Benzylic C-H addition of aromatic amines to alkenes by a scandium catalyst

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General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. High resolution mass spectrometry was measured with a BRUKER micrOTOF-Q III. Melting points were determined using an Electrotherman IA9000. $[PhNMe_2H][B(C_6F_5)_4]$ was purchased from Strem. Complexes **1**[1], **2**[2], $RE(CH_2SiMe_3)_3(THF)_2$ (RE = Sc, Y)[3] and 2-(2-bromophenyl)-4-isopropyl-4,5-dihydrooxazole[4] were prepared according to the literature procedures. All substrates were distilled from CaH_2 or molecular sieves before use.

References:

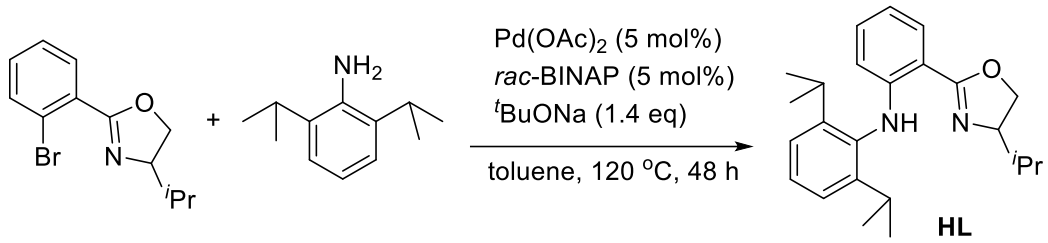
1. Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533.

2. Su, J.; Zhou, Y.; Xu, X. *Org. Biomol. Chem.* **2019**, *17*, 2013.

3. Lappert, M. F.; Pearce, R.; *J. Chem. Soc. Chem. Commun.* **1973**, 126.

4. Giereth, R.; Mengele, A. K.; Frey, W.; Kloß, M.; Steffen, A.; Karnahl, M.; Tschierlei, S. *Chem. - Eur. J.* **2020**, *26*, 2675.

Preparation of HL



Scheme S1.

An oven dried Schlenk flask was charged with $Pd(OAc)_2$ (113 mg, 0.5 mmol), *rac*-BINAP (312 mg, 0.5 mmol), 2-(2-bromophenyl)-4-isopropyl-4,5-dihydrooxazole (2.68 g, 10.0 mmol), 2,6-diisopropylaniline (2.13 g, 12.0 mmol), ^{t}BuONa (1.35 g, 14.0 mmol) and toluene (30 mL). The reaction mixture was heated at 120 °C for 48 h under N_2 flow. After workup, the crude product was purified by column chromatography on silica gel eluting with a mixture of petroleum ether and ethyl acetate (30/1) to afford **HL** as a colorless solid (2.95 g, 81% yield).

HRMS (ESI) *m/z* calcd. For $C_{24}H_{33}N_2O$ $[M + H]^+$: 365.2587; found: 365.2584.

MP: 62-63 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 9.93 (s, 1H, N*H*), 7.74 (m, 1H, Ar-H), 7.28 (m, 1H, Ar-H), 7.21 (m, 2H, Ar-H), 7.07 (m, 1H, Ar-H), 6.57 (m, 1H, Ar-H), 6.17 (m, 1H, Ar-H), 4.32 (m, 1H, CH_2), 4.15 (m, 1H, C*H*), 4.03 (m, 1H, CH_2), 3.11 (m, 2H, C*H*Me$_2$), 1.77 (m, 1H, C*H*Me$_2$), 1.12 (m, 9H, CH*Me*$_2$), 1.07 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH*Me*$_2$), 0.96 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH*Me*$_2$), 0.90 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 164.0, 149.4, 148.0, 147.8, 135.4, 132.2, 129.7, 127.4, 123.88, 123.86, 114.9, 111.9, 108.2, 72.9, 68.7, 33.2, 28.6, 28.5, 25.1, 24.9, 23.03, 23.01, 18.7, 18.6.

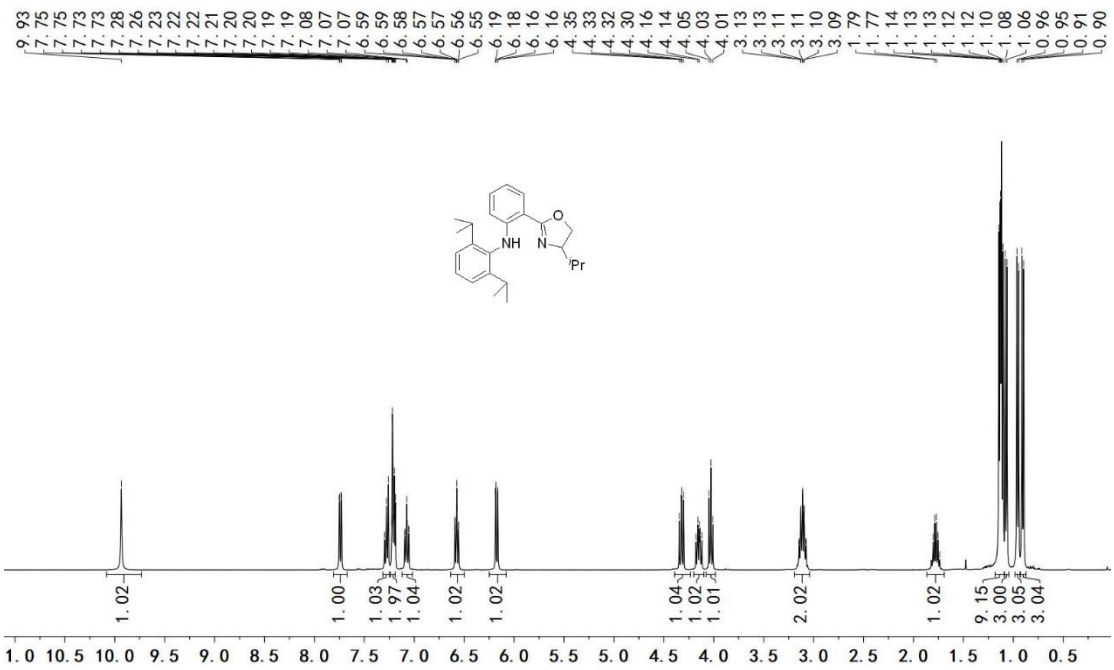


Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

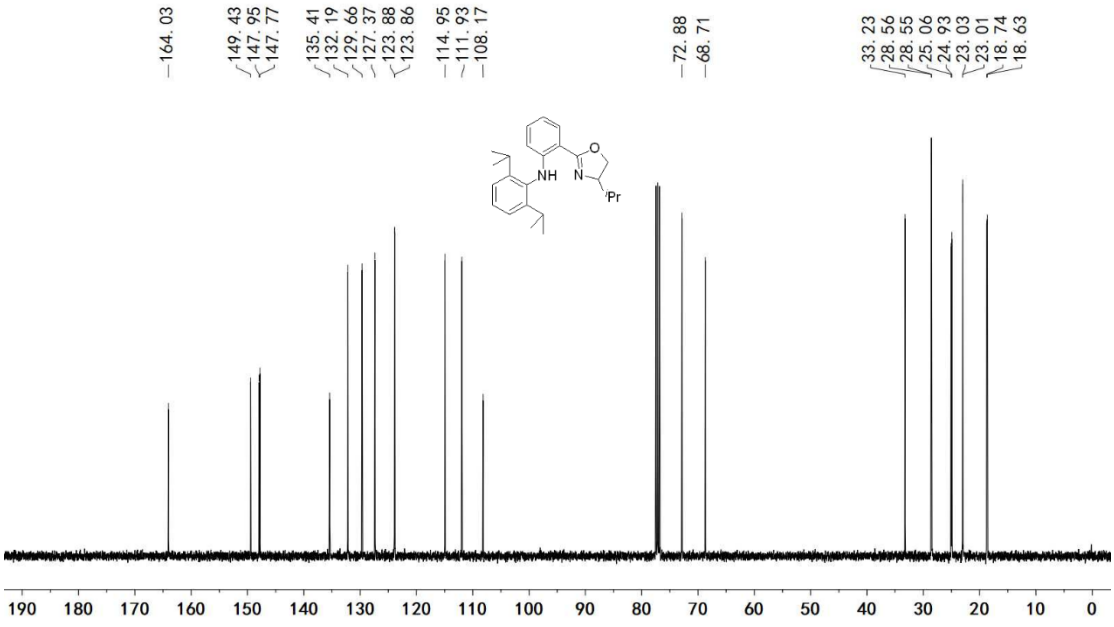
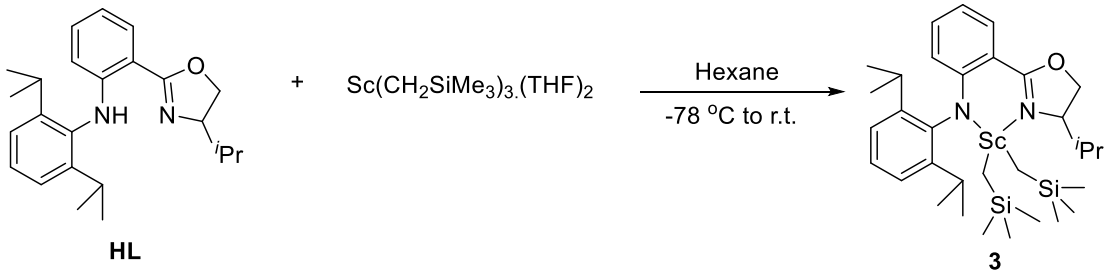


Fig. S2. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)

Preparation of complex 3



HL **3**

Scheme S2.

A solution of **HL** (182 mg, 0.5 mmol) in 3 mL hexane was added dropwise to a solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (247 mg, 0.55 mmol) in 3 mL of hexane at -78 °C. The mixture was stirred at room temperature for 2 h, and then the volatiles were removed under vacuum. The resulting residue was washed with hexane (0.5 mL*3) to finally give **3** as a pale yellow solid (219 mg, 75%). *Note: Complex **3** is thermally stable, with no decomposition observed over 12 h at 60 °C in C_6D_6 solution. However, it is air- and moisture-sensitive, thus should be stored in the glove box.*

Elemental Analysis: calcd. for $C_{32}H_{53}N_2OScSi_2$: C, 65.94; H, 9.16; N, 4.81; found: C, 65.90; H, 9.31; N, 4.62.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.96 (m, 1H, Ar-H), 7.27 (m, 3H, Ar-H), 6.87 (m, 1H, Ar-H), 6.42 (m, 1H, Ar-H), 6.21 (m, 1H, Ar-H), 4.59 (m, 1H, C*H*$_2$), 3.86 (m, 2H, OC*H*$_2$), 3.65 (m, 1H, C*H*Me$_2$), 3.01 (m, 1H, C*H*Me$_2$), 2.22 (m, 1H, C*H*Me$_2$), 1.57 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH*Me*$_2$), 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*$_2$), 0.87 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH*Me*$_2$), 0.59 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH*Me*$_2$), 0.57 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH*Me*$_2$), 0.27-0.11 (m, 22H, CH_2Si*Me*$_3$, C*H*$_2$SiMe$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 171.4, 157.0, 146.8, 146.6, 138.5, 135.4, 132.1, 127.5, 125.9, 124.8, 118.0, 116.0, 107.6, 68.6, 67.8, 45.0 (br), 44.3 (br), 32.2, 28.9, 28.6, 26.1, 25.9, 25.0, 24.3, 18.6, 14.2, 3.4.

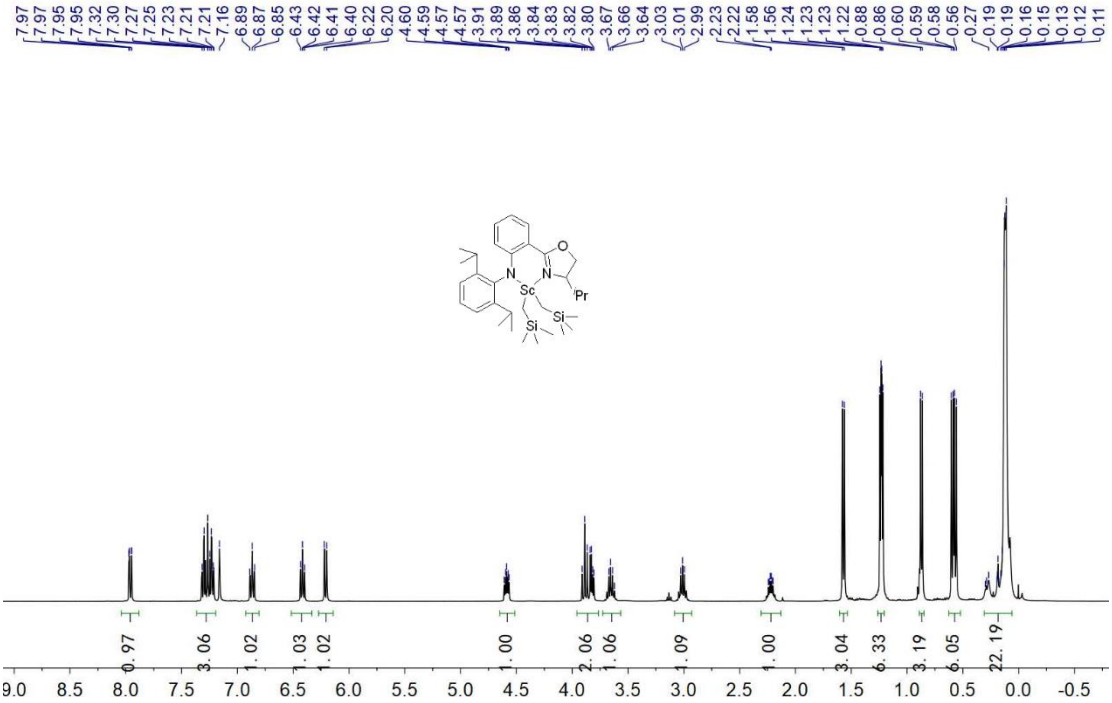


Fig. S3. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

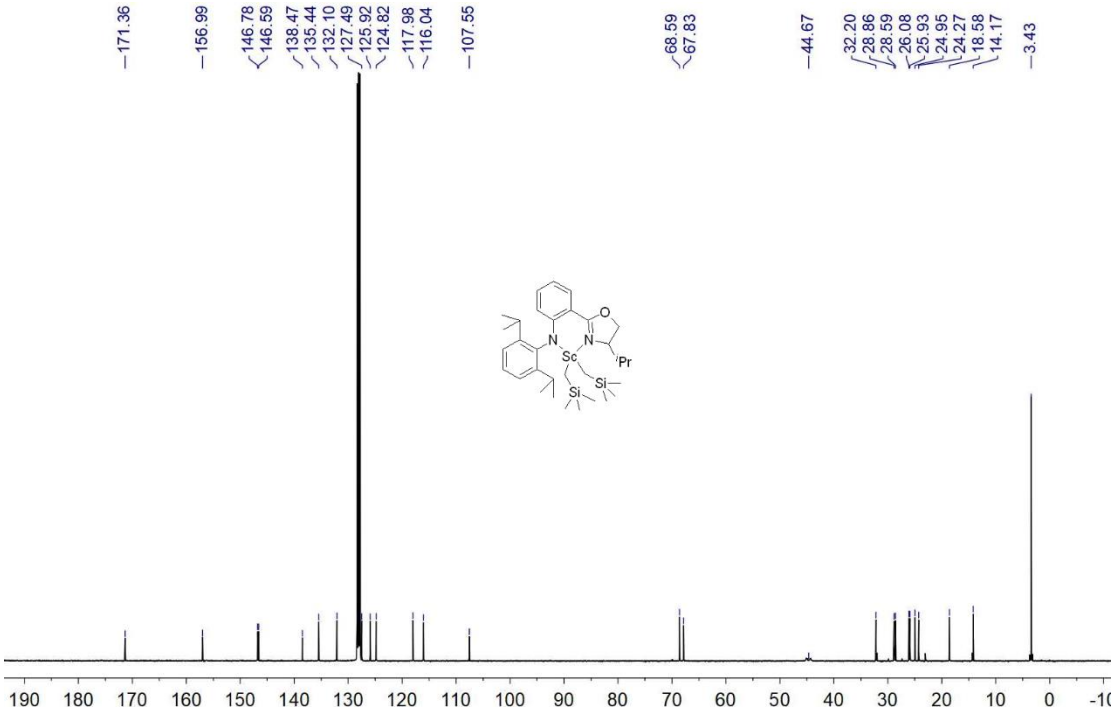
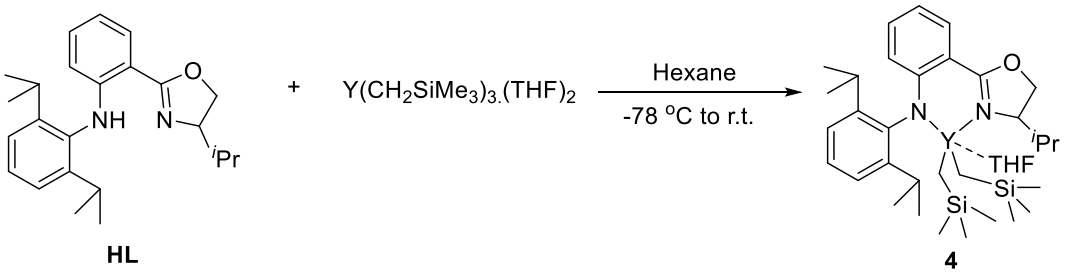


Fig. S4. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

Preparation of complex 4



Scheme S3.

Following the procedure described for **3**, reaction of **HL** (197 mg, 0.5 mmol) with $Y(CH_2SiMe_3)_3(THF)_2$ (271 mg, 0.55 mmol) gave complex **4** as a pale yellow solid (206 mg, 63%).

Elemental Analysis: calcd. for $C_{36}H_{61}N_2O_2Si_2Y$: C, 61.86; H, 8.80; N, 4.01; found: C, 61.89; H, 8.96; N, 4.33.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.20 (m, 1H, Ar-H), 7.17 (m, 1H, Ar-H), 7.10 (m, 2H, Ar-H), 6.89 (m, 1H, Ar-H), 6.44 (m, 1H, Ar-H), 6.03 (m, 1H, Ar-H), 4.88 (m, 1H, CH_2), 4.03 (m, 1H, CH), 4.02 (m, 1H, CH_2), 3.43 (m, 1H, CHMe$_2$), 3.29 (m, 4H, THF), 3.14 (m, 1H, CHMe$_2$), 2.71 (m, 1H, CHMe$_2$), 1.29 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, CHMe_2), 1.14 (m, 7H, CHMe_2, THF), 1.10 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CHMe_2), 0.96 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CHMe_2), 0.80 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, CHMe_2), 0.76 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CHMe_2), 0.26 (s, 18H, CH$_2$SiMe_3), -0.46 (m, 4H, CH_2SiMe$_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 169.5, 157.7, 148.7, 147.4, 142.3, 133.5, 132.4, 126.3, 125.3, 125.0, 117.8, 113.6, 108.1, 70.5, 70.3, 66.0, 34.9 (br), 31.3, 28.8, 28.5, 26.1, 25.5, 25.1, 24.9, 24.2, 19.1, 14.0, 4.6.

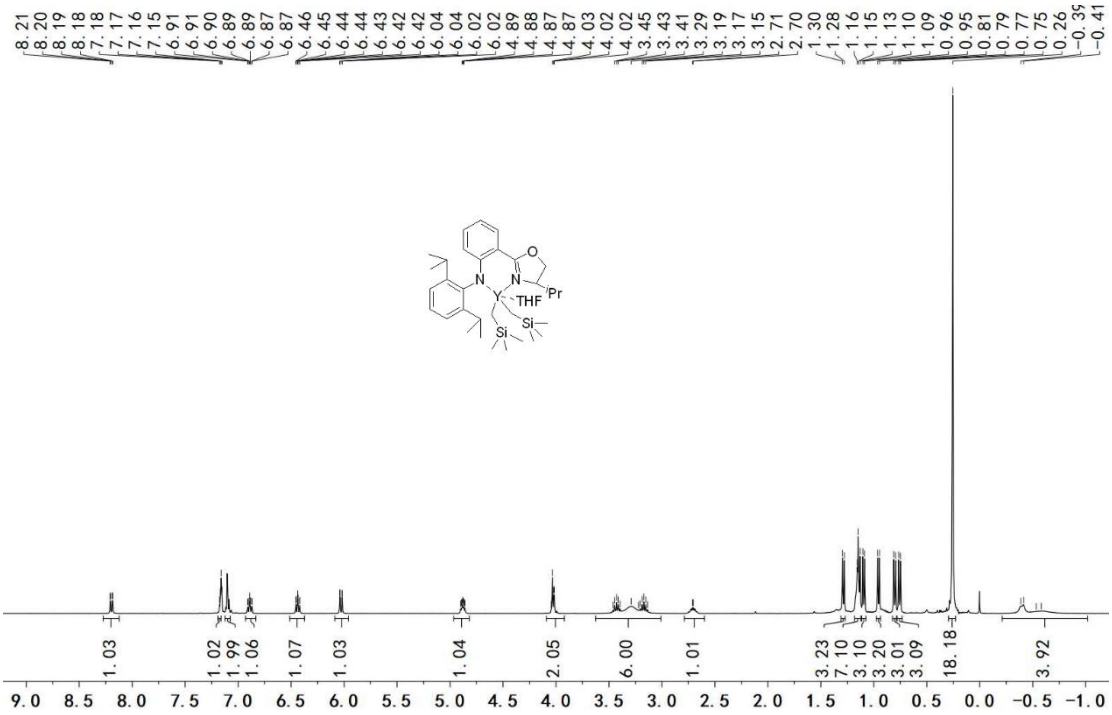


Fig. S5. ^1H NMR (400 MHz, C_6D_6, 298 K)

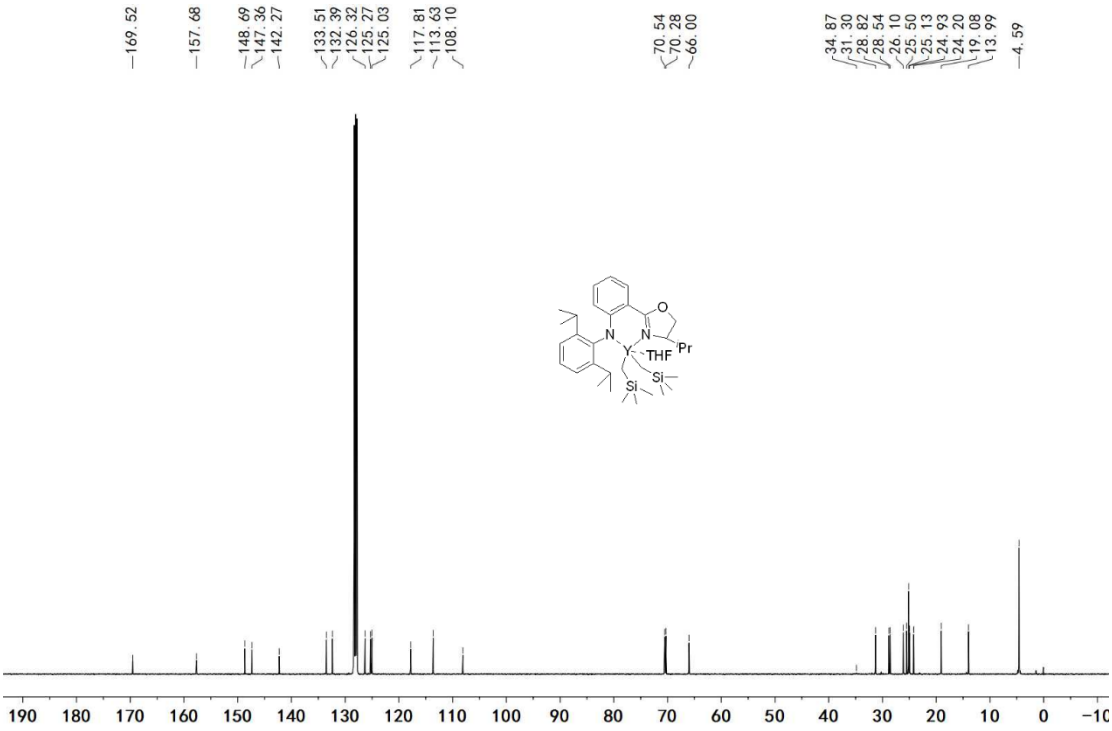
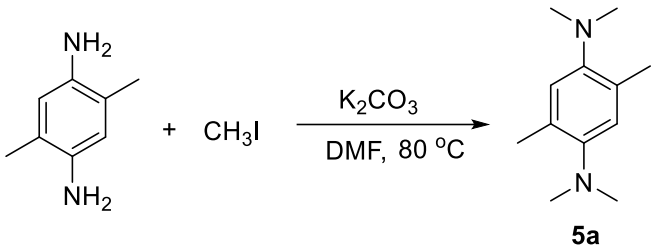


Fig. S6. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K)

Preparation of substrates



Scheme S4.

A mixture of 2,5-dimethylbenzene-1,4-diamine (1.36 g, 10 mmol), CH_3I (6.25 g, 44 mmol) and K_2CO_3 (6.08 g, 44 mmol) in DMF (80 mL) was stirred at 80 °C for 24 h. The reaction was then cooled and diluted with ethyl acetate (100 mL) and H_2O (100 mL). The layers were separated and the organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and purified by flash chromatography to afford **5a** as a colorless solid (0.89 g, 46%).

MP: 63-64 ℃.

HRMS (ESI) *m/z* calcd. For $C_{12}H_{21}N_2$ $[M + H]^+$: 193.1699; found: 193.1706.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.88 (s, 2H, Ar-H), 2.68 (s, 12H, N*Me*$_2$), 2.31 (s, 6H, *Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 147.8, 130.2, 121.4, 44.8, 18.1.

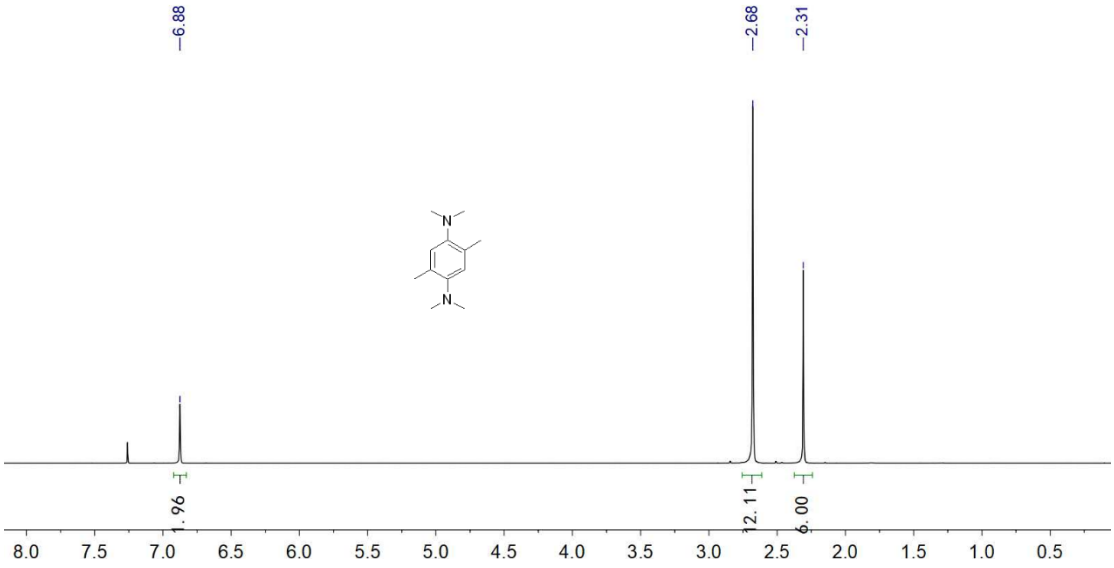


Fig. S7. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

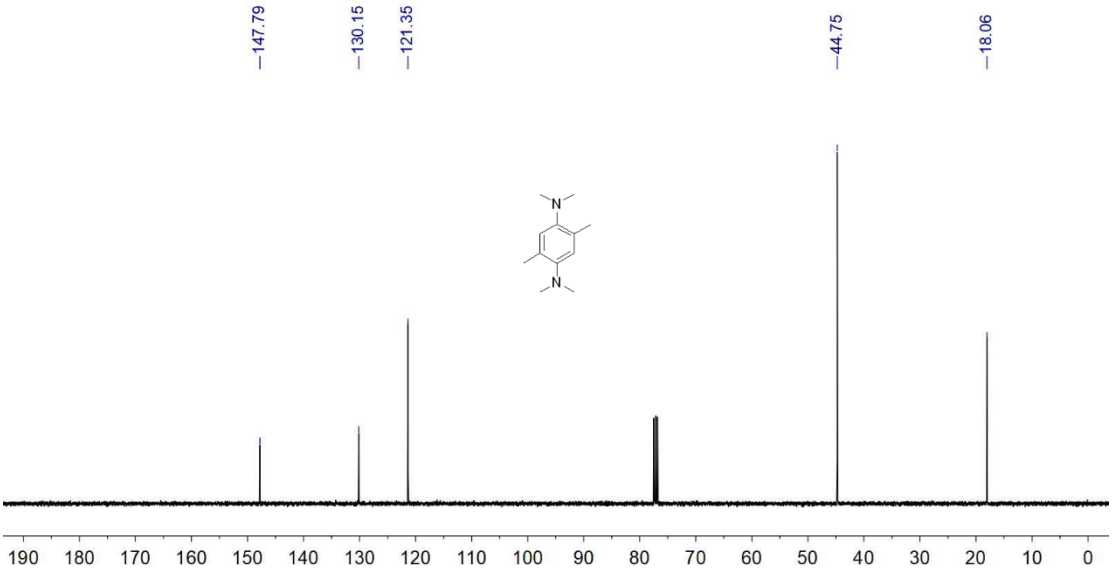
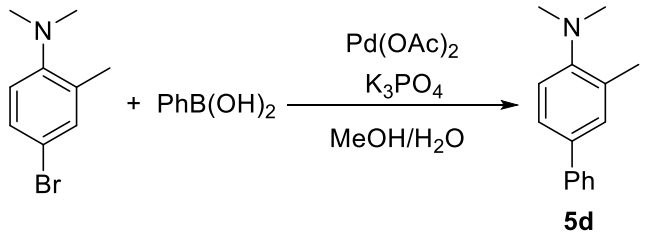


Fig. S8. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



5d

Scheme S6.

4-Bromo-*N,N*-dimethyl-*o*-toluidine (1.07 g, 5.0 mmol) was dissolved in a mixture of MeOH and H_2O (1:1, 10 mL) under an argon atmosphere. Phenylboronic acid (0.67 g, 5.5 mmol), $Pd(OAc)_2$ (6 mg, 0.025 mmol) and K_3PO_4 (2.10 g, 10 mmol) were added. The reaction mixture was stirred at 100 °C for 16 h, and then cooled and diluted with ethyl acetate (100 mL) and H_2O (100 mL). The layers were separated and the organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and purified by flash chromatography to afford **5d** as a colorless solid (0.96 g, 91%).

MP: 78-79 °C.

HRMS (ESI) *m/z* calcd. For $C_{15}H_{18}N$ $[M + H]^+$: 212.1434; found: 212.1439.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.64 (m, 2H, Ar-H), 7.48 (m, 4H, Ar-H), 7.37 (m, 1H, Ar-H), 7.16 (m, 1H, Ar-H), 2.81 (s, 6H, N*Me*$_2$), 2.47 (s, 3H, Ar-*Me*).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.3, 141.2, 135.4, 132.3, 130.1, 128.8, 126.9, 126.7, 125.2, 118.7, 44.3, 18.8.

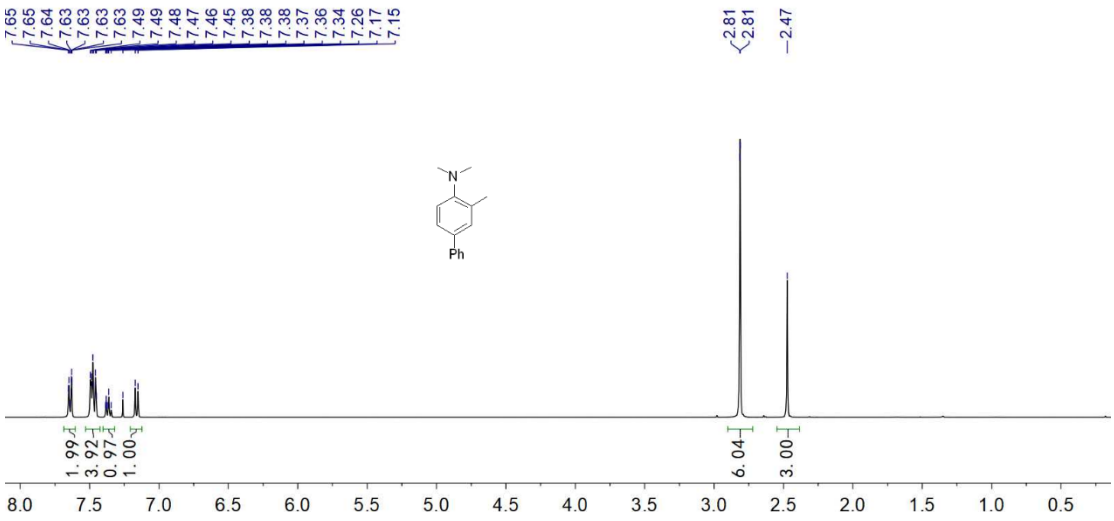


Fig. S11. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

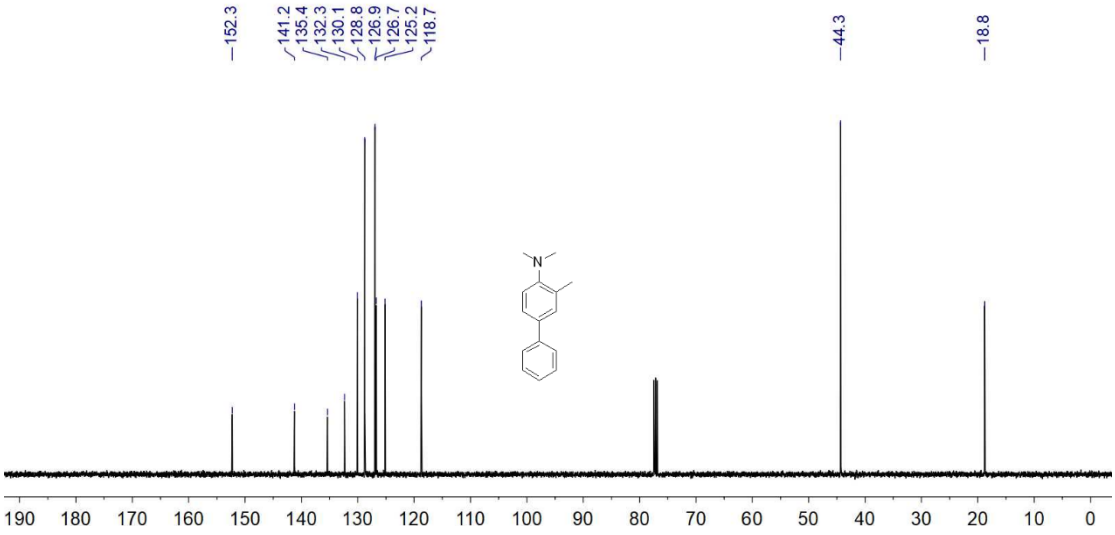
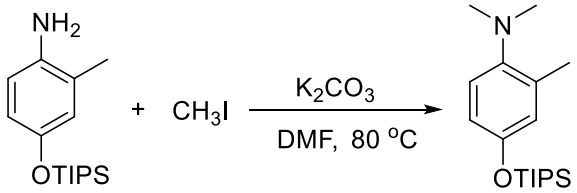


Fig. S12. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



TIPS: $^{i}Pr_3Si$ **5i**

Scheme S5.

Following the procedure described for **5a**, reaction of 2-methyl-4-((triisopropylsilyl)oxy)aniline (1.36 g, 10 mmol), CH_3I (3.13 g, 22 mmol) and K_2CO_3 (3.04 g, 44 mmol) afforded **5i** as a yellow oil (1.21 g, 79%).

HRMS (ESI) *m/z* calcd. For $C_{18}H_{34}NOSi$ $[M + H]^+$: 308.2404; found: 308.2410.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.90 (m, 1H, Ar-H), 6.71 (m, 1H, Ar-H), 6.66 (m, 1H, Ar-H), 2.63 (s, 6H, N*Me*$_2$), 2.27 (s, 3H, Ar-*Me*), 1.24 (m, 3H, C*H*Me$_2$), 1.11 (d, $^3J_{HH}$ = 7.3 Hz, 18H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 151.6, 146.5, 133.8, 122.4, 119.3, 117.2, 45.0, 18.3, 18.1, 12.8.

