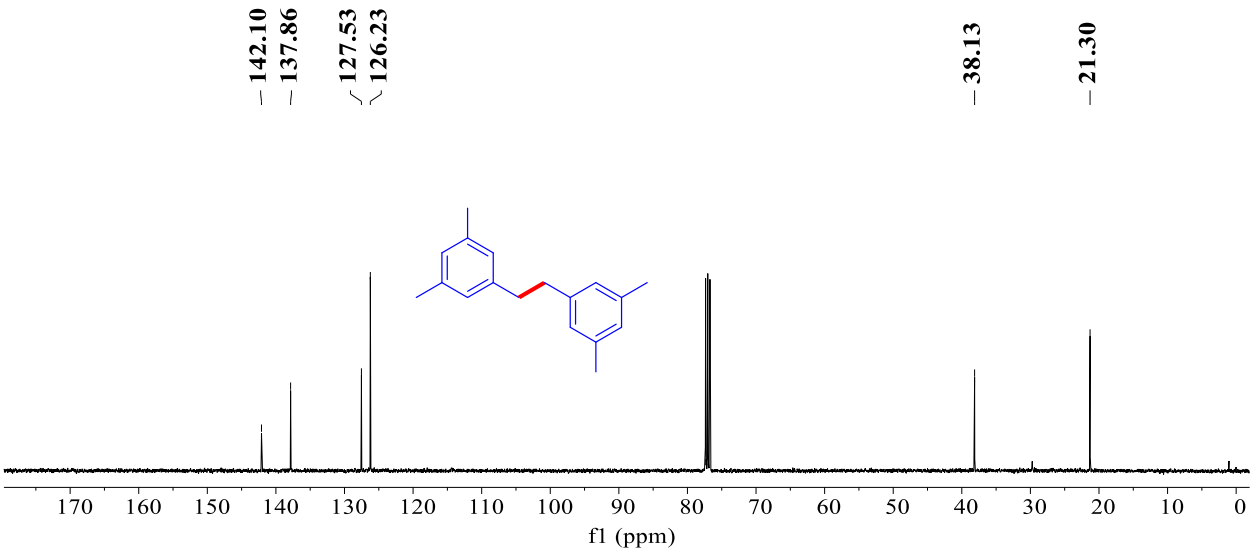


Figure S12. ^{13}C NMR spectrum of 1, 2-di-p-tolylethane (**vi**) (126 MHz, $CDCl_3$)

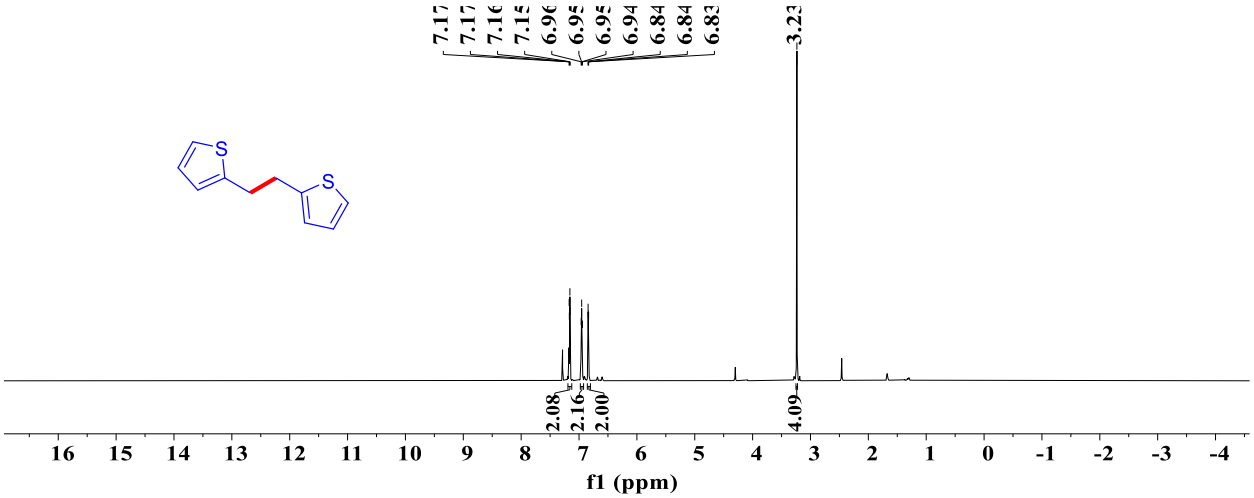


Figure S13. ^{1}H NMR spectrum of 1, 2-di(thiophen-2-yl)ethane (**vii**) (400 MHz, $CDCl_3$)

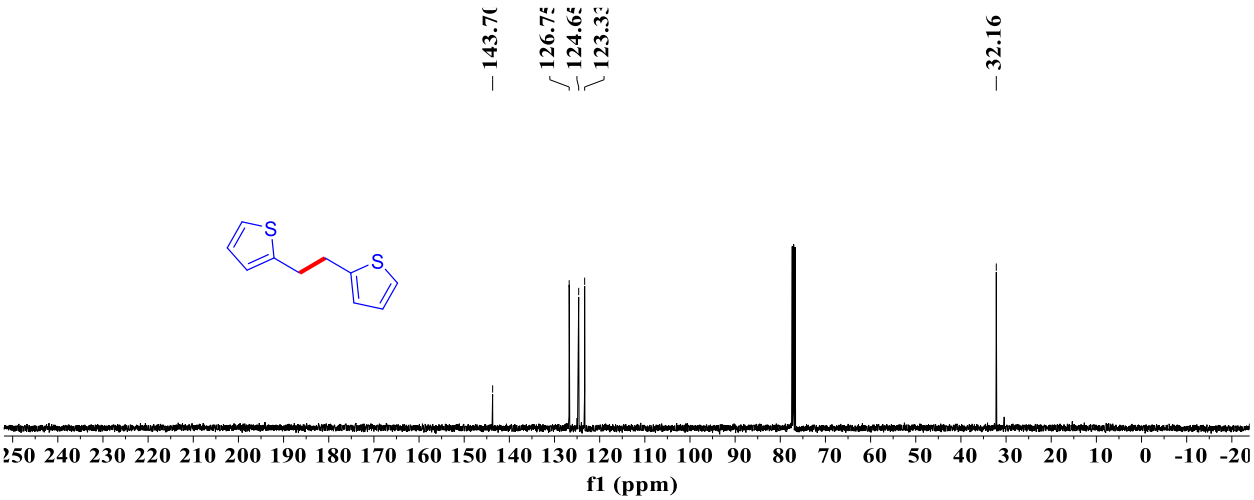


Figure S14. ^{13}C NMR spectrum of 1, 2-di(thiophen-2-yl)ethane (**vii**) (101 MHz, $CDCl_3$)

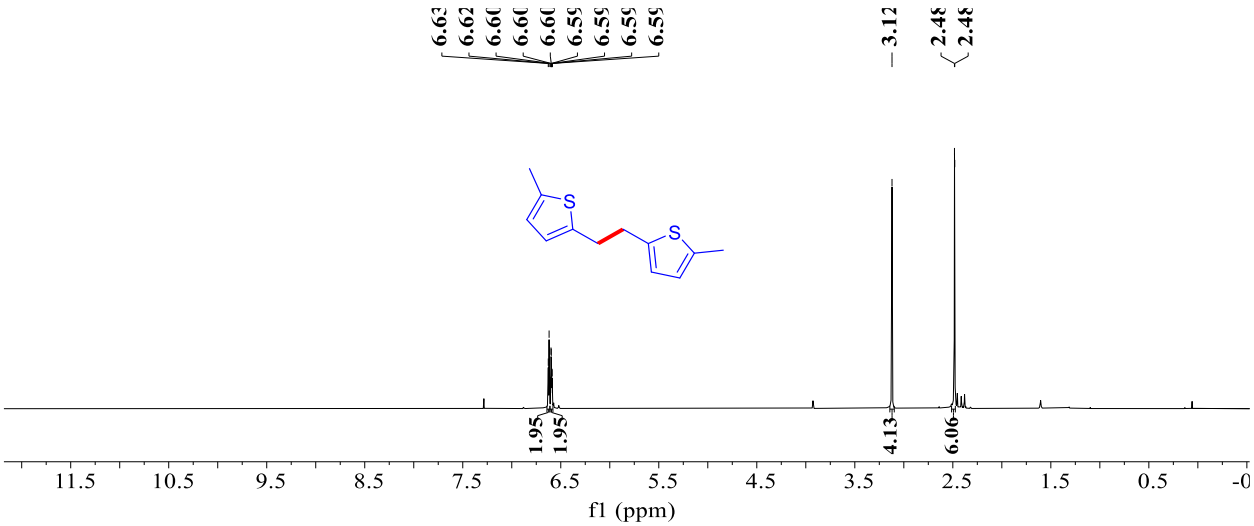


Figure S15. ^{1}H NMR spectrum of 1, 2-bis(5-methylthiophen-2-yl)ethane (**viii**) (400 MHz, $CDCl_3$)

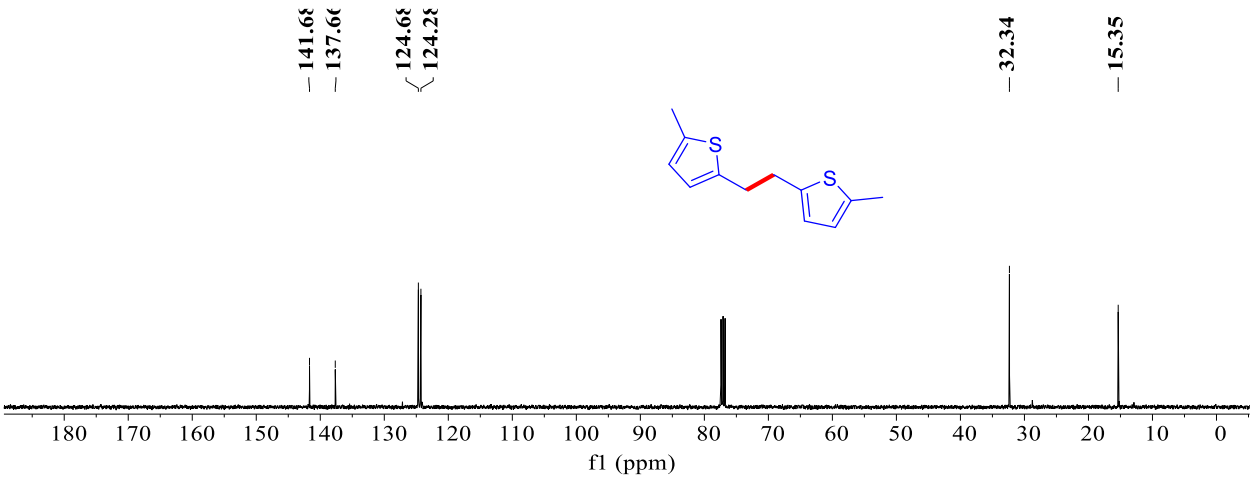


Figure S16. ^{13}C NMR spectrum of 1, 2-bis(5-methylthiophen-2-yl)ethane (**viii**) (101 MHz, $CDCl_3$)

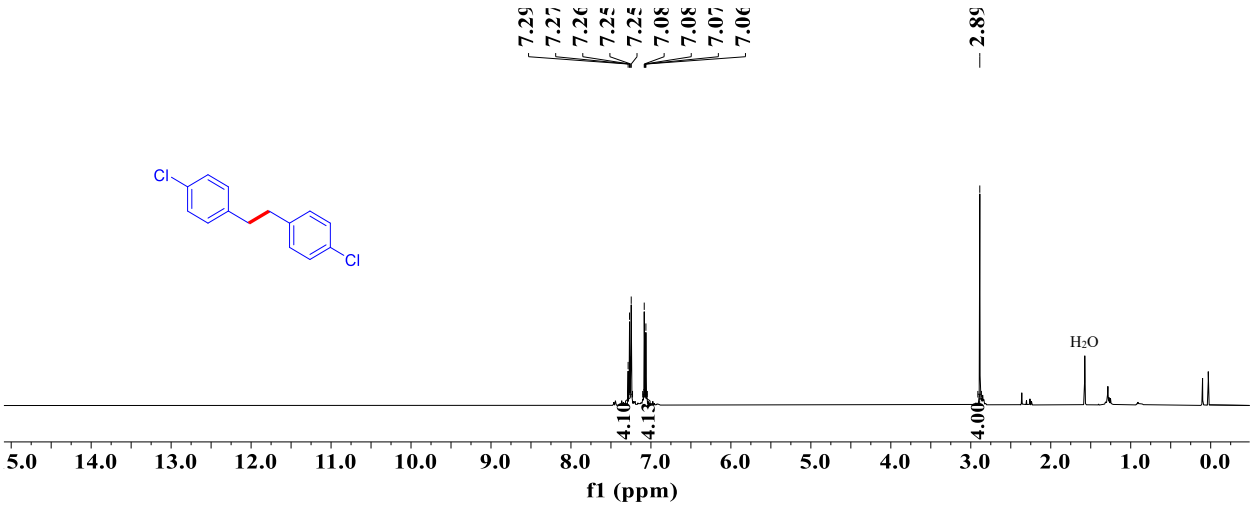


Figure S17. ^{1}H NMR spectrum of 1, 4-bis(2-chlorophenyl)ethane (**ix**) (400 MHz, $CDCl_3$)

