Electronic Supplementary Material (ESI) for Chemical Communications

Sterically demanding imidazolinium salts through the activation and cyclization of formamides

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SUPPORTING INFORMATION

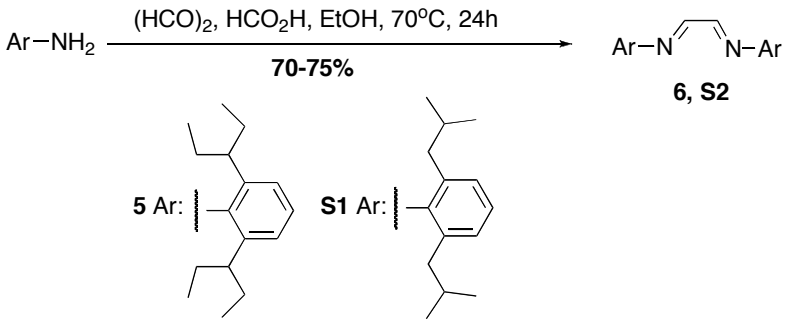
General experimental

All air sensitive reactions were carried out under an atmosphere of argon using Schlenk techniques. Glovebox manipulations were performed in an MBraun Unilab glove-box under an atmosphere of dry argon. All solvents were purchased from either Fischer Scientific or Sigma Aldrich. $CDCl_3$ was purchased from Sigma Aldrich. THF and Et_2O were dried under argon over sodium-benzophenone; toluene and dichloromethane were dried under argon over CaH_2. All reagents were purchased from commercial sources and were used without further purification, unless indicated otherwise. Thin layer chromatography (TLC) was performed on Whattman 60 F254 glass plates and were visualized using UV light (254 nm). Sonication was performed using a Fisher Bioblock Scientific Sonicator operating at 35 kHz. Column chromatography purifications were carried out using the flash technique on Silicycle silica gel 60 (230-400 mesh) or using a Biotage Isolera™ version 1.2.1. Gas chromatography was performed on Agilent (formerly Varian) Series GC/MS/MS 4000 System. Microwave reactions were conducted in a Biotage Initiator microwave operating at 2.45 GHz, with a maximal power setting of 400 W. NMR spectra were recorded on Bruker 600, 400 and 300 MHz AV spectrometers. The chemical shifts (δ) for ^1H spectra are given in ppm and are referenced to the residual proton signal of the deuterated solvent. The chemical shifts (δ) for ^{13}C spectra are referenced relative to the signal from the carbon of the deuterated solvent. ^{13}C JMOD spectra represent a positive set of peaks (indicated by (+)) for quaternary carbons as well as carbon atoms attached to an even number of protons and a negative set of peaks (indicated by (-)) for carbon atoms attached to an odd number of protons. Abbreviations used to define multiplicies are as follows: s = singlet; d = doublet; t =

triplet; q = quartet; p = pentet, sept = septet, m = multiplet; br = broad. Elemental analyses were performed by Chemisar Laboratories, Inc. in Guelph, Ontario. HRMS analyses were performed by the McMaster Regional Centre for Mass Spectrometry in Hamilton, Ontario and by the Queen's Mass Spectrometry Facility at Queen's University in Kingston, Ontario. Melting points were acquired using a Fisher-Johns melting point apparatus. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer 341 MC digital polarimeter with a 10 cm cell (c given in g per 100 mL) and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

Synthetic procedures

All glassware was flame dried and cooled under argon before use. Standard Schlenk techniques were employed for air sensitive reagents. Anilines **5** and S**1** were donated by Total Synthesis Ltd. Acetic formic anhydride was prepared according to literature procedures.[1] Compound **20**, was prepared according to literature procedures using the acetic formic anhydride formylation procedure.[2] Compound **S5**, was prepared according to literature procedures.[3]



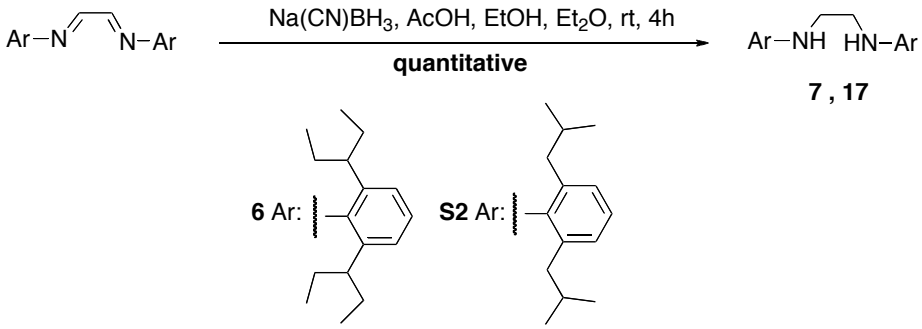
*General procedure for the preparation of bis imines **6** and **S2**:* A round bottom flask containing a stir bar was charged with the corresponding aniline (1 equiv.), EtOH (1 M in aniline) and glyoxal in H_2O 40% w/w (0.5 equiv.) producing a bright-yellow solution.

Formic acid (0.12 equiv.) was added, the flask was fitted with a reflux condensor and the reaction was heated at 70ºC for 24 h. At this time the reaction was brown and contained a dark-orange solid. After cooling to rt and removing the solvent *in vacuo*, methanol (1 mL per mmol aniline) was added to the resulting thick oil/crystals and the solution was again concentrated *in vacuo*. The procedure was repeated once more and the solid material was sonicated in solution of methanol and water 10:1) (0.5 mL of solution per mmol aniline) solution until bright-yellow crystals could be isolated. The crystals were collected in a medium porosity fritted funnel and washed with a small amount of cold methanol and then dried under vacuum.

(*E*)-N-((*E*)-2-(2,6-di(pentan-3-yl)phenylimino)ethylidene)-2,6-di(pentan-3-yl)benzenamine (6): Using the general procedure aniline **5** (10.7 mmol, 2.5 g) provided compound **6** as yellow needles (1.98 g, 75%). M.p. = 57-60ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (s, 2H), 7.25-7.05 (m, 6H), 2.52 (p, J = 6.3 Hz, 4H), 1.80-1.45 (m, 16H), 0.82 (t, J = 7.5 Hz, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9, 150.9, 133.8, 124.8, 123.9, 42.5, 28.9, 12.2. HRMS *m/e* calcd. for $C_{34}H_{52}N_2$ (M^+) 488.4122, found 488.4131.

(*E*)-N-((*E*)-2-(2,6-diisobutylphenylimino)ethylidene)-2,6-diisobutylbenzenamine (S2): Using the general procedure aniline S**1** (2.5 mmol, 510 mg) provided compound **S2** as yellow needles (376 mg, 70%). M.p. = 76-78ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 2H), 7.07 (m, 6H), 2.41 (d, J = 7.2 Hz, 8H), 1.82 (sept, J = 6.4 Hz, 4H), 0.90 (d, J = 6.4 Hz, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.4, 150.0, 129.7, 128.3, 124.1, 40.9,

29.0, 22.6. Anal. Calcd. For $C_{30}H_{44}N_2$: C, 83.28; H, 10.25; N, 6.47. Found: C, 83.58; H, 10.52; N, 6.49.

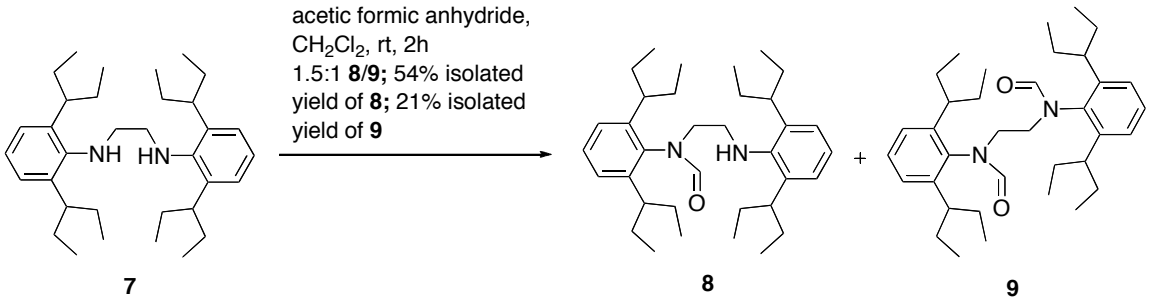


*General procedure for preparation of bis-amines **7** and **17**:* To a round bottom flask equipped with a stir bar was added bis-imine (1 equiv.), and $Na(CN)BH_3$ (2 Equiv.) after which the flask was fitted with a reflux condensor. EtOH (0.07 M in bis-imine), Et_2O (0.14 M in bis-imine), and AcOH (0.7 M in bis-imine) were then added, producing a nearly clear, yellow solution. After stirring at room temperature for 4 h, the yellow color abated. The solution was concentrated *in vacuo* and the residue was then dissolved in DCM (20 mL / mmol bis-imine) and then transferred to a separatory funnel. The organic layer was washed successively with equal volumes of 1 M $NaOH_{(aq)}$, water, and saturated $NaCl_{(aq)}$ after which it was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give the bis-amine as a pale yellow oil and required no further purification.

N-(2-(2,6-di(pentan-3-yl)phenylamino)ethyl)-2,6-di(pentan-3-yl)benzenamine (7): Using the general procedure, 1.50 g of bis-imine **6** provided 1.51 g (>99%) of **7** as a pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 (t, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 4H), 3.32 (br, 2H), 3.03 (s, 4H), 2.95 (p, J = 7.2 Hz, 4H), 1.85-1.65 (m, 8H), 1.65-1.45

(m, 8H), 0.83 (t, J = 7.2 Hz, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.4, 140.2, 123.9, 123.6, 52.0, 41.9, 29.6, 12.3. HRMS *m/e* calcd. for $C_{34}H_{56}N_2$ (M^+) 492.4443, found 492.4436.

N-(2-(2,6-diisobutylphenylamino)ethyl)-2,6-diisobutylbenzenamine (17): Using the general procedure, 0.38 g of **S2** produced 0.38 g (>99%) of **17** as a pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (d, J = 7.2 Hz, 4H), 7.01 (t, J = 7.2 Hz, 2H), 3.43 (br, 2H), 3.22 (s, 4H), 2.65 (d, J = 7.5 Hz, 8H), 2.06 (m, 4H), 1.03 (d, J = 6.6 Hz, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 134.7, 128.5, 122.3, 50.7, 41.0, 29.5, 22.7. HRMS *m/e* calcd. for $C_{30}H_{48}N_2$ (M^+) 436.3817, found 436.3805.



7 **8** **9**

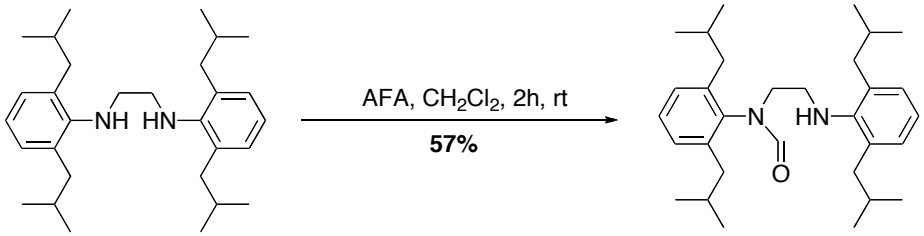
N-(2,6-di(pentan-3-yl)phenyl)-N-(2-(2,6-di(pentan-3-yl)phenylamino)ethyl) formamide (8): *Orthoformate procedure:* To a microwave vial equipped with a stir bar, was added a solution of **7** (0.51 mmol, 250 mg) in dioxane (670 μL), $HC(OEt)_3$ (0.51 mmol, 86 μL) and 4 M HCl in dioxane (0.31 mmol, 76 μL). The reaction was heated at

140ºC for 45 min using microwave irradiation. After cooling to rt, the solution was diluted with an equal volume of CH_2Cl_2, loaded onto silica and flashed. Compound **8** (109 mg, 41%) (R_f = 0.3 in 1:9 Et_2O/pentane) was collected as a beige solid. M.p = 61-63°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 8.4, 6.6 Hz, 1H), 6.94 (d, *J* = 6.6 Hz, 2H), 3.80 (t, *J* = 7.5 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.81 (m, 2H), 2.55 (m, 2H), 1.78-1.60 (8H), 1.60-1.35 (8H), 0.83 (t, *J* = 7.5 Hz, 6H), 0.78-0.65 (18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 145.9, 145.0, 140.0, 138.8, 129.1, 124.7, 123.9, 123.6, 49.5, 48.9, 42.1, 41.7, 29.5, 29.0, 12.3, 12.1. HRMS *m/e* calcd. for $C_{35}H_{56}N_2O$ (M^+) 520.4381, found 520.4393.

Acetic Formic Anhydride (AFA) procedure: A round bottom flask with a stir bar was charged with **7** (2.84 mmol, 1.47 g), CH_2Cl_2 (7.2 mL) and acetic formic anhydride (4.36 mmol, 320 μL). The reaction was stirred under argon for 2 h at rt and then transferred to a separatory funnel, diluted with CH_2Cl_2 (60 mL), and washed successively with saturated $NaHCO_{3(aq)}$ (50 mL), water (50 mL), and saturated $NaCl_{(aq)}$, after which it was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography (gradient: 1:9 Et_2O/pentane to 1:5 Et_2O/pentane). Compound **8** (796 mg, 54%) was collected as a beige solid with spectra identical to those reported above.

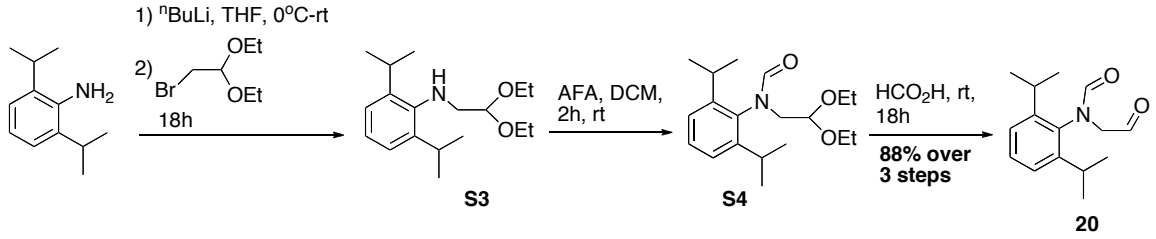
N-(2,6-di(pentan-3-yl)phenyl)-N-(2-(N-(2,6-di(pentan-3-yl)phenyl)-N-(formyl)ethyl) formamide (9): Using the AFA procedure 330 mg (21%) of compound **9** were collected

as a beige solid (R_f = 0.4 in 1:5 Et_2O/pentane). M.p. = 210-214ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 4H), 3.90 (s, 4H), 2.50 (p, *J* = 7.0 Hz, 4H), 1.75-1.6 (12H), 1.50-1.35 (4H), 0.88 (t, *J* = 6.8 Hz, 12H), 0.71 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 145.0, 138.7, 129.1, 124.8, 45.5, 42.4, 29.3, 28.8, 12.4, 12.2. HRMS *m/e* calcd. for $C_{36}H_{56}N_2O_2$ (M^+) 548.4342, found 548.4329.

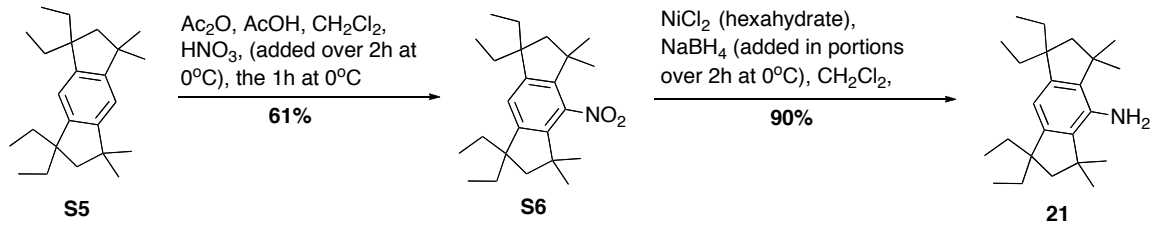


17 **18**

N-(2,6-diisobutylphenyl)-N-(2-(2,6-diisobutylphenylamino)ethyl)formamide (18): Using the AFA procedure, 380 mg of **17** provided 229 mg of **18** (57%) as a beige solid (R_f = 0.3 in 1:9 Et_2O/pentane). M.p. 49-52°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 3.82 (t, *J* = 7.6 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.42 (m, 8H), 1.90 (m, 4H), 0.94 (d, *J* = 6.4 Hz, 6H). 0.91-0.85 (18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 145.8, 140.4, 138.4, 133.3, 128.5, 128.4, 128.2, 121.5, 48.5, 47.5, 41.1, 40.2, 29.4, 28.9, 22.6, 22.5. HRMS *m/e* calcd. for $C_{31}H_{48}N_2O$ (M^+) 464.3767, found 464.3779.



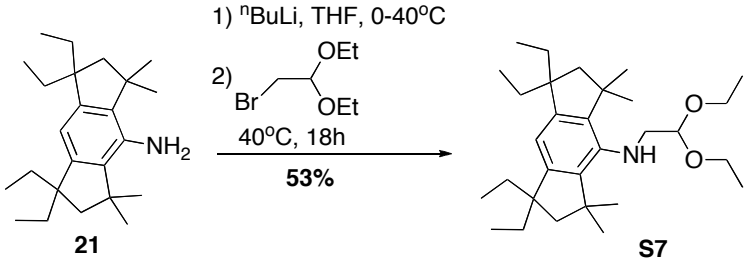
N-(2,6-diisopropylphenyl)-N-(2-oxoethyl)formamide (20): Prepared according to literature procedure.[3] Spectral data of the light brown solid were identical to reported values. M.p. 65-72ºC (reported M.p. 83-84ºC).



1,1,7,7-Tetraethyl-1,2,3,5,6,7-hexahydro-3,3,5,5-tetramethyl-4-nitro-*s*-indacene (EMindNO_2) (S6): To a mixture of 1,1,7,7-tetraethyl-1,2,3,5,6,7-hexahydro-3,3,5,5-tetramethyl-*s*-indacene (EMindH (**S5**),[3] 24.5 g, 75 mmol), 1,2-dichloromethane (300 mL), acetic anhydride (200 mL), and acetic acid (150 mL) was added fuming nitric acid (30 mL) at 0 °C over a period of 2 h. The mixture was stirred for an additional hour at 0 °C, and then water (300 mL) and dichloromethane (200 mL) were added. The organic layer was separated, and washed successively with water (200 mL × 3), aqueous sodium carbonate (200 mL), and brine (200 mL). After drying over anhydrous magnesium sulfate, the crude material was filtered and evaporated. The residue was washed with hexane (100 mL) to afford EMindNO_2 as a colorless solid (first crop, 15.0 g, 54%). Evaporation of the rinse solution and washing of the resulting solid with hexane (70 mL)

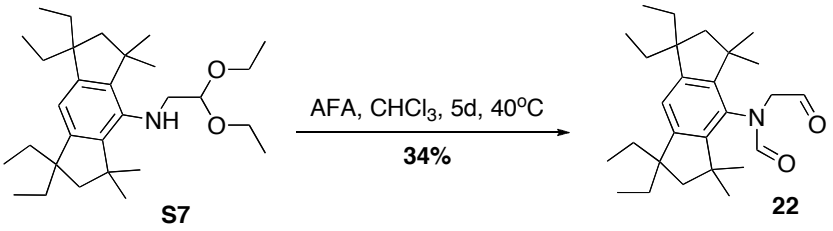
afforded a second crop of crystals as a colorless solid (second crop, 1.84 g, 7%). M.p. 120 °C (sublimation), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 1.91 (s, 4H), 1.71–1.54 (m, 8H), 1.32 (s, 12H), 0.79 (t, J = 7.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 145.4, 138.8, 121.5, 53.0, 48.5, 43.0, 32.4, 30.0, 9.0; HRMS (EI) Calcd for $C_{24}H_{37}NO_2$: 371.2824. Found: 371.2829.

4-Amino-1,1,7,7-tetraethyl-1,2,3,5,6,7-hexahydro-3,3,5,5-tetramethyl-*s*-indacene (EMindNH$_2$) (21): To a vigorously stirred mixture of EMindNO$_2$ (**S6**) (16.0 g, 43.1 mmol), CH_2Cl_2 (250 mL), MeOH (125 mL), and nickel(II) chloride hexahydrate (2.04 g, 8.6 mmol) was added sodium borohydride (7.50 g, 198 mmol) portionwise over a period of 2 h at 0 °C. The mixture was stirred for an additional hour and then filtered through a plug of Celite®. The organic layer was separated, and washed successively with water (100 mL × 2) and brine, and dried over anhydrous sodium sulfate. After filtration the solvent was removed *in vacuo* and the residue was loaded atop a short silica gel column and flashed using dichloromethane:hexane (1:3, v/v) as eluent affording the pure EMindNH$_2$ (13.2 g, 38.5 mmol, 90 %) as a colorless solid. M.p. 92–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 1H), 3.62 (br, 2H, NH_2), 1.86 (s, 4H), 1.65–1.49 (m, 8H), 1.44 (s, 12H), 0.79 (t, J = 7.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 138.9, 133.3, 109.9, 53.1, 48.9, 42.1, 33.0, 29.4, 9.2. HRMS (EI) Calcd for $C_{24}H_{39}N$: 341.3083. Found: 341.3091. Anal. Calcd for $C_{24}H_{39}N$: C, 84.39; H, 11.51; N, 4.10. Found: C, 84.14; H, 11.67; N, 4.01.



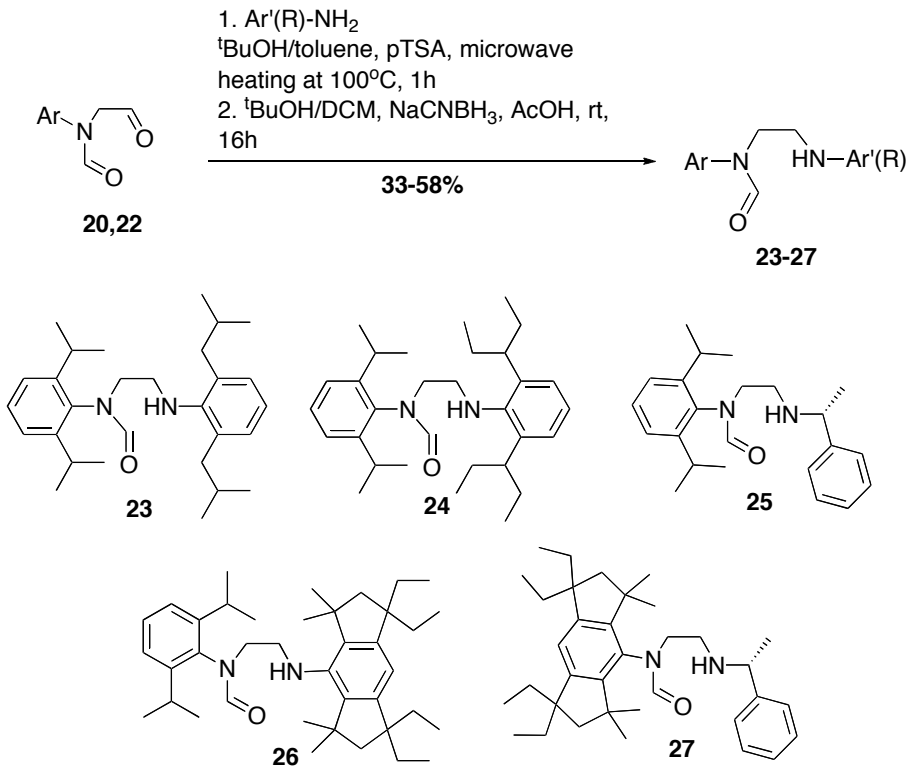
N-(2,2-diethoxyethyl)-1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-1,2,3,5,6,7-hexahydros-indacen-4-amine (S7): A round bottom flask equipped with a stir bar and fitted with a reflux condenser was charged with the EMind aniline (**21**) (3.5 mmol, 1.2 g) and THF (0.5M). ^{n}BuLi in hexanes (3.9 mmol, 3.4 mL based on 1.15 M titre value) was added drop-wise to the reaction during which the yellow solution slightly intensifies. After stirred for 2h at room temperature and the 1h at 40°C bromoacetaldehyde diethyl acetal (3.9 mmol, 590 μL) was added quickly and the mixture was stirred at 40°C for 18h. The solution was concentrated under reduced pressure, the residue redissolved in DCM (~5 mL/mmol aniline) and then it was washed with an equal volume of saturated $NaHCO_{3\,(aq)}$. The aqueous layer was back extracted twice with about half the volume of DCM and the combined organic layers were washed successively with an equal volume of water, and saturated $NaCl_{(aq)}$. After drying over anhydrous Na_2SO_4 the mixture was concentrated *in vacuo* and the residue was purified using flash chromatography. Due to the very similar R_f values of the product and the EMind aniline up to 3 columns were required to obtain analytically pure material. Compound **S7** (848 mg, 53%) (99.5:0.5 hexanes/EtOAc, R_f = 0.2) was collected as a thick orange oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.39 (s, 1H), 4.71 (t, J = 6.0 Hz, 1H), 3.80 (m, 2H), 3.60 (m, 2H), 3.18 (d, J = 6.4 Hz, 2H), 1.84 (s, 4H), 1.70-1.50 (8H), 1.47 (s, 12H), 1.26 (t, J = 7.0 Hz, 6H), 0.79 (t, J = 7.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 143.2, 142.7, 114.9, 103.3,

63.1, 55.1, 53.8, 48.3, 43.1, 32.7, 31.3, 15.5, 9.1. HRMS *m/e* calcd. for $C_{30}H_{52}NO_2$ ($M+H^+$) 458.4002, found 458.3998.



