Electronic Supplementary information

FLP reactivity of $[Ph_3C]+$ and $(o\text{-tolyl})_3P$ and the capture of a Staudinger reaction intermediate

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This PDF file includes:

1. Materials and Methods

General Remarks

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N_2. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (dichloromethane, chlorobenzene, *n*-pentane and *n*-hexane) were prepared using an Innovative Technologies solvent purification system. Deuterated chloroform ($CDCl_3$), dichloromethane (CD_2Cl_2) and bromobenzene (C_6D_5Br) purchased from Cambridge Isotope Laboratories Inc. were degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Commercial reagents were used without further purification unless indicated otherwise. $[Ph_3C][BF_4]$[S1] and pentafluorophenyl azide[S2] were prepared according to literature procedures. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer. ^{1}H, $^{13}C\{^{1}H\}$, ^{31}P, ^{19}F, $^{11}B\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR chemical shifts (δ/ppm) are referenced to Me_4Si, Me_4Si, H_3PO_4, $CFCl_3$, $BF_3{\cdot}OEt_2$ and Me_4Si, respectively. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JMS-T100LC JOEL (DART). Elemental analyses were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyzer.

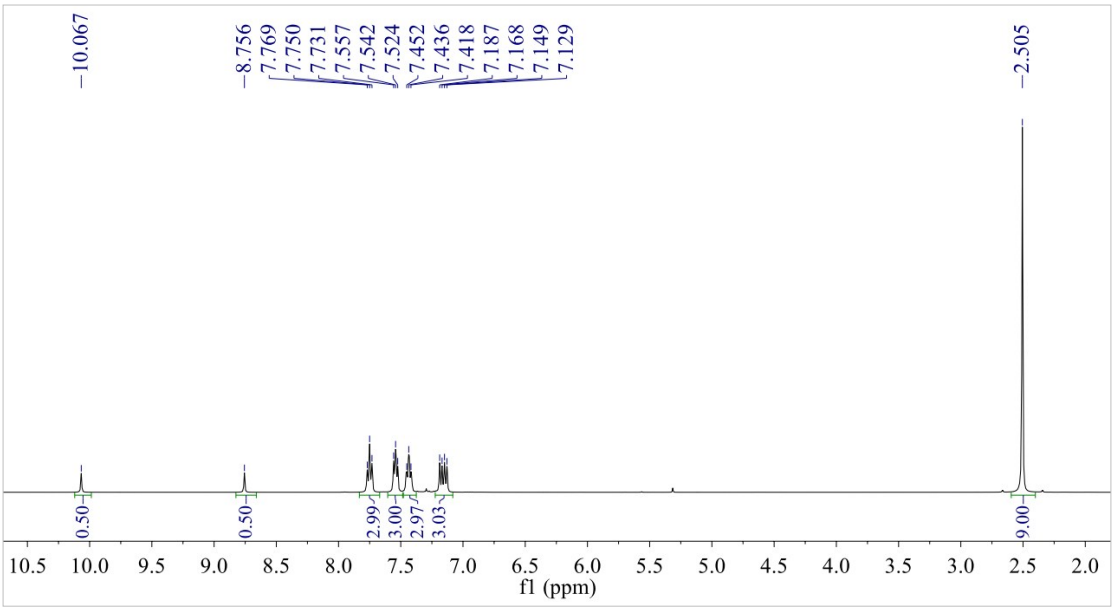
2. Syntheses and Spectroscopic Data

2.1. The reaction of $[Ph_3C][BF_4]$/P(*o*-tolyl)$_3$ with 1,4-cyclohexadiene

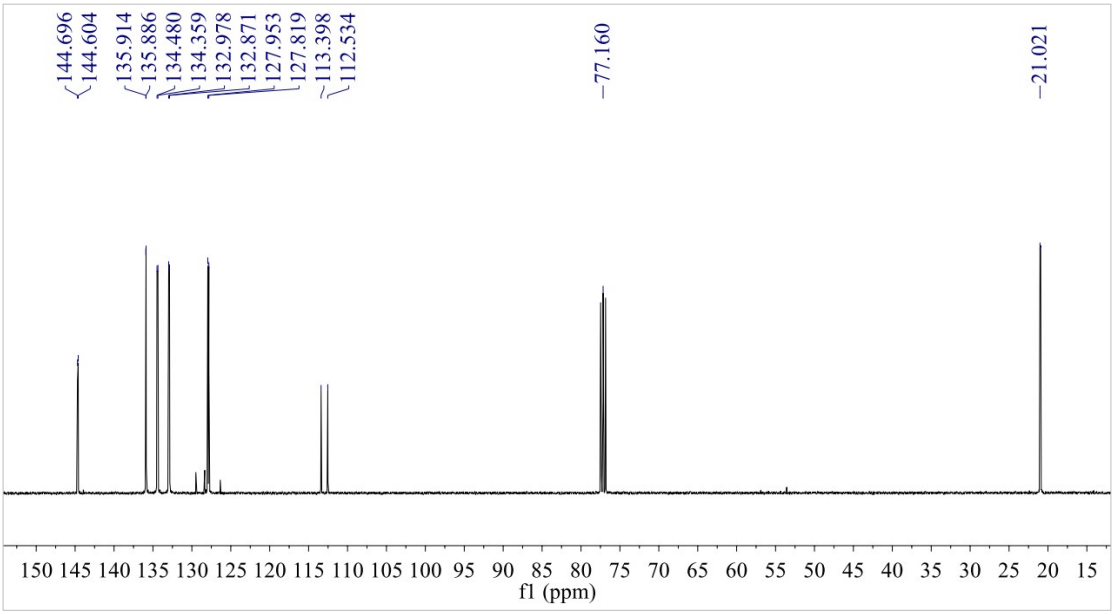
Dichloromethane solution (2 mL) of 1,4-cyclohexadiene (29 mg, 0.36 mmol) was added to dichloromethane solution (2 mL) of $[Ph_3C][BF_4]$ (99 mg, 0.30 mmol) and P(*o*-tolyl)$_3$ (91 mg, 0.30 mmol), and the solution stood at room temperature for 30 minutes. The volatiles of the solution were removed under vacuum to give a white solid. The solid was washed with *n*-pentane (2 mL × 4) and dried under vacuum to give **1** as a white solid (115 mg, 97% yield). The washing solution was combined and evaporated under vacuum to give triphenylmethane as a white solid (72 mg, 98% yield). Single crystals of **1** were obtained by slow diffusion of *n*-pentane into a dichloromethane solution at room temperature.

1: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.41 (d, $^{1}J_{P\text{-}H}$ = 524 Hz, 1H, P*H*), 7.75 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 3H, *o*-tolyl-*H*), 7.54 (m, 3H, *o*-tolyl-*H*), 7.44 (m, 3H, *o*-tolyl-*H*), 7.16 (dd, $^{3}J_{P\text{-}H}$ = 15.2 Hz, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 3H, *o*-tolyl-*H*), 2.51 (s, 9H, *o*-tolyl-*Me*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7 (d, $J_{C\text{-}P}$ = 9.2 Hz), 135.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 134.4 (d, $J_{C\text{-}P}$ = 12.1 Hz), 132.9 (d, $J_{C\text{-}P}$ = 10.7 Hz), 127.9 (d, $J_{C\text{-}P}$ = 13.4 Hz), 113.0 (d, $J_{C\text{-}P}$ = 86.4 Hz) (*o*-tolyl-*C*), 21.0 (d, $J_{C\text{-}P}$ = 8.4 Hz, *o*-tolyl-*Me*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ (ppm) -14.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) -14.2 (d, $^{1}J_{P\text{-}H}$ = 535 Hz). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ (ppm) -0.8 (s). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -150.9 (s). MS (ESI) [M] $C_{21}H_{22}P^{+}$ calc. 305.1454 m/z found 305.1457 m/z. Anal. Calcd for $C_{21}H_{22}BF_4P$: C, 64.31; H, 5.65. Found: C, 63.82; H, 5.58.

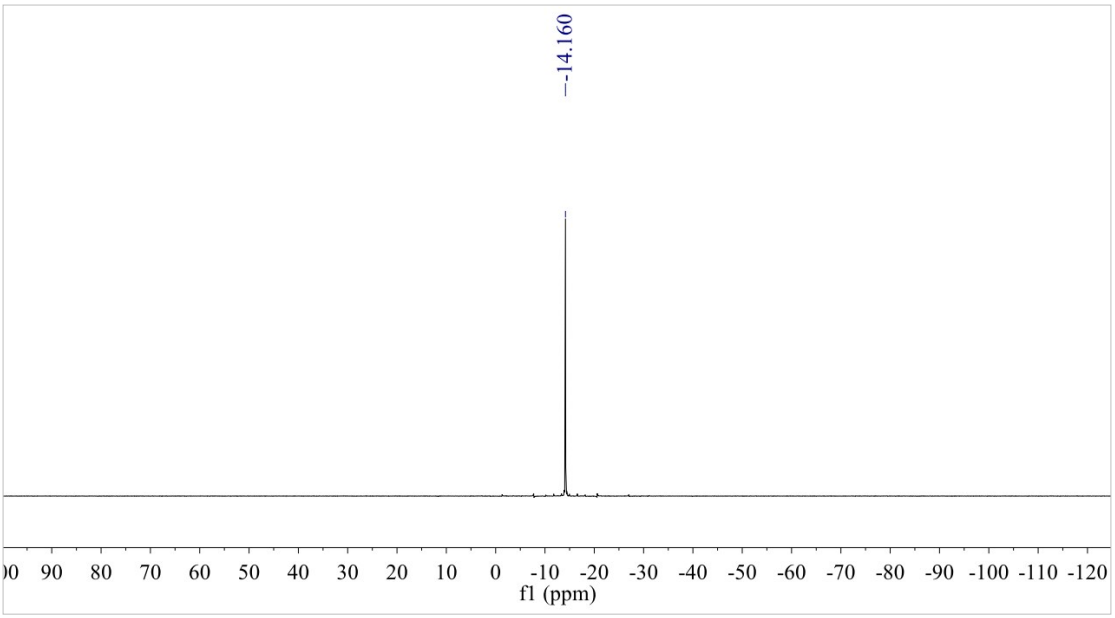
Triphenylmethane: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 6H, Ph-*H*), 7.20 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 3H, Ph-*H*), 9.12 (d, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 6H, Ph-*H*), 5.55 (s, 1H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 144.1, 129.6, 128.4, 126.4 (Ph-*C*), 57.0 (*C*H).



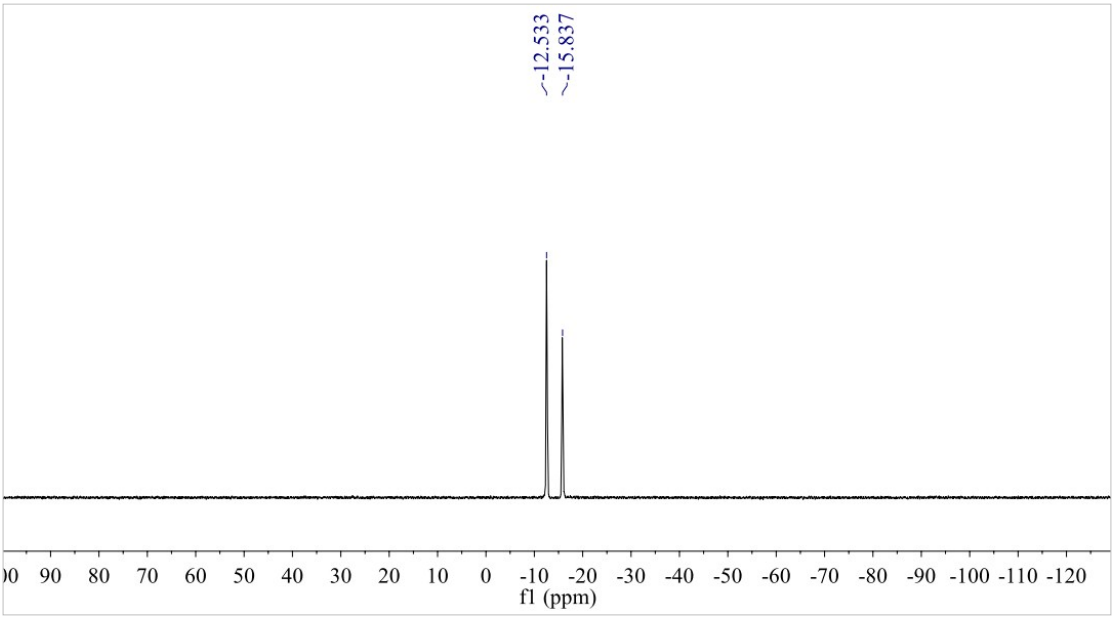
^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$).



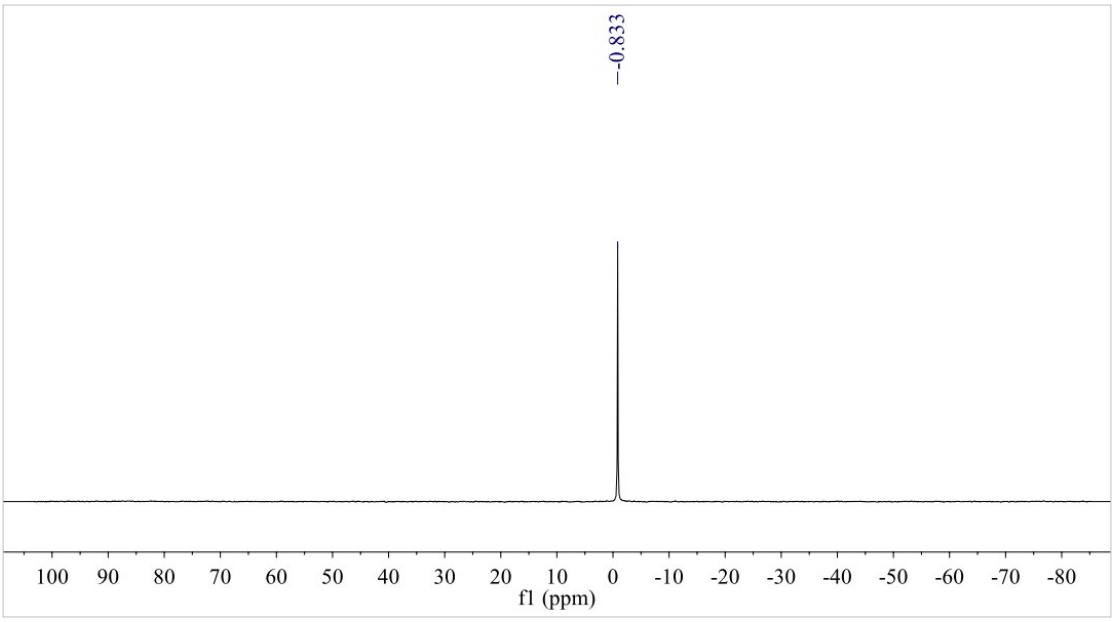
^{13}C{^{1}H} NMR spectrum of **1** (100 MHz, $CDCl_3$).