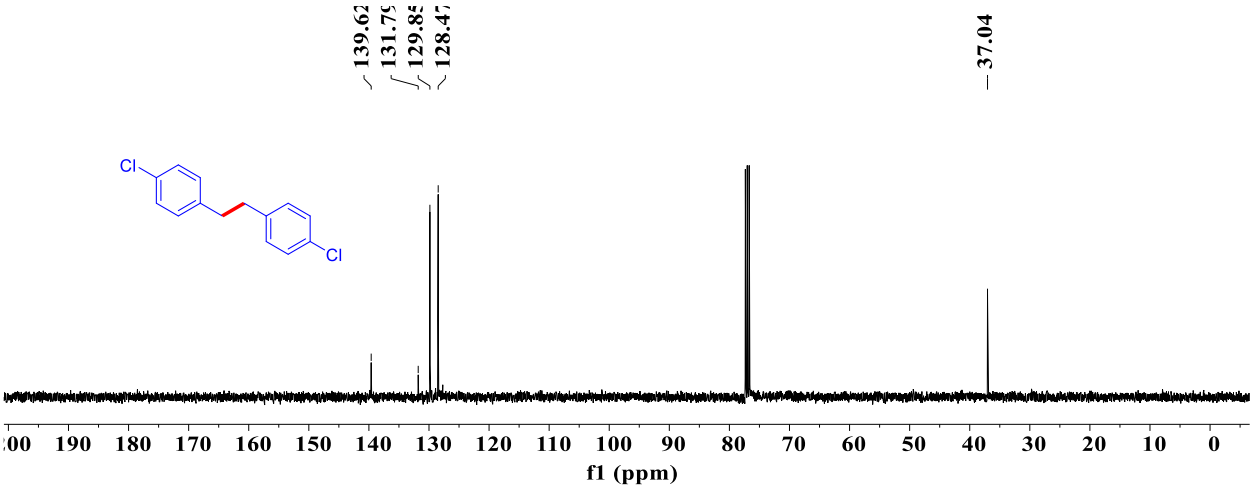


Figure S18. ^{13}C NMR spectrum of 1, 4-bis(2-chlorophenyl)ethane (**ix**) (101 MHz, $CDCl_3$)

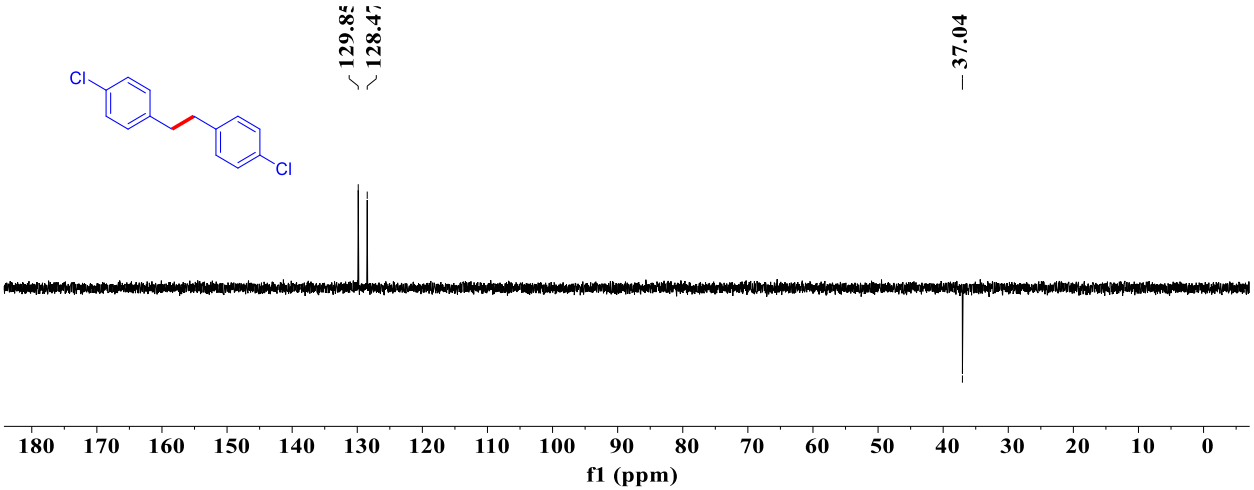


Figure S19. ^{13}C DEPT 135 NMR spectrum of 1, 4-bis(2-chlorophenyl)ethane (**ix**) (101 MHz, $CDCl_3$)

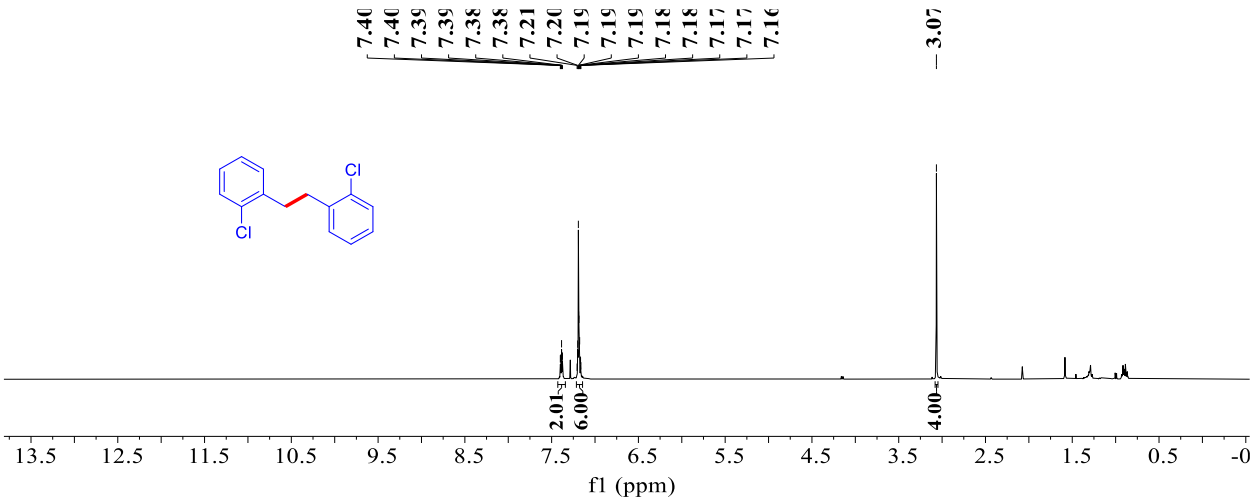


Figure S20. ^{1}H NMR spectrum of 1, 2-bis(2-chlorophenyl)ethane (**x**) (400 MHz, $CDCl_3$)

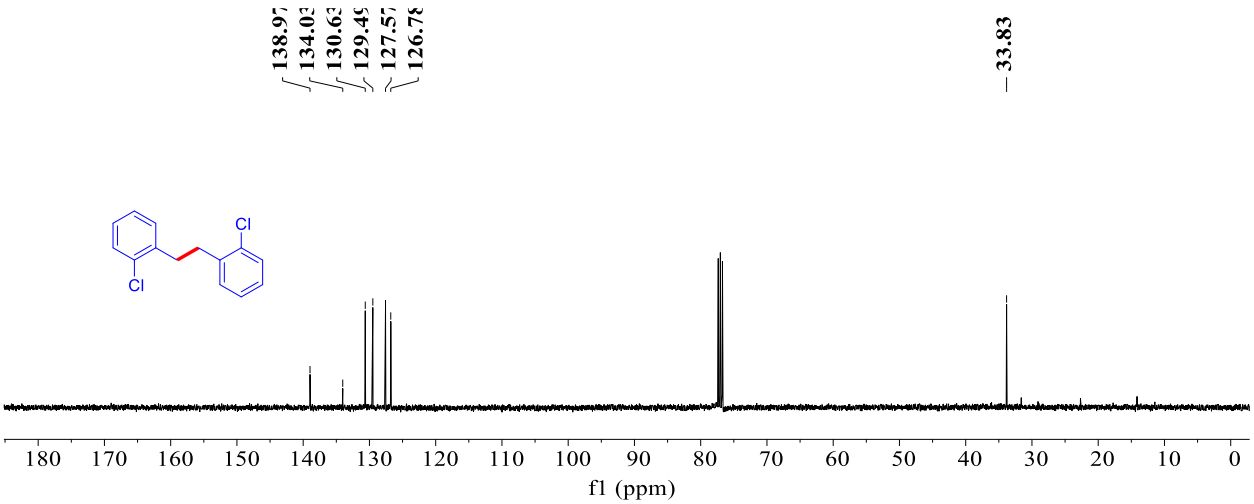


Figure S21. ^{13}C NMR spectrum of 1, 2-bis(2-chlorophenyl)ethane (**x**) (101 MHz, $CDCl_3$)

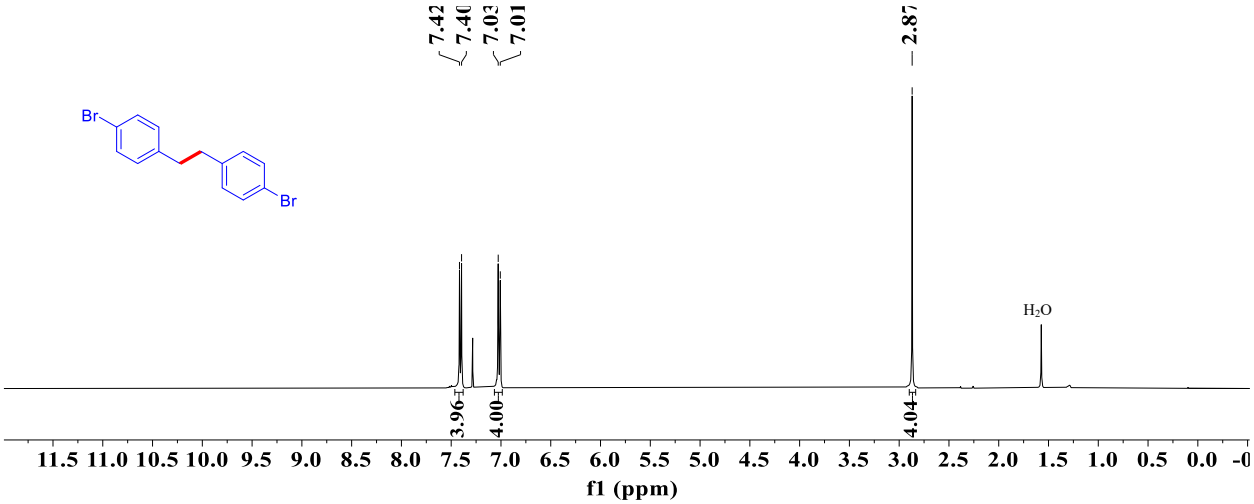


Figure S22. ^{1}H NMR spectrum of 1, 2-bis(4-bromophenyl)ethane (**xi**) (400 MHz, $CDCl_3$)

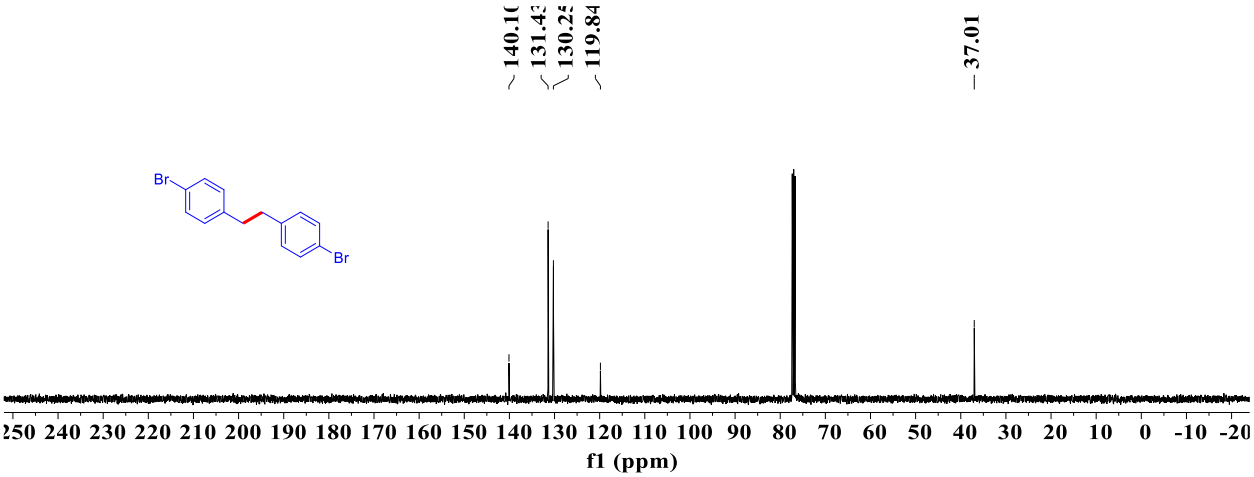


Figure S23. ^{13}C NMR spectrum of 1, 2-bis(4-bromophenyl)ethane (**xi**) (101 MHz, $CDCl_3$)