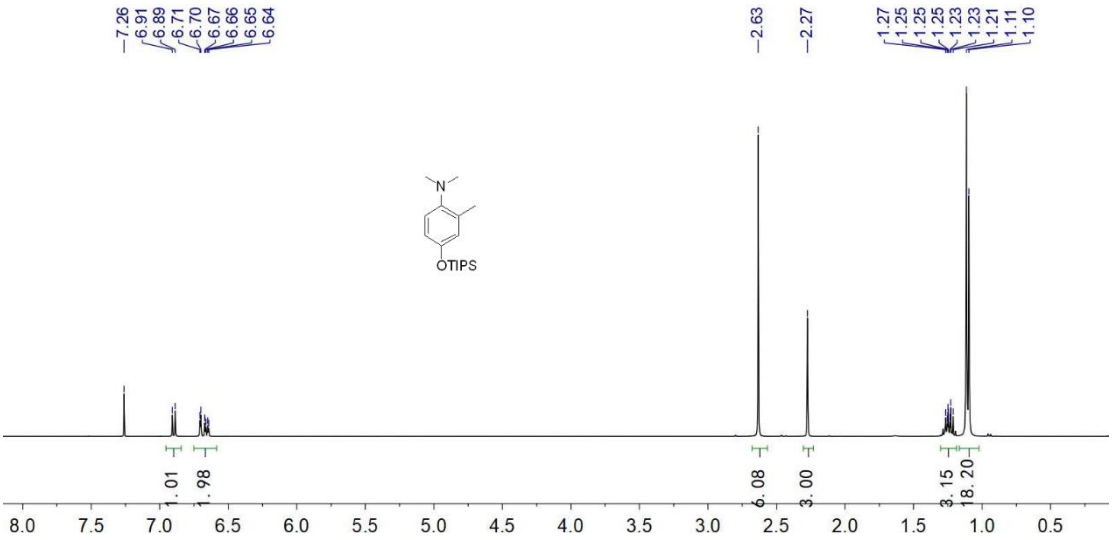


Fig. S9. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

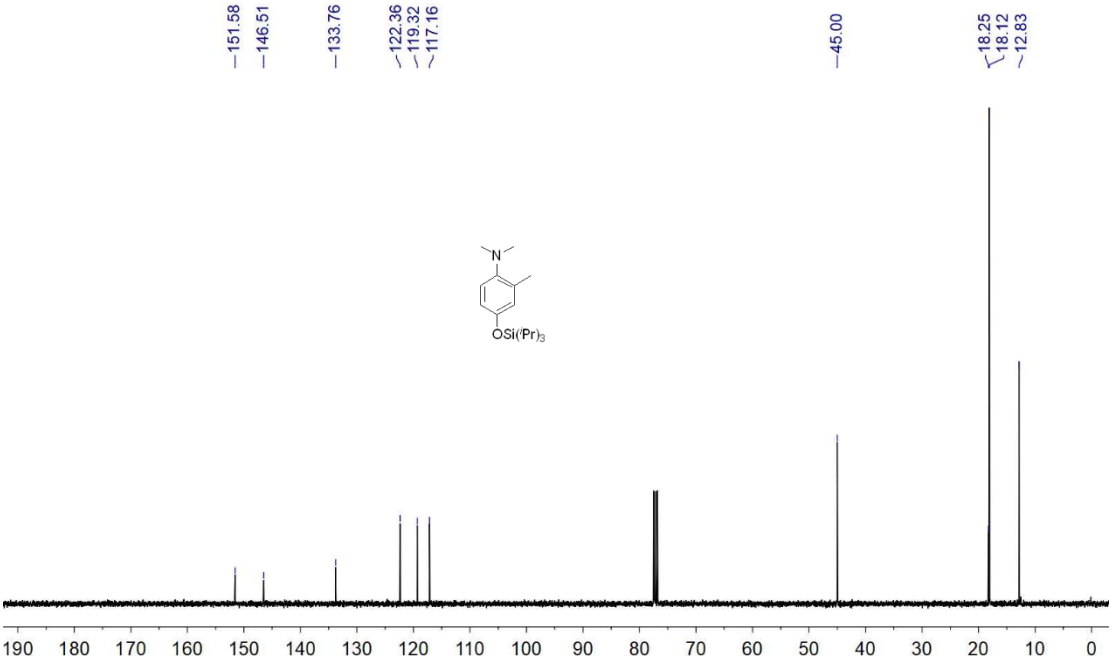
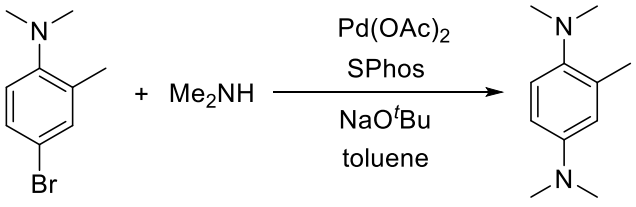


Fig. S10. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



5j

Scheme S7.

4-Bromo-*N,N*-dimethyl-*o*-toluidine (1.07 g, 5 mmol), dimethylamine (1.0 M in THF, 7.5 mL, 7.5 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), NaO^tBu (0.67 g, 7 mmol), SPhos (25 mg, 0.04 mmol) and toluene (15 mL) were added to a Schlenk tube. The reaction mixture was stirred at 110 ℃ for 12 h, and then cooled and diluted with ethyl acetate (100 mL) and H_2O (100 mL). The layers were separated and the organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and purified by flash chromatography to afford **5j** as a yellow oil (0.65 g, 73%).

HRMS (ESI) *m/z* calcd. For $C_{11}H_{19}N_2$ $[M + H]^+$: 179.1543; found: 179.1551.

^{1}H NMR (400 MHz,$CDCl_3$, 298 K): δ = 7.03 (m, 1H, Ar-H), 6.64 (m, 2H, Ar-H), 2.92 (s, 6H, N*Me*$_2$), 2.67 (s, 6H, N*Me*$_2$), 2.36 (s, 3H, Ar-*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 147.2, 143.6, 133.6, 119.6, 116.2, 111.4, 45.1, 41.4, 18.5.

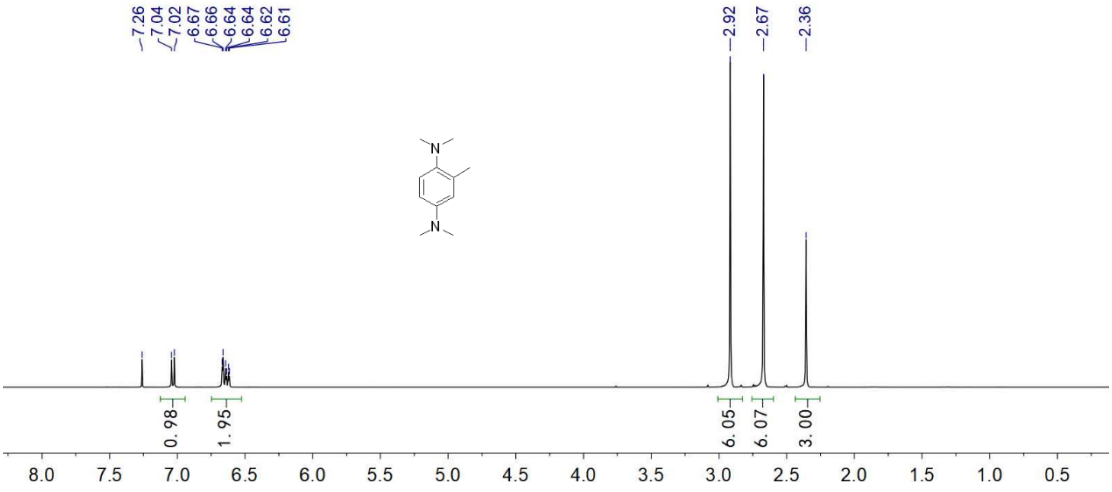


Fig. S13. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

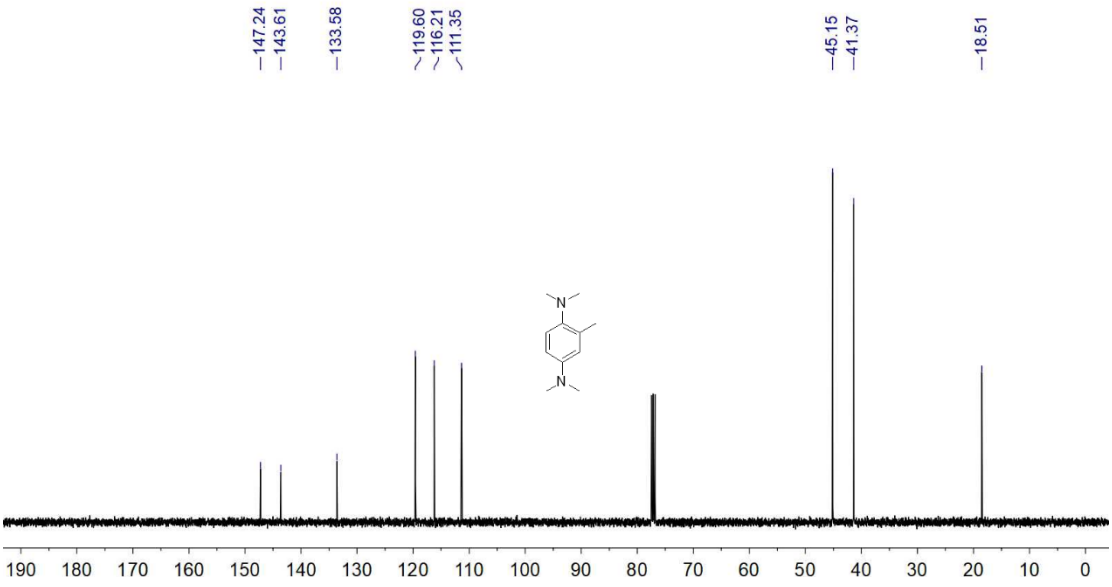
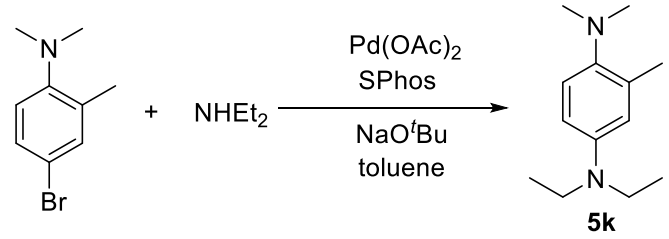


Fig. S14. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



Scheme S8.

Following the procedure described for **5j**, treatment of 4-bromo-*N,N*-dimethyl-*o*-toluidine (1.07 g, 5 mmol), diethylamine (0.55 g, 7.5 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), NaO^{t}Bu (0.67 g, 7 mmol), and SPhos (25 mg, 0.04 mmol) afforded **5k** as a yellow oil (0.67 g, 65%).

HRMS (ESI) *m/z* calcd. For $C_{13}H_{23}N_2$ $[M + H]^+$: 207.1856; found: 207.1865.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.00 (m, 1H, Ar-H), 6.56 (m, 2H, Ar-H), 3.32 (q, $^{3}J_{HH}$ = 7.1 Hz, 4H, C*H*$_2$CH$_3$), 2.66 (s, 6H, N*Me*$_2$), 2.33 (s, 3H, Ar-*Me*), 1.16 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH$_2$C*H*$_3$).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 144.4, 142.5, 133.8, 119.8, 115.4, 110.6, 45.3, 44.7, 18.6, 12.8.

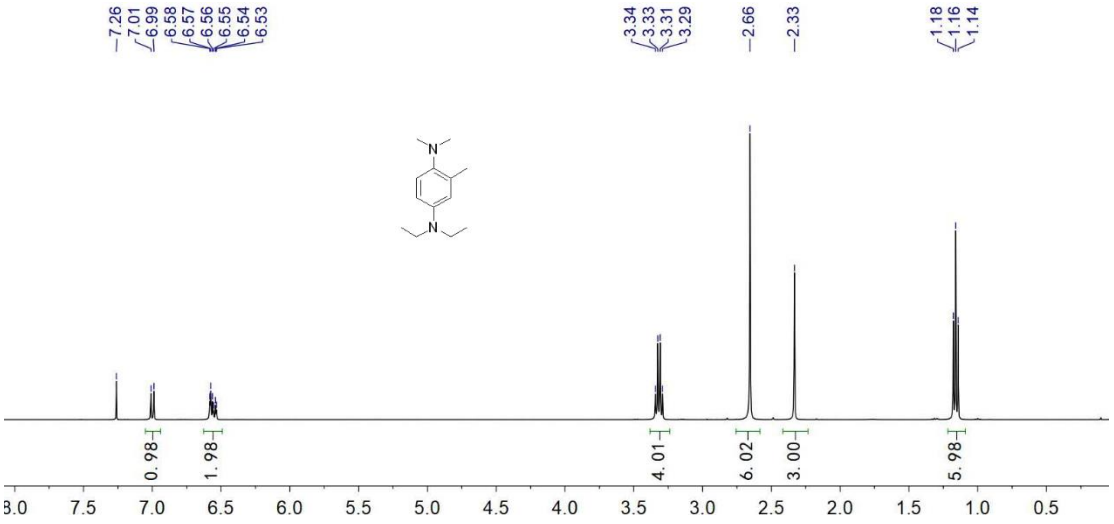


Fig. S15. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

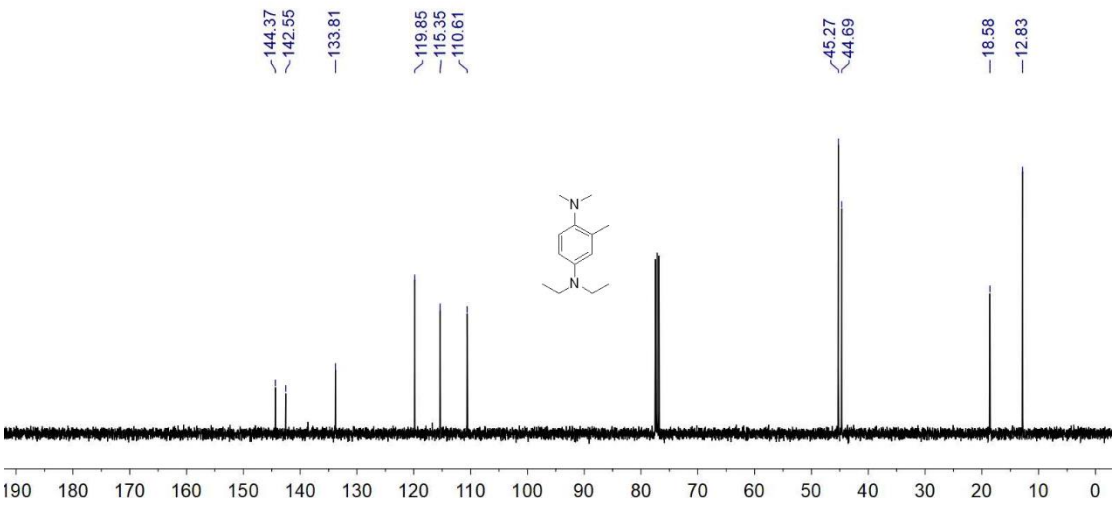
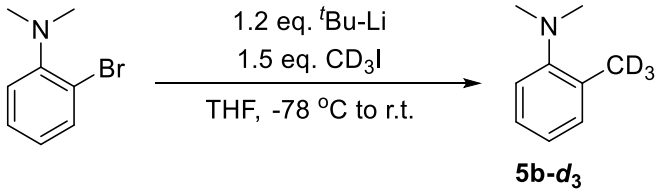


Fig. S16. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)

Preparation of deuterium labeled substrates



5b-*d*$_3$

Scheme S9.

t-BuLi (1.0 M in hexane, 6 mL, 6 mmol) was added dropwise to a solution of 2-bromo-*N*,*N*-dimethylaniline (1.07 g, 5.0 mmol) in 40 mL of THF at -78 °C. The reaction mixture was stirred at -78 °C for 40 min, and subsequently, CD_3I (1.10 g, 7.5 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 14 h, and then an appropriate amount of water was added under an ice-bath until all the lithium salts precipitate was dissolved. Diethyl ether (30 mL) was added and the

mixture was washed with saturated NaCl solution. The organic layer was collected and dried over anhydrous $MgSO_4$. After column chromatography (petroleum ether/ethyl acetate = 30/1), **5b-*d*$_3$** was obtained as a yellow oil (138 mg, 20%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.16 (m, 2H, Ar-H), 7.03 (m, 1H, Ar-H), 6.95 (m, 1H, Ar-H), 2.70 (s, 6H, N*Me*$_2$).

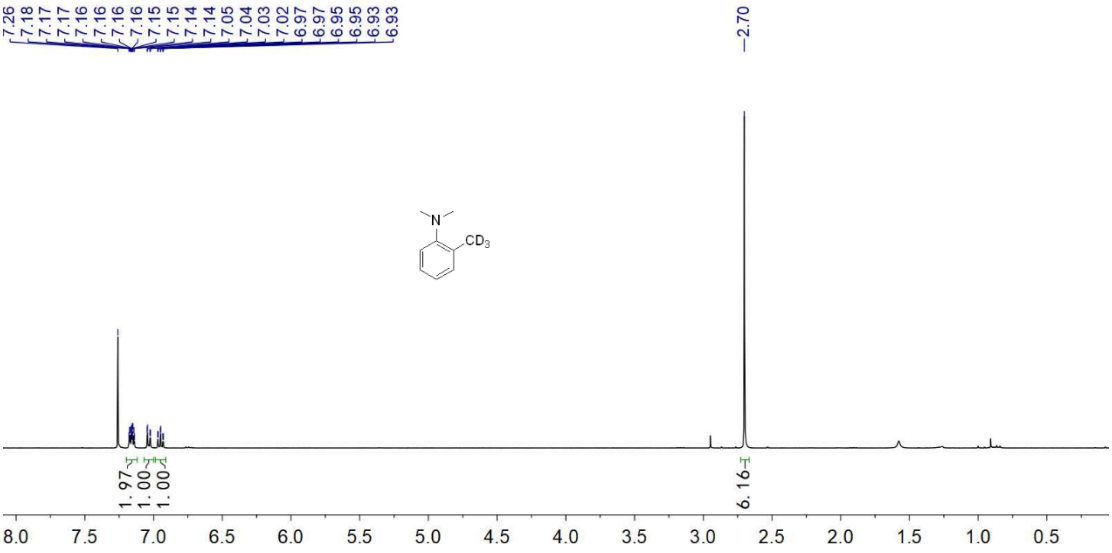


Fig. S17. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

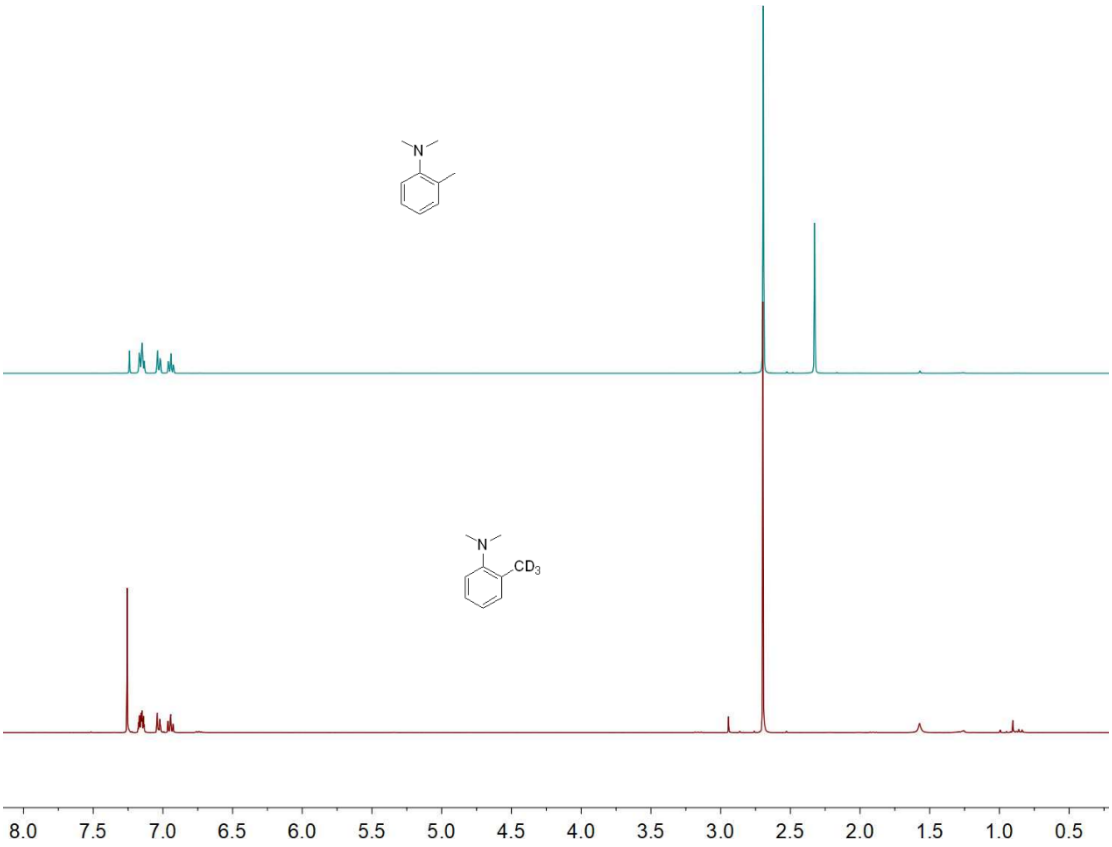
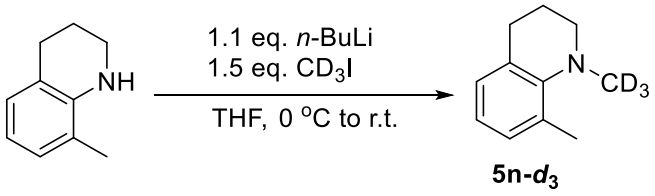


Fig. S18. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



Scheme S10.

n-BuLi (2.4 M in hexane, 2.3 mL, 5.5 mmol) was added to a solution of 8-methyl-1,2,3,4-tetrahydroquinoline (0.74 g, 5 mmol) in THF at 0 °C. The mixture was allowed to warm to room temperature for 1 h, and CD_3I (1.10 g, 7.5 mmol) was added. After 12 h, the reaction mixture was cooled and diluted with ethyl acetate (100 mL) and H_2O (100 mL). The layers were separated and the organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and purified by flash chromatography to afford **5n-*d*3** as a yellow oil (0.71 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.04 (m, 1H, Ar-H), 6.94 (m, 1H, Ar-H), 6.88 (m, 1H, Ar-H), 3.16 (m, 2H, C*H*$_2$), 2.85 (t, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*$_2$), 2.35 (s, 3H, Ar-*Me*), 1.89 (m, 2H, C*H*$_2$).

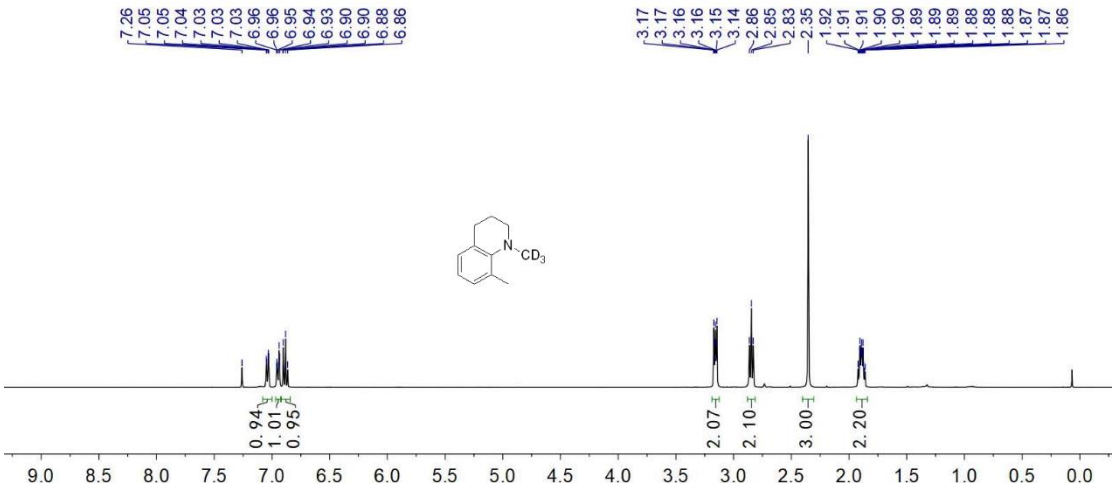


Fig. S19. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

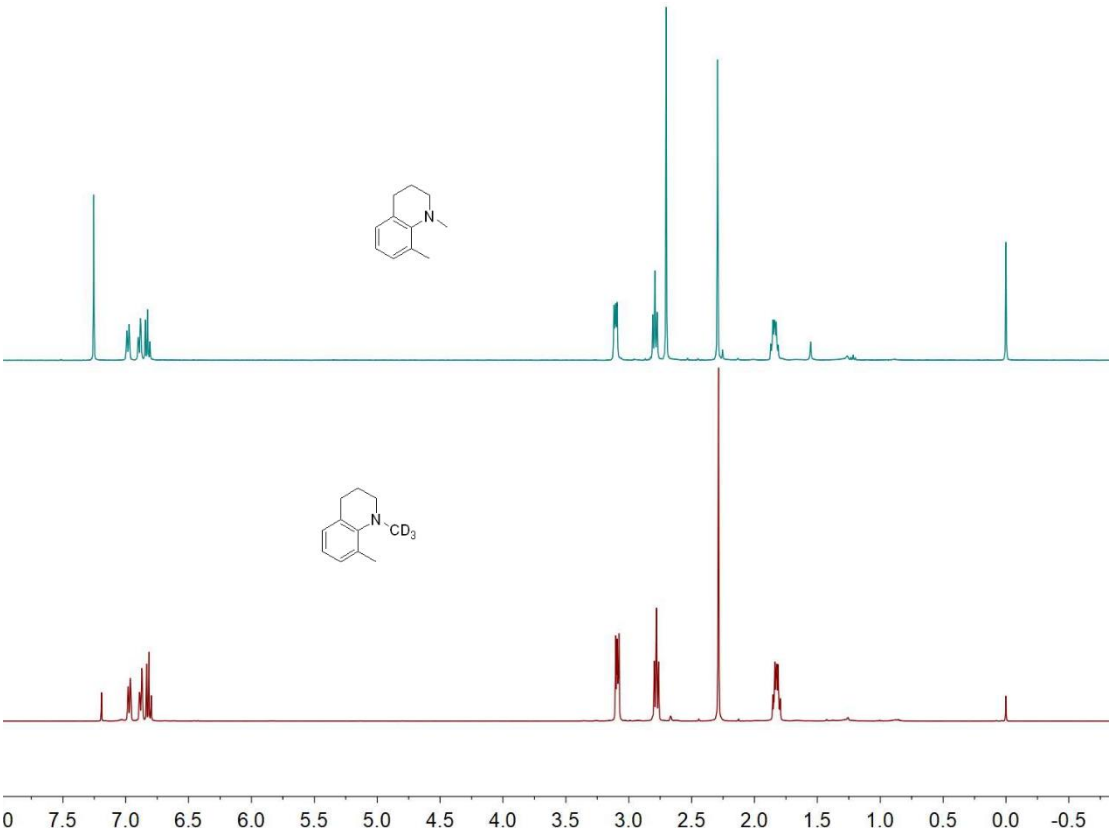
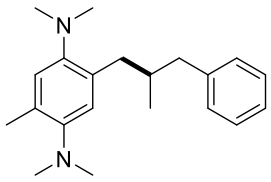


Fig. S20. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

General procedure for benzylic C-H alkylation of aromatic amines with alkenes

Complex **3** (18 mg, 0.03 mmol) in 0.5 mL of toluene was added to a solution of $[PhNHMe_2][B(C_6F_5)_4]$ (24 mg, 0.03 mmol) in 0.5 mL of toluene. After stirring at room temperature for 5 min, a mixture of amine (0.45 mmol) and alkene (0.3 mmol) in 1 mL of toluene was added and the reaction mixture was heated at 80 °C for 12 h. Then, the mixture was cooled to room temperature and the volatiles were removed under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, a small amount of Et_3N if necessary) to eventually afford the target alkylation product.

Characterization of alkylation products



7a (colorless oil, 86 mg, 92%)

HRMS (ESI) *m/z* calcd. For $C_{21}H_{31}N_2$ $[M + H]^+$: 311.2482; found: 311.2478.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.27 (m, 2H, Ar-H), 7.18 (m, 3H, Ar-H), 6.94

(m, 1H, Ar-H), 6.86 (m, 1H, Ar-H), 2.74 (m, 2H, CH_2), 2.69 (s, 6H, NMe_2), 2.60 (s, 6H, NMe_2), 2.50 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, CH_2), 2.41 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, CH_2), 2.31 (s, 3H, Ar-*Me*), 2.19 (m, 1H, C*H*), 0.86 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.4, 148.3, 142.0, 134.6, 130.3, 129.3, 128.2, 125.7, 122.7, 120.3, 45.6, 44.8, 43.6, 38.2, 36.3, 19.6, 18.1.

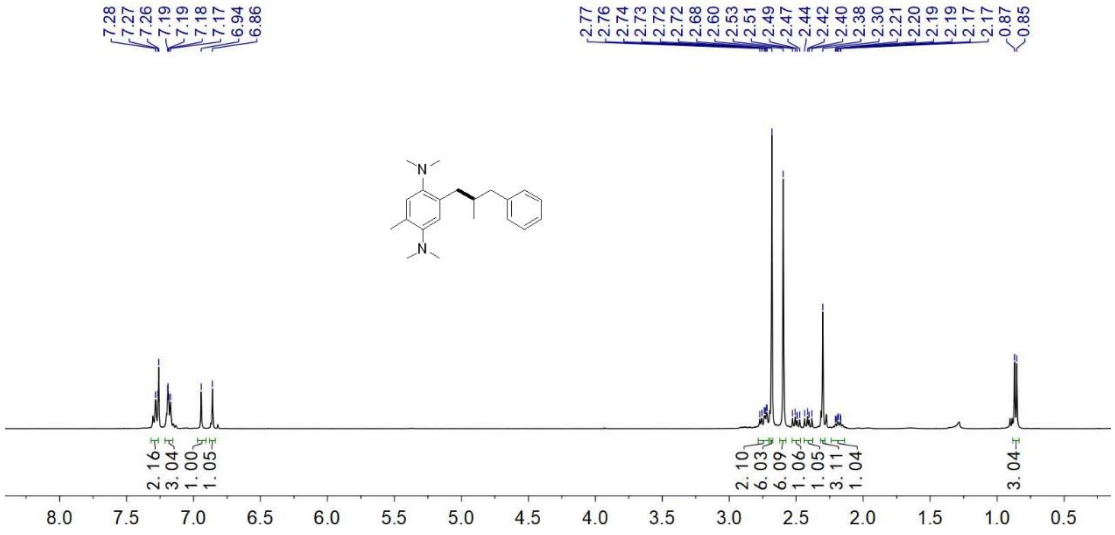


Fig. S21. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

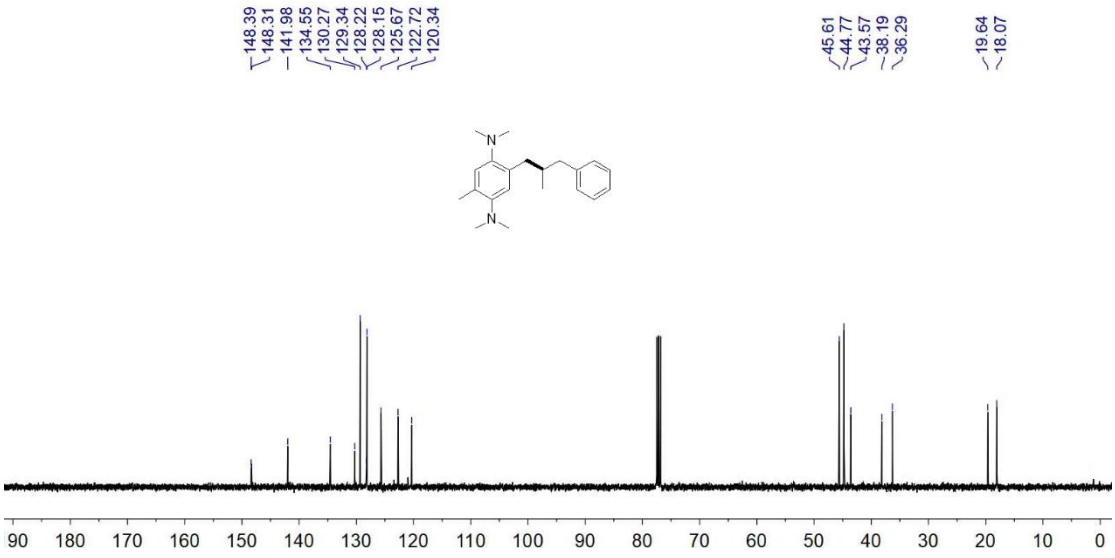


Fig. S22. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)

7a' (colorless oil, 116 mg, 90%)

HRMS (ESI) *m/z* calcd. For $C_{30}H_{41}N_2$ $[M + H]^+$: 429.3264; found: 429.3286.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.30 (m, 4H, Ar-H), 7.20 (m, 6H, Ar-H), 6.96 (s, 2H, Ar-H), 2.74 (m, 4H, CH_2), 2.63 (s, 12H, NMe_2), 2.53 (m, 2H, CH_2), 2.42 (m, 2H, CH_2), 2.20 (m, 2H, C*H*Me), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 149.0, 142.0, 134.6, 129.3, 128.2, 125.7, 121.7, 45.6, 43.6, 38.2, 36.3, 19.7.

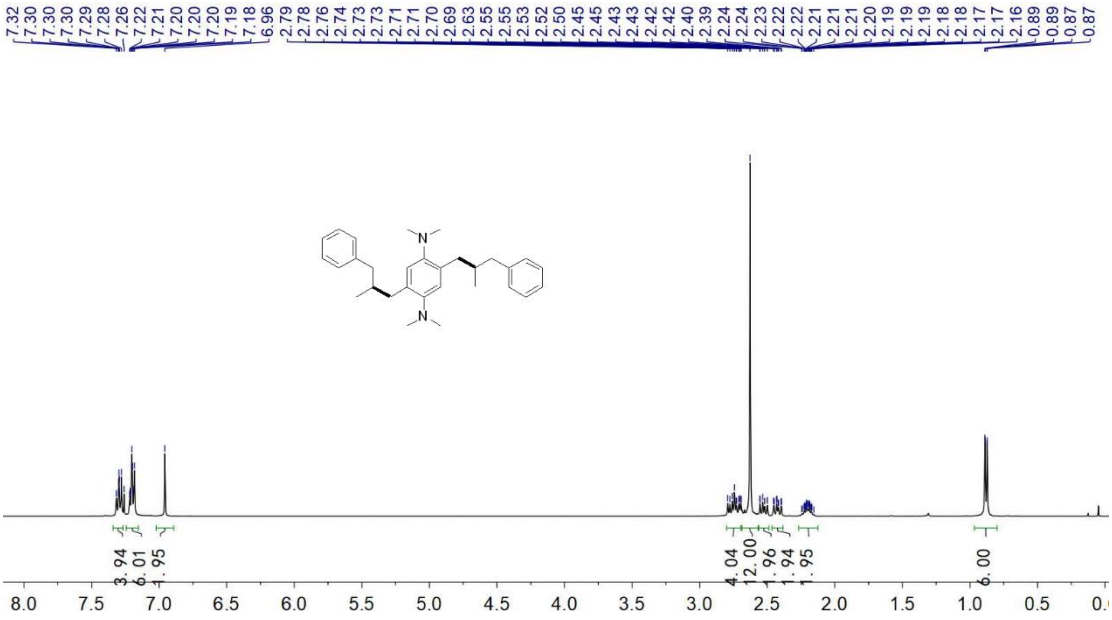


Fig. S23. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

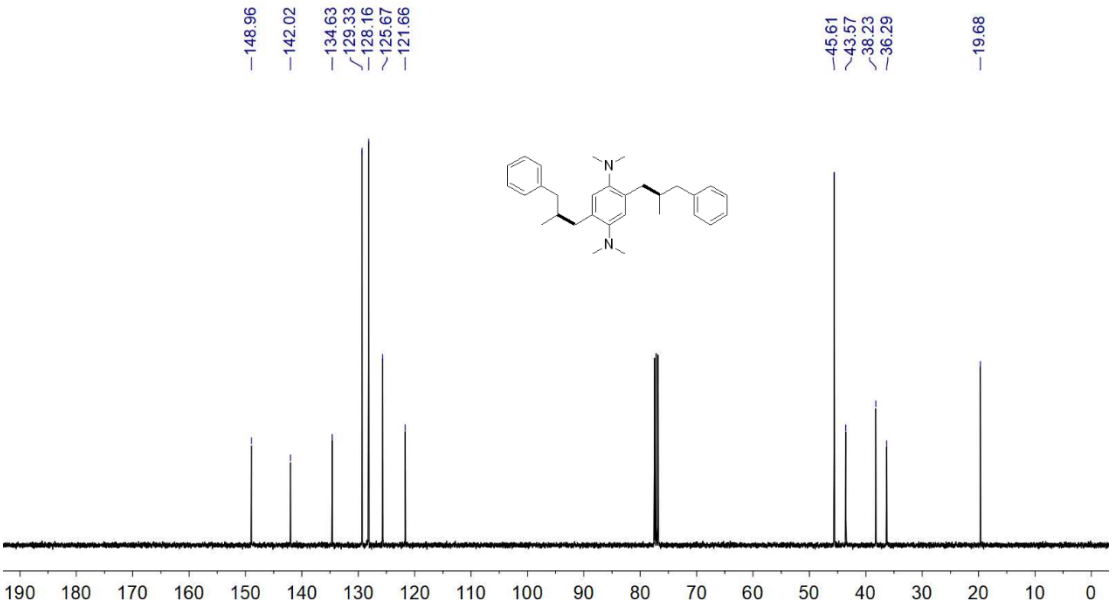
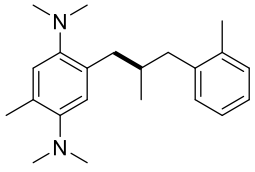


Fig. S24. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7b (colorless oil, 86 mg, 88%)

HRMS (ESI) *m/z* calcd. For $C_{22}H_{33}N_2$ $[M + H]^+$: 325.2638; found: 325.2631.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.13 (m, 4H, Ar-H), 6.95 (m, 1H, Ar-H), 6.87 (m, 1H, Ar-H), 2.80 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 6.3 Hz, 1H, C*H*$_2$), 2.72 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, C*H*$_2$), 2.68 (s, 6H, N*Me*$_2$), 2.59 (s, 6H, N*Me*$_2$), 2.50 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*$_2$), 2.40 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 8.9 Hz, 1H, C*H*$_2$), 2.31 (s, 3H, Ar-*Me*), 2.25 (s, 3H, Ar-*Me*), 2.15 (m, 1H, C*H*Me), 0.89 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.3, 148.2, 140.2, 136.4, 134.6, 130.3, 130.2, 130.1, 125.8, 125.6, 122.7, 120.5, 45.6, 44.7, 40.9, 38.7, 35.1, 19.8, 19.6, 18.1.

