Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 334–336

Highly basic alkyl-substituted bis(benzhydryl) Ca^{II} and Yb^{II} complexes with β-CH–M agostic interactions

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Experimental Section

General Procedures. All reactions were performed under a dry argon or nitrogen atmosphere using standard Schlenk techniques or under nitrogen atmosphere in a glovebox, unless indicated. Dry, oxygen-free solvents were used throughout. After being dried over KOH, THF was purified by distillation from sodium benzophenone ketyl. Hexane, benzene and toluene were distilled from sodium/potassium alloy prior to use. Benzene-d_6 was refluxed over Na/K alloy, vacuum-transferred, and stored over 4 Å molecular sieves in a nitrogen-filled glovebox. $(4\text{-Bu}^t\text{C}_6\text{H}_4)_2\text{CH}_2$ [S1] and *n*-BuNa [S2] were prepared according to literature procedures. Unsolvated YbI_2 and CaI_2 were synthesized by heating $YbI_2(THF)_2$ [S3] and $CaI_2(THF)_4$ [S4] at 180 °C in dynamic vacuum.[S5] Other reagents and solvents were used as purchased from commercial suppliers.

Instruments and Measurements. NMR spectra were recorded on a Bruker DPX 200 or Bruker Avance DRX-400 spectrometer. Chemical shifts for ^{1}H and ^{13}C{^{1}H} spectra were referenced internally using the residual solvent resonances and are reported relative to TMS; coupling constants are given in Hz. The assignment of ^{1}H and ^{13}C{^{1}H} resonances was assisted with gHSQC and gHMBC spectra. The hmbcgplpndqf (2D H/X correlation via heteronuclear zero and double quantum coherence optimized on long-range couplings with low-pass J-filter to suppress one-bond correlations without decoupling during acquisition, using gradient pulses for selection) pulse program was used for Yb−H long-range correlation. The delay between pulses (d1) was set to 1.5 s. The gpz1, gpz2, and gpz3 parameters were set to 70%, 30%, and 57.5%, respectively. The cnst2 was set to 250 and cnst13 to 15. IR spectra were recorded as Nujol mulls or KBr pellets on FSM 1201 and Bruker Vertex 70 instruments. The N, C, H elemental analyses were carried out in the microanalytical laboratory of the IOMC by means of a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of 0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Lanthanide metal analysis was carried out by complexonometric titration.[S6]

Synthesis of $(4\text{-Bu}^t\text{C}_6\text{H}_4)_2\text{CHMe}$ (1a). A solution of $(4\text{-Bu}^t\text{C}_6\text{H}_4)_2\text{CH}_2$ (5.00 g, 17.8 mmol) in hexane (30 ml) was added to Bu^tOK (2.00 g, 17.8 mmol), and the mixture was cooled to −78 °C. Then *n*-BuLi (8 ml, 2.5 M in hexanes, 19.5 mmol) was slowly syringed to a stirred suspension. The mixture was warmed to room temperature and allowed to stir for additional 24 hours. The orange-red suspension was filtered, and the resulting solid was washed twice with hexane (20 ml). The precipitate was dissolved in THF, and MeI (2.60 g, 18.0 mmol) was slowly added to the deep-red solution at 0 °C. A white precipitate of KI formed immediately, and the solution became colourless. The solution was washed three times with water and HCl (1 M), extracted with Et_2O (3×50 ml) and dried with $MgSO_4$, after this all volatiles were removed on a rotary evaporator. $(4\text{-Bu}^t\text{C}_6\text{H}_4)_2\text{CHMe}$ (**1a**) was obtained as white solid in 82% yield (4.30 g) after purification by flash chromatography on silica gel with petroleum ether as eluent (R_f = 0.9). ^{1}H NMR (200 MHz, $CDCl_3$, 293 K): δ 1.31 (s, 18H, *t*Bu), 1.63 (d, 3H, Me, $^3J_{HH}$ = 7.2 Hz), 4.10 (q, 1H, CH, $^3J_{HH}$ = 7.3 Hz), 7.17 (d, 4H, *o*-CH, C_6H_4, $^3J_{HH}$ = 8.3 Hz), 7.31 (d, 4H, *m*-CH, C_6H_4, $^3J_{HH}$ = 8.4 Hz). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 293 K): δ 22.0 (s, CH_3), 31.4 (s, $C(CH_3)_3$), 34.3 (s, $C(CH_3)_3$), 43.9 (s, CH), 125.2 (s, *o*-CH, C_6H_4), 127.2 (s, *m*-CH, C_6H_4), 143.5 (s, *ipso*-C), 148.6 (s, *ipso*-C). IR (KBr): 1898 (m), 1511 (s), 1410 (m), 1360 (s), 1266 (s), 1201

(m), 1130 (m), 1111 (m), 1048 (w), 1015 (s), 841 (s), 773 (m), 670 (m), 637 (m), 578 (s). Anal. Calcd for $C_{22}H_{30}$ (294.48 g/mol): C 89.73; H 10.27. Found: C 89.77; H 10.23. MS(EI): *m/z* 294.44 [M^+].

Synthesis of (4-Bu^{t}C$_6$H$_4$)$_2$CHBu^i (1b). The synthetic protocol analogous to that for **1a** was applied. Hydrocarbon (4-Bu^{t}C$_6$H$_4$)$_2$CH$_2$ (7.00 g, 25.0 mmol), Bu^{t}OK (2.80 g, 25.0 mmol) and Bu^{n}Li (11 ml, 2.5 M in hexanes, 27.5 mmol) were used in the synthesis. The reaction of {[(4-Bu^{t}C$_6$H$_4$)$_2$CH]K}$_n$ with Bu^{i}I (4.60 g, 25.0 mmol) was carried out in THF (20 m;) at 0 °C. A white precipitate of KI formed immediately, and the solution became colourless. The solution was washed three times with water and HCl (1M), extracted with Et_2O (3×50 ml) and dried with $MgSO_4$, after this all volatiles were removed on a rotary evaporator. Product **1b** was obtained as white solid in 90% yield (7.56 g) after purification by flash chromatography on silica gel with petroleum ether as eluent (R_f = 0.91). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ 0.91 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 1.29 (s, 18H, *t*Bu), 1.36-1.51 (m, 1H, C*H*(CH$_3$)$_2$), 1.89 (t, 2H, -CH$_2$-, $^3J_{HH}$ = 10.0 Hz), 3.96 (t, 1H, CH, $^3J_{HH}$ = 8.0 Hz), 7.18 (d, 4H, *o*-CH-Ph, $^3J_{HH}$ = 8.4 Hz), 7.28 (d, 4H, *o*-CH-Ph, $^3J_{HH}$ = 8.3 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 296 K): δ 22.7 (s, CH(*C*H$_3$)$_2$), 25.4 (s, *C*H(CH$_3$)$_2$), 31.4 (s, C(*C*H$_3$)$_3$), 34.3 (s, *C*(CH$_3$)$_3$), 45.3 (s, CH$_2$), 48.0 (s, CH), 125.2 (s, *o*-CH, C$_6$H$_4$), 127.4 (s, *m*-CH, C$_6$H$_4$), 142.4 (s, *ipso*-C), 148.5 (s, *ipso*-C). IR (KBr): 1899 (m), 1786 (w), 1500 (s), 1407 (s), 1266 (s), 1205 (m), 1170 (m), 1134 (s), 1111(s), 1018 (s), 924 (w), 833 (s), 811 (s), 778 (s), 689 (m), 670 (m), 637 (m), 579 (s), 556 (s). Anal. Calcd for $C_{22}H_{30}$ (336.56 g/mol): C 89.22; H 10.78. Found: C 89.35; H 10.65. MS (EI): *m/z* 336.28 [M^+].