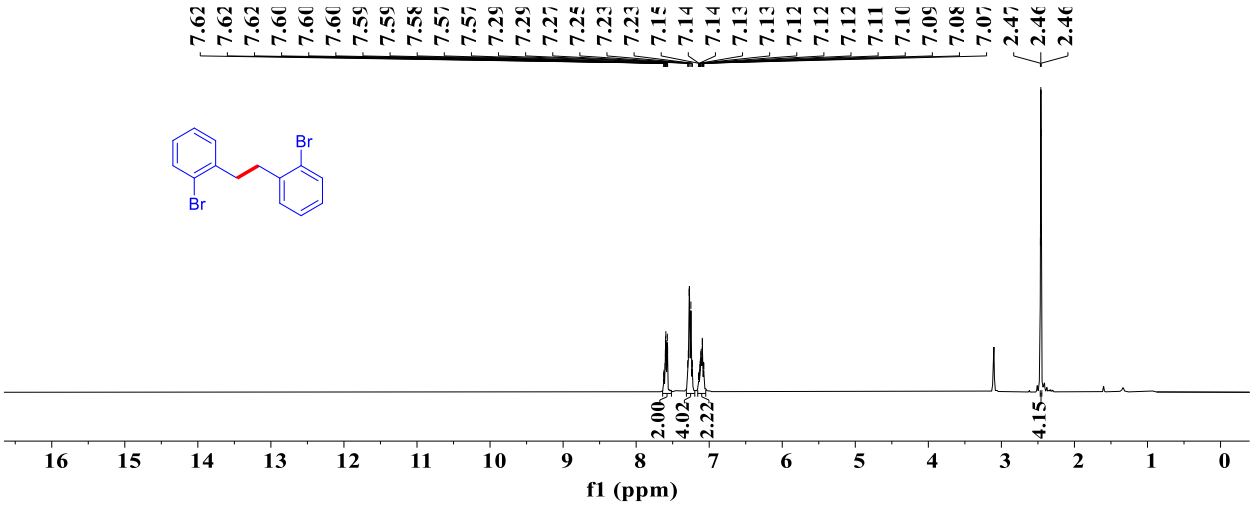


Figure S24. ^{1}H NMR spectrum of 1, 2-bis(2-bromophenyl)ethane (**xii**) (400 MHz, $CDCl_3$)

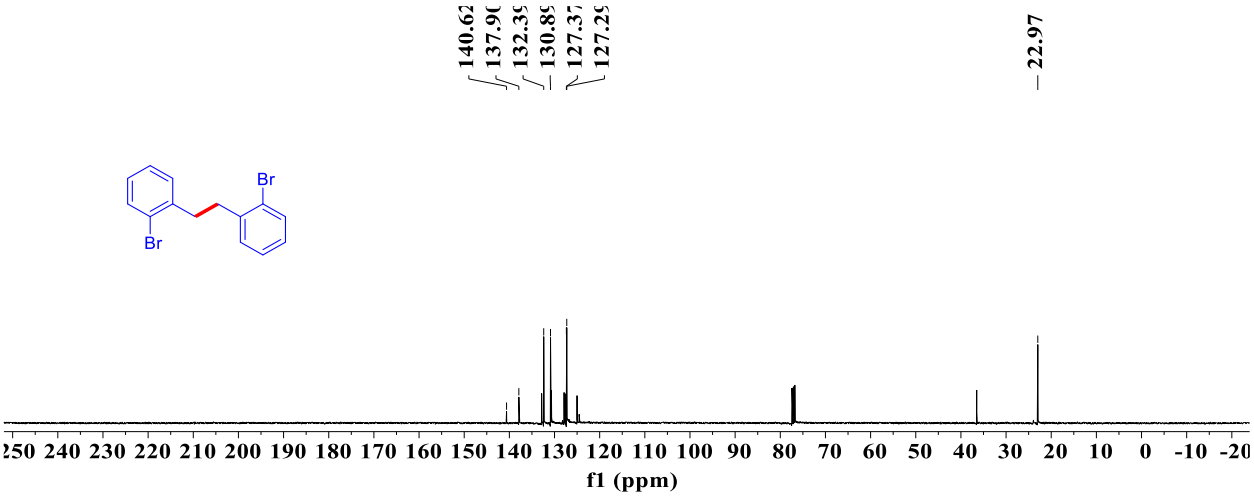


Figure S25. ^{13}C NMR spectrum of 1, 2-bis(2-bromophenyl)ethane (**xii**) (101 MHz, $CDCl_3$)

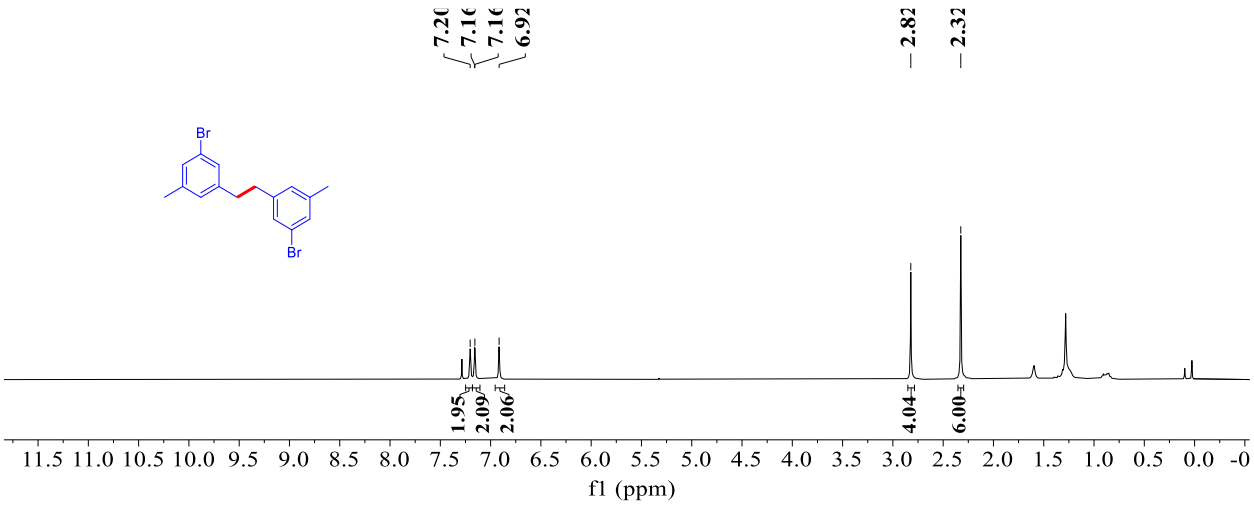


Figure S26. ^{1}H NMR spectrum of 1, 2-bis(3-bromo-5-methylphenyl)ethane (**xiii**) (400 MHz, $CDCl_3$)

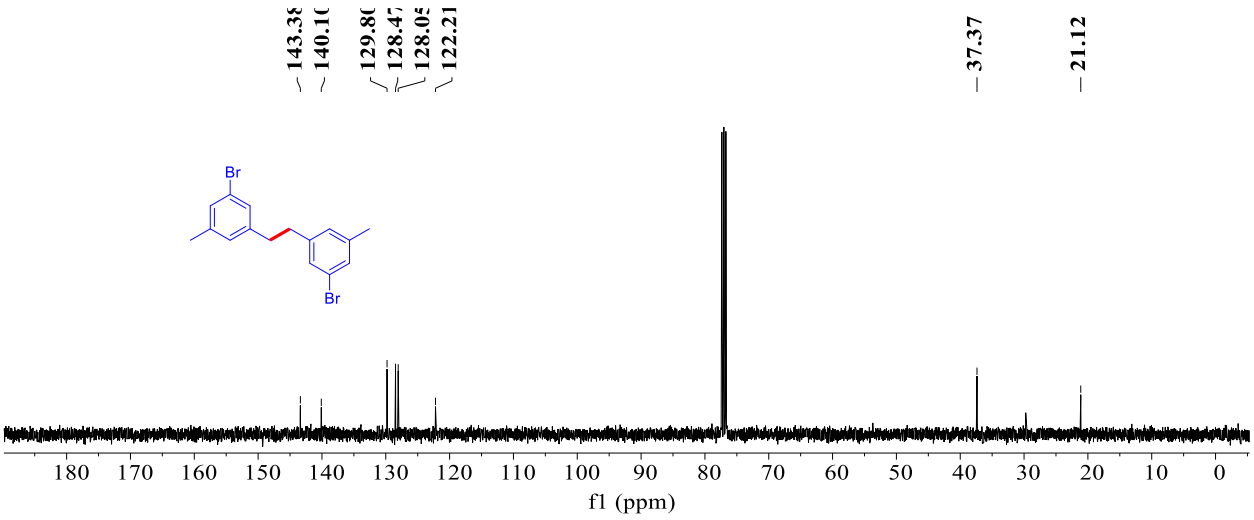


Figure S27. ^{13}C NMR spectrum of 1, 2-bis(3-bromo-5-methylphenyl)ethane (**xiii**) (101 MHz, $CDCl_3$)

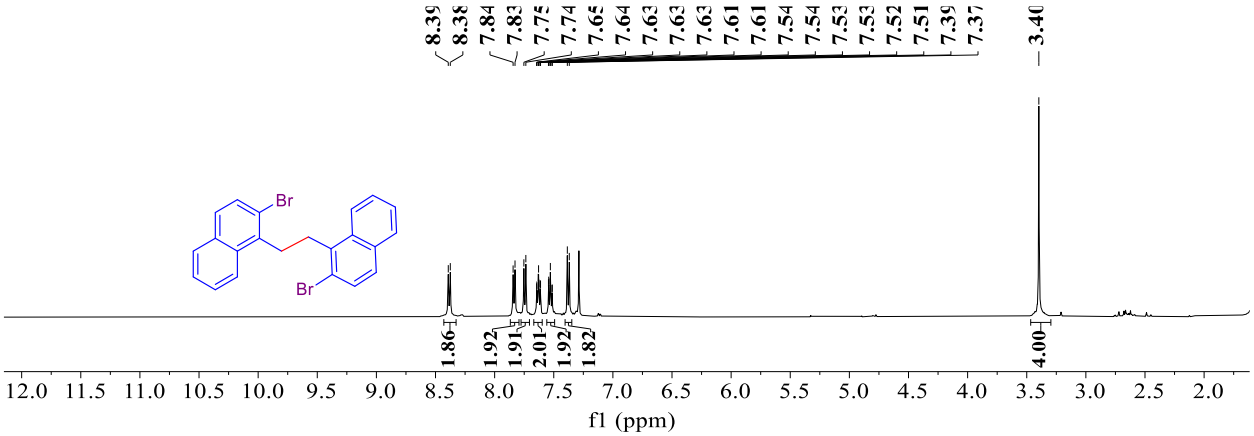


Figure S28. ^{1}H NMR spectrum of 1,2-bis(1-bromonaphthalen-2-yl)ethane (**xiv**) (500 MHz, $CDCl_3$)

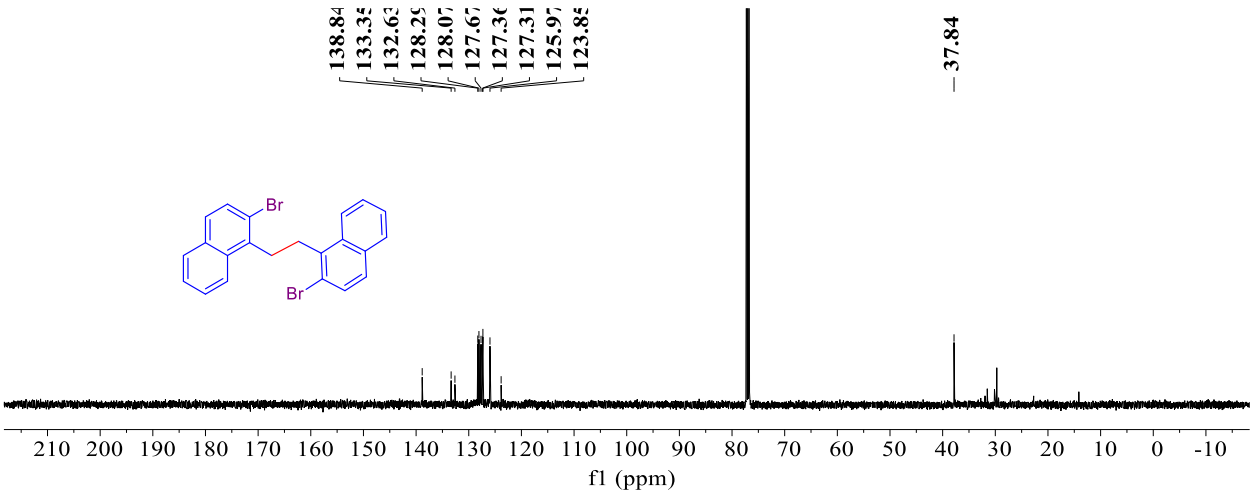


Figure S29. ^{13}C NMR spectrum of 1, 2-bis(1-bromonaphthalen-2-yl)ethane (**xiv**) (126 MHz, $CDCl_3$)

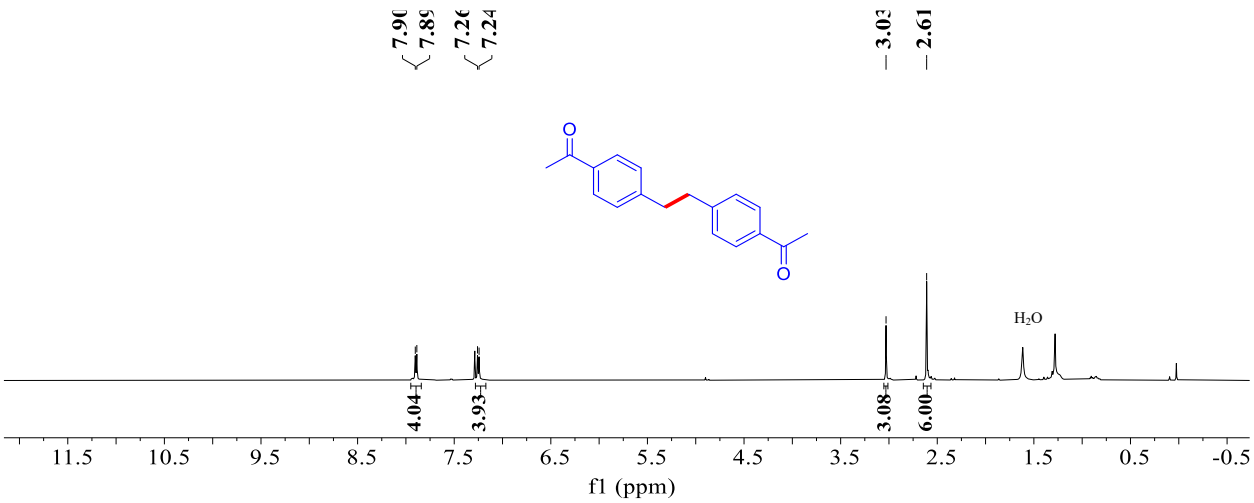


Figure S30. ^{1}H NMR spectrum of 1, 1'-(ethane-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) (**xv**) (500 MHz, $CDCl_3$)