S7 22

N-(2-oxoethyl)-N-(1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-1,2,3,5,6,7-hexahydros-indacen-4-yl)formamide (25): A round bottom flask equipped with a stir bar and fitted with a reflux condenser was charged with **S7** (0.87 mmol, 400 mg) and $CHCl_3$ (0.1M). AFA (5.22 mmol, 380 μL) was added and the reaction heated at 40°C for 5 days after which it was diluted with DCM (~5 mL/mmol aniline) and washed carefully with enough of a saturated $NaHCO_{3\,(aq)}$ to adjust the pH of the aqueous layer to approximately 8. The aqueous layer was back extracted twice with about half the volume of DCM and the combined organic layers were washed with an equal volume of water and saturated $NaCl_{(aq)}$. The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* and the residue was purified using flash chromatography providing **22** (122 mg, 34%) (93:7 hexanes/EtOAc, $R_f = 0.3$) as a white solid. M.p. = 134-137ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.22 (s, 1H), 6.78 (s, 1H), 4.13 (s, 2H), 1.89 (m, 4H), 1.75-1.45 (8H), 1.37 (s, 6H), 1.32 (s, 6H), 0.85 (t, $J = 4.5$ Hz, 6H), 0.76 (t, $J = 4.5$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 166.0, 151.0, 147.8, 133.1, 121.6, 59.3, 53.3, 48.3, 43.5, 33.0, 31.8, 31.6, 31.2, 9.1, 8.9. HRMS *m/e* calcd. for $C_{27}H_{41}NO_2$ (M^+) 648.3573, found 648.3557



*General procedure for preparation of unsymmetric formamides **23-27***: A microwave vial was charged with **20** or **22** (1 equiv.), pTSA•H_2O (0.1 equiv.) and the corresponding amine or aniline (1 equiv.) and then purged with argon. The vial was then charged with ^{t}BuOH/toluene, 10:1 (0.25 M in **20** or **22**), after which it was flushed with argon and quickly sealed. The vial was heated briefly with a heat gun and stirred as it cooled to rt to dissolve all the solids after which it was heated at 100ºC for 1 h using microwave irradiation whereupon a clear orange solution was observed. After being cooled to rt the reaction was probed by ^{1}H-NMR spectroscopy to ensure imine formation. The solution was transferred to a round bottom flask and $Na(CN)BH_3$ (1 equiv.) was added followed by CH_2Cl_2 (0.15 M) and AcOH (1.5 M). The cloudy light-orange reaction was stirred at rt for 16 h and then concentrated to dryness *in vacuo*. The residue was partitioned between CH_2Cl_2 and 1 M $NaOH_{(aq)}$ (30 mL of each per mmol of aldehyde). Prior to layer

separation the pH of the aqueous layer was verified to be 12. The organic layer was collected and the aqueous layer was extracted twice with half the volume of CH_2Cl_2. The pooled organic layers were washed with water, and saturated $NaCl_{(aq)}$ solution, after which they were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography.

***N*-(2-(2,6-diisobutylphenylamino)ethyl)-*N*-(2,6-diisopropylphenyl)formamide (23):** Using the general procedure, **20** (1.1 mmol, 272 mg) was reacted with 2,6-diisobutylaniline (1.1 mmol, 226 mg) to give 140 mg (33%) of **23** as a yellow solid. (R_f = 0.3 in 93:7 hexanes/EtOAc). M.p. = 118-122°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.85 (t, *J* = 7.8 Hz, 1H), 3.83 (t, *J* = 7.2 Hz, 2H), 3.38 (br, 1H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.99 (sept, *J* = 6.9 Hz, 2H), 2.44 (d, *J* = 7.5 Hz, 4H), 1.89 (sept, *J* = 6.9 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.14 (d, *J* = 6.6 Hz, 6H), 0.88 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.8, 147.6, 145.6, 135.3, 133.4, 129.5, 128.4, 124.5, 121.7, 48.6, 47.4, 41.1, 28.9, 28.2, 25.4, 23.5, 22.6. HRMS *m/e* calcd. for $C_{29}H_{44}N_2O$ (M^+) 436.3454, found 436.3461.

***N*-(2-(2,6-di(pentan-3-yl)phenylamino)ethyl)-*N*-(2,6-diisopropylphenyl)formamide (24):** Using the general procedure, **20** (2.42 mmol, 600 mg) was reacted with 2,6-di(3-pentyl)aniline (2.42 mmol, 566 mg) to give 647 mg (58%) of **24** as an off white solid. (R_f = 0.3 in 93:7 hexanes/EtOAc). M.p. = 95-99°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 2H), 3.91 (t, *J* = 7.5 Hz, 2H), 3.14 (br, 1H), 3.10-2.90 (4H), 2.77 (m, 2H), 1.66

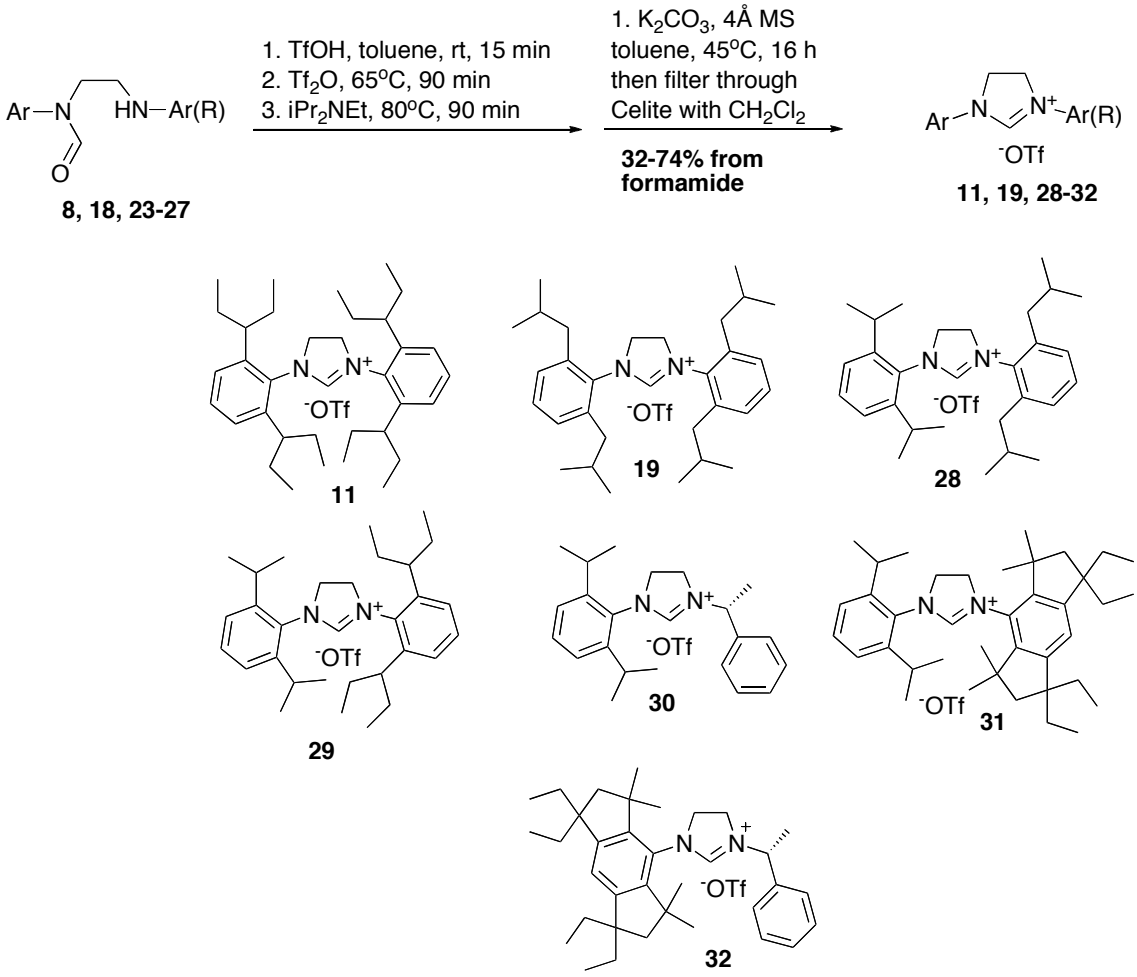
(m, 4H), 1.49 (m, 4H), 1.23 (d, J = 6.9 Hz, 6H), 1.16 (d, J = 6.9 Hz, 6H), 0.71 (t, J = 7.2 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7, 147.5, 146.1, 139.8, 135.1, 129.4, 124.4, 123.9, 123.6, 48.5, 48.1, 41.8, 29.5, 28.1, 25.4, 23.4, 12.0. HRMS *m/e* calcd. for $C_{31}H_{48}N_2O$ (M^+) 464.3767, found 464.3782.

(R)-N-(2,6-diisopropylphenyl)-N-(2-(1-phenylethylamino)ethyl)formamide (25): Using the general procedure, **20** (2.0 mmol, 495 mg) was reacted with (R)-(+)-α-methylbenzylamine (2.0 mmol, 248 mg, 260 μL) to give 401 mg (57%) of **25** as a yellow solid. (R_f = 0.4 in 2:1 hexanes/EtOAc). M.p. = 62-66°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.40-7.15 (8H), 3.85-3.70 (2H), 3.58 (m, 1H), 2.93 (m, 2H), 2.67 (m, 2H), 1.35 (d, J = 6.3 Hz, 3H), 1.20-1.05 (12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.6 (-), 147.5 (2 overlapping signals (+)), 145.2 (+), 135.5 (+), 129.3 (-), 128.4 (-), 126.9 (-), 126.5 (-), 124.3 (-), 58.3 (-), 48.0 (+), 44.9 (+), 28.1 (-), 28.0 (-), 25.4 (-), 25.3 (-), 24.1 (-), 23.4 (2 overlapping signals (-)). HRMS *m/e* calcd. for $C_{23}H_{33}N_2O$ $(M+H)^+$ 353.2587, found 353.2587. $[\alpha]^{20}_D$ +38.6 (c = 3.56, CH_2Cl_2)

***N*-(2,6-diisopropylphenyl)-*N*-(2-(1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-1,2,3,5,6,7-hexahydro*s*-indacen-4-ylamino)ethyl)formamide (26):** Using the general procedure, **22** (1.43 mmol, 355 mg) was reacted with the EMind aniline (1.43 mmol, 489 mg) to give 281 mg (34%) of **26** as an off white solid. (R_f = 0.3 in 93:7 hexanes/EtOAc). M.p. = 104-106°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 6.38 (s, 1H), 3.83 (t, J = 8.1 Hz, 2H), 3.24 (t, J = 8.1 Hz, 2H), 3.00 (sept, J = 7.2 Hz, 2H), 2.79 (br, 1H), 1.80 (s, 4H), 1.70-1.45 (8H), 1.38 (s, 12H), 1.24 (d, J = 6.6

Hz, 6H), 1.14 (d, *J* = 6.6 Hz, 6H), 0.76 (t, *J* = 7.2 Hz, 12H) ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5, 149.7, 147.6, 143.4, 142.6, 135.6, 129.4, 124.4, 115.3, 53.5, 49.8, 48.5, 48.3, 43.1, 32.7, 31.4, 28.3, 25.4, 23.4, 9.0. HRMS *m/e* calcd. for $C_{39}H_{60}N_2O$ $(M+H)^+$ 572.4784, found 572.4772.

(*R*)-*N*-(2-(1-phenylethylamino)ethyl)-*N*-(1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-1,2,3,5,6,7-hexahydro*s*-indacen-4-yl)formamide (27): Using the general procedure, **22** (0.38 mmol, 158 mg) was reacted with (R)-(+)-α-methylbenzylamine (0.38 mmol, 50 mg, 53 μL) to give 83 mg (42%) of **27** as a pale yellow solid. (R_f = 0.3 in 4:1 hexanes/EtOAc). M.p. = 88-90°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.30-7.10 (5H), 6.67 (s, 1H), 3.80-3.65 (2H), 3.58 (m, 1H), 2.75 (m, 1H), 2.66 (m, 1H), 1.81 (s, 2H), 1.78 (s, 1H), 1.76 (s, 1H), 1.72-1.40 (8H), 1.35-1.15 (12H), 0.85-0.65 (12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 150.4, 150.3, 147.7, 147.6, 145.2, 132.9, 128.3, 126.8, 126.5, 120.8, 58.1, 52.9, 52.7, 50.1, 48.1, 48.0, 44.4, 43.5 (2 overlapping signals), 33.0, 32.9, 32.4, 32.1, 31.7, 31.5, 30.5, 24.2, 9.0, 8.9 (2 overlapping signals). HRMS *m/e* calcd. for $C_{35}H_{52}N_2O$ $(M)^+$ 516.4080, found 516.4069. $[\alpha]^{20}_D$ +26.8 (c = 0.83, CH_2Cl_2)



General procedure for preparation of imidazolinium triflate salts ***11,19, 28-32***: To a round bottom flask was added the corresponding formamide (1 equiv.), freshly distilled toluene (0.037 M), and TfOH (1 equiv.) whereupon the yellow colour of the solution intensified. After stirring at rt for 15 min, Tf_2O (1 equiv.) was added and the reaction stirred at 65°C for 90 min, during which the colour darkened to brown. Upon addition of DIPEA (3 equiv.) white fumes were observed and the colour gradually changed to red. The reaction was heated at 80ºC for 90 min and then cooled to rt during which time a small amount of a red oil began to form at the bottom of the flask. The solvent was removed *in vacuo* and pentane was added to the reddish brown microcrystalline material.

The suspension was sonicated for 30 seconds, inducing the formation of a flaky solid that was amenable to filtration. The solid was filtered on a medium porosity filter funnel and washed with pentane. The light-brown solid consisted of a mixture of the imidazolinium and Huniginium triflate salts. This mixture was transferred to another round bottom flask where K_2CO_3 (1:1 w/w), crushed hot 4Å molecular sieves (1:1 w/w), and freshly distilled toluene (3 mL/100 mg of solids) were added. The mixture was heated at 45ºC for 16 h, cooled to rt, filtered through Celite and washed with methylene chloride. The filtrate was concentrated *in vacuo* and the resulting solid was triturated once with a minimal amount of Et_2O. After decantation or filtration the imidazolinium salt was obtained in pure form.

1,3-Bis(2,6-di(pentan-3-yl)phenyl)-4,5-dihydroimidazolium trifluoromethanesulfonate (11): Using the general procedure, formamide **8** (0.6 mmol, 310 mg) produced **11** (247 mg, 64%) as an off white solid. M.p. = decomposes at >258°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, *J* = 8.0 Hz, 2H), 7.40 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 4H), 4.62 (s, 4H), 2.52 (p, *J* = 7.2 Hz, 4H), 1.90-1.80 (8H), 1.80-1.55 (8H), 0.95 (t, *J* = 7.2 Hz, 12H), 0.74 (t, *J* = 7.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (-), 143.3 (+), 132.2 (+), 131.5 (-), 125.6 (-), (q, 120.7 (+), *J* = 319 Hz), 55.4 (+), 43.4 (-), 29.1 (+), 12.4 (-), 12.1 (-). Anal. Calcd. for $C_{36}H_{55}F_3N_2O_3S$: C 66.23, H 8.49, N 4.29. Found: C 66.46, H 8.42, N 4.65.

1,3-Bis(2,6-diisobutylphenyl)-4,5-dihydroimidazolium trifluoromethanesulfonate (19): Using the general procedure, formamide **18** (0.3 mmol, 140 mg) produced **19** (125 mg, 65%) as a light-brown solid. M.p. = 238-244°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95

(s, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 4H), 4.58 (s, 4H), 2.54 (m, 8H), 2.03 (sept, *J* = 6.6 Hz, 4H), 0.99 (d, *J* = 6.6 Hz, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 138.8, 132.1, 130.6, 128.4, (q, 120.7, *J* = 319), 53.7, 40.0, 29.2, 22.8, 22.5. HRMS *m/e* calcd. for $C_{31}H_{47}N_2$ $(M\text{-}OTf)^+$ 447.3739, found 447.3734.

1-(2,6-diisopropylphenyl)-3-(2,6-diisobutylphenyl)-4,5-dihydroimidazolium trifluoromethanesulfonate (28): Using the general procedure, formamide **23** (0.32 mmol, 140 mg) produced **28** (102 mg, 57%) as a light-brown solid. M.p. = decomposes at >291°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.60 (s, 4H), 2.99 (sept, *J* = 6.9 Hz, 2H), 2.54 (m, 4H), 1.93 (sept, *J* = 6.6 Hz, 2H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.28 (d, *J* = 6.9 Hz, 6H), 0.98 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 146.0, 138.8, 132.1, 131.6, 130.5, 129.0, 125.1, (q, 120.7, *J* = 319), 54.5, 53.6, 40.4, 29.4, 29.1, 25.0, 24.2, 22.8, 22.4. HRMS *m/e* calcd. for $C_{29}H_{43}N_2(M\text{-}OTf)^+$ 419.3426, found 419.3441.

1-(2,6-di-(3-pentyl)phenyl)-3-(2,6-diisopropylphenyl)-4,5-dihydroimidazolium trifluoromethanesulfonate (29): Using the general procedure, formamide **24** (0.65 mmol, 300 mg) produced **29** (284 mg, 74%) as a light-brown solid. M.p. = 230-234°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.55-7.45 (2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 4.62 (m, 4H), 3.00 (sept, *J* = 6.9 Hz, 2H), 2.51 (p, *J* = 6.3 Hz, 2H), 1.90-1.50 (8H), 1.39 (d, *J* = 6.9 Hz, 6H), 1.28 (d, *J* = 6.9 Hz, 6H), 0.91 (t, *J* = 7.5 Hz, 6H), 0.75 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9, 146.0, 143.4,

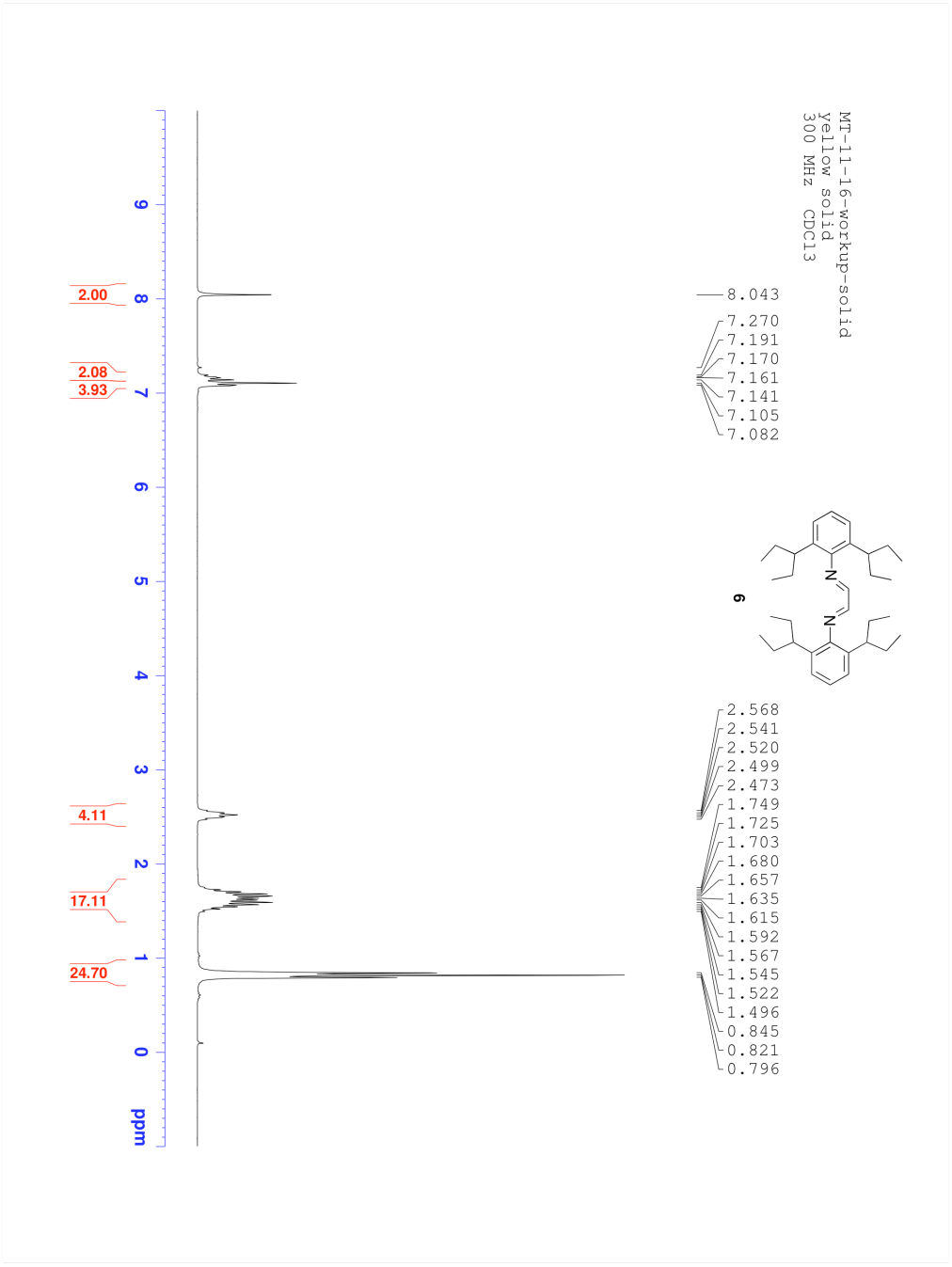
132.4, 131.6, 131.4, 128.8, 125.5, 125.2, (q, 120.7, J = 319), 55.0, 54.6, 43.5, 29.5, 29.1, 28.8, 24.7, 24.4, 12.4, 12.2. . HRMS *m/e* calcd. for $C_{31}H_{47}N_2$ $(M\text{-}OTf)^+$ 447.3739, found 447.3746.

1-(2,6-diisopropylphenyl)-3-(R)-1-phenylethyl)-4,5-dihydroimidazolium trifluoromethanesulfonate (30): Using the general procedure, formamide **25** (1.49 mmol, 527 mg) produced **30** as a light-brown solid (369 mg, 52%). M.p. = 62-68ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.50-7.25 (6H), 7.21 (d, J = 7.8 Hz, 2H), 5.32 (q, J = 6.9 Hz, 1H), 4.25-4.10 (4H), 2.87 (sept, J = 6.9 Hz, 1H), 2.80 (sept, J = 6.9 Hz, 1H), 1.77 (d, J = 6.9 Hz, 3H), 1.30-1.10 (12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0 (-), 146.5 (+), 146.4 (+), 137.1 (+), 131.0 (-), 129.9 (+), 129.4 (-), 129.3 (-), 127.0 (-), 124.8 (-), (q, 120.7 (+), J = 319 Hz), 57.9 (-), 53.3 (+), 46.7 (+), 28.7 (-), 28.6 (-), 24.7 (-), 24.6 (-), 24.0 (-), 23.9 (-), 18.4 (-).HRMS *m/e* calcd. for $C_{23}H_{31}N_2$ $(M\text{-}OTf)^+$ 335.2487, found 335.2479. $[\alpha]^{20}_D$ +50.0 (c = 0.50, CH_2Cl_2)

***1*-(1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-1,2,3,5,6,7-hexahydro*s*-indacen-4-yl)-3-(2,6-diisopropylphenyl)4,5-dihydroimidazolium trifluoromethanesulfonate (31):** Using the general procedure, formamide **26** (0.49 mmol, 280 mg) produced **31** as a light brown solid (248 mg, 72%). M.p. = 274-278ºC; ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.99 (s, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 6.91 (s, 1H), 4.78 (t, J = 11.4 Hz, 2H), 4.50 (t, J = 11.4 Hz, 2H), 3.08 (sept, J = 6.6 Hz, 2H), 2.01 (d, J = 13.2 Hz, 2H), 1.95 (d, J = 13.2 Hz, 2H), 1.80-1.50 (14H), 1.40 (s, 6H), 1.38 (d, J = 6.6 Hz, 6H), 1.27 (d, J = 6.6 Hz, 6H), 0.82 (t, J = 7.2 Hz, 6H), 0.79 (t, J = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2):

δ 159.0 (-), 152.7 (+), 146.8 (+), 146.6 (+), 132.1 (-), 129.2 (+), 127.7 (+), 125.8 (-), 123.7 (-), (q, 121.3 (+), J = 320 Hz), 56.3 (+), 54.5 (+), 52.6 (+), 49.1 (+), 44.2 (+), 33.2 (+), 33.0 (-), 32.6 (+), 31.5 (-), 29.5 (-), 24.9 (-), 24.6 (-), 9.2 (-), 9.11 (-). HRMS *m/e* calcd. for $C_{39}H_{59}N_2$ $(M\text{-}OTf)^+$ 555.4669, found 555.4687.