Synthesis of [(4-Bu^{t}C$_6$H$_4$)$_2$CMe]$_2$Ca(TMEDA) (2a). Hydrocarbon **1a** (1.00 g, 3.4 mmol) was dissolved in hexane (7 ml), the solution was cooled to 0 °C, and TMEDA (1 ml, 6.70 mmol) was condensed. *n*-Butylsodium (0.29 g, 3.6 mmol) was added to the solution under vigorous stirring. The suspension was stirred at 0 °C for 2 h, then brought to room temperature and was stirred for more 24 hours. Voluminous finely crystalline precipitate of sodium salt was centrifuged from the mother liquor and redissolved in benzene. The resulting deep-red solution was slowly added to a suspension of CaI_2 (0.50 g, 1.7 mmol) in TMEDA (2 ml) at room temperature, and the resulting orange solution was stirred at 50 °C for 1 h and at room temperature for 24 h. The solution was centrifuged from the precipitate of NaI, and the precipitate was once extracted with benzene (5 ml). Complex **2a** was obtained as orange crystals by slowly concentrating the mother liquor in benzene in 53% yield (0.67 g). ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 1.29 (s, 12H, NMe$_2$-TMEDA), 1.33 (s, 36H, *t*Bu), 1.43 (s, 4H, -CH$_2$-CH$_2$-TMEDA), 2.07 (s, 6H, Me), 7.21 (d, 8H, *o*-CH-Ph, $^3J_{HH}$ = 8.3 Hz), 7.11 (d, 8H, *m*-CH-Ph, $^3J_{HH}$ = 7.8 Hz). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 296 K): δ 22.9 (s, Me), 31.5 (s, C(*C*H$_3$)$_3$), 33.6 (s, *C*(CH$_3$)$_3$), 45.1 (s, N(CH$_3$)$_2$), 56.5 (s, -CH$_2$CH$_2$-), 60.9 (s, C), 119.9 (s, *o*-CH), 127.2 (s, *m*-CH), 137.9 (s, *ipso*-C), 146.9 (s, *ipso*-C). IR (KBr): 1594 (s), 1510 (s), 1412 (w), 1263 (s), 1190 (m), 1128 (w), 1107 (w), 1068 (m), 1023 (s), 950 (s), 816 (s), 666 (m), 650 (m), 621 (m), 551 (s). Anal. Calcd for $C_{50}H_{74}N_2Ca$ (743.23 g/mol): C 80.80; H 10.04; N 3.77. Found: C 80.76; H 10.10; N 3.78.

Synthesis of [(4-Bu^{t}C$_6$H$_4$)$_2$C*i*Bu]$_2$Yb(TMEDA) (2b). Hydrocarbon **1b** (1.00 g, 3.0 mmol) was dissolved in hexane (5 ml), the solution was cooled to 0 °C, and TMEDA (1 ml, 6.70 mmol) was condensed. *n*-Butylsodium (0.26 g, 3.2 mmol) was added to the solution under vigorous stirring. The suspension was stirred at 0 °C for 2 h, then brought to room temperature and stirred for more 100 hours. A red precipitate of [(4-Bu^{t}C$_6$H$_4$)$_2$C*i*Bu]Na(TMEDA) was formed. Hexane was removed in vacuum, and benzene (10 ml) was added. The resulting suspension was slowly added to the suspension of YbI_2 (0.64 g, 1.5 mmol) in TMEDA (2 ml) at room temperature, and the resulting dark red solution was stirred at 50 °C for 1 h and at room temperature for 24 h. The solution was centrifuged from the precipitate of NaI, and the precipitate was once extracted with benzene (5 ml). The extracts were combined, all volatiles were removed in vacuum, and hexane (10 ml) was condensed. Complex **2b** was obtained as dark red large crystals (1.30 g, 90%) by slow concentration of the solution. ^{1}H NMR (400 MHz, C_6D_6, 296 K): δ 1.03 (d, 12H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 1.30 (s, 36H, *t*Bu), 1.32 (s, 12H, NMe$_2$-TMEDA), 1.48 (s, 4H, -CH$_2$-CH$_2$-TMEDA), 2.10-2.29 (m, 2H, C*H*(CH$_3$)$_2$), 2.65 (d, 4H, -CH$_2$-CH, $^3J_{HH}$ = 6.7 Hz), 7.09-7.29 (compl. m, 16H, CH-aryl). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 296 K): δ 23.2 (s, CH(*C*H$_3$)$_2$), 28.5 (s, *C*H(CH$_3$)$_2$), 31.4 (s, C(*C*H$_3$)$_3$), 33.6 (s, *C*(CH$_3$)$_3$), 43.6 (s, -*C*H$_2$CH), 45.6 (s, N(CH$_3$)$_2$), 56.7 (s, -CH$_2$CH$_2$-), 71.2 (s, C), 119.4 (s, *o*-CH), 127.5 (s, *m*-CH), 137.1 (s, *ipso*-C), 144.8 (s, *ipso*-C). IR (KBr): 1592(s), 1493(s), 1358(m), 1330 (s), 1300(w), 1266 (m), 1231 (w), 1186 (s), 1126 (w), 1092 (m), 1021 (m), 996 (w), 950 (m), 838(m), 814 (s), 791 (m), 571 (s), 543 (m). Anal. Calcd for $C_{56}H_{86}N_2Yb$ (960.30 g/mol): C 70.04; H 9.03; N 2.92; Yb 18.01. Found: C 70.13; H 9.07; N 2.89; Yb 17.91.

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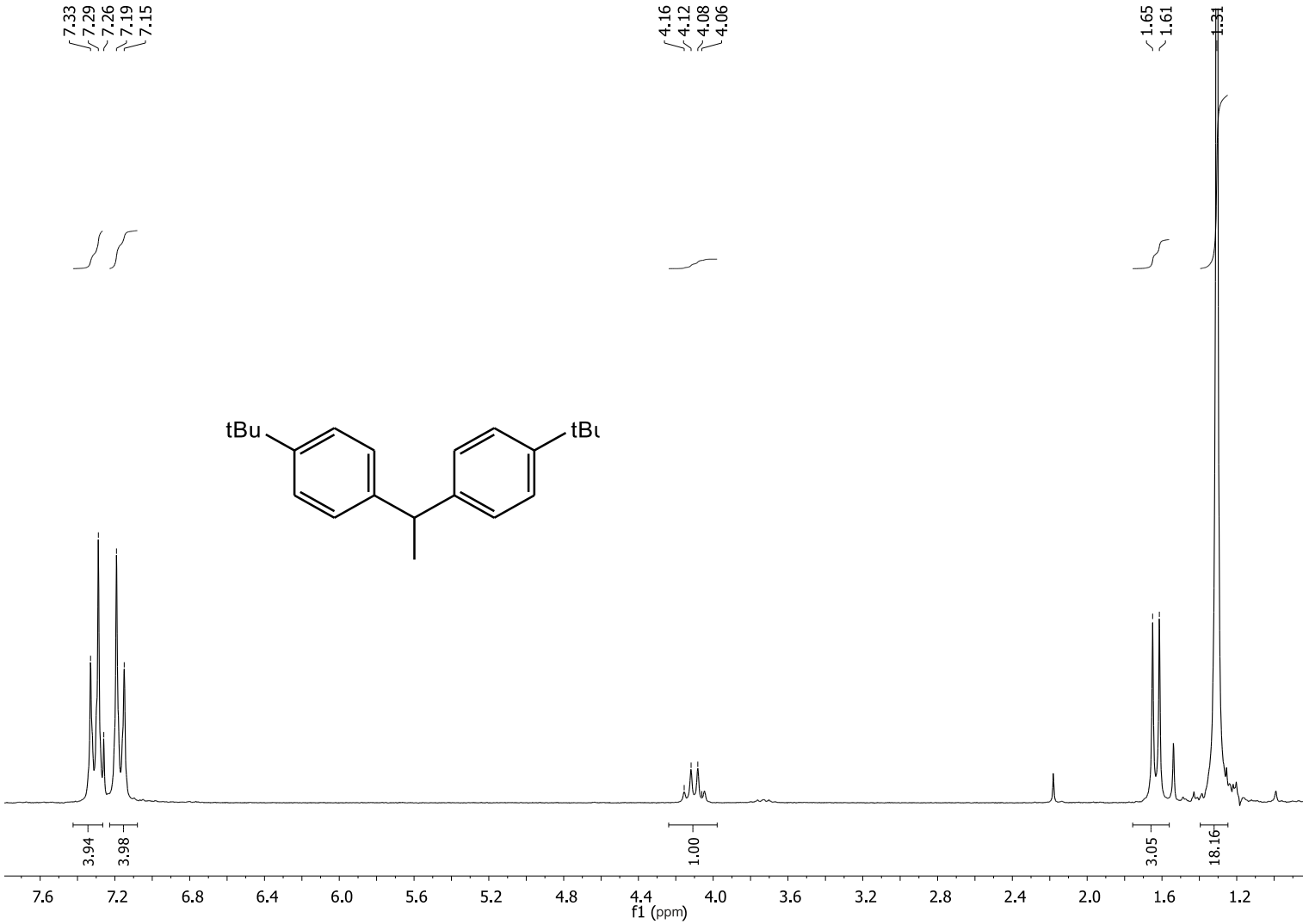