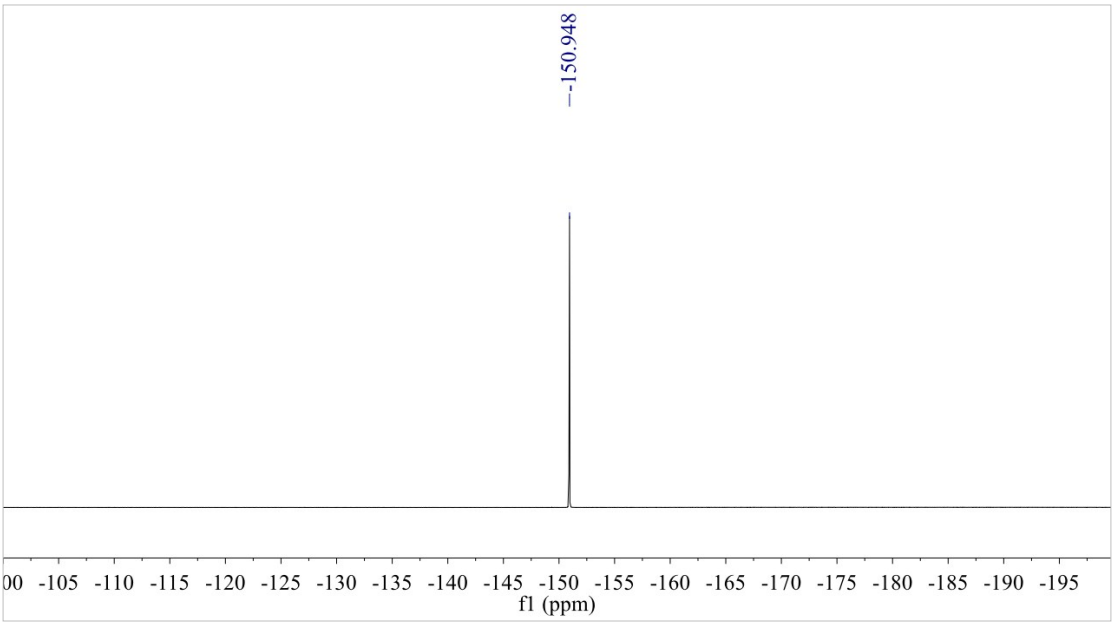
$^{31}P\{^{1}H\}$ NMR spectrum of **1** (162 MHz, $CDCl_3$).



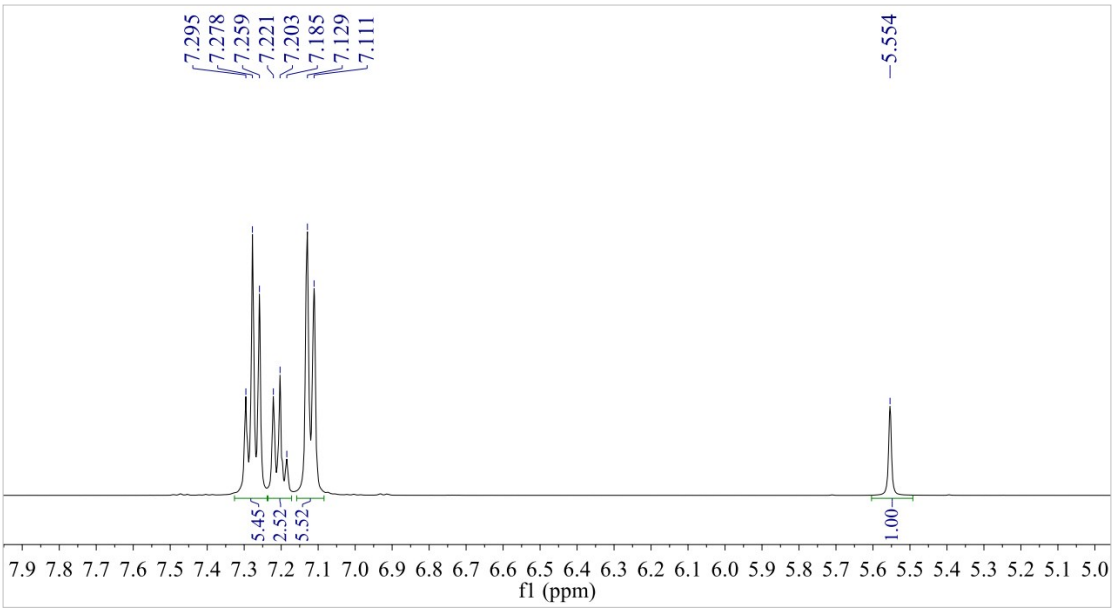
^{31}P NMR spectrum of **1** (162 MHz, $CDCl_3$):



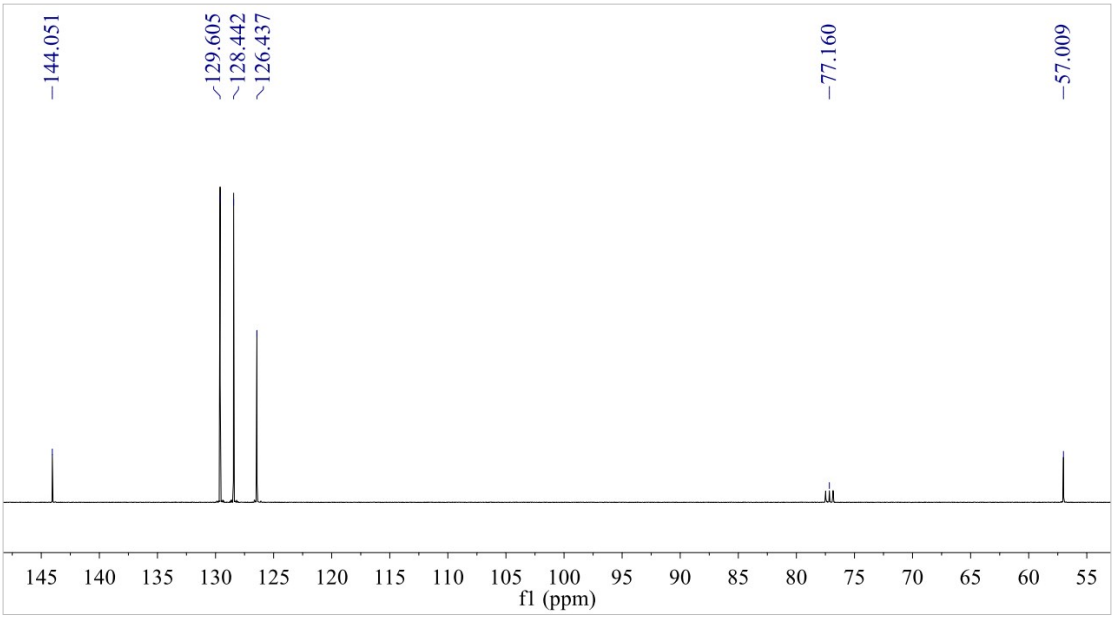
$^{11}B\{^{1}H\}$ NMR spectrum of **1** (128 MHz, $CDCl_3$).



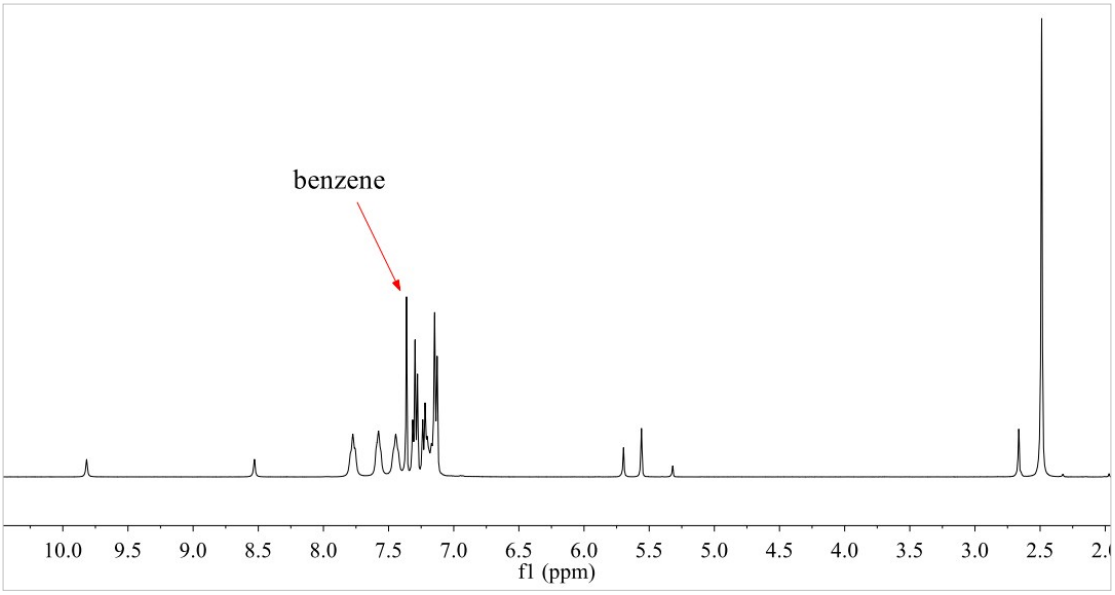
^{19}F NMR spectrum of **1** (377 MHz, $CDCl_3$).



^{1}H NMR spectrum of triphenylmethane (400 MHz, $CDCl_3$).



^{13}C{^{1}H} NMR spectrum of triphenylmethane (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of the reaction at 30 minutes (400 MHz, CD_2Cl_2)

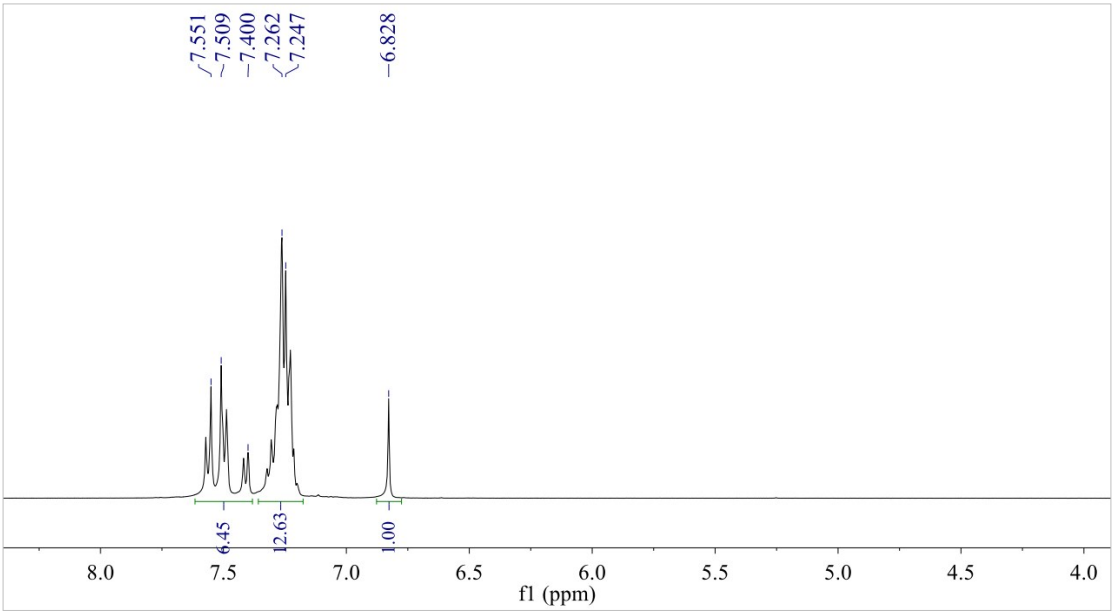
(the proof of formation of benzene):

2.2. The reaction of $[Ph_3C][BF_4]$/P(*o*-tolyl)$_3$ with 1-bromo-4-ethynylbenzene

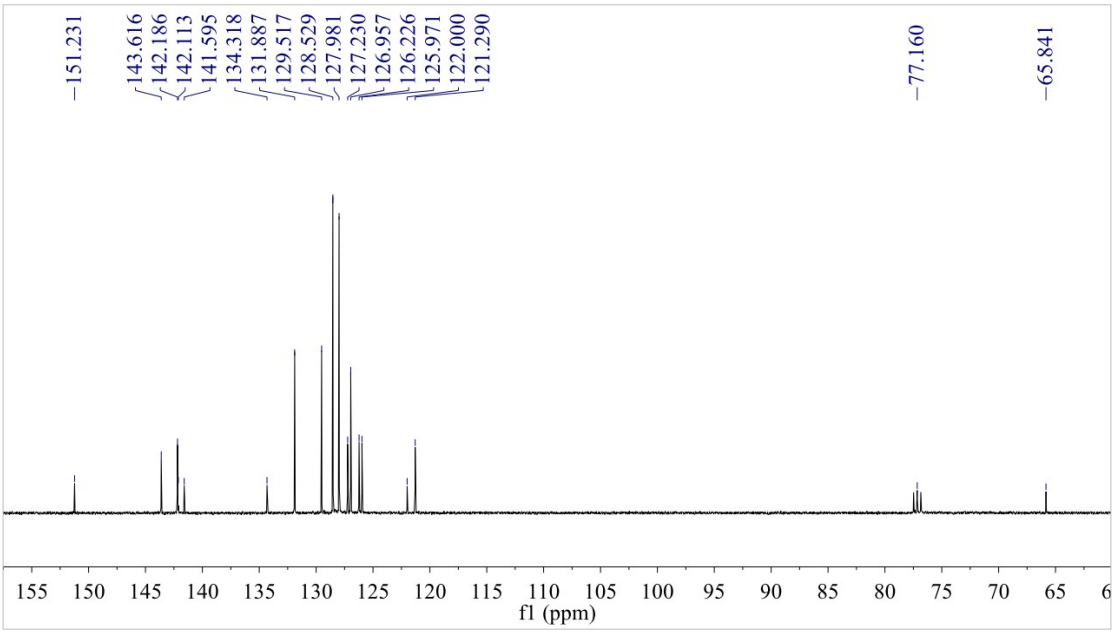
Dichloromethane solution (1 mL) of 1-bromo-4-ethynylbenzene (54 mg, 0.30 mmol) was added to dichloromethane solution (2 mL) of $[Ph_3C][BF_4]$ (99 mg, 0.30 mmol) and P(*o*-tolyl)$_3$ (91 mg, 0.30 mmol), and the solution stood at room temperature for 12 hours. The solution was reduced to 1 mL under vacuum, and 4 mL of *n*-pentane was added with rigorous stirring to give a precipitate. After decanting the supernatant, the precipitate was washed with a solution of dichloromethane and *n*-pentane (1 : 4, 5 mL × 2) and dried under vacuum to give **1** as a white solid (112 mg, 95% yield). The washing solution was combined and evaporated under vacuum to give a pale yellow solid. The solid was extracted with 4 mL of *n*-pentane. The *n*-pentane solution was evaporated under vacuum to give **2a** as a pale yellow solid (121 mg, 95% yield). Single crystals of **2a** were obtained by slow evaporation of an *n*-pentane solution at room temperature.

2a: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62-7.38 (m, 6H, Ar-*H*), 7.36-7.18 (m, 12H, Ar-*H*), 6.83 (s, 1H, vinylic-*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 151.2, 143.6, 142.2, 142.1, 141.6, 134.3, 131.9, 129.5, 128.5, 128.0, 127.2, 127.0,

126.2, 126.0, 122.0, 121.3 (Ar-*C* and vinylic-*C*), 65.8 (*C*Ph_2). MS (DART) [M+H] $C_{27}H_{20}Br^+$ calc. 423.07484 m/z found 423.07399 m/z.