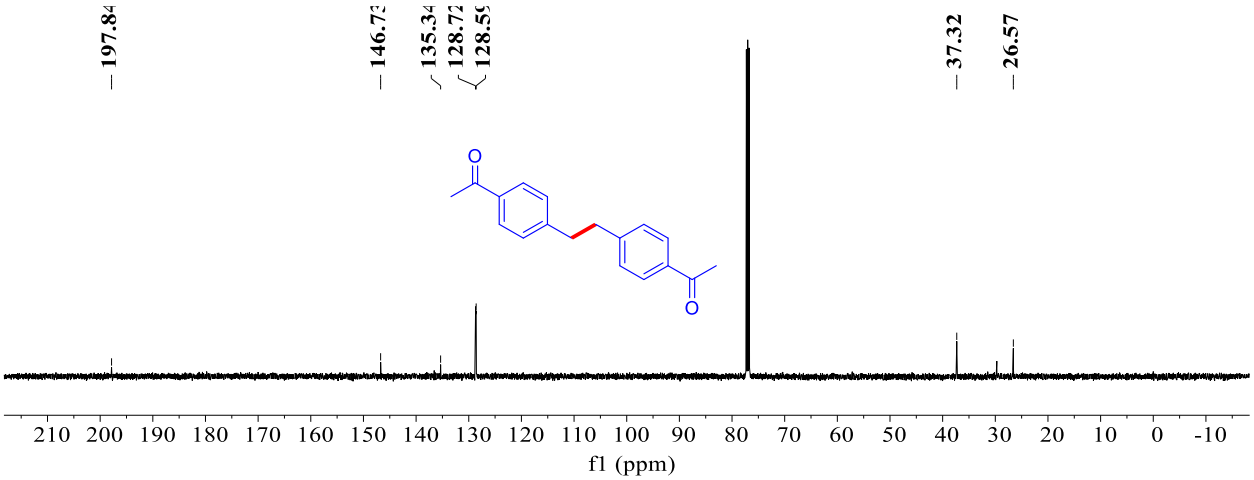


Figure S31. ^{13}C NMR spectrum of 1, 1'-(ethane-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) (**xv**) (126 MHz, $CDCl_3$)

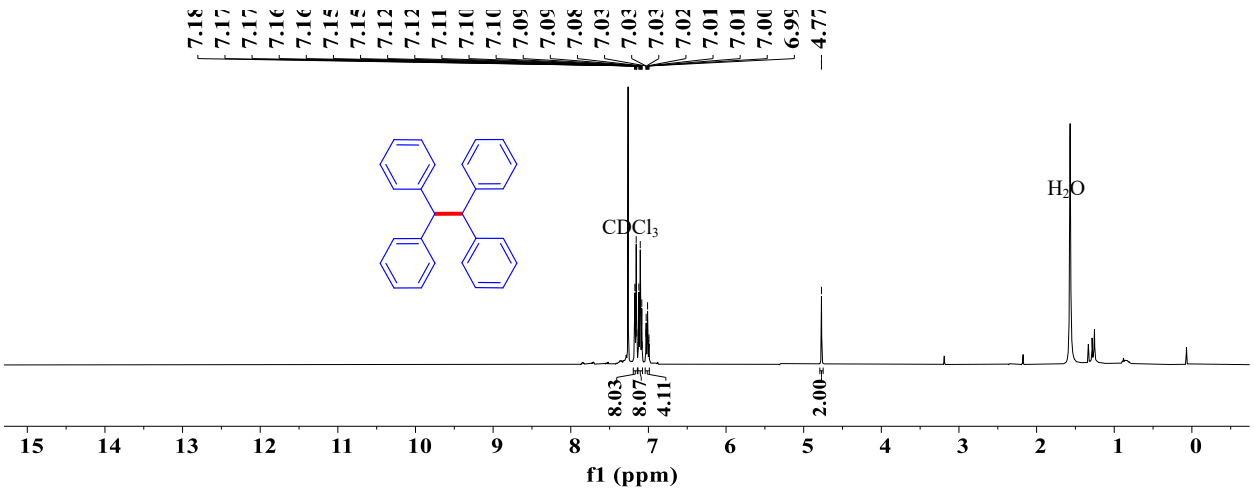


Figure S32. ^{1}H NMR spectrum of 1,1,2,2-tetraphenylethane (**xvi**) (400 MHz, $CDCl_3$)

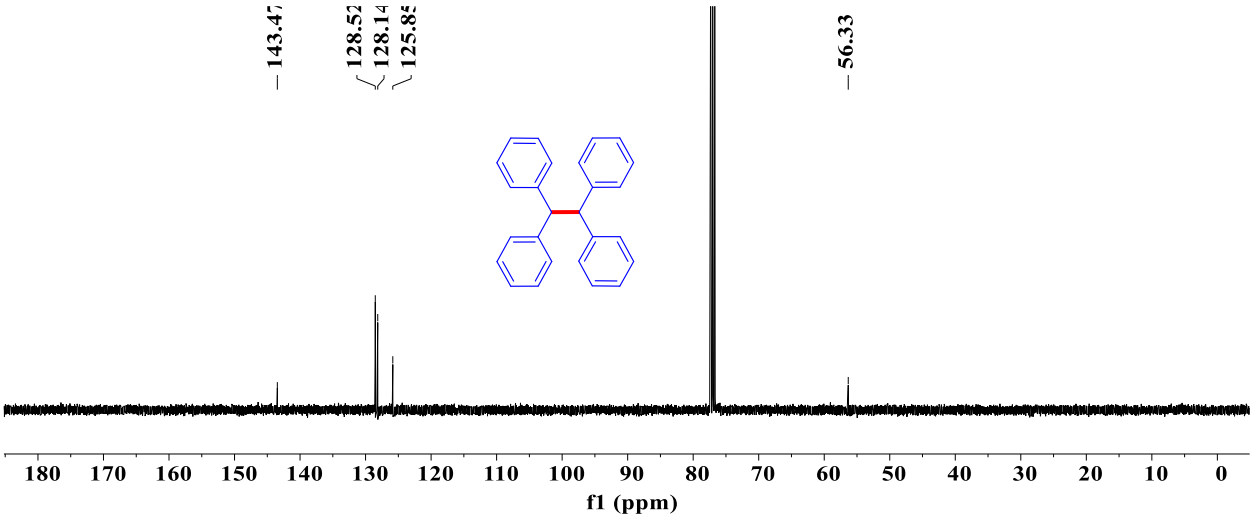
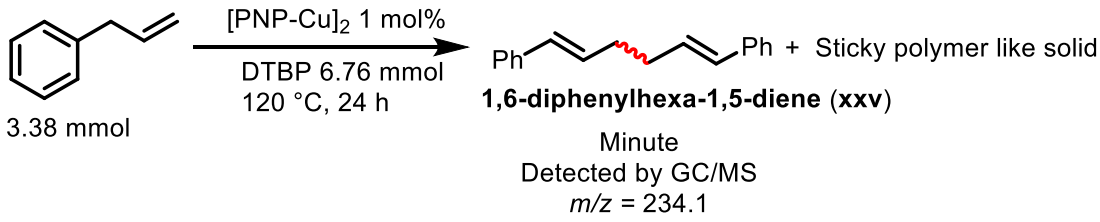


Figure S33. ^{13}C NMR spectrum of 1, 1, 2, 2-tetraphenylethane (**xvi**) (101 MHz, $CDCl_3$)

7. [PNP-Cu]$_2$ catalysed homocoupling reaction of allyl benzene

The reaction between allyl benzene and DTBP in a 1:2 molar ratio, conducted in the presence of [PNP-Cu]2 (1 mol%) at 120°C for 24 hours, yielded traces of 1,6-diphenylhexa-1,5-diene (**xxv**), accompanied by an insoluble grey-coloured sticky solid with apparent polymeric characteristics. Analysis of the solid via GC/MS revealed a molecular ion peak $[M]^+$ at 234.1, confirming the formation of 1,6-diphenylhexa-1,5-diene (**xxv**).



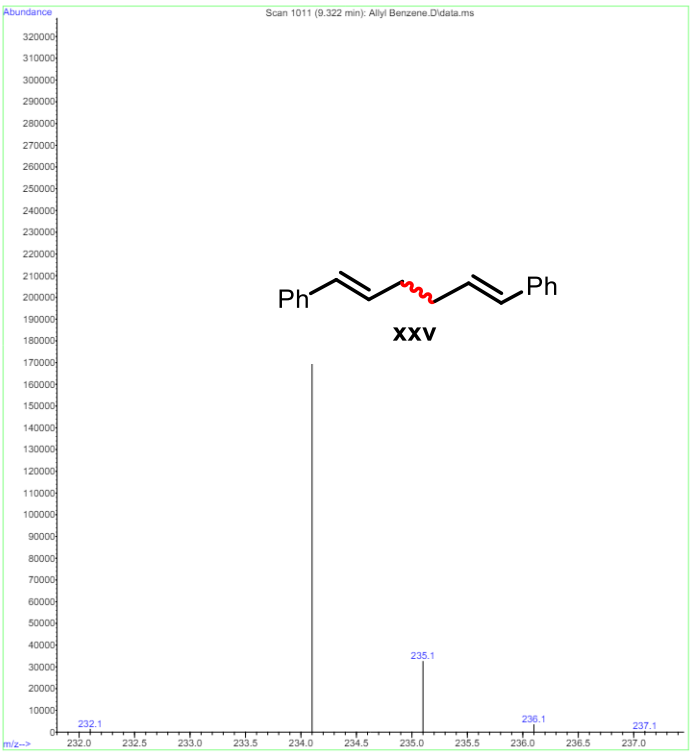


Figure 34. GC/MS spectrum of 1,6-diphenylhexa-1,5-diene (**xxv**)

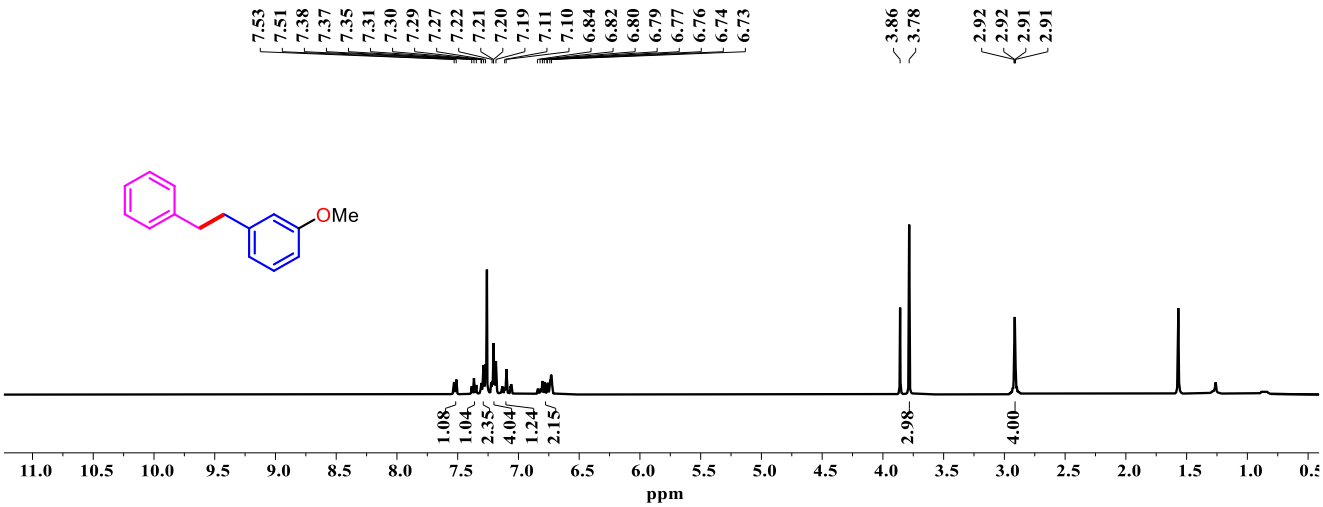


Figure S35. ^{1}H NMR spectrum of 1-methoxy-3-phenethylbenzene **c** (400 MHz, $CDCl_3$)

Cpd. 1: C15 H16 O

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C15 H16 O	235.1115	235.111483409919	3.19384611944429	15.0567810009261	31.32