***1*-(1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-1,2,3,5,6,7-hexahydro*s*-indacen-4-yl)-3-(R)-(1-phenylethyl)-4,5-dihydroimidazolium trifluoromethanesulfonate (32):** Using the general procedure, formamide **27** (0.43 mmol, 222 mg) produced **32** as a pale yellow solid (86 mg, 32%). M.p. = 65-72ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.50-7.30 (5H), 6.79 (s, 1H), 5.46 (q, J = 6.9 Hz, 1H), 4.45-4.25 (m, 2H), 4.16 (m, 1H), 3.96 (dd, J = 21.9,11.7 Hz, 1H), 1.87 (d, J = 2.1 Hz, 2H), 1.85 (s, J = 2.1 Hz, 2H), 1.75 (d, J = 6.6 Hz, 3H), 1.70-1.45 (m, 8H), 1.39 (s, 3H), 1.30 (s, 6H), 1.24 (s, 3H), 0.80-0.74 (12H); ^{1}H NMR (100 MHz, $CDCl_3$): δ 157.9 (-), 151.5 (+), 146.7 (+), 146.6 (+), 136.3 (+), 129.3 (-), 129.2 (-), 127.7 (+), 127.2 (-), 122.7 (-), (q, 120.6 (+), J = 319 Hz), 57.4 (-), 54.2 (+), 52.8 (+), 48.3 ((+), two overlapping signals), 45.8 (+), 43.4 ((+), two overlapping signals), 32.2 (+), 32.0 (+), 31.9 (+), 31.8 (-), 31.6 (-), 31.4 (-), 18.0 (-), 8.9 (-), 8.8 (-). HRMS *m/e* calcd. for $C_{36}H_{51}F_3N_2O_3S$ $(M)^+$ 648.3573, found 648.3557. $[\alpha]^{20}_D$ 0 degrees (c = 0.78, CH_2Cl_2).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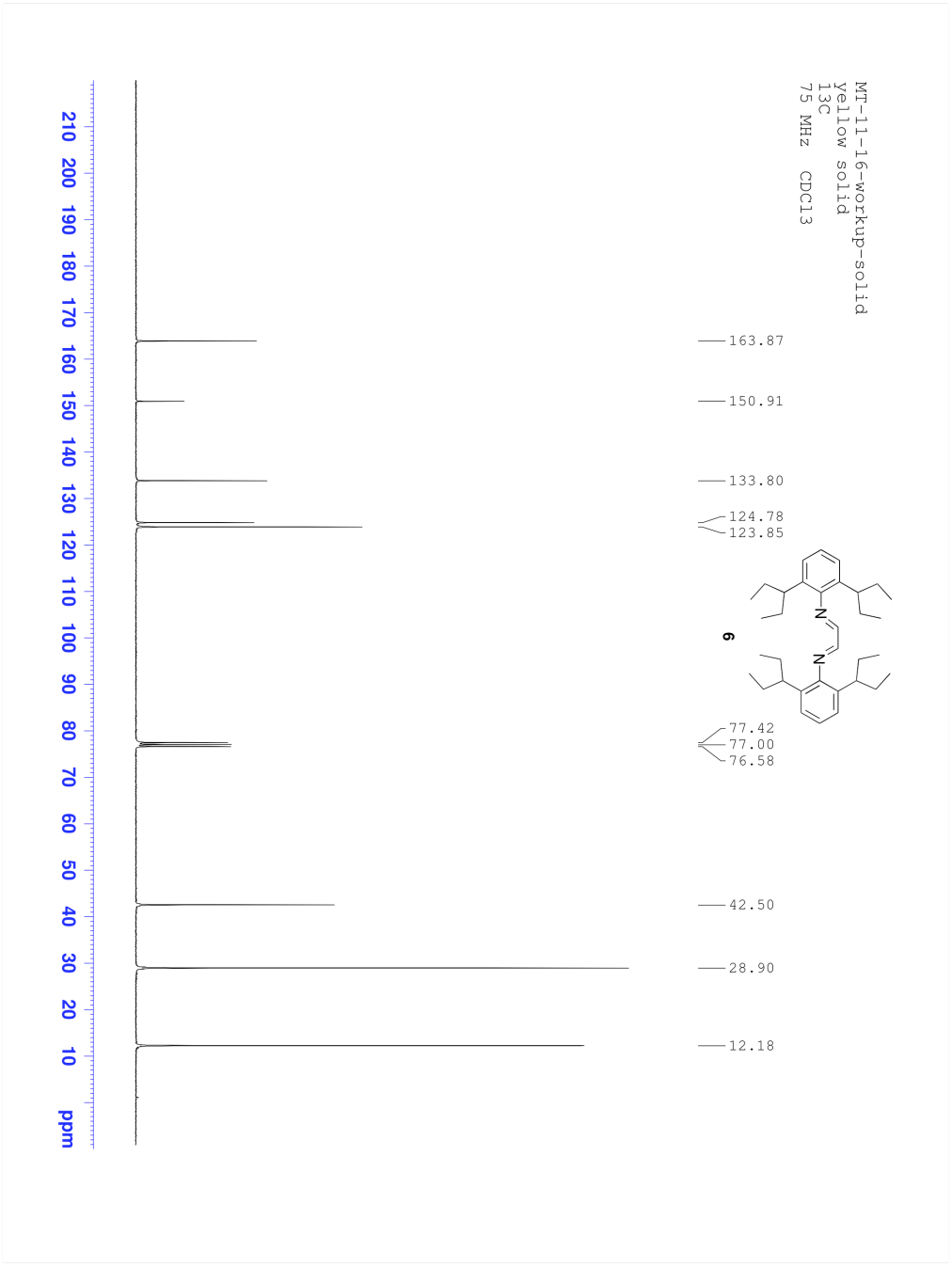
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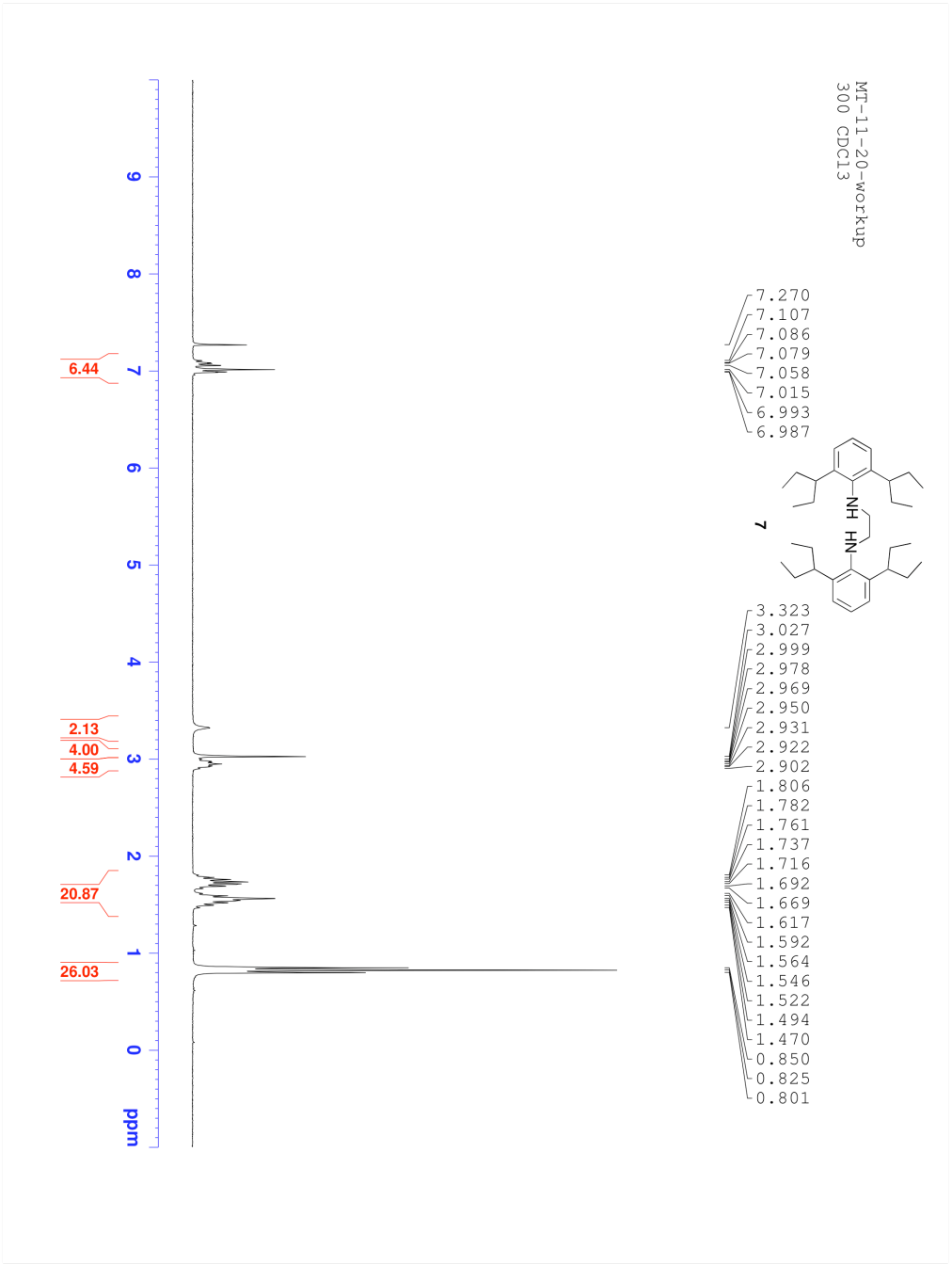
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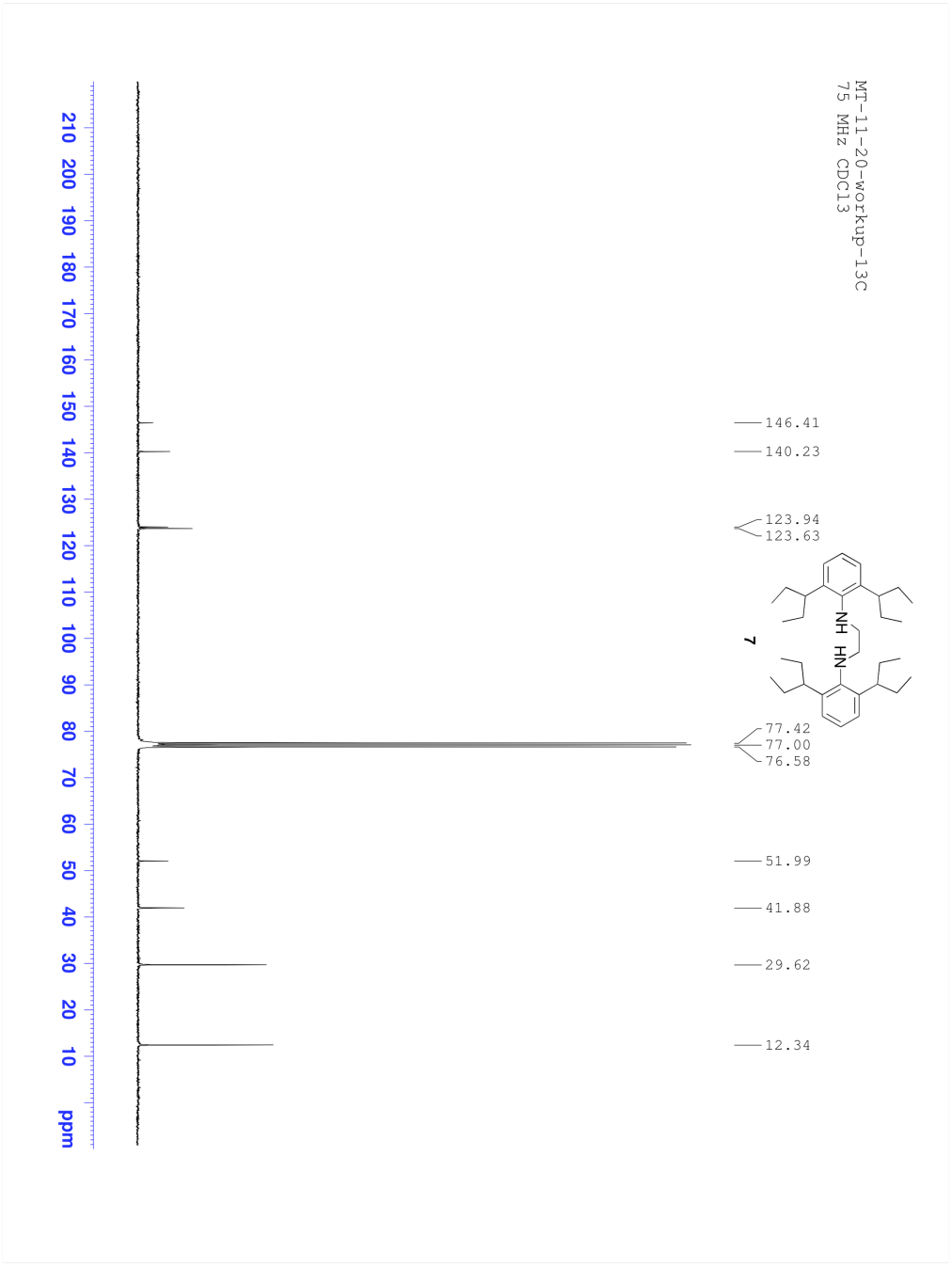

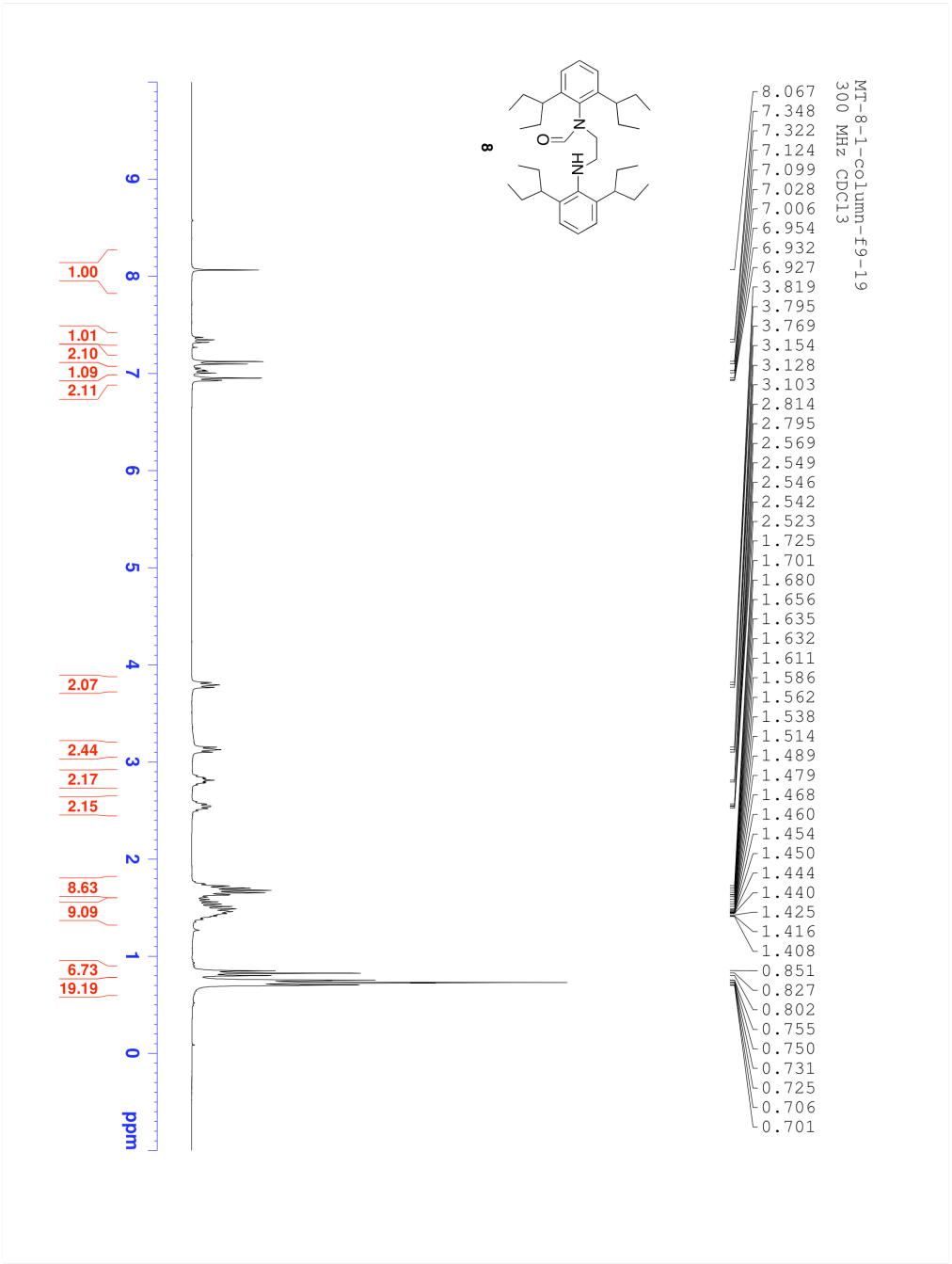
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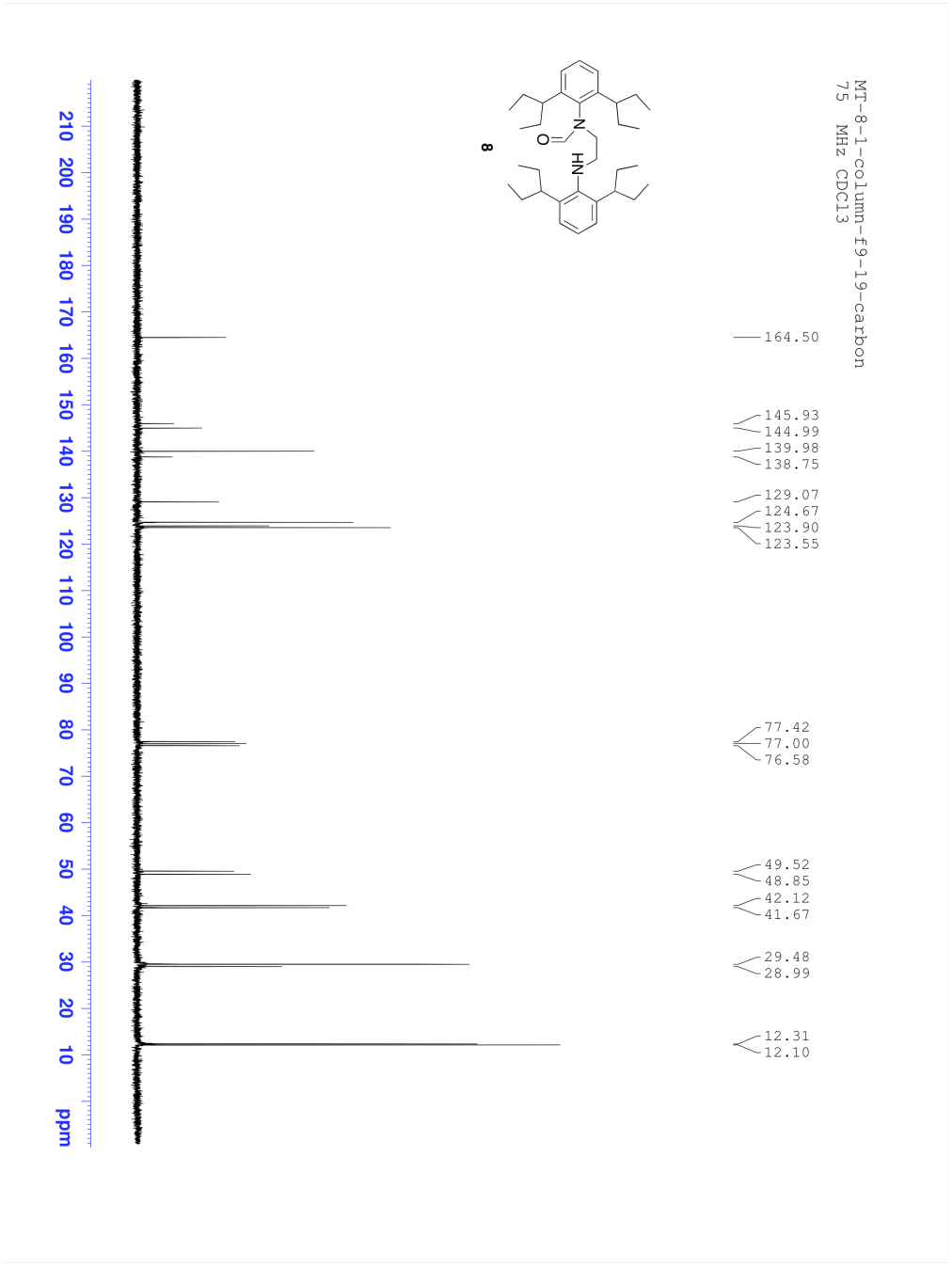
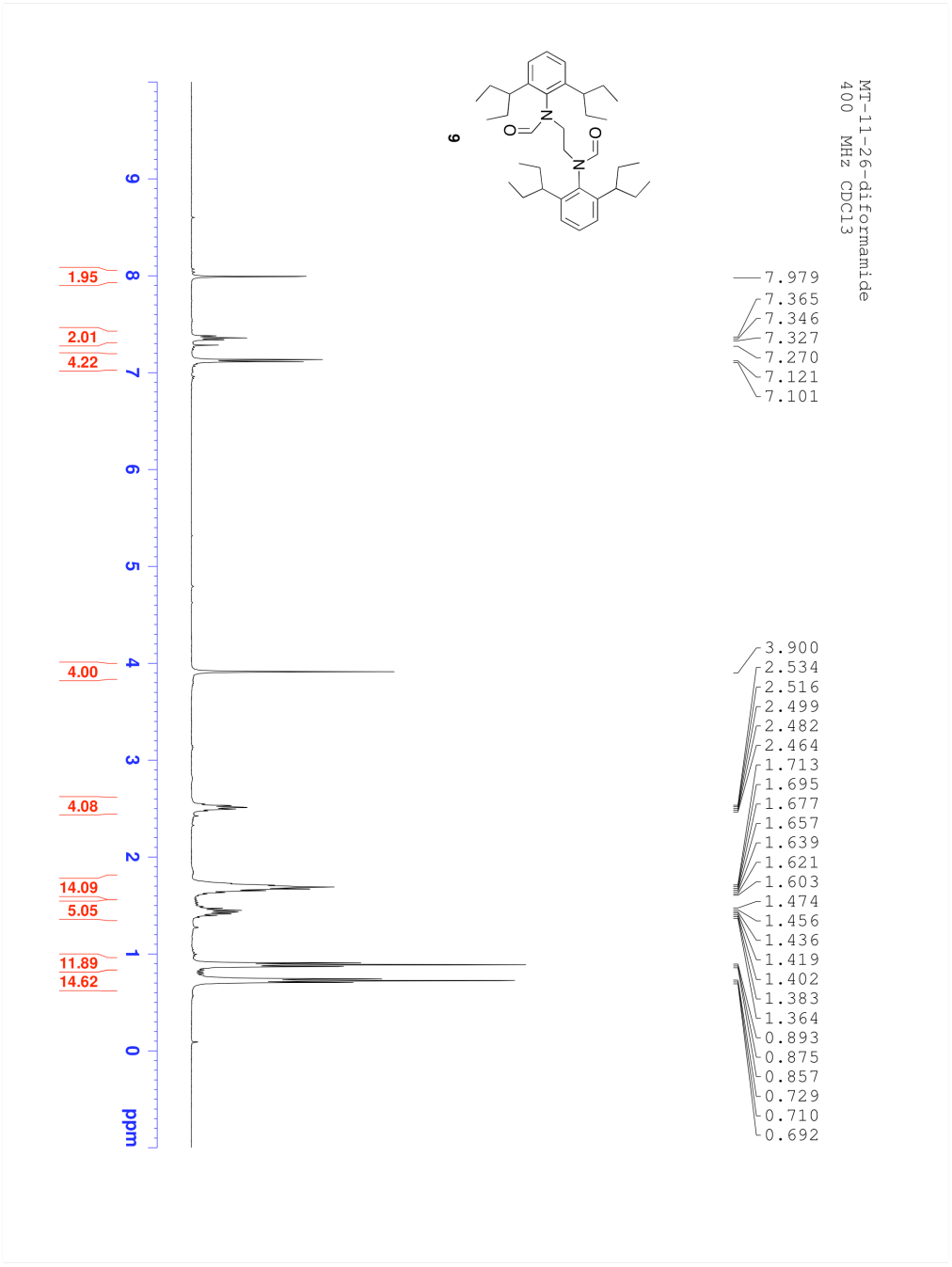
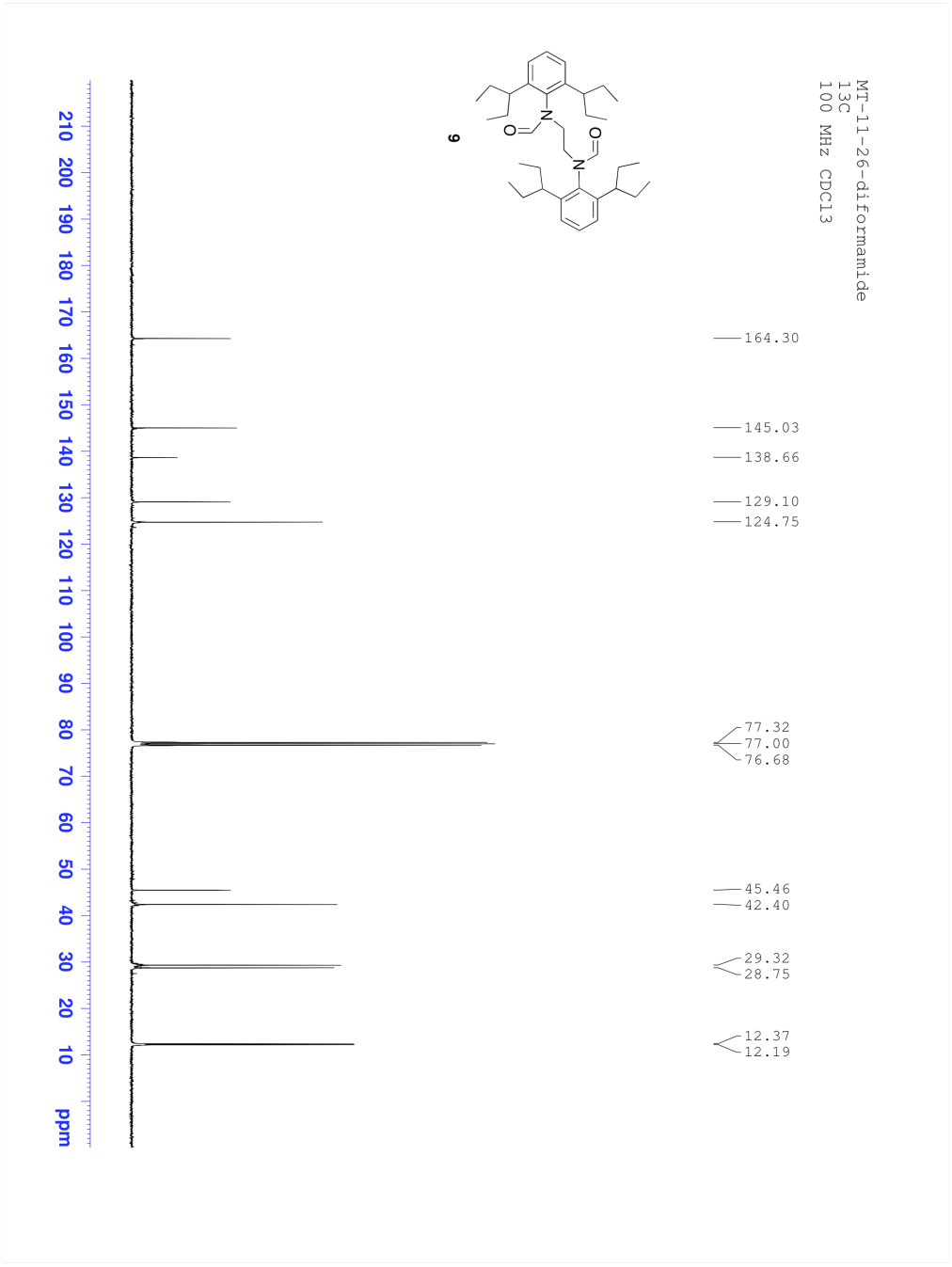
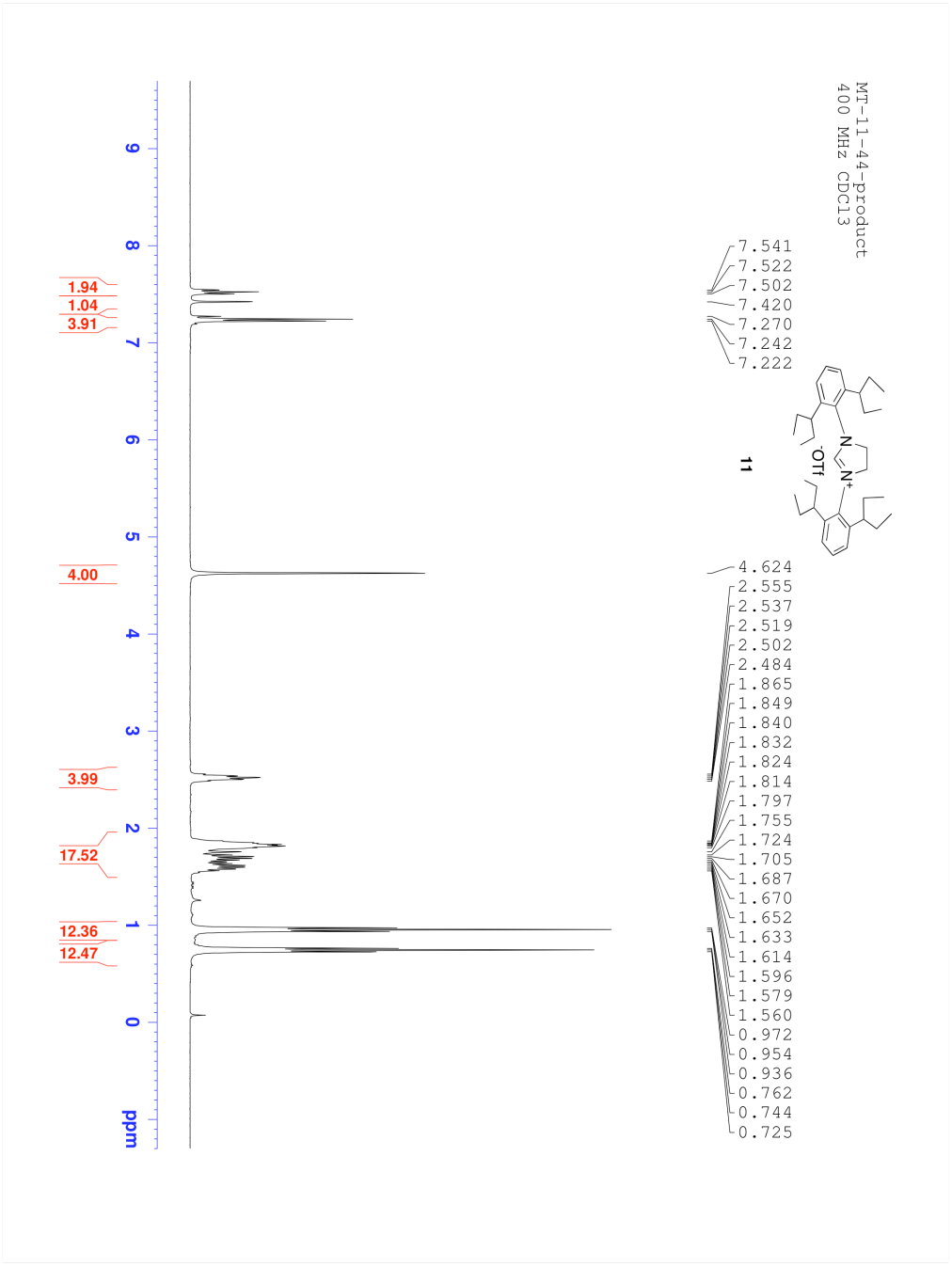
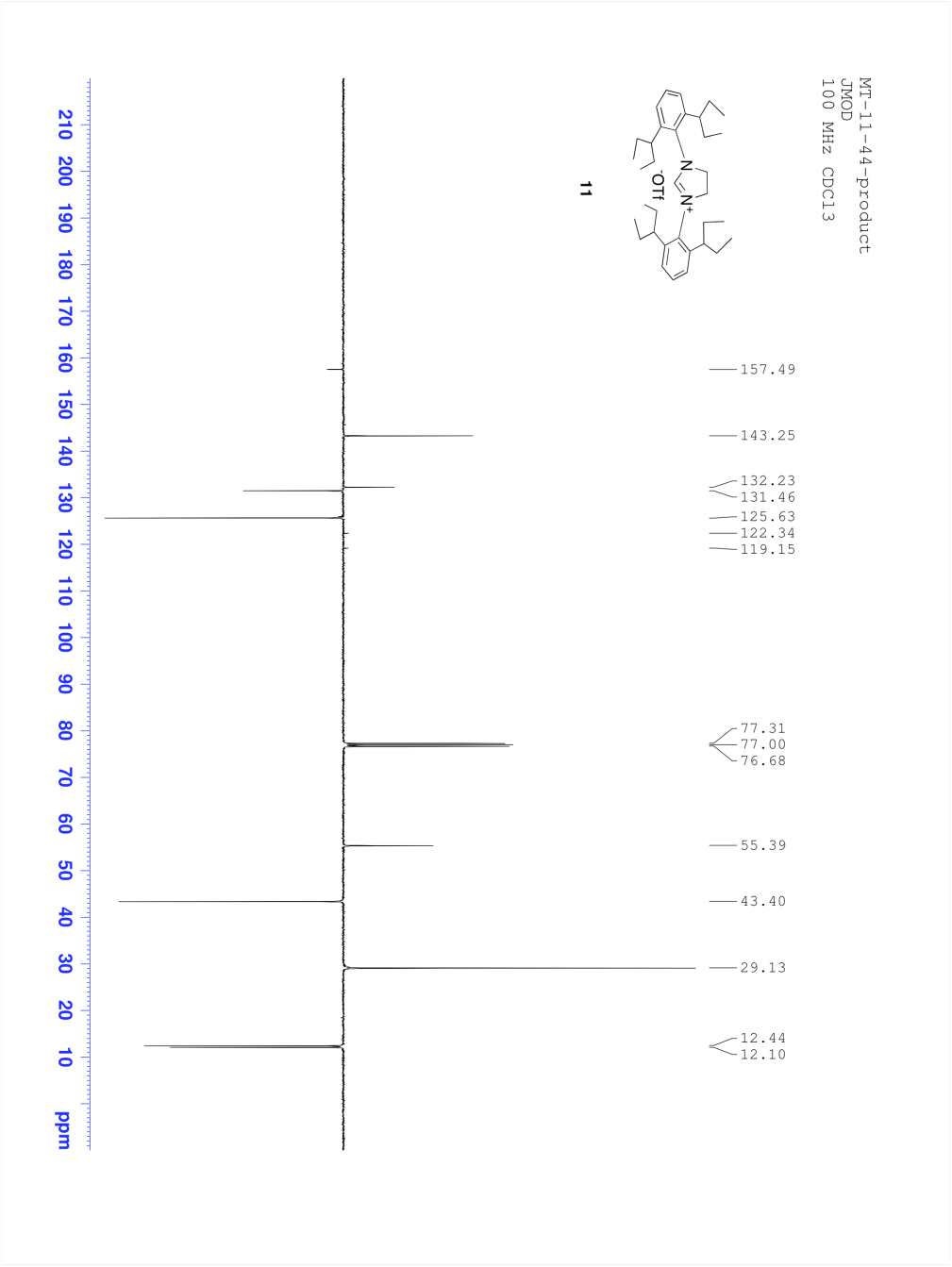
19.19
ppm