^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$).



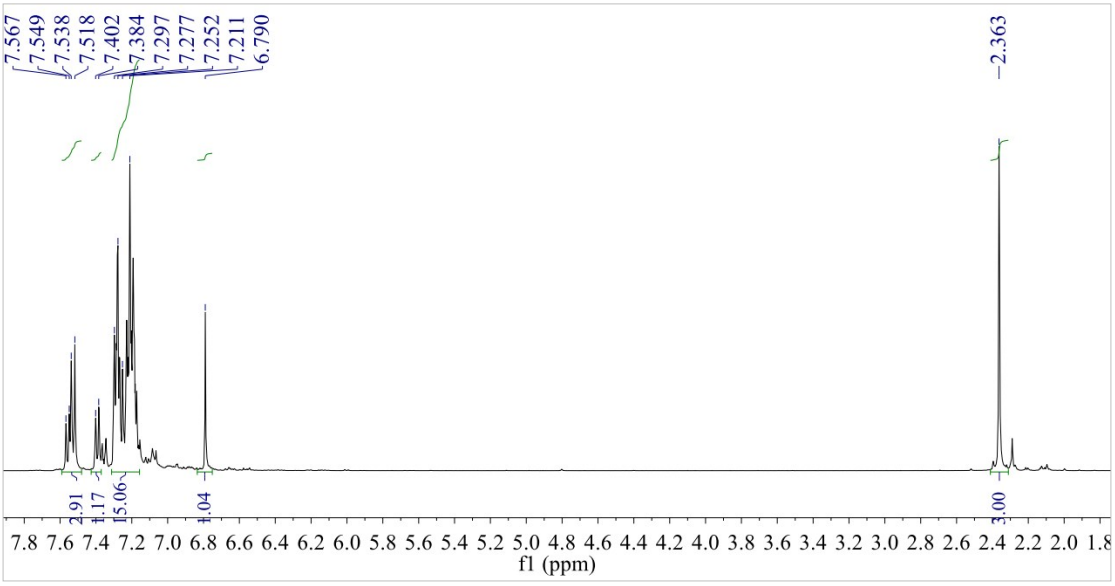
^{13}C{^{1}H} NMR spectrum of **2a** (100 MHz, $CDCl_3$).

2.3. The reaction of $[Ph_3C][BF_4]$/P(*o*-tolyl)$_3$ with 4-ethynyltoluene

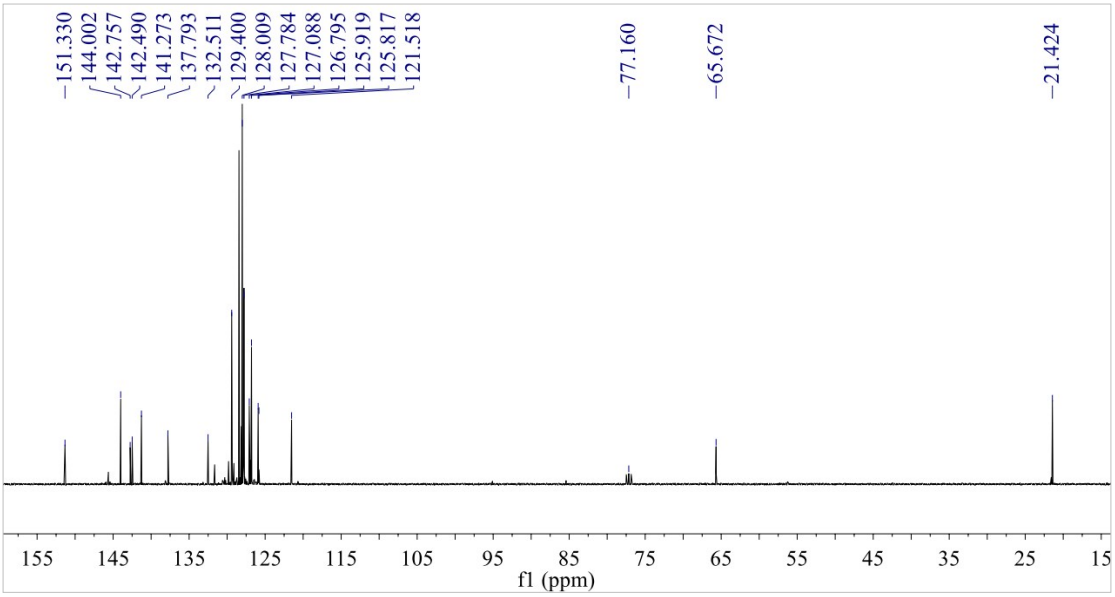
Dichloromethane solution (1 mL) of 4-ethynyltoluene (35 mg, 0.30 mmol) was added

to dichloromethane solution (2 mL) of $[Ph_3C][BF_4]$ (99 mg, 0.30 mmol) and P(*o*-tolyl)$_3$ (91 mg, 0.30 mmol), and the solution stood at room temperature for 2 hours. The solution was reduced to 1 mL under vacuum, and 4 mL of *n*-pentane was added with rigorous stirring to give a precipitate. After decanting the supernatant, the precipitate was washed with a solution of dichloromethane and *n*-pentane (1 : 4, 5 mL × 2) and dried under vacuum to give **1** as a pale yellow solid (108 mg, 92% yield). The washing solution was combined and evaporated under vacuum. The residue was extracted with 2 mL of *n*-pentane. The *n*-pentane solution was evaporated under vacuum to give **2b** with minor impurities as pale yellow oil (105 mg, 98% yield).

2b: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, Ar-*H*), 7.53 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar-*H*), 7.39 (d, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, Ar-*H*), 7.31-7.16 (m, 14H, Ar-*H*), 6.79 (s, 1H, vinylic-*H*), 2.36 (s, 3H, *Me*),. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 151.3, 144.0, 142.8, 142.5, 141.3, 137.8, 132.5, 129.4, 128.4, 128.0, 127.8, 127.1, 126.8, 125.9, 125.8, 121.5 (Ar-*C* and vinylic-*C*), 65.7 (*C*Ph$_2$), 21.4 (*Me*). MS (DART) [M+H] $C_{28}H_{23}^+$ calc. 359.17998 m/z found 359.17974 m/z.



^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$).



$^{13}C\{^{1}H\}$ NMR spectrum of **2b** (100 MHz, $CDCl_3$).

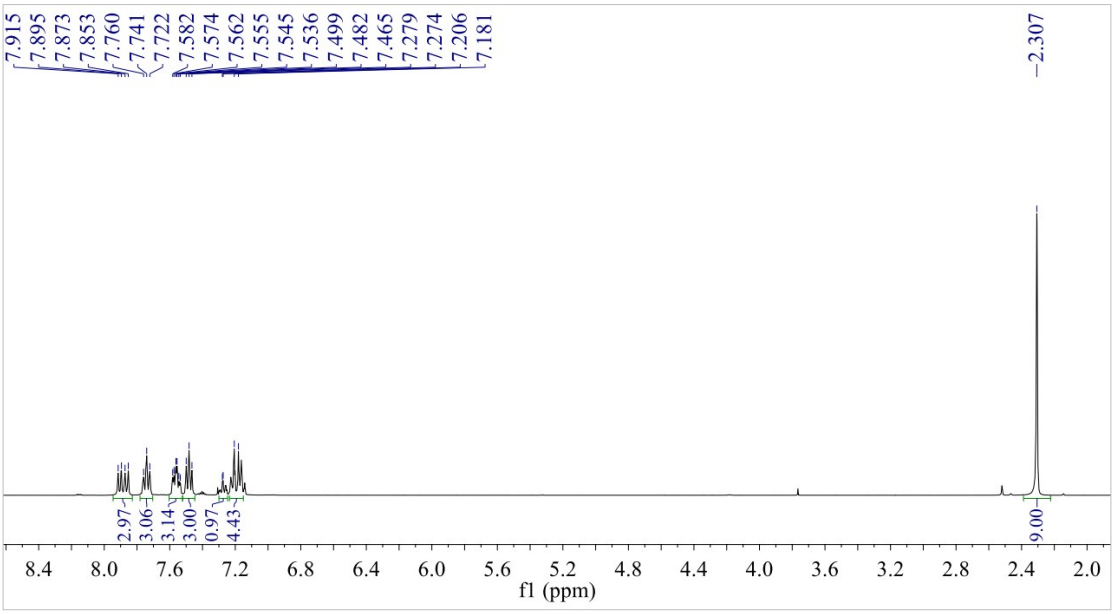
2.4. The reaction of $[Ph_3C][BF_4]$/P(*o*-tolyl)$_3$ with diphenyl disulfide

Dichloromethane solution (2 mL) of diphenyl disulfide (66 mg, 0.30 mmol) was added to dichloromethane solution (2 mL) of $[Ph_3C][BF_4]$ (99 mg, 0.30 mmol) and P(*o*-tolyl)$_3$ (91 mg, 0.30 mmol), and the solution stood at room temperature for 12 hours. The solution was reduced to 1 mL under vacuum, and 4 mL of *n*-pentane was added with rigorous stirring to give a precipitate. After decanting the supernatant, the precipitate was washed with *n*-pentane (4 mL × 3) and dried under vacuum to give **3** as a pale yellow solid (120 mg, 80% yield). The washing solution was combined and evaporated under vacuum to give a pale yellow solid. The solid was recrystallized in *n*-pentane solution at -30 ^{o}C to give pale yellow crystals, and the crystals were dried under vacuum to give triphenylmethyl phenyl sulfide as a pale yellow solid (54 mg, 51% yield). Single crystals of **3** were obtained by slow diffusion of *n*-pentane into a dichloromethane solution at room temperature.

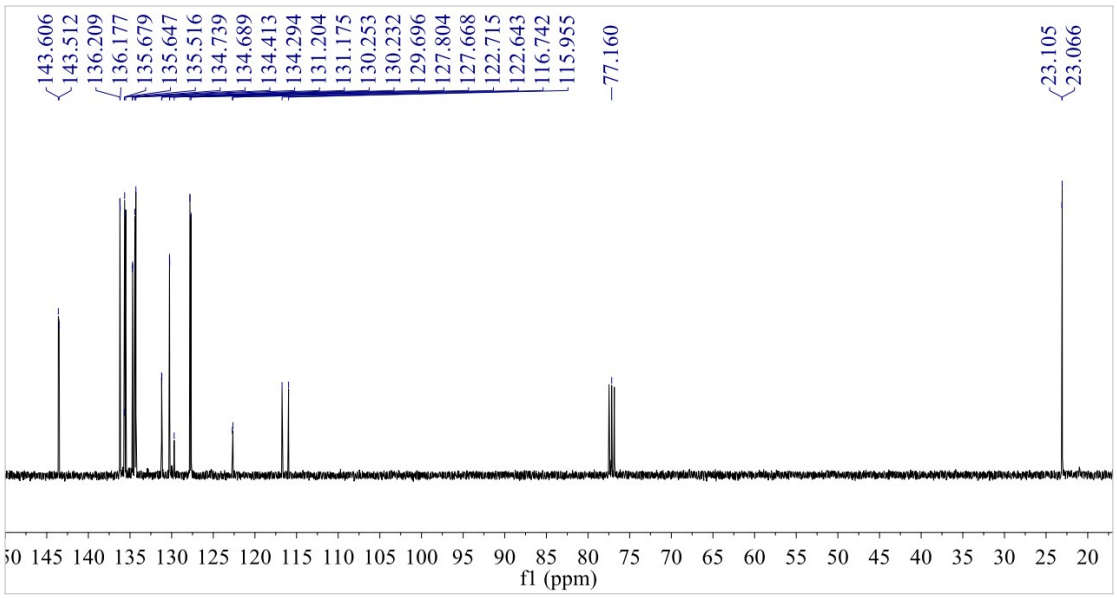
3: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (dd, $^{3}J_{P\text{-}H}$ = 16.8 Hz, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 3H, *o*-tolyl-*H*), 7.74 (tt, $^{3}J_{H\text{-}H}$ = 7.6 Hz, *J* = 1.6 Hz, 3H, *o*-tolyl-*H*), 7.56 (td, $^{3}J_{H\text{-}H}$ = 7.6 Hz, *J* = 3.2 Hz, 3H, *o*-tolyl-*H*), 7.48 (t, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 3H, *o*-tolyl-*H*), 7.28 (m, 1H, Ph-*H*), 7.19 (m, 4H, Ph-*H*), 2.31 (s, 9H, *o*-tolyl-*Me*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ

(ppm) 143.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 136.2 (d, $J_{C\text{-}P}$ = 3.2 Hz), 135.7 (s), 135.6 (d, $J_{C\text{-}P}$ = 13.1 Hz), 134.7 (d, $J_{C\text{-}P}$ = 5.0 Hz), 134.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.2 (d, $J_{C\text{-}P}$ = 2.1 Hz), 129.7 (s), 127.7 (d, $J_{C\text{-}P}$ = 13.6 Hz), 122.7 (d, $J_{C\text{-}P}$ = 7.2 Hz), 116.3 (d, $J_{C\text{-}P}$ = 78.7 Hz) (*o*-tolyl-*C* and Ph-*C*), 23.1 (d, $J_{C\text{-}P}$ = 3.9 Hz, *o*-tolyl-*Me*). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ (ppm) 51.0 (s). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ (ppm) -0.8 (s). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -150.9 (s). MS (ESI) [M] $C_{27}H_{26}PS^{+}$ calc. 413.1487 m/z found 413.1491 m/z. Anal. Calcd for $C_{27}H_{26}BF_4PS$: C, 64.82; H, 5.24. Found: C, 64.34; H, 4.83.

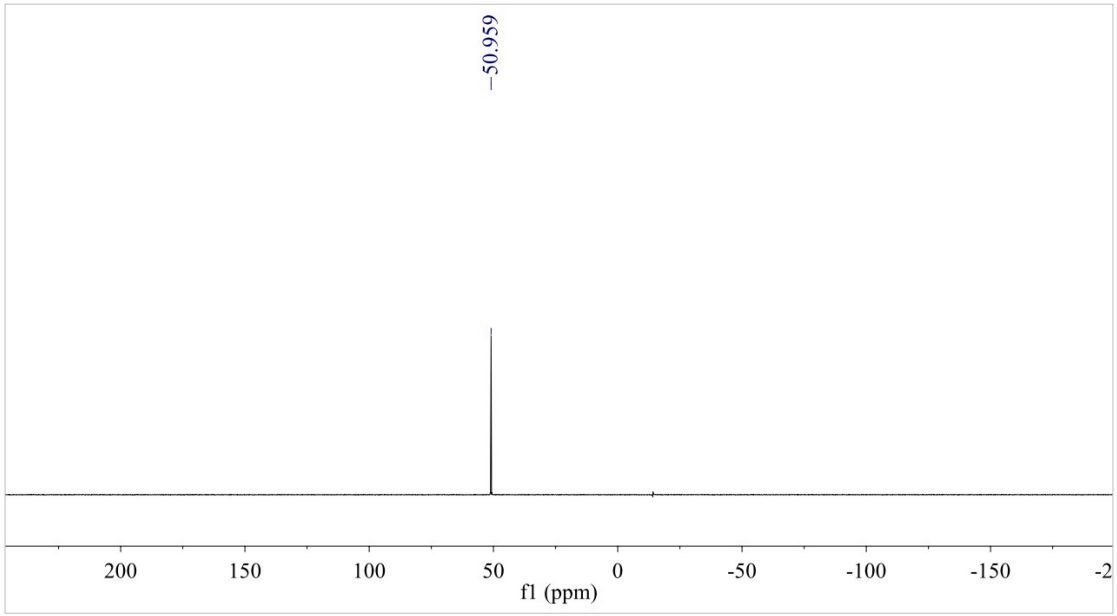
Triphenylmethyl phenyl sulfide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 6H, *Ph*$_3$C), 7.20 (m, 9H, *Ph*$_3$C), 7.08 (m. 1H, *Ph*S), 6.97 (m, 4H, *Ph*S). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 134.6, 130.1, 128.2, 127.8, 127.7, 126.8 (Ph-*C*), 70.9 (Ph$_3$*C*).