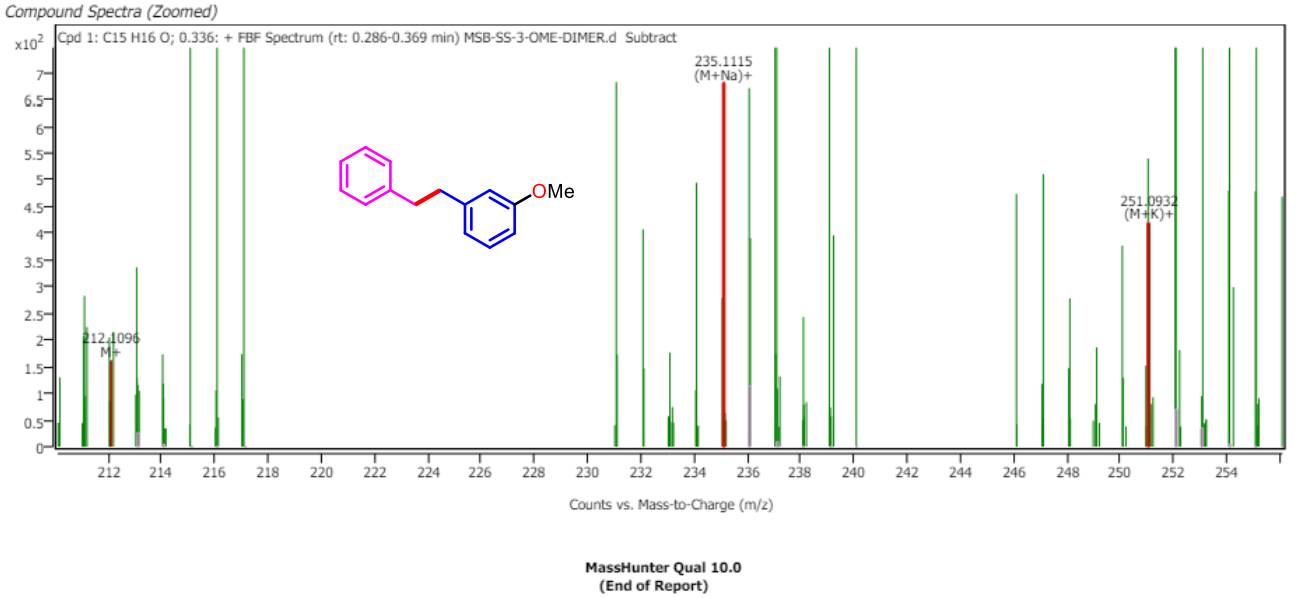


Figure S36. HRMS of 1-methoxy-3-phenethylbenzene **c**

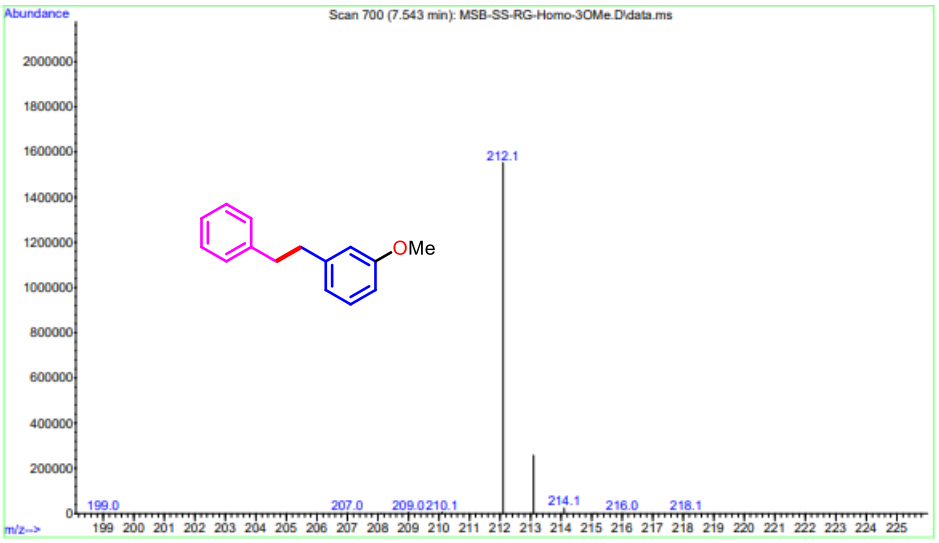


Figure S37. GC/MS spectrum of 1-methoxy-3-phenethylbenzene **c**

8. Free Energy Profile Diagram and Computational Details

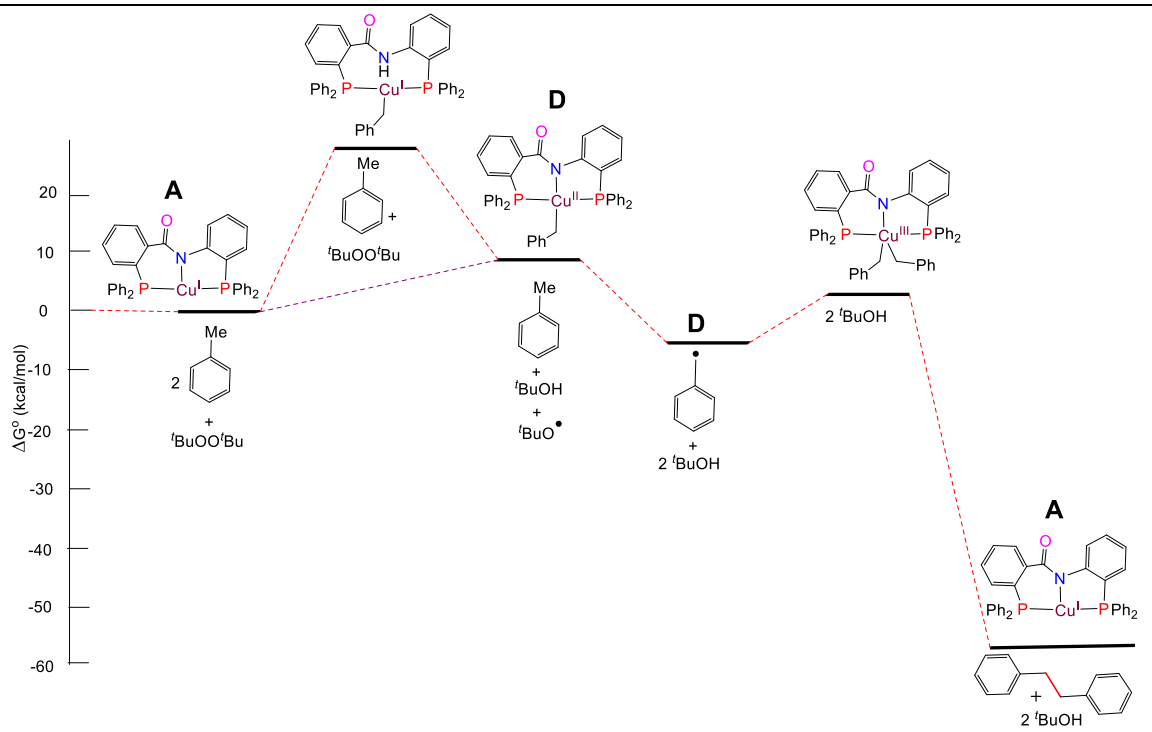


Figure S38. Standard state free energy profile for the homocoupling of toluene mediated by [Cu(I)PNP], in the absence of exogenous ^{t}BuOH, as calculated from DFT (Level of theory: ωB97xD/LANL2DZ(Cu)/6-311G**(C, H, P, N, O)/SMD(Toluene).

Computational details: Quantum chemical calculations were performed using density functional theory[4] (DFT) with the Gaussian16 software package.[5] The intermediates' lowest energy structures were obtained by geometry optimisation using the unrestricted formalism of a long-range corrected hybrid functional, ωB97xD.[6] An effective core potential with relativistic corrections, viz. LANL2DZ[7] was employed for Cu, and a triple zeta basis set with polarization (6-311G**) was employed for all the other atoms (including hydrogens).[8] Gibbs free energies[9] were obtained by performing harmonic analyses on the optimised structures. The polarisable continuum solvation model, SMD (Solvation Model Density).[10] was employed to calculate the solvation free energy of optimised intermediates. The Gibbs free energy of a reaction for any given set of reactants and products was calculated using equation 1. The free energy of intermediates was corrected to account for the standard state corrections from 1 mol per 24.46 L (gas phase) to 1 M (solution phase), which corresponds to RT ln (24.46) or 1.89 kcal mol^{-1}

Eq. (1) $$\Delta G^{\circ\,(SMD-toluene)}_{reaction} = \Delta G^{\circ\,(SMD-toluene)}_{products} - \Delta G^{\circ\,(SMD-toluene)}_{reactants}$$

9. GC/MS spectra of xxvi-xxxi

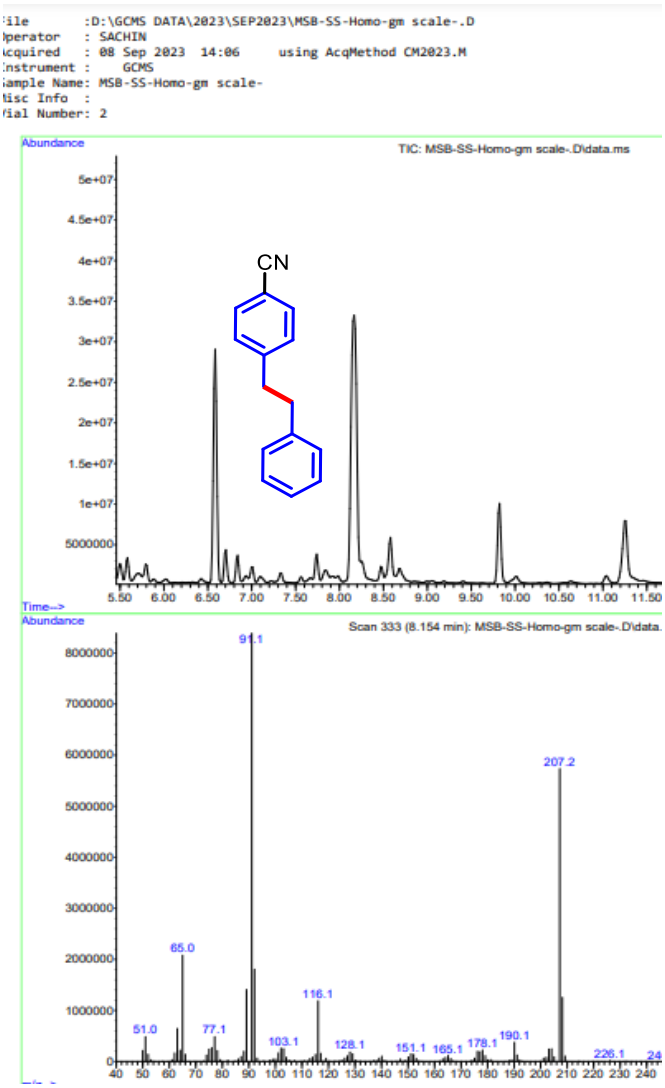


Figure S39. GC/MS spectrum of **xxvi**

```
File       :D:\GCMS DATA\2023\OCT2023\MSB-RG-02-223.D
Operator   : RG
Acquired   : 29 Oct 2023  15:59     using AcqMethod CF_29SEP2023.M
Instrument :   GCMS-01
Sample Name: MSB-RG-02-223
Misc Info  :
Vial Number: 1
```