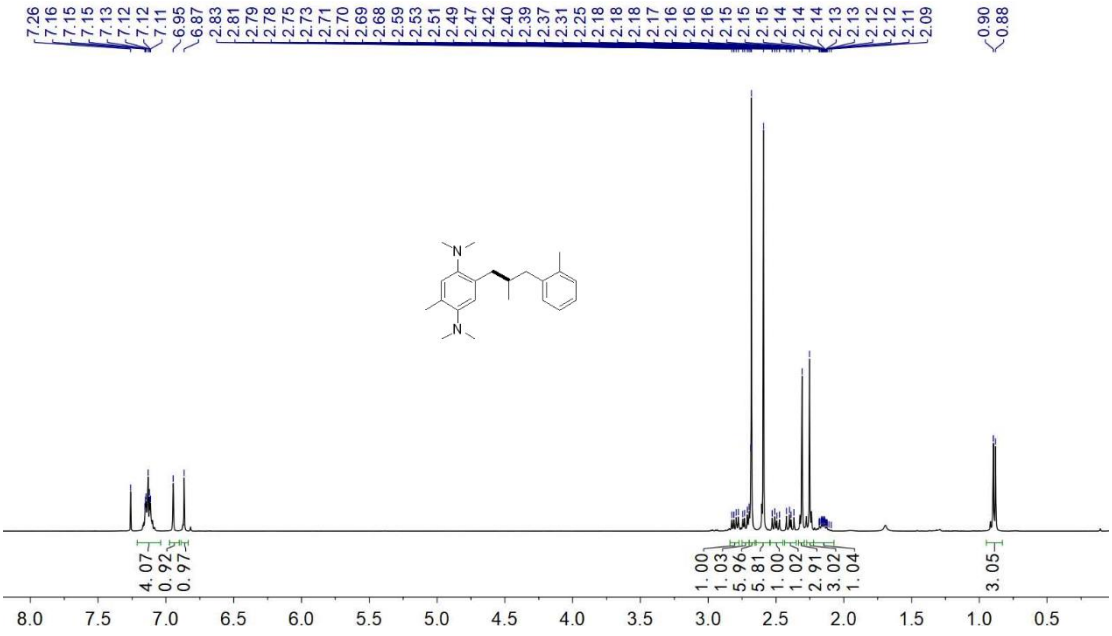


Fig. S25. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

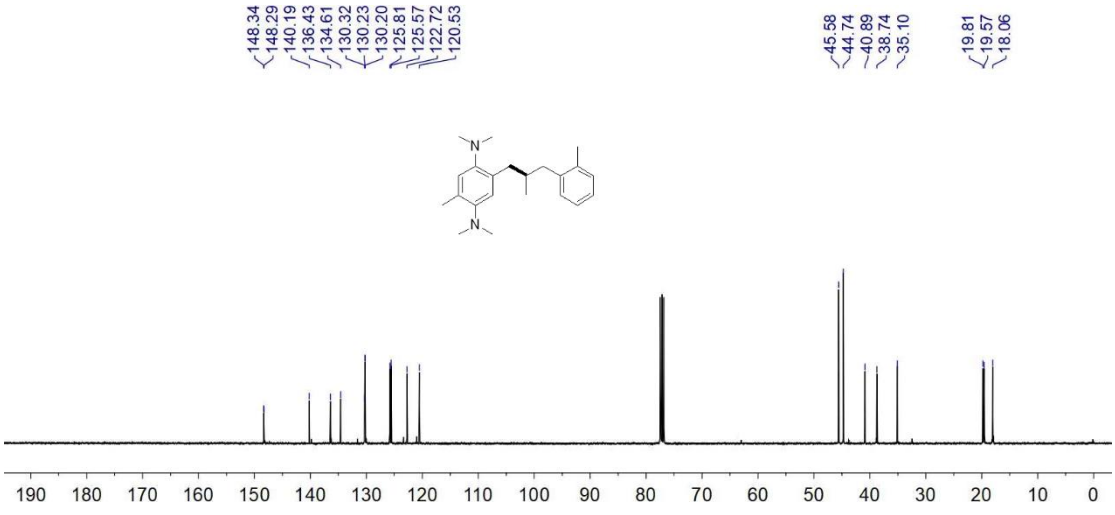
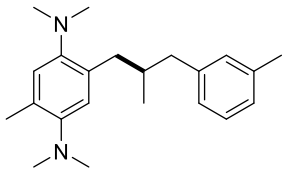


Fig. S26. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7c (colorless oil, 89 mg, 91%)

HRMS (ESI) *m/z* calcd. For $C_{22}H_{33}N_2$ $[M + H]^+$: 325.2638; found: 325.2647.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.21 (m, 1H, Ar-H), 7.04 (m, 3H, Ar-H), 6.98 (m, 1H, Ar-H), 6.90 (m, 1H, Ar-H), 2.73 (m, 2H, C*H*$_2$), 2.72 (s, 6H, N*Me*$_2$), 2.64 (s, 6H, N*Me*$_2$), 2.54 (m, 1H, C*H*$_2$), 2.42 (m, 1H, C*H*$_2$), 2.38 (s, 3H, Ar-*Me*), 2.34 (s, 3H, Ar-*Me*), 2.21 (m, 1H, C*H*Me), 0.90 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.4, 148.3, 141.9, 137.6, 134.6, 130.3, 130.1, 128.0, 126.4, 126.3, 122.7, 120.4, 45.6, 44.8, 43.5, 38.2, 36.2, 21.6, 19.7, 18.1.

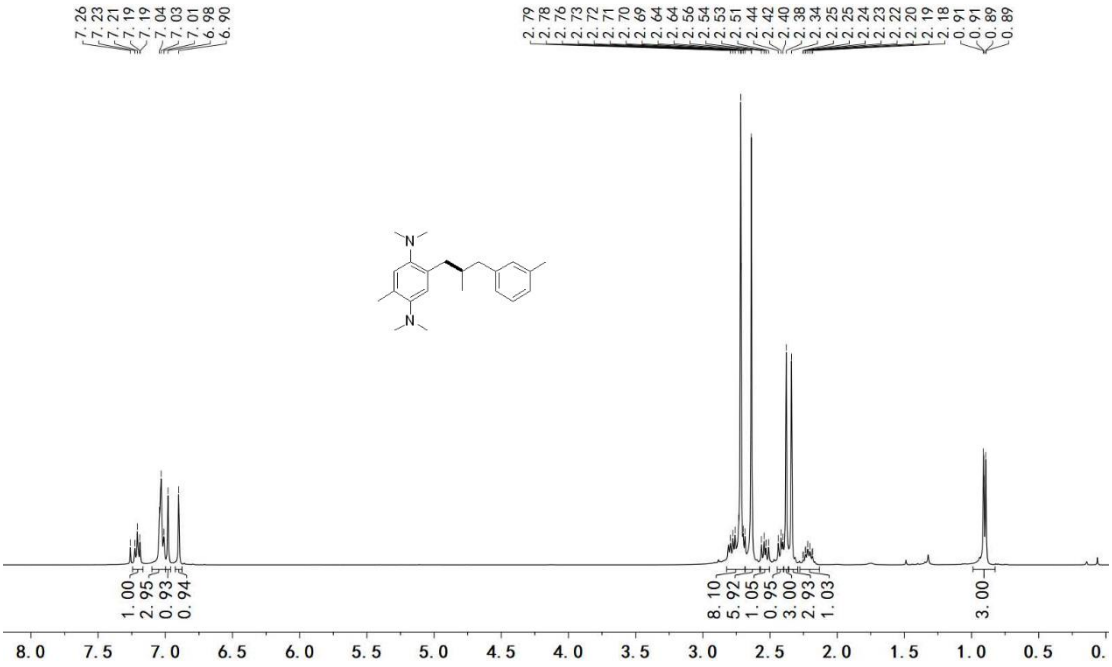


Fig. S27. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

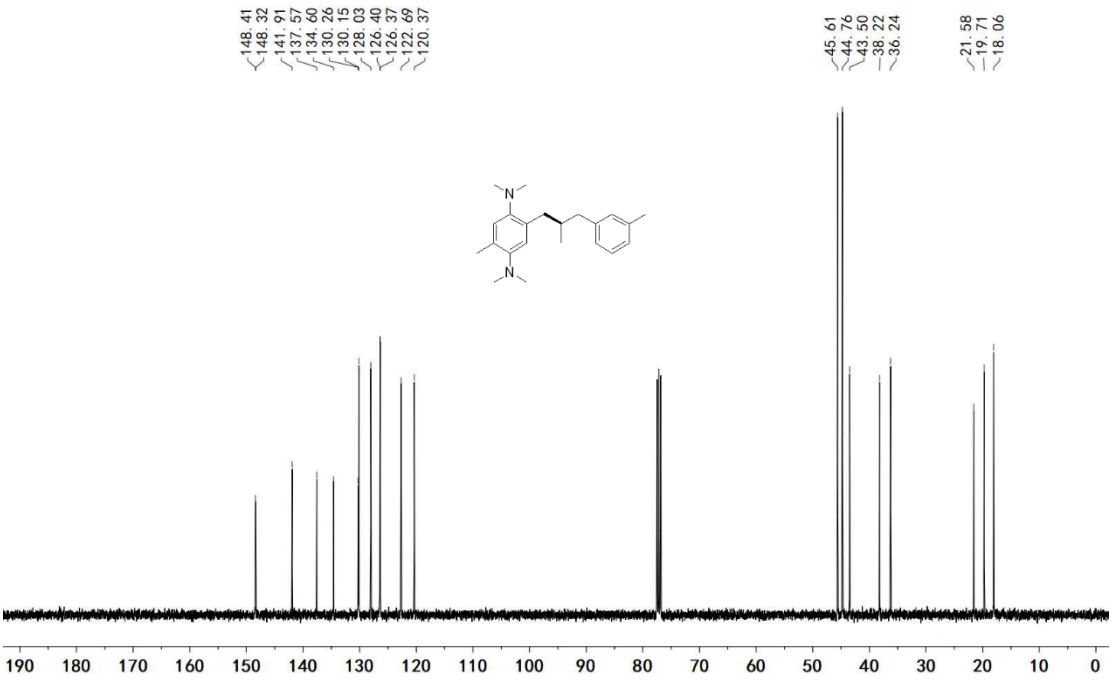
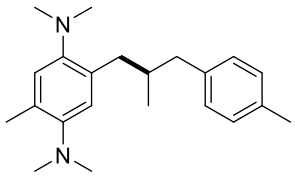


Fig. S28. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



7d (colorless oil, 88 mg, 90%)

HRMS (ESI) *m/z* calcd. For $C_{22}H_{33}N_2$ $[M + H]^+$: 325.2638; found: 325.2641.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.09 (m, 4H, Ar-H), 6.95 (m, 1H, Ar-H), 6.87 (m, 1H, Ar-H), 2.74 (m, 2H, C*H*$_2$), 2.69 (s, 6H, N*Me*$_2$), 2.61 (s, 6H, N*Me*$_2$), 2.51 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*$_2$), 2.38 (m, 1H, C*H*$_2$), 2.34 (s, 3H, Ar-*Me*), 2.31 (s, 3H, Ar-*Me*), 2.16 (m, 1H, C*H*Me), 0.86 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.4, 148.3, 138.8, 135.0, 134.6, 130.2, 129.2, 128.9, 122.7, 120.3, 45.6, 44.8, 43.1, 38.1, 36.3, 21.2, 19.6, 18.1.

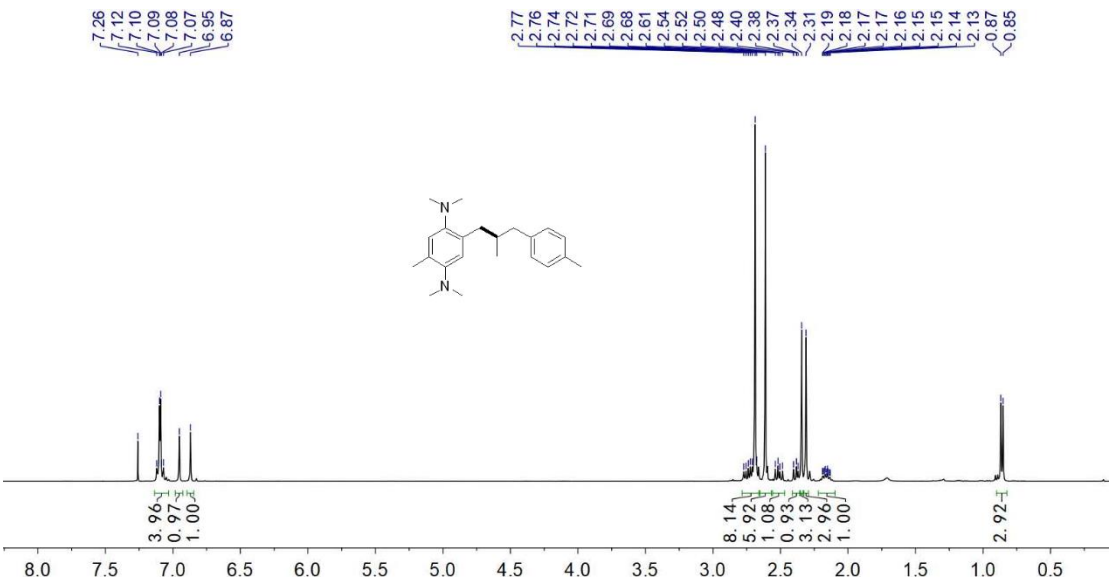


Fig. S29. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

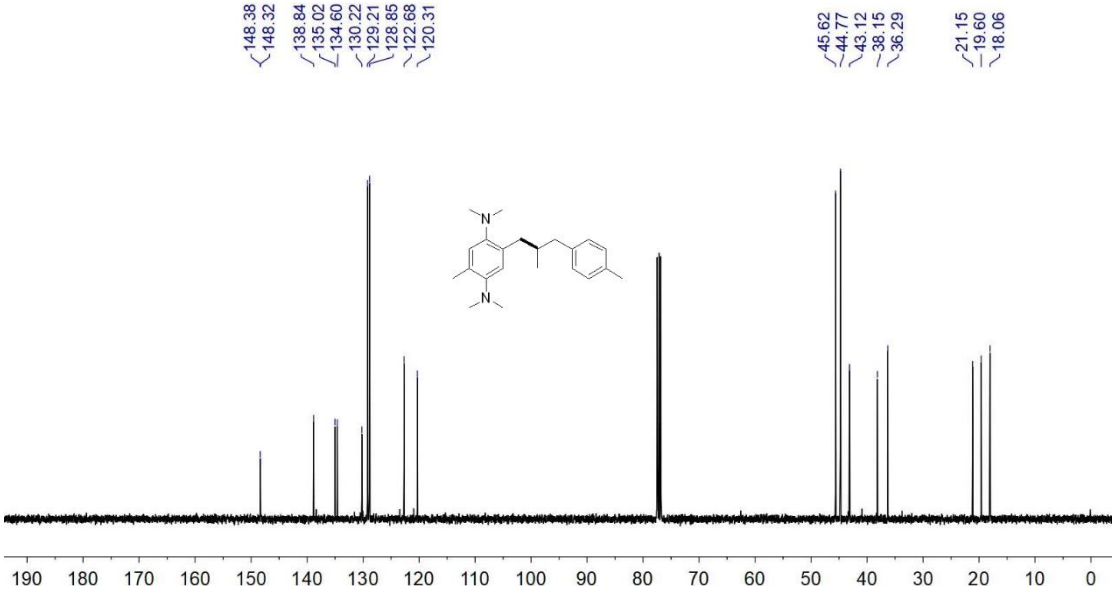
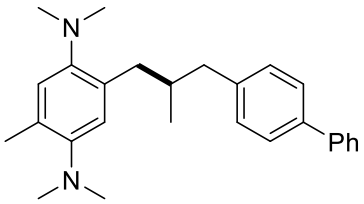


Fig. S30. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7e (colorless oil, 105 mg, 91%).

HRMS (ESI) *m/z* calcd. For $C_{27}H_{35}N_2$ $[M + H]^+$: 387.2795; found: 387.2787.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.61 (m, 2H, Ar-H), 7.53 (m, 2H, Ar-H), 7.44 (m, 2H, Ar-H), 7.34 (m, 1H, Ar-H), 7.27 (m, 2H, Ar-H), 6.95 (m, 1H, Ar-H), 6.88 (m, 1H, Ar-H), 2.76 (m, 2H, C*H*$_2$), 2.69 (s, 6H, N*Me*$_2$), 2.61 (s, 6H, N*Me*$_2$), 2.49 (m, 2H,

CH_2), 2.31 (s, 3H, Ar-*Me*), 2.23 (m, 1H, C*H*Me), 0.90 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.3, 148.2, 141.2, 141.0, 138.5, 134.4, 130.2, 129.7, 128.7, 127.0, 126.9, 126.8, 122.6, 120.2, 45.5, 44.7, 43.1, 38.1, 36.2, 19.6, 18.0.

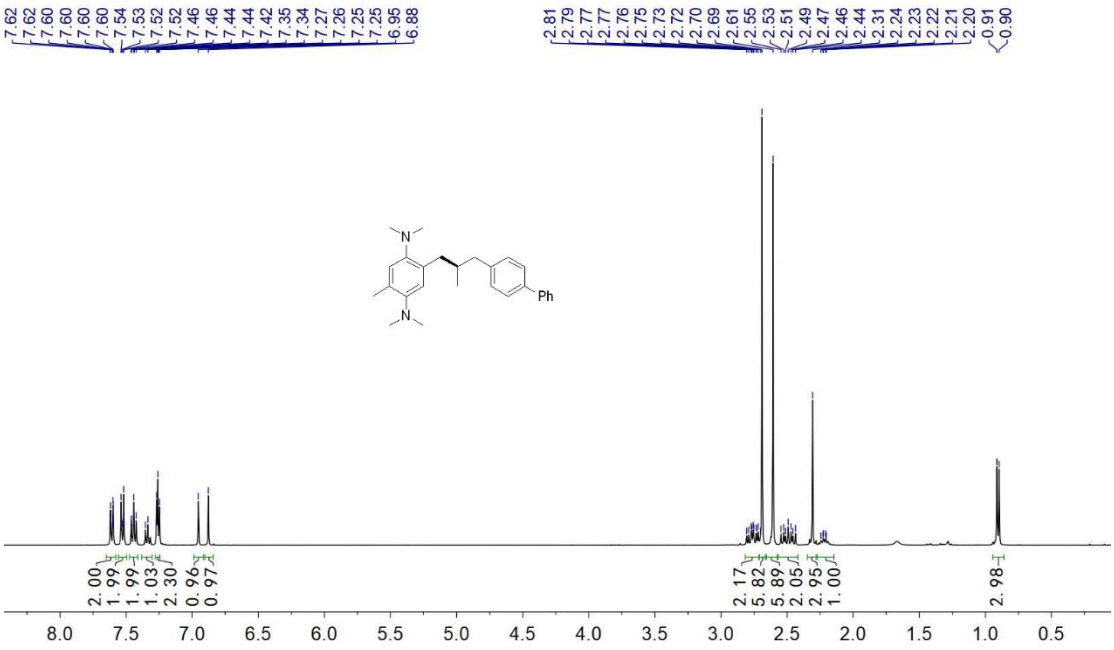


Fig. S31. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

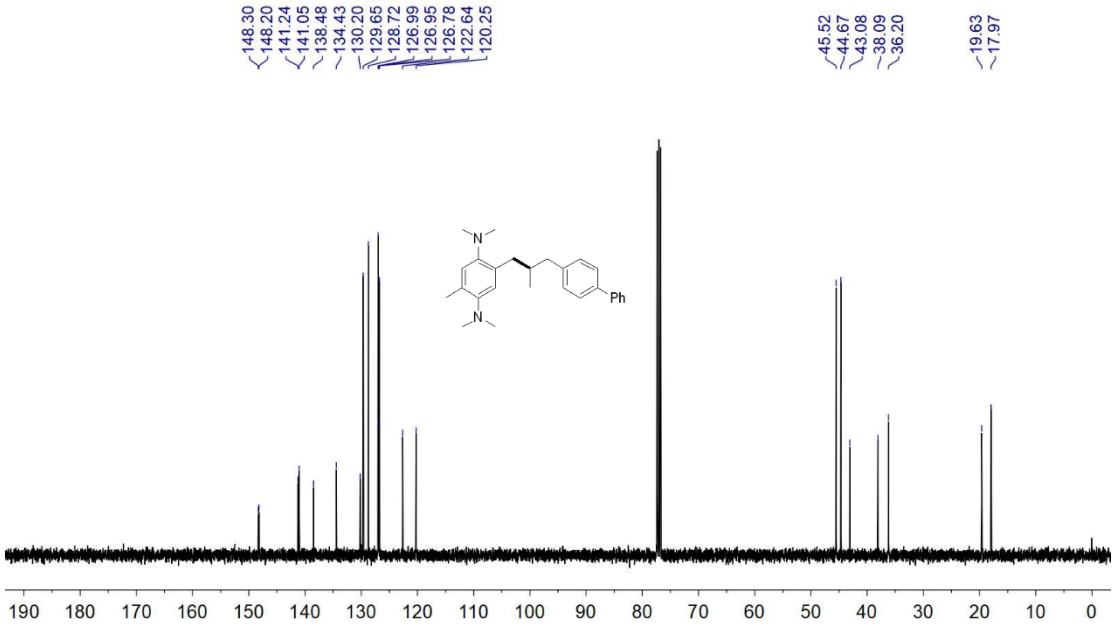
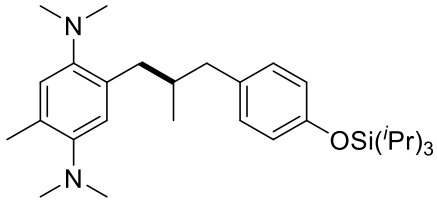


Fig. S32. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298K)



7f (colorless oil, 134 mg, 93%)

HRMS (ESI) *m/z* calcd. For $C_{30}H_{51}N_2OSi$ $[M + H]^+$: 483.3765; found: 483.3783.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.01 (m, 2H, Ar-H), 6.93 (m, 1H, Ar-H), 6.84 (m, 1H, Ar-H), 6.80 (m, 2H, Ar-H), 2.73 (dd, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, CH_2), 2.68 (s, 6H, NMe_2), 2.63 (m, 1H, CH_2), 2.59 (s, 6H, NMe_2), 2.46 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.1 Hz, 1H, CH_2), 2.35 (m, 1H, CH_2), 2.30 (s, 3H, Ar-*Me*), 2.12 (m, 1H, C*H*Me), 1.25 (m, 3H, C*H*Me_2), 1.11 (d, $^3J_{HH}$ = 7.2 Hz, 18H, CHMe_2), 0.83 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 154.0, 148.3, 134.7, 134.4, 130.2, 130.1, 130.0, 122.7, 120.4, 119.6, 45.6, 44.8, 42.8, 38.1, 36.4, 19.6, 18.1, 12.8.

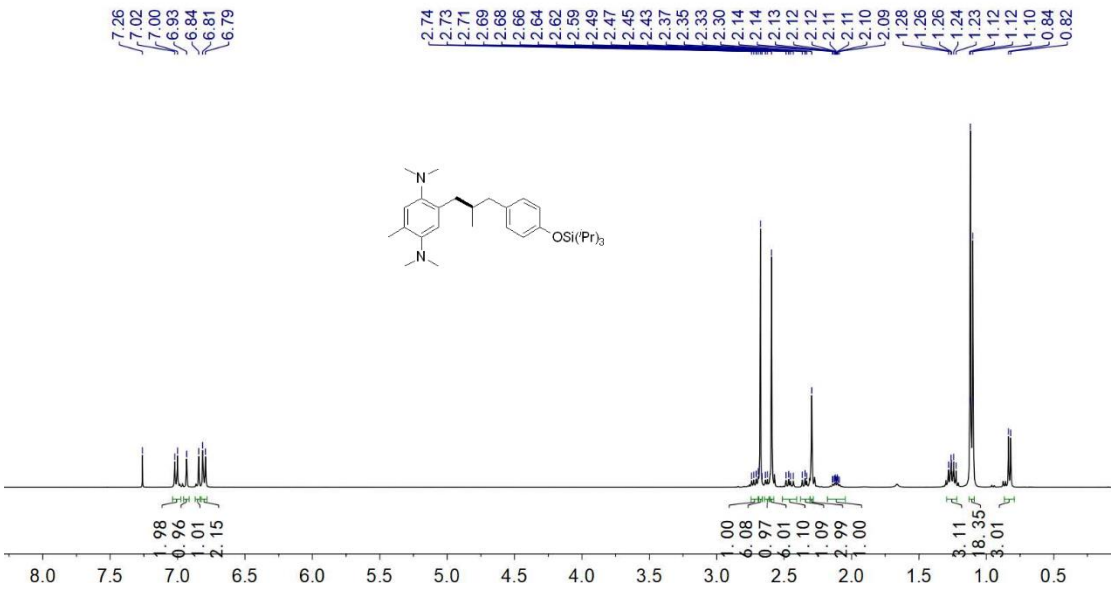


Fig. S33. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

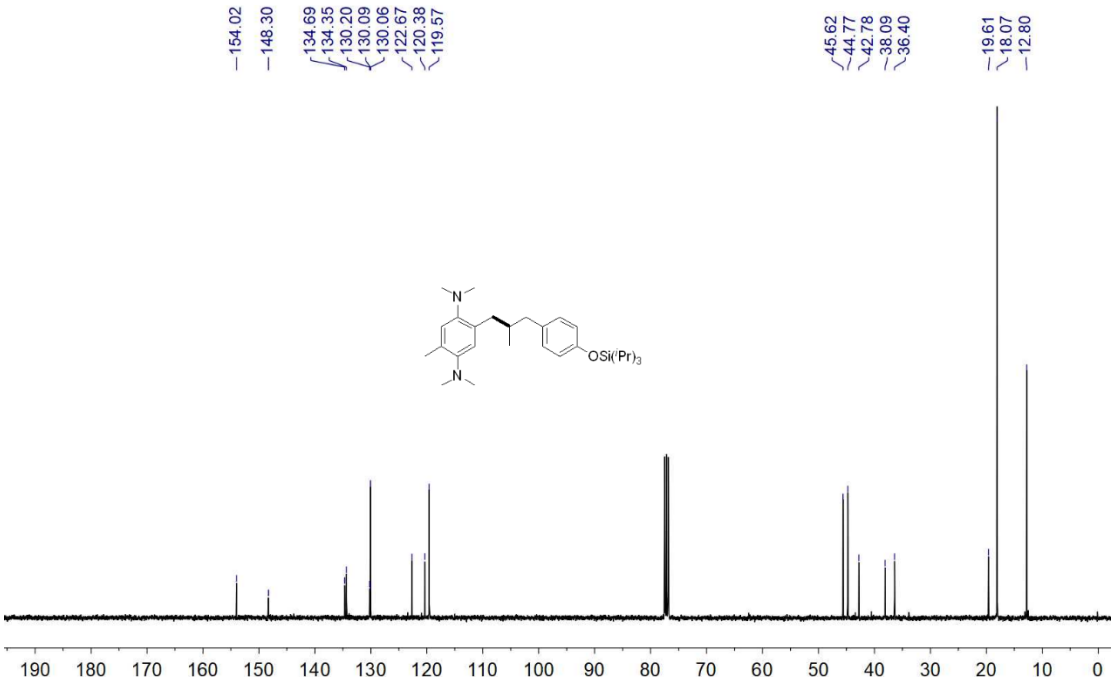
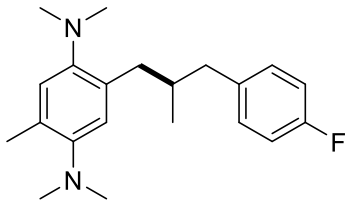


Fig. S34. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



7g (colorless oil, 86 mg, 87%)

HRMS (ESI) *m/z* calcd. For $C_{21}H_{30}FN_2$ $[M + H]^+$: 329.2388; found: 329.2398.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.12 (m, 2H, Ar-H), 6.96 (m, 3H, Ar-H), 6.84 (m, 1H, Ar-H), 2.69 (m, 2H, CH_2), 2.68 (m, 6H, NMe_2), 2.58 (s, 6H, NMe_2), 2.46 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 8.0 Hz, 1H, CH_2), 2.38 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 8.4 Hz, 1H, CH_2), 2.30 (s, 3H, Ar-*Me*), 2.14 (m, 1H, C*H*Me), 0.84 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 161.3 ($^{1}J_{FC}$ = 242.9 Hz), 148.4, 148.3, 137.5 ($^{4}J_{FC}$ = 3.2 Hz), 134.4, 130.6, 130.6 ($^{3}J_{FC}$ = 7.6 Hz), 122.8, 120.3, 114.83 ($^{2}J_{FC}$ = 21.0 Hz), 45.6, 44.8, 42.6, 38.1, 36.4, 19.6, 18.1.

^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ = -118.3.

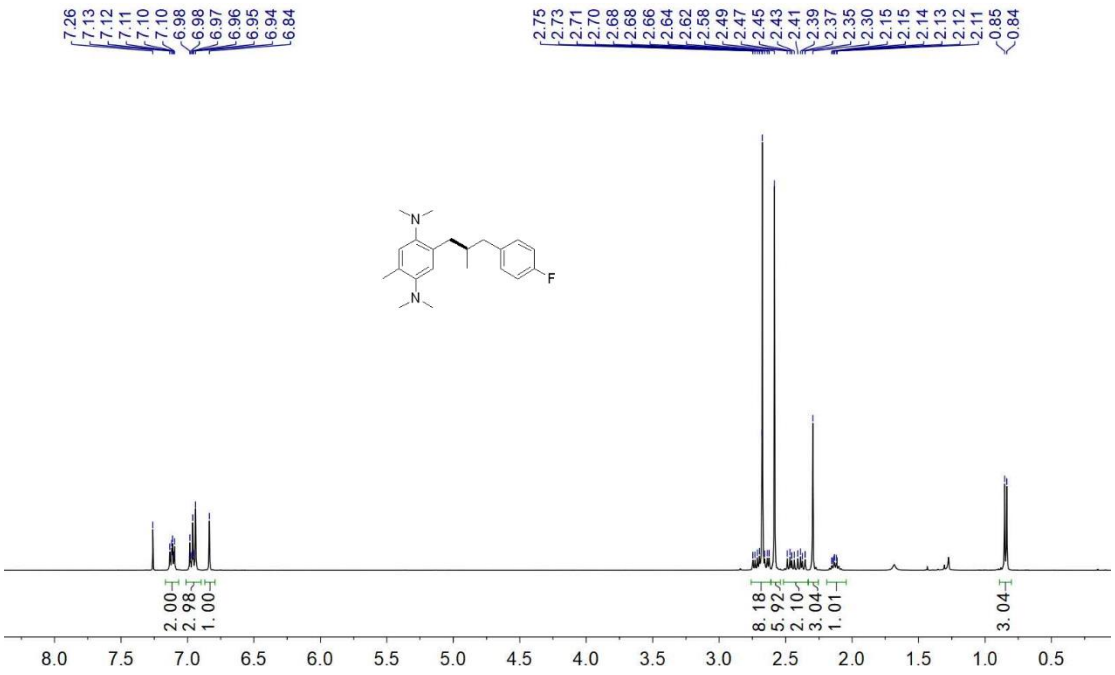


Fig. S35. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

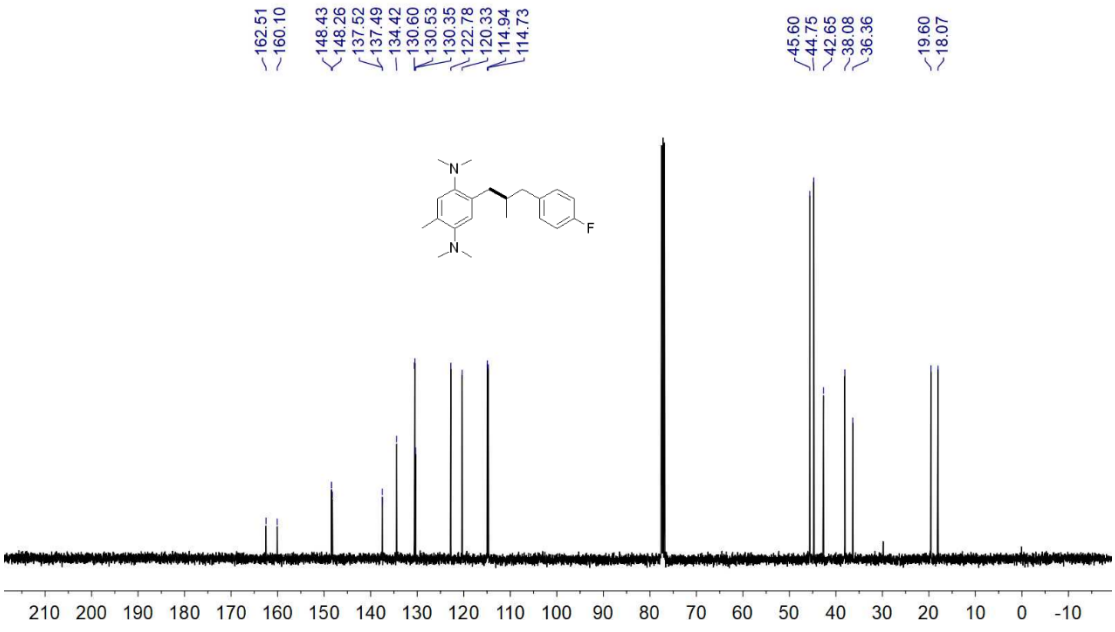


Fig. S36. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)

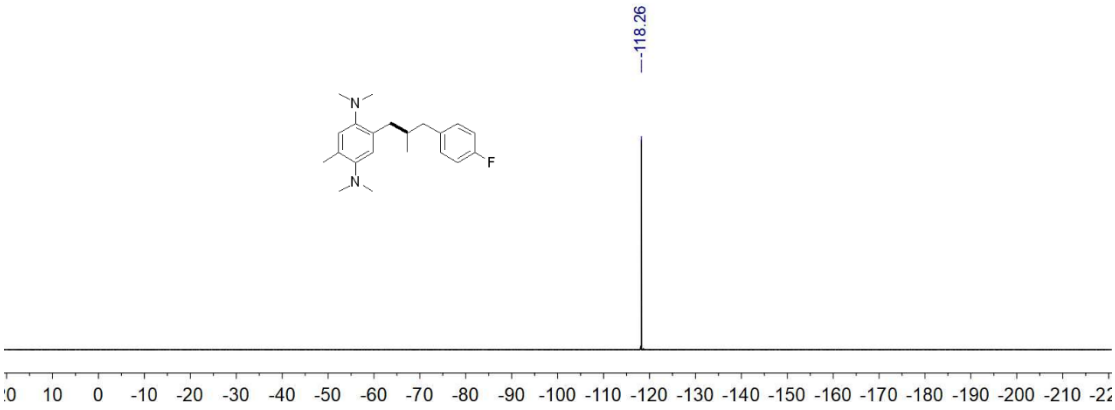
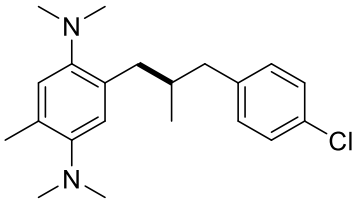


Fig. S37. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K)



7h (colorless oil, 82 mg, 79%)

HRMS (ESI) *m/z* calcd. For $C_{21}H_{30}ClN_2$ $[M + H]^+$: 345.2092; found: 345.2079.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.28 (m, 2H, Ar-H), 7.13 (m, 2H, Ar-H), 6.97 (m, 1H, Ar-H), 6.86 (m, 1H, Ar-H), 2.76 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, CH_2), 2.70 (s, 6H, NMe_2), 2.67 (m, 1H, CH_2), 2.61 (s, 6H, NMe_2), 2.49 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, CH_2), 2.41 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.4 Hz, 1H, CH_2), 2.33 (s, 3H, Ar-*Me*), 2.17 (m, 1H, C*H*Me), 0.87 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.5, 148.3, 140.4, 134.3, 131.4, 130.6, 130.4, 128.2, 122.8, 120.3, 45.6, 44.7, 42.8, 38.1, 36.2, 19.6, 18.1.