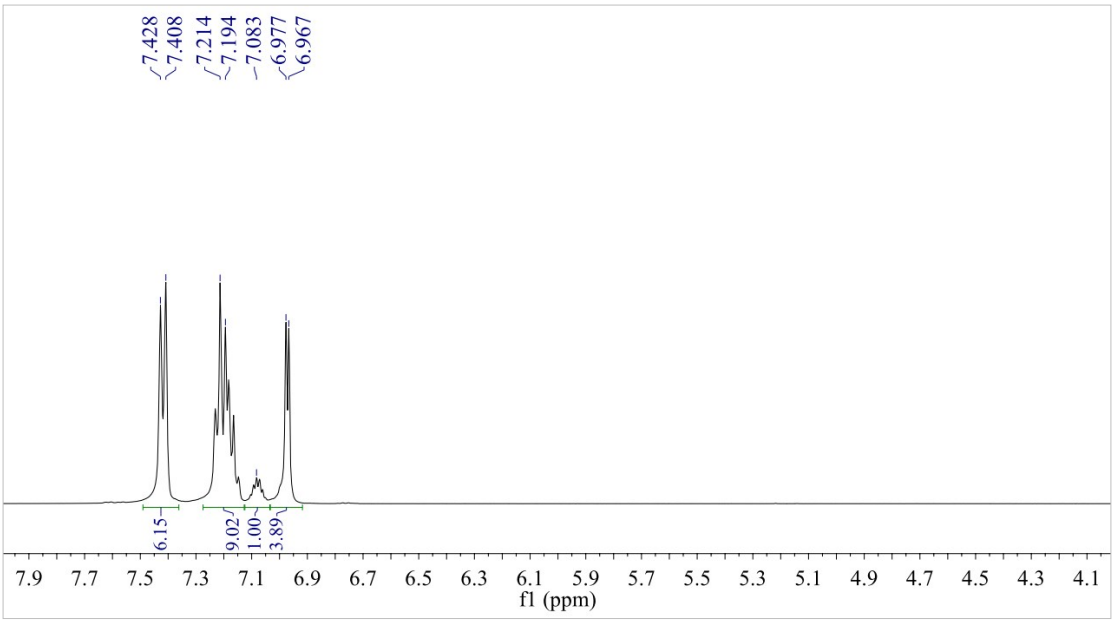
^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).



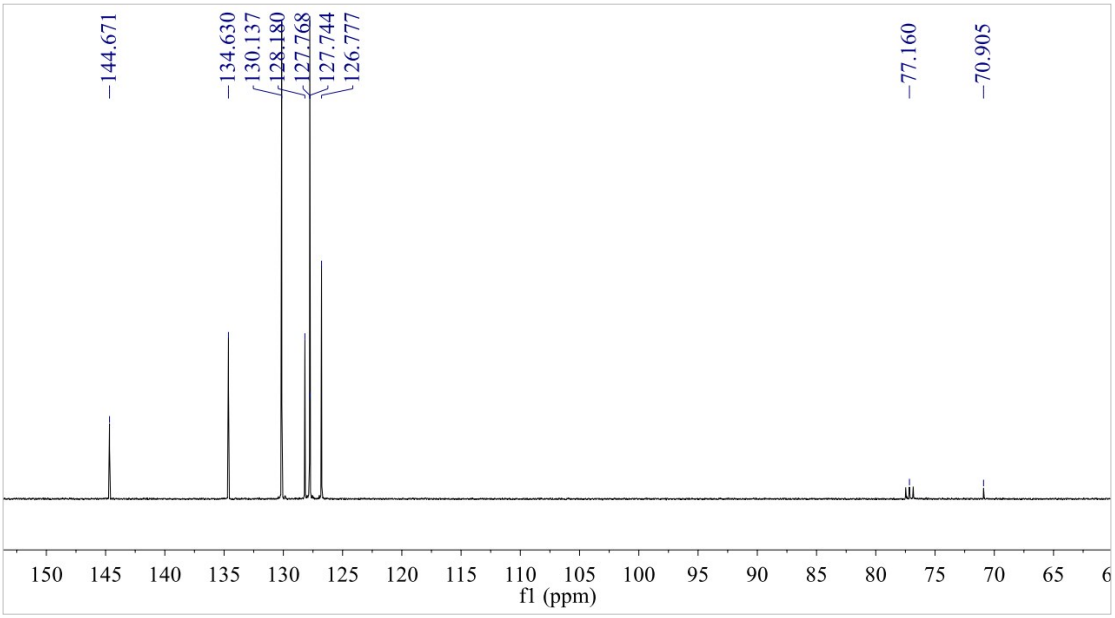
$^{13}C\{^{1}H\}$ NMR spectrum of **3** (100 MHz, $CDCl_3$).



$^{31}P\{^{1}H\}$ NMR spectrum of **3** (162 MHz, $CDCl_3$).



^{1}H NMR spectrum of triphenylmethyl phenyl sulfide (400 MHz, $CDCl_3$).



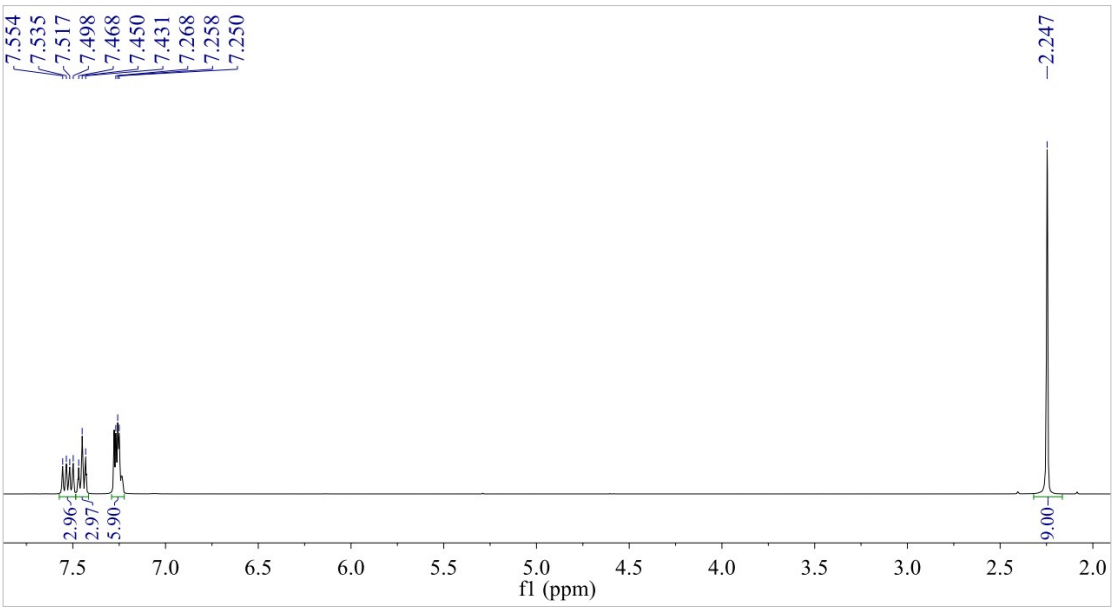
^{13}C{^{1}H} NMR spectrum of triphenylmethyl phenyl sulfide (100 MHz, $CDCl_3$).

2.5. The reaction of P(*o*-tolyl)$_3$ with pentafluorophenyl azide

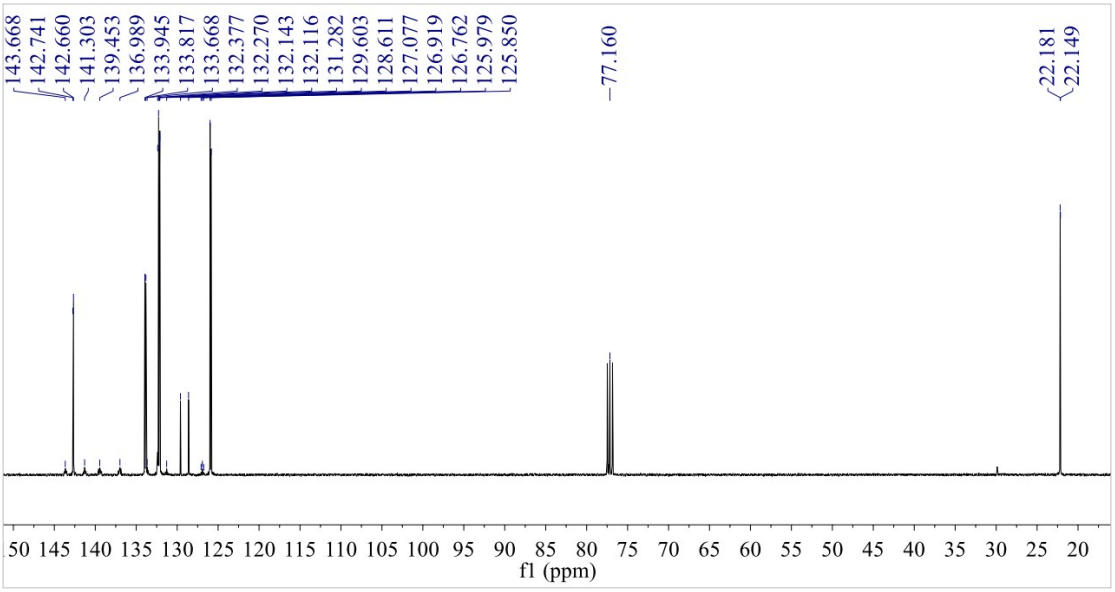
Toluene solution (2 mL) of pentafluorophenyl azide (115 mg, 0.55 mmol) was added to toluene solution (2 mL) of P(*o*-tolyl)$_3$ (152 mg, 0.50 mmol), and the solution was stirred at 100 ^{o}C for 24 hours. The volatiles of the solution were removed under vacuum and the residue was purified by silica gel column chromatography to afford **5**

as a pale yellow solid (150 mg, 62% yield).

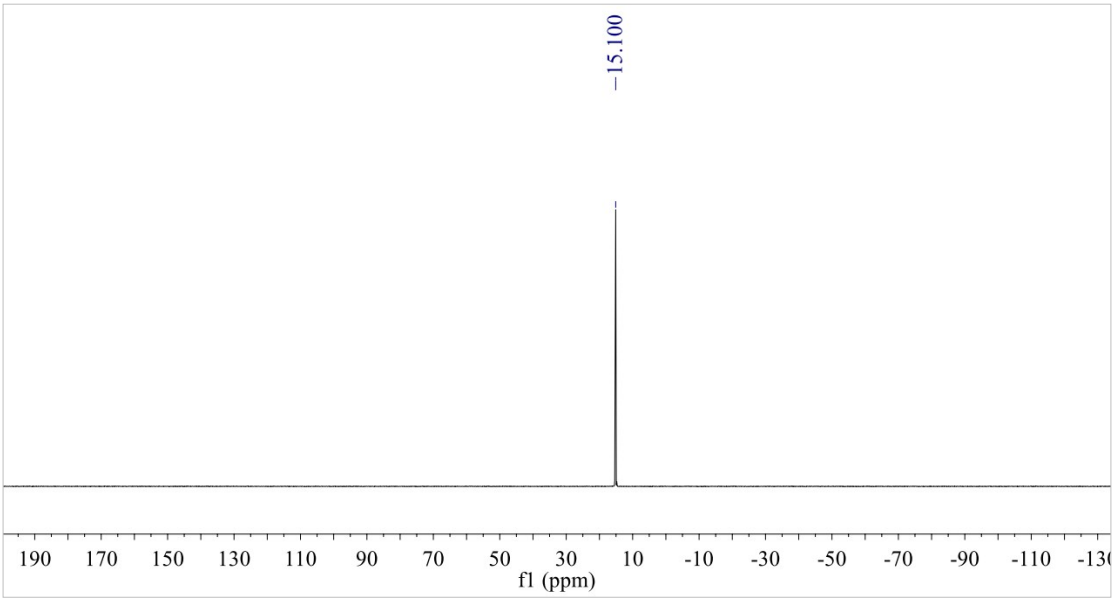
4: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53 (dd, $^{3}J_{P\text{-}H}$ = 14.8 Hz, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 3H, *o*-tolyl-*H*), 7.54 (tt, $^{3}J_{H\text{-}H}$ = 7.6 Hz, *J* = 1.6 Hz, 3H, *o*-tolyl-*H*), 7.26 (m, 6H, *o*-tolyl-*H*), 2.25 (s, 9H, *o*-tolyl-*Me*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 142.7 (d, $J_{C\text{-}P}$ = 8.1 Hz, *o*-tolyl-*C*), 142.5 (d(br), $^{1}J_{C\text{-}F}$ = 237 Hz, C_6F_5), 138.2 (d(br), $^{1}J_{C\text{-}F}$ = 246 Hz, C_6F_5), 133.9 (d, $J_{C\text{-}P}$ = 12.8 Hz, *o*-tolyl-*C*), 132.5 (d(br), $^{1}J_{C\text{-}F}$ = 239 Hz, C_6F_5), 132.3 (d, $J_{C\text{-}P}$ = 10.7 Hz, *o*-tolyl-*C*), 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz, *o*-tolyl-*C*), 129.1 (d, $J_{C\text{-}P}$ = 99.2 Hz, *o*-tolyl-*C*), 126.9 (t(br), $^{1}J_{C\text{-}F}$ = 15.8 Hz, C_6F_5), 125.9 (d, $J_{C\text{-}P}$ = 12.9 Hz, *o*-tolyl-*C*), 22.1 (d, $J_{C\text{-}P}$ = 3.2 Hz, *o*-tolyl-*Me*). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ (ppm) 15.1 (s). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -154.2 (m, 2F, C_6F_5), -167.3 (m, 2F, C_6F_5), -175.6 (tt, $^{3}J_{F\text{-}F}$ = 22.2 Hz, $^{4}J_{F\text{-}F}$ = 7.5 Hz, 1F, C_6F_5). MS (ESI) [M+H] $C_{27}H_{22}F_5NP^+$ calc. 486.14100 m/z found 486.14139 m/z.