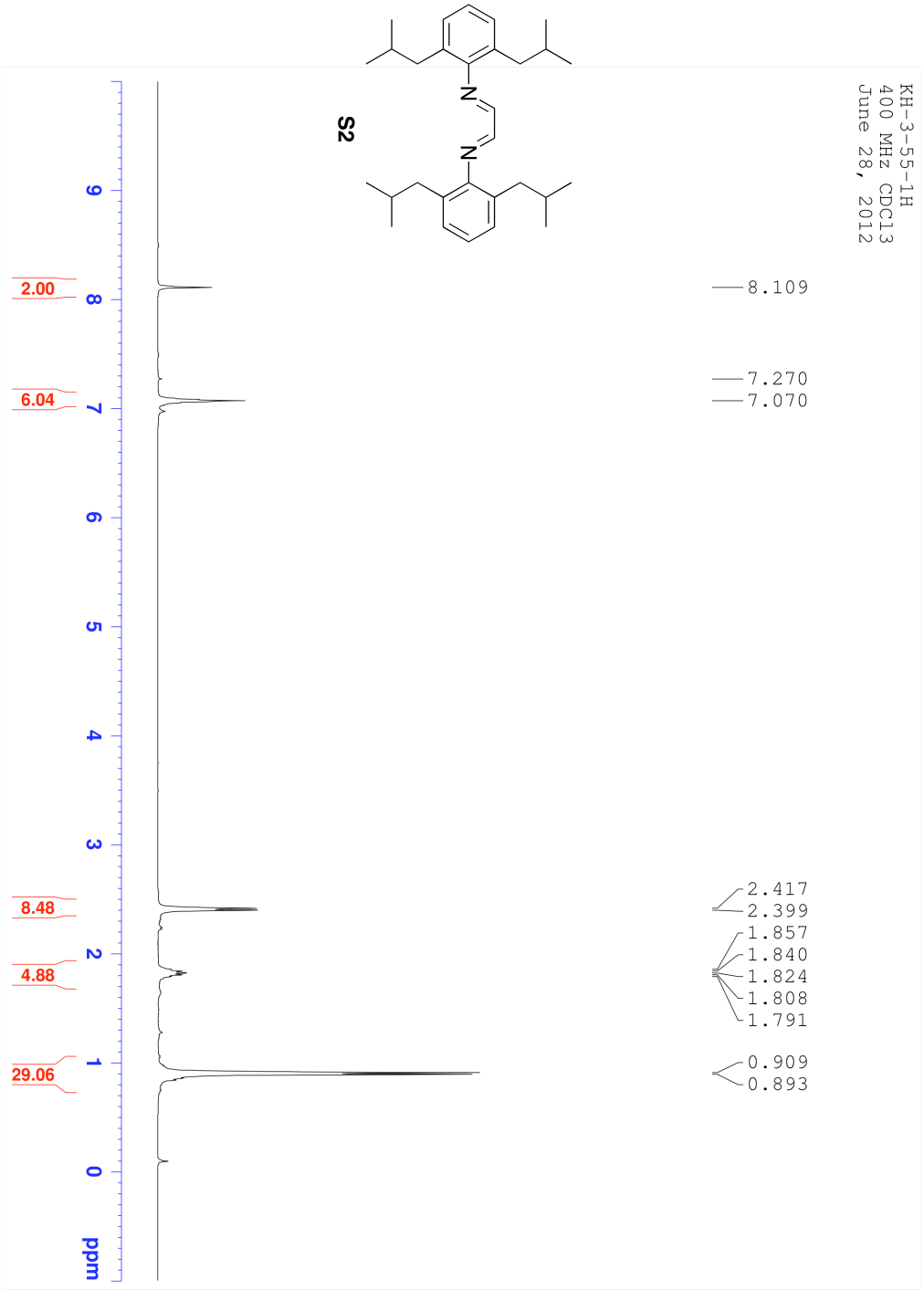

MT-8-1-column-f9-19-carbon
75 MHz CDCl3
8
O
N
HN
164.50
145.93
144.99
139.98
138.75
129.07
124.67
123.90
123.55
77.42
77.00
76.58
49.52
48.85
42.12
41.67
29.48
28.99
12.31
12.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

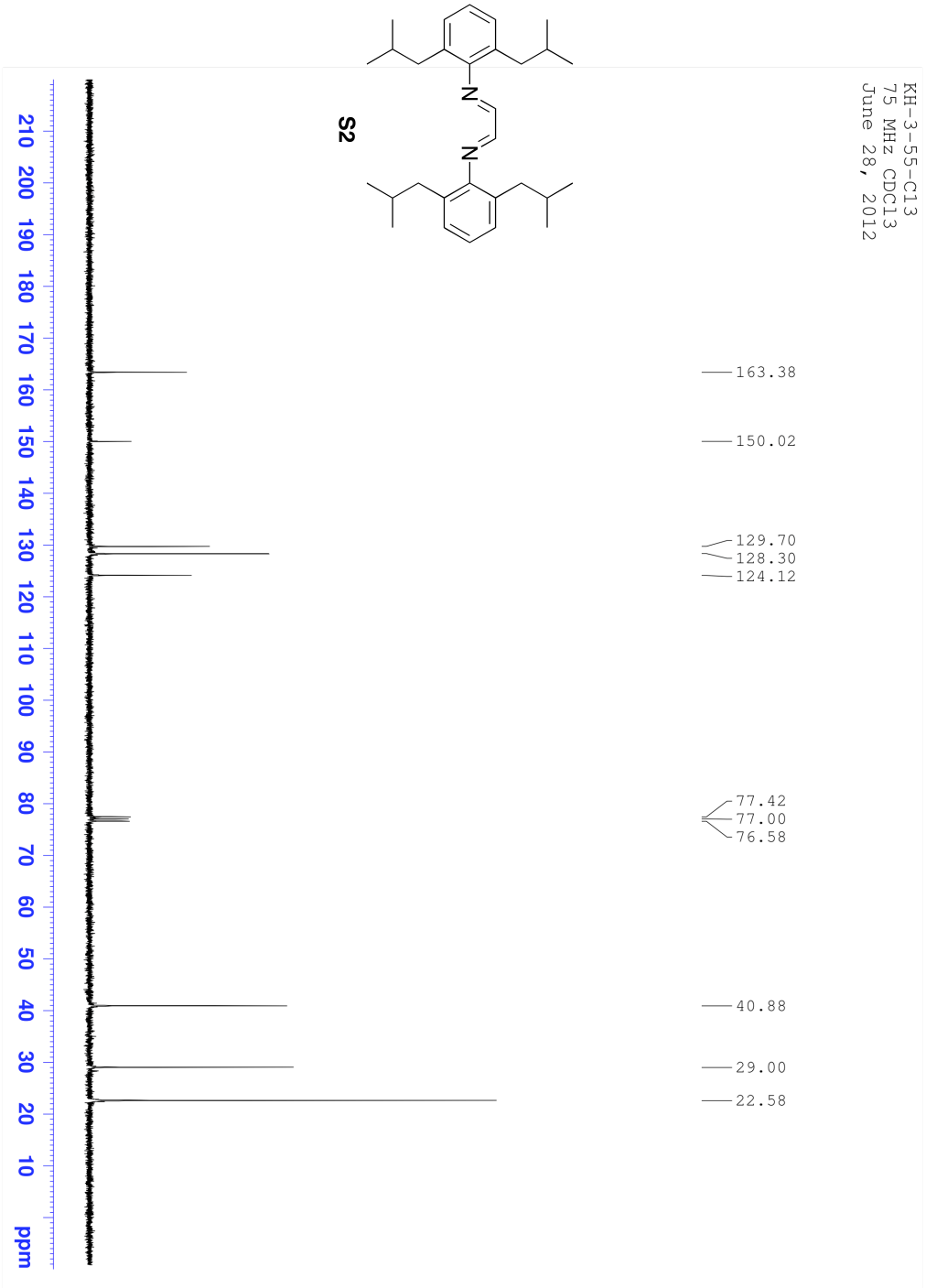

MT-11-26-diformamide
400 MHz CDCl3
9
1.95
2.01
4.22
4.00
4.08
14.09
5.05
11.89
14.62
ppm
7.979
7.365
7.346
7.327
7.270
7.121
7.101
3.900
2.534
2.516
2.499
2.482
2.464
1.713
1.695
1.677
1.657
1.639
1.621
1.603
1.474
1.456
1.436
1.419
1.402
1.383
1.364
0.893
0.875
0.857
0.729
0.710
0.692

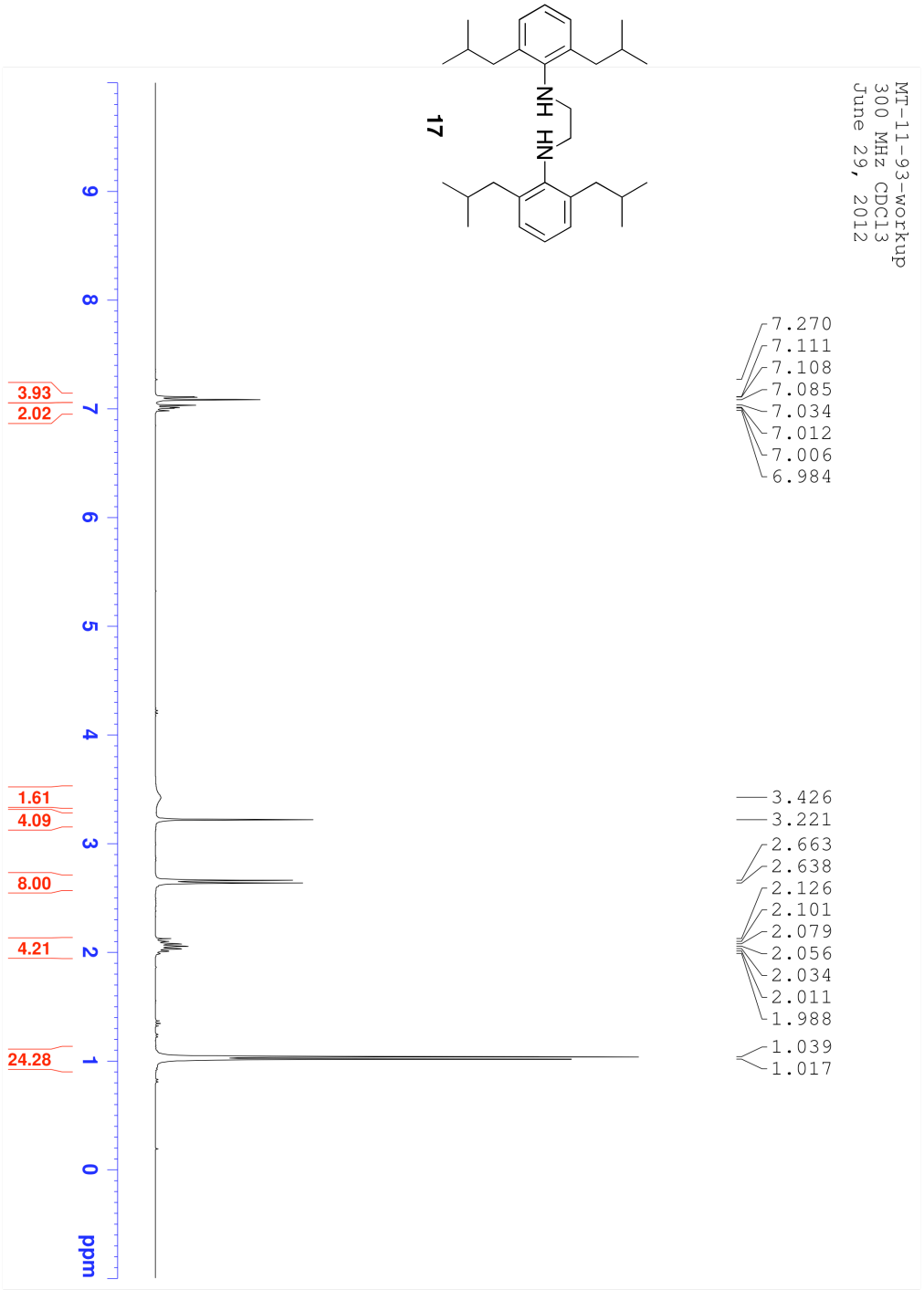

MT-11-26-diformamide
13C
100 MHz CDCl3
6
164.30
145.03
138.66
129.10
124.75
77.32
77.00
76.68
45.46
42.40
29.32
28.75
12.37
12.19
ppm

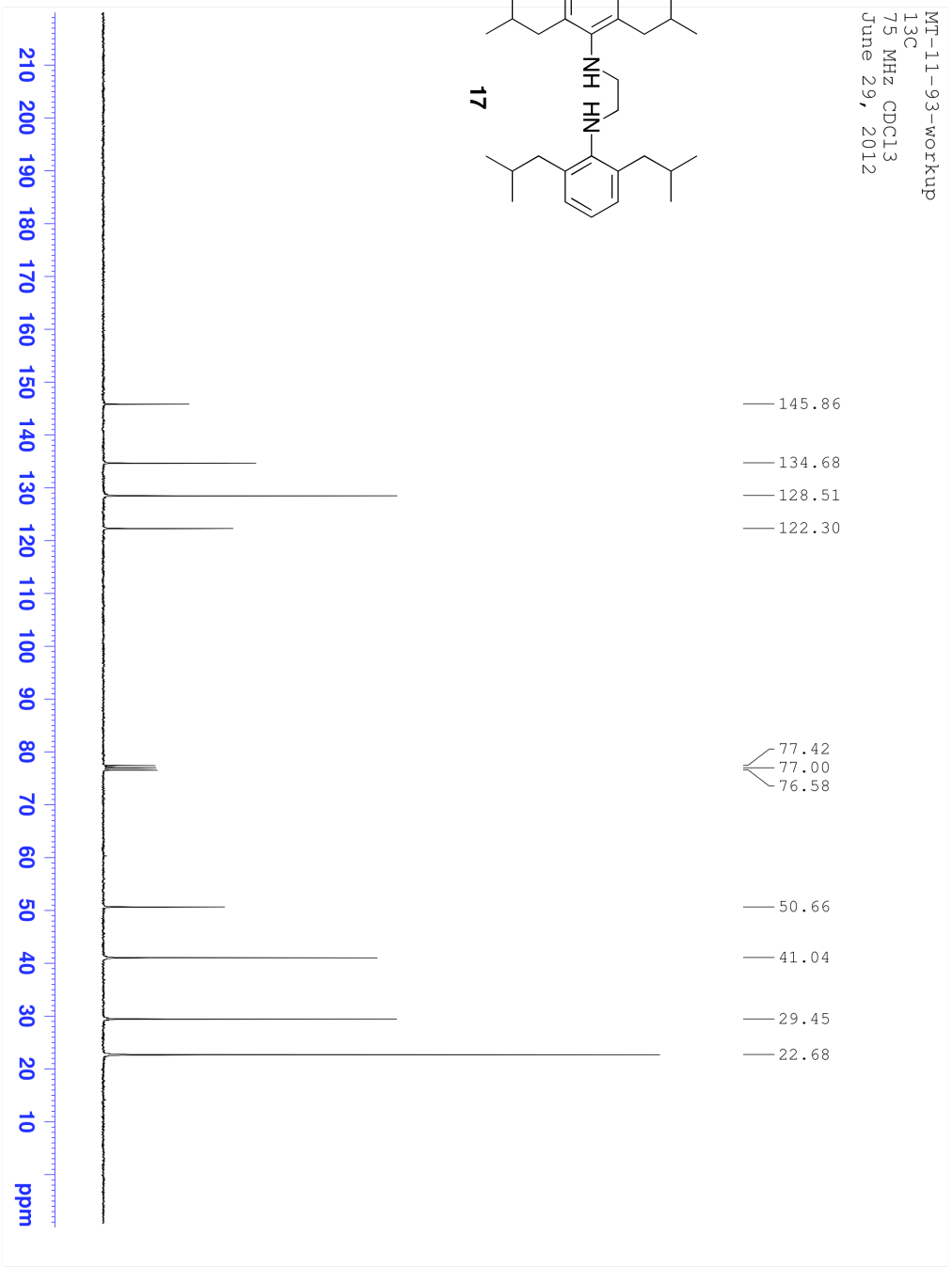

MT-11-44-product
400 MHz CDCl3
7.541
7.522
7.502
7.420
7.270
7.242
7.222
11
4.624
2.555
2.537
2.519
2.502
2.484
1.865
1.849
1.840
1.832
1.824
1.814
1.797
1.755
1.724
1.705
1.687
1.670
1.652
1.633
1.614
1.596
1.579
1.560
0.972
0.954
0.936
0.762
0.744
0.725
1.94
1.04
3.91
4.00
3.99
17.52
12.36
12.47
ppm