Figure S1. ^{1}H NMR spectrum of **(4-Bu^{t}C$_6$H$_4$)$_2$CHMe (1a)**. (200 MHz, $CDCl_3$, 293 K).

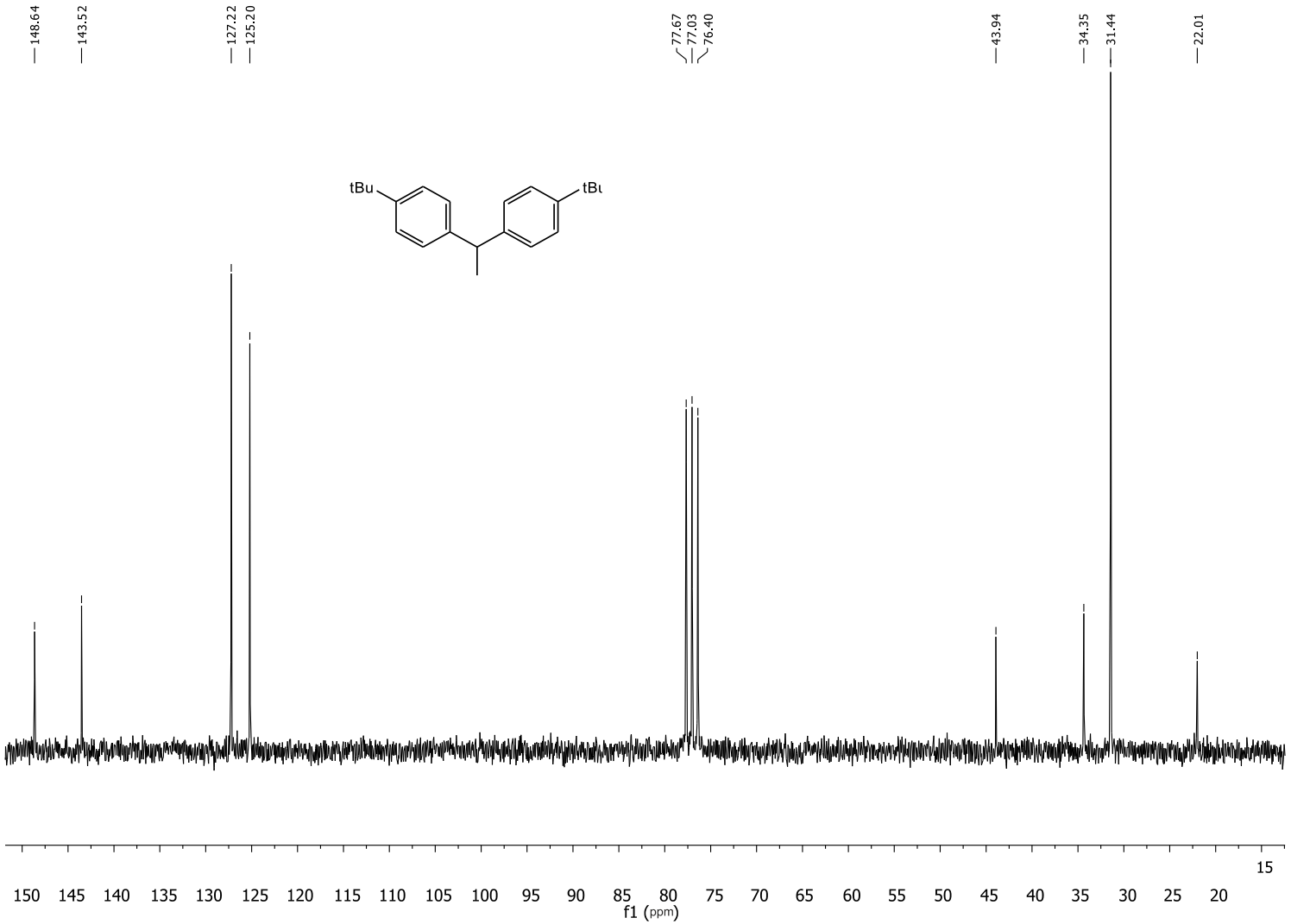

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **(4-Bu^{t}C$_6$H$_4$)$_2$CHMe (1a)**. (50 MHz, $CDCl_3$, 293 K).

Figure S3. ^{1}H NMR spectrum of **(4-Bu^{t}C$_6$H$_4$)$_2$CHBu^{i} (1b)**. (300 MHz, $CDCl_3$, 296 K).