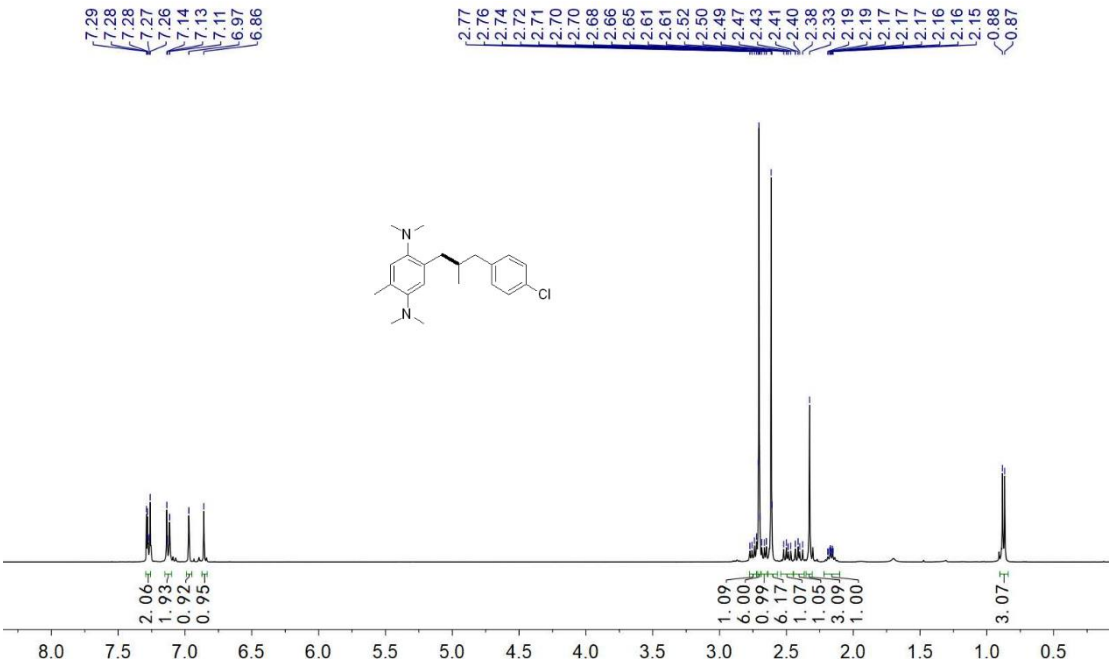


Fig. S38. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

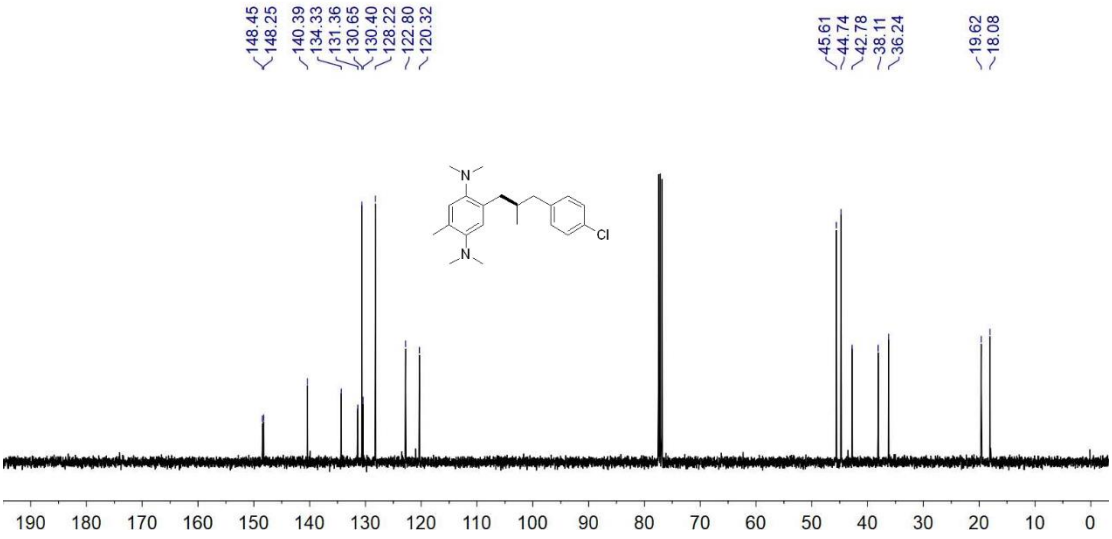
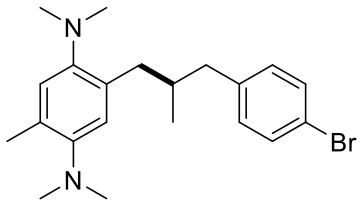


Fig. S39. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7i (colorless oil, 96 mg, 82%)

HRMS (ESI) *m/z* calcd. For $C_{21}H_{30}BrN_2$ $[M + H]^+$: 389.1587; found: 389.1589.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.39 (m, 2H, Ar-H), 7.04 (m, 2H, Ar-H), 6.94 (m, 1H, Ar-H), 6.82 (m, 1H, Ar-H), 2.71 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 6.4 Hz, 1H, CH_2), 2.67 (s, 6H, NMe_2), 2.63 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 5.7 Hz, 1H, CH_2), 2.58 (s, 6H,

N*Me*$_2$), 2.46 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*$_2$), 2.36 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.4 Hz, 1H, C*H*$_2$), 2.29 (s, 3H, Ar-*Me*), 2.13 (m, 1H, C*H*Me), 0.84 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 148.3, 148.1, 140.8, 134.2, 131.1, 131.0, 130.3, 122.7, 120.2, 119.3, 45.5, 44.6, 42.7, 38.0, 36.1, 19.5, 18.0.

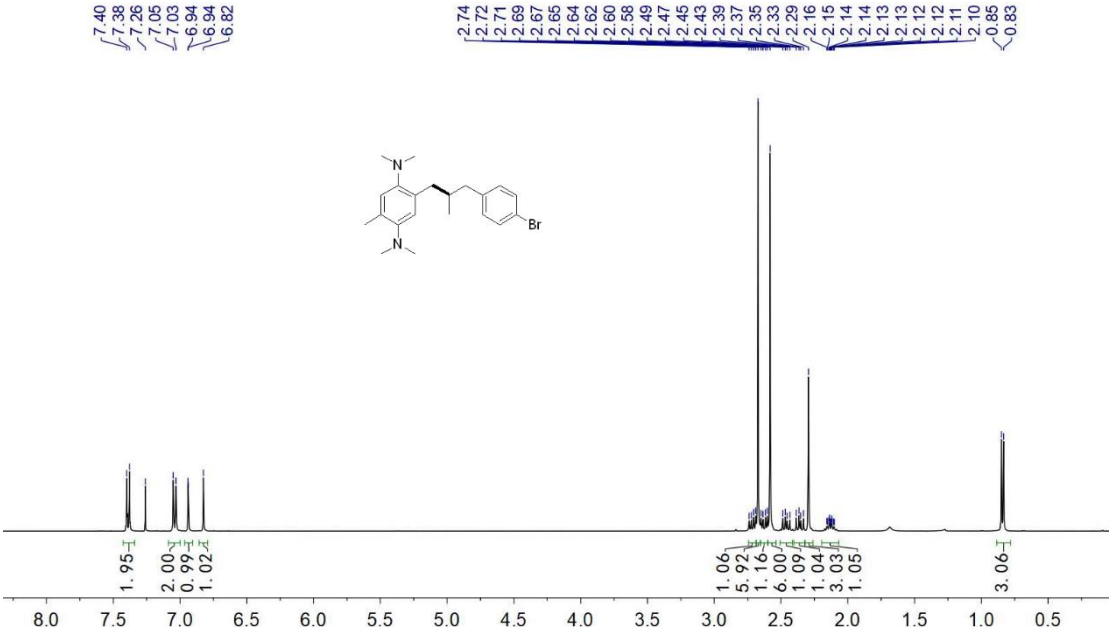


Fig. S40. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

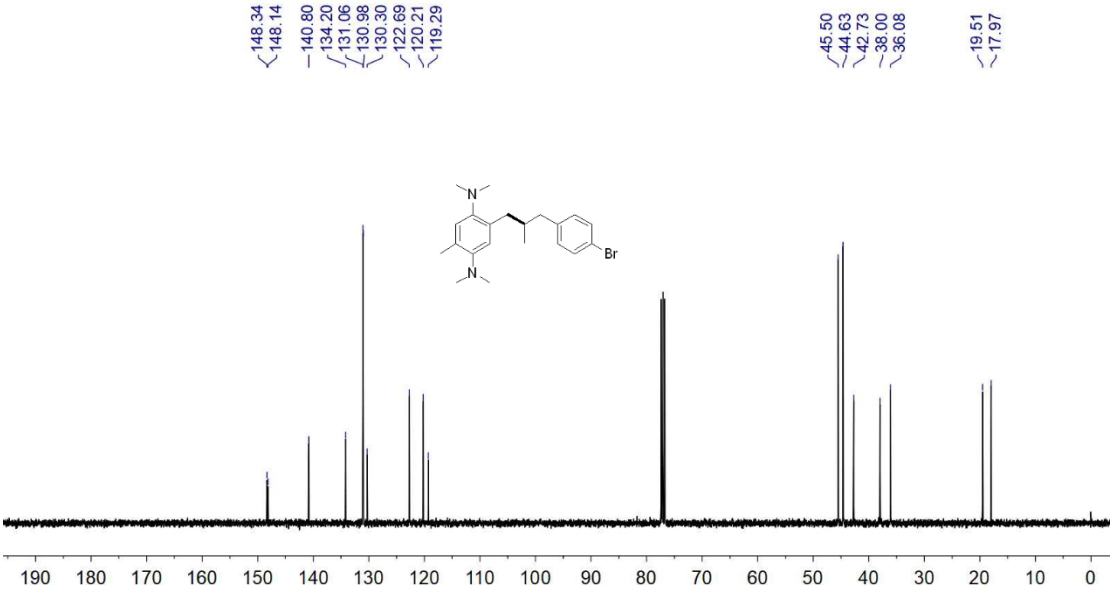
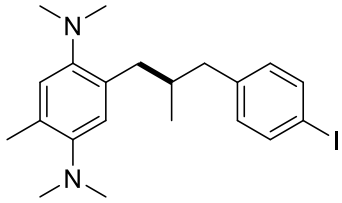


Fig. S41. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7j (colorless oil, 109 mg, 83%)

HRMS (ESI) *m/z* calcd. For $C_{21}H_{30}IN_2$ $[M + H]^+$: 437.1448; found: 437.1456.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.58 (m, 2H, Ar-H), 6.93 (m, 3H, Ar-H), 6.82 (m, 1H, Ar-H), 2.70 (m, 1H, CH_2), 2.67 (s, 6H, NMe_2), 2.60 (m, 1H, CH_2), 2.58 (s, 6H, NMe_2), 2.46 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, CH_2), 2.34 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.4 Hz, 1H, CH_2), 2.29 (s, 3H, Ar-*Me*), 2.12 (m, 1H, C*H*Me), 0.84 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.4, 148.2, 141.6, 137.2, 134.3, 131.5, 130.4, 122.8, 120.3, 90.7, 45.6, 44.7, 42.9, 38.1, 36.2, 19.6, 18.1.

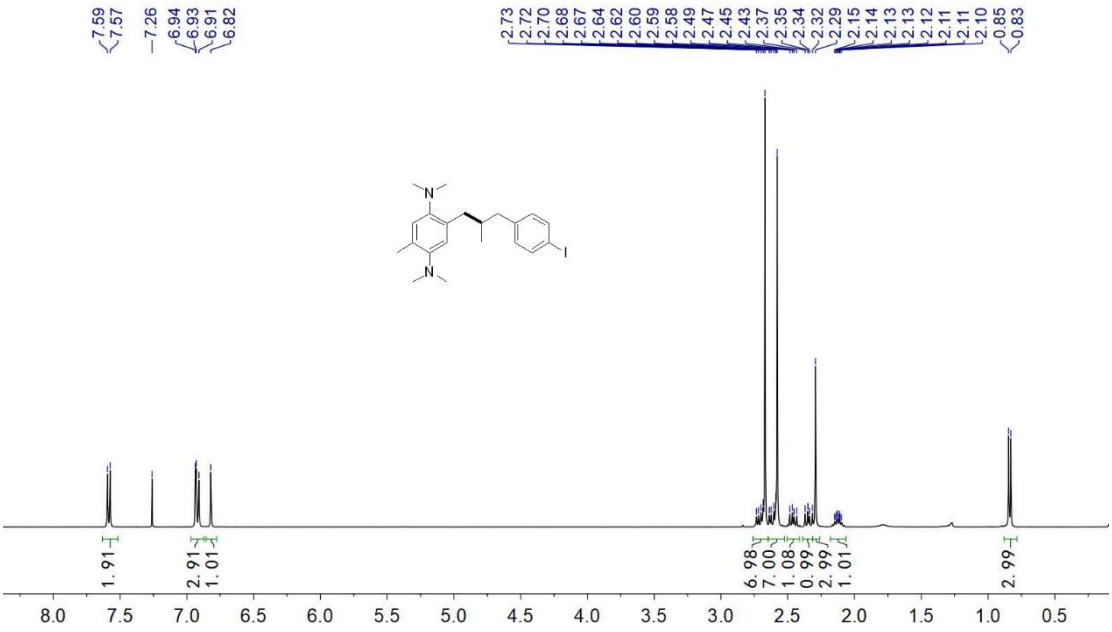


Fig. S42. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

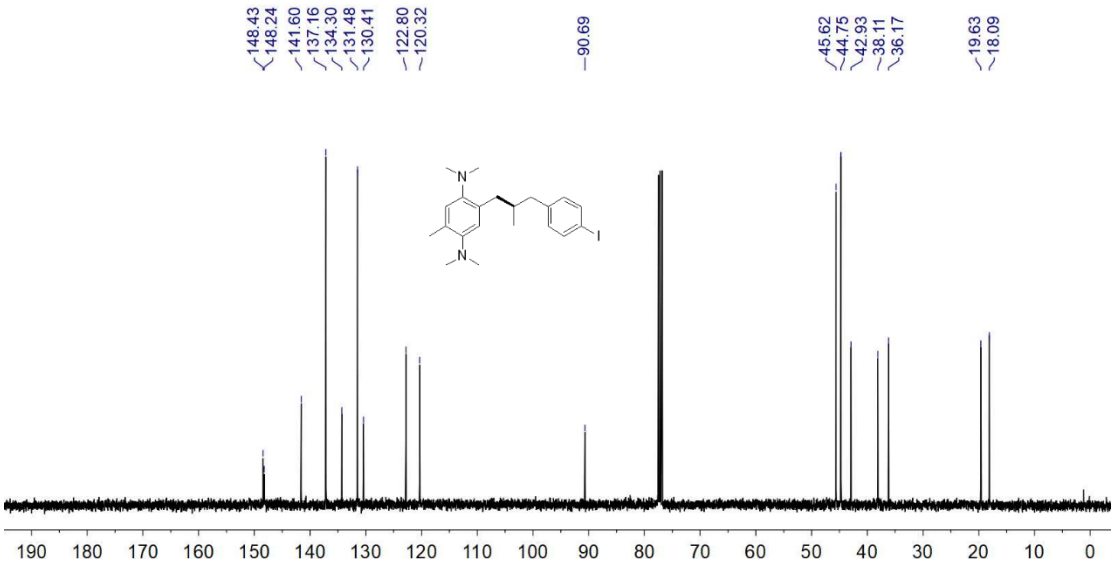
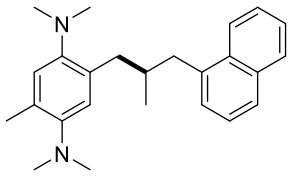


Fig. S43. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



7k (colorless oil, 96 mg, 89%)

HRMS (ESI) *m/z* calcd. For $C_{25}H_{33}N_2$ $[M + H]^+$: 361.2638; found: 361.2650.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.81 (m, 3H, Ar-H), 7.64 (m, 1H, Ar-H), 7.45 (m, 2H, Ar-H), 7.34 (m, 1H, Ar-H), 6.97 (m, 1H, Ar-H), 6.90 (m, 1H, Ar-H), 2.88 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 5.7 Hz, 1H, CH_2), 2.81 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 6.4 Hz, 1H, CH_2), 2.70 (s, 6H, NMe_2), 2.61 (overlapped, 8H, NMe_2 and CH_2), 2.34 (overlapped, 4H, Ar-*Me* and C*H*Me), 0.91 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.3, 148.2, 139.5, 134.5, 133.6, 132.0, 130.3, 128.1, 127.6, 127.5, 127.4, 127.3, 125.8, 125.0, 122.7, 120.3, 45.6, 44.7, 43.6, 38.2, 36.1, 19.7, 18.0.

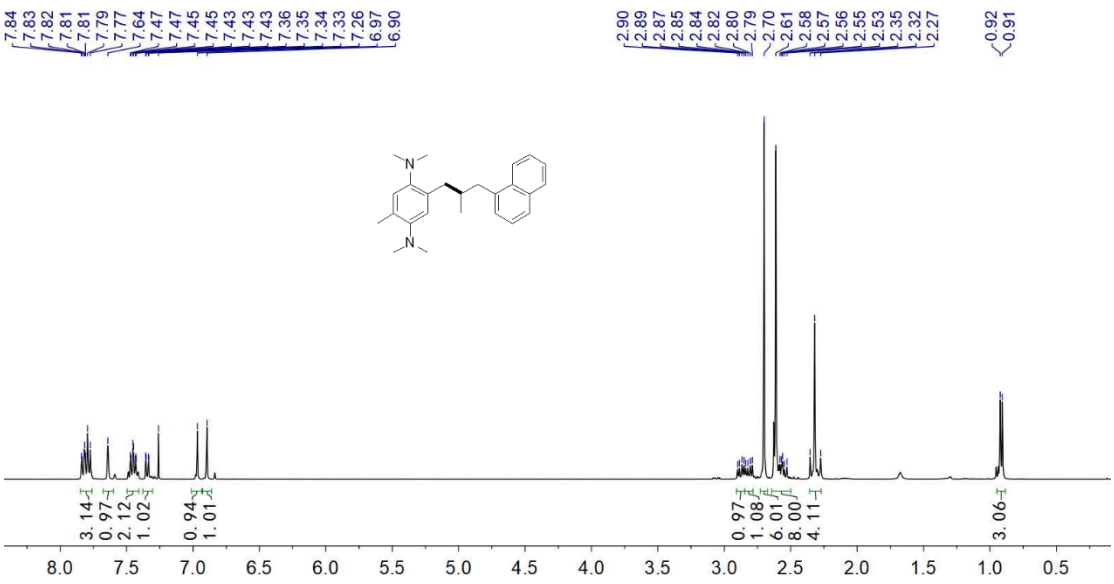


Fig. S44. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

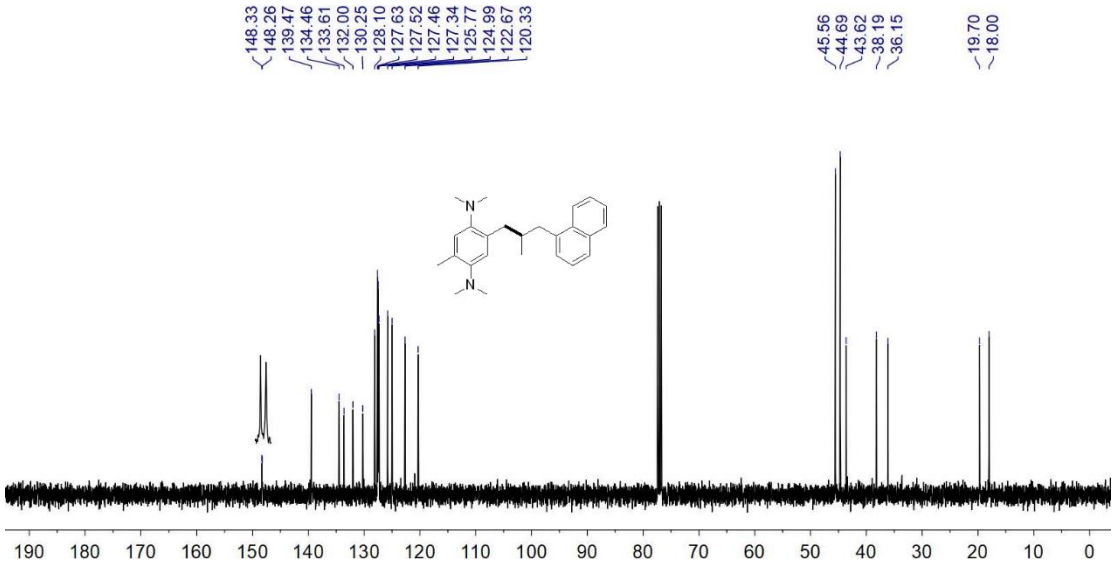
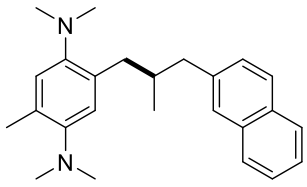


Fig. S45. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7l (colorless oil, 94 mg, 87%)

HRMS (ESI) *m/z* calcd. For $C_{25}H_{33}N_2$ $[M + H]^+$: 361.2638; found: 361.2645.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.83 (m, 2H, Ar-H), 7.72 (m, 1H, Ar-H), 7.42 (m, 3H, Ar-H), 7.34 (m, 1H, Ar-H), 6.98 (s, 1H, Ar-H), 6.92 (m, 1H, Ar-H), 3.25 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 4.9 Hz, 1H, CH_2), 2.89 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH_2), 2.71 (overlapped, 7H, NMe_2 and CH_2), 2.56 (overlapped, 7H, NMe_2 and CH_2),

2.34 (overlapped, 4H, Ar-*Me* and C*H*Me), 0.93 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.5, 148.4, 138.1, 134.7, 134.1, 132.4, 130.5, 128.7, 127.3, 126.5, 125.5, 125.4, 125.3, 124.5, 122.8, 120.6, 45.6, 44.8, 40.7, 39.1, 35.7, 20.3, 18.1.

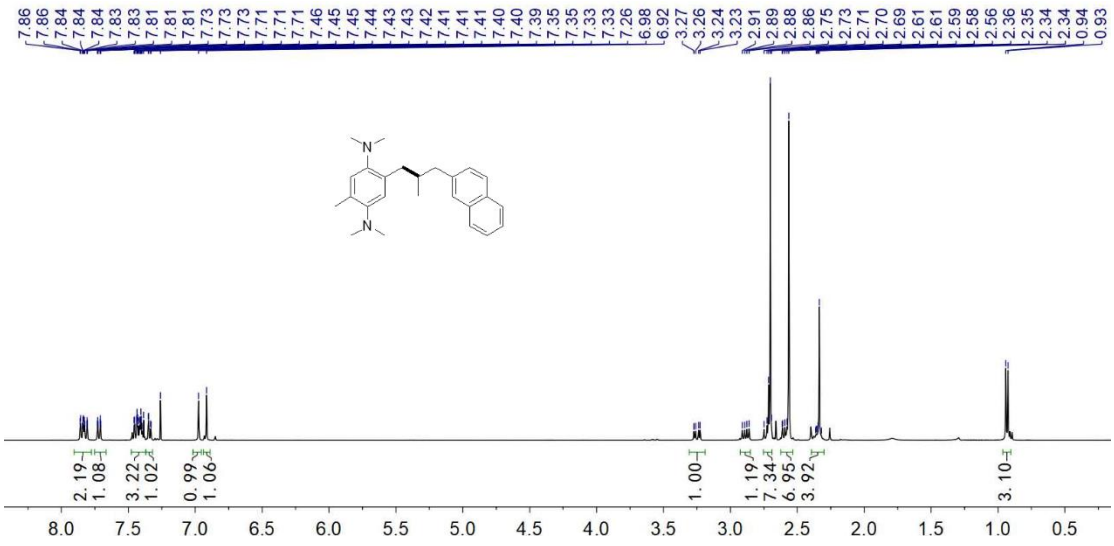


Fig. S46. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

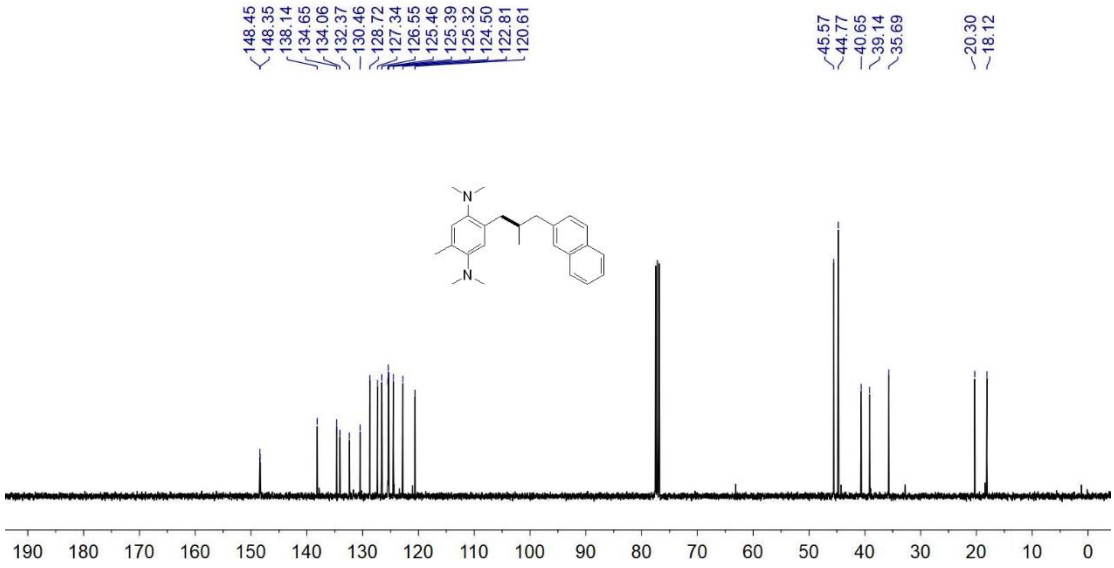
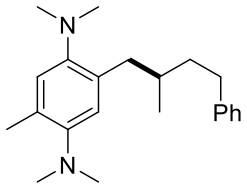


Fig. S47. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7m (colorless oil, 81 mg, 83%)

HRMS (ESI) *m/z* calcd. For $C_{22}H_{33}N_2$ $[M + H]^+$: 325.2638; found: 325.2641.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.27 (m, 2H, Ar-H), 7.19 (m, 3H, Ar-H), 6.94 (m, 1H, Ar-H), 6.82 (m, 1H, Ar-H), 2.74 (m, 2H, CH_2), 2.67 (s, 6H, NMe_2), 2.62 (s, 6H, NMe_2), 2.49 (m, 1H, CH_2), 2.30 (s, 3H, Ar-*Me*), 1.91 (m, 1H, C*H*Me), 1.70 (m, 2H, CH_2), 1.53 (m, 1H, CH_2), 0.96 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, C*H*Me).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.4, 148.3, 143.3, 134.7, 130.2, 128.5, 128.3, 125.6, 122.7, 120.3, 45.7, 44.7, 38.7, 38.0, 33.6, 33.5, 19.9, 18.1.

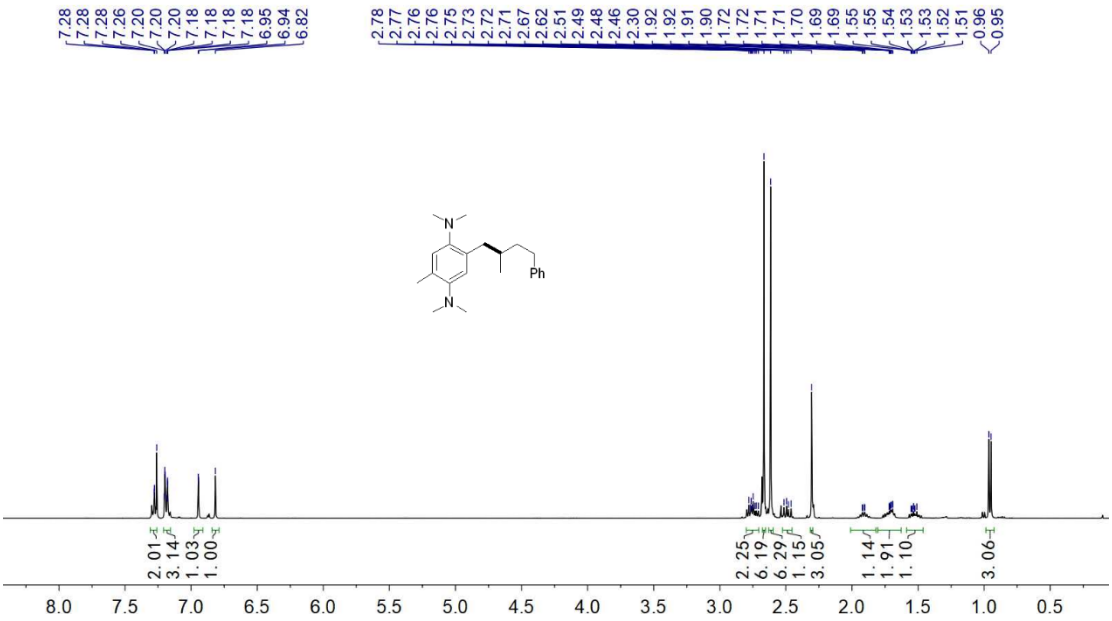


Fig. S48. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

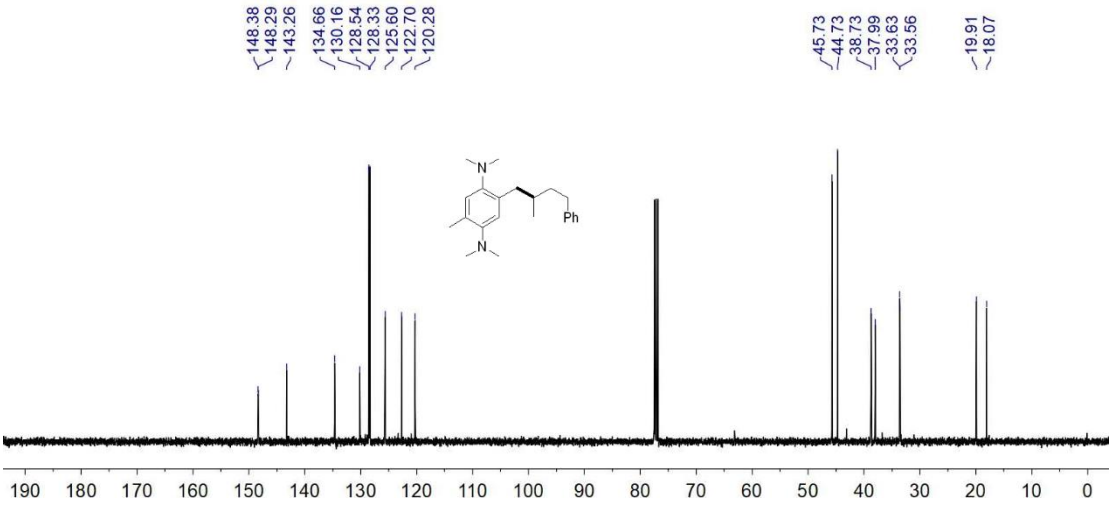
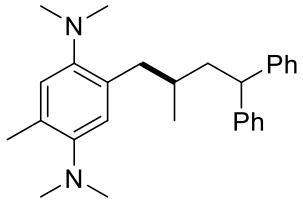


Fig. S49. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7n (colorless oil, 112 mg, 93%)

HRMS (ESI) *m/z* calcd. For $C_{28}H_{37}N_2$ $[M + H]^+$: 401.2951; found: 401.2961.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.28 (m, 5H, Ar-H), 7.24 (m, 1H, Ar-H), 7.20 (m, 4H, Ar-H), 6.96 (m, 1H, Ar-H), 6.73 (m, 1H, Ar-H), 4.13 (m, 1H, Ph_2CH), 2.83 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, CH_2), 2.67 (s, 6H, NMe_2), 2.57 (s, 6H, NMe_2), 2.49 (m, 1H, CH_2), 2.34 (s, 3H, Ar-*Me*), 2.20 (m, 1H, C*H*Me), 1.85 (m, 2H, CH_2), 0.99 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.4, 148.3, 146.0, 144.9, 134.6, 130.2, 128.5, 128.4, 128.2, 127.9, 126.0, 125.9, 122.7, 120.4, 48.8, 45.7, 44.7, 42.9, 38.5, 31.9, 20.2, 18.1.

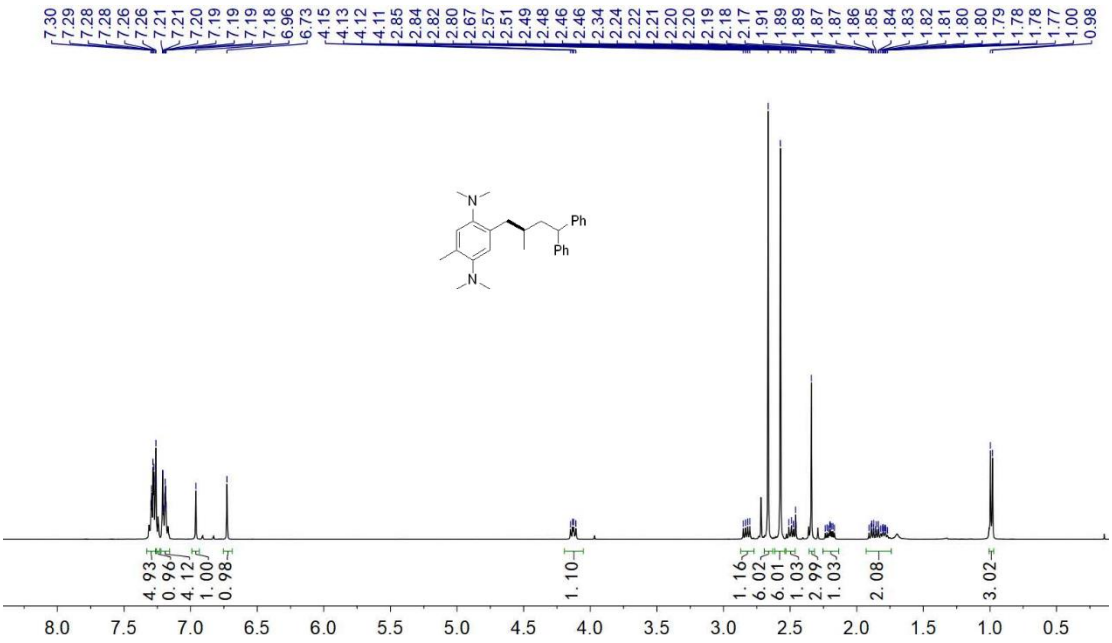


Fig. S50. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

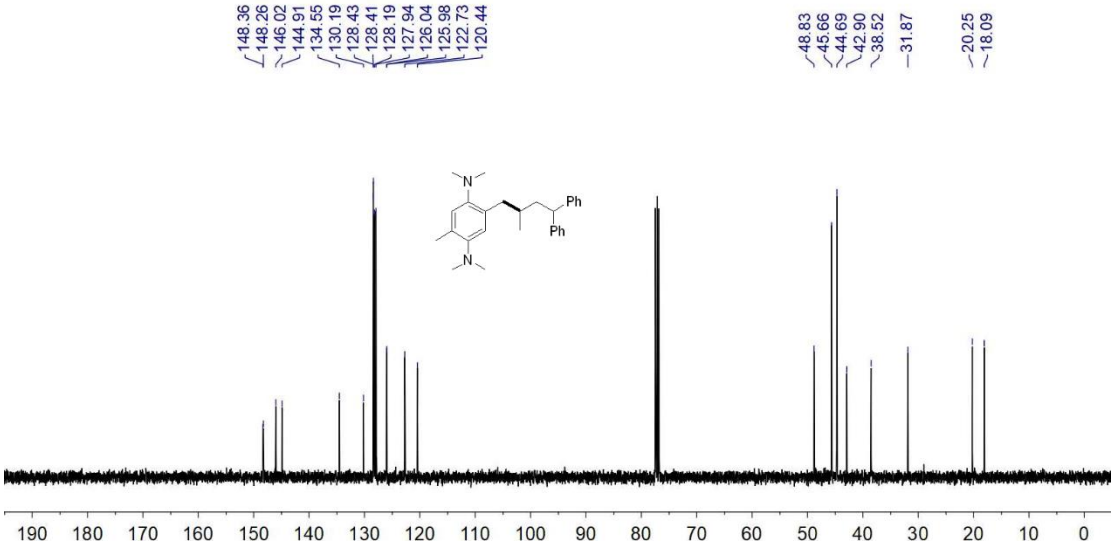
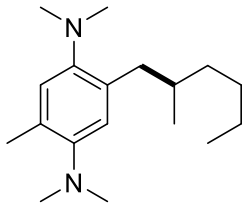


Fig. S51. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



7o (colorless oil, 62 mg, 75%)

HRMS (ESI) *m/z* calcd. For $C_{18}H_{33}N_2$ $[M + H]^+$: 277.2638; found: 277.2635.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 6.93 (m, 1H, Ar-H), 6.82 (m, 1H, Ar-H), 2.67 (m, 2H, C*H*$_2$), 2.63 (s, 6H, N*Me*$_2$), 2.59 (s, 6H, N*Me*$_2$), 2.40 (m, 1H, C*H*$_2$), 2.25 (s, 3H, Ar-*Me*), 1.80 (m, 1H, C*H*), 1.30 (m, 5H, C*H*$_2$), 0.89 (m, 3H, CH$_2$C*H*$_3$), 0.84 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ = 148.8, 148.7, 135.3, 130.4, 122.9, 120.7, 45.8, 44.8, 38.5, 37.1, 34.4, 29.8, 23.4, 19.9, 18.0, 14.4.

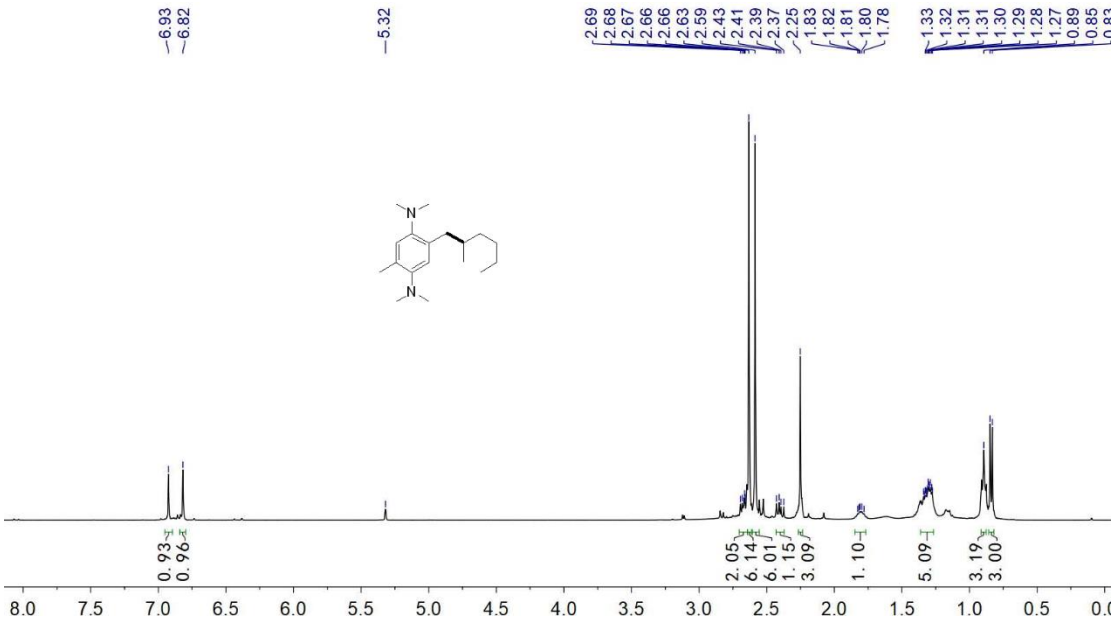


Fig. S52. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K)

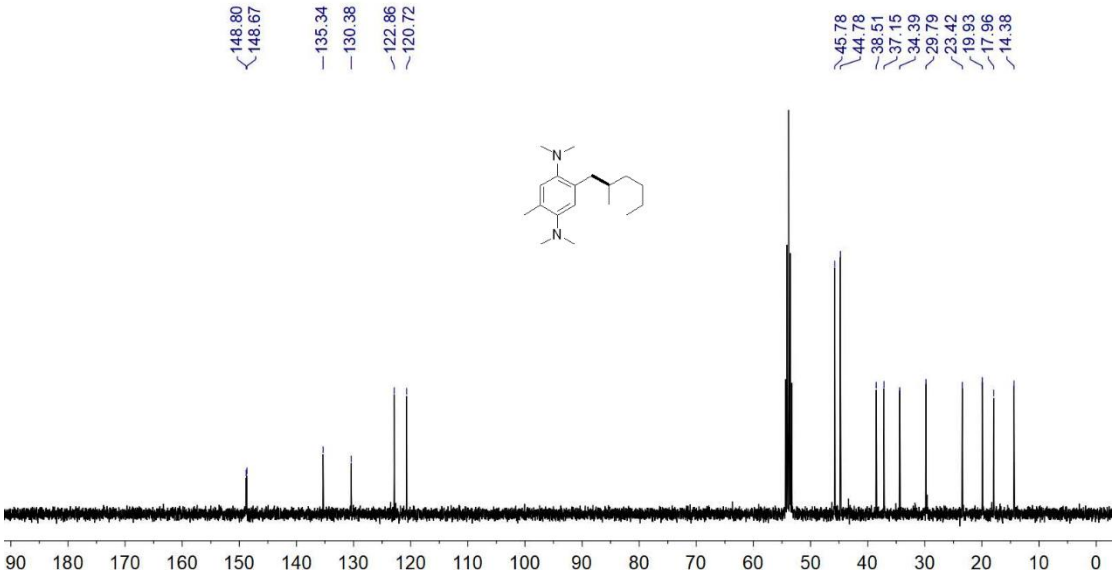
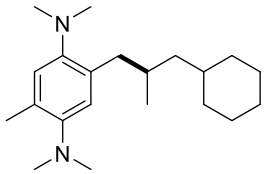


Fig. S53. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K)



7p (colorless oil, 82 mg, 86%)

HRMS (ESI) *m/z* calcd. For $C_{21}H_{37}N_2$ $[M + H]^+$: 317.2951; found: 317.2942.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.94 (m, 1H, Ar-H), 6.84 (m, 1H, Ar-H), 2.71 (m, 1H, C*H*$_2$), 2.68 (s, 6H, N*Me*$_2$), 2.62 (s, 6H, N*Me*$_2$), 2.35 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, C*H*$_2$), 2.30 (s, 3H, Ar-*Me*), 1.97 (m, 1H, C*H*Me), 1.72 (m, 5H, Cy, C*H*$_2$),

1.39 (m, 1H, Cy), 1.21 (m, 3H, Cy), 1.08 (m, 1H, Cy), 0.84 (m, 5H, Cy, CH*Me*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.3, 148.3, 135.0, 130.0, 122.7, 120.4, 45.7, 45.4, 44.8, 38.6, 35.2, 34.2, 33.4, 30.7, 27.0, 26.7, 26.6, 20.3, 18.0.