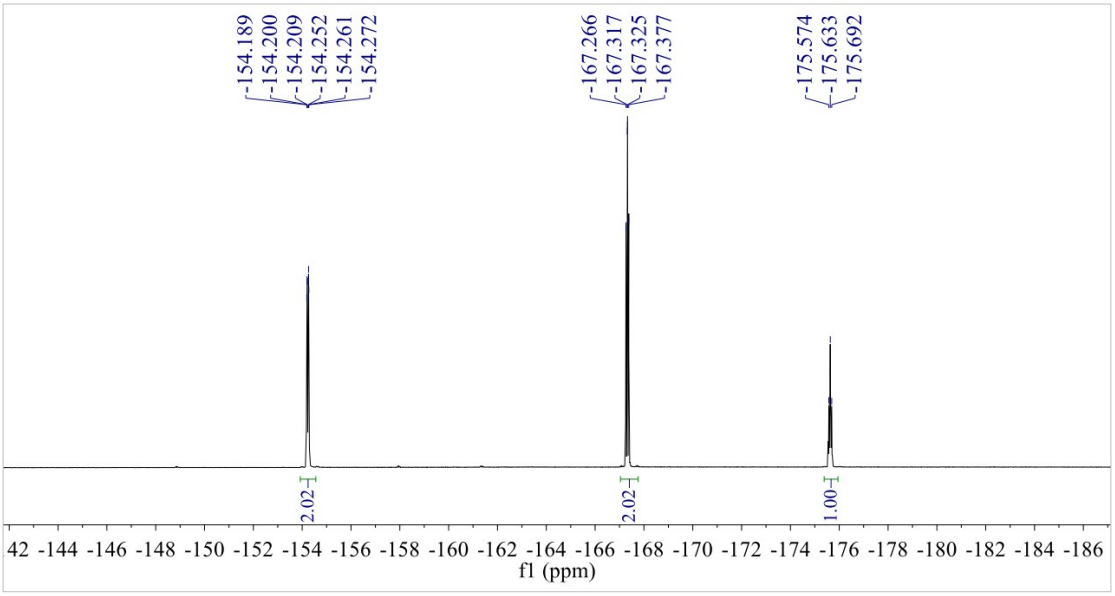
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).



$^{13}C\{^{1}H\}$ NMR spectrum of **5** (100 MHz, $CDCl_3$).



$^{31}P\{^{1}H\}$ NMR spectrum of **5** (162 MHz, $CDCl_3$).



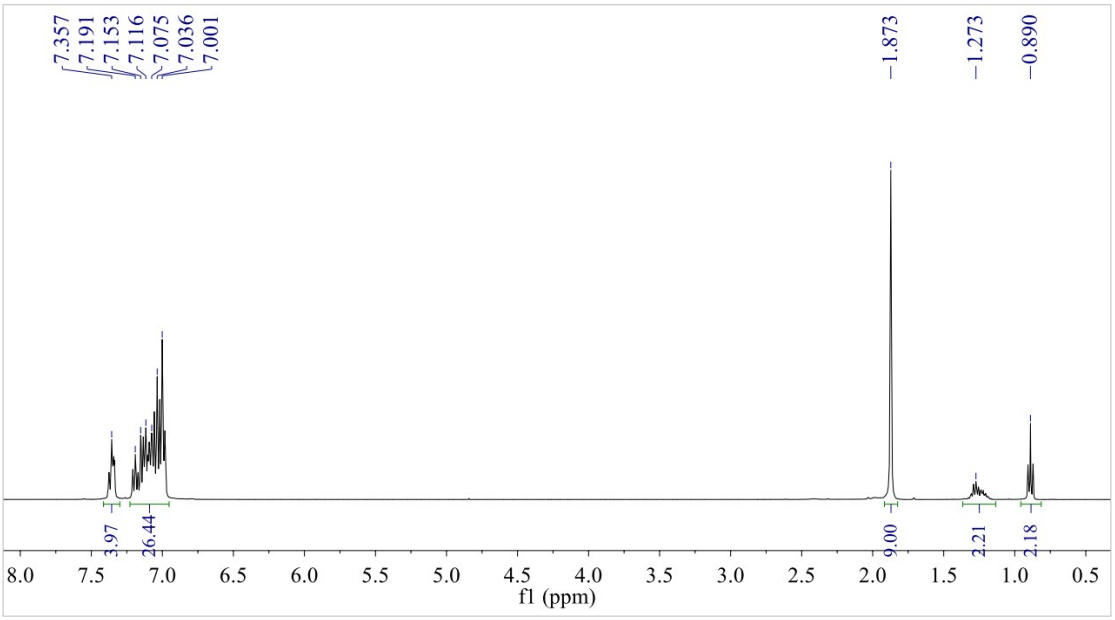
^{19}F NMR spectrum of **5** (377 MHz, $CDCl_3$).

2.6. The reaction of $[Ph_3C][B(C_6F_5)_4]$/P(*o*-tolyl)$_3$ with pentafluorophenyl azide

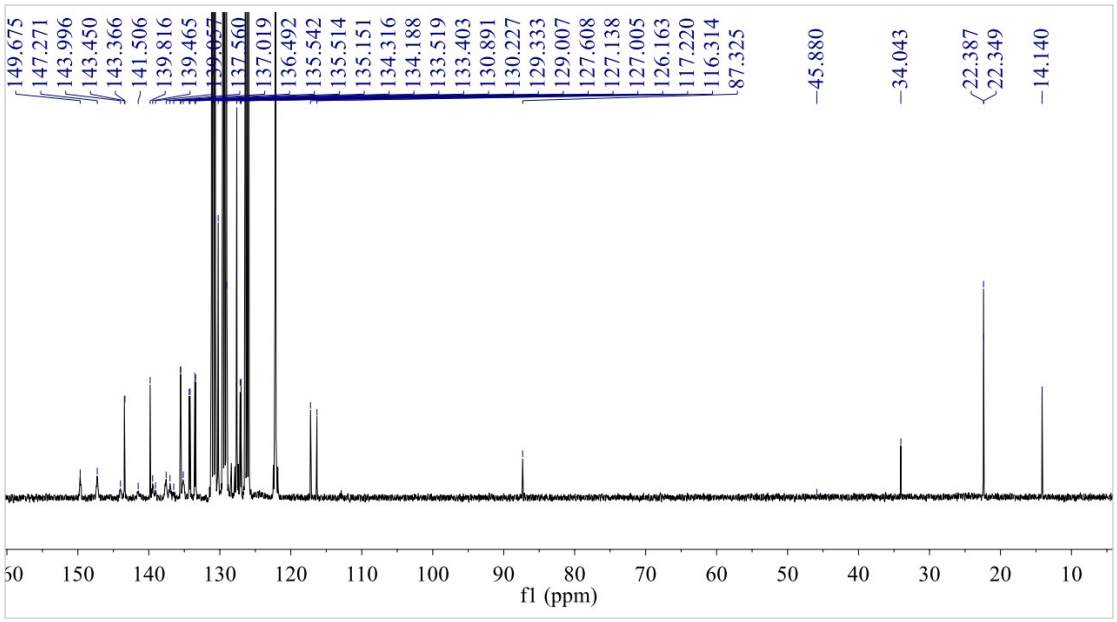
Dichloromethane solution (1 mL) of pentafluorophenyl azide (38 mg, 0.18 mmol) was added to dichloromethane solution (3 mL) of $[Ph_3C][B(C_6F_5)_4]$ (138 mg, 0.15 mmol), and P(*o*-tolyl)$_3$ (46 mg, 0.15 mmol), and the solution stood at room temperature for 12 hours. The solution was reduced to 2 mL under vacuum, and 4 mL of *n*-pentane was added with rigorous stirring to give a precipitate. After decanting the supernatant, the precipitate was washed with 4 mL of *n*-pentane and dried under vacuum to give **5**·0.5pentane as a pale yellow solid (218 mg, 99% yield). Single crystals of **5**·CH_2Cl_2 were obtained by slow diffusion of *n*-pentane into a dichloromethane solution at room temperature.

5·0.5pentane: ^{1}H NMR (400 MHz, C_6D_5Br): δ (ppm) 7.36 (m, 4H, Ar-*H*), 7.23-6.96 (m, overlap with C_6D_5Br signals, Ar-*H*), 1.87 (s, 9H, *o*-tolyl-*Me*), 1.27 (m, 3H, *n*-pentane-CH_2), 0.89 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, *n*-pentane-CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): 148.5 (d(br), $^1J_{C\text{-}F}$ = 240 Hz, C_6F_5), 143.4 (d, $J_{C\text{-}P}$ = 8.4 Hz, *o*-tolyl-*C*), 142.8 (d(br), $^1J_{C\text{-}F}$ = 249 Hz, C_6F_5), 139.8 (s, Ph-*C*), 138.2 (d(br), $^1J_{C\text{-}F}$ = 245 Hz, C_6F_5), 137.8 (d(br), $^1J_{C\text{-}F}$ = 257 Hz, C_6F_5), 136.4 (d(br), $^1J_{C\text{-}F}$ = 241 Hz, C_6F_5), 135.5 (d, $J_{C\text{-}P}$ = 2.8 Hz, *o*-tolyl-*C*), 134.3 (d, $J_{C\text{-}P}$ = 12.8 Hz, *o*-tolyl-*C*), 133.5 (d, $J_{C\text{-}P}$ = 11.6 Hz, *o*-

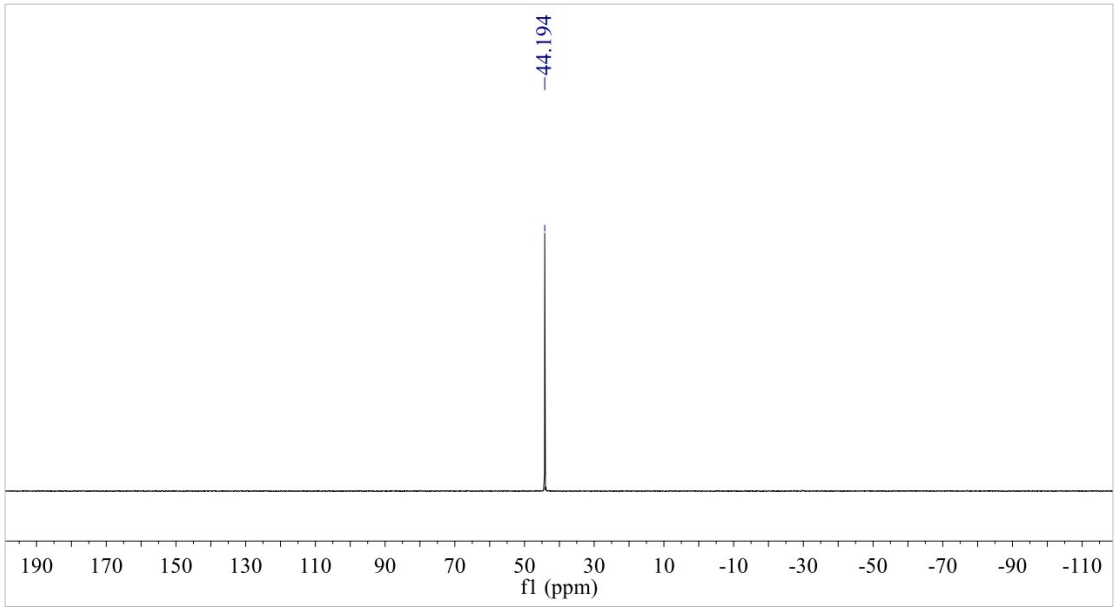
tolyl-*C*), 130.2 (s, Ph-*C*), 129.0 (s, Ph-*C*), 127.6 (s, Ph-*C*), 127.1 (d, $J_{C\text{-}P}$ = 13.3 Hz, *o*-tolyl-*C*), 116.8 (d, $J_{C\text{-}P}$ = 90.6 Hz, *o*-tolyl-*C*), 87.3 (s, Ph_3C), 34.0 (s, *n*-pentane-*C*), 22.4 (s, *o*-tolyl-*Me*), 22.3 (s, *n*-pentane-*C*), 14.1 (s, *n*-pentane-*C*). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_5Br): δ (ppm) 44.2 (s). ^{19}F NMR (377 MHz, C_6D_5Br): δ (ppm) -131.6 (d, $^3J_{F\text{-}F}$ = 10.6 Hz, 8F, $B(C_6F_5)_4$), -136.8 (d, $^3J_{F\text{-}F}$ = 20.0 Hz, 2F, NC_6F_5), -145.5 (t, $^3J_{F\text{-}F}$ = 22.2 Hz, 1F, NC_6F_5), -159.0 (t, $^3J_{F\text{-}F}$ = 20.7, 2F, NC_6F_5), -162.2 (t, $^3J_{F\text{-}F}$ = 21.1 Hz, 4F, $B(C_6F_5)_4$), -166.0 (t, $^3J_{F\text{-}F}$ = 18.5 Hz, 8F, $B(C_6F_5)_4$). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_5Br): δ (ppm) -16.1 (s). MS (ESI) [M] $C_{46}H_{36}F_5N_3P^+$ calc. 756.2562 m/z found 756.2559 m/z. Anal. Calcd for $C_{70}H_{36}BF_{25}N_3P \cdot 0.5$pentane: C, 59.16; H, 2.88; N, 2.85. Found: C, 59.68; H, 2.61; N, 2.59.



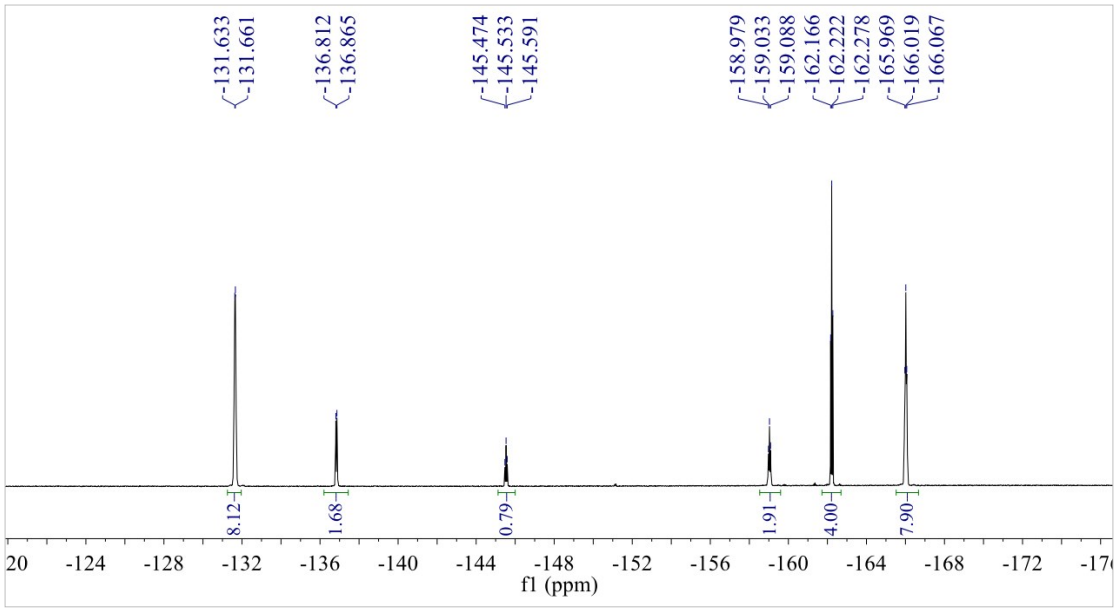
^1H NMR spectrum of **4** (400 MHz, C_6D_5Br).