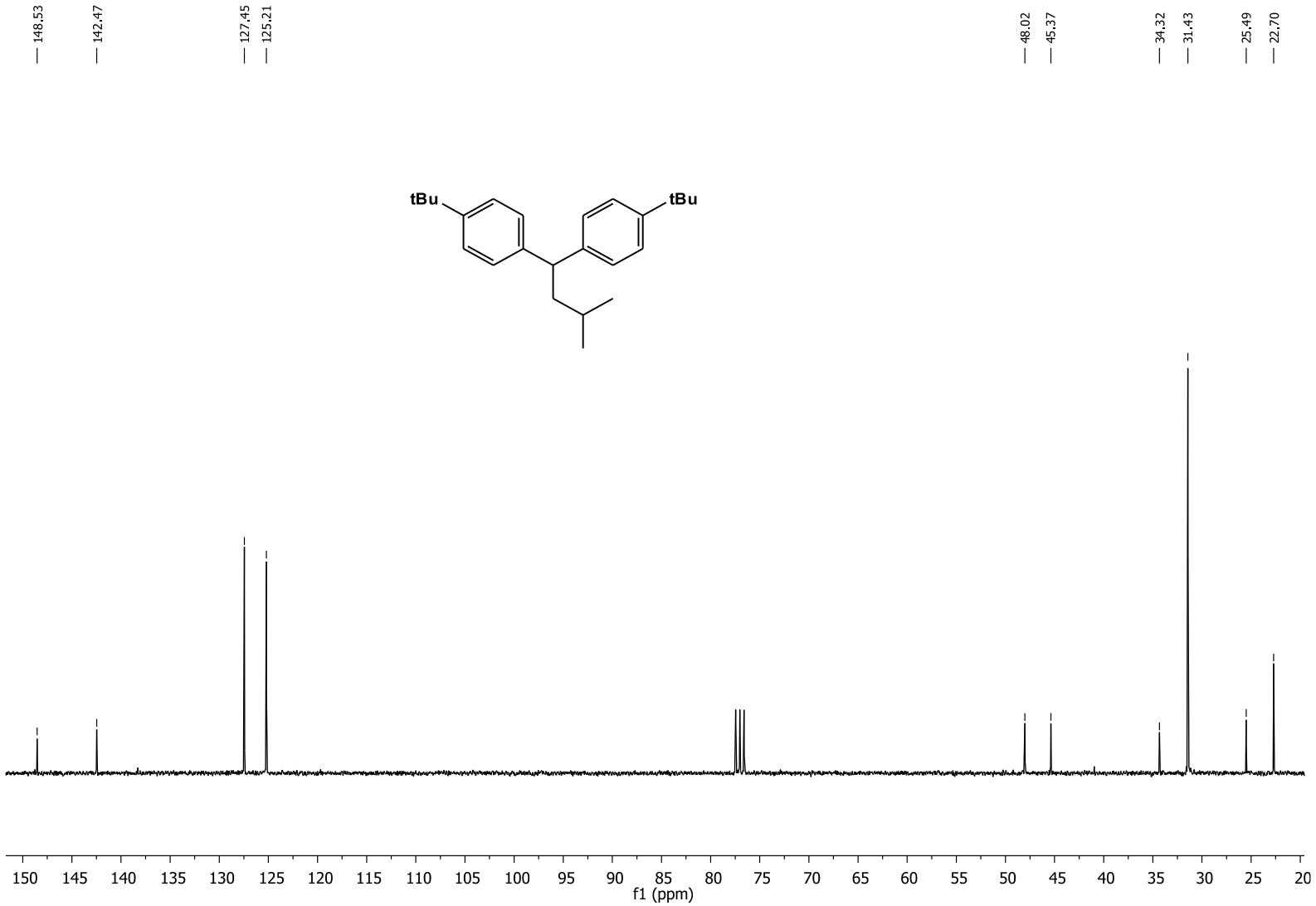

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **(4-Bu^{t}C$_6$H$_4$)$_2$CHBu^{i} (1b)**. (75 MHz, $CDCl_3$, 296 K).

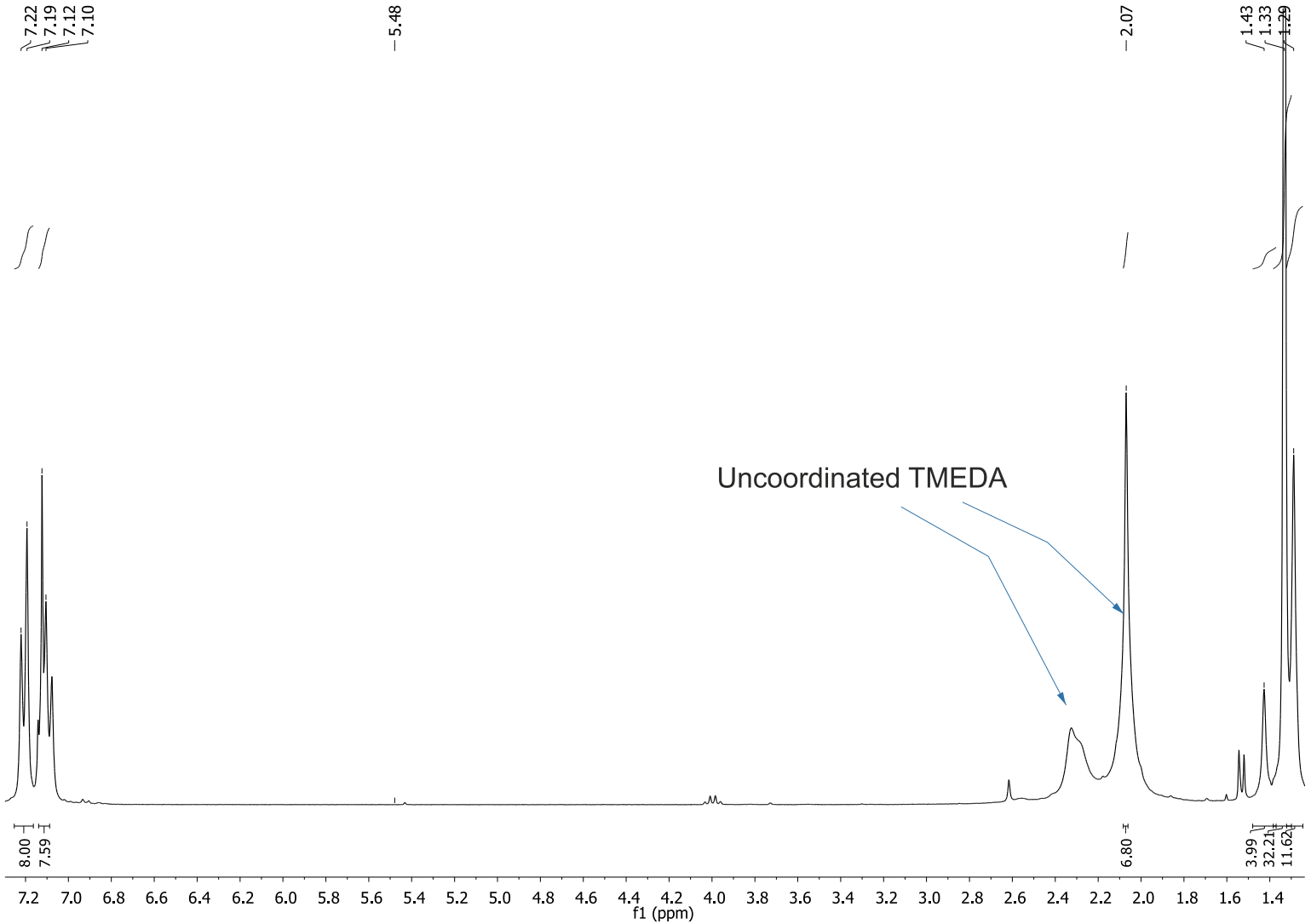

Figure S5. ^{1}H NMR spectrum of **[(4-Bu^{t}C$_6$H$_4$)$_2$CMe]$_2$Ca(TMEDA) (2a)**. (300 MHz, C_6D_6, 296 K).