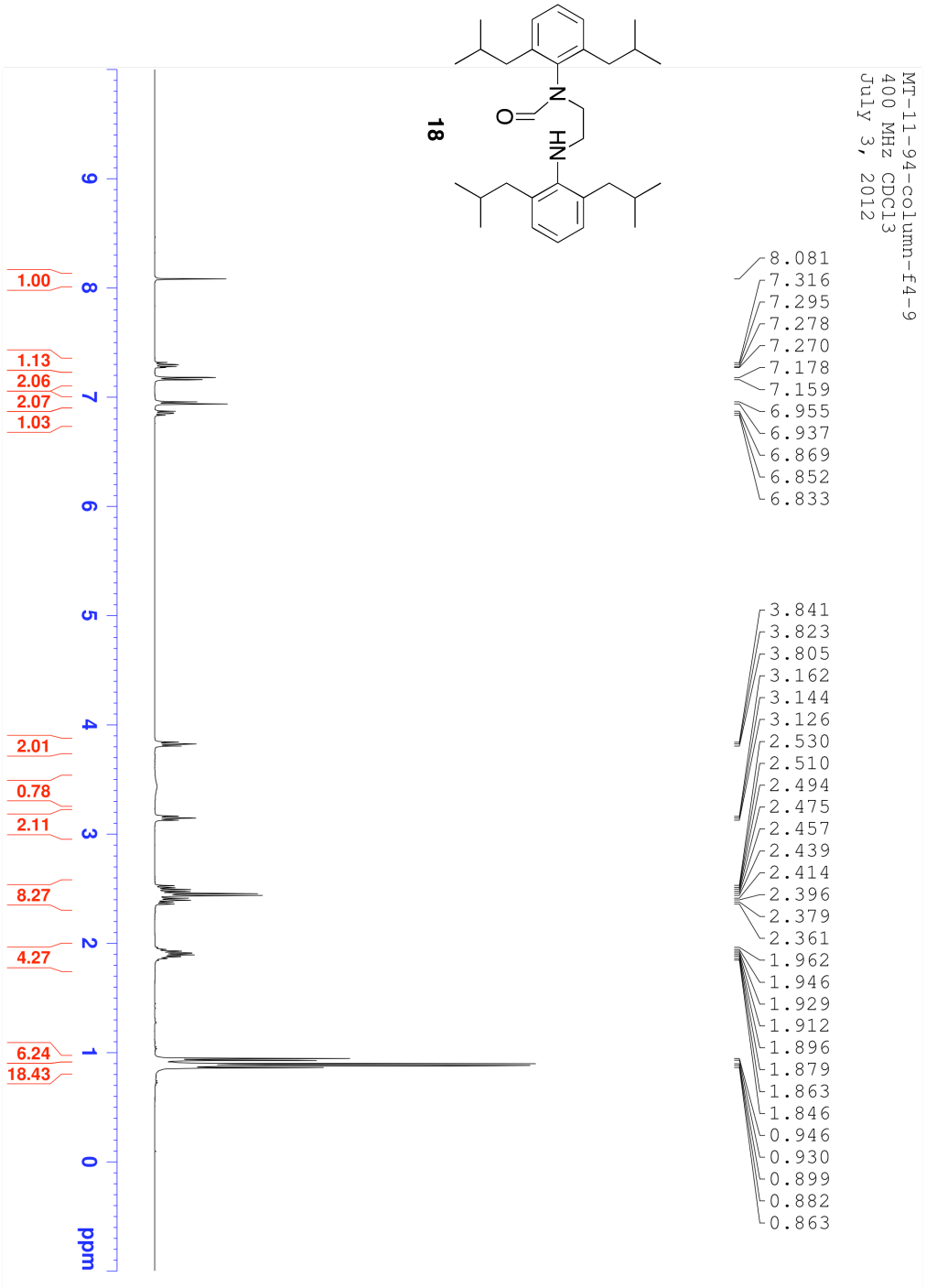

MT-11-44-product
JMOD
100 MHz CDCl3
11
OTf
157.49
143.25
132.23
131.46
125.63
122.34
119.15
77.31
77.00
76.68
55.39
43.40
29.13
12.44
12.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

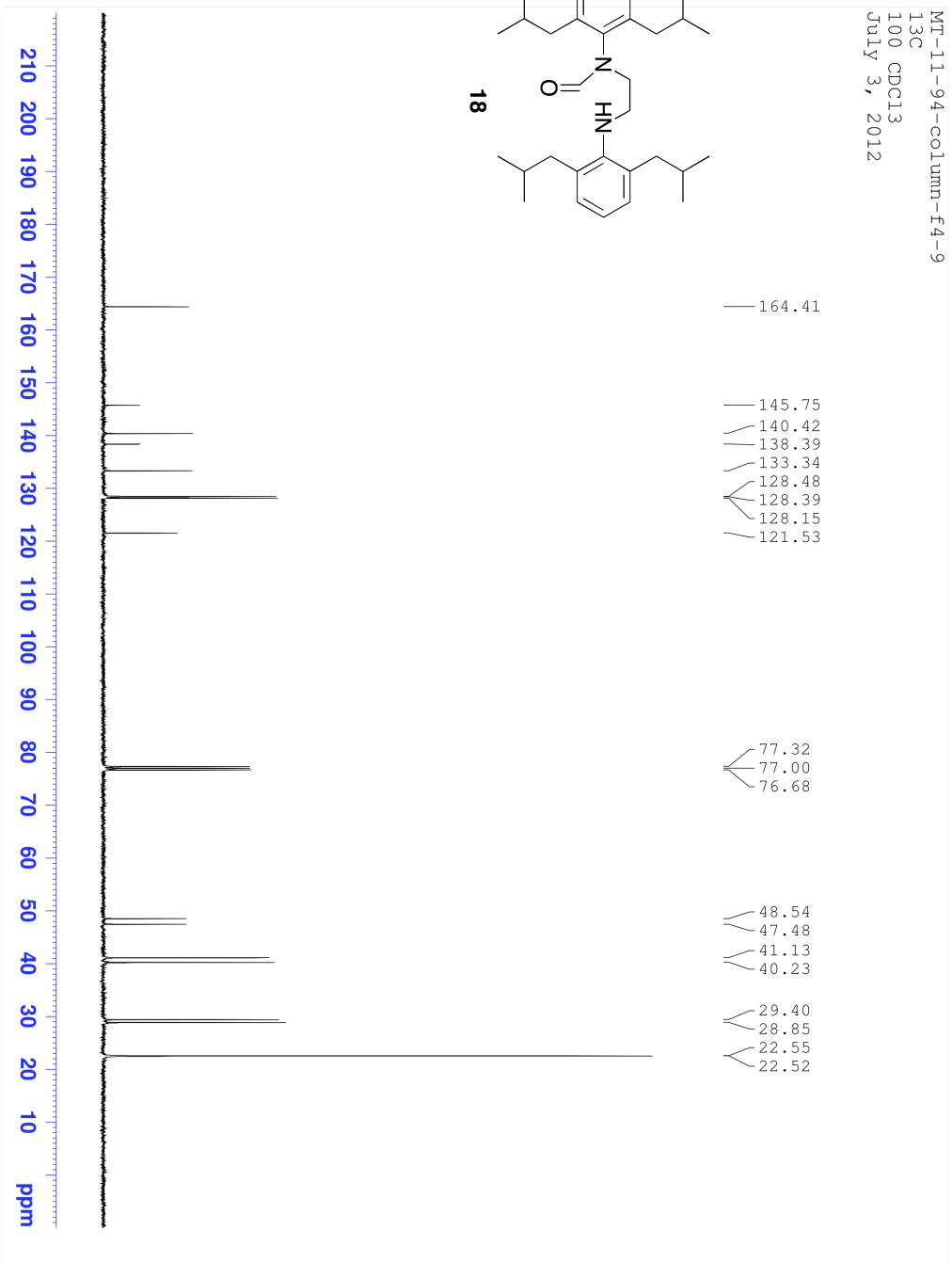

S2
KH-3-55-1H
400 MHz CDCl3
June 28, 2012
8.109
7.270
7.070
2.417
2.399
1.857
1.840
1.824
1.808
1.791
0.909
0.893
2.00
6.04
8.48
4.88
29.06
ppm

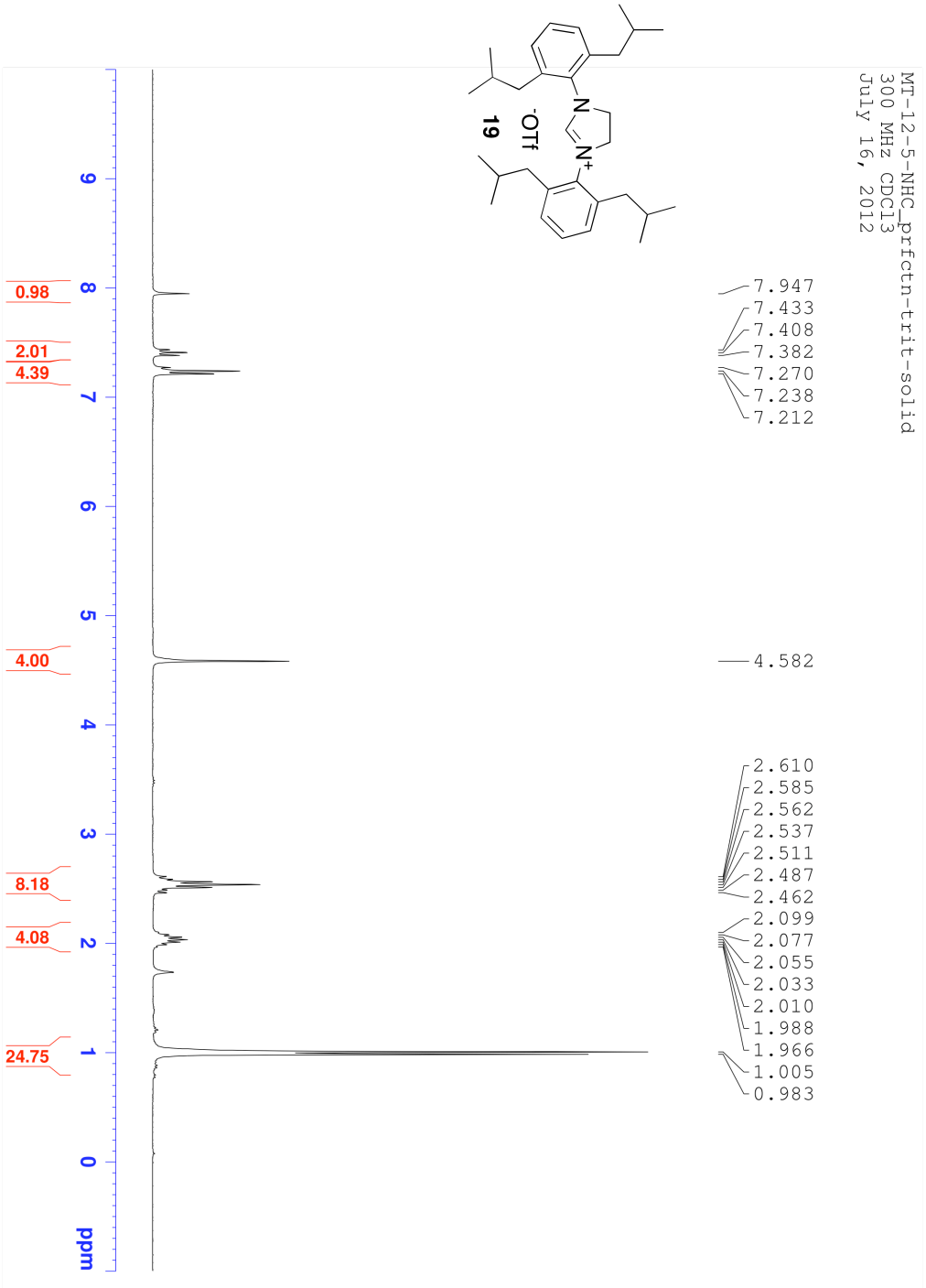

KH-3-55-C13
75 MHz CDCl3
June 28, 2012
S2
163.38
150.02
129.70
128.30
124.12
77.42
77.00
76.58
40.88
29.00
22.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

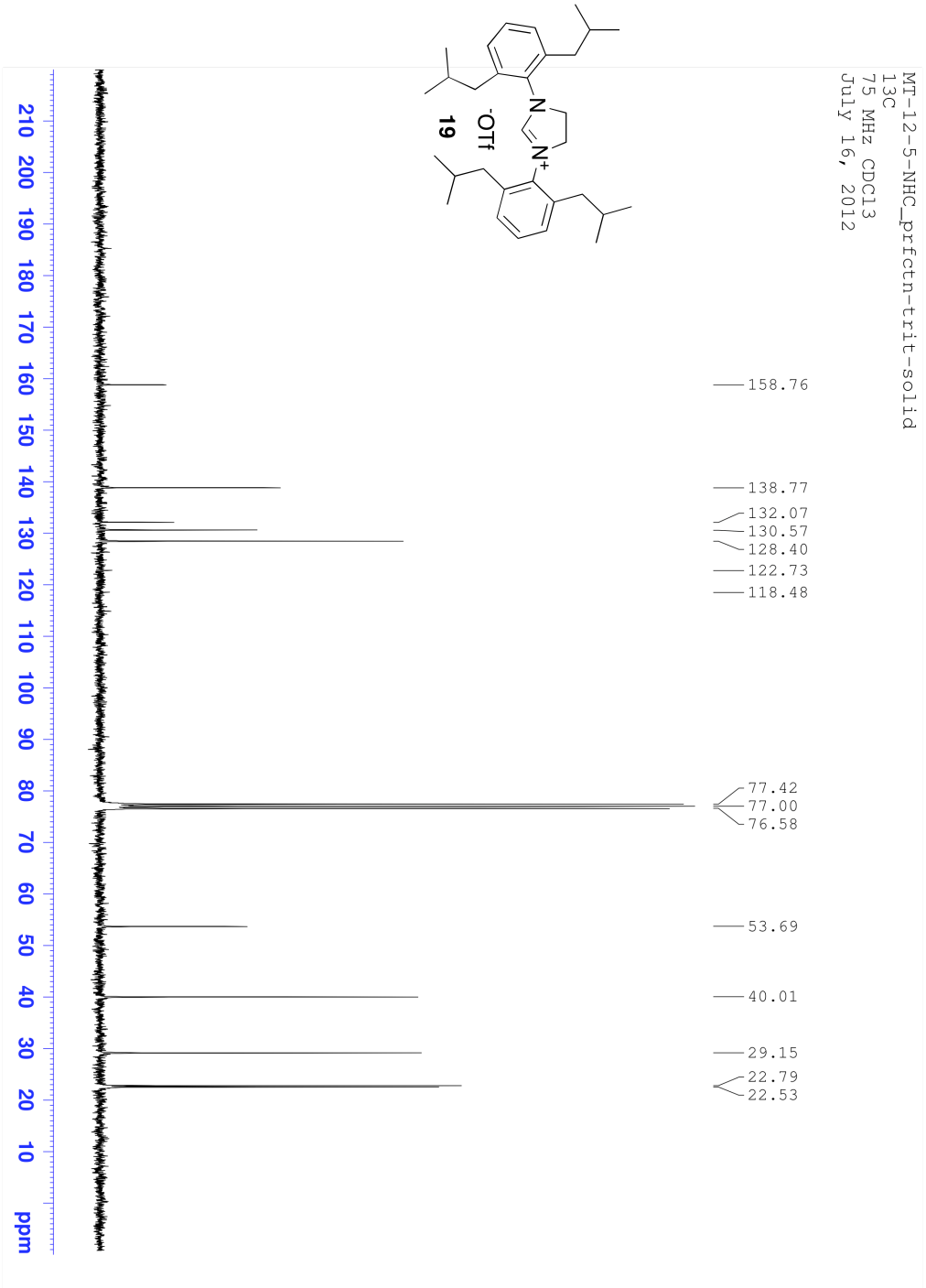

MT-11-93-workup
300 MHz CDCl3
June 29, 2012
17
NH HN
7.270
7.111
7.108
7.085
7.034
7.012
7.006
6.984
3.426
3.221
2.663
2.638
2.126
2.101
2.079
2.056
2.034
2.011
1.988
1.039
1.017
3.93
2.02
1.61
4.09
8.00
4.21
24.28
ppm

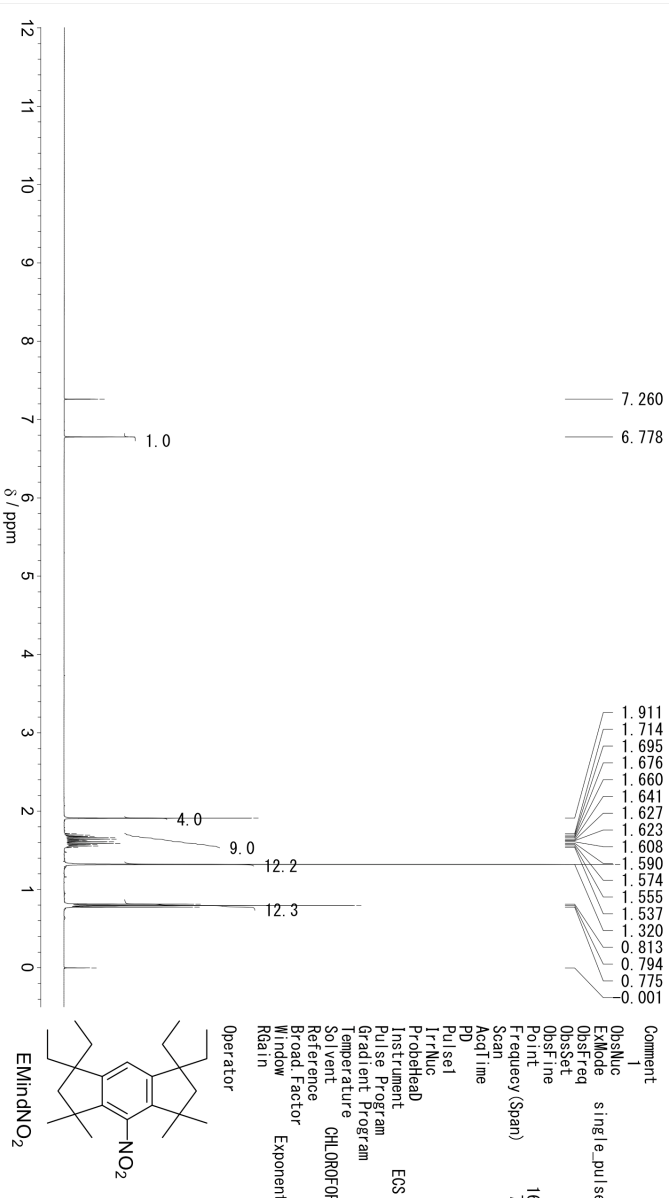

MT-11-93-workup
13C
75 MHz CDCl3
June 29, 2012
17
NH HN
145.86
134.68
128.51
122.30
77.42
77.00
76.58
50.66
41.04
29.45
22.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


MT-11-94-column-f4-9
400 MHz CDCl3
July 3, 2012
18
8.081
7.316
7.295
7.278
7.270
7.178
7.159
6.955
6.937
6.869
6.852
6.833
3.841
3.823
3.805
3.162
3.144
3.126
2.530
2.510
2.494
2.475
2.457
2.439
2.414
2.396
2.379
2.361
1.962
1.946
1.929
1.912
1.896
1.879
1.863
1.846
0.946
0.930
0.899
0.882
0.863
1.00
1.13
2.06
2.07
1.03
2.01
0.78
2.11
8.27
4.27
6.24
18.43
ppm

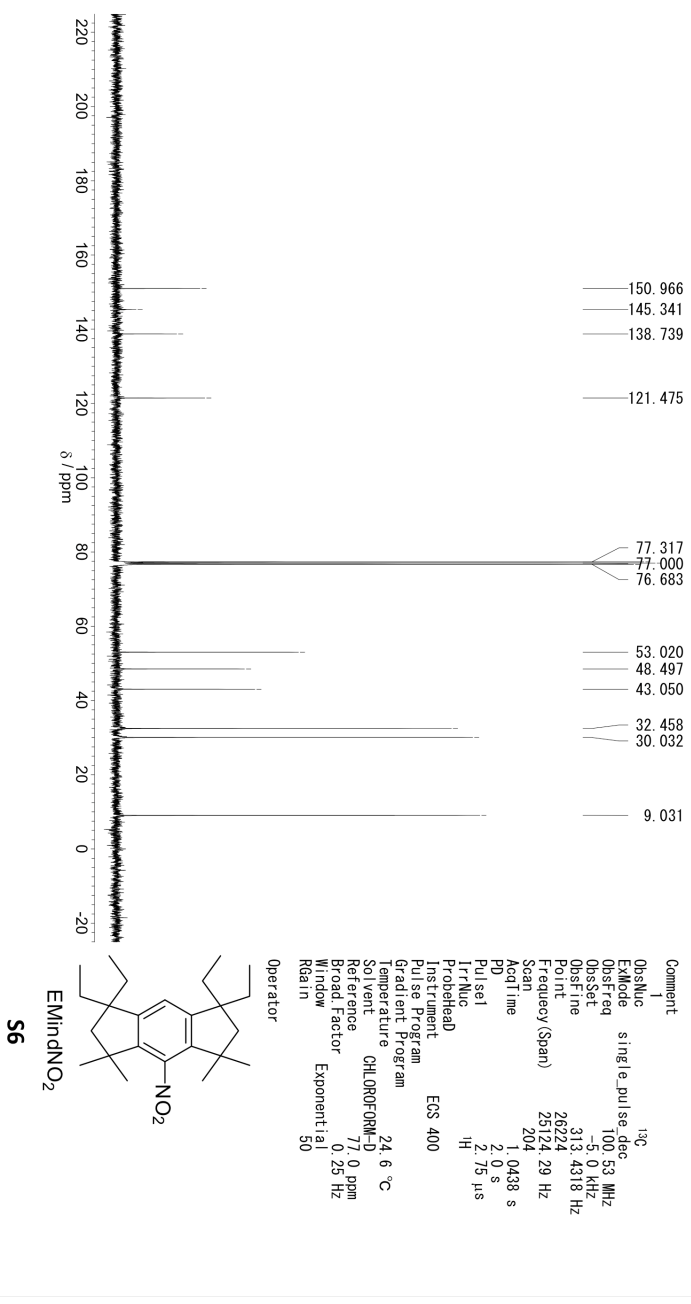

MT-11-94-column-f4-9
13C
100 CDCl3
July 3, 2012
18
N
O
HN
164.41
145.75
140.42
138.39
133.34
128.48
128.39
128.15
121.53
77.32
77.00
76.68
48.54
47.48
41.13
40.23
29.40
28.85
22.55
22.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


MT-12-5-NHC_prfctn-trit-solid
300 MHz CDCl3
July 16, 2012
19
-OTf
7.947
7.433
7.408
7.382
7.270
7.238
7.212
4.582
2.610
2.585
2.562
2.537
2.511
2.487
2.462
2.099
2.077
2.055
2.033
2.010
1.988
1.966
1.005
0.983
0.98
2.01
4.39
4.00
8.18
4.08
24.75
ppm


MT-12-5-NHC_prfctn-trit-solid
13C
75 MHz CDC13
July 16, 2012
19
-OTf
158.76
138.77
132.07
130.57
128.40
122.73
118.48
77.42
77.00
76.58
53.69
40.01
29.15
22.79
22.53
ppm