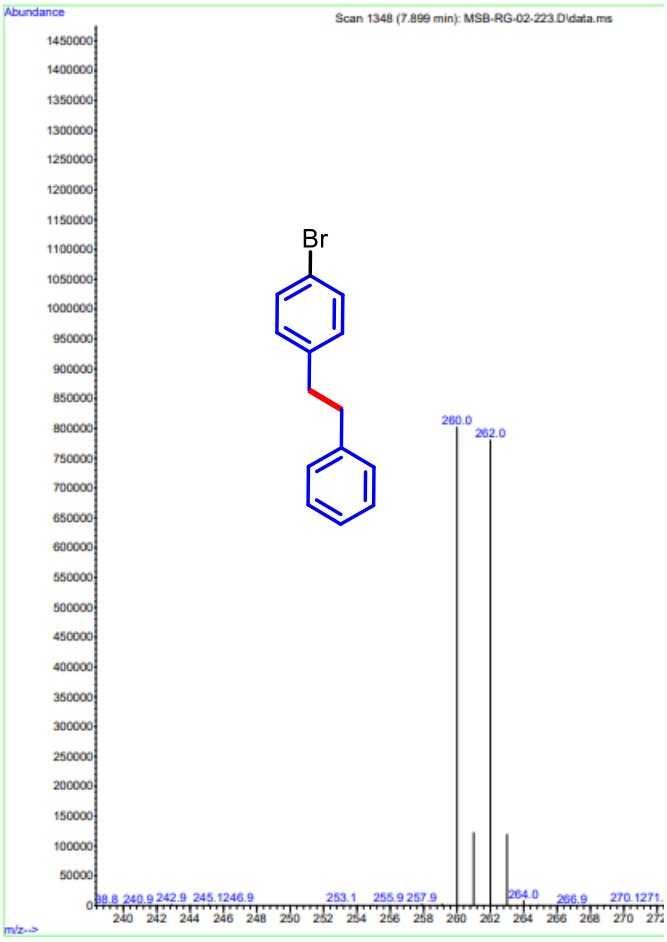


Figure S40. GC/MS spectrum of **xxvii**

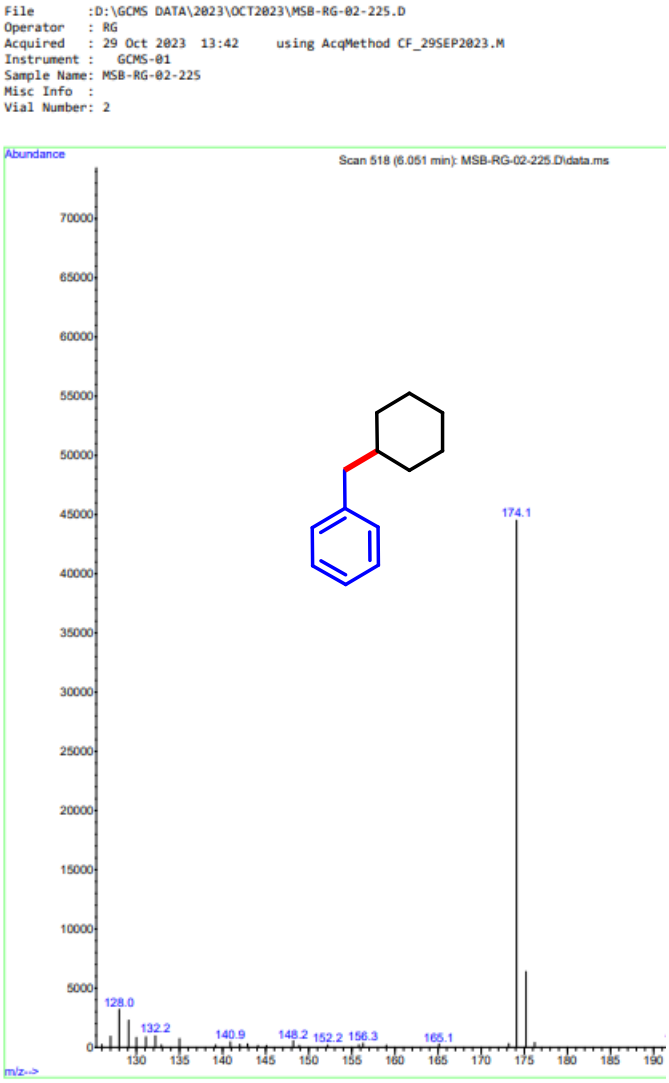


Figure S41. GC/MS spectrum of **xxix**

```
File       :D:\GCMS DATA\2023\OCT2023\MSB-RG-02-232.D
Operator   : BHP
Acquired   : 01 Nov 2023  16:11     using AcqMethod CF_29SEP2023.M
Instrument :   GCMS-01
Sample Name: MSB-RG-02-232
Misc Info  :
Vial Number: 2
```

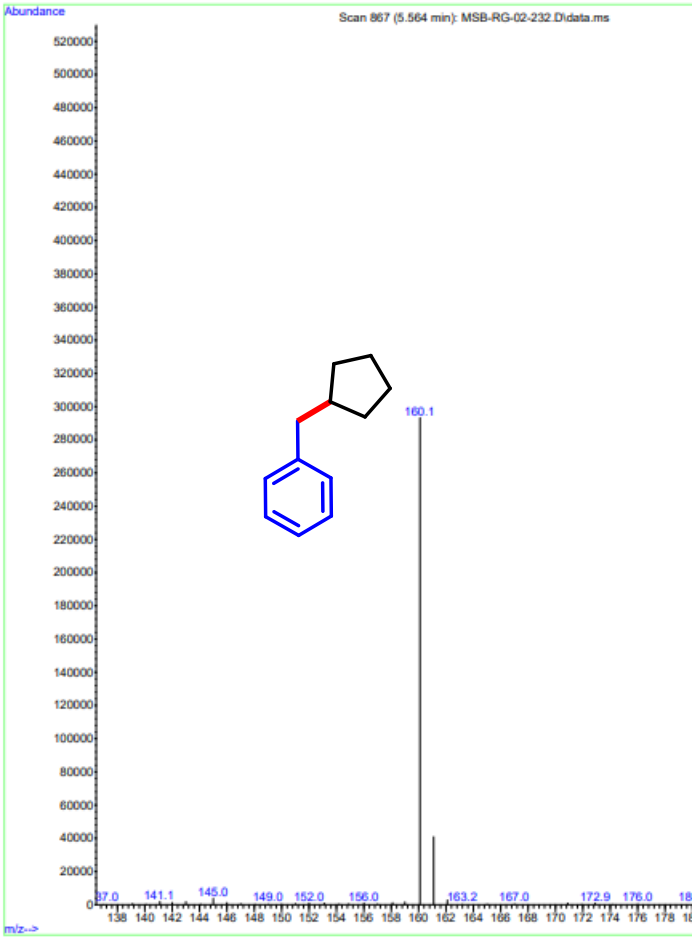


Figure S42. GC/MS spectrum of **xxx**

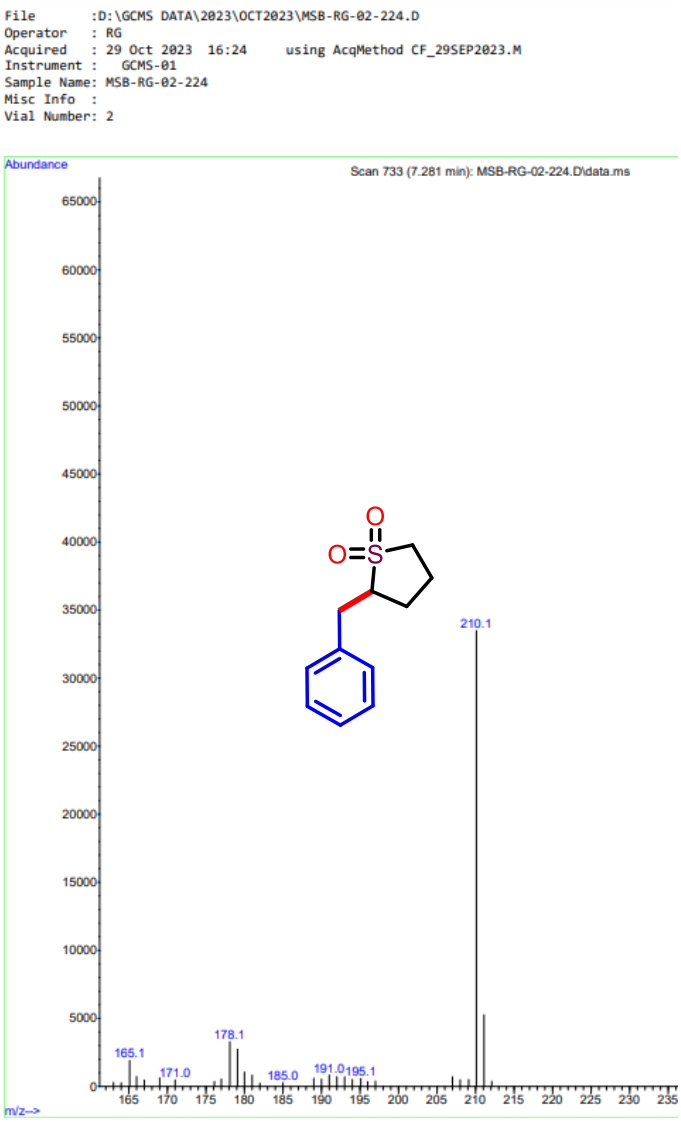
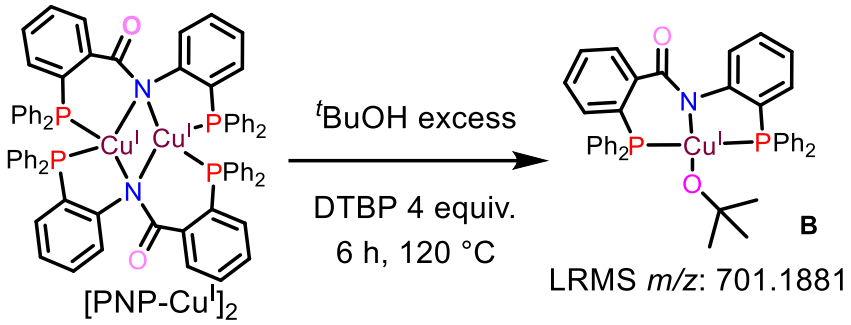


Figure S43. GC/MS spectrum of **xxxi**

10. Identification of Intermediate B, in Homomcoupling Reaction

To investigate the formation of intermediate **B**, $[PNP\text{-}Cu]_2$ (1 equiv.) was treated with an excess of ^{t}BuOH in the presence of DTBP (4 equiv.) at 120 °C for 6 hours. Analysis of the reaction mixture via mass spectrometry LRMS (ESI) resulted a mass spectrum with *m/z*: 701.1596 $[M]^+$ calcd for $C_{41}H_{37}CuNO_2P_2$, found 701.188, which indicates the formation of intermediate **B**.



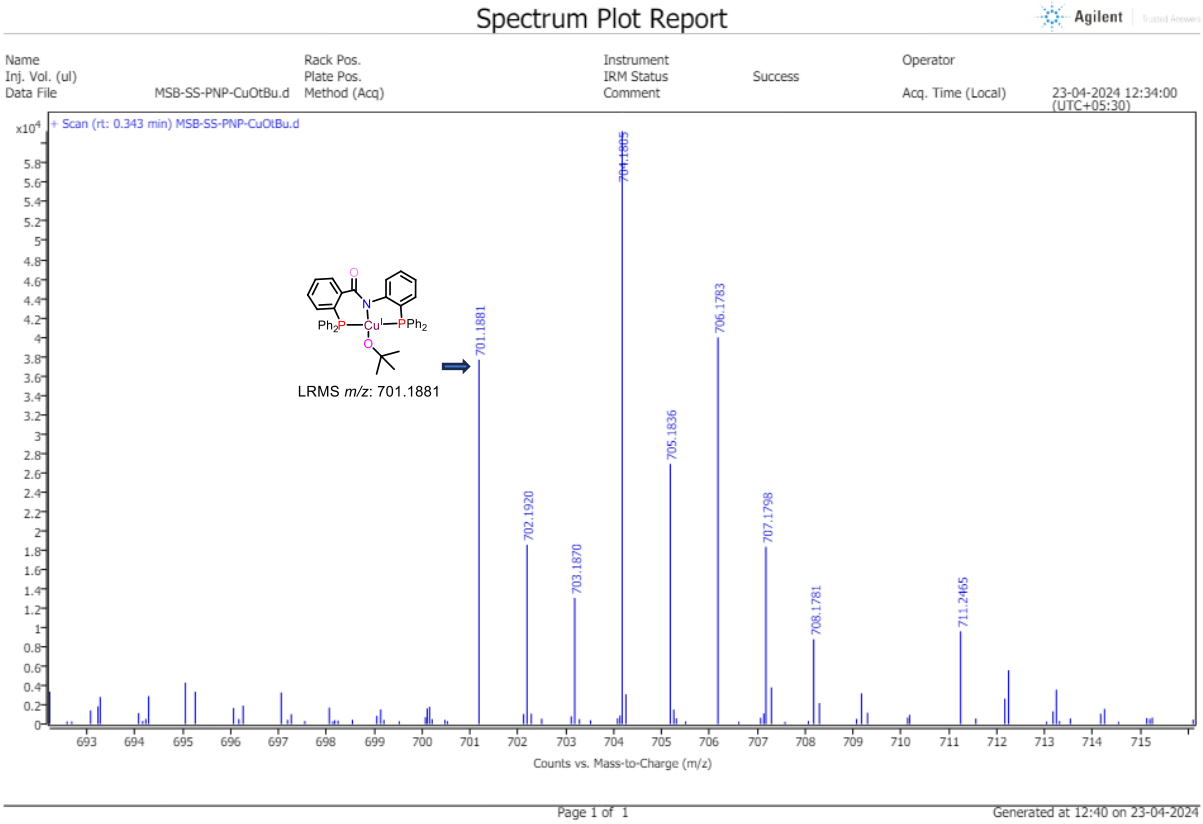


Figure 44. LRMS of Intermediate **B**

11. Cartesian Coordinates of Optimized Geometries

Intermediate A

E_{gas}	-2435.555323 hartree
E_{solv}	-2435.597186 hartree
G_{solv}	-2435.121340 hartree

Cu	-0.044653	0.072436	-0.968771
P	2.071652	-0.34381	-0.418822
P	-2.20782	-0.23769	-0.465742
O	0.899228	3.45986	1.179248
C	-2.252077	-1.18187	1.102997
C	3.231559	-1.62449	-0.998062
N	-0.200832	1.975373	-0.217055
C	-2.577579	1.477352	0.003336
C	2.082149	-0.49874	1.401816
C	4.291329	-2.07662	-0.211001
H	4.42693	-1.68319	0.790503
C	-1.49173	2.380306	0.139353
C	-3.654222	-0.8254	-1.408268
C	4.739151	2.497326	-1.703239
H	5.711339	2.504853	-2.182575
C	2.751046	0.397146	2.232751
H	3.29471	1.233389	1.809323
C	3.054472	-2.1462	-2.279203
H	2.220265	-1.80722	-2.885077
C	-2.313588	-0.54448	2.339673
H	-2.391786	0.535461	2.386776
C	4.137791	1.291108	-1.378146
H	4.653084	0.364274	-1.600669
C	-3.891861	1.880609	0.251055
H	-4.699538	1.167295	0.124096
C	4.091514	3.685882	-1.397694
H	4.552415	4.637838	-1.636156
C	4.992383	-3.54138	-1.989572
H	5.677309	-4.28872	-2.373864
C	-1.813815	3.688535	0.557795
H	-1.014828	4.398169	0.704246
C	5.166327	-3.0339	-0.706724
H	5.985946	-3.3846	-0.090084
C	2.879474	1.25585	-0.772427
C	-2.095092	-3.31607	2.225521