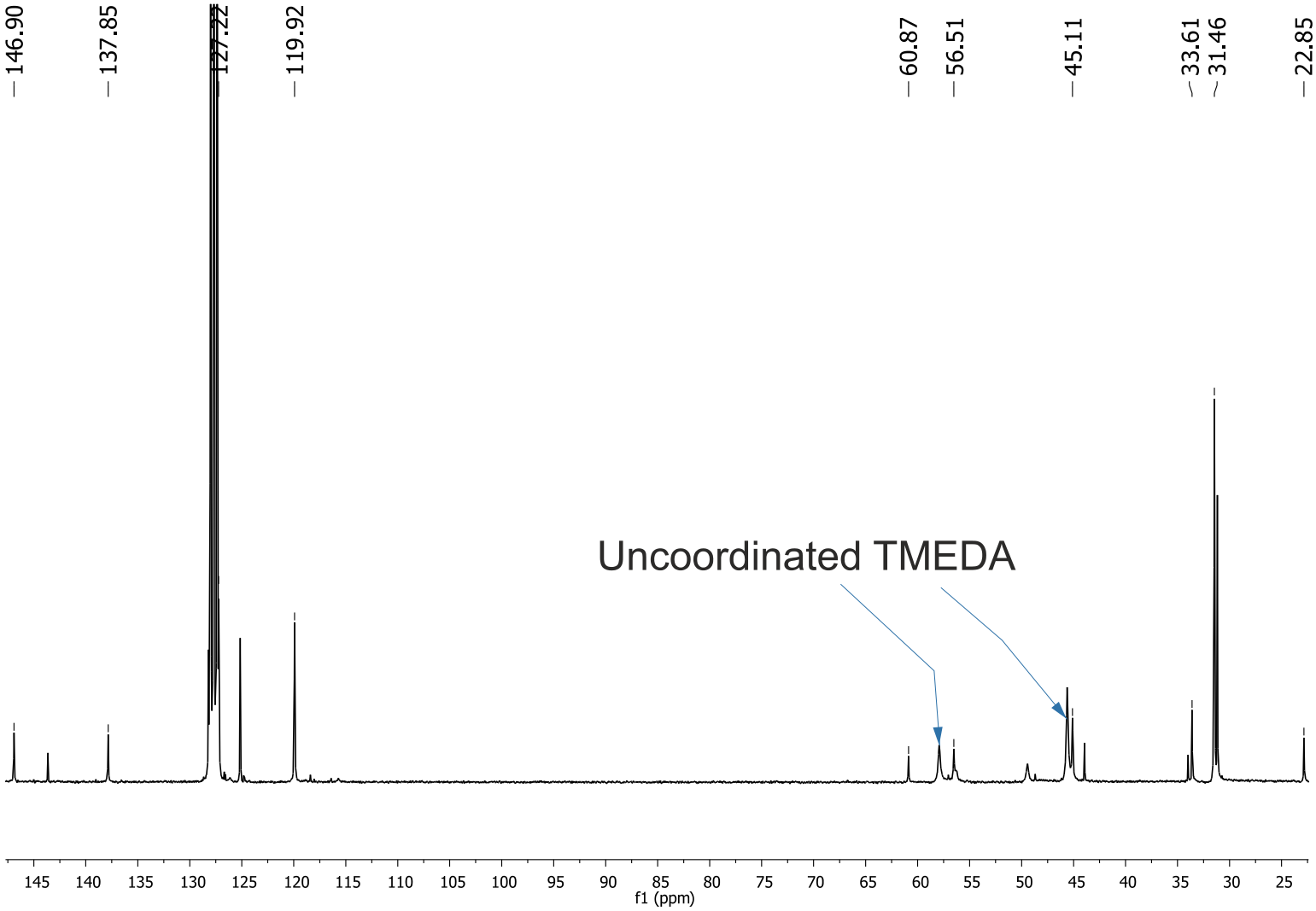

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **[(4-Bu^{t}C$_6$H$_4$)$_2$CMe]$_2$Ca(TMEDA) (2a)**. (75 MHz, C_6D_6, 296 K).

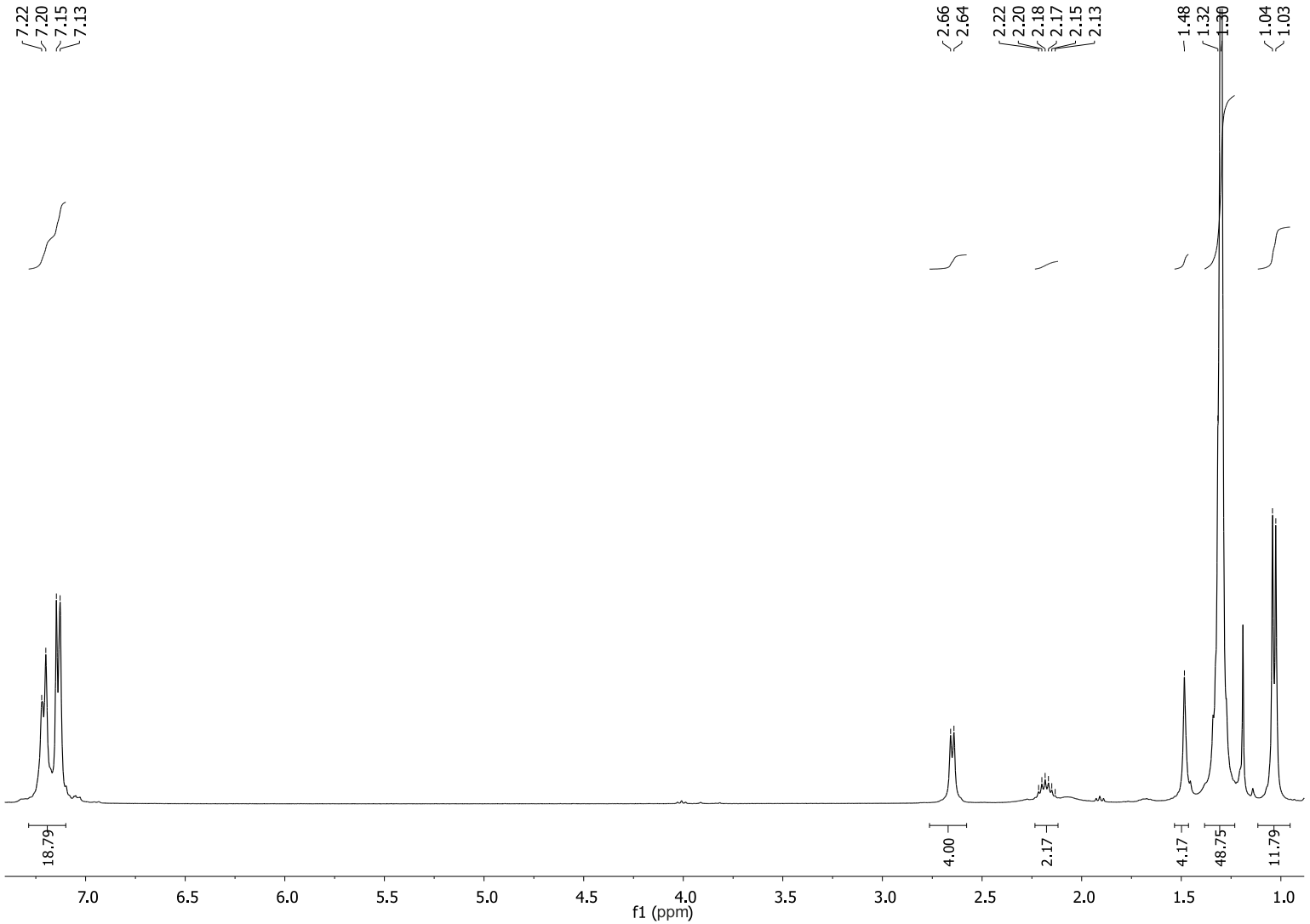

Figure S7. ^{1}H NMR spectrum of **[(4-Bu^{t}C$_6$H$_4$)$_2$CBu^{i}]$_2$Yb(TMEDA) (2b)**. (400 MHz, C_6D_6, 296 K).