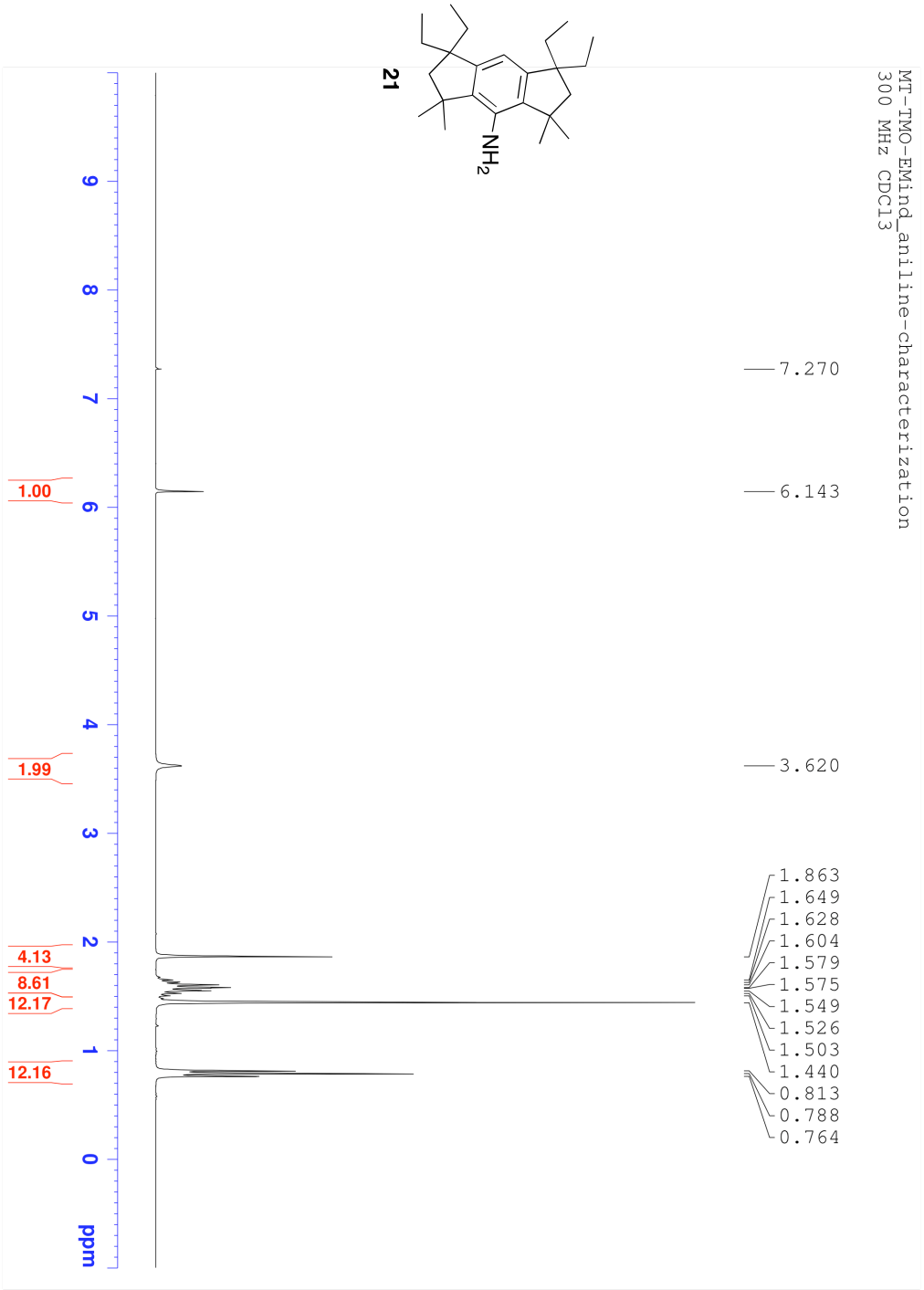

7.260
6.778
1.0
4.0
9.0
12.2
12.3
δ/ppm
1.911
1.714
1.695
1.676
1.660
1.641
1.627
1.623
1.608
1.590
1.574
1.555
1.537
1.320
0.813
0.794
0.775
-0.001
Comment
1
ObsNuc
1H
ExMode
single_pulse.ex2
ObsFreq
399.78 MHz
ObsSet
2.0 kHz
ObsFine
199.599 Hz
Point
16384
Frequecy(Span)
7503.001 Hz
Scan
8
AcqTime
2.1837 s
PD
2.0 s
Pulse1
4.925 µs
IrrNuc
1H
ProbeHead
Instrument
EOS 400
Pulse Program
Gradient Program
Temperature
24.5 °C
Solvent
CHLOROFORM-D
Reference
5.0125 ppm
Broad.Factor
0.25 Hz
Window
Exponential
RGain
36
Operator
EMindNO2
NO2

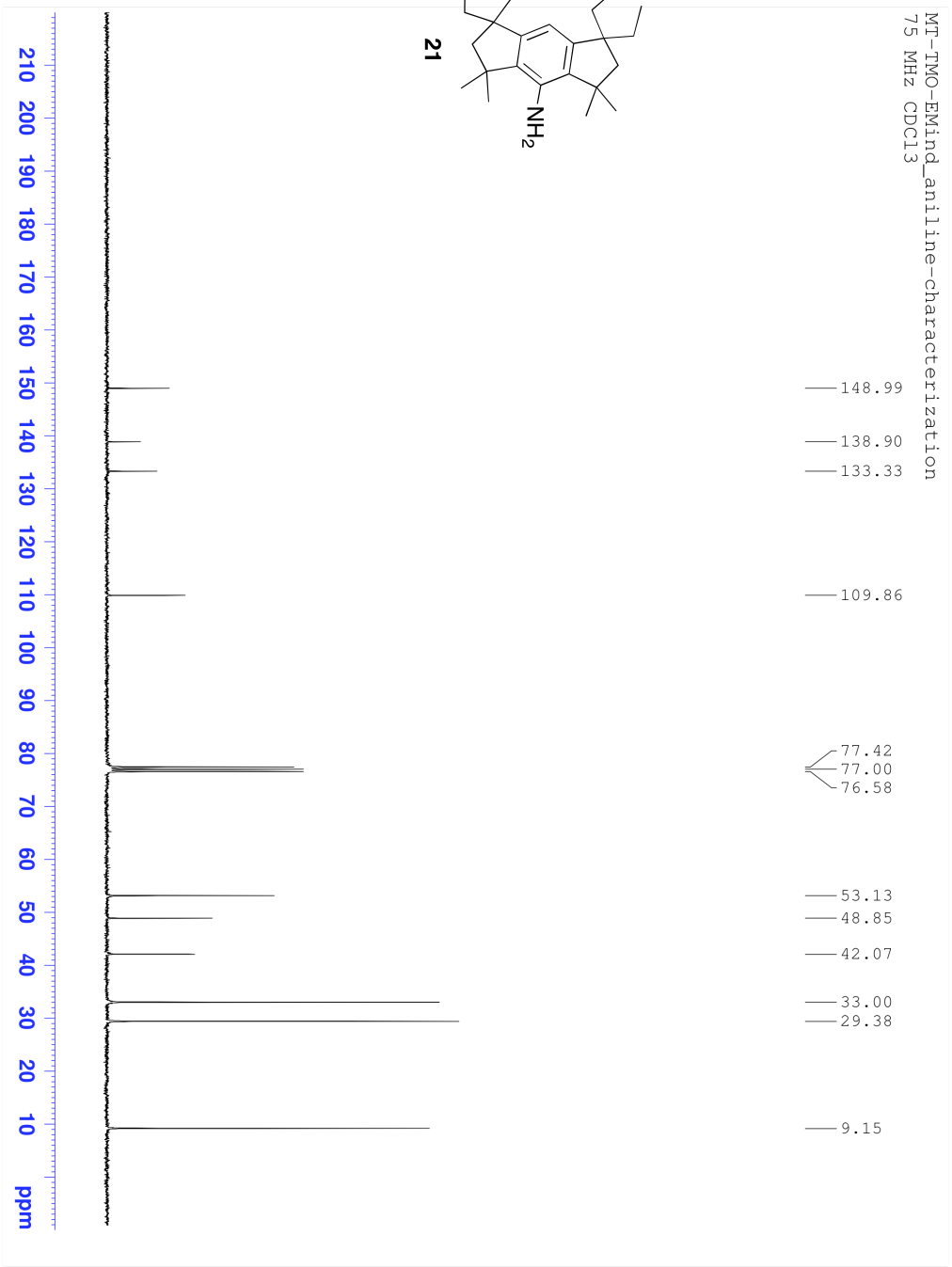
S6

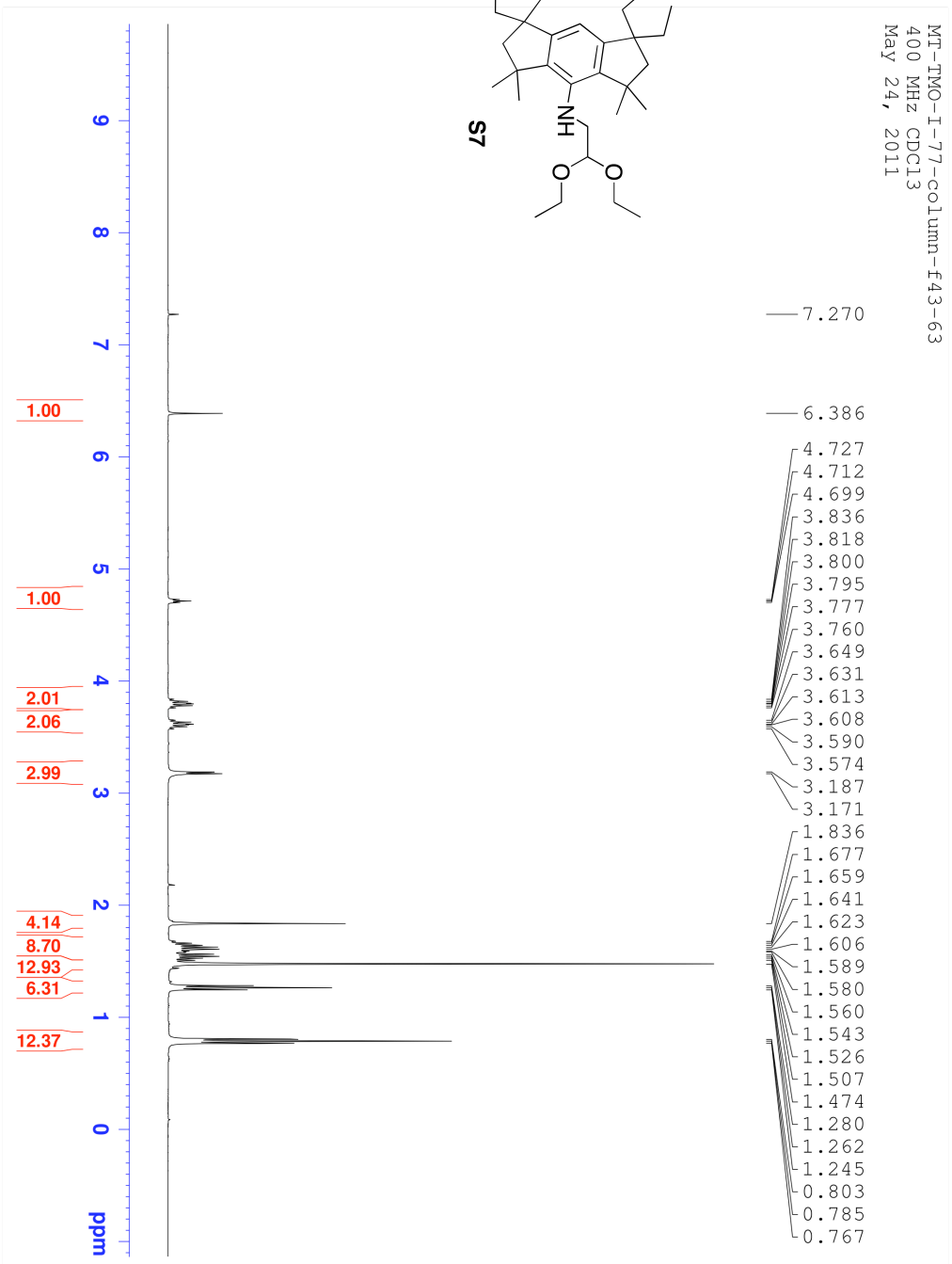

150.966
145.341
138.739
121.475
77.317
77.000
76.683
53.020
48.497
43.050
32.458
30.032
9.031
δ/ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
NO2
Comment 1
ObsNuc 13C
ExMode single_pulse_dec
ObsFreq 100.53 MHz
ObsSet -5.0 kHz
ObsFine 313.4318 Hz
Point 26224
Frequecy(Span) 25124.29 Hz
Scan 204
AcqTime 1.0438 s
PD 2.0 s
Pulse1 2.75 µs
IrrNuc 1H
ProbeHeaD
Instrument EOS 400
Pulse Program
Gradient Program
Temperature 24.6 ℃
Solvent CHLOROFORM-D
Reference 77.0 ppm
Broad Factor 0.25 Hz
Window Exponential
RGain 50
Operator

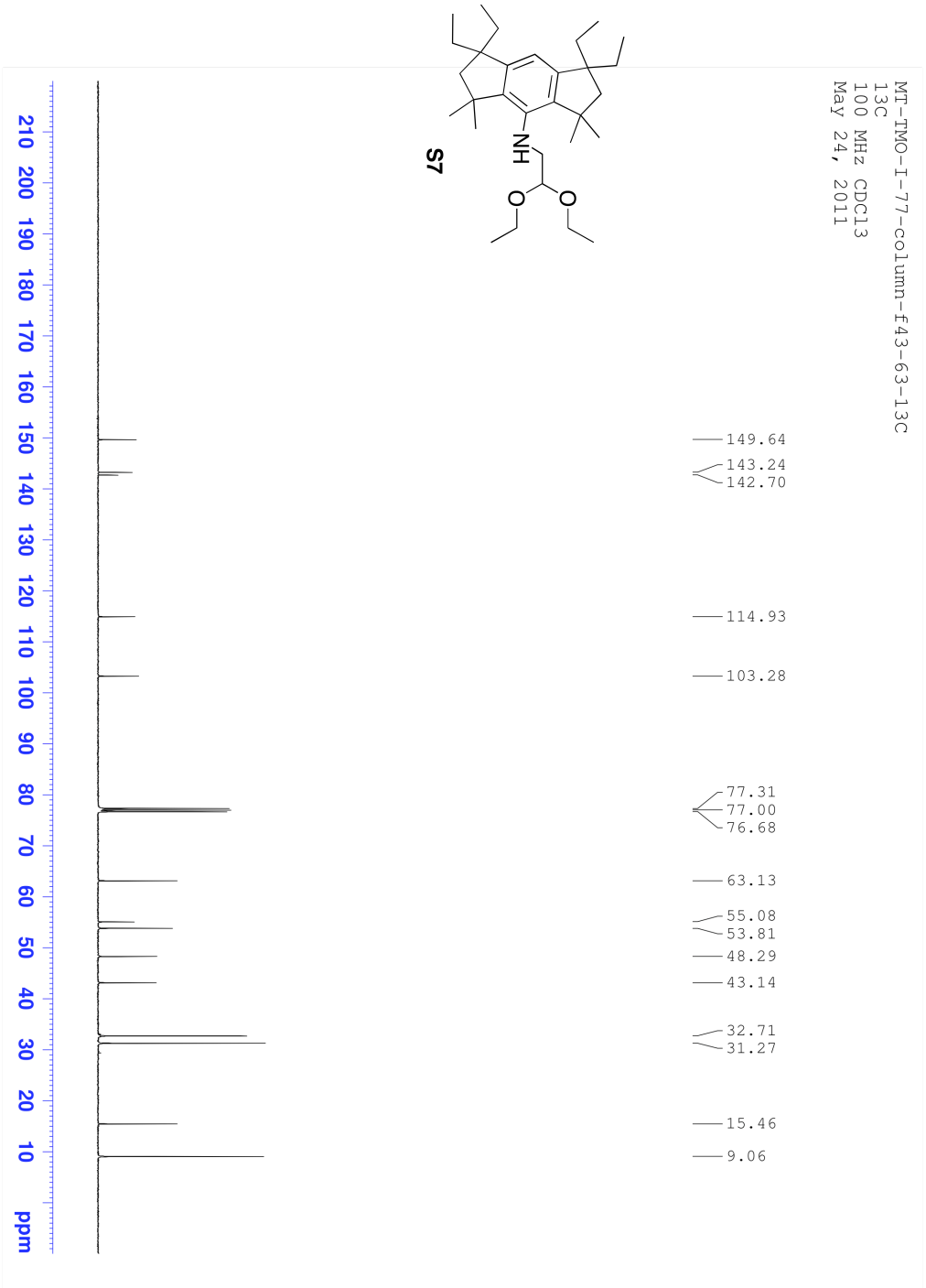
S6

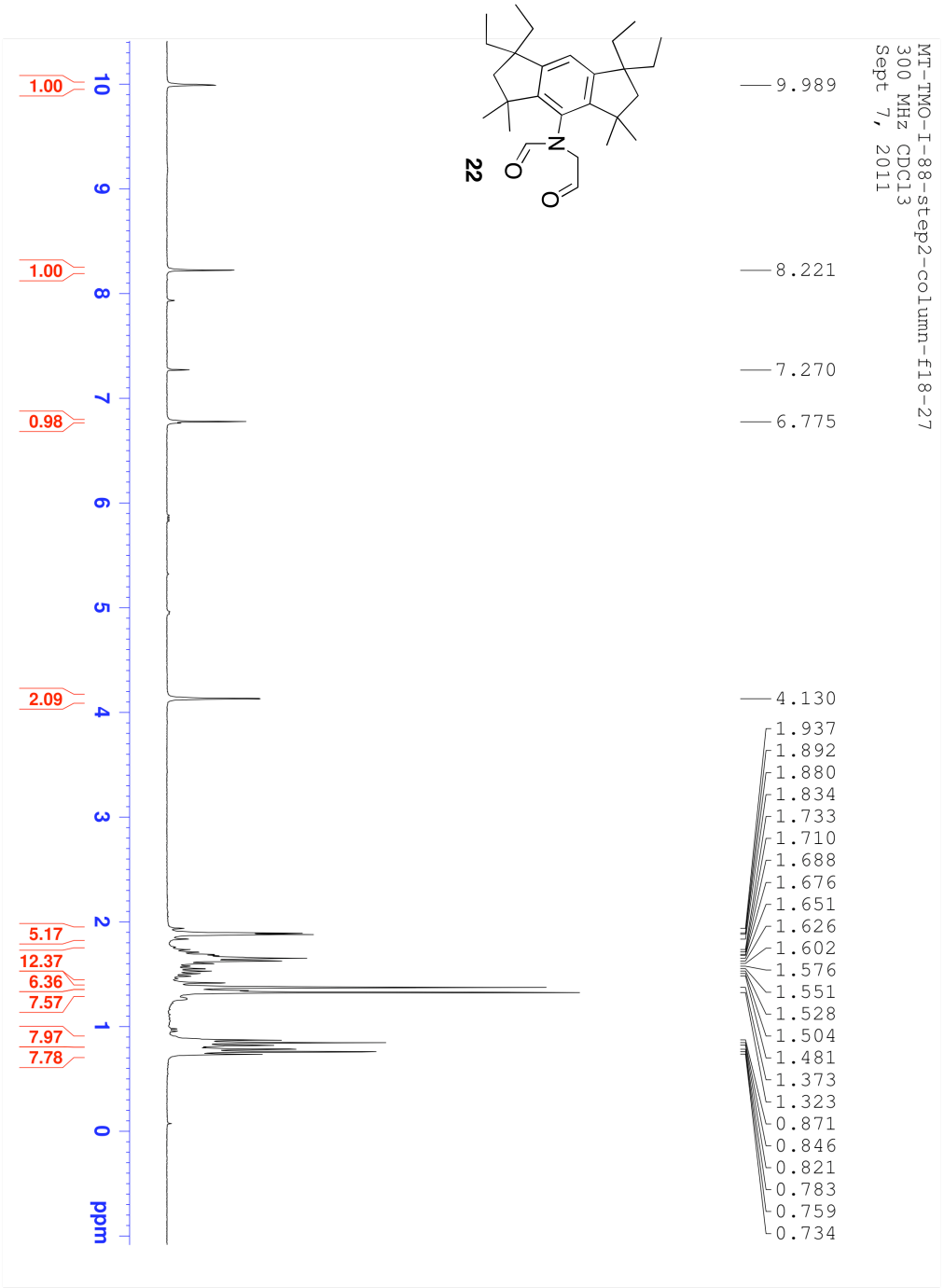
EMindNO2

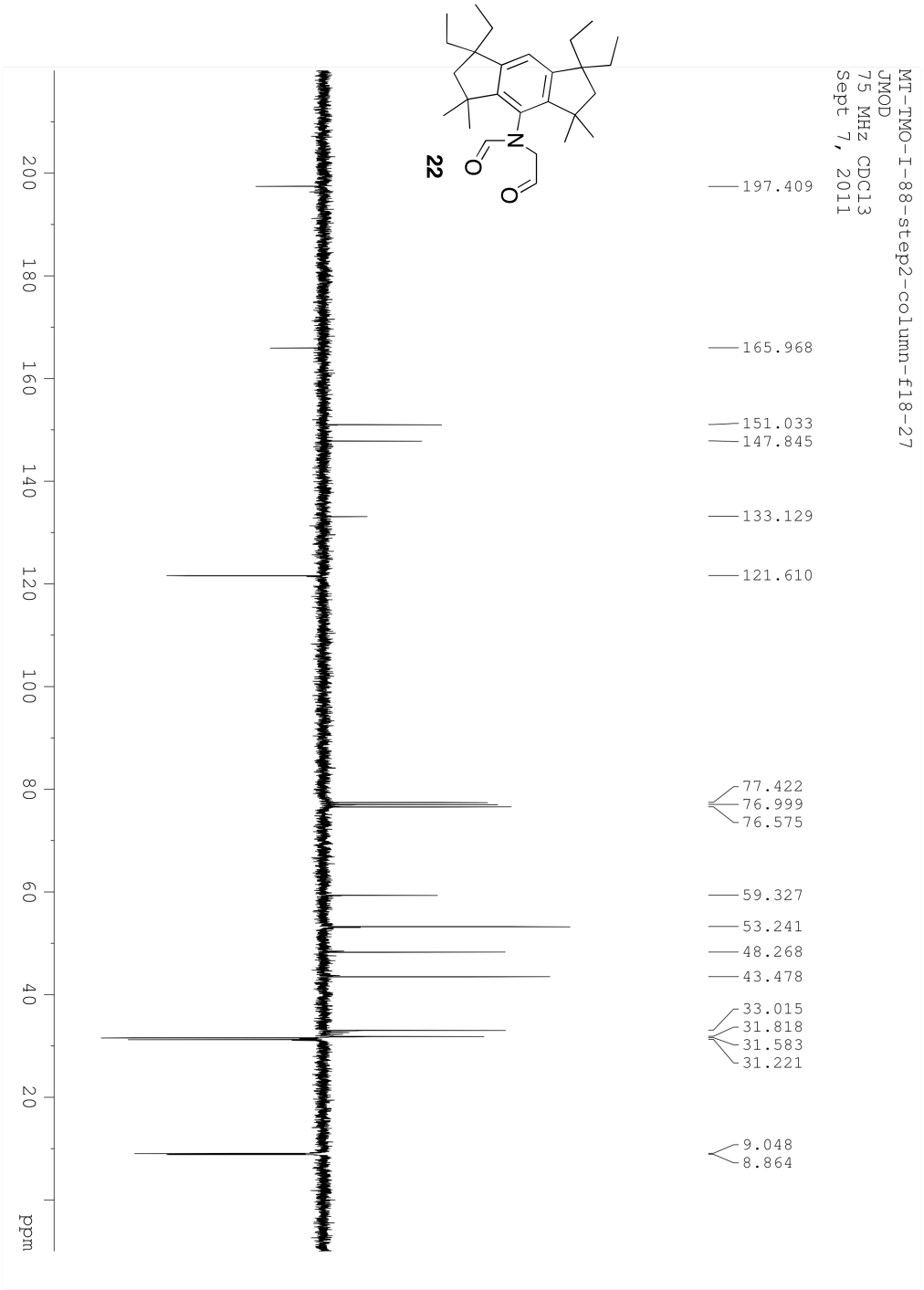

21
NH2
MT-TMO-EMind_aniline-characterization
300 MHz CDCl3
7.270
6.143
3.620
1.863
1.649
1.628
1.604
1.579
1.575
1.549
1.526
1.503
1.440
0.813
0.788
0.764
1.00
1.99
4.13
8.61
12.17
12.16
ppm