H	-2.009913	-4.39589	2.177114
C	-2.269308	-1.29122	3.512113
H	-2.313116	-0.78478	4.46939
C	-2.127047	-2.57346	1.054686
H	-2.061028	-3.07704	0.095046
C	2.699356	0.234215	3.612295
H	3.210281	0.943128	4.2533
C	-2.168196	-2.67413	3.458663
H	-2.141004	-3.25386	4.3747
C	3.93653	-3.097	-2.776205
H	3.794105	-3.4968	-3.773546
C	-3.120709	4.068525	0.797123
H	-3.318815	5.088941	1.10858
C	-4.177165	3.173339	0.646946
H	-5.199188	3.479767	0.835204
C	-3.666688	-0.60094	-2.785691
H	-2.814516	-0.12401	-3.259179
C	2.211129	2.455697	-0.469389
C	0.874803	2.647036	0.260853
C	2.855913	3.657239	-0.770517
H	2.3651	4.580178	-0.488534
C	1.989055	-0.82239	4.165742
H	1.948902	-0.94382	5.242392
C	-5.839071	-1.83667	-1.574474
H	-6.684753	-2.32109	-1.099732
C	1.353268	-1.54962	1.963665
H	0.801887	-2.23265	1.325282
C	-5.848674	-1.60221	-2.943851
H	-6.701617	-1.90521	-3.540426
C	-4.761624	-0.98174	-3.548799
H	-4.763587	-0.79973	-4.617332
C	-4.748153	-1.44787	-0.806719
H	-4.746671	-1.63253	0.261806
C	1.316661	-1.7163	3.339269
H	0.743665	-2.53179	3.763636

Intermediate B

E_{gas}	-2669.255480 hartree
E_{solv}	-2669.295192 hartree
G_{solv}	-2668.686794 hartree

Cu	-0.055487	0.755708	0.669162

P	-1.977216	-0.3618	0.252776
P	2.022605	-0.22528	0.371474
O	0.315641	2.629558	0.182894
O	-0.170056	-0.80312	-2.86024
C	2.15778	-2.04693	0.415557
C	-3.339426	-0.29772	1.468826
N	0.61267	1.182966	-2.060087
H	0.416663	1.95669	-1.376528
C	2.739118	0.198224	-1.266338
C	-1.867294	-2.13289	-0.167807
C	-4.365195	-1.24354	1.496853
H	-4.355486	-2.07246	0.797548
C	1.975309	0.819329	-2.258655
C	3.283003	0.455863	1.508467
C	-4.416604	1.738869	-2.314525
H	-5.44204	2.089648	-2.318422
C	-2.305054	-2.65766	-1.379804
H	-2.701539	-2.00195	-2.145048
C	-3.349867	0.752849	2.386364
H	-2.54503	1.480451	2.376821
C	1.986674	-2.77719	-0.762218
H	1.831872	-2.26315	-1.704784
C	-3.965245	0.945517	-1.267851
H	-4.642775	0.701408	-0.458667
C	4.075163	-0.10929	-1.53509
H	4.678479	-0.58122	-0.767558
C	-3.551823	2.090739	-3.339593
H	-3.893033	2.721072	-4.152611
C	-5.404901	-0.07042	3.326076
H	-6.208473	0.016209	4.048666
C	2.550559	1.105193	-3.494738
H	1.937325	1.584484	-4.248344
C	-5.392749	-1.12852	2.423826
H	-6.185368	-1.86782	2.442541
C	-2.649542	0.486399	-1.232725
C	2.282667	-4.11488	1.658537
H	2.393995	-4.63195	2.605216
C	1.98452	-4.1649	-0.725885
H	1.845577	-4.72077	-1.645767
C	2.27526	-2.7262	1.630098
H	2.372559	-2.17142	2.557538
C	-2.203683	-4.02329	-1.619778

H	-2.535488	-4.42518	-2.570188
C	2.147528	-4.83681	0.478814
H	2.153663	-5.92091	0.501131
C	-4.382544	0.870303	3.307351
H	-4.382905	1.691992	4.014102
C	3.872884	0.785774	-3.751393
H	4.30604	1.01492	-4.718298
C	4.641479	0.177062	-2.765308
H	5.679209	-0.07166	-2.954569
C	3.107445	1.804237	1.835432
H	2.249026	2.340586	1.430846
C	-1.780853	0.837545	-2.277214
C	-0.367962	0.309979	-2.40438
C	-2.240122	1.636627	-3.318259
H	-1.556728	1.906653	-4.115618
C	-1.676114	-4.86642	-0.651567
H	-1.599824	-5.93115	-0.842149
C	5.308018	0.408769	2.815839
H	6.164837	-0.13548	3.19706
C	-1.312846	-2.98061	0.793395
H	-0.937375	-2.57137	1.726061
C	5.13189	1.748338	3.140989
H	5.850831	2.249408	3.779587
C	4.035534	2.444944	2.645109
H	3.898559	3.491912	2.891555
C	4.390192	-0.23728	1.996059
H	4.539365	-1.28062	1.740663
C	-1.230435	-4.34323	0.557551
H	-0.794973	-4.9926	1.307257
C	-0.386314	3.779877	0.538488
C	0.319432	4.984577	-0.098891
H	1.359245	5.021711	0.237763
H	0.321567	4.876039	-1.187467
H	-0.167153	5.932431	0.155044
C	-1.837628	3.715414	0.038374
H	-2.396308	4.626653	0.277191
H	-1.856519	3.570922	-1.04593
H	-2.358752	2.867918	0.492603
C	-0.37966	3.932415	2.066944
H	-0.846011	3.054253	2.528047
H	0.649856	3.991219	2.432362
H	-0.919527	4.825	2.400701

Intermediate C

E_{gas}	-2668.604790 hartree
E_{solv}	-2668.645160 hartree
G_{solv}	-2668.049315 hartree

Cu	0.322116	0.864127	-0.95322
P	-1.83508	0.018167	0.27825
P	2.129573	-0.097138	0.117989
O	0.648829	2.656613	-1.09289
O	-1.13995	-1.957089	-3.49383
C	1.859922	-0.844231	1.757959
C	-3.06898	0.579765	1.515515
N	0.128791	-0.874327	-1.88144
C	2.323649	-1.467345	-1.04068
C	-1.9562	-1.800638	0.456995
C	-4.27646	-0.097313	1.707488
H	-4.49719	-0.980638	1.118185
C	1.221158	-1.754548	-1.88346
C	3.693648	0.813425	0.250226
C	-4.2143	1.756022	-2.5884
H	-5.04359	2.454169	-2.59411
C	-2.57776	-2.642161	-0.46343
H	-3.02828	-2.23961	-1.36245
C	-2.78979	1.701754	2.293572
H	-1.85256	2.229427	2.161736
C	1.964387	-2.214899	1.984357
H	2.213719	-2.882923	1.16879
C	-3.70438	1.307233	-1.37968
H	-4.14848	1.660108	-0.45705
C	3.480399	-2.245821	-1.06064
H	4.316507	-1.971552	-0.42539
C	-3.66805	1.302501	-3.78118
H	-4.0649	1.641733	-4.73105
C	-4.90681	1.478924	3.414954
H	-5.62165	1.827344	4.151921
C	1.324127	-2.91047	-2.68228
H	0.498918	-3.170875	-3.32352
C	-5.18942	0.350943	2.650036
H	-6.12331	-0.181228	2.791054
C	-2.62682	0.418048	-1.33546
C	1.250944	-0.518111	4.072172

H	0.964804	0.144229	4.880929
C	1.726004	-2.730348	3.253626
H	1.812014	-3.797887	3.421199
C	1.498941	0.001539	2.810625
H	1.410911	1.068854	2.63979
C	-2.60898	-4.014323	-0.24415
H	-3.08094	-4.659791	-0.97577
C	1.36574	-1.887232	4.295869
H	1.171043	-2.293531	5.281877
C	-3.70675	2.152757	3.237322
H	-3.47881	3.028329	3.834418
C	2.472312	-3.684518	-2.66954
H	2.512598	-4.559722	-3.30932
C	3.568314	-3.358391	-1.87765
H	4.468853	-3.960316	-1.8955
C	3.831476	1.971061	-0.51886
H	2.992616	2.318166	-1.11622
C	-2.0667	-0.030909	-2.54553
C	-0.95867	-1.06619	-2.67461
C	-2.61765	0.400148	-3.7518
H	-2.20528	0.001087	-4.67029
C	-2.03613	-4.554759	0.899346
H	-2.06174	-5.625728	1.066233
C	5.917603	1.124146	1.123819
H	6.726278	0.80077	1.769202
C	-1.38101	-2.349933	1.604027
H	-0.89551	-1.704622	2.329369
C	6.061365	2.266258	0.343403
H	6.985159	2.832623	0.380401
C	5.019116	2.690164	-0.47238
H	5.124441	3.589752	-1.06792
C	4.735118	0.39815	1.08162
H	4.61667	-0.482606	1.7042
C	-1.42633	-3.717991	1.82683
H	-0.97355	-4.128586	2.722263
C	0.26808	3.737649	-0.29396
C	1.019844	4.970238	-0.80887
H	2.098263	4.808713	-0.72863
H	0.775265	5.138135	-1.86033
H	0.756361	5.867002	-0.23955
C	-1.2451	3.96026	-0.39792
H	-1.57317	4.820614	0.194388

H	-1.52314	4.124112	-1.44189
H	-1.78497	3.077185	-0.04788
C	0.669209	3.460801	1.162717
H	0.166357	2.554424	1.51295
H	1.749357	3.300701	1.22887
H	0.395084	4.291176	1.820699

Intermediate D

E_{gas}	-2706.467476 hartree
E_{solv}	-2706.510533 hartree
G_{solv}	-2705.924339 hartree

Cu	-0.09973	-0.228843	-1.03105
P	-2.22243	0.222291	-0.15497
P	2.007639	-0.537864	-0.09906
O	-1.64231	-3.896812	0.346004
C	2.206561	0.000476	1.630233
C	-3.13506	1.787564	-0.36773
N	-0.32731	-2.295437	-0.6809
C	2.054384	-2.339909	-0.12876
C	-2.15727	-0.077125	1.639366
C	-3.56895	2.55782	0.70944
H	-3.43976	2.194931	1.722259
C	0.849486	-3.015301	-0.40934
C	3.532908	-0.038731	-0.96312
C	-5.35722	-1.753464	-1.92539
H	-6.34937	-1.510395	-2.288
C	-2.92728	-1.047246	2.275976
H	-3.6214	-1.654307	1.706758
C	-3.31524	2.271232	-1.6679
H	-2.99195	1.676149	-2.51575
C	2.286606	-0.905907	2.685209
H	2.254667	-1.970884	2.48625
C	-4.58425	-0.775212	-1.32096
H	-4.98478	0.224689	-1.20747
C	3.257186	-3.030581	0.058759
H	4.164422	-2.468206	0.255826
C	-4.8566	-3.043493	-2.04812
H	-5.45284	-3.819105	-2.51539
C	-4.33064	4.272981	-0.80366
H	-4.78817	5.241148	-0.97144

C	0.925501	-4.421849	-0.49329
H	0.028834	-4.985241	-0.69995
C	-4.16061	3.797062	0.48918
H	-4.49119	4.389679	1.33455
C	-3.29758	-1.065817	-0.8584
C	2.34072	1.829147	3.201538
H	2.356025	2.895987	3.394719
C	2.402627	-0.44331	3.991184
H	2.463959	-1.154661	4.806791
C	2.213402	1.373059	1.897765
H	2.12293	2.087257	1.08631
C	-2.7832	-1.256151	3.642441
H	-3.37319	-2.022912	4.130713
C	2.441015	0.920422	4.2509
H	2.539799	1.276477	5.270514
C	-3.91378	3.502613	-1.88447
H	-4.04661	3.86594	-2.89683
C	2.117291	-5.09153	-0.30389
H	2.127737	-6.173484	-0.38431
C	3.298899	-4.407273	-0.01745
H	4.229645	-4.94167	0.130757
C	3.602911	-0.347221	-2.32441
H	2.794752	-0.902413	-2.79085
C	-2.79411	-2.369128	-0.96263
C	-1.49883	-2.901987	-0.35743
C	-3.60206	-3.347347	-1.54612
H	-3.23029	-4.363695	-1.58132
C	-1.88165	-0.496004	4.375497
H	-1.77012	-0.665914	5.440481
C	5.66576	1.072624	-1.13018
H	6.471344	1.624956	-0.6596
C	-1.23651	0.672408	2.376481
H	-0.61193	1.408797	1.879487
C	5.725447	0.77348	-2.48446
H	6.575061	1.095057	-3.07595
C	4.693773	0.053199	-3.07992
H	4.737825	-0.190861	-4.13513
C	4.575254	0.666073	-0.3686
H	4.535249	0.911271	0.686028
C	-1.10978	0.472366	3.742163
H	-0.38946	1.055036	4.302931
C	0.271386	1.48559	-2.23296

H	0.925588	1.062354	-2.99604
H	-0.73906	1.666275	-2.59267
C	0.857107	2.585732	-1.4669
C	2.221493	2.900284	-1.57133
C	0.082105	3.357031	-0.58252
C	2.786784	3.917665	-0.8152
H	2.844369	2.339037	-2.25867
C	0.647464	4.37198	0.172887
H	-0.97875	3.156599	-0.49418
C	2.006991	4.656373	0.068059
H	3.845121	4.130965	-0.91823
H	0.021343	4.947566	0.846177
H	2.449142	5.450643	0.658726