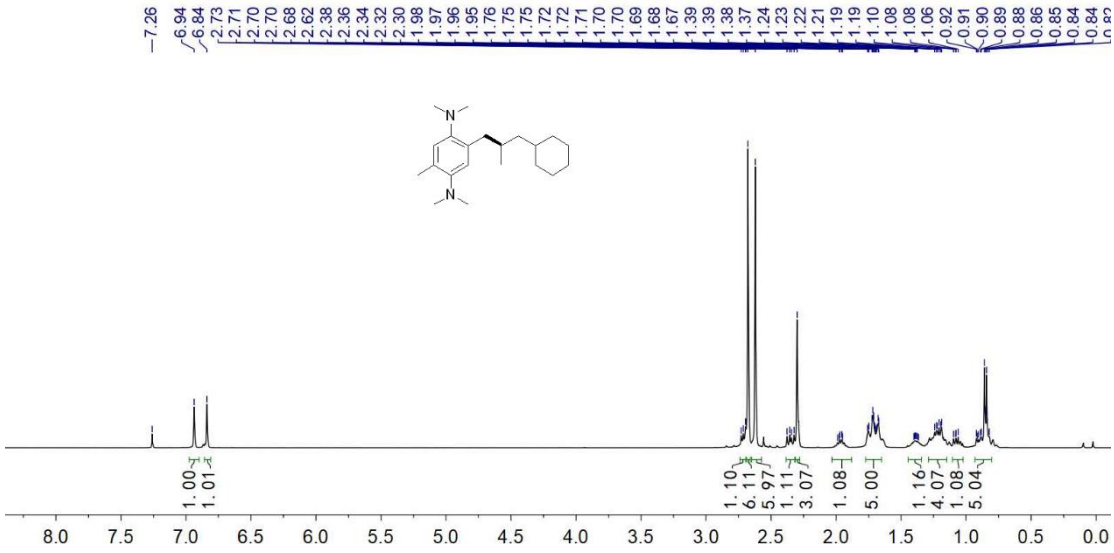


Fig. S54. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

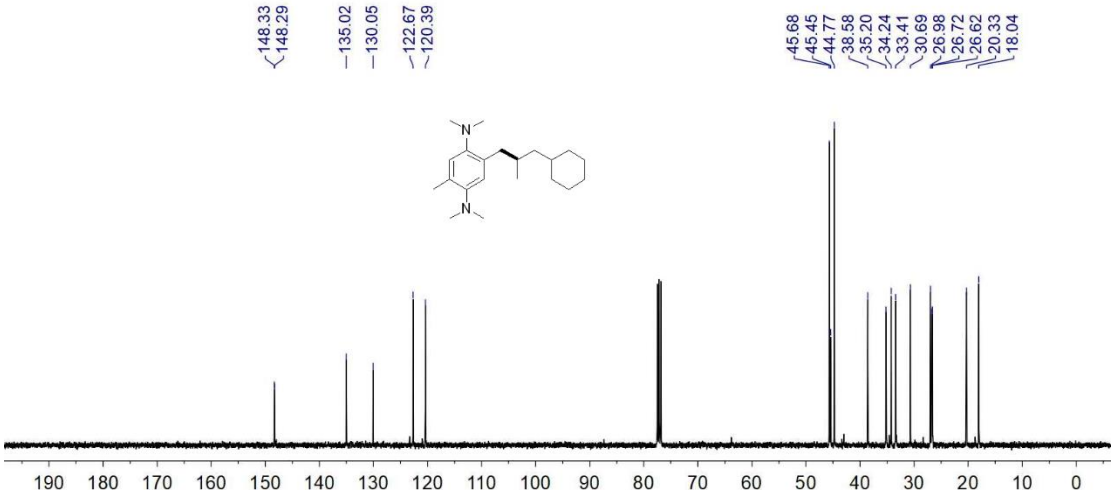
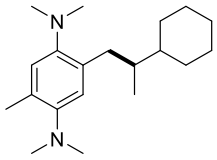


Fig. S55. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



7q (colorless oil, 80 mg, 88%)

HRMS (ESI) *m/z* calcd. For $C_{20}H_{35}N_2$ $[M + H]^+$: 303.2795; found: 303.2801.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.93 (m, 1H, Ar-H), 6.82 (m, 1H, Ar-H), 2.74 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 6.6 Hz, 1H, CH_2), 2.67 (s, 6H, NMe_2), 2.61 (s, 6H, NMe_2), 2.39 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 7.2 Hz, 1H, CH_2), 2.29 (s, 3H, Ar-*Me*), 1.78 – 1.61 (m,

6H, Cy and C*H*), 1.30 – 1.05 (m, 6H, Cy), 0.79 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH*Me*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.2, 148.1, 135.4, 129.9, 122.6, 120.3, 45.6, 44.6, 42.5, 39.4, 35.1, 31.0, 28.6, 27.0, 26.9, 26.8, 17.9, 15.9.

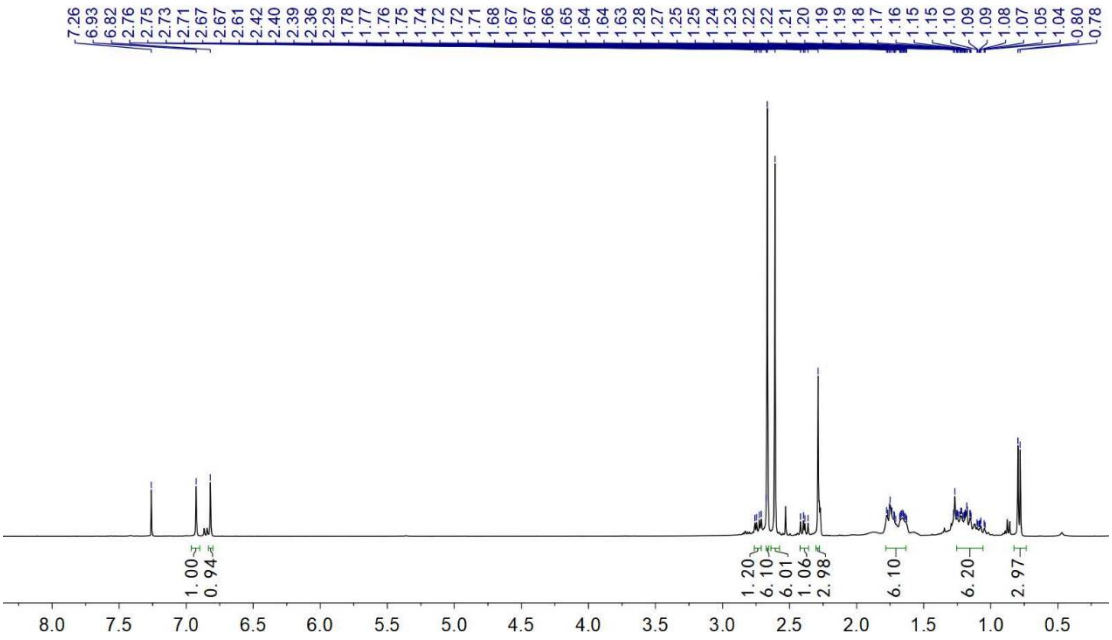


Fig. S56. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

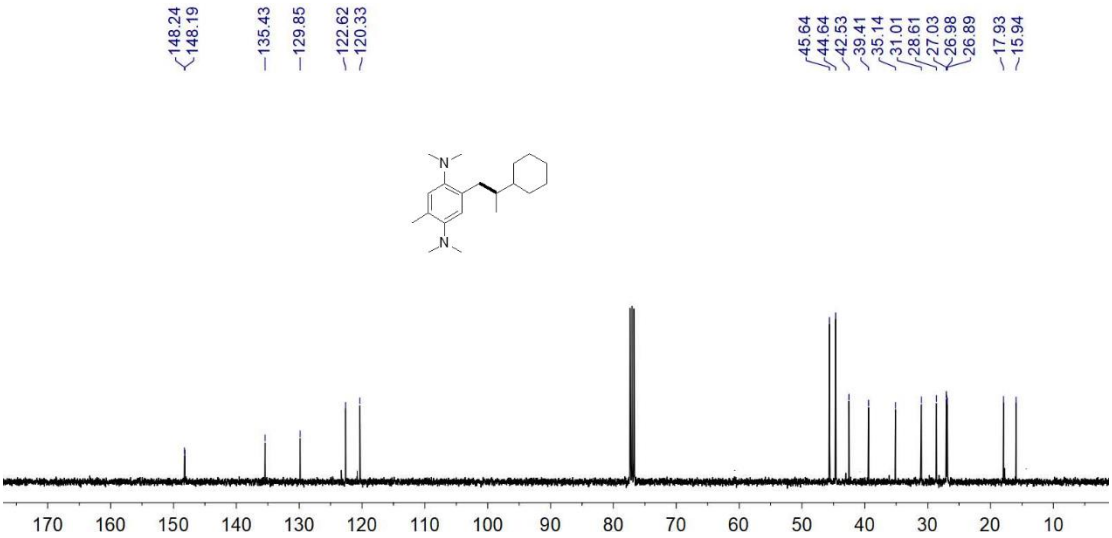
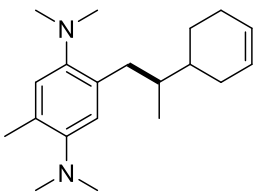


Fig. S57. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



7r (colorless oil, 78 mg, 86%), dr = 1:1

HRMS (ESI) *m/z* calcd. For $C_{20}H_{33}N_2$ $[M + H]^+$: 301.2638; found: 301.2636.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.93 (m, 2H, Ar-H), 6.83 (m, 2H, Ar-H), 5.67 (m, 4H, C*H*=C*H*), 2.80 (m, 2H, CH_2), 2.67 (s, 12H, NMe_2), 2.61 (s, 12H, NMe_2), 2.40 (m, 2H, CH_2), 2.29 (s, 6H, Ar-*Me*), 2.08 (m, 6H, Cy and C*H*Me), 1.85 (m, 6H, Cy), 1.73 (m, 2H, Cy), 1.54 (m, 2H, Cy), 1.37 (m, 4H, Cy), 0.84 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH*Me*), 0.82 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.3, 135.2, 135.1, 130.0, 129.9, 127.4, 127.3, 127.1, 127.0, 122.7, 122.6, 120.3, 120.2, 45.7, 45.6, 44.6, 38.8, 38.6, 38.5, 38.2, 35.2, 35.1, 29.7, 27.6, 27.0, 26.3, 26.2, 24.8, 18.0, 16.0, 15.7.

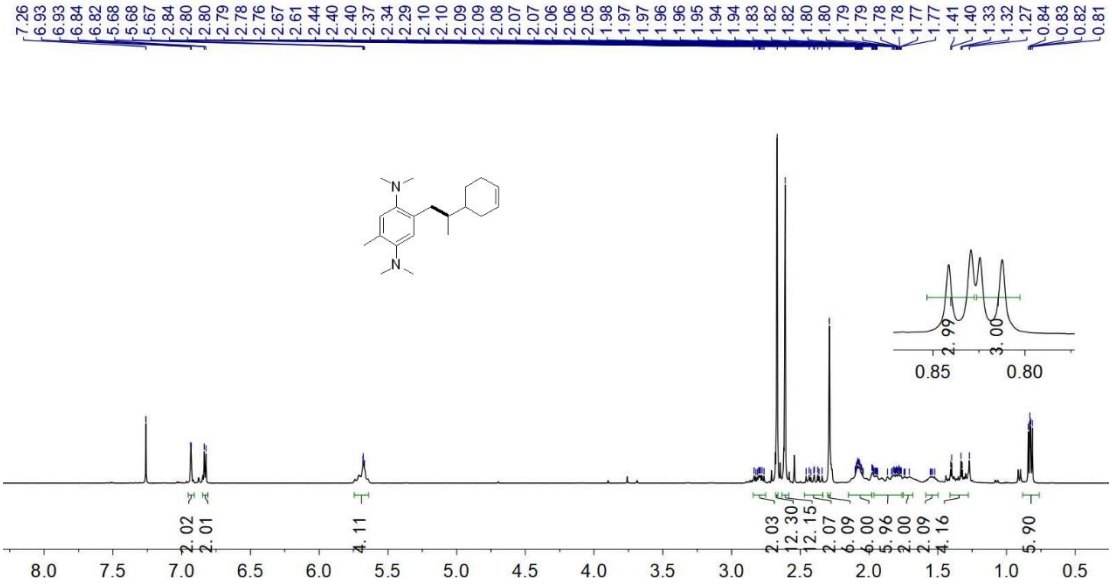


Fig. S58. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

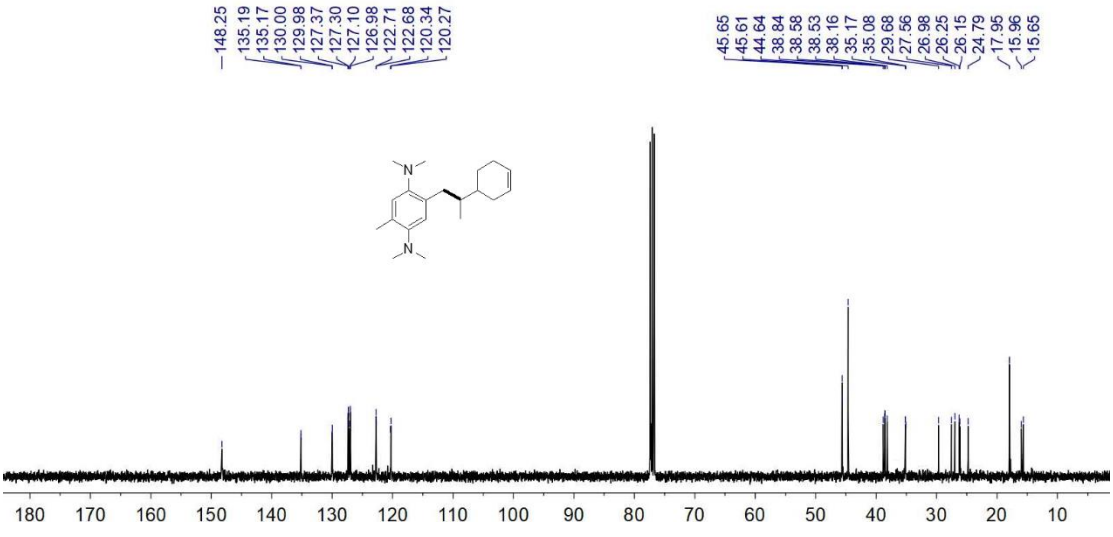
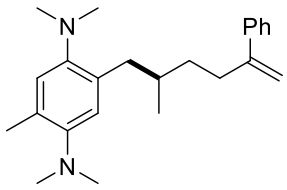


Fig. S59. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7s (colorless oil, 89 mg, 91%)

HRMS (ESI) *m/z* calcd. For $C_{24}H_{34}N_2Na$ $[M + Na]^+$: 351.2795; found: 351.2803.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.39 (m, 2H, Ar-H), 7.32 (m, 3H, Ar-H), 6.93 (m, 1H, Ar-H), 6.82 (m, 1H, Ar-H), 5.26 (s, 1H, =CH_2), 5.06 (s, 1H, =CH_2), 2.70 (m, 2H, CH_2), 2.66 (s, 6H, NMe_2), 2.61 (s, 6H, NMe_2), 2.51 (m, 2H, CH_2), 2.30 (s, 3H, Ar-*Me*), 1.90 (m, 1H, C*H*Me), 1.57 (m, 1H, CH_2), 1.39 (m, 1H, CH_2), 0.92 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 149.1, 148.2, 148.1, 141.7, 134.6, 130.0, 128.2, 127.2, 126.1, 122.6, 120.3, 111.8, 45.6, 44.6, 37.9, 35.6, 33.9, 32.9, 19.7, 18.0.

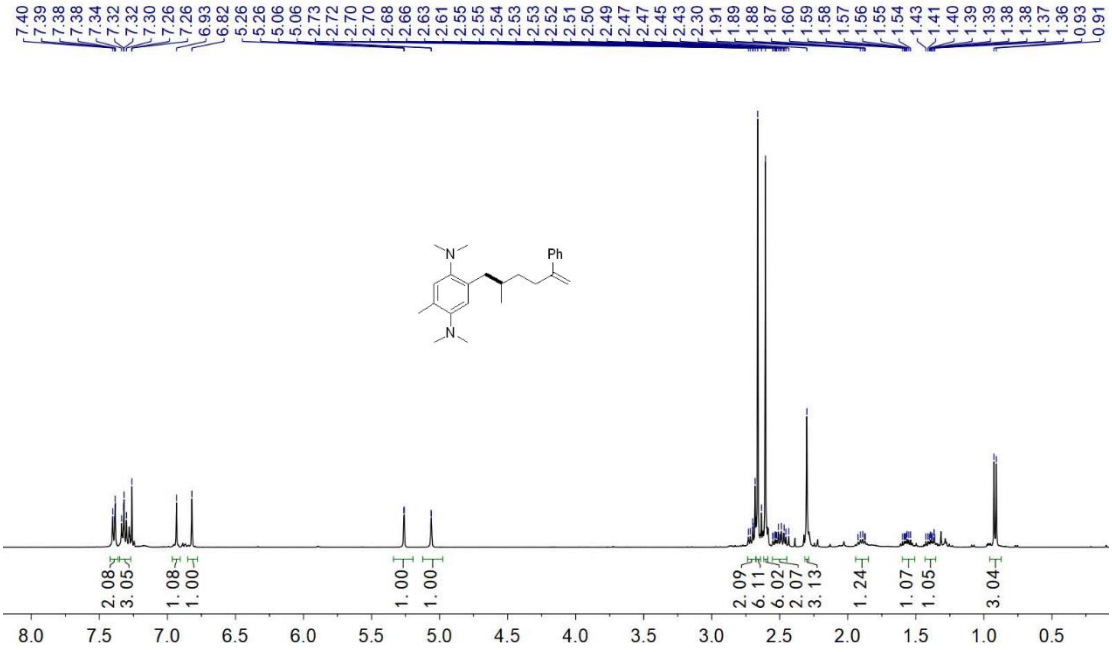


Fig. S60. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

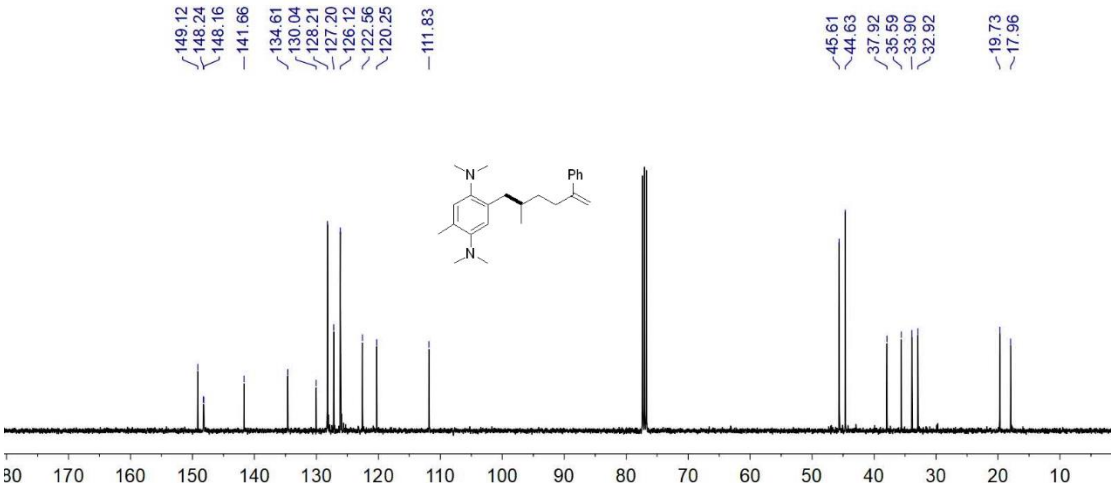
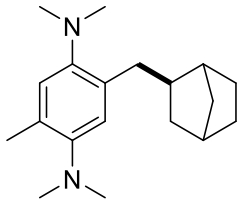


Fig. S61. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



7t (colorless oil, 63 mg, 73%)

HRMS (ESI) *m/z* calcd. For $C_{19}H_{31}N_2$ $[M + H]^+$: 287.2482; found: 287.2486.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.92 (m, 1H, Ar-H), 6.88 (m, 1H, Ar-H), 2.67 (s, 6H, N*Me*$_2$), 2.62 (s, 6H, N*Me*$_2$), 2.59 (m, 1H, C*H*$_2$), 2.50 (dd, $^{2}J_{HH}$ = 14.3 Hz, $^{3}J_{HH}$ = 7.5 Hz, 1H, C*H*$_2$), 2.29 (s, 3H, Ar-*Me*), 2.21 (m, 1H, C_7H_{11}), 2.00 (m, 1H, C_7H_{11}), 1.84 (m, 1H, C_7H_{11}), 1.46 (m, 4H, C_7H_{11}), 1.13 (m, 4H, C_7H_{11}).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.3, 148.2, 135.0, 130.0, 122.5, 120.0, 45.7, 44.8, 42.7, 41.0, 38.4, 37.3, 37.0, 35.4, 30.3, 29.1, 18.1.

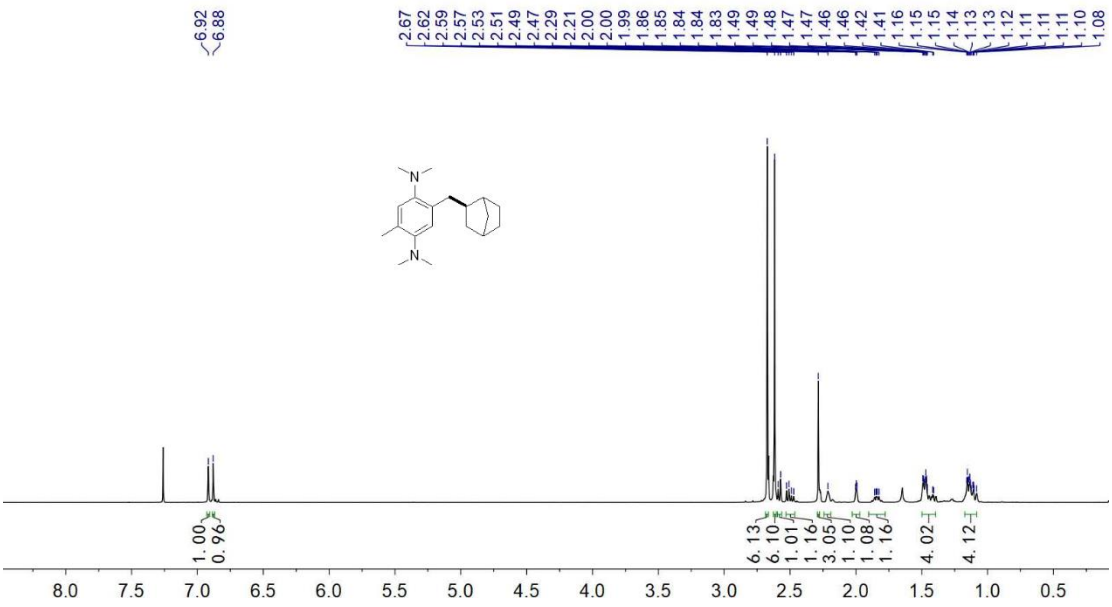


Fig. S62. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

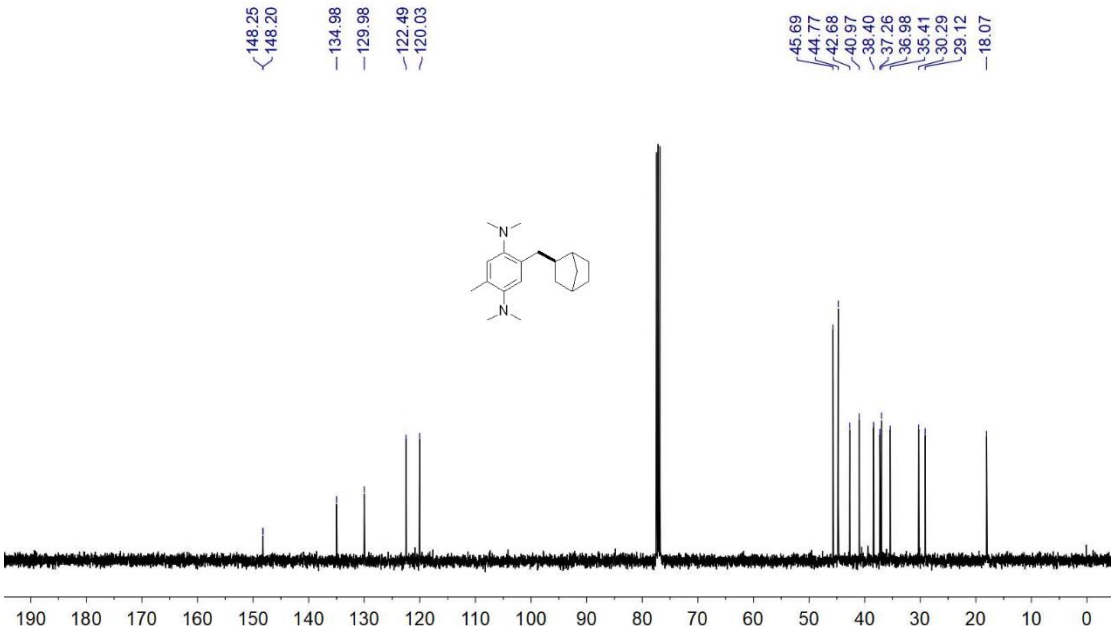
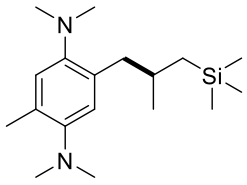


Fig. S63. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7u (colorless oil, 72 mg, 78%)

HRMS (ESI) *m/z* calcd. For $C_{18}H_{35}N_2Si$ $[M + H]^+$: 307.2564; found: 307.2567.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 6.94 (m, 1H, Ar-H), 6.81 (m, 1H, Ar-H), 2.69 (m, 1H, CH_2), 2.66 (s, 6H, NMe_2), 2.61 (s, 6H, NMe_2), 2.43 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$

= 7.6 Hz, 1H, CH_2), 2.29 (s, 3H, Ar-*Me*), 2.01 (m, 1H, C*H*Me), 0.90 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH*Me*), 0.69 (dd, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, CH_2Si), 0.47 (dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, CH_2Si), 0.02 (s, 9H, SiMe_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 148.4, 148.3, 135.1, 130.1, 122.8, 120.4, 45.8, 44.7, 41.8, 30.8, 25.4, 23.1, 18.1, -0.4.

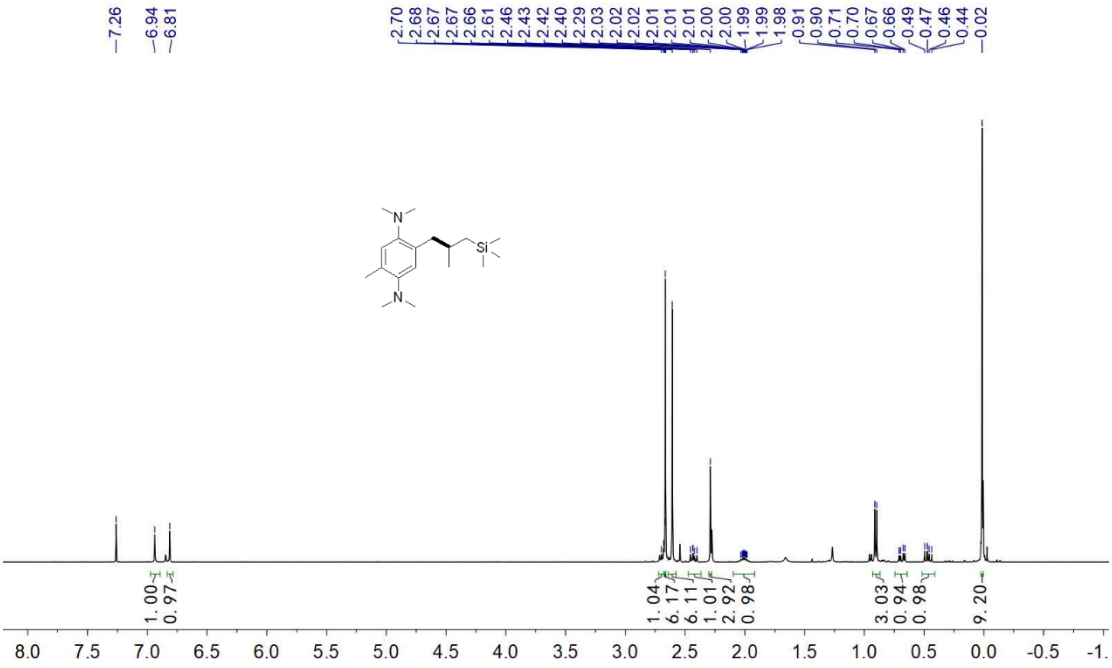


Fig. S64. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

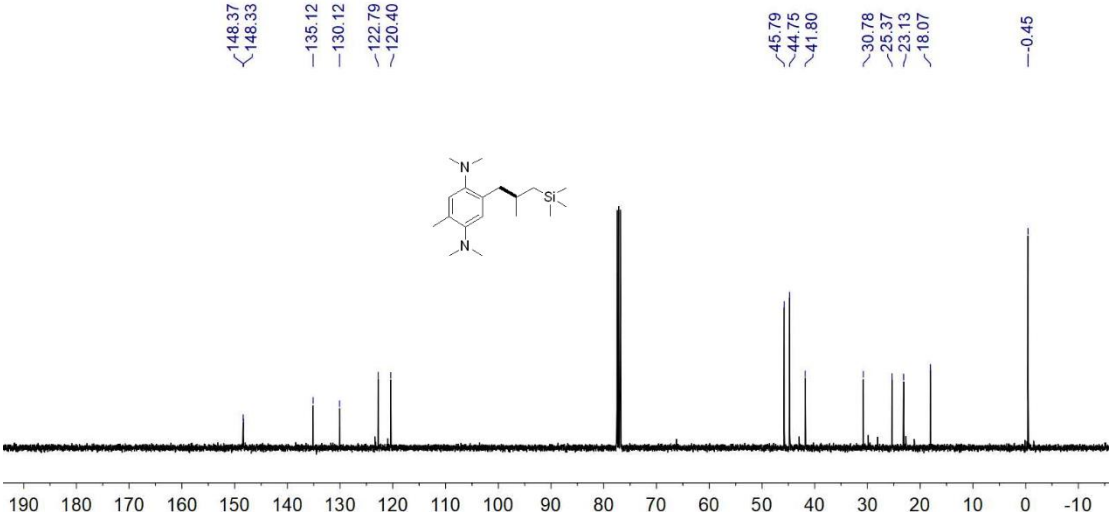
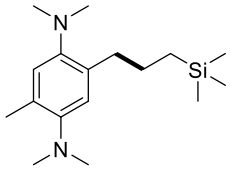


Fig. S65. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7v (colorless oil, 80 mg, 91%)

HRMS (ESI) *m/z* calcd. For $C_{17}H_{33}N_2Si$ $[M + H]^+$: 293.2408; found: 293.2407.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.92 (m, 1H, Ar-H), 6.87 (m, 1H, Ar-H), 2.68 (overlapped, 7H, N*Me*$_2$ and C*H*$_2$), 2.64 (overlapped, 7H, N*Me*$_2$ and C*H*$_2$), 2.29 (s, 3H, Ar-*Me*), 1.64 (m, 2H, C*H*$_2$), 0.61 (m, 2H, C*H*$_2$), 0.00 (s, 9H, Si*Me*$_3$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.4, 147.7, 135.7, 130.1, 122.4, 119.7, 45.7, 44.7, 34.6, 25.6, 18.1, 17.2, -1.5.

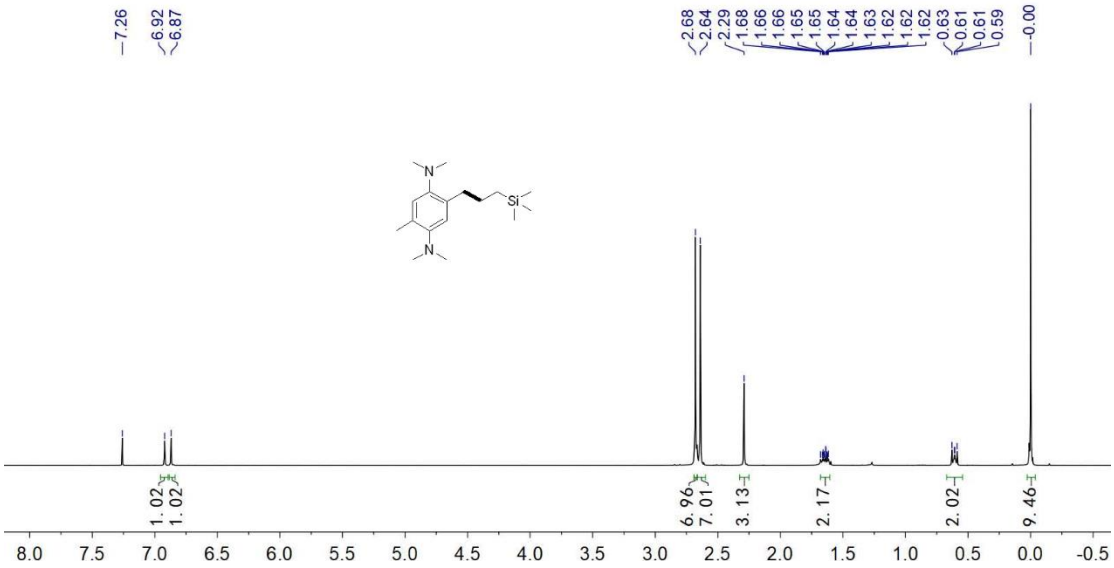


Fig. S66. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

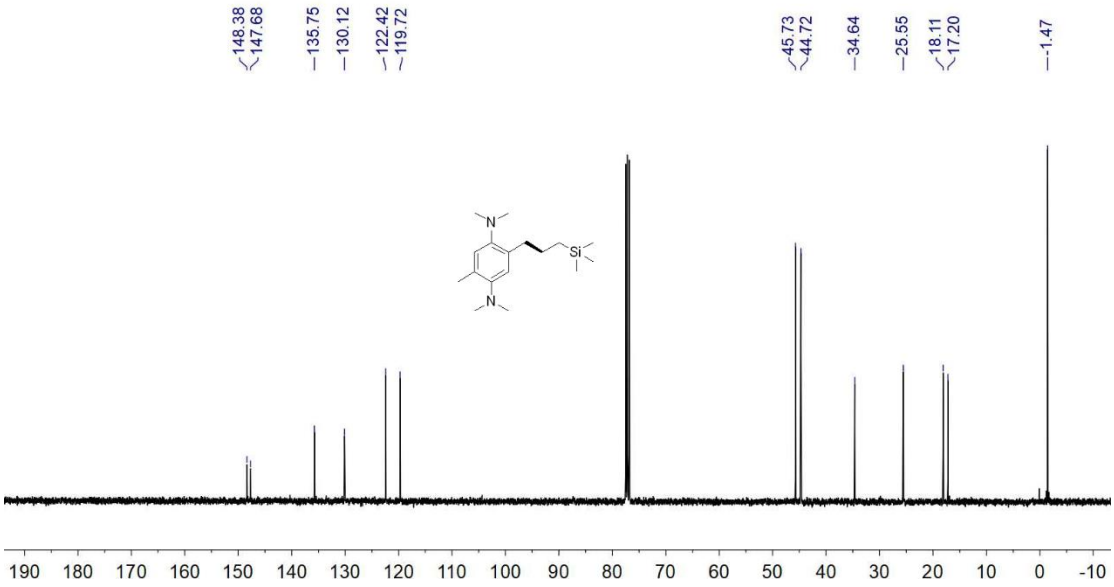
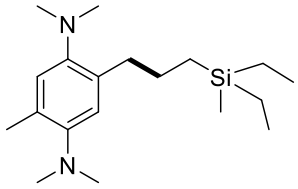


Fig. S67. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7w (colorless oil, 86 mg, 89%)

HRMS (ESI) *m/z* calcd. For $C_{19}H_{37}N_2Si$ $[M + H]^+$: 321.2721; found: 321.2721.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.92 (m, 1H, Ar-H), 6.87 (m, 1H, Ar-H), 2.68 (overlapped, 7H, N*Me*$_2$ and C*H*$_2$), 2.64 (overlapped, 7H, N*Me*$_2$ and C*H*$_2$), 2.29 (s, 3H, Ar-*Me*), 1.63 (m, 2H, C*H*$_2$), 0.93 (t, $^3J_{HH}$ = 7.9 Hz, 6H, CH_2CH_3), 0.62 (m, 2H, C*H*$_2$), 0.51 (q, $^3J_{HH}$ = 7.9 Hz, 4H, CH_2CH_3), -0.06 (s, 3H, Si*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.4, 147.7, 135.7, 130.1, 122.4, 119.7, 45.7, 44.7, 34.9, 25.4, 18.1, 13.6, 7.6, 5.3, -6.0.