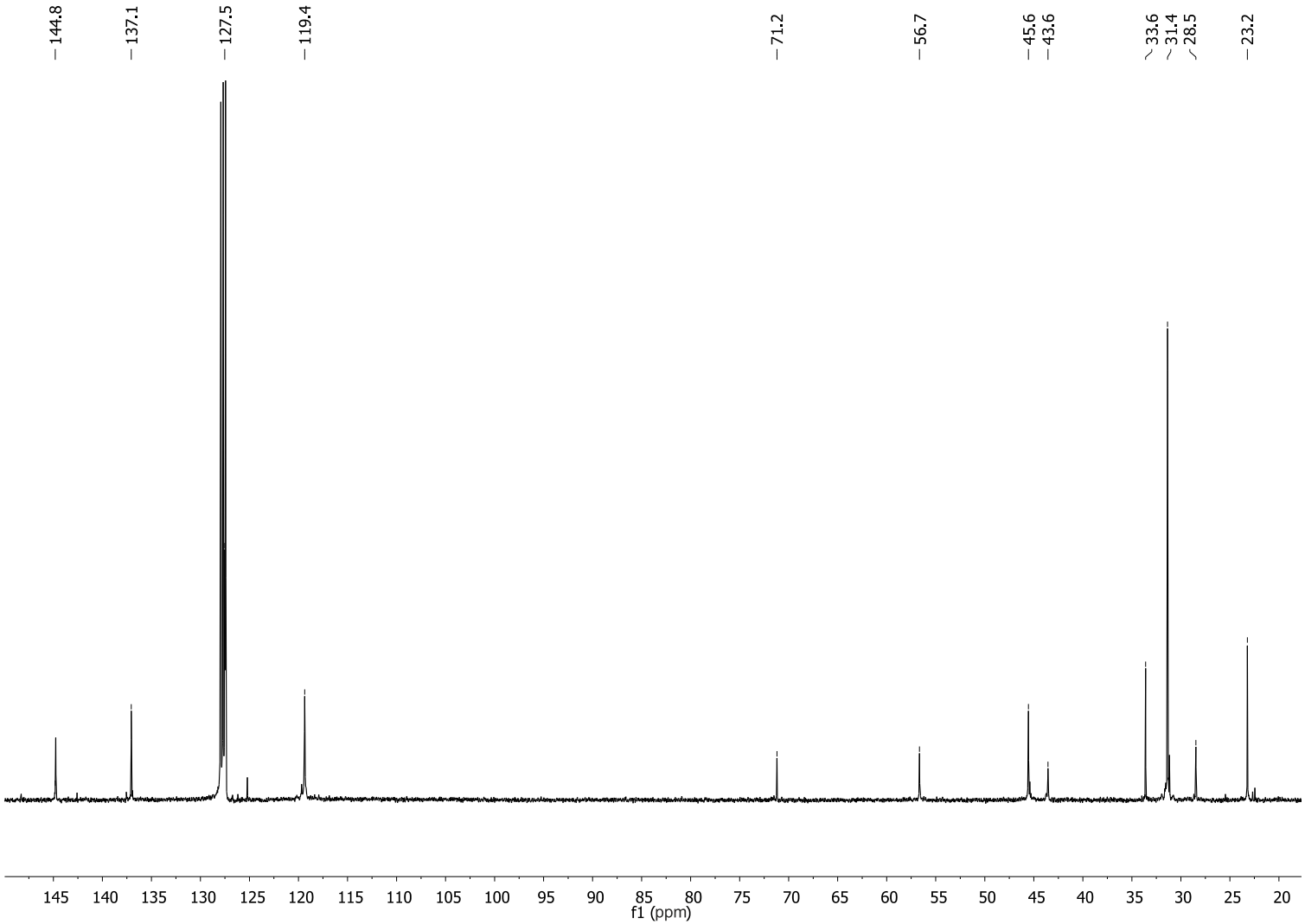

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **[(4-Bu^{t}C$_6$H$_4$)$_2$CBu^{i}]$_2$Yb(TMEDA) (2b)**. (100 MHz, C_6D_6, 296 K).

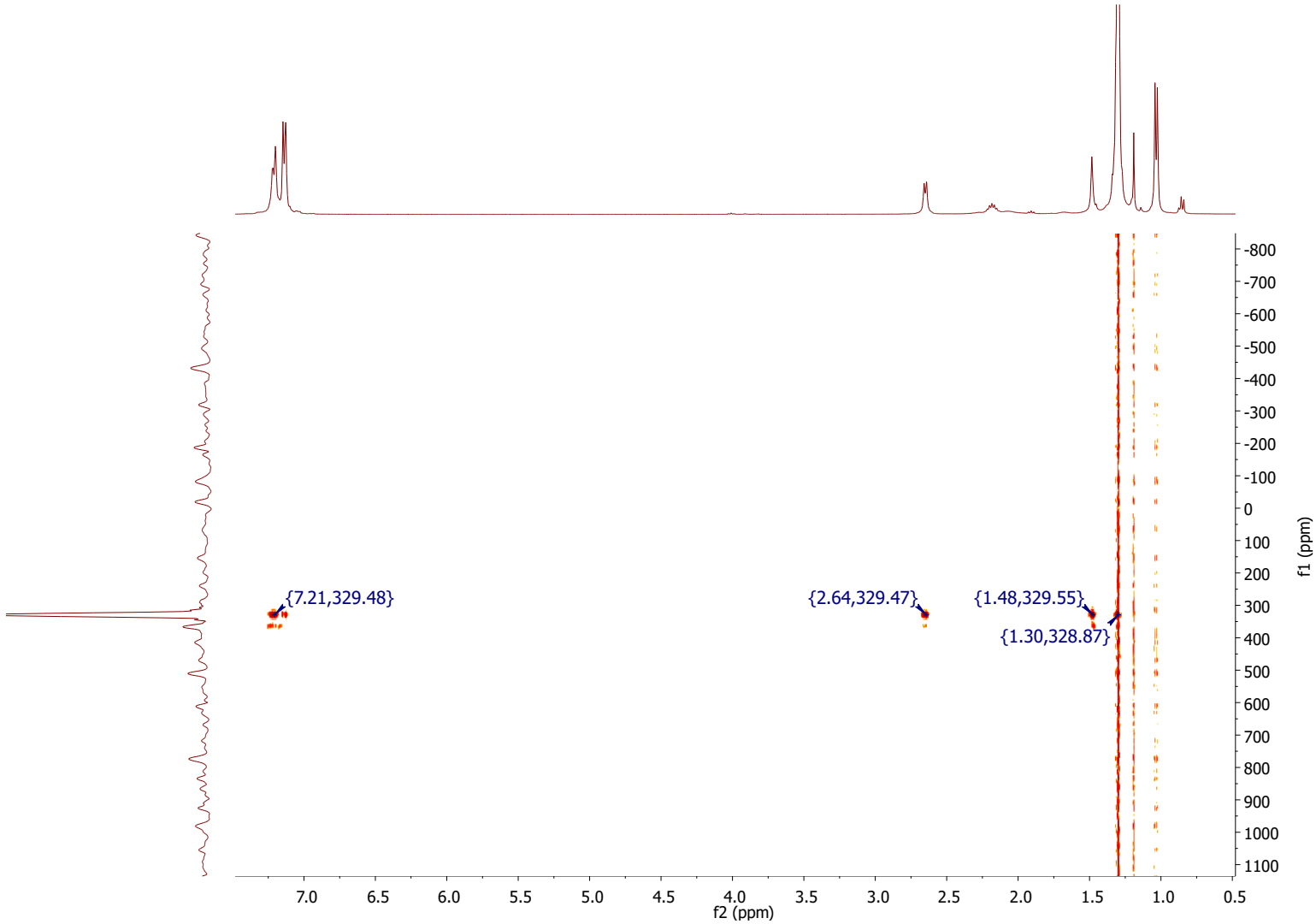

Figure S9. ^{171}Yb-^{1}H 2D *ge*-HMBC NMR spectrum of **[(4-Bu^{t}C$_6$H$_4$)$_2$CBu^{i}]$_2$Yb(TMEDA) (2b)**. (400 MHz, C_6D_6, 296 K).