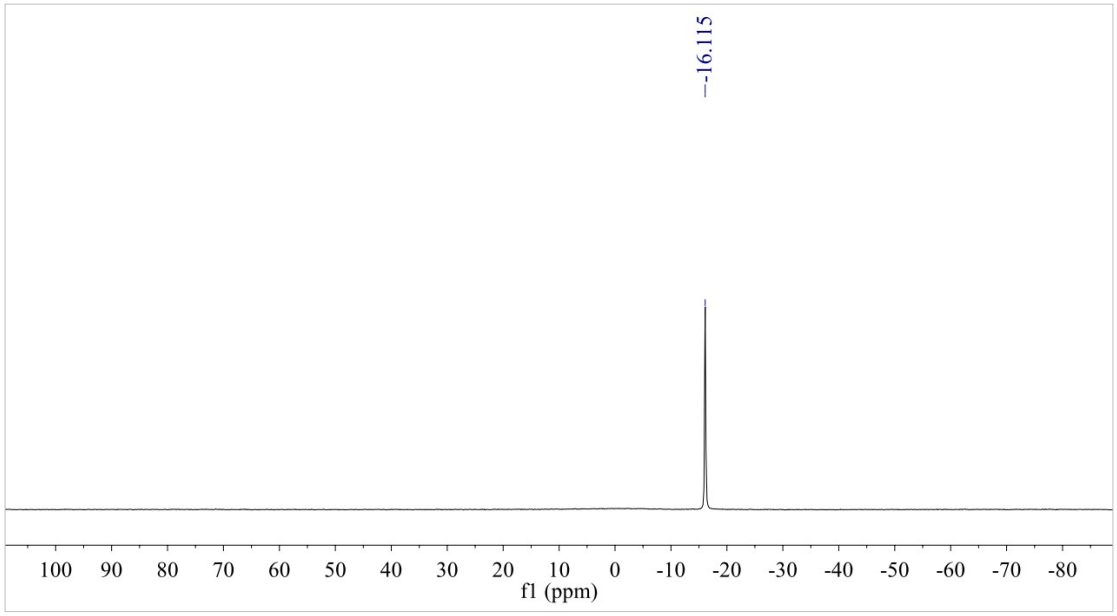
$^{13}C\{^{1}H\}$ NMR spectrum of **4** (100 MHz, C_6D_5Br).



$^{31}P\{^{1}H\}$ NMR spectrum of **4** (162 MHz, C_6D_5Br).



^{19}F NMR spectrum of **4** (377 MHz, C_6D_5Br):



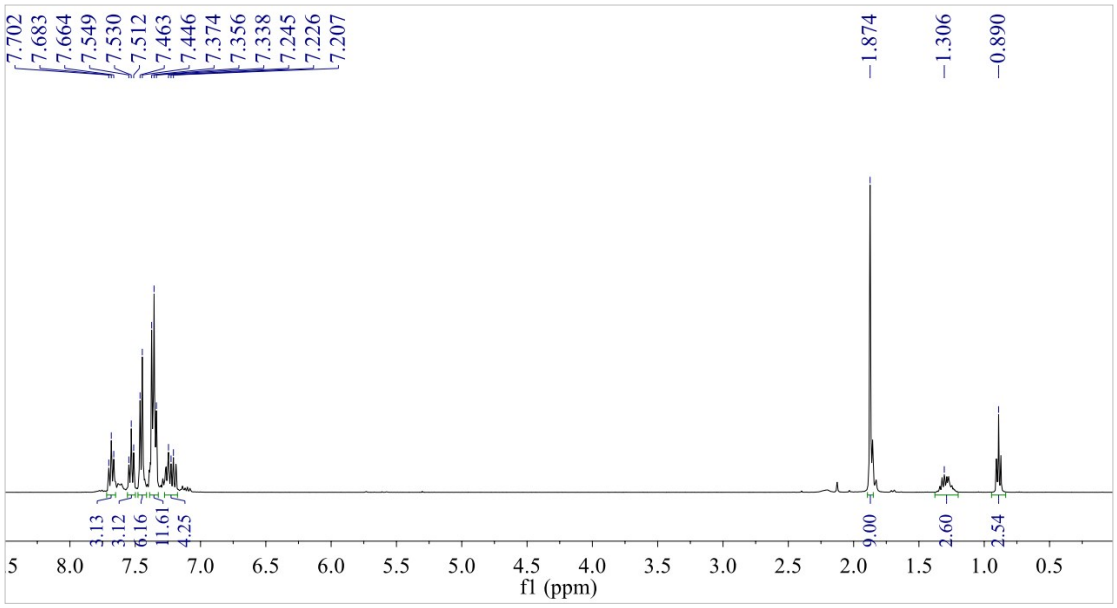
^{11}B{^{1}H} NMR spectrum of **4** (128 MHz, C_6D_5Br).

2.7. The reaction of 5 with triphenylsilane

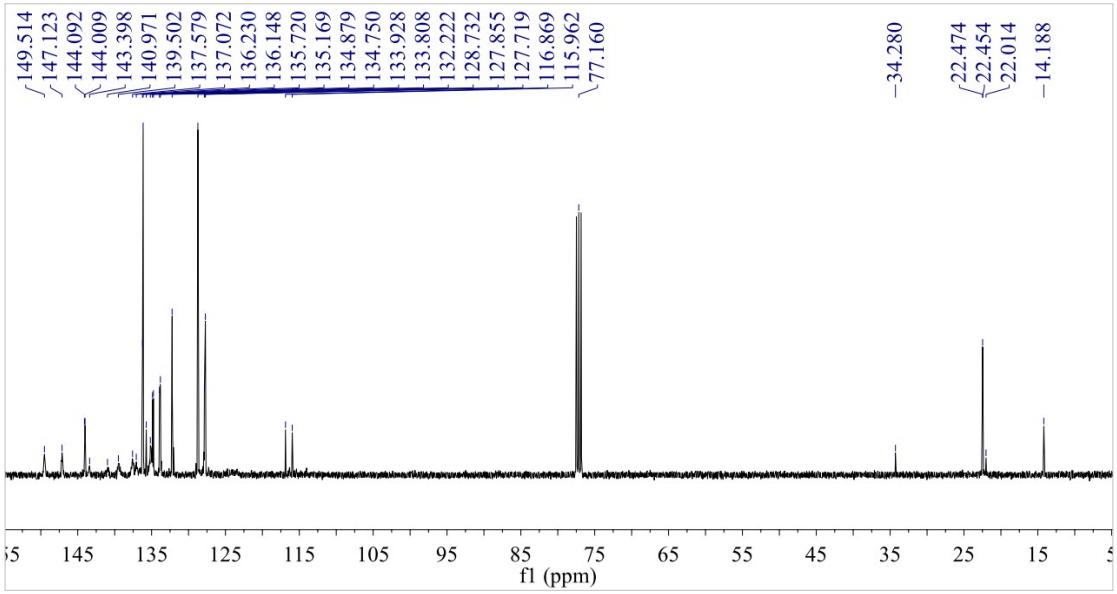
Chlorobenzene solution (1 mL) of triphenylsilane (26 mg, 0.10 mmol) was added to chlorobenzene suspension (1 mL) of **5**·0.5pentane (147 mg, 0.10 mmol), and the mixture was stirred at room temperature for 1 hour. The solution was reduced to 1 mL under vacuum, and 4 mL of *n*-pentane was added with rigorous stirring to give a

precipitate. After decanting the supernatant, the precipitate was washed with *n*-pentane (4 mL × 2) and dried under vacuum to give a white solid in which **6**·0.5pentane is the dominant product (138 mg, 93% yield). It is hard to remove some impurities in the solid even by recrystallization. Single crystals of **6**·0.5hexane were obtained by slow diffusion of *n*-hexane into a chlorobenzene solution at room temperature.

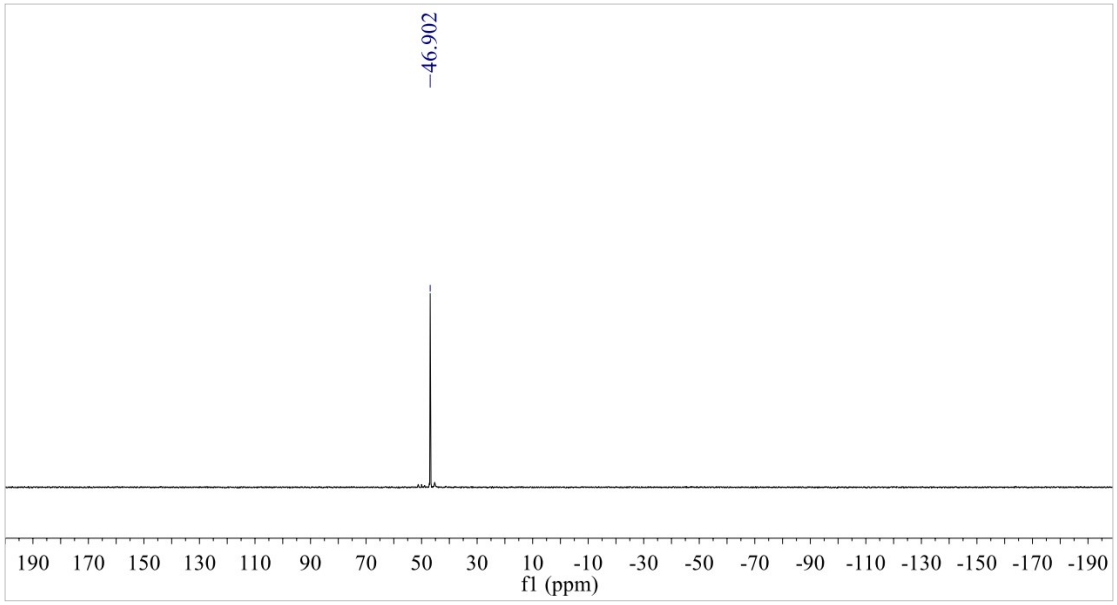
6·0.5pentane: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 3H, Ar-*H*), 7.53 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 3H, Ar-*H*), 7.45 (m, 6H, Ar-*H*), 7.36 (m, 11H, Ar-*H*), 7.23 (m, 4H, Ar-*H*), 1.87 (s, 9H, *o*-tolyl-*Me*), 1.31 (m, 3H, *n*-pentane-CH_2), 0.89 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 3H, *n*-pentane-CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 148.3 (d(br), $^{1}J_{C\text{-}F}$ = 239 Hz, C_6F_5), 144.0 (d, $J_{C\text{-}P}$ = 8.3 Hz, *o*-tolyl-*C*), 142.2 (d(br), $^{1}J_{C\text{-}F}$ = 243 Hz, C_6F_5), 138.3, (d(br), $^{1}J_{C\text{-}F}$ = 243 Hz, C_6F_5), 137.6 (br, C_6F_5), 136.2 (d, $J_{C\text{-}P}$ = 8.2 Hz, *o*-tolyl-*C*), 136.1 (s, Ph-*C*), 135.2 (br, C_6F_5), 134.8 (d, $J_{C\text{-}P}$ = 12.9 Hz, *o*-tolyl-*C*), 133.9 (d, $J_{C\text{-}P}$ = 12.0 Hz, *o*-tolyl-*C*), 132.2 (s, Ph-*C*), 128.7 (s, Ph-*C*), 127.8 (d, $J_{C\text{-}P}$ = 13.6 Hz, *o*-tolyl-*C*), 127.7 (s, Ph-*C*), 116.4 (d, $J_{C\text{-}P}$ = 90.7 Hz, *o*-tolyl-*C*), 34.3 (s, *n*-pentane-*C*), 22.5 (d, $J_{C\text{-}P}$ = 2.0 Hz, *o*-tolyl-*Me*), 22.0 (s, *n*-pentane-*C*), 14.2 (s, *n*-pentane-*C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ (ppm) 46.9 (s). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -132.6 (m, 8F, B(C_6F_5)$_4$), -141.0 (d, $^{3}J_{F\text{-}F}$ = 18.9 Hz, 2F, NC$_6F_5$), -148.3 (t, $^{3}J_{F\text{-}F}$ = 21.5 Hz, 1F, NC$_6F_5$), -159.5 (m, 2F, NC$_6F_5$), -163.3 (t, $^{3}J_{F\text{-}F}$ = 20.7 Hz, 4F, B(C_6F_5)$_4$), -167.0 (m, 8F, B(C_6F_5)$_4$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ (ppm) -16.6 (s). ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): δ (ppm) -3.5 (s). MS (ESI) [Ph_3Si] $C_{18}H_{15}Si^+$ calc. 259.0938 m/z found 259.0944 m/z, and [($C_6F_5N_3P$(*o*-tolyl)$_3$+H] $C_{27}H_{22}F_5N_3P^+$ calc. 514.1466 m/z found 514.1466 m/z.



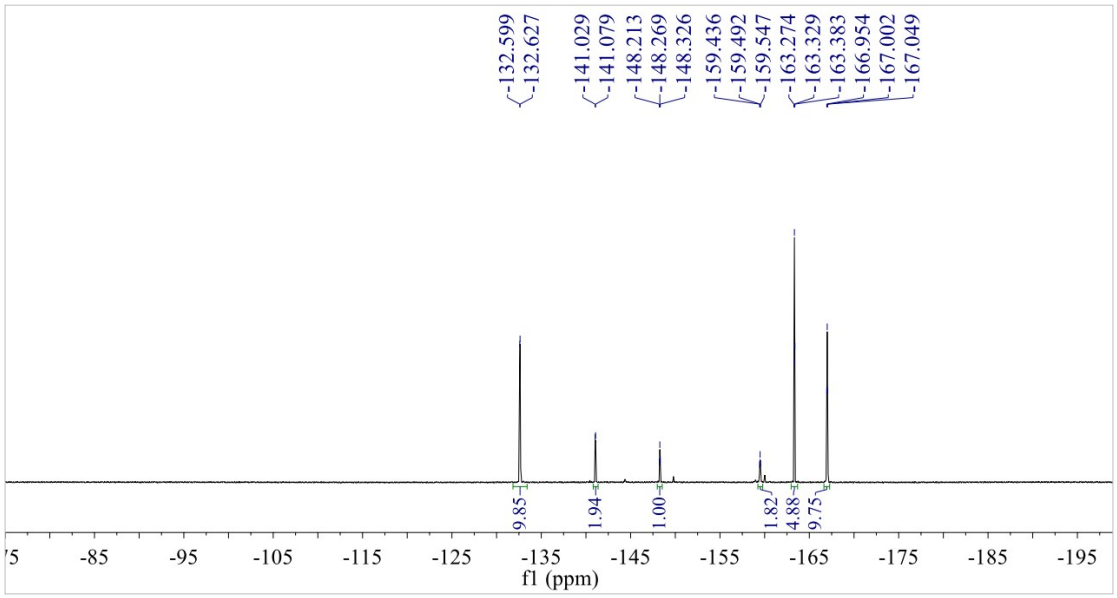
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).