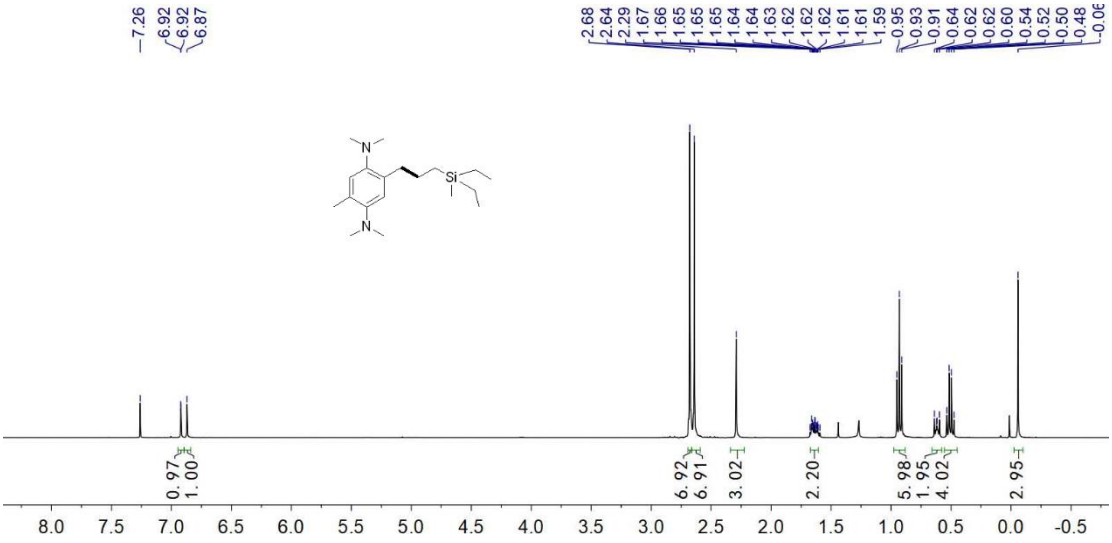


Fig. S68. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

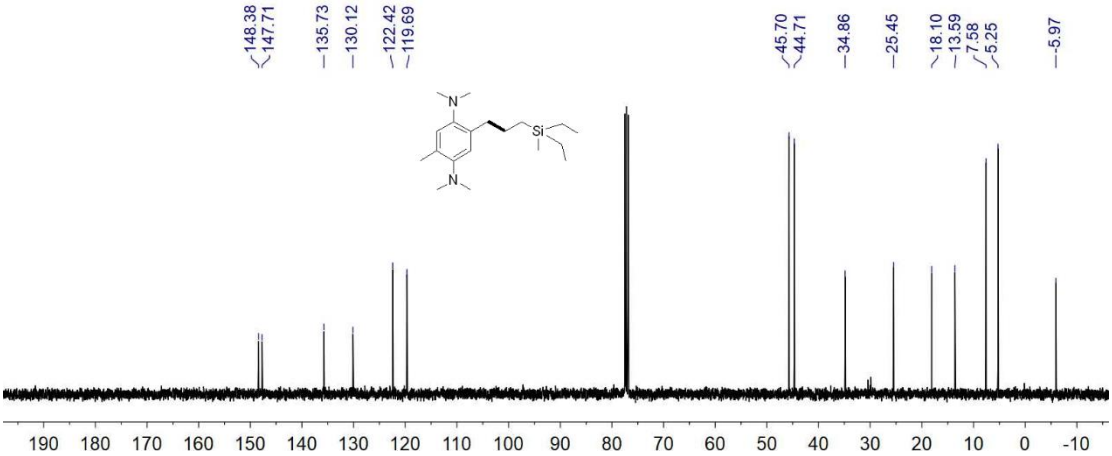
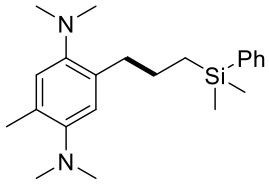


Fig. S69. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



7x (colorless oil, 98 mg, 92%)

HRMS (ESI) *m/z* calcd. For $C_{22}H_{35}N_2Si$ $[M + H]^+$: 355.2564; found: 355.2570.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.53 (m, 2H, Ar-H), 7.35 (m, 3H, Ar-H), 6.92 (m, 1H, Ar-H), 6.83 (m, 1H, Ar-H), 2.67 (overlapped, 7H, N*Me*$_2$ and C*H*$_2$), 2.62 (overlapped, 7H, N*Me*$_2$ and C*H*$_2$), 2.29 (s, 3H, Ar-*Me*), 1.69 (m, 2H, C*H*$_2$), 0.87 (m, 2H, C*H*$_2$), 0.29 (s, 6H, Si*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.4, 147.7, 139.8, 135.5, 133.7, 130.2, 128.9, 127.8, 122.4, 119.7, 45.7, 44.7, 34.6, 25.4, 18.1, 16.1, -2.8.

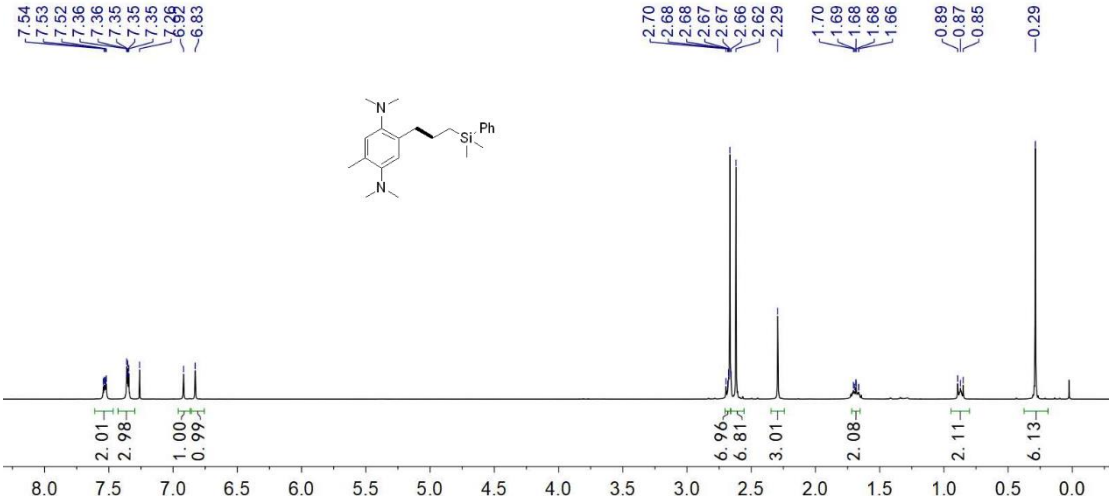


Fig. S70. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

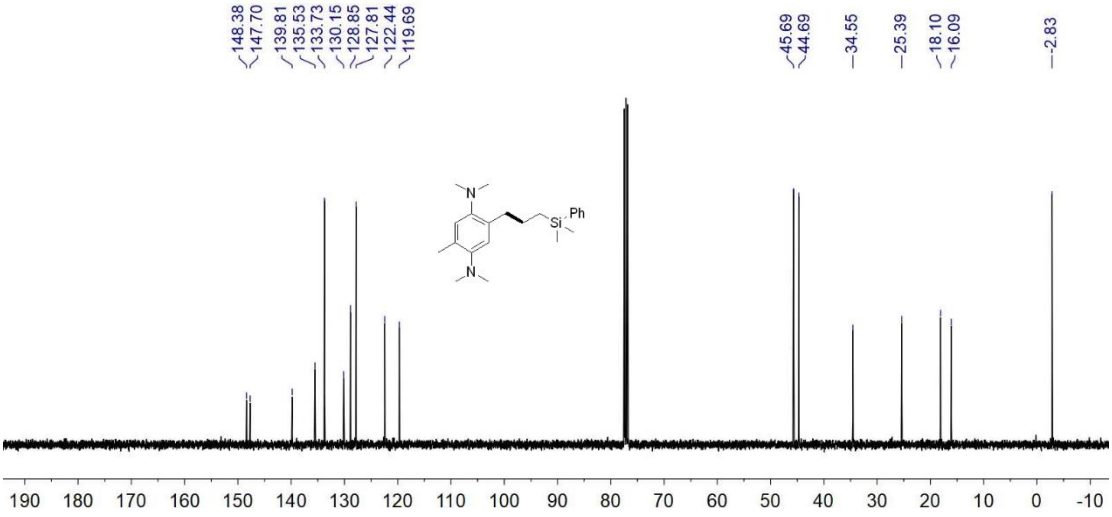
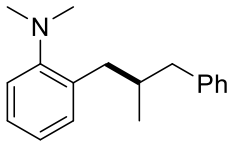


Fig. S71. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8a (colorless oil, 68 mg, 89%)

HRMS (ESI) *m/z* calcd. For $C_{18}H_{24}N$ $[M + H]^+$: 254.1903; found: 254.1913.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.33 (m, 2H, Ar-H), 7.21 (m, 6H, Ar-H), 7.08 (m, 1H, Ar-H), 2.83 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, CH_2), 2.72 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2), 2.67 (s, 6H, NMe_2), 2.58 (dd, $^2J_{HH}$ = 13.6 Hz, $^2J_{HH}$ = 8.3 Hz, 1H, CH_2), 2.49 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, CH_2), 2.27 (m, 1H, C*H*Me), 0.89 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 153.5, 141.8, 136.6, 130.4, 129.3, 128.2, 126.6, 125.7, 123.4, 119.9, 45.2, 43.6, 38.3, 36.2, 19.6.

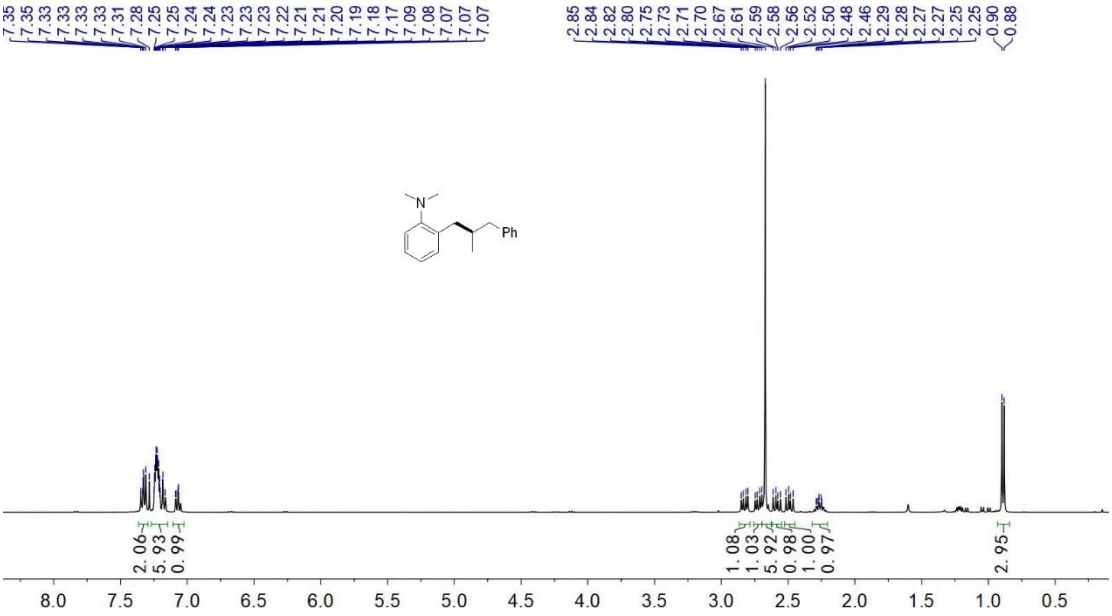


Fig. S72. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

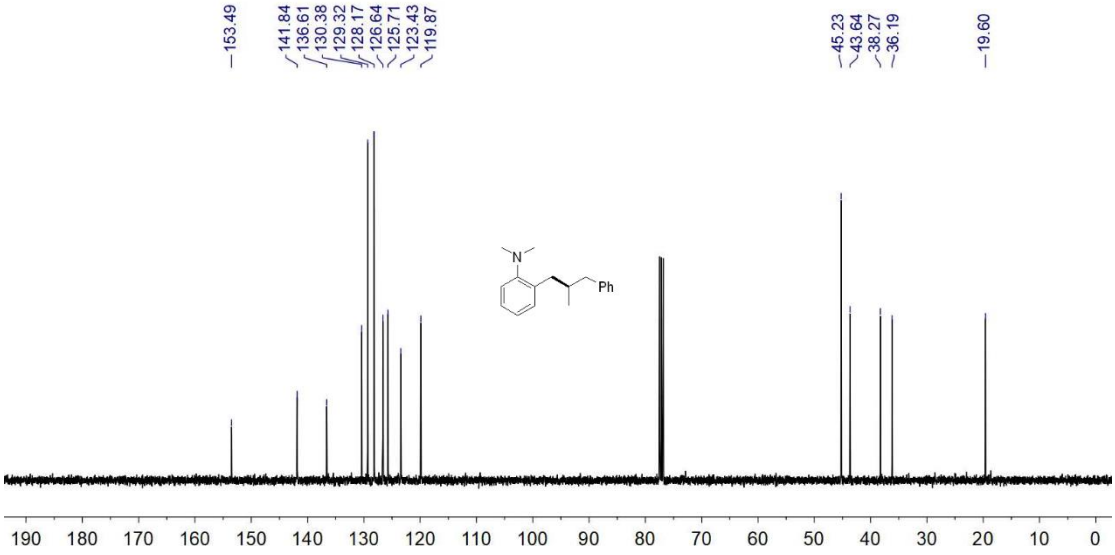
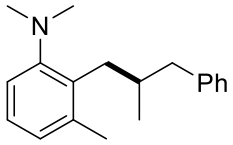


Fig. S73. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



8b (colorless oil, 71 mg, 88%)

HRMS (ESI) *m/z* calcd. For $C_{19}H_{26}N$ $[M + H]^+$: 268.2060; found: 268.2066.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.27 (m, 2H, Ar-H), 7.17 (m, 3H, Ar-H), 7.06 (m, 2H, Ar-H), 6.91 (m, 1H, Ar-H), 2.73 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 5.9 Hz, 1H, CH_2), 2.64 (m, 2H, CH_2), 2.57 (s, 6H, NMe_2), 2.49 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.2 Hz, 1H, CH_2), 2.25 (s, 3H, Ar-*Me*), 2.08 (m, 1H, C*H*Me), 0.82 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH*Me*).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 154.1, 142.1, 137.8, 136.4, 129.3, 128.1, 126.5, 126.2, 125.7, 118.3, 45.7, 43.9, 36.2, 34.4, 20.5, 19.6.

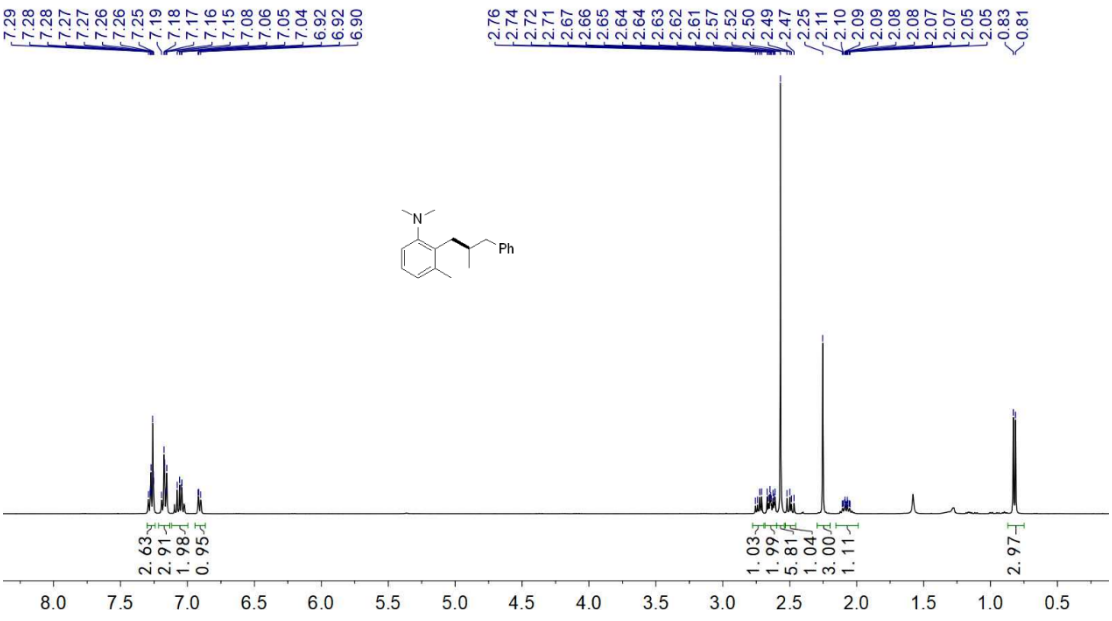


Fig. S74. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

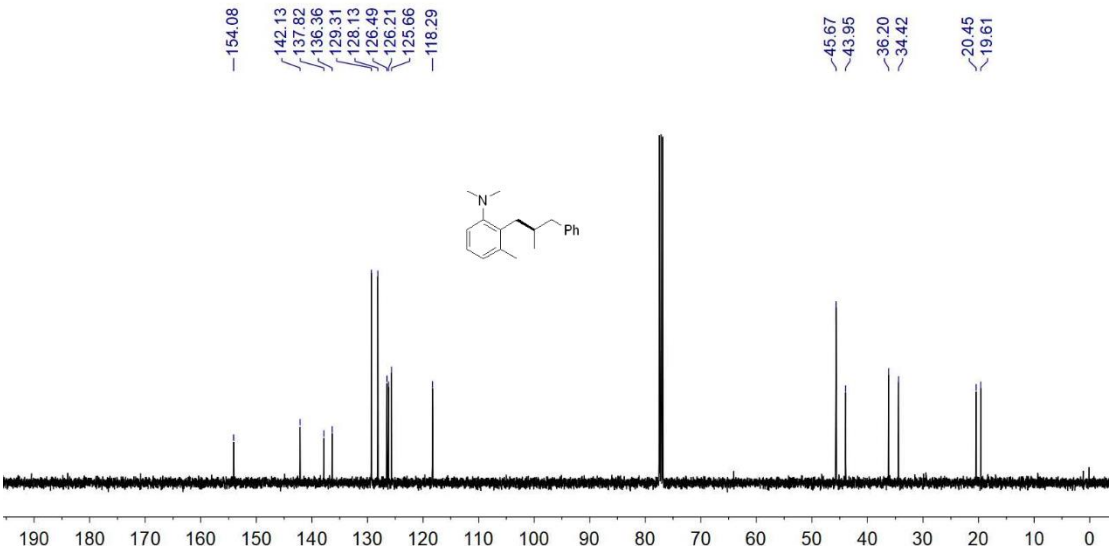
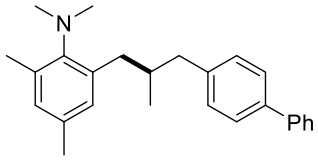


Fig. S75. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8c (colorless oil, 99 mg, 92%)

HRMS (ESI) *m/z* calcd. For $C_{26}H_{32}N$ $[M + H]^+$: 358.2529; found: 358.2526.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.62 (m, 2H, Ar-H), 7.54 (m, 2H, Ar-H), 7.45 (m, 2H, Ar-H), 7.35 (m, 1H, Ar-H), 7.27 (m, 2H, Ar-H), 6.83 (m, 2H, Ar-H), 2.76 (overlapped, 8H, Ar-*Me* and CH_2), 2.52 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 8.1 Hz, 1H, CH_2), 2.39 (dd, $^{2}J_{HH}$ = 13.0 Hz, $^{3}J_{HH}$ = 8.7 Hz, 1H, CH_2), 2.28 (s, 6H, NMe_2), 2.12 (m, 1H,

C*H*Me), 0.90 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 147.3, 141.4, 141.1, 140.8, 138.6, 137.4, 134.3, 130.2, 129.8, 129.1, 128.8, 127.1, 127.0, 126.9, 43.7, 43.1, 39.7, 36.7, 21.0, 19.8, 19.4.

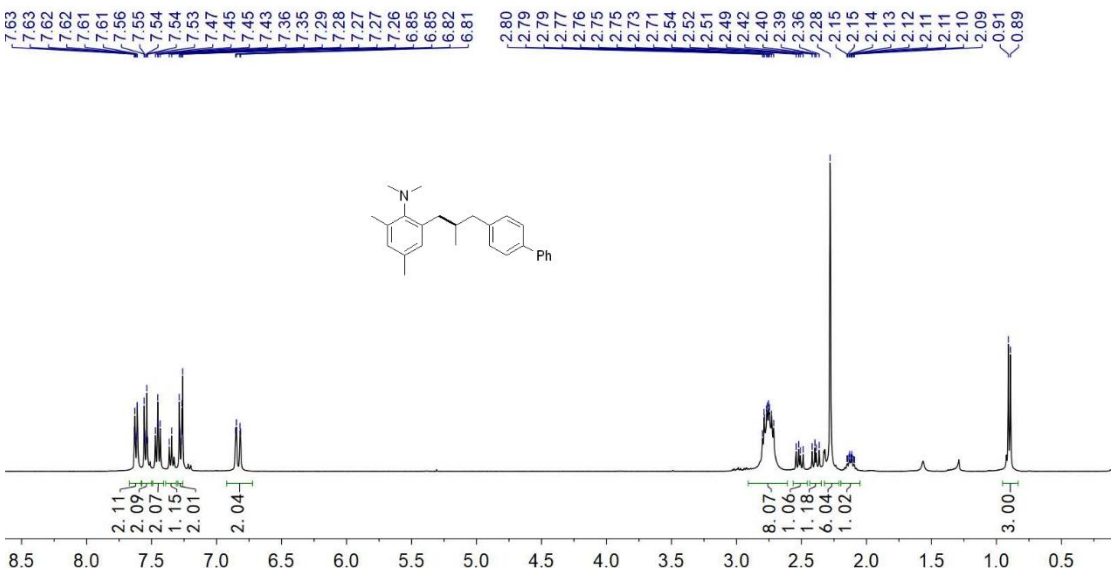


Fig. S76. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

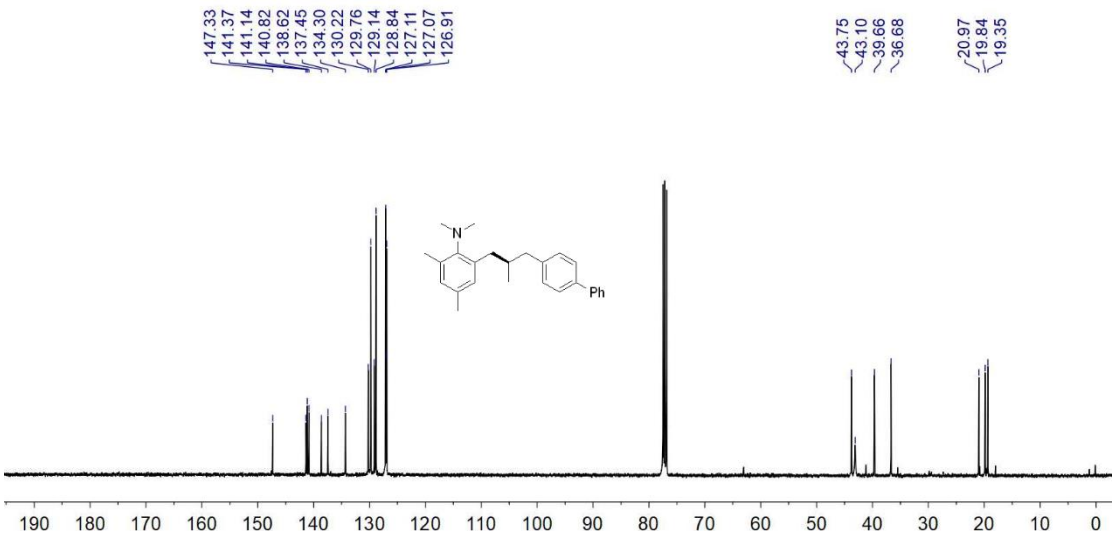
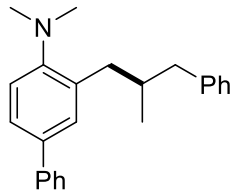


Fig. S77. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8d (colorless oil, 85 mg, 86%)

HRMS (ESI) *m/z* calcd. For $C_{24}H_{28}N$ $[M + H]^+$: 330.2216; found: 330.2222.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.59 (m, 2H, Ar-H), 7.43 (m, 4H, Ar-H), 7.31 (m, 3H, Ar-H), 7.19 (m, 4H, Ar-H), 2.84 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 6.0 Hz, 1H, CH_2), 2.67 (overlapped, 7H, NMe_2 and CH_2), 2.60 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 8.4 Hz, 1H, CH_2), 2.48 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 8.2 Hz, 1H, CH_2), 2.27 (m, 1H, C*H*Me), 0.88 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.8, 141.6, 141.3, 136.6, 136.0, 129.2, 129.1, 128.7, 128.1, 126.9, 126.7, 125.6, 125.2, 120.0, 45.1, 43.6, 38.4, 36.1, 19.6.

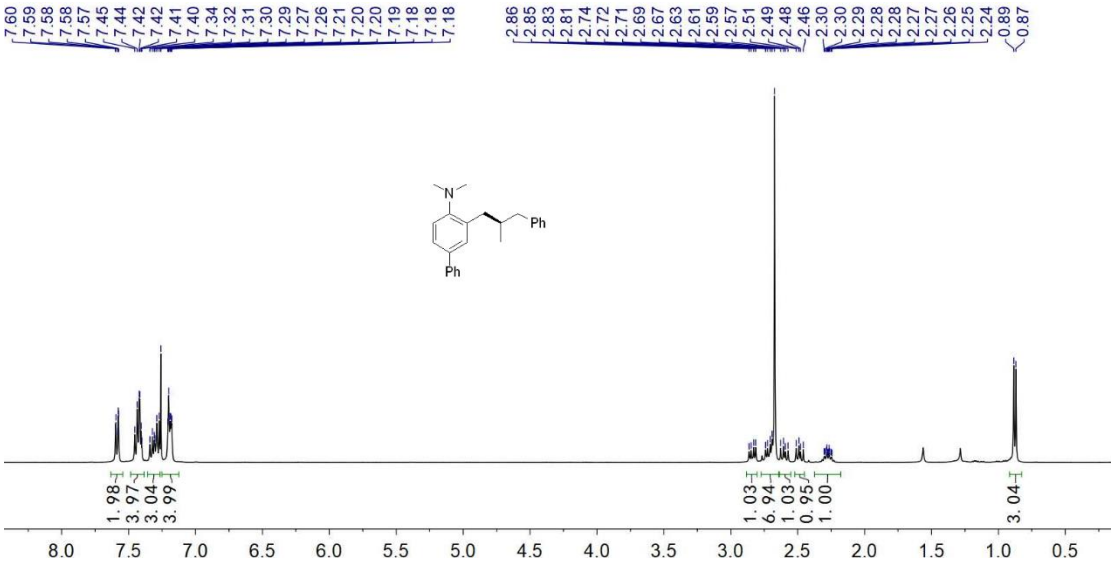


Fig. S78. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

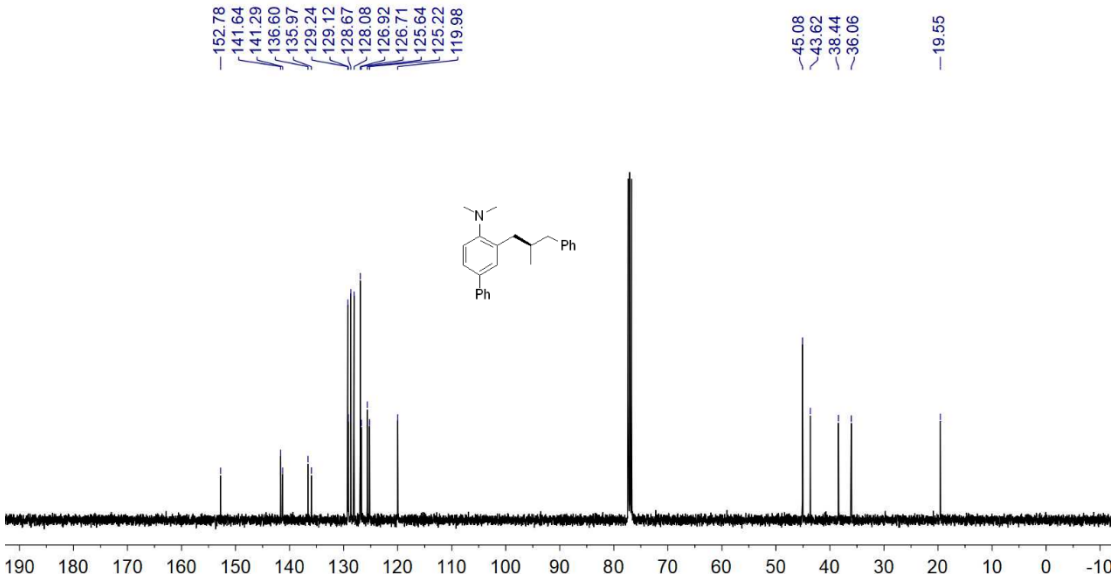
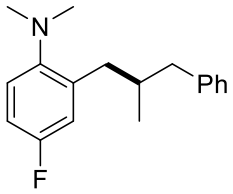


Fig. S79. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8e (colorless oil, 72 mg, 88%)

HRMS (ESI) *m/z* calcd. For $C_{18}H_{23}FN$ $[M + H]^+$: 272.1809; found: 272.1807.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.28 (m, 2H, Ar-H), 7.18 (m, 3H, Ar-H), 7.08 (m, 1H, Ar-H), 6.87 (m, 2H, Ar-H), 2.74 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2), 2.65 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, CH_2), 2.57 (s, 6H, NMe_2), 2.48 (m, 2H, CH_2), 2.16 (m, 1H, C*H*Me), 0.84 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 159.3 (J_{FC} = 241.3 Hz), 149.5 (J_{FC} = 2.7 Hz), 141.6, 139.3 (J_{FC} = 7.1 Hz), 129.3, 128.2, 125.8, 121.38 (J_{FC} = 8.6 Hz), 116.6 (J_{FC} = 21.6 Hz), 112.9 (J_{Fc} = 21.8 Hz), 45.6, 43.6, 38.0, 36.3, 19.5.

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ = -120.1.

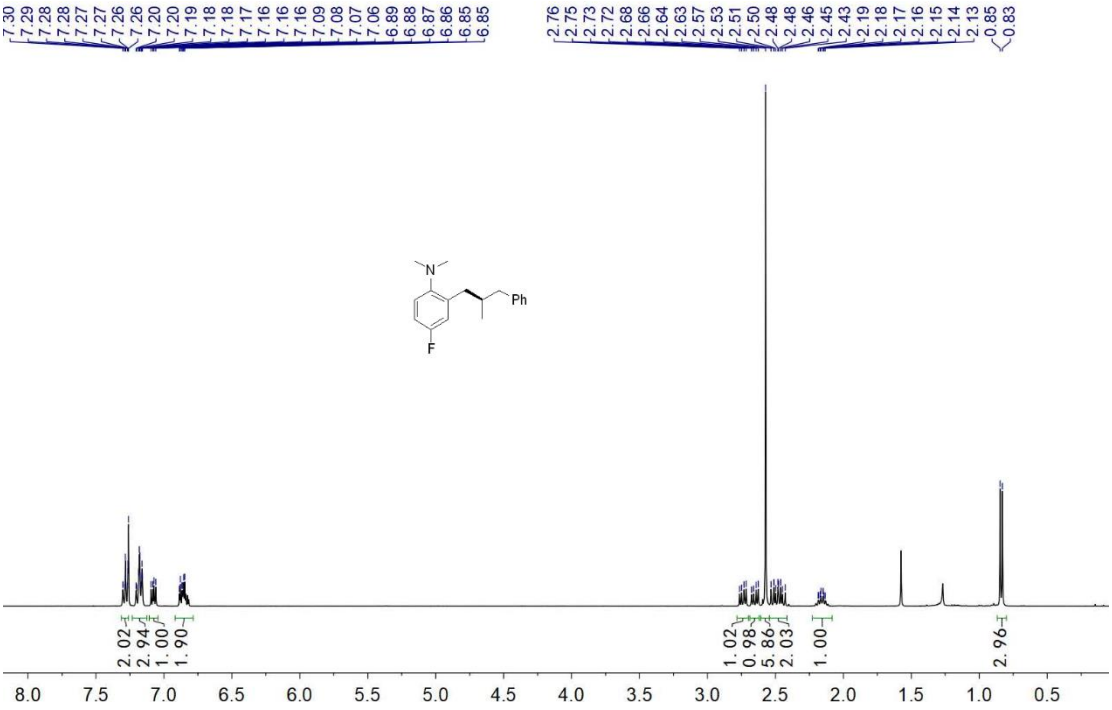


Fig. S80. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

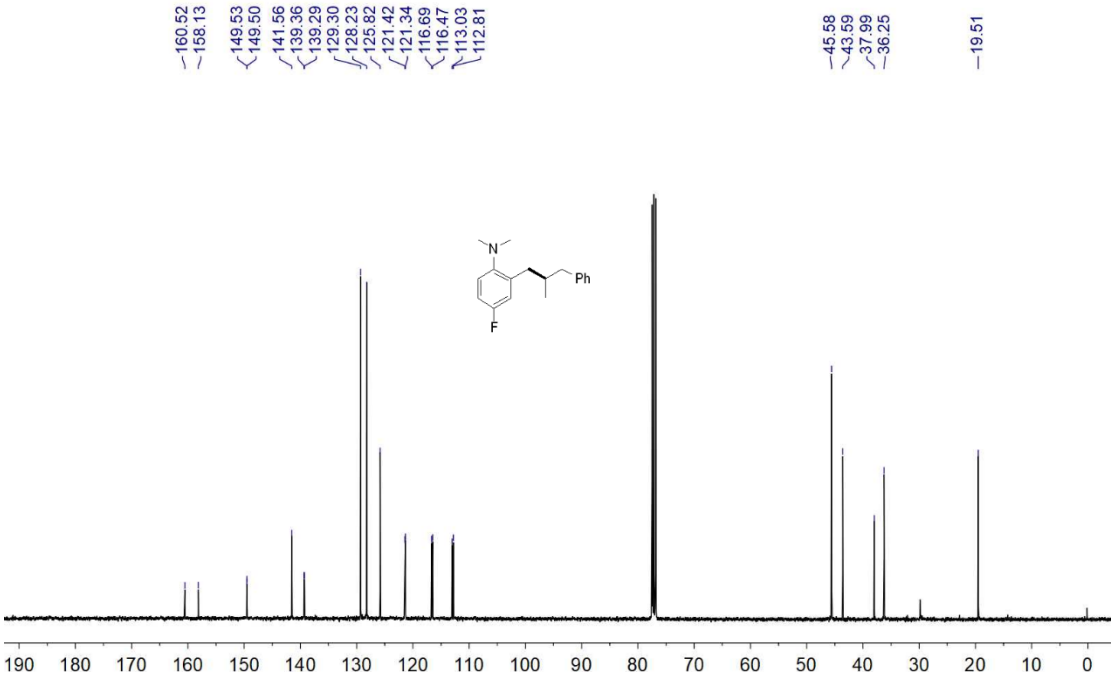


Fig. S81. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, $CDCl_3$, 298 K)

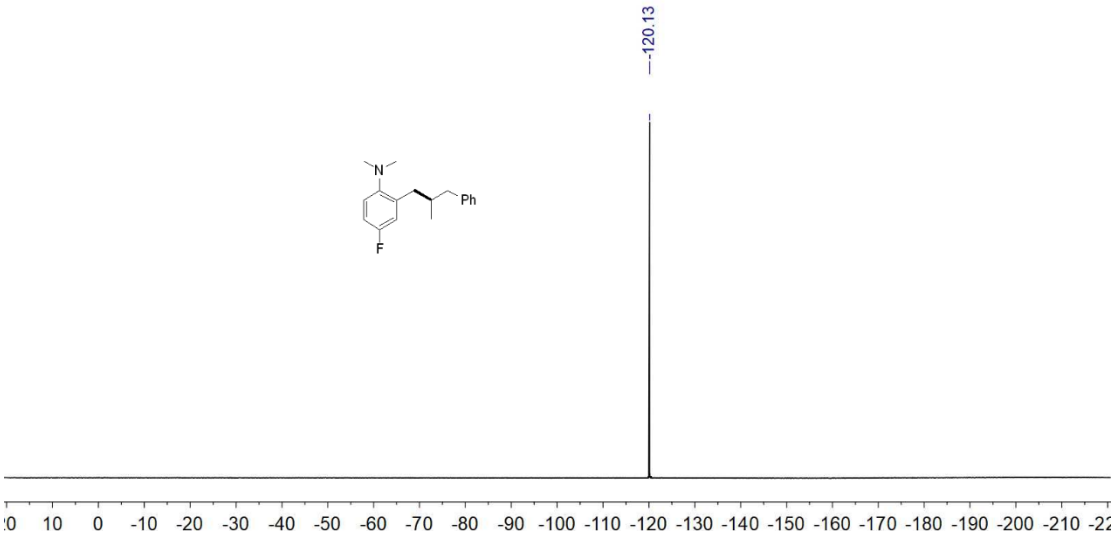
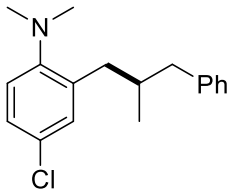


Fig. S82. ^{19}F **NMR** (376 MHz, $CDCl_3$, 298 K)



8f (colorless oil, 79 mg, 91%)

HRMS (ESI) *m/z* calcd. For $C_{18}H_{23}ClN$ $[M + H]^+$: 288.1514; found: 288.1517.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.28 (m, 2H, Ar-H), 7.18 (m, 3H, Ar-H), 7.12 (m, 2H, Ar-H), 7.03 (m, 1H, Ar-H), 2.72 (dd, $^{2}J_{HH}$ = 13.7 Hz, $^{3}J_{HH}$ = 5.9 Hz, 1H, CH_2),

2.64 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 6.2 Hz, 1H, CH_2), 2.58 (s, 6H, NMe_2), 2.48 (m, 2H, CH_2), 2.18 (m, 1H, C*H*Me), 0.83 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.1, 141.5, 138.6, 130.1, 129.3, 128.5, 128.2, 126.5, 125.8, 121.2, 45.1, 43.6, 38.0, 36.1, 19.5.