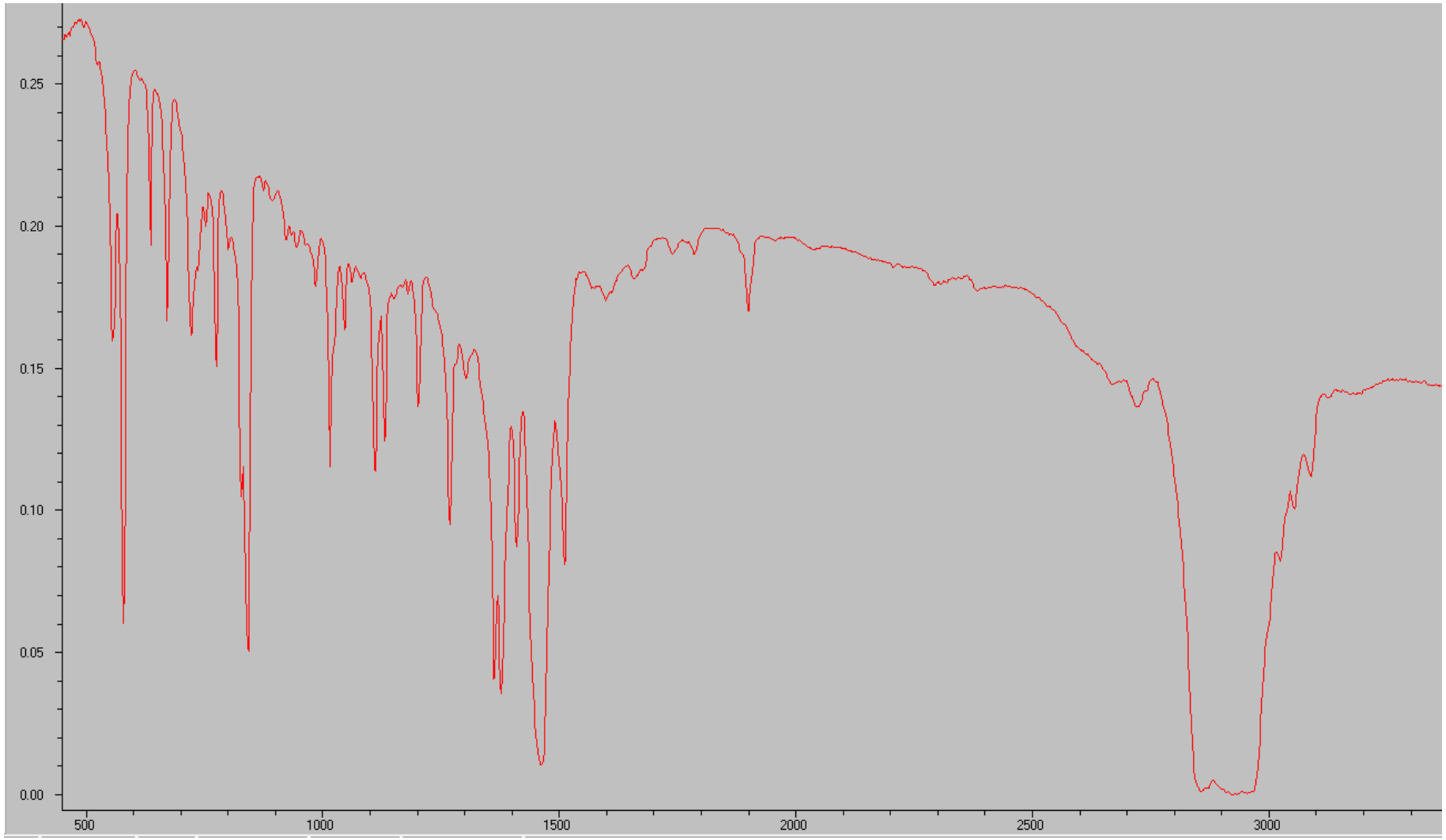

Figure S10. IR (KBr) spectrum of **(4-Bu^{t}C$_6$H$_4$)$_2$CHMe (1a)**.

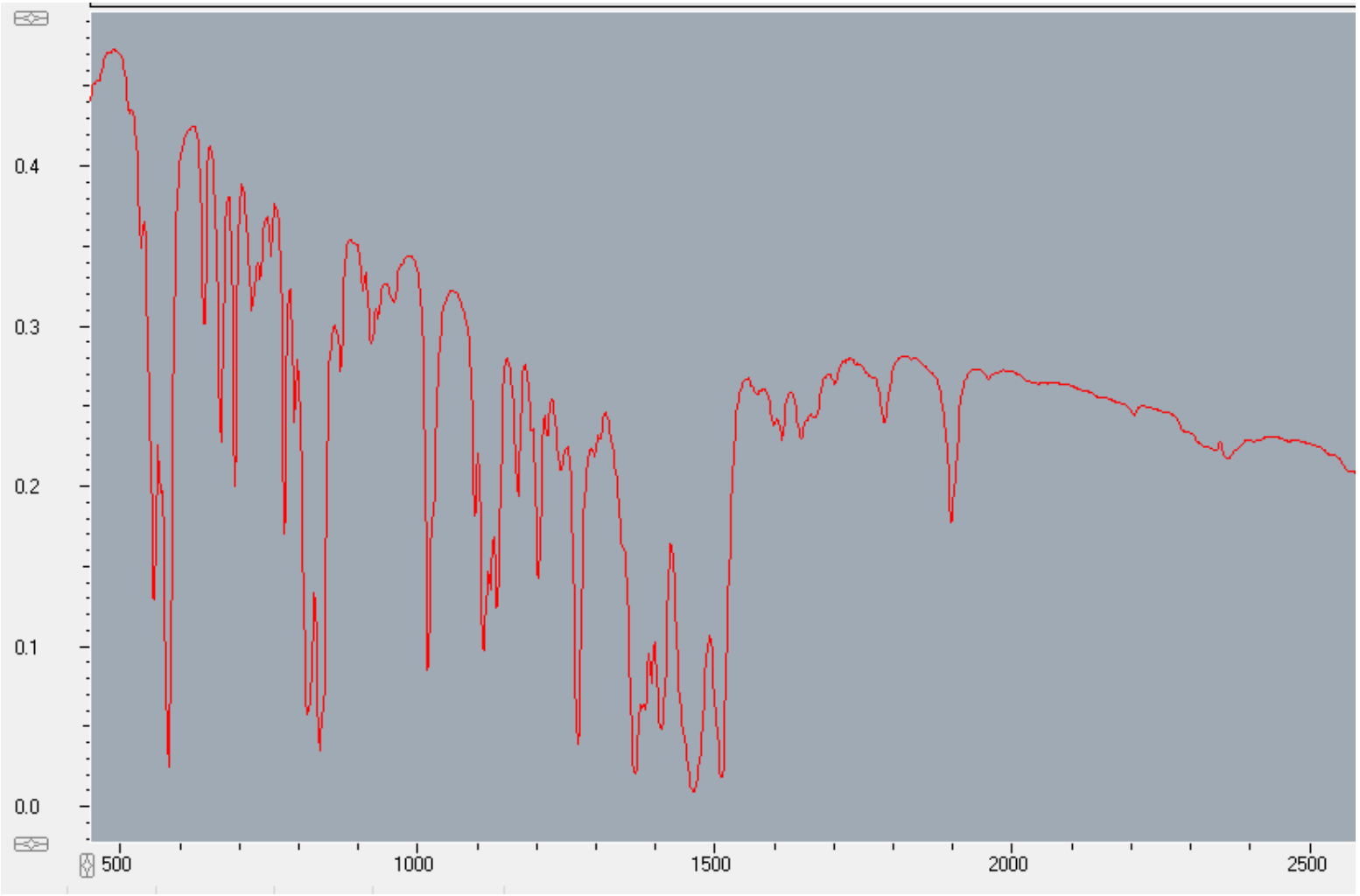

Figure S11. IR (KBr) spectrum of **(4-Bu^{t}C$_6$H$_4$)$_2$CHBu^i (1b)**.