(Cu^{III}-penta-coordinated)

E_{gas}	-2977.370290 hartree
E_{solv}	-2977.419045 hartree
G_{solv}	-2976.713474 hartree

Cu	-0.27793	-1.324895	0.90478
P	-2.28118	-0.571211	-0.2069
P	1.224942	1.496456	-0.35849
O	-1.43898	2.084678	3.141838
C	0.60568	3.224867	-0.51168
C	-3.24206	-1.76535	-1.2134
N	-0.42714	0.417172	1.947122
C	1.734885	1.46717	1.410745
C	-2.33519	0.986042	-1.153
C	-3.72667	-1.486491	-2.4901
H	-3.59361	-0.500916	-2.91926
C	0.826702	0.952374	2.343989
C	2.869666	1.546535	-1.18211
C	-5.52734	-0.472057	2.312903
H	-6.55768	-0.807538	2.282719
C	-3.06703	2.085856	-0.71527
H	-3.59897	2.049453	0.227701
C	-3.45112	-3.040408	-0.67568
H	-3.11037	-3.264529	0.330437
C	-0.08244	3.830326	0.542397
H	-0.21169	3.319931	1.491271
C	-4.70185	-0.685402	1.22041
H	-5.10442	-1.17543	0.342996

C	2.989628	1.904415	1.848253
H	3.699744	2.29527	1.13015
C	-5.03005	0.184202	3.43101
H	-5.66697	0.362547	4.289984
C	-4.58789	-3.730795	-2.67933
H	-5.10568	-4.492747	-3.25038
C	1.199867	0.895799	3.692744
H	0.482916	0.518098	4.412158
C	-4.39176	-2.4673	-3.21846
H	-4.76256	-2.235988	-4.21046
C	-3.36538	-0.274267	1.23734
C	0.214887	5.200478	-1.85762
H	0.337829	5.728963	-2.79707
C	-0.61416	5.105242	0.392111
H	-1.14477	5.556347	1.223157
C	0.727019	3.917511	-1.71922
H	1.236	3.456475	-2.55912
C	-3.10984	3.245374	-1.48175
H	-3.66173	4.104697	-1.1204
C	-0.4601	5.799228	-0.80123
H	-0.86314	6.800435	-0.908
C	-4.12252	-4.013591	-1.39959
H	-4.28029	-4.994123	-0.96557
C	2.4488	1.317511	4.108149
H	2.718395	1.251382	5.156317
C	3.353564	1.82497	3.181044
H	4.335553	2.158401	3.496199
C	3.366777	0.3066	-1.5831
H	2.758912	-0.58065	-1.44768
C	-2.86636	0.406234	2.356745
C	-1.48973	1.038132	2.495603
C	-3.72106	0.636098	3.436416
H	-3.33056	1.202343	4.272122
C	-2.44434	3.304538	-2.6952
H	-2.47661	4.210903	-3.28797
C	4.920944	2.572019	-1.95099
H	5.525266	3.461042	-2.09451
C	-1.62826	1.068033	-2.35683
H	-1.00888	0.241446	-2.68333
C	5.41047	1.327752	-2.3354
H	6.394896	1.246075	-2.78292
C	4.631255	0.193684	-2.14743

H	4.99667	-0.782198	-2.44756
C	3.662373	2.68156	-1.37373
H	3.297034	3.654485	-1.0645
C	-1.70161	2.212625	-3.13229
H	-1.15346	2.264868	-4.06601
C	0.007015	-3.061957	-0.07577
H	0.42454	-3.859885	0.525707
H	-1.02918	-3.282518	-0.32245
C	0.817406	-2.790761	-1.28618
C	2.1511	-3.207027	-1.3777
C	0.245295	-2.182866	-2.41167
C	2.882787	-3.010061	-2.54208
H	2.612645	-3.714004	-0.5409
C	0.977394	-1.974553	-3.56879
H	-0.80279	-1.908305	-2.38377
C	2.305928	-2.383406	-3.63832
H	3.911212	-3.351557	-2.58661
H	0.507526	-1.504493	-4.42578
H	2.880622	-2.221139	-4.54285
C	0.855672	-2.287504	2.276219
H	0.833355	-1.432305	2.945923
H	0.226676	-3.095606	2.647516
C	2.227898	-2.707248	1.943578
C	3.186721	-1.771174	1.539984
C	2.610989	-4.05055	2.027646
C	4.47335	-2.166314	1.209218
H	2.914287	-0.725032	1.479013
C	3.903469	-4.44721	1.708063
H	1.887383	-4.791125	2.354608
C	4.837752	-3.506847	1.288539
H	5.19062	-1.420972	0.884073
H	4.18041	-5.492798	1.784748
H	5.844939	-3.815858	1.032745

Intermediate A” (A+ toluene) SI fig.

E_{gas}	-2707.076592 hartree
E_{solv}	-2707.123766 hartree
G_{solv}	-2706.524444 hartree

Cu	0.041556	0.89022	-0.15557
P	-2.2463	0.41505	-0.14506
P	1.627545	-0.81523	-0.04456

O	-1.1636	-2.552998	-0.12223
C	1.486739	-1.183727	1.744117
C	-3.19703	1.979163	-0.17261
N	-0.16621	-2.372212	-2.1517
H	-0.30397	-2.124431	-3.11786
C	1.897434	-2.482301	-0.80613
C	-2.71634	-0.347457	1.44535
C	-4.30372	2.216282	0.641596
H	-4.62784	1.460349	1.348222
C	1.048069	-3.014607	-1.77986
C	3.304335	-0.10337	-0.24507
C	-4.89509	-0.914573	-3.03456
H	-5.83555	-0.584107	-3.46025
C	-3.76644	-1.252315	1.581
H	-4.34282	-1.550336	0.712321
C	-2.77583	2.970867	-1.05993
H	-1.88941	2.806349	-1.66403
C	0.989474	-2.397509	2.21425
H	0.730284	-3.182456	1.515203
C	-4.31167	-0.182172	-2.00665
H	-4.79844	0.719295	-1.65446
C	3.038522	-3.213705	-0.4654
H	3.710534	-2.825159	0.289929
C	-4.27581	-2.058449	-3.51471
H	-4.7279	-2.632853	-4.31481
C	-4.57203	4.399639	-0.34109
H	-5.10368	5.342523	-0.40193
C	1.358914	-4.217565	-2.41095
H	0.675254	-4.609042	-3.15624
C	-4.98655	3.424094	0.557152
H	-5.84192	3.60383	1.198563
C	-3.10845	-0.586913	-1.43029
C	1.558103	-0.350583	4.010972
H	1.778199	0.452106	4.705934
C	0.787729	-2.586304	3.575933
H	0.393361	-3.531516	3.930836
C	1.753493	-0.15368	2.651436
H	2.113902	0.802667	2.288535
C	-4.06294	-1.791746	2.825734
H	-4.87636	-2.501829	2.924155
C	1.077787	-1.569882	4.476348
H	0.921906	-1.723324	5.538551

C	-3.4647	4.171944	-1.15049
H	-3.12572	4.937316	-1.83903
C	2.50967	-4.9114	-2.07774
H	2.743739	-5.844056	-2.5776
C	3.346049	-4.412879	-1.0867
H	4.241871	-4.952785	-0.80334
C	3.528678	0.640815	-1.40321
H	2.706733	0.84405	-2.08126
C	-2.48631	-1.741965	-1.92685
C	-1.22304	-2.256187	-1.29636
C	-3.06795	-2.465962	-2.96256
H	-2.58208	-3.366203	-3.32456
C	-3.31497	-1.429617	3.939779
H	-3.54587	-1.855673	4.909776
C	5.606664	0.240529	0.390588
H	6.4122	0.097849	1.102335
C	-1.96159	0.006884	2.563934
H	-1.12638	0.692783	2.460592
C	5.828546	0.953491	-0.78028
H	6.807218	1.37326	-0.9836
C	4.786645	1.155659	-1.67574
H	4.941083	1.750204	-2.56751
C	4.35089	-0.289632	0.657308
H	4.185322	-0.837858	1.578339
C	-2.26476	-0.529793	3.807231
H	-1.66563	-0.2557	4.667221
C	0.534635	2.73918	0.528147
H	-0.30354	3.382969	0.24019
H	0.547653	2.695513	1.623944
C	1.804616	3.284666	0.007913
C	1.894407	3.808229	-1.29403
C	2.982705	3.310924	0.771744
C	3.072661	4.347226	-1.7883
H	1.00373	3.802076	-1.91769
C	4.16566	3.840969	0.277556
H	2.958442	2.925474	1.787484
C	4.223363	4.372057	-1.00584
H	3.093045	4.757848	-2.79359
H	5.052082	3.841914	0.904078
H	5.145334	4.794769	-1.38938

Toluene

E_{gas}	-271.534596 hartree
E_{solv}	-271.543333 hartree
G_{solv}	-271.445291 hartree

C	-1.19548	1.19998	0.002009
C	0.193741	1.197148	-0.00875
C	0.908923	0.000001	-0.01193
C	0.193742	-1.19715	-0.00875
C	-1.19548	-1.19998	0.002009
C	-1.89591	0	0.008188
H	-1.73219	2.142295	0.002145
H	0.732861	2.139524	-0.01706
H	0.732863	-2.13952	-0.01706
H	-1.73219	-2.1423	0.002145
H	-2.97993	-1E-06	0.013864
C	2.415536	0	0.009411
H	2.788458	-2.3E-05	1.03862
H	2.819864	-0.88441	-0.48788
H	2.819865	0.884435	-0.48784

Benzyl radical

E_{gas}	-270.878758 hartree
E_{solv}	-270.886857 hartree
G_{solv}	-270.801359 hartree

C	-1.12902	1.206796	-0.000001
C	0.251199	1.213156	-0.000004
C	0.989282	0.000007	0.000011
C	0.251212	-1.213147	-0.000005
C	-1.12901	-1.2068	-0.000001
C	-1.83084	-0.000008	0.000004
H	-1.67137	2.145798	-0.000003
H	0.791426	2.154137	-0.000015
H	0.791443	-2.154126	-0.000014
H	-1.67134	-2.145809	0
H	-2.91453	-0.000014	0.000004
C	2.392791	0.000004	-0.000001
H	2.950333	-0.928698	0.000003
H	2.950391	0.928666	0.000006

di *tert*-butyl peroxide

E_{gas}	-466.051770 hartree
E_{solv}	-466.059772 hartree
G_{solv}	-465.845483 hartree

	x	y	z
C	2.669126	1.182757	-0.084632
C	1.743806	-0.027250	-0.007695
H	2.693244	1.581421	-1.101030
H	2.329042	1.970469	0.591640
H	3.682744	0.892102	0.201029
C	1.651414	-0.557998	1.420820
C	2.183902	-1.119124	-0.980979
H	0.934367	-1.378041	1.477194
H	2.627040	-0.926415	1.748593
H	1.332518	0.233841	2.102813
H	3.176787	-1.489361	-0.711534
H	1.482985	-1.954500	-0.961212
H	2.221613	-0.722309	-1.998089
O	0.487836	0.524605	-0.429312
O	-0.487836	-0.524560	-0.429368
C	-1.743806	0.027251	-0.007693
C	-1.651415	0.557849	1.420877
C	-2.183901	1.119226	-0.980863
C	-2.669126	-1.182748	-0.084758
H	-1.332514	-0.234060	2.102786
H	-0.934370	1.377889	1.477336
H	-2.627041	0.926227	1.748690
H	-2.221614	0.722518	-1.998015
H	-3.176786	1.489437	-0.711378
H	-1.482984	1.954600	-0.961010
H	-3.682744	-0.892123	0.200930
H	-2.693242	-1.581307	-1.101197
H	-2.329043	-1.970530	0.591433

***tert*-butoxy radical**

E_{gas}	-232.994268 hartree
E_{solv}	-233.0002068 hartree
G_{solv}	-232.9069398 hartree

	x	y	z
C	1.27069	-0.789353	-0.312717
C	0.000002	-0.024962	0.082084
H	2.156524	-0.222387	-0.019669
H	1.297627	-1.757058	0.194233
H	1.302025	-0.966718	-1.391356
C	-1.270584	-0.789526	-0.312714
C	-0.000096	1.380355	-0.578116
H	-2.15649	-0.222712	-0.01959
H	-1.301936	-0.966825	-1.391363
H	-1.297352	-1.757268	0.194174
H	-0.000052	1.247787	-1.662731
H	-0.889548	1.939607	-0.284742
H	0.889246	1.939754	-0.284691
O	-0.000015	0.263341	1.424314

***tert*-butanol**

E_{gas} -233.671201 hartree
E_{solv} -233.677024 hartree
G_{solv} -233.569494 hartree

	x	y	z
C	0.682977	1.258895	-0.513100
C	-0.006032	0.000000	0.017387
H	0.206277	2.149699	-0.097779
H	1.740037	1.270138	-0.225939
H	0.632902	1.310278	-1.604373
C	0.683004	-1.258878	-0.513104
C	-1.485747	-0.000015	-0.345729
H	0.206323	-2.149694	-0.097787
H	0.632930	-1.310258	-1.604377
H	1.740064	-1.270100	-0.225943
H	-1.619908	-0.000014	-1.430372
H	-1.973194	-0.885237	0.068920
H	-1.973213	0.885194	0.068924
O	0.027017	-0.000002	1.445001
H	0.946437	0.000000	1.715992

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