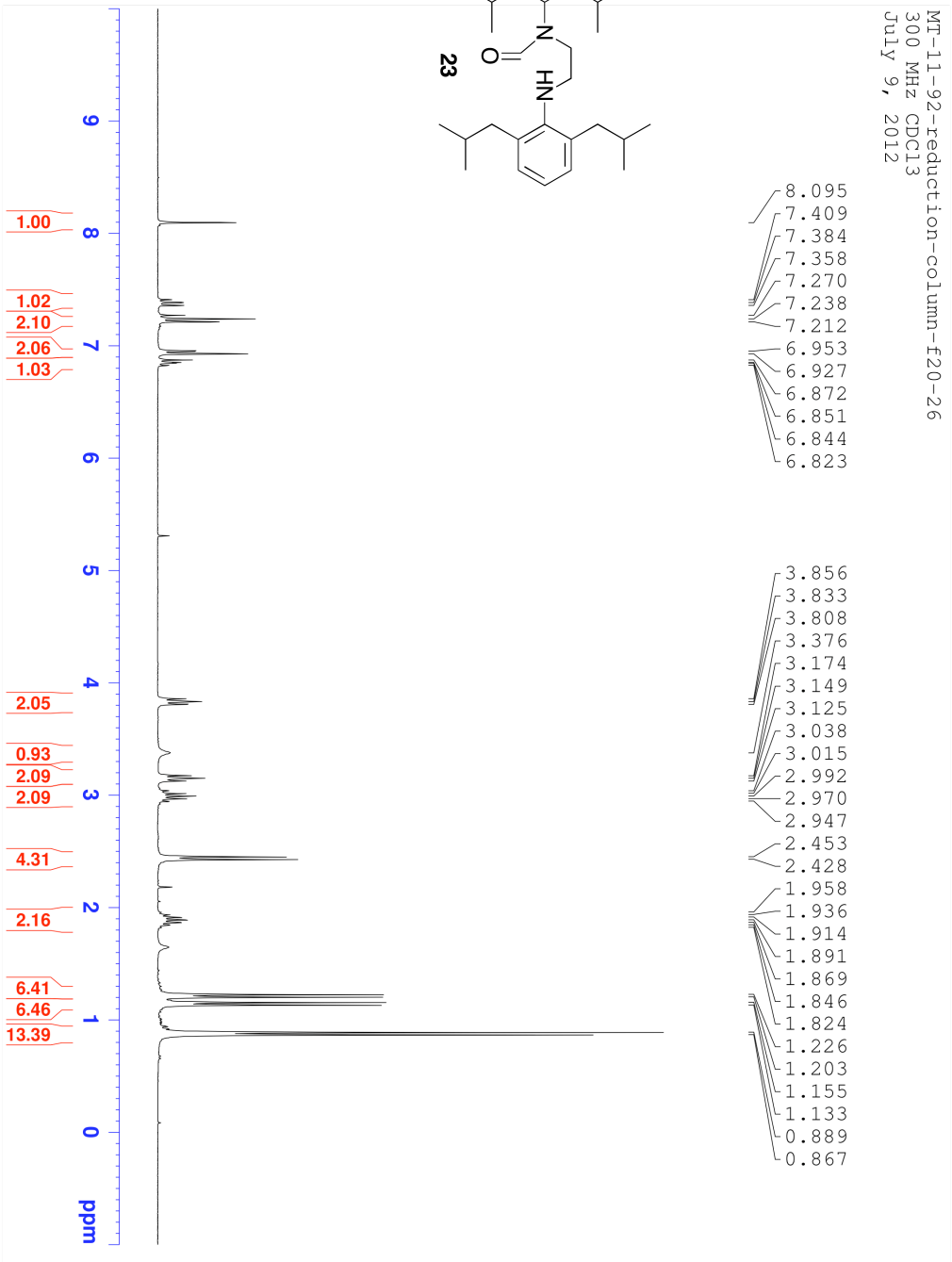

MT-TMO-EMind_aniline-characterization
75 MHz CDCl3
21
NH2
148.99
138.90
133.33
109.86
77.42
77.00
76.58
53.13
48.85
42.07
33.00
29.38
9.15
ppm

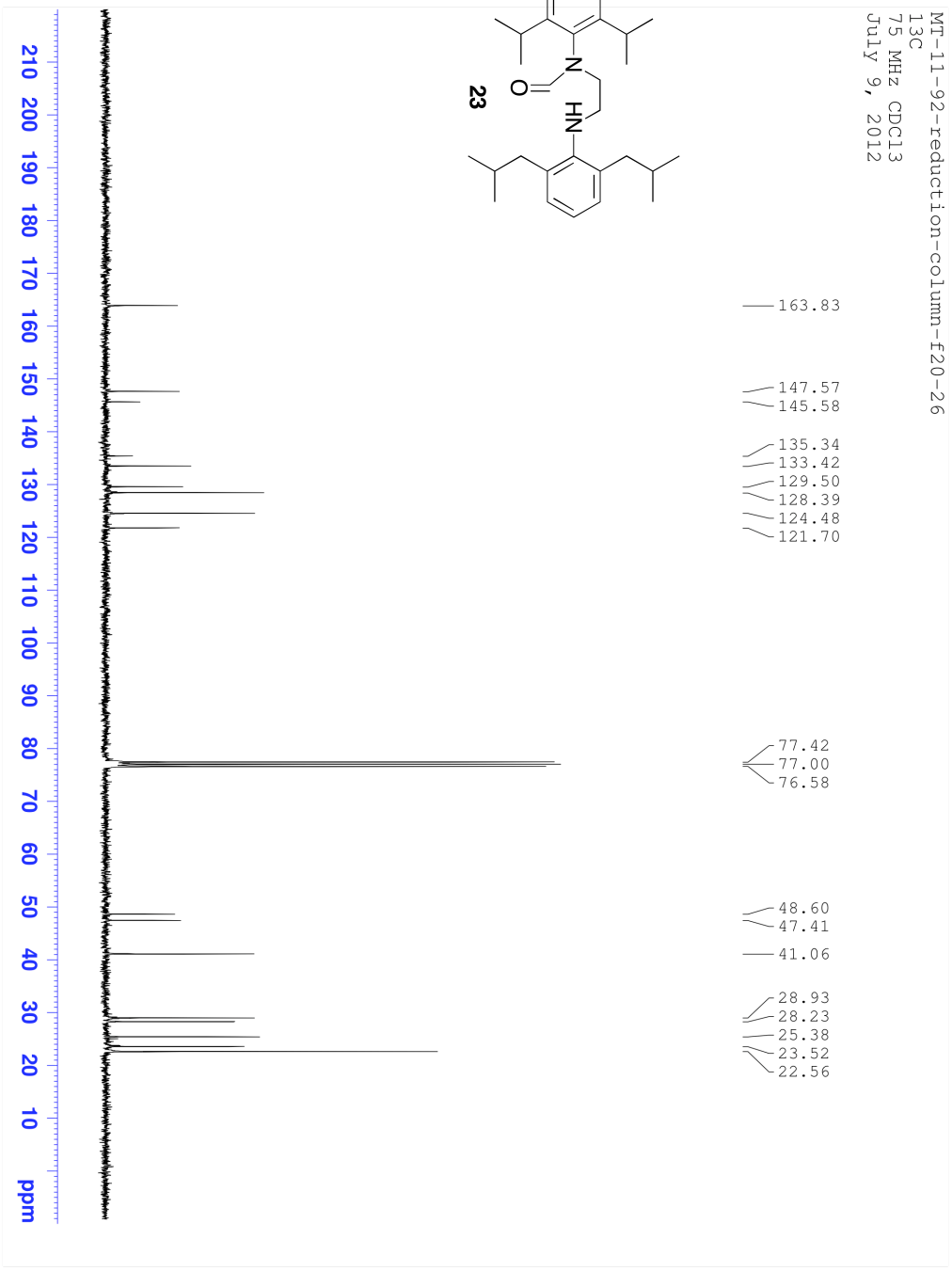

MT-TMO-I-77-column-f43-63
400 MHz CDCl3
May 24, 2011
S7
NH
O
O
7.270
6.386
4.727
4.712
4.699
3.836
3.818
3.800
3.795
3.777
3.760
3.649
3.631
3.613
3.608
3.590
3.574
3.187
3.171
1.836
1.677
1.659
1.641
1.623
1.606
1.589
1.580
1.560
1.543
1.526
1.507
1.474
1.280
1.262
1.245
0.803
0.785
0.767
1.00
1.00
2.01
2.06
2.99
4.14
8.70
12.93
6.31
12.37
ppm

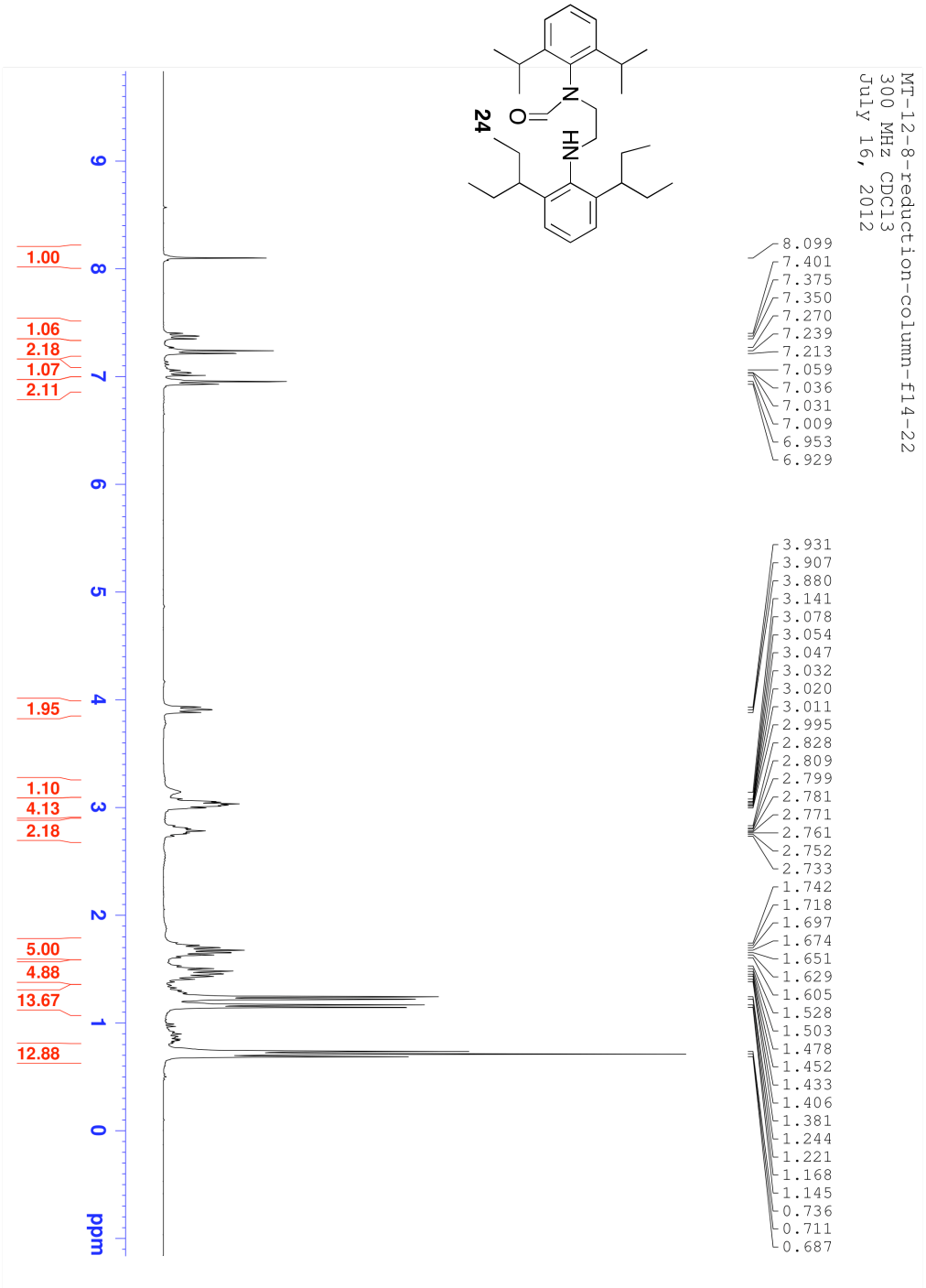

MT-TMO-I-77-column-f43-63-13C
13C
100 MHz CDCl3
May 24, 2011
S7
NH
O
O
149.64
143.24
142.70
114.93
103.28
77.31
77.00
76.68
63.13
55.08
53.81
48.29
43.14
32.71
31.27
15.46
9.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

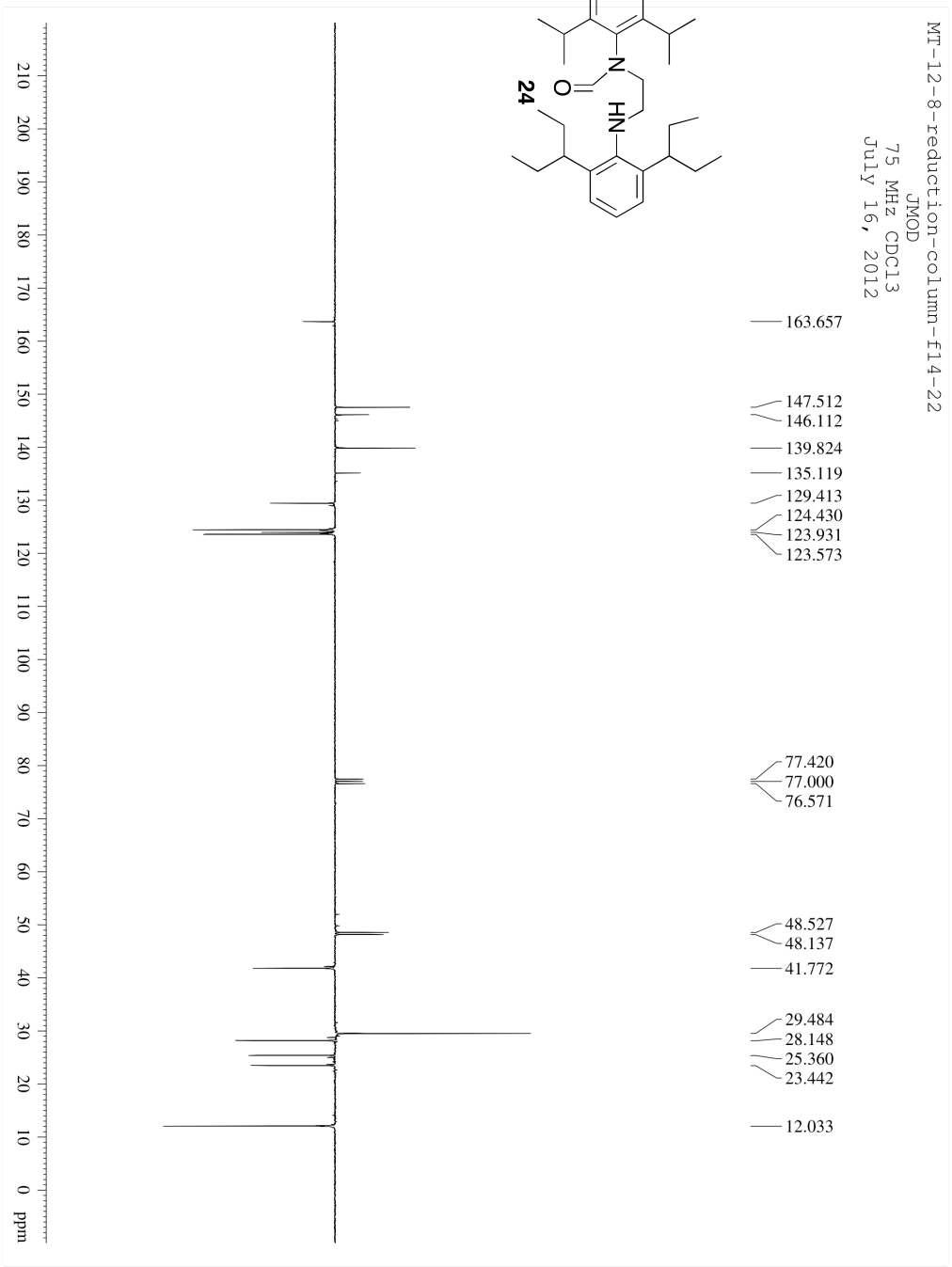

MT-TMO-I-88-step2-column-f18-27
300 MHz CDCl3
Sept 7, 2011
22
9.989
8.221
7.270
6.775
4.130
1.937
1.892
1.880
1.834
1.733
1.710
1.688
1.676
1.651
1.626
1.602
1.576
1.551
1.528
1.504
1.481
1.373
1.323
0.871
0.846
0.821
0.783
0.759
0.734
1.00
1.00
0.98
2.09
5.17
12.37
6.36
7.57
7.97
7.78
ppm

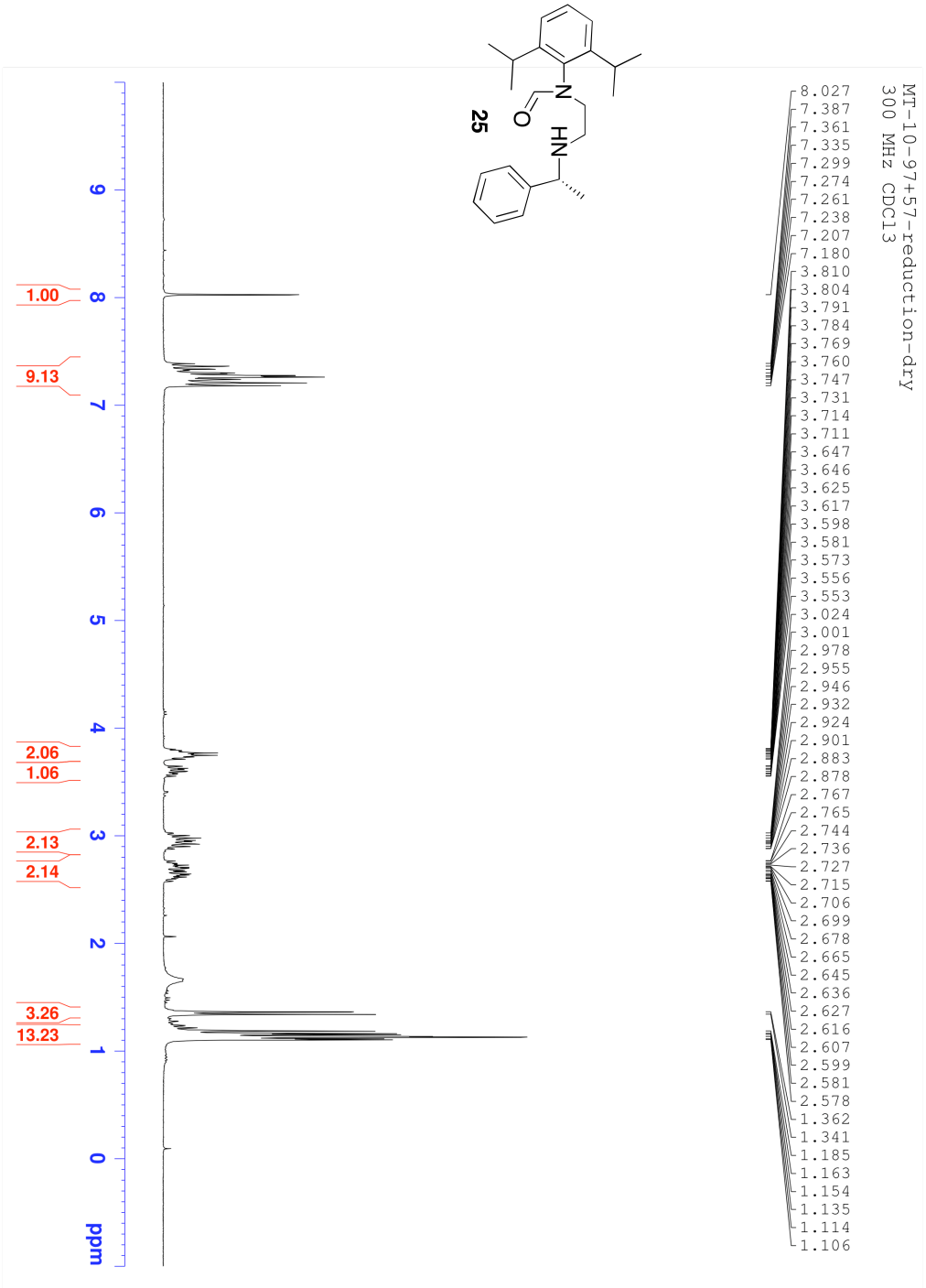

MT-TMO-I-88-step2-column-f18-27
JMOD
75 MHz CDCl3
Sept 7, 2011
22
197.409
165.968
151.033
147.845
133.129
121.610
77.422
76.999
76.575
59.327
53.241
48.268
43.478
33.015
31.818
31.583
31.221
9.048
8.864
200
180
160
140
120
100
80
60
40
20
ppm

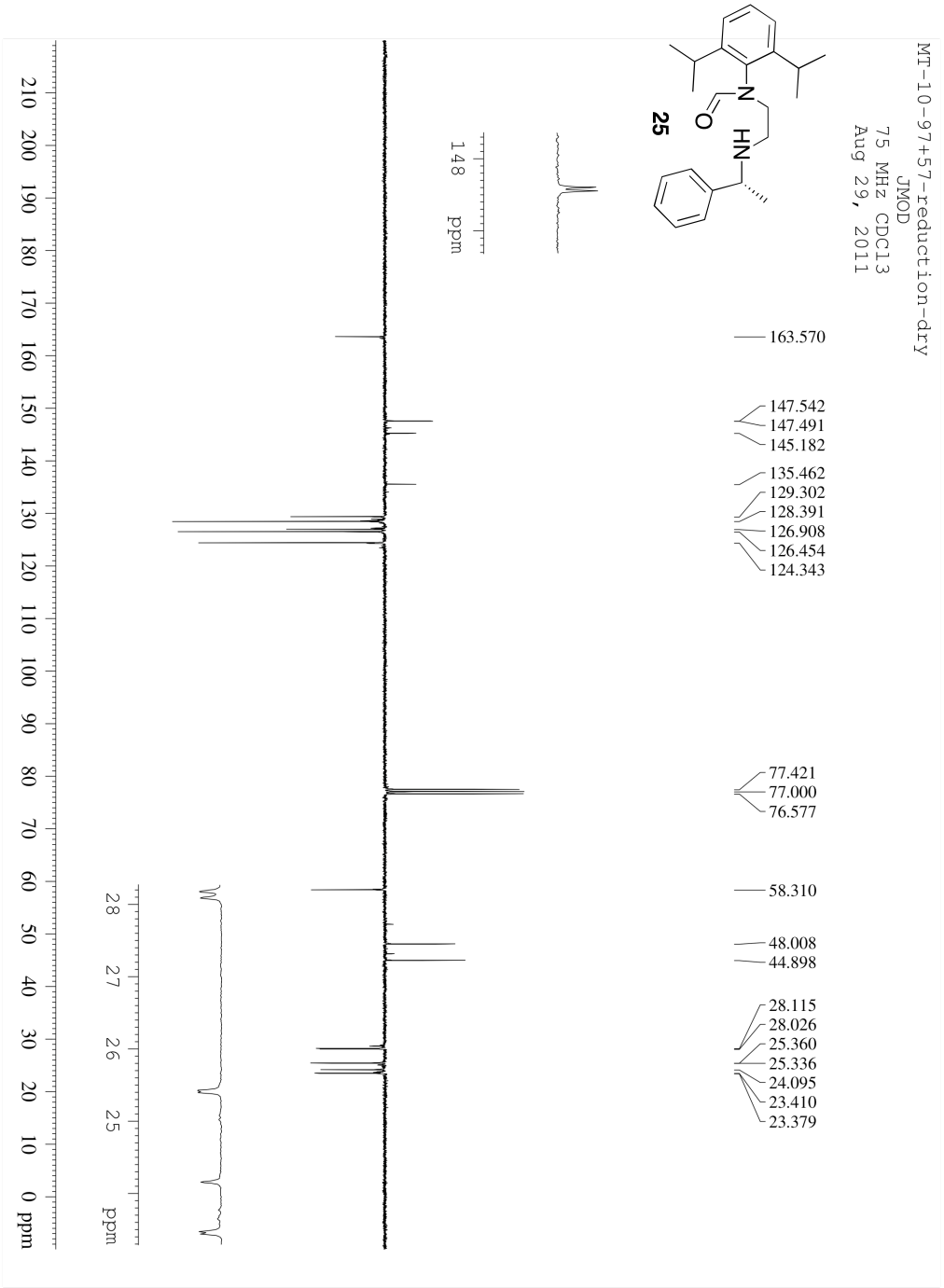

MT-11-92-reduction-column-f20-26
300 MHz CDCl3
July 9, 2012
23
O
N
NH
8.095
7.409
7.384
7.358
7.270
7.238
7.212
6.953
6.927
6.872
6.851
6.844
6.823
3.856
3.833
3.808
3.376
3.174
3.149
3.125
3.038
3.015
2.992
2.970
2.947
2.453
2.428
1.958
1.936
1.914
1.891
1.869
1.846
1.824
1.226
1.203
1.155
1.133
0.889
0.867
1.00
1.02
2.10
2.06
1.03
2.05
0.93
2.09
2.09
4.31
2.16
6.41
6.46
13.39
ppm