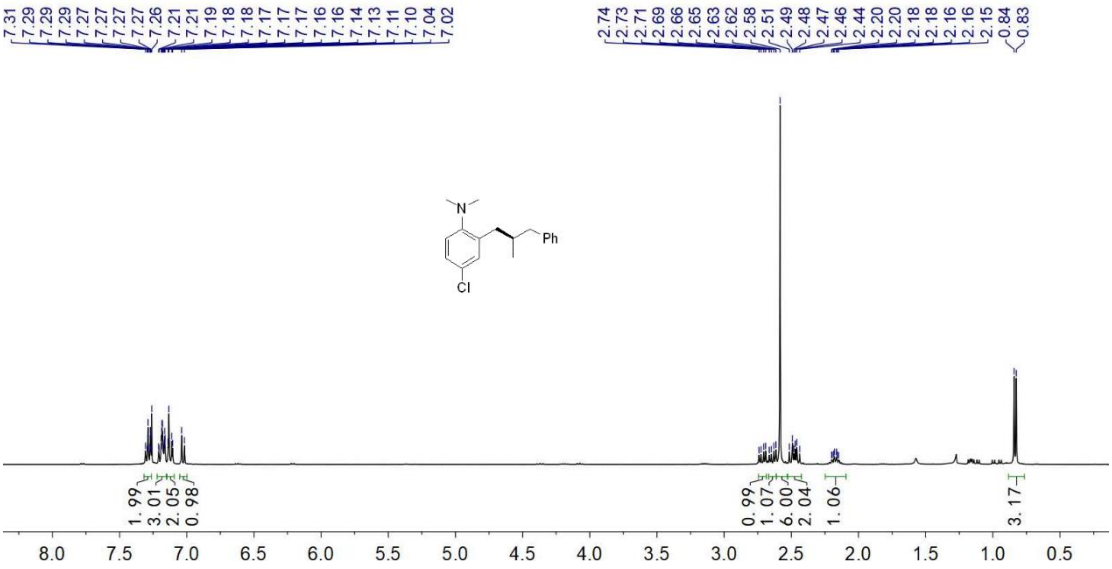


Fig. S83. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

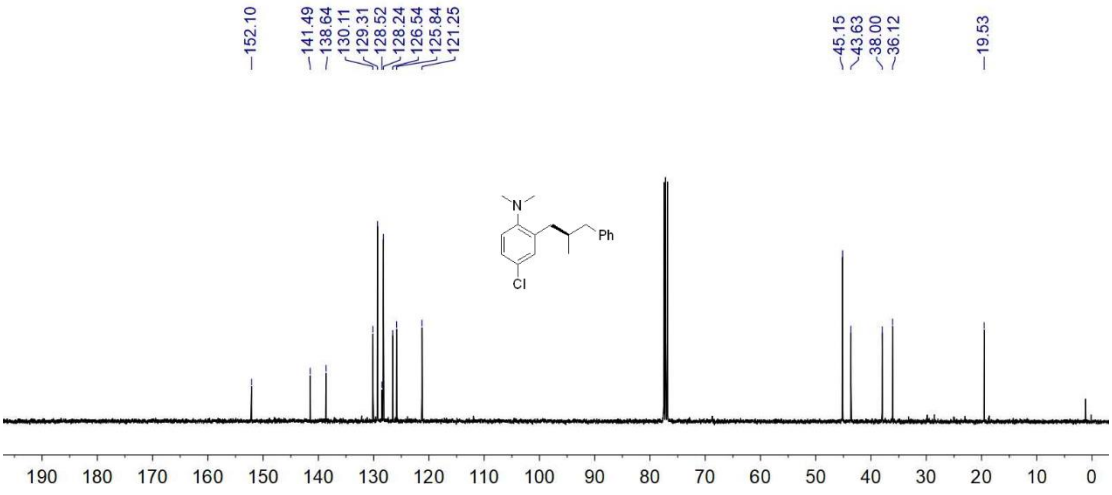
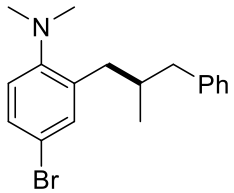


Fig. S84. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8g (colorless oil, 93 mg, 93%)

HRMS (ESI) *m/z* calcd. For $C_{18}H_{23}BrN$ $[M + H]^+$: 332.1008; found: 332.1003.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.26 (m, 4H, Ar-H), 7.18 (m, 3H, Ar-H), 6.96

(m, 1H, Ar-H), 2.70 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 5.9 Hz, 1H, CH_2), 2.63 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 6.3 Hz, 1H, CH_2), 2.58 (s, 6H, NMe_2), 2.46 (m, 2H, CH_2), 2.16 (m, 1H, C*H*Me), 0.82 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.6, 141.5, 139.0, 133.0, 129.5, 129.3, 128.2, 125.8, 121.7, 116.4, 45.0, 43.6, 38.0, 36.1, 19.5.

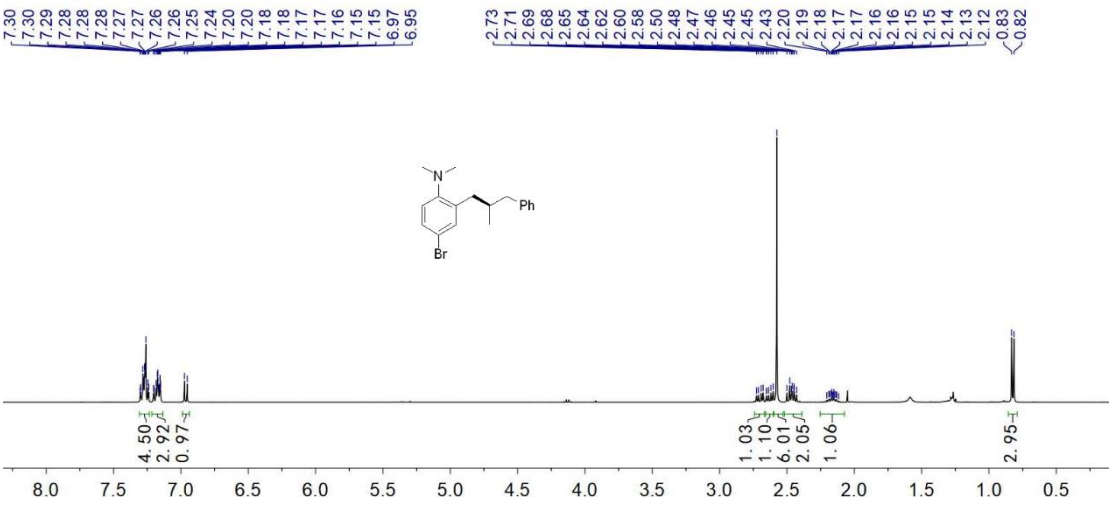


Fig. S85. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

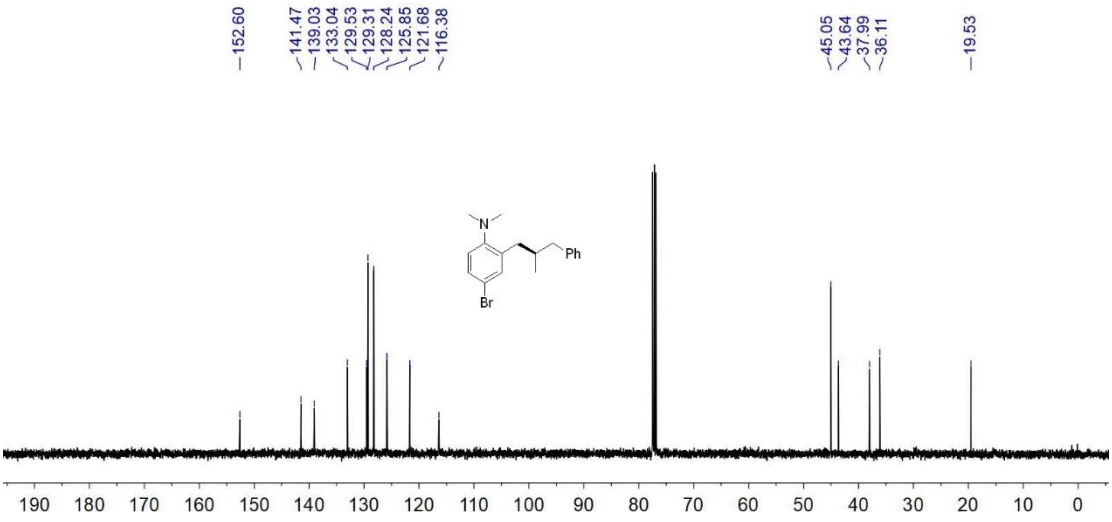
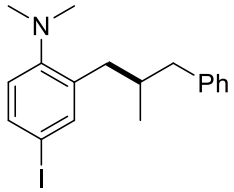


Fig. S86. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8h (colorless oil, 98 mg, 86%)

HRMS (ESI) *m/z* calcd. For $C_{18}H_{23}IN$ $[M + H]^+$: 380.0870; found: 380.0871.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.46 (m, 2H, Ar-H), 7.28 (m, 2H, Ar-H), 7.18

(m, 3H, Ar-H), 6.84 (m, 1H, Ar-H), 2.65 (m, 2H, CH_2), 2.58 (s, 6H, NMe_2), 2.45 (m, 2H, CH_2), 2.16 (m, 1H, CHMe), 0.82 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CHMe).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 153.3, 141.5, 139.3, 139.0, 135.6, 129.3, 128.2, 125.8, 122.1, 87.3, 44.9, 43.6, 37.9, 36.1, 19.5.

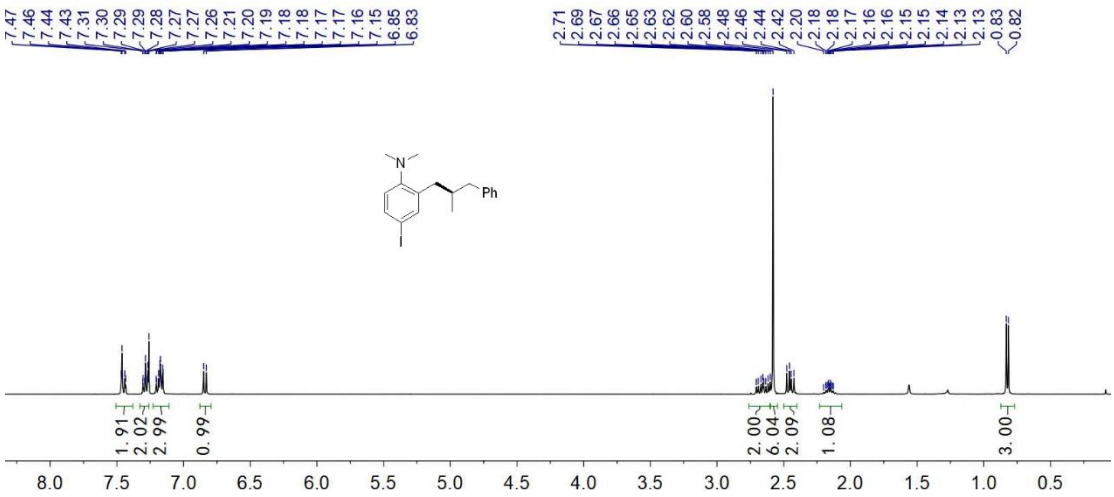


Fig. S87. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

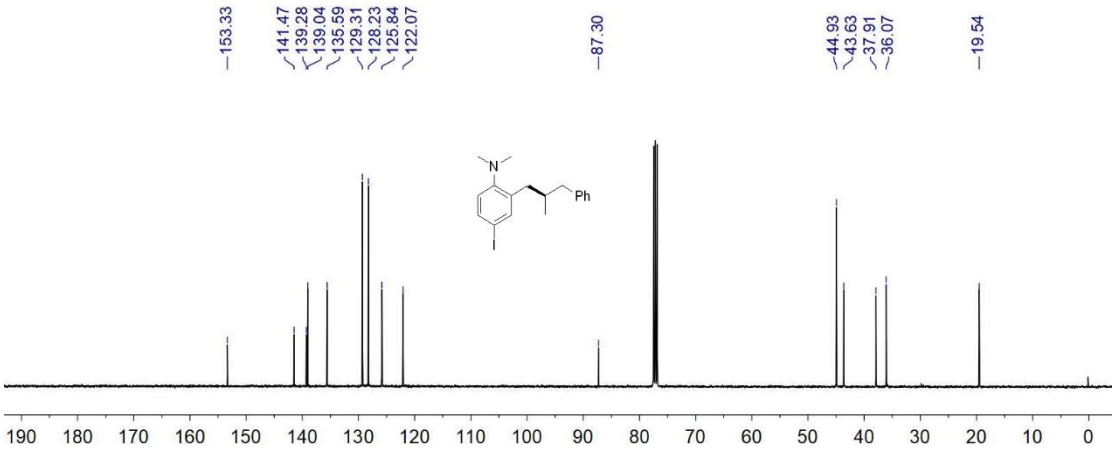
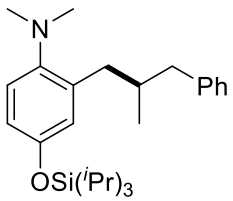


Fig. S88. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8i (colorless oil, 118 mg, 92%)

HRMS (ESI) *m/z* calcd. For $C_{27}H_{44}NOSi$ $[M + H]^+$: 426.3187; found: 426.3186.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 2H, Ar-H), 7.19 (m, 3H, Ar-H), 7.01 (m, 1H, Ar-H), 6.70 (m, 2H, Ar-H), 2.71 (m, 2H, CH_2), 2.57 (s, 6H, NMe_2), 2.44 (m,

2H, CH_2), 2.16 (m, 1H, CH), 1.26 (m, 3H, CHMe$_2$), 1.12 (d, $^3J_{HH}$ = 7.3 Hz, 18H, CHMe_2), 0.85 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CHMe).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.1, 147.1, 141.9, 138.2, 129.3, 128.2, 125.7, 121.5, 120.9, 117.6, 45.8, 43.4, 38.2, 36.4, 19.6, 18.1, 12.8.

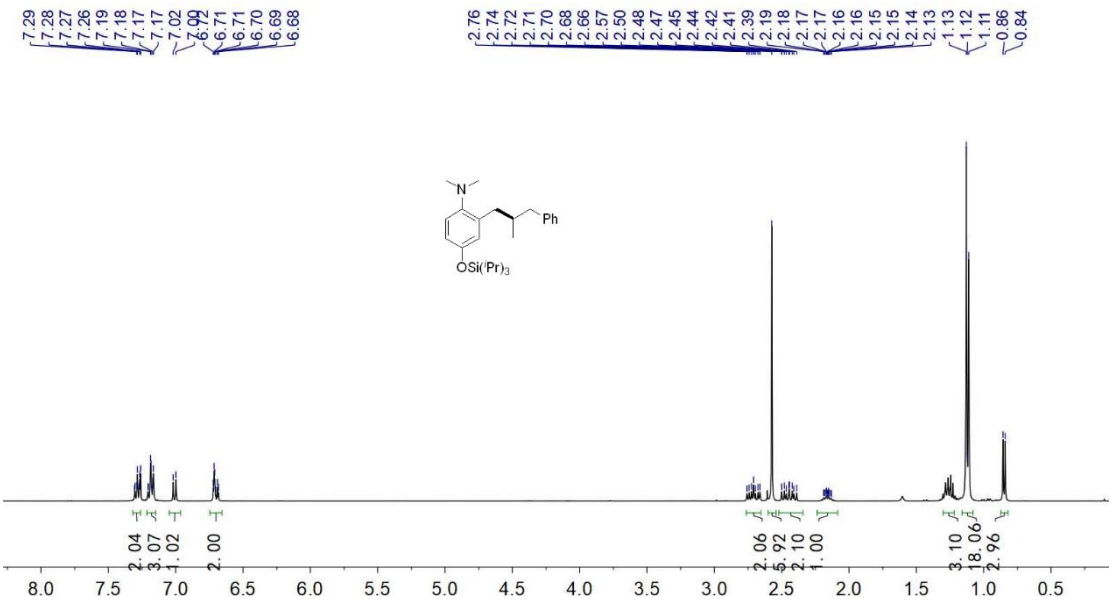


Fig. S89. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

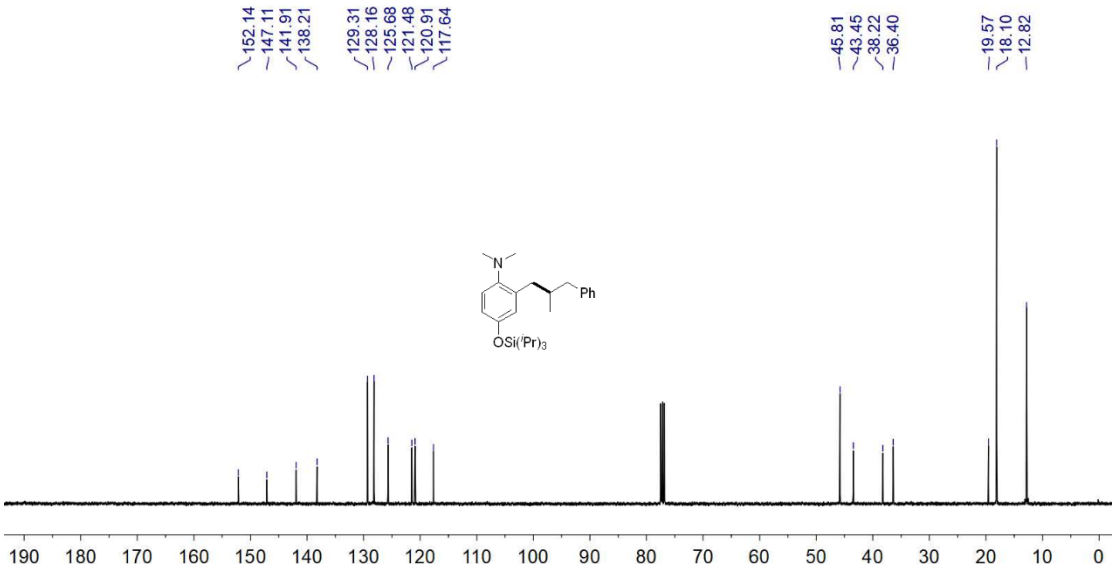
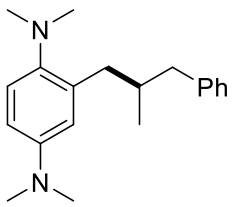


Fig. S90. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8j (colorless oil, 78 mg, 87%)

HRMS (ESI) *m/z* calcd. For $C_{20}H_{29}N_2$ $[M + H]^+$: 297.2325; found: 297.2334.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 2H, Ar-H), 7.19 (m, 3H, Ar-H), 7.10 (m, 1H, Ar-H), 6.63 (m, 2H, Ar-H), 2.92 (s, 6H, N*Me*$_2$), 2.74 (m, 2H, C*H*$_2$), 2.58 (overlapped, 7H, N*Me*$_2$ and C*H*$_2$), 2.44 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, C*H*$_2$), 2.22 (m, 1H, C*H*Me), 0.88 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 147.6, 144.1, 142.0, 137.9, 129.3, 128.1, 125.6, 121.1, 115.4, 111.5, 45.9, 43.7, 41.4, 38.7, 36.4, 19.6.

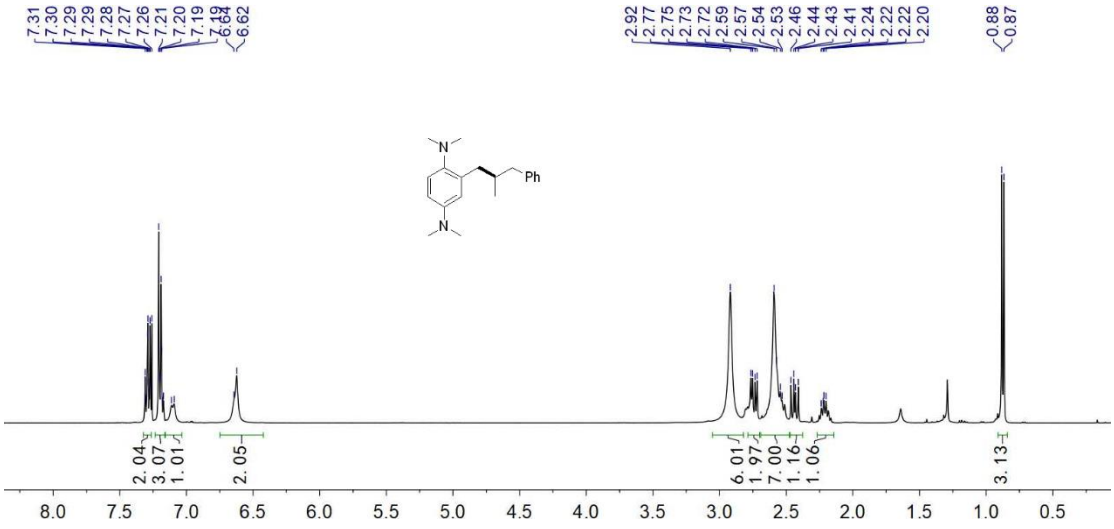


Fig. S91. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

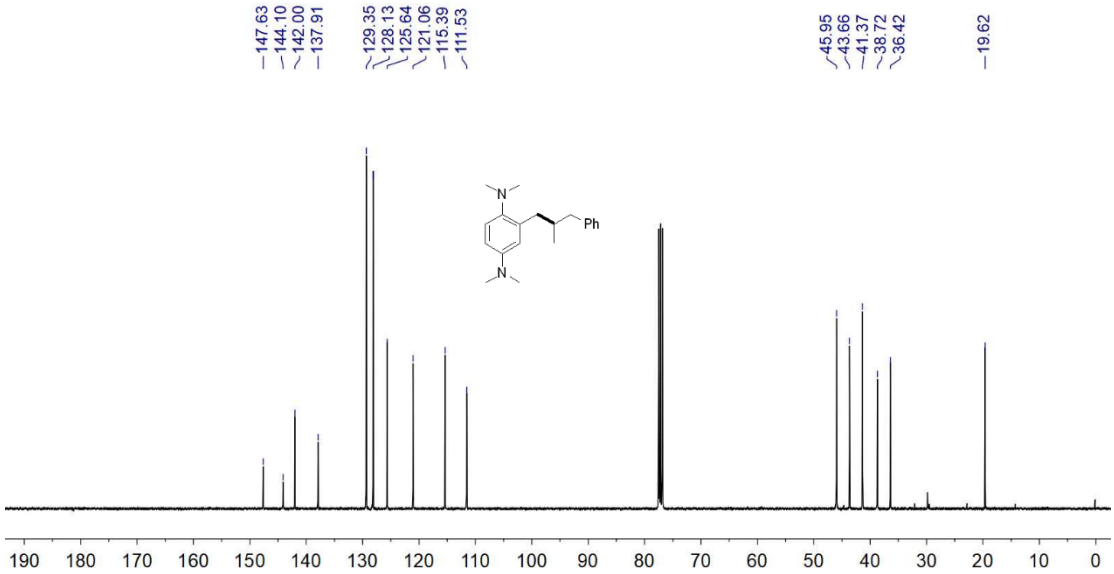
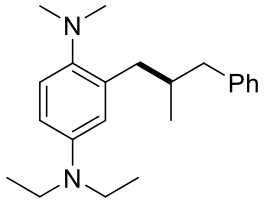


Fig. S92. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8k (colorless oil, 83 mg, 85%)

HRMS (ESI) *m/z* calcd. For $C_{22}H_{33}N_2$ $[M + H]^+$: 325.2638; found: 325.2646.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.28 (m, 1H, Ar-H), 7.26 (m, 1H, Ar-H), 7.18 (m, 3H, Ar-H), 7.06 (m, 1H, Ar-H), 6.53 (m, 2H, Ar-H), 3.31 (q, $^3J_{HH}$ = 7.1 Hz, 4H, C*H*$_2$CH$_3$), 2.75 (m, 2H, C*H*$_2$), 2.57 (s, 6H, N*Me*$_2$), 2.49 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*$_2$), 2.41 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, C*H*$_2$), 2.19 (m, 1H, C*H*Me), 1.15 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH$_2$C*H*$_3$), 0.87 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 144.7, 143.1, 142.1, 138.0, 129.3, 128.1, 125.6, 121.3, 114.7, 111.0, 46.1, 44.8, 43.6, 38.8, 36.4, 19.7, 12.9.

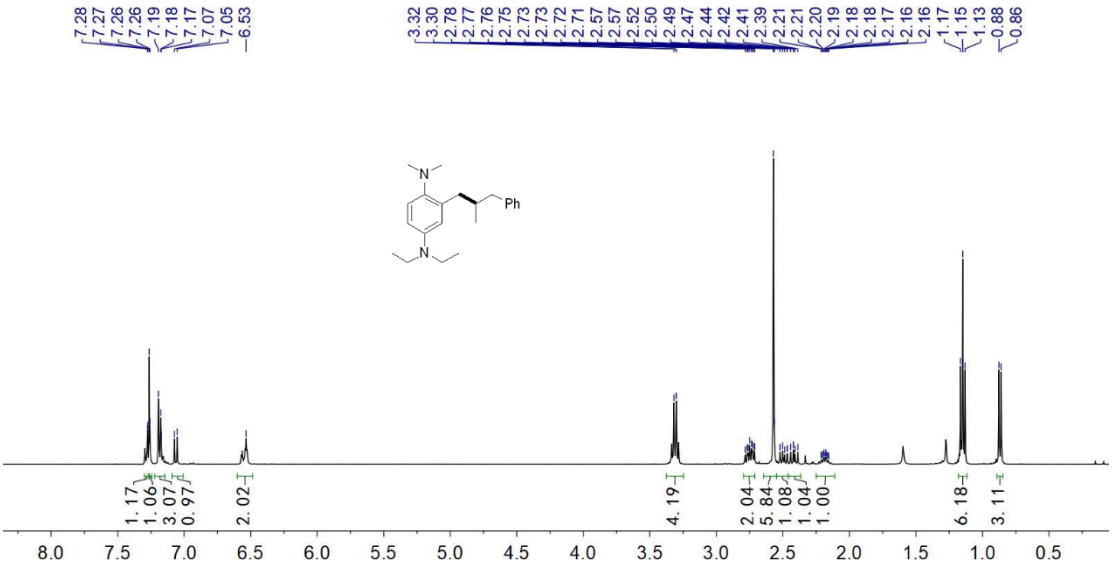


Fig. S93. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

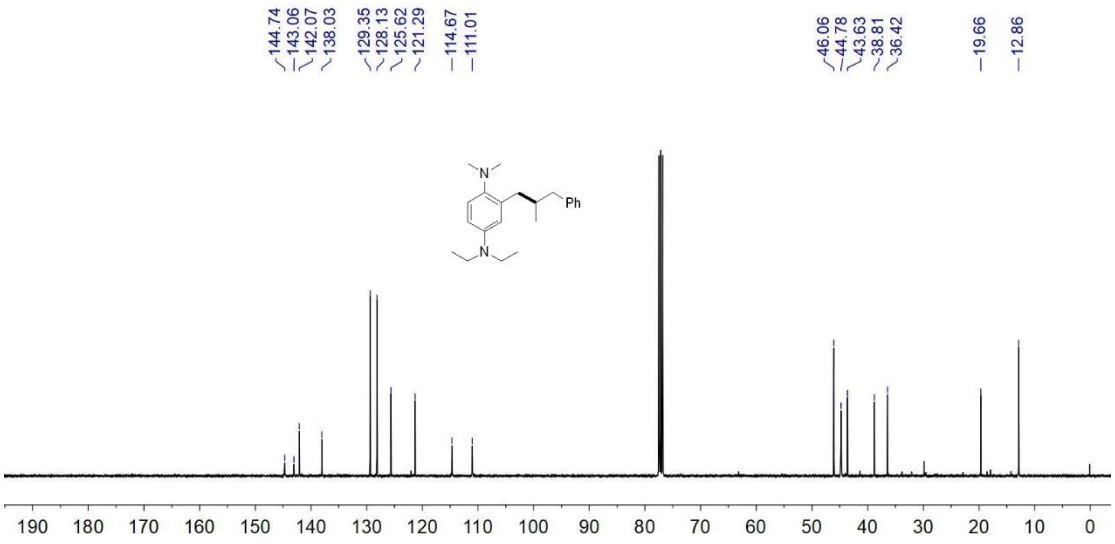
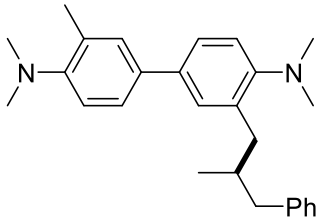


Fig. S94. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



8l (colorless oil, 108 mg, 93%)

HRMS (ESI) *m/z* calcd. For $C_{27}H_{35}N_2$ $[M + H]^+$: 387.2795; found: 387.2785.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.38 (m, 4H, Ar-H), 7.29 (m, 2H, Ar-H), 7.19 (m, 4H, Ar-H), 7.10 (m, 1H, Ar-H), 2.83 (dd, $^{2}J_{HH}$ = 13.6 Hz, $^{3}J_{HH}$ = 6.0 Hz, 1H, CH_2), 2.76 (s, 6H, NMe_2), 2.71 (m, 1H, CH_2), 2.67 (s, 6H, NMe_2), 2.60 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{3}J_{HH}$ = 8.4 Hz, 1H, CH_2), 2.48 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, CH_2), 2.42 (s, 3H, Ar-*Me*), 2.28 (m, 1H, C*H*Me), 0.87 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.3, 151.7, 141.8, 136.6, 136.1, 135.6, 132.3, 129.9, 129.4, 128.9, 128.2, 125.7, 125.0, 124.9, 120.0, 118.7, 45.3, 44.4, 43.7, 38.5, 36.2, 19.7, 18.8.

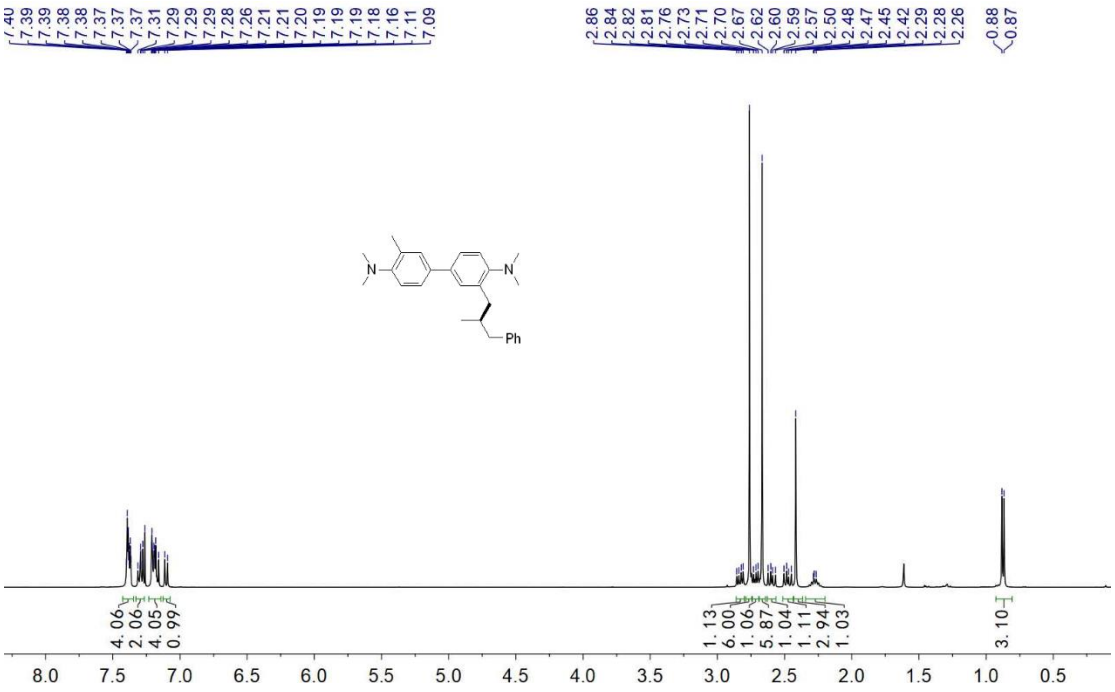


Fig. S95. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

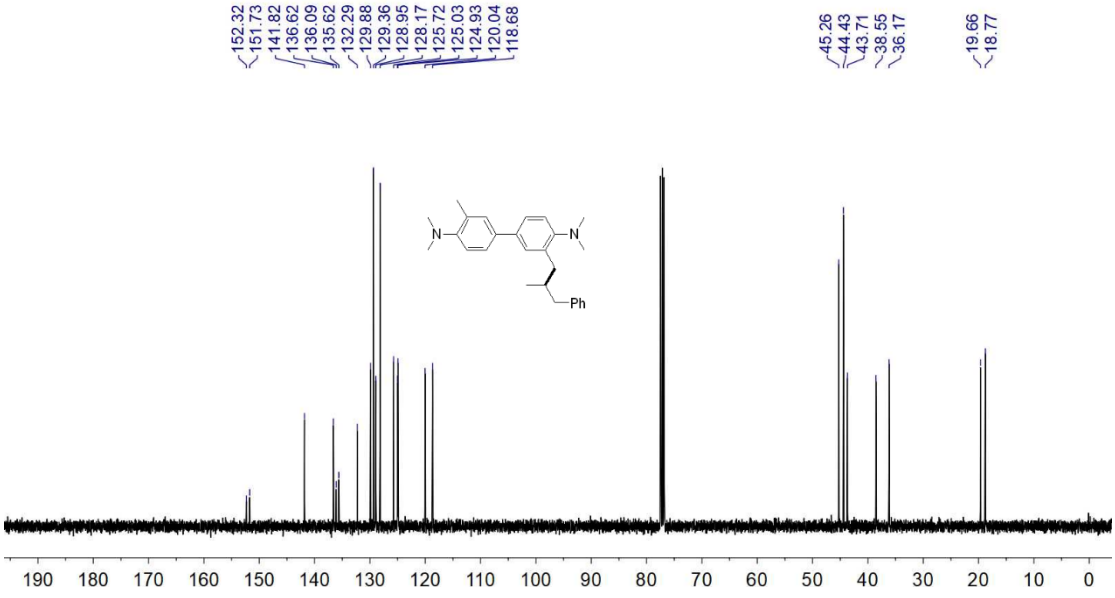
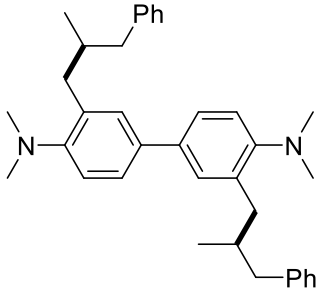


Fig. S96. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K)



8m (colorless oil, 139 mg, 92%)

HRMS (ESI) *m/z* calcd. For $C_{36}H_{45}N_2$ $[M + H]^+$: 505.3577; found: 505.3574.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.41 (m, 4H, Ar-H), 7.32 (m, 4H, Ar-H), 7.22 (m, 8H, Ar-H), 2.87 (dd, $^2J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 5.8 Hz, 2H, CH_2), 2.76 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2), 2.70 (s, 12H, NMe_2), 2.64 (m, 2H, CH_2), 2.51 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 8.2 Hz, 2H, CH_2), 2.31 (m, 2H, C*H*Me), 0.92 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.4, 141.8, 136.7, 136.3, 129.4, 129.0, 128.2, 125.7, 125.1, 120.0, 45.3, 43.7, 38.6, 36.2, 19.7.