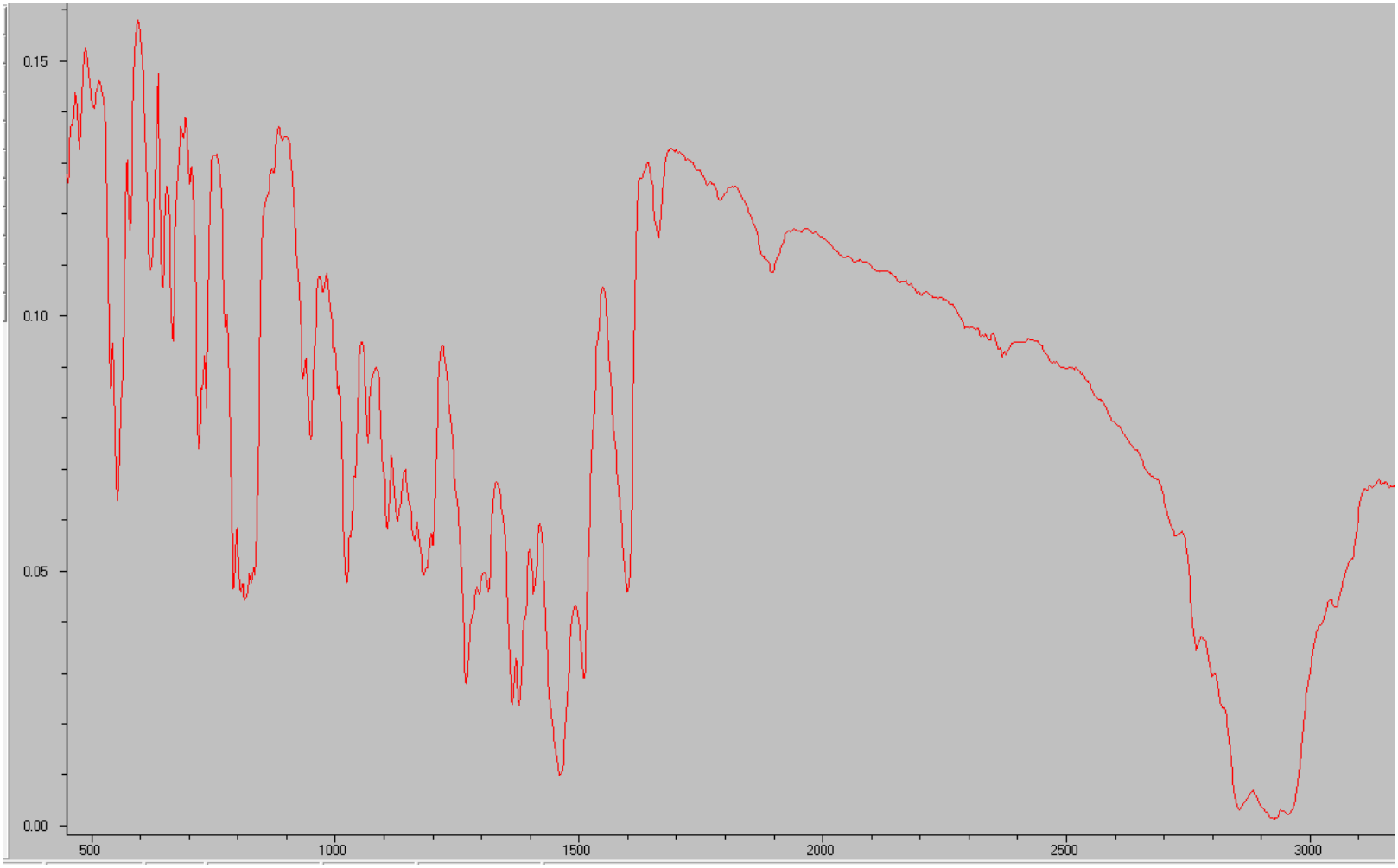

Figure S12. IR (KBr) spectrum of **[(4-Bu^{t}C$_6$H$_4$)$_2$CMe]$_2$Ca(TMEDA) (2a)**.

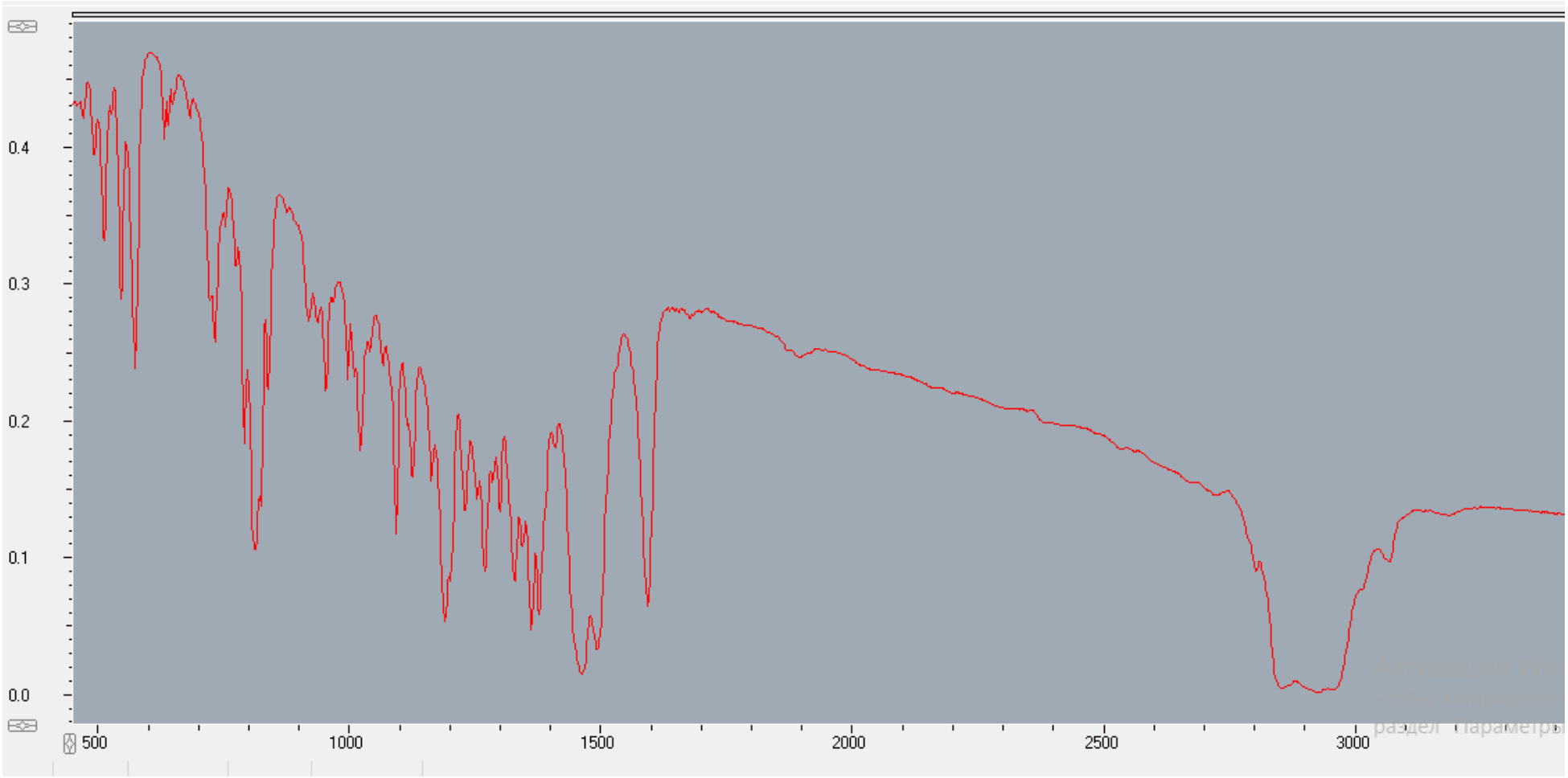

Figure S13. IR (KBr) spectrum of **[(4-Bu^{t}C$_6$H$_4$)$_2$CBu^i]$_2$Yb(TMEDA) (2b)**.