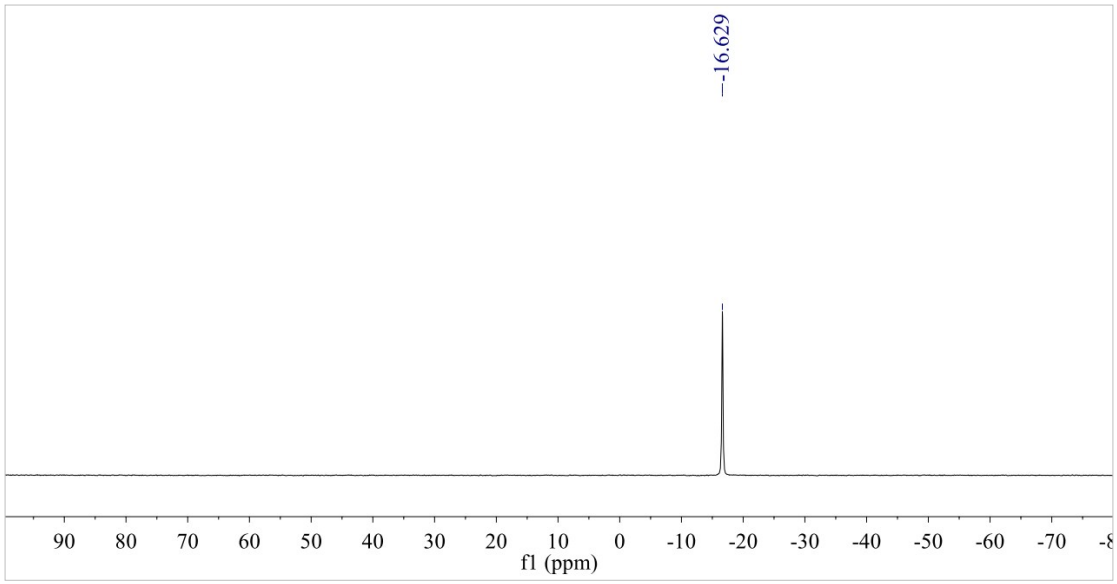
^{13}C{^{1}H} NMR spectrum of **6** (100 MHz, $CDCl_3$).



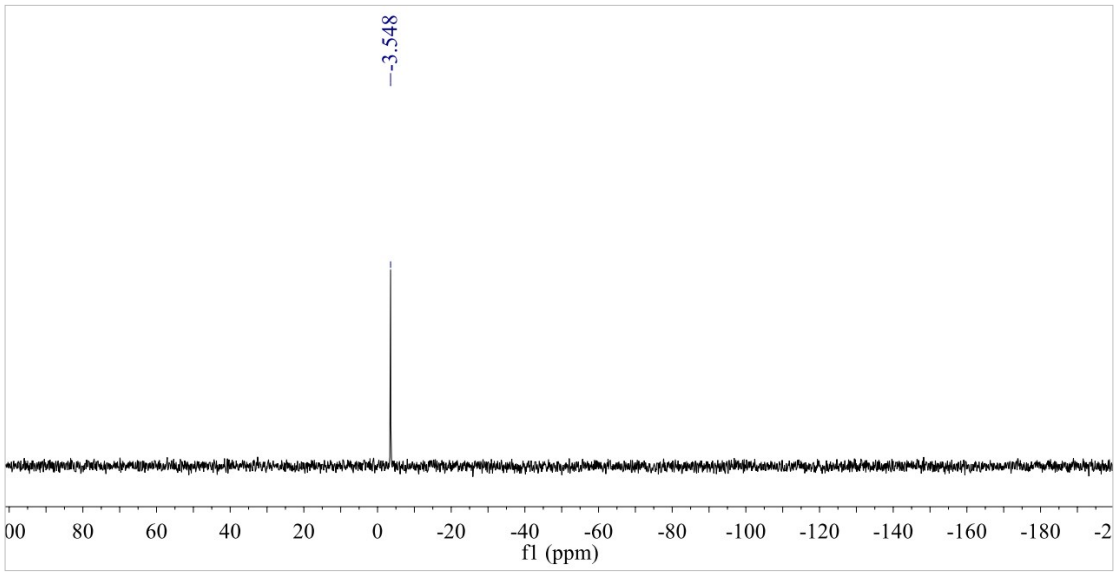
$^{31}P\{^{1}H\}$ NMR spectrum of **6** (162 MHz, $CDCl_3$).



^{19}F NMR spectrum of **6** (377 MHz, $CDCl_3$).



$^{11}B\{^{1}H\}$ NMR spectrum of **6** (128 MHz, $CDCl_3$)



$^{29}Si\{^{1}H\}$ NMR spectrum of **6** (79.5 MHz, $CDCl_3$).

3. Crystallographic Details

Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were placed at calculated positions (except for P–*H1* of compound **1**) and were included in the structure calculation. Calculations were carried out using the SHELXL-97, SHELXL-2014 or Olex2 program.[S3]

Table S1 Crystallographic data and refinement parameters for **1-3**, **5**, **6**.

	1	**2**	**3**
formula	$C_{21}H_{11}BF_4P$	$C_{27}H_{19}Br$	$C_{27}H_{26}BF_4PS$
formula Mass	392.16	423.33	500.32
color	colorless	colorless	brown
cryst system	Monoclinic	Monoclinic	Monoclinic
space group	*C*2/c	$P2_1/n$	$P2_1/n$
a, Å	23.468(7)	15.169(3)	9.406(3)
b, Å	12.135(4)	8.4035(14)	23.181(6)
c, Å	15.927(4)	31.814(6)	12.247(4)
α, deg	90.00	90.00	90.00
β, deg	123.650(6)	100.259(11)	111.409(9)
γ, deg	90.00	90.00	90.00
V, Å^3	3775.8(19)	3990.7(12)	2486.2(12)
Z	8	8	4
D_{calcd}, (mg/m^3)	1.380	1.409	1.337
F(000)	1632	1728	1040
T(K)	150.01	149.99	150.01
θ range, deg	1.976 to 26.732	1.613 to 27.633	1.990 to 26.552
no. of reflns measured	35183	32584	39353
no. of independent reflns	4021	9188	5141
no. of obsd reflns ($I > 2\sigma(I)$)	2518	5370	3261
No. of params	251	505	310
final R_1, *wR* ($I > 2\sigma(I)$)	0.0494, 0.1032	0.0470, 0.0778	0.0578, 0.1246
goodness of fit on F^2	1.022	0.981	1.019
$\Delta\rho_{max, min}$, eÅ^{-3}	0.293, -0.325	0.361, -0.411	0.775, -0.551

	5·CH_2Cl_2	0.5**6**·0.25hexane
formula	$C_{71}H_{38}BF_{25}N_3PCl_2$	$C_{36}H_{21.5}B_{0.5}F_{12.5}N_{1.5}P_{0.5}Si_{0.5}$
formula Mass	1520.72	423.33
color	colorless	colorless
cryst system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.961(8)	13.156(13)
b, Å	14.618(9)	14.543(15)
c, Å	17.917(11)	18.353(19)
α, deg	94.169(17)	93.34(2)
β, deg	109.880(16)	110.49(2)
γ, deg	96.001(17)	95.19(2)
V, Å^3	3153(3)	3261(6)
Z	2	4
D_{calcd}, (mg/m^3)	1.602	1.523
F(000)	1528	1510
T(K)	150.0	149.99
θ range, deg	1.410 to 26.855	1.413 to 25.334
no. of reflns measured	51393	67143
no. of independent reflns	13236	11763
no. of obsd reflns ($I > 2\sigma(I)$)	6700	5924
No. of params	931	932
final R_1, *wR* (I > 2σ(I))	0.0662, 0.1404	0.0680, 0.1318
goodness of fit on F^2	1.004	1.020
$\Delta\rho_{max, min}$, eÅ^{-3}	0.700, -1.028	0.330, -0.411

4. Computational Details

All geometry optimizations were performed using the Gaussian 09 software package.[S4] Optimizations of the structures with frequency calculations were carried out with the M06-2X functional[S5] with 6-31G(d) basis set, using crystallographic coordinates as the starting geometry when possible. Transition states with only one imaginary frequency were examined by vibrational analysis and then submitted to intrinsic reaction coordinate (IRC)[S6] calculations to ensure that such structures indeed connected two minima. Energies in solution (DCM) were calculated by means of single-point calculations (IEF-PCM method with the Bondi radii)[S7] with the same functional using 6-311++G(2d,p) basis set for all of the atoms. The gas-phase geometry was used for all of the solution-phase calculations. A similar treatment was also used in many recent computational studies.[S8] The free energy correction from the frequency calculation was added to the single-point energy to obtain the free energy in solution. All of the solution-phase free energies reported herein correspond to the reference state of 1 mol/L, 298 K. NBO calculations were performed at M06-2X/TZVP//M06-2X/Def2-SVP for compound **5** with the NBO 5.9 program.[S9]

Table S2. Energies for the TS calculation

$$G = E(SCRF) + G_{corr}$$

	E [a.u.]	**G_{corr} [a.u.]**	**ΔG [kcal/mol]**
INT 1	-2046.11198	0.363555	0
TS 1	-2046.067191	0.36212	27.2
INT 2	-2046.125264	0.364114	-7.985
INT 3	-2778.908135	0.631469	-1.134
TS 3	-2778.905671	0.63299	1.367
Product	-2778.937396	0.6369	-16.09

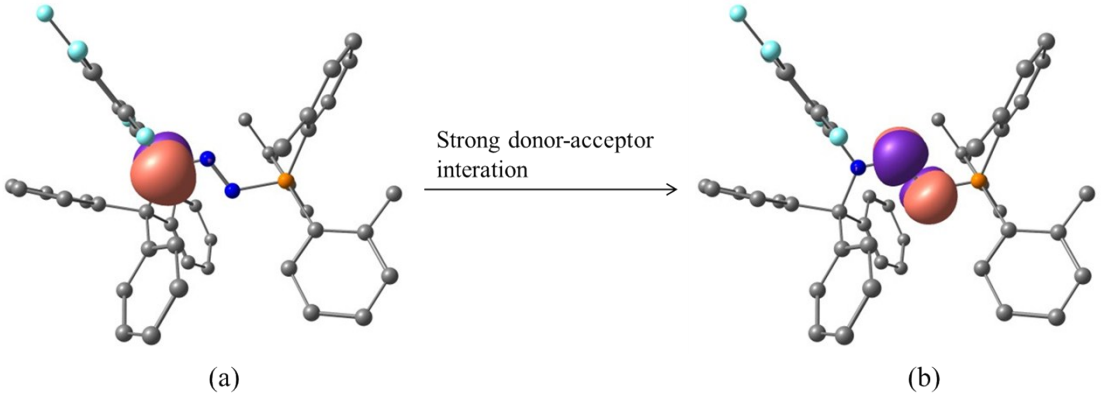


Fig. S1 Selected NBOs of the cation of **5**. (a) Lone pair of N1; (b) N2–N3 π* antibonding.

Cartesian coordinates:

5^+:

P	-2.41963	0.50374	0.06091	C	-1.23518	-3.60311	1.71953
F	2.74576	0.68397	2.31959	H	-1.92984	-4.39893	1.46871
F	2.10551	1.30955	-2.31530	C	-5.41987	-0.88739	-2.34184
F	4.16711	3.03763	-2.35782	H	-6.44597	-0.63205	-2.59043
F	4.82022	2.37562	2.25522	C	5.27694	-1.57814	-0.54131
F	5.54868	3.56184	-0.07507	H	5.97440	-1.33742	-1.33740
N	0.11027	0.60331	0.00050	C	-2.67397	0.35173	4.13891
N	1.28612	0.00838	-0.00993	H	-2.16840	0.77951	5.00065
N	-0.87635	-0.17051	-0.12435	C	1.55161	-3.40205	-1.69100
C	2.98811	-1.74621	0.25427	H	2.03444	-3.98087	-0.90750
C	1.49153	-1.51164	-0.03952	C	-3.72981	-0.53351	4.33124
C	2.36937	0.93963	-0.00129	H	-4.04384	-0.78443	5.33966
C	1.19528	-2.07011	-1.44063	C	-1.01985	1.59844	2.74489
C	-2.91706	0.15028	1.76148	H	-0.10867	0.98924	2.70624
C	0.55029	-1.57707	2.32271	H	-0.94652	2.24889	3.61987
H	1.24750	-0.78703	2.57398	H	-1.02222	2.23037	1.85514
C	0.55304	-2.11536	1.03209	C	-5.45891	1.07378	-0.78622
C	-3.41368	-0.45973	-1.09995	H	-5.29215	1.13967	0.29426
C	-4.74372	-0.10175	-1.40729	H	-6.53512	0.98313	-0.94793
C	-2.52805	2.26833	-0.31646	H	-5.13049	2.02037	-1.22886
C	-0.33409	-2.03510	3.29430	C	-2.80620	-1.56952	-1.70419
H	-0.31322	-1.59372	4.28662	H	-1.78493	-1.83247	-1.45046
C	2.75423	1.57091	-1.18096	C	-4.81386	-1.97832	-2.95891
C	-0.34703	-3.14509	0.74858	H	-5.37103	-2.56054	-3.68615
H	-0.38870	-3.58245	-0.24175	C	4.15924	2.11024	1.13859
C	-2.22986	0.70470	2.86276	C	3.82260	2.45436	-1.21903
C	-3.97102	-0.75284	1.95370	C	-2.28034	4.12456	-1.81494
H	-4.47225	-1.19283	1.09669	H	-1.93781	4.52900	-2.76319
C	3.07993	1.23874	1.15819	C	4.53041	2.72075	-0.05317
C	-3.16650	3.10860	0.60662	C	-3.50504	-2.32304	-2.63996
H	-3.52753	2.70571	1.54927	H	-3.02199	-3.17201	-3.11226
C	0.61688	-1.33140	-2.46886	C	4.83784	-2.36704	1.68753
H	0.36308	-0.29044	-2.31904	H	5.19014	-2.74492	2.64181
C	3.91318	-1.44835	-0.75872	C	5.74564	-2.03443	0.69134
H	3.55481	-1.11214	-1.72881	H	6.81159	-2.14379	0.86370
C	3.46545	-2.22523	1.47303	C	-3.35649	4.45225	0.31935
H	2.77996	-2.50638	2.26282	H	-3.85336	5.09612	1.03695
C	-2.07088	2.76768	-1.55204	C	1.29646	-3.98802	-2.92387
C	-1.24144	-3.04669	2.99425	H	1.57748	-5.02229	-3.09484
H	-1.94112	-3.39921	3.74564	C	0.36630	-1.91647	-3.71159
C	-4.37760	-1.09688	3.23668	H	-0.08354	-1.31973	-4.49963
H	-5.19534	-1.79556	3.37652	C	-1.34803	1.93352	-2.58028
				H	-0.27479	1.90362	-2.35980

H	-1.46858	2.37360	-3.57270
H	-1.71112	0.90226	-2.62873
C	0.69571	-3.24609	-3.94117
H	0.50497	-3.69974	-4.90850
C	-2.91169	4.95862	-0.89970
H	-3.06055	6.00651	-1.14016

INT 1:

P	-1.23471	0.06457	0.42009
F	2.01268	2.10655	1.99726
F	2.96813	-2.46945	1.43299
F	4.08875	-1.93940	-0.95566
F	3.02440	2.62076	-0.45576
F	4.10957	0.59645	-1.93335
N	0.90368	0.18476	3.39335
N	1.78656	-0.57343	2.95507
N	0.09106	0.76470	3.91107
C	2.38794	-0.20559	1.74023
C	-2.31441	1.50805	0.00677
C	-2.40106	-1.36419	0.35013
C	-2.98488	-1.92619	-0.80594
C	-0.19007	-0.15475	-1.09103
C	2.99617	-1.21466	0.99292
C	-1.79031	2.80989	0.15632
C	-3.66007	1.35497	-0.34418
H	-4.08752	0.35986	-0.41837
C	2.47154	1.09799	1.24995
C	-0.04063	0.86886	-2.03637
H	-0.62124	1.78211	-1.93580
C	0.53946	-1.34996	-1.25518
C	-4.47244	2.45883	-0.58690
H	-5.51351	2.31215	-0.85779
C	-3.80786	-3.04599	-0.65134
H	-4.26039	-3.48477	-1.53733
C	-2.61494	3.90470	-0.10801
H	-2.20443	4.90537	-0.00011
C	-3.94486	3.74003	-0.48104
H	-4.56677	4.60897	-0.67395
C	-0.38159	3.03937	0.63577
H	-0.23278	2.56997	1.61272
H	-0.17101	4.10702	0.73706
H	0.36818	2.61772	-0.04426
C	-2.75404	-1.39654	-2.20132
H	-1.80232	-1.75638	-2.60908
H	-2.71878	-0.30468	-2.22960
H	-3.55439	-1.73298	-2.86620
C	-2.66508	-1.93867	1.59958
H	-2.19911	-1.50649	2.48235
C	-4.06161	-3.60848	0.59591
H	-4.70470	-4.48005	0.67402
C	3.02062	1.37383	0.00632
C	3.58009	-0.94461	-0.23413
C	1.37043	-1.48277	-2.37294
H	1.92486	-2.40919	-2.50165
C	3.58202	0.34831	-0.74079
C	-3.49164	-3.04925	1.73327
H	-3.67939	-3.47535	2.71375
C	0.81654	0.73025	-3.12292
H	0.91997	1.54219	-3.83615
C	0.43723	-2.50871	-0.29307
H	0.37818	-2.17762	0.75074
H	1.30966	-3.16094	-0.38896
H	-0.45998	-3.10820	-0.48625
C	1.52350	-0.45557	-3.29717
H	2.19495	-0.57869	-4.14124

TS 1:

P	-1.82858	0.08903	-0.38307
F	1.71927	-1.62676	-0.32691
F	4.08775	2.04101	-2.16107
F	6.16257	1.48370	-0.55141
F	3.76159	-2.11339	1.31252
F	6.01958	-0.58642	1.21599
N	0.61710	0.39737	-1.68259
N	1.78817	0.60667	-2.19219
N	-0.49357	0.55925	-2.09283
C	2.80442	0.25943	-1.28906
C	-3.00597	-1.28564	-0.56438
C	-2.78975	1.58433	-0.00998
C	-3.29148	1.92634	1.26202
C	-0.69328	-0.28387	0.96680
C	3.98829	1.00729	-1.32709
C	-2.57602	-2.48080	-1.17952
C	-4.33548	-1.14310	-0.15107
H	-4.66689	-0.20540	0.28628
C	2.78295	-0.81872	-0.39600
C	-0.67173	-1.56749	1.53248
H	-1.43569	-2.28962	1.25579

C	0.28543	0.66558	1.33098	N	0.75133	0.40096	-0.69660
C	-5.23995	-2.18810	-0.30384	N	1.71317	0.62242	-1.48746
H	-6.26724	-2.06760	0.02466	N	-0.43792	0.57756	-1.26901
C	-3.98514	3.13317	1.38275	C	2.95244	0.38175	-0.86380
H	-4.37918	3.41400	2.35611	C	-2.53479	-1.28660	-1.10438
C	-3.50004	-3.51911	-1.30855	C	-2.86105	1.49048	-0.20994
H	-3.17922	-4.44803	-1.77234	C	-3.92115	1.55916	0.71660
C	-4.81605	-3.38267	-0.87620	C	-1.21589	-0.38742	1.38155
H	-5.51233	-4.20687	-0.99720	C	4.04802	1.12777	-1.31317
C	-1.18051	-2.64389	-1.72941	C	-1.78638	-2.39591	-1.55635
H	-1.02794	-1.98179	-2.58809	C	-3.91704	-1.23582	-1.30785
H	-1.01829	-3.67339	-2.05734	H	-4.47781	-0.36002	-0.99516
H	-0.40355	-2.39741	-0.99820	C	3.21561	-0.60491	0.09741
C	-3.09991	1.05962	2.48255	C	-1.44304	-1.70351	1.79250
H	-2.07885	1.14003	2.87232	H	-1.88869	-2.41642	1.10441
H	-3.27232	0.00060	2.26671	C	-0.64787	0.55011	2.26766
H	-3.78925	1.36508	3.27367	C	-4.58394	-2.28638	-1.92981
C	-2.98705	2.43566	-1.10446	H	-5.65672	-2.23287	-2.08357
H	-2.56892	2.16447	-2.07070	C	-4.73718	2.69265	0.68370
C	-4.18365	3.97626	0.29307	H	-5.55878	2.76418	1.39158
H	-4.72692	4.90700	0.42562	C	-2.48228	-3.43909	-2.17035
C	3.84478	-1.09568	0.45263	H	-1.92167	-4.30271	-2.51783
C	5.06485	0.72963	-0.49802	C	-3.86102	-3.39392	-2.35578
C	1.26670	0.27408	2.24889	H	-4.36636	-4.22260	-2.84242
H	2.03078	0.99485	2.53045	C	-0.28418	-2.48459	-1.43782
C	4.99527	-0.32333	0.40477	H	0.19604	-1.80132	-2.14642
C	-3.68741	3.62805	-0.95823	H	0.04727	-3.50332	-1.65349
H	-3.83607	4.28052	-1.81243	H	0.08501	-2.21050	-0.44501
C	0.31320	-1.92802	2.43926	C	-4.19686	0.49389	1.75182
H	0.31993	-2.92649	2.86431	H	-3.48926	0.56075	2.58565
C	0.26899	2.10277	0.86481	H	-4.11461	-0.51794	1.34388
H	-0.03152	2.21628	-0.17840	H	-5.20586	0.61503	2.15371
H	1.26266	2.54432	0.97629	C	-2.64067	2.52850	-1.12174
H	-0.43189	2.69408	1.46827	H	-1.80358	2.45035	-1.80943
C	1.29739	-1.00560	2.78749	C	-4.52166	3.72395	-0.22600
H	2.08964	-1.28364	3.47537	H	-5.17659	4.58995	-0.22241
				C	4.49605	-0.81296	0.59313
INT 2:				C	5.32970	0.93031	-0.82183
P	-1.67983	0.10947	-0.30868	C	-0.32774	0.11505	3.55504
F	2.25611	-1.41537	0.55132	H	0.11214	0.82528	4.24984
F	3.86850	2.07535	-2.23029	C	5.55817	-0.04588	0.13779
F	6.34137	1.67593	-1.26386	C	-3.47127	3.64386	-1.13306
F	4.71103	-1.76444	1.50245	H	-3.29485	4.44284	-1.84567
F	6.78475	-0.24582	0.61535	C	-1.11391	-2.11181	3.08037

H	-1.29338	-3.13717	3.38666	H	5.07569	-1.42509	-2.11825
C	-0.41263	1.99283	1.89575	H	5.38063	-1.28164	-0.38664
H	0.10247	2.07824	0.93533	H	6.56323	-0.65985	-1.54085
H	0.19973	2.48271	2.65646	C	3.01040	2.13145	-0.85038
H	-1.35856	2.54187	1.82076	H	2.02543	2.29809	-0.42987
C	-0.55444	-1.19594	3.96331	C	4.99748	2.95358	-1.91744
H	-0.29022	-1.49929	4.97174	H	5.57391	3.76791	-2.34518
				C	-3.81955	-2.54899	0.55440
INT 3:				C	-4.09811	-1.90166	-1.74483
P	2.49312	-0.46359	-0.11865	C	2.28469	-3.09814	-3.22543
F	-2.00467	-1.73730	1.78223	H	1.92668	-3.10218	-4.25113
F	-2.55756	-0.42694	-2.71575	C	-4.54291	-2.60399	-0.63045
F	-4.79563	-1.94063	-2.87441	C	3.73315	3.18934	-1.38860
F	-4.25645	-3.19521	1.62954	H	3.30981	4.18888	-1.39208
F	-5.66038	-3.31501	-0.69542	C	3.36148	-4.24353	-1.39708
N	0.00877	-0.68492	-0.24361	H	3.83989	-5.12562	-0.98516
N	-1.13219	-0.14641	-0.40229	C	1.41998	-0.75247	-3.08718
N	0.97442	0.20542	-0.11852	H	0.37911	-0.68396	-2.75172
C	-2.18438	-1.08269	-0.48716	H	1.41779	-0.85505	-4.17455
C	3.13079	-0.79716	1.55412	H	1.90660	0.19554	-2.83828
C	3.54142	0.83522	-0.83854	C	2.89585	-4.23548	-2.70845
C	4.83088	0.58720	-1.35245	H	3.00933	-5.11602	-3.33315
C	2.59762	-1.96011	-1.13764	C	-0.71198	2.14376	1.56290
C	-2.93912	-1.14485	-1.65919	C	-1.87720	2.19074	0.70530
C	2.45887	-1.67441	2.43259	C	-3.14425	1.60571	1.09085
C	4.26893	-0.10390	1.98593	C	-0.70425	2.86968	-1.38310
H	4.77221	0.58564	1.31515	H	0.04387	2.10929	-1.16684
C	-2.65299	-1.80003	0.61154	C	-1.81404	2.97668	-0.52315
C	3.21361	-3.10375	-0.61790	C	-0.63581	3.65891	-2.52073
H	3.59285	-3.09868	0.40086	H	0.20614	3.55539	-3.19802
C	2.11386	-1.94011	-2.46205	C	-2.84726	3.88087	-0.82882
C	4.76255	-0.27675	3.27488	H	-3.69477	3.97613	-0.15665
H	5.64766	0.26459	3.59226	C	-4.06643	1.23838	0.08326
C	5.53233	1.67001	-1.88997	H	-3.80139	1.39609	-0.95764
H	6.52563	1.49588	-2.29397	C	-0.48681	1.06268	2.44353
C	2.98248	-1.83788	3.71759	H	-1.16993	0.22018	2.43171
H	2.48128	-2.51942	4.39996	C	0.23861	3.18442	1.51028
C	4.11642	-1.15079	4.14184	H	0.06002	4.04103	0.86887
H	4.49455	-1.30230	5.14810	C	-1.65227	4.57519	-2.80121
C	1.17757	-2.38279	2.07614	H	-1.58992	5.19736	-3.68860
H	0.33181	-1.68930	2.12435	C	-2.75306	4.68915	-1.95396
H	0.98703	-3.19759	2.77854	H	-3.53777	5.40609	-2.17048
H	1.17608	-2.79446	1.06379	C	0.64591	1.02910	3.23745
C	5.49388	-0.76934	-1.34750	H	0.82197	0.18533	3.89704

C	-3.48382	1.36974	2.44085	C	1.14118	-2.39353	2.06582
H	-2.82040	1.70940	3.22894	H	0.29715	-1.69851	2.12642
C	1.37406	3.14142	2.30634	H	0.94951	-3.21662	2.75811
H	2.09413	3.95202	2.26254	H	1.13793	-2.79385	1.04903
C	1.58280	2.06299	3.16495	C	5.48134	-0.80389	-1.34184
H	2.47773	2.02190	3.77873	H	5.05812	-1.45894	-2.11053
C	-4.68484	0.75795	2.76399	H	5.36523	-1.31233	-0.37911
H	-4.94245	0.58937	3.80392	H	6.55132	-0.70273	-1.53600
C	-5.26263	0.62225	0.41390	C	3.01519	2.11366	-0.85053
H	-5.95469	0.32752	-0.36850	H	2.03234	2.28910	-0.42808
C	-5.56845	0.37421	1.75326	C	5.00485	2.92006	-1.92538
H	-6.50413	-0.11226	2.01173	H	5.58447	3.72968	-2.35777
				C	-3.86785	-2.49389	0.54625
TS 2:				C	-4.09189	-1.83663	-1.75814
P	2.48939	-0.47854	-0.11535	C	2.23551	-3.10252	-3.22657
F	-2.07295	-1.69840	1.81405	H	1.87320	-3.10083	-4.25074
F	-2.52622	-0.35914	-2.68434	C	-4.56389	-2.54033	-0.65594
F	-4.76211	-1.87065	-2.90353	C	3.74269	3.16483	-1.39550
F	-4.32786	-3.14934	1.60499	H	3.32402	4.16621	-1.40286
F	-5.67862	-3.25027	-0.75007	C	3.30827	-4.26272	-1.40466
N	-0.00221	-0.64925	-0.23846	H	3.77950	-5.15055	-0.99686
N	-1.14979	-0.10202	-0.33825	C	1.39477	-0.74873	-3.07915
N	0.97403	0.21156	-0.09749	H	0.35180	-0.68038	-2.74994
C	-2.20856	-1.02735	-0.45198	H	1.39805	-0.84146	-4.16735
C	3.10838	-0.81756	1.55960	H	1.88345	0.19561	-2.82015
C	3.54059	0.81481	-0.83589	C	2.83719	-4.24695	-2.71418
C	4.82779	0.55716	-1.35079	H	2.93894	-5.12731	-3.34107
C	2.56858	-1.97262	-1.13777	C	-0.66032	2.07255	1.55107
C	-2.93332	-1.08313	-1.64246	C	-1.80486	2.05977	0.64811
C	2.42416	-1.69216	2.43107	C	-3.10504	1.55309	1.05752
C	4.24429	-0.12670	2.00090	C	-0.65106	2.76125	-1.46235
H	4.75483	0.56171	1.33437	H	0.07971	1.97494	-1.28858
C	-2.70161	-1.74832	0.63363	C	-1.73446	2.87384	-0.57469
C	3.17520	-3.12350	-0.62223	C	-0.56622	3.60027	-2.56298
H	3.55798	-3.12421	0.39527	H	0.25994	3.49212	-3.25895
C	2.07997	-1.94440	-2.46009	C	-2.72429	3.84143	-0.81260
C	4.72524	-0.30138	3.29409	H	-3.55250	3.94761	-0.11867
H	5.60826	0.23806	3.62029	C	-4.06590	1.25128	0.06522
C	5.53404	1.63405	-1.89319	H	-3.81530	1.41159	-0.97889
H	6.52599	1.45352	-2.29771	C	-0.43461	1.02642	2.46863
C	2.93712	-1.85877	3.71978	H	-1.10231	0.17141	2.46876
H	2.42745	-2.53833	4.39780	C	0.26047	3.13501	1.49734
C	4.06915	-1.17494	4.15410	H	0.08526	3.96538	0.82134
H	4.43774	-1.32803	5.16364	C	-1.54468	4.57299	-2.78244

H	-1.47213	5.23094	-3.64274	C	1.59116	2.09467	3.21737
C	-2.61805	4.69563	-1.90474	H	2.47255	2.08979	3.85152
H	-3.37553	5.45459	-2.06899	C	-4.67420	0.79776	2.74845
C	0.67690	1.04114	3.29346	H	-4.92579	0.64355	3.79216
H	0.85274	0.21963	3.98084	C	-5.29279	0.70683	0.40964
C	-3.44190	1.33708	2.40969	H	-6.01422	0.46467	-0.36434
H	-2.75165	1.63209	3.19204	C	-5.59404	0.46975	1.75183
C	1.37488	3.14383	2.32681	H	-6.55407	0.04134	2.02335
H	2.07451	3.97198	2.27846				

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