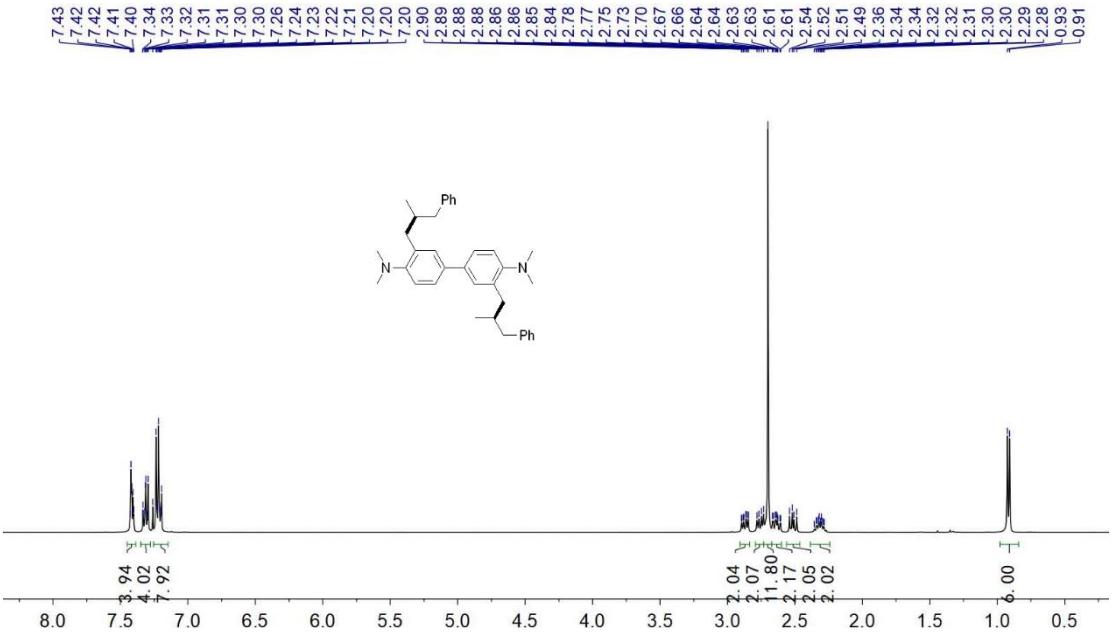


Fig. S97. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

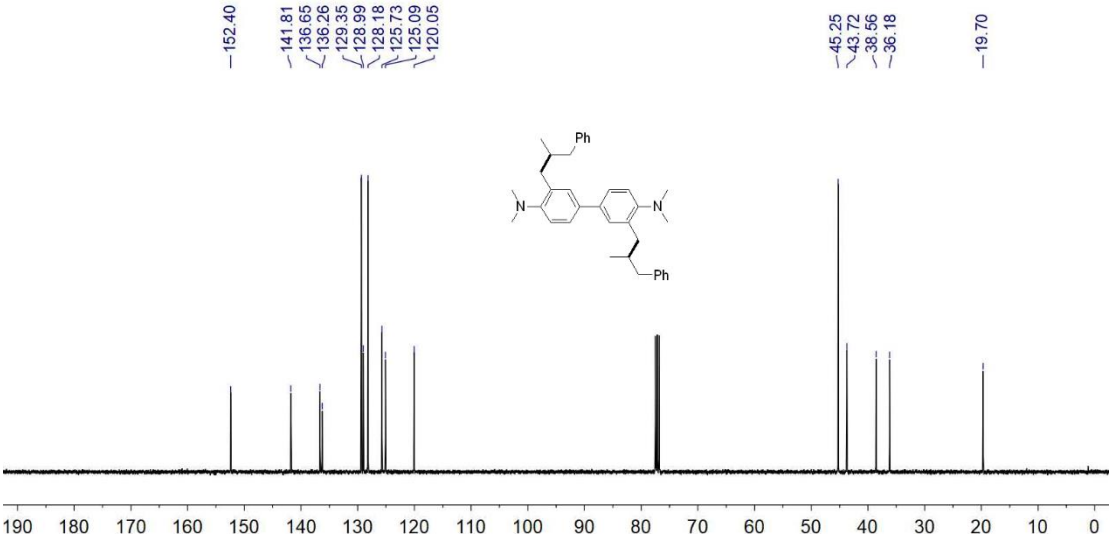
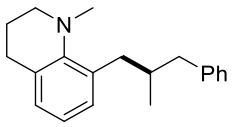


Fig. S98. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8n (colorless oil, 66 mg, 78%)

HRMS (ESI) *m/z* calcd. For $C_{20}H_{26}N$ $[M + H]^+$: 280.2060; found: 280.2068.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 2H, Ar-H), 7.20 (m, 3H, Ar-H), 7.03 (m, 1H, Ar-H), 6.90 (m, 2H, Ar-H), 3.09 (m, 2H, CH_2), 2.83 (m, 2H, CH_2), 2.74 (dd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, CH_2), 2.69 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, CH_2), 2.64 (s, 3H, N*Me*), 2.55 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 8.1 Hz, 1H, CH_2), 2.43 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, CH_2), 2.28 (m, 1H, C*H*Me), 1.87 (m, 2H, CH_2), 0.86 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 148.6, 141.9, 135.0, 129.4, 129.4, 128.2, 127.7, 127.4, 125.7, 121.9, 51.7, 43.9, 43.5, 38.4, 35.8, 27.8, 19.7, 16.7.

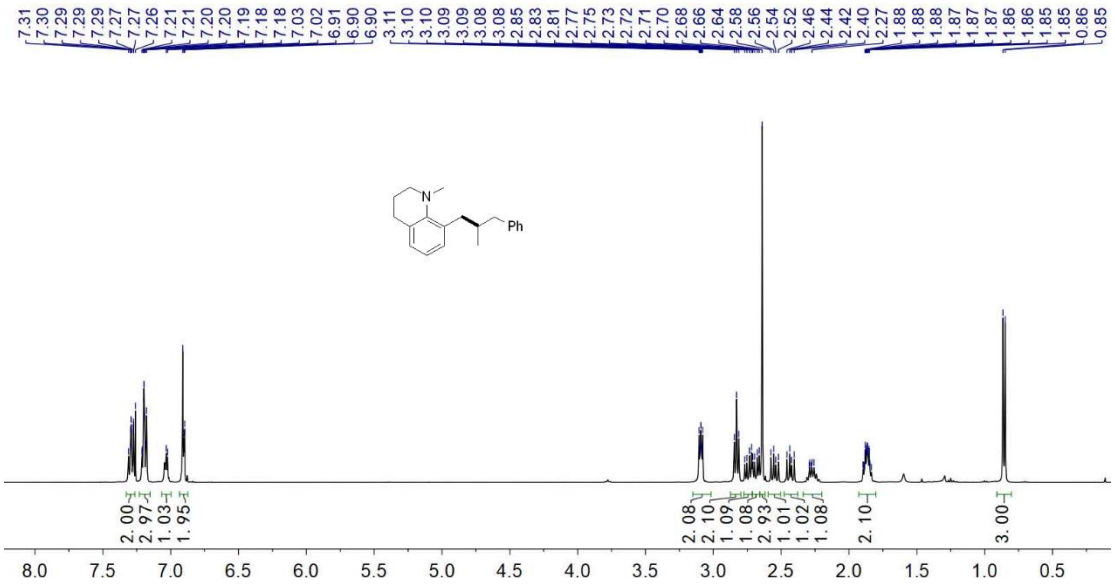


Fig. S99. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

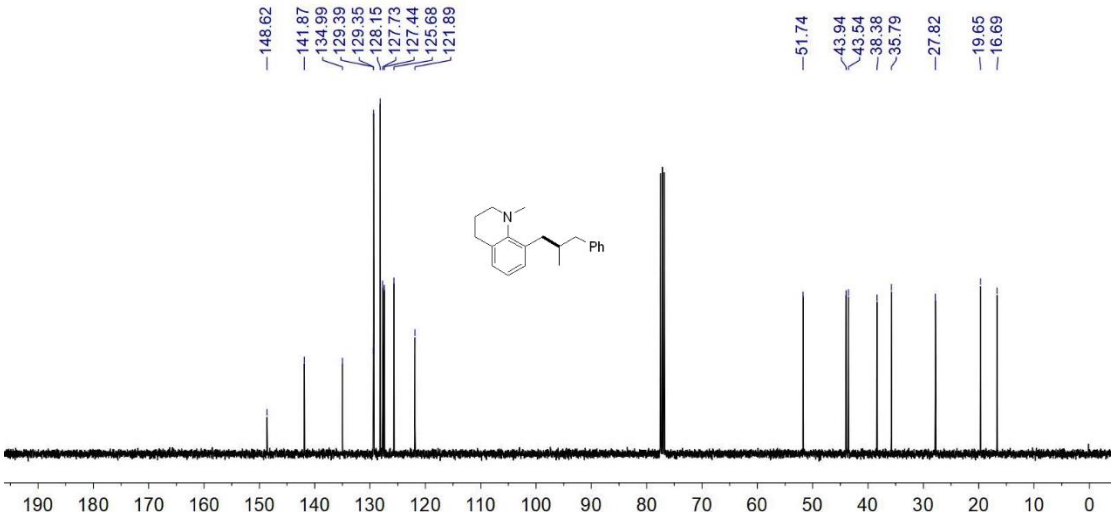
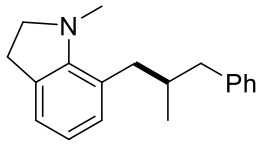


Fig. S100. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, $CDCl_3$, 298 K)



8o (colorless oil, 43 mg, 54%)

HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}N$ $[M + H]^+$: 266.1903; found: 266.1906.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.27 (m, 2H, Ar-H), 7.19 (m, 3H, Ar-H), 6.98 (m, 1H, Ar-H), 6.85 (m, 1H, Ar-H), 6.68 (m, 1H, Ar-H), 3.32 (m, 1H, CH_2), 3.22 (m, 1H, CH_2), 2.91 (m, 3H, CH_2), 2.72 (overlapped, 4H, N*Me* and CH_2), 2.44 (m, 2H, CH_2), 2.11 (m, 1H, C*H*Me), 0.83 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH*Me*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 151.0, 141.4, 131.9, 131.3, 129.5, 128.2, 125.9, 123.8, 122.6, 119.0, 57.7, 43.8, 40.1, 39.9, 35.3, 28.9, 19.4.

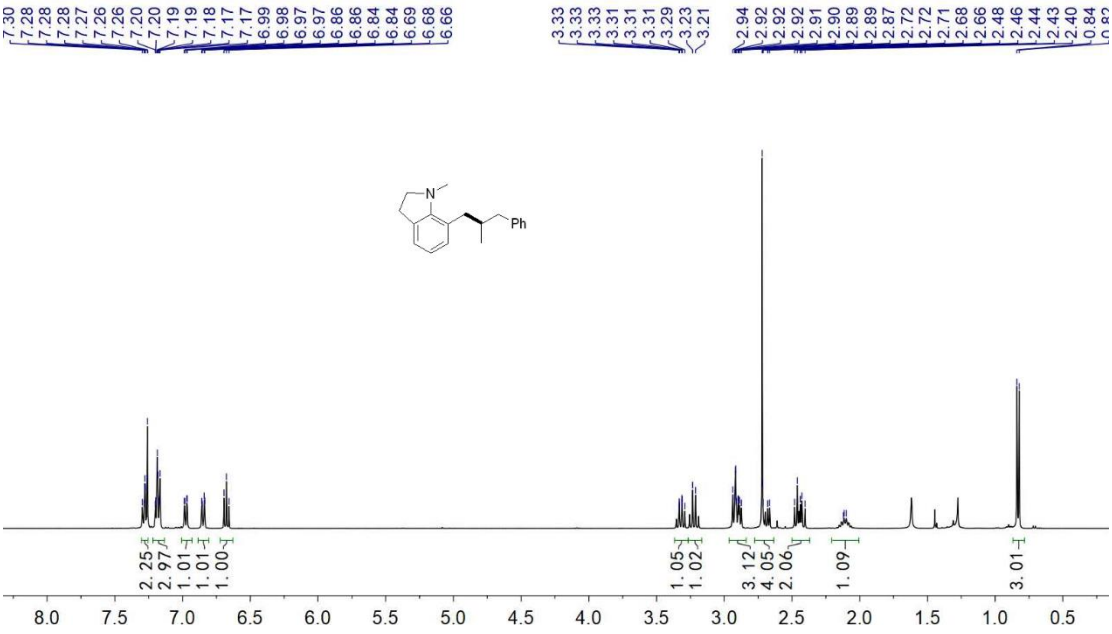


Fig. S101. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

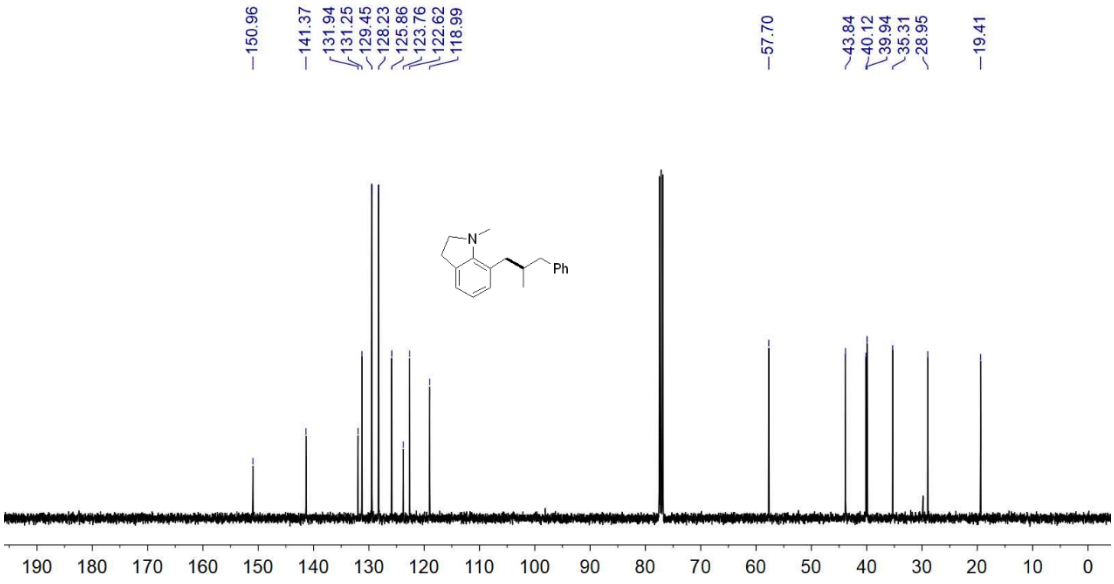
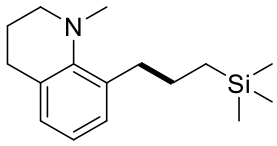


Fig. S102. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)



8p (colorless oil, 64 mg, 81%)

HRMS (ESI) *m/z* calcd. For $C_{16}H_{28}NSi$ $[M + H]^+$: 262.1986; found: 262.1982.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.06 (m, 1H, Ar-H), 6.92 (m, 2H, Ar-H), 3.12 (m, 2H, C*H*$_2$), 2.84 (m, 2H, C*H*$_2$), 2.72 (overlapped, 5H, N*Me* and C*H*$_2$), 1.87 (m, 2H,

CH_2), 1.70 (m, 2H, CH_2), 0.65 (m, 2H, CH_2), 0.03 (s, 9H, SiMe_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 147.9, 136.4, 129.3, 127.3, 127.1, 122.0, 52.0, 44.2, 34.7, 27.9, 25.1, 17.4, 16.7, -1.5.

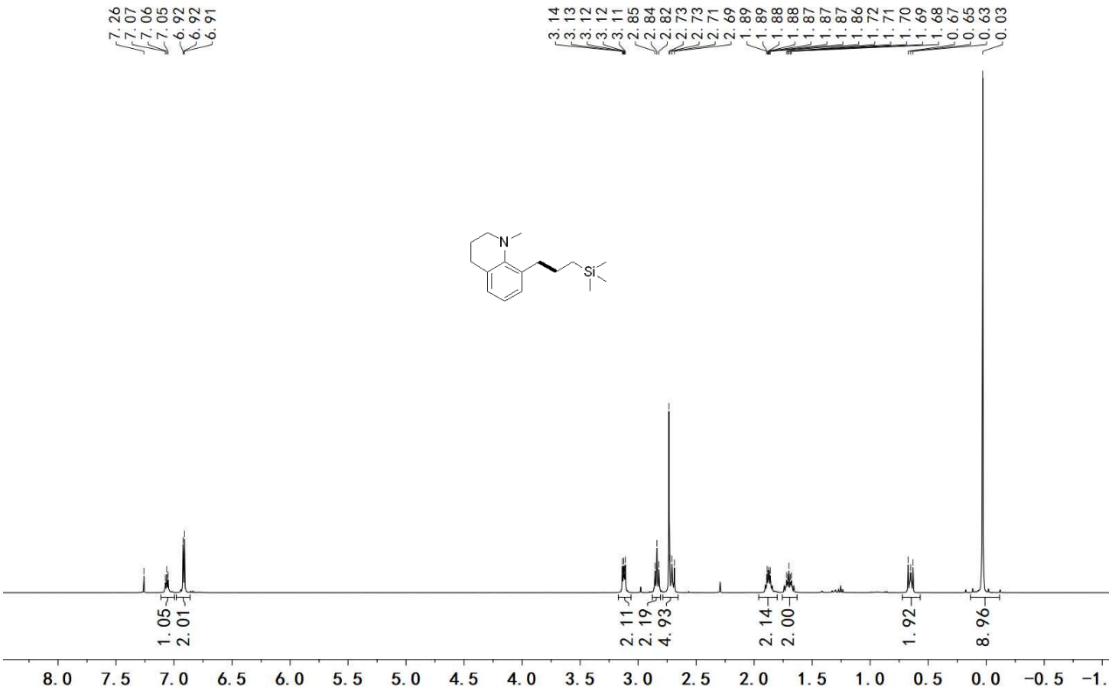


Fig. S103. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

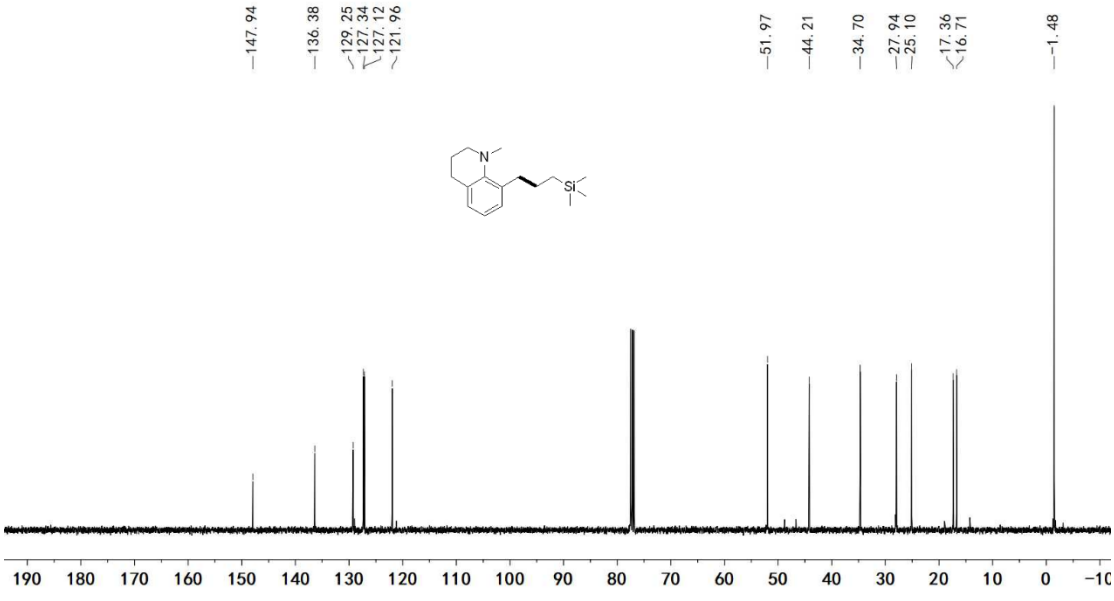
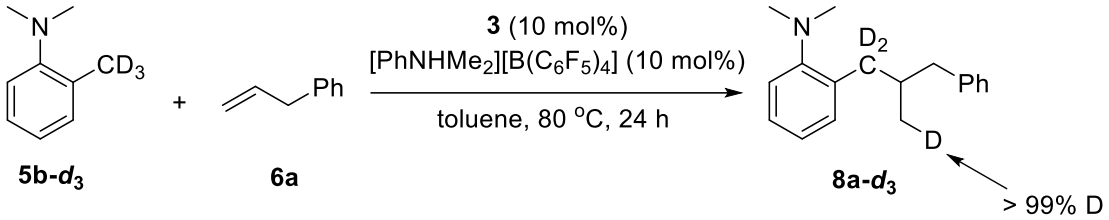


Fig. S104. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)

Deuterium labeling experiments

C(sp^3)-H alkylation of aniline 5b-*d*$_3$ with alkene 6a



Scheme S11.

Complex **3** (9 mg, 0.015 mmol, in 0.5 mL of toluene) was added to a solution of [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] (12 mg, 0.015 mmol) in 0.5 mL of toluene. After stirring at room temperature for 5 min, amine **5b-*d*$_3$** (31 mg, 0.225 mmol) and alkene **6a** (18 mg, 0.15 mmol) were added and the reaction mixture was heated at 80 °C for 24 h. Then, the mixture was cooled to room temperature and the volatiles were removed under vacuum. The residue was purified by silica gel column chromatography to afford alkylation product **8a-*d*$_3$** (12 mg, 31%).

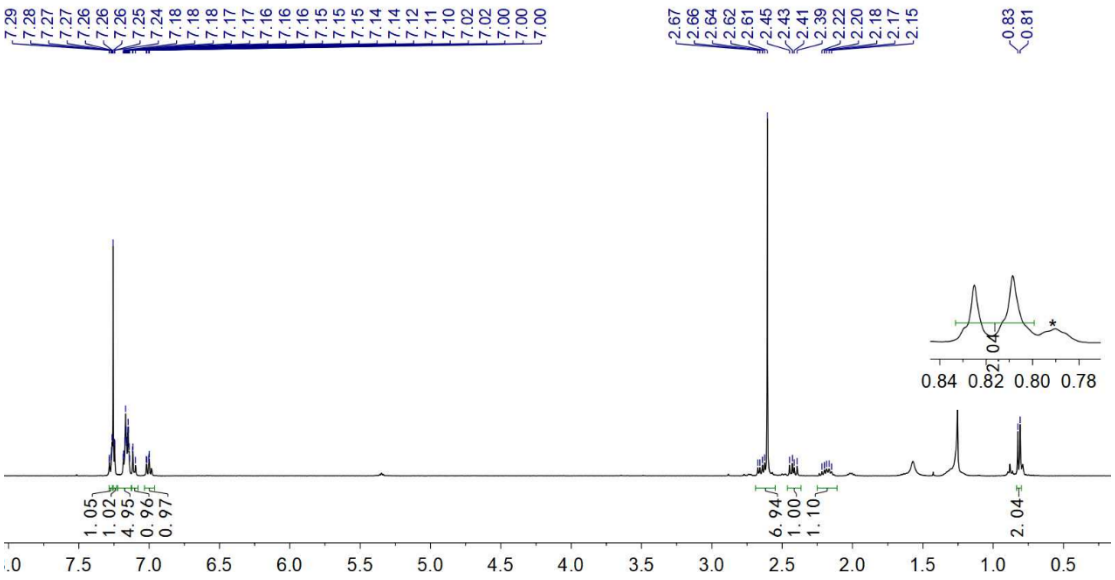
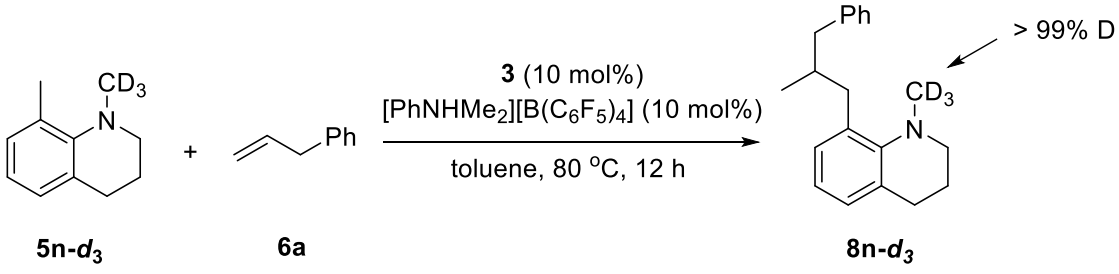


Fig. S105. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) [*: petroleum ether]

C(sp^3)-H alkylation of 5n-*d*$_3$ with 6a



Scheme S12.

Complex **3** (9 mg, 0.015 mmol, in 0.5 mL of toluene) was added to a solution of $[PhNHMe_2][B(C_6F_5)_4]$ (12 mg, 0.015 mmol) in 0.5 mL of toluene. After stirring at room temperature for 5 min, amine **5n-*d*$_3$** (37 mg, 0.225 mmol) and alkene **6a** (18 mg, 0.15 mmol) were added and the reaction mixture was heated at 80 ^oC for 12 h. Then, the mixture was cooled to room temperature and the volatiles were removed under vacuum. The residue was purified by silica gel column chromatography to afford alkylation product **8n-*d*$_3$** (32 mg, 75%).

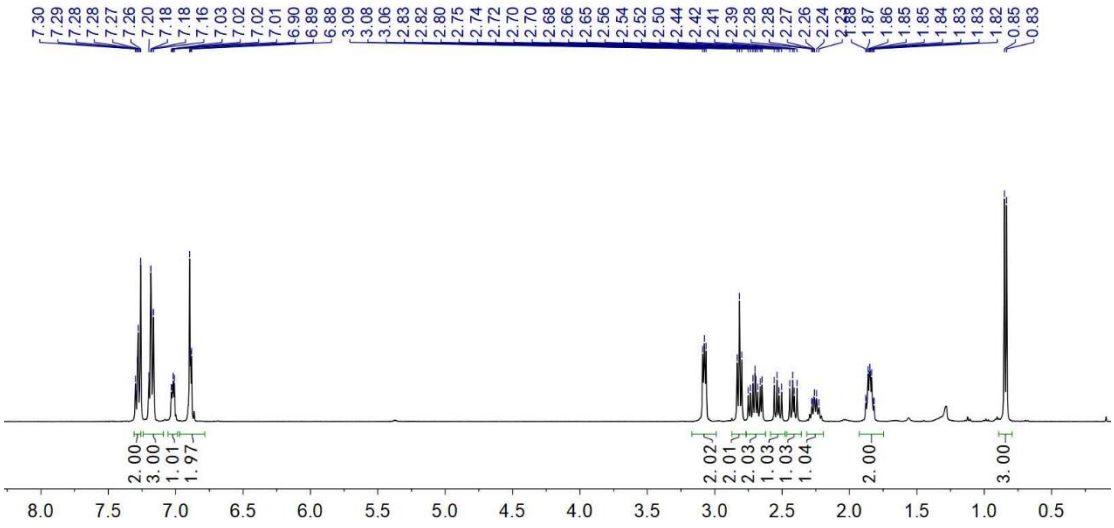


Fig. S106. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

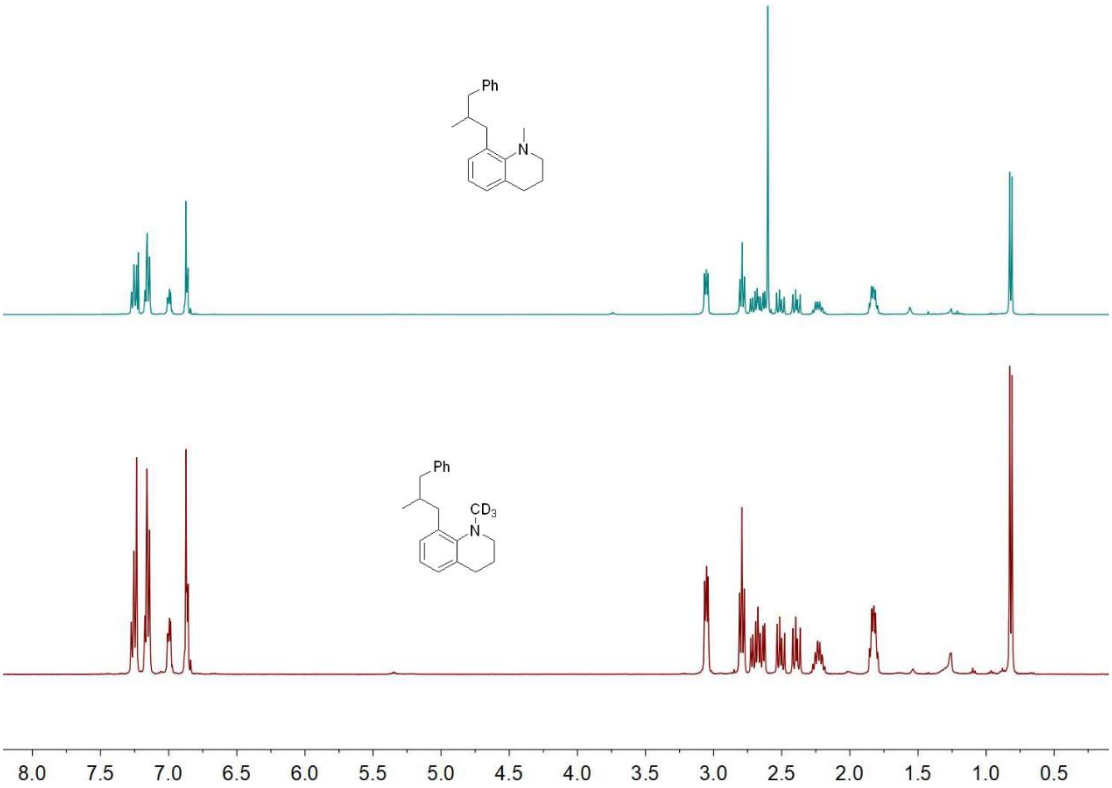
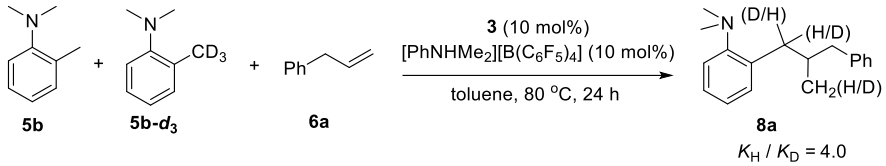


Fig. S107. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

Intermolecular competition experiment



Scheme S13.

Complex **3** (9 mg, 0.015 mmol, in 0.5 mL of toluene) was added to a solution of $[PhNHMe_2][B(C_6F_5)_4]$ (12 mg, 0.015 mmol) in 0.5 mL of toluene. After stirring at room temperature for 5 min, **5b** (30 mg, 0.225 mmol), **5b-*d*$_3$** (30 mg, 0.225 mmol) and alkene **6a** (18 mg, 0.15 mmol) were added and the reaction mixture was heated at 80 °C for 24 h. The mixture was cooled to room temperature and the volatiles were removed under vacuum. The residue was purified by silica gel column chromatography to afford alkylation products **8a** (31 mg). The product was analyzed by ^{1}H NMR and KIE value of 4.0 was calculated the integration values of ArCH_2 (dd, 2.77 and 2.52 ppm) (KIE = 0.8/0.2 = 4.0).

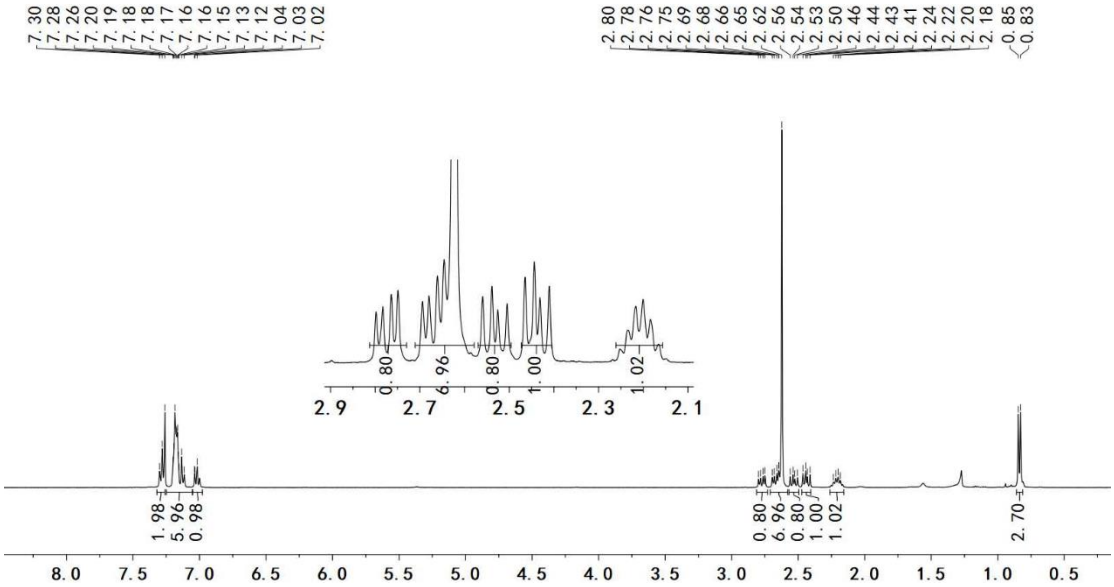
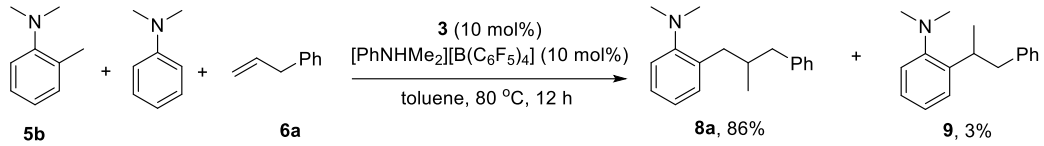


Fig. S108. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

Intermolecular C-H Bond competition reaction



Scheme S14.

Complex **3** (36 mg, 0.06 mmol, in 1 mL of toluene) was added to a solution of $[PhNHMe_2][B(C_6F_5)_4]$ (48 mg, 0.06 mmol) in 1 mL of toluene. After stirring at room temperature for 5 min, **5b** (122 mg, 0.9 mmol), *N,N*-dimethylaniline (109 mg, 0.9 mmol) and alkene **6a** (71 mg, 0.6 mmol) were added and the reaction mixture was heated at 80 °C for 12 h. The mixture was cooled to room temperature and the volatiles were removed under vacuum. The residue was purified by silica gel column chromatography to afford alkylation products **8a** (131 mg, 86%) and **9** (yellow oil, 6 mg, 3%).

Data of compound 9

HRMS (ESI) *m/z* calcd. For $C_{17}H_{22}N$ $[M + H]^+$: 240.1747; found: 240.1749.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.31 (m, 1H, Ar-H), 7.21 (m, 2H, Ar-H), 7.13 (m, 6H, Ar-H), 3.74 (m, 1H, C*H*Me), 2.92 (dd, $^{2}J_{HH}$ = 13.3 Hz, $^{3}J_{HH}$ = 6.2 Hz, 1H, CH_2), 2.71 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 8.7 Hz, 1H, CH_2), 2.59 (s, 6H, NMe_2), 1.19 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 152.5, 142.9, 141.5, 129.3, 128.1, 126.9, 126.5, 125.8, 124.2, 120.3, 45.9, 45.0, 34.0, 21.2.

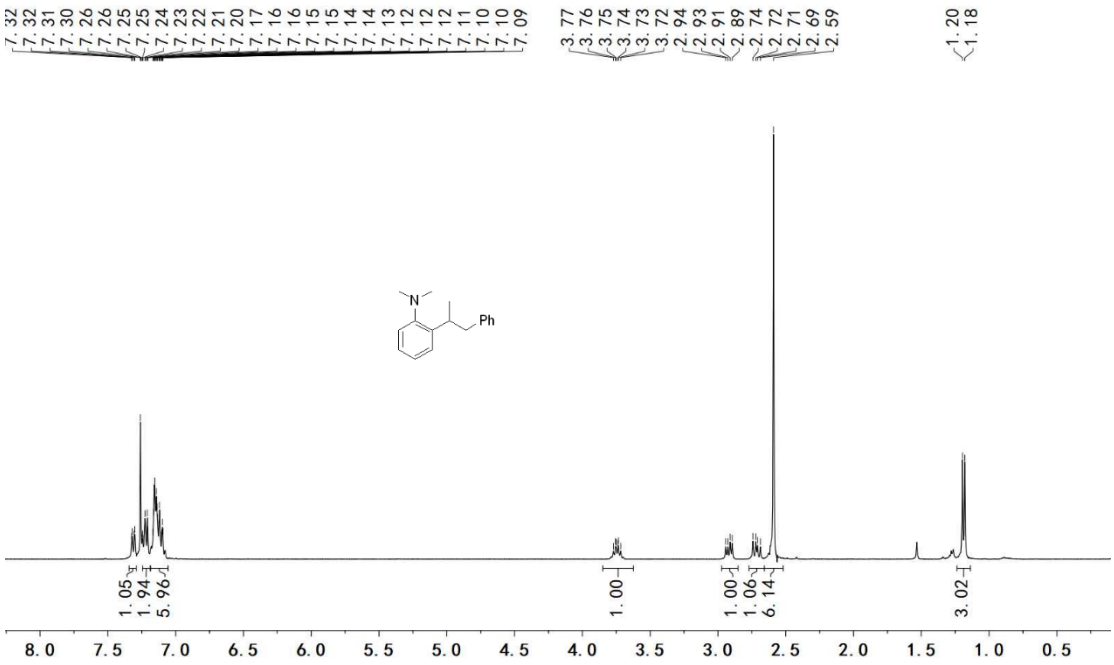


Fig. S109. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

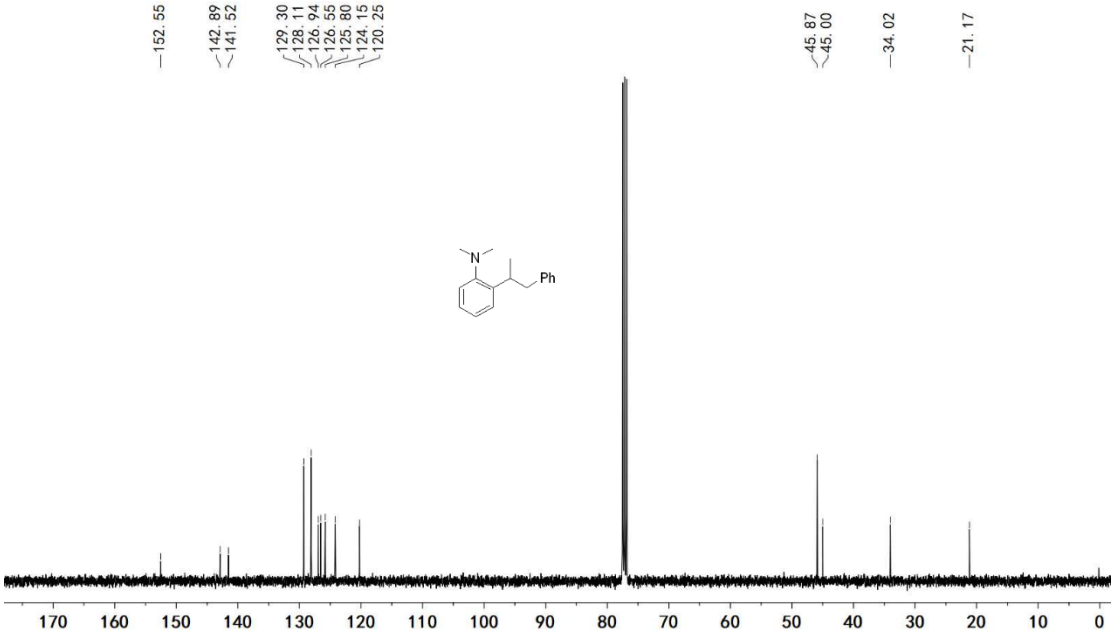


Fig. S110. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K)