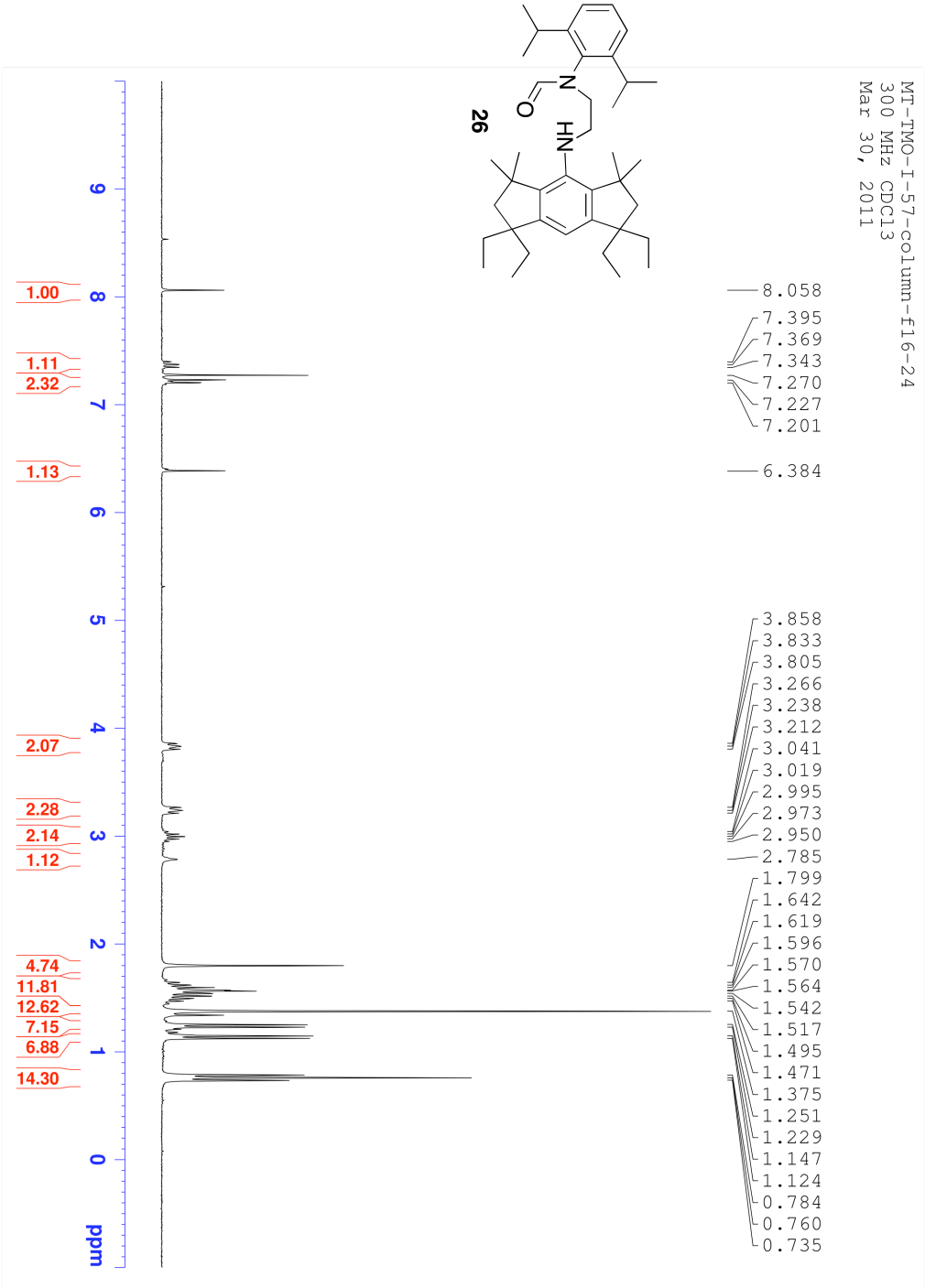

MT-11-92-reduction-column-f20-26
13C
75 MHz CDCl3
July 9, 2012
23
O
N
HN
163.83
147.57
145.58
135.34
133.42
129.50
128.39
124.48
121.70
77.42
77.00
76.58
48.60
47.41
41.06
28.93
28.23
25.38
23.52
22.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

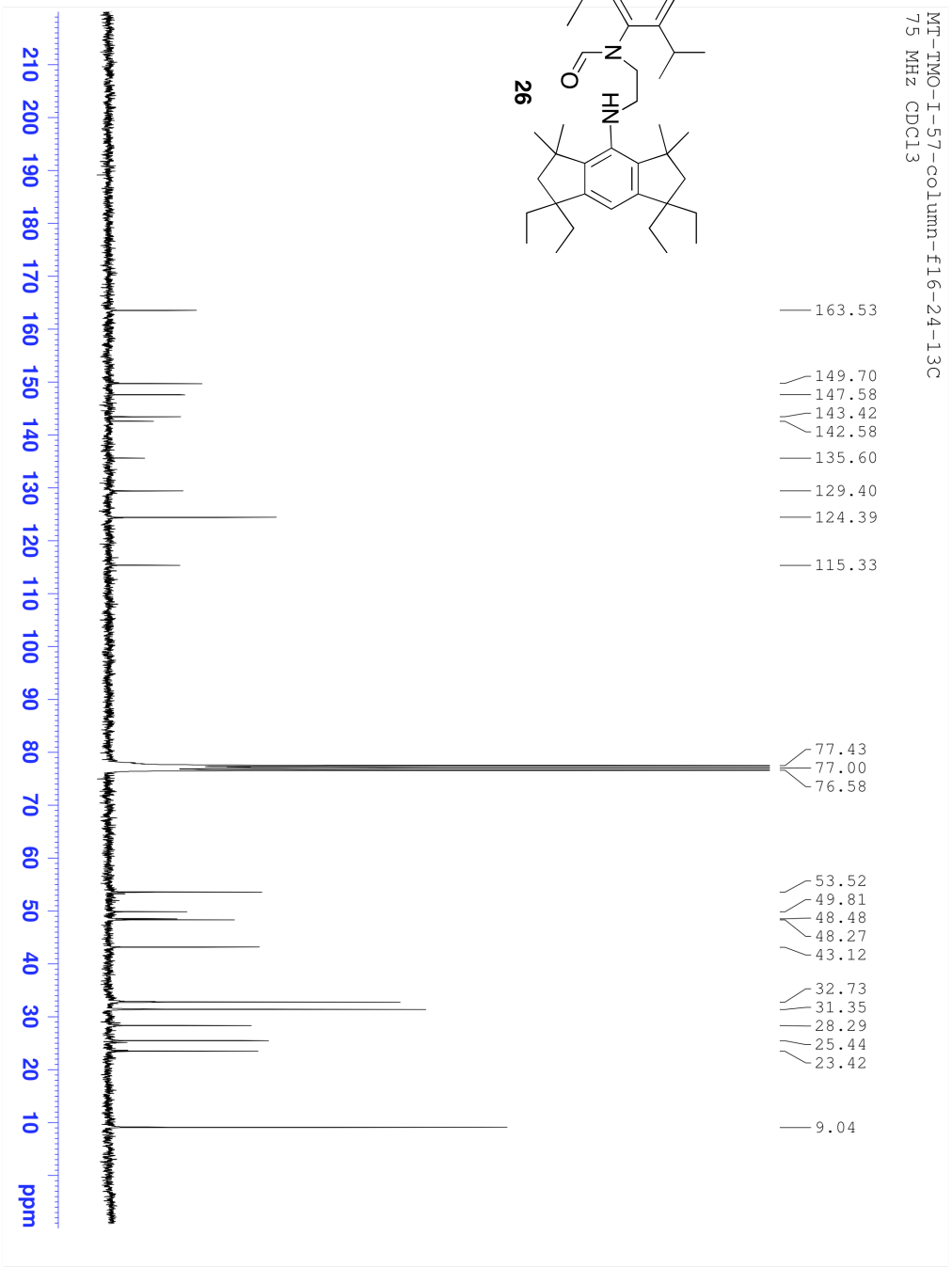

MT-12-8-reduction-column-f14-22
300 MHz CDCl3
July 16, 2012
24
N
O
HN
8.099
7.401
7.375
7.350
7.270
7.239
7.213
7.059
7.036
7.031
7.009
6.953
6.929
3.931
3.907
3.880
3.141
3.078
3.054
3.047
3.032
3.020
3.011
2.995
2.828
2.809
2.799
2.781
2.771
2.761
2.752
2.733
1.742
1.718
1.697
1.674
1.651
1.629
1.605
1.528
1.503
1.478
1.452
1.433
1.406
1.381
1.244
1.221
1.168
1.145
0.736
0.711
0.687
1.00
1.06
2.18
1.07
2.11
1.95
1.10
4.13
2.18
5.00
4.88
13.67
12.88
ppm

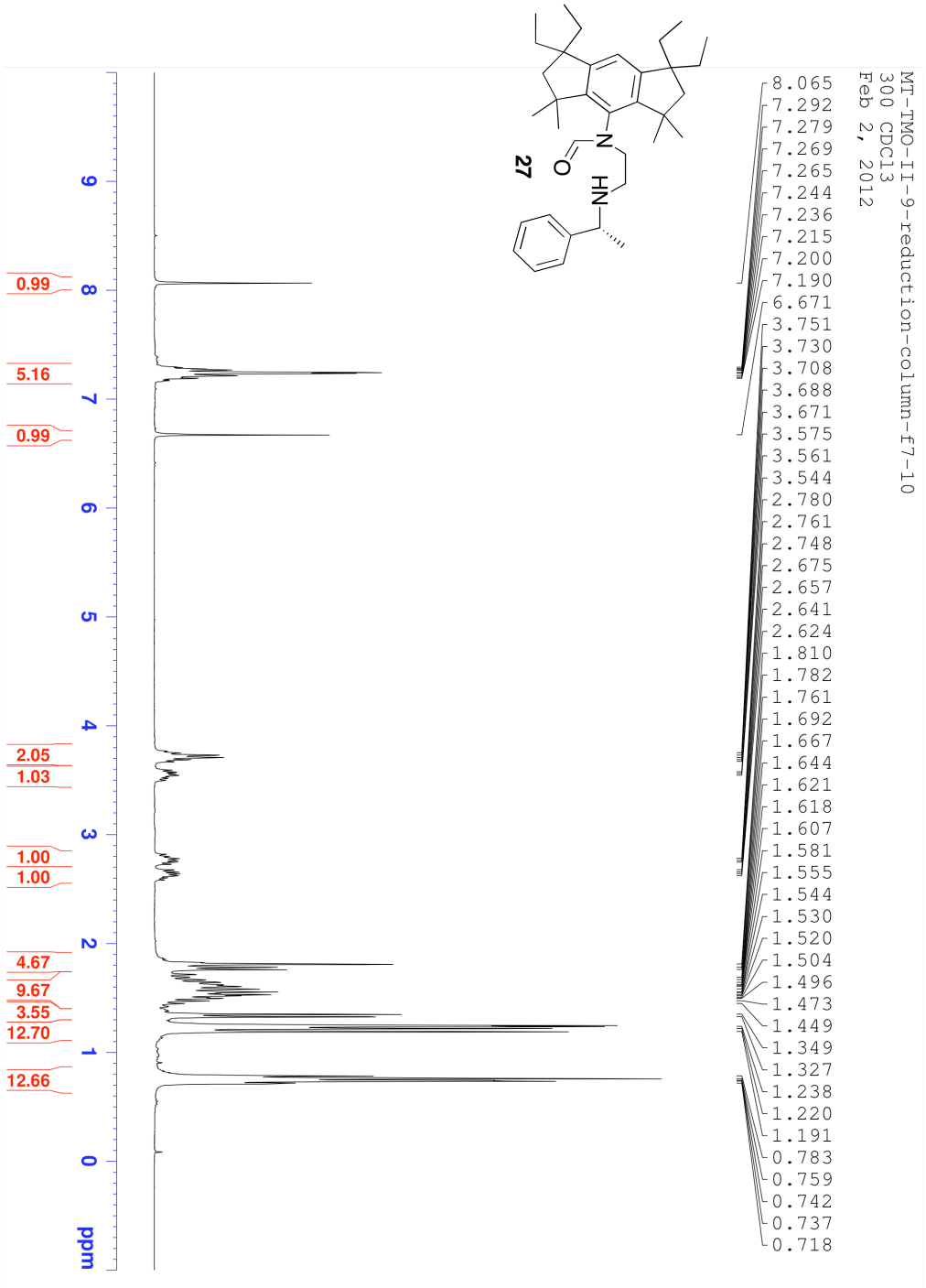

MT-12-8-reduction-column-f14-22
JMOD
75 MHz CDC13
July 16, 2012
24
163.657
147.512
146.112
139.824
135.119
129.413
124.430
123.931
123.573
77.420
77.000
76.571
48.527
48.137
41.772
29.484
28.148
25.360
23.442
12.033
ppm

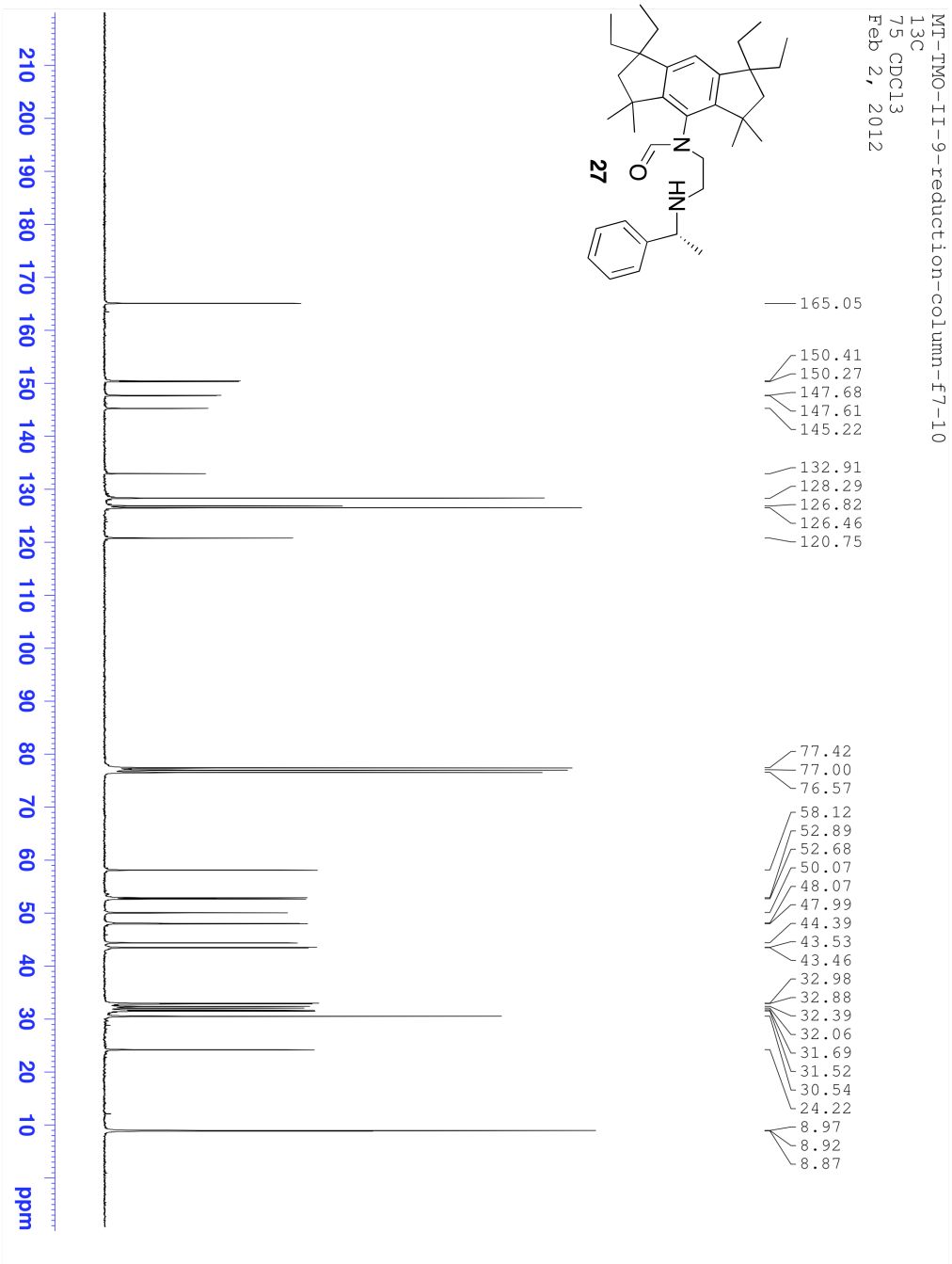

25
N
O
HN
MT-10-97+57-reduction-dry
300 MHz CDCl3
8.027
7.387
7.361
7.335
7.299
7.274
7.261
7.238
7.207
7.180
3.810
3.804
3.791
3.784
3.769
3.760
3.747
3.731
3.714
3.711
3.647
3.646
3.625
3.617
3.598
3.581
3.573
3.556
3.553
3.024
3.001
2.978
2.955
2.946
2.932
2.924
2.901
2.883
2.878
2.767
2.765
2.744
2.736
2.727
2.715
2.706
2.699
2.678
2.665
2.645
2.636
2.627
2.616
2.607
2.599
2.581
2.578
1.362
1.341
1.185
1.163
1.154
1.135
1.114
1.106
1.00
9.13
2.06
1.06
2.13
2.14
3.26
13.23
9
8
7
6
5
4
3
2
1
0
ppm

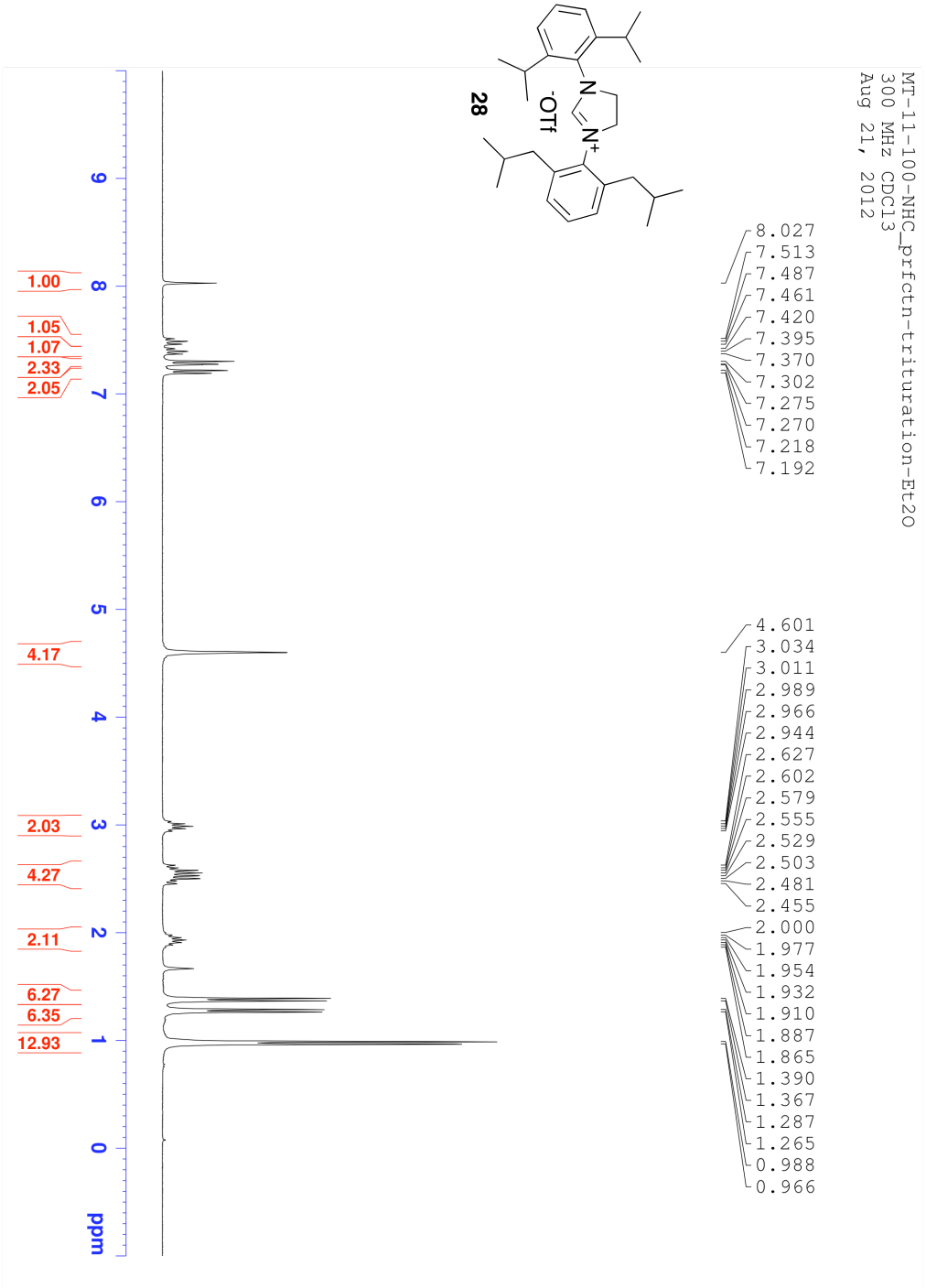

MT-10-97+57-reduction-dry
JMOD
75 MHz CDCl3
Aug 29, 2011
25
163.570
147.542
147.491
145.182
135.462
129.302
128.391
126.908
126.454
124.343
77.421
77.000
76.577
58.310
48.008
44.898
28.115
28.026
25.360
25.336
24.095
23.410
23.379
148 ppm
28 27 26 25 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

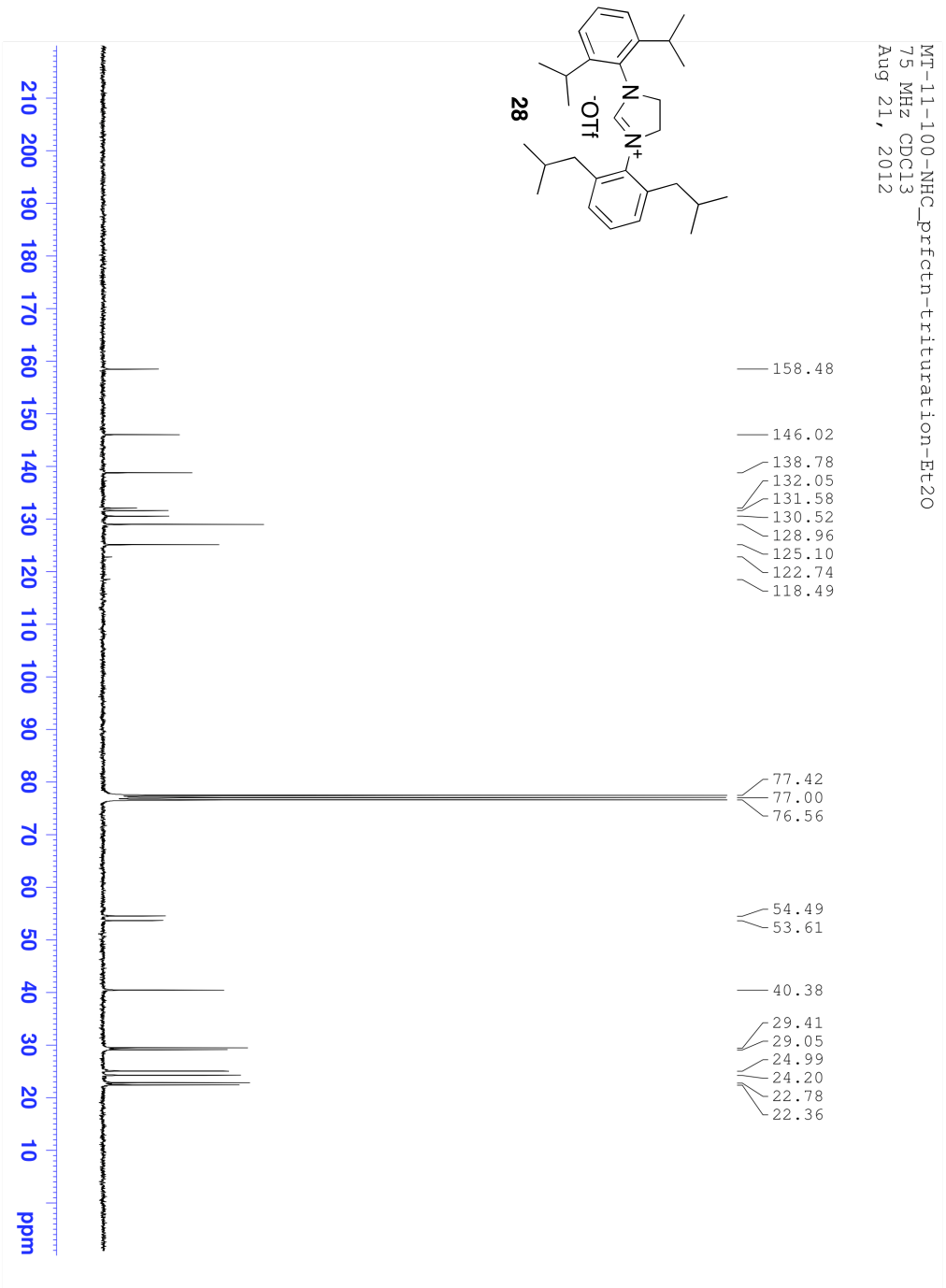

MT-TMO-I-57-column-f16-24
300 MHz CDCl3
Mar 30, 2011
26
N
O
HN
8.058
7.395
7.369
7.343
7.270
7.227
7.201
6.384
3.858
3.833
3.805
3.266
3.238
3.212
3.041
3.019
2.995
2.973
2.950
2.785
1.799
1.642
1.619
1.596
1.570
1.564
1.542
1.517
1.495
1.471
1.375
1.251
1.229
1.147
1.124
0.784
0.760
0.735
1.00
1.11
2.32
1.13
2.07
2.28
2.14
1.12
4.74
11.81
12.62
7.15
6.88
14.30
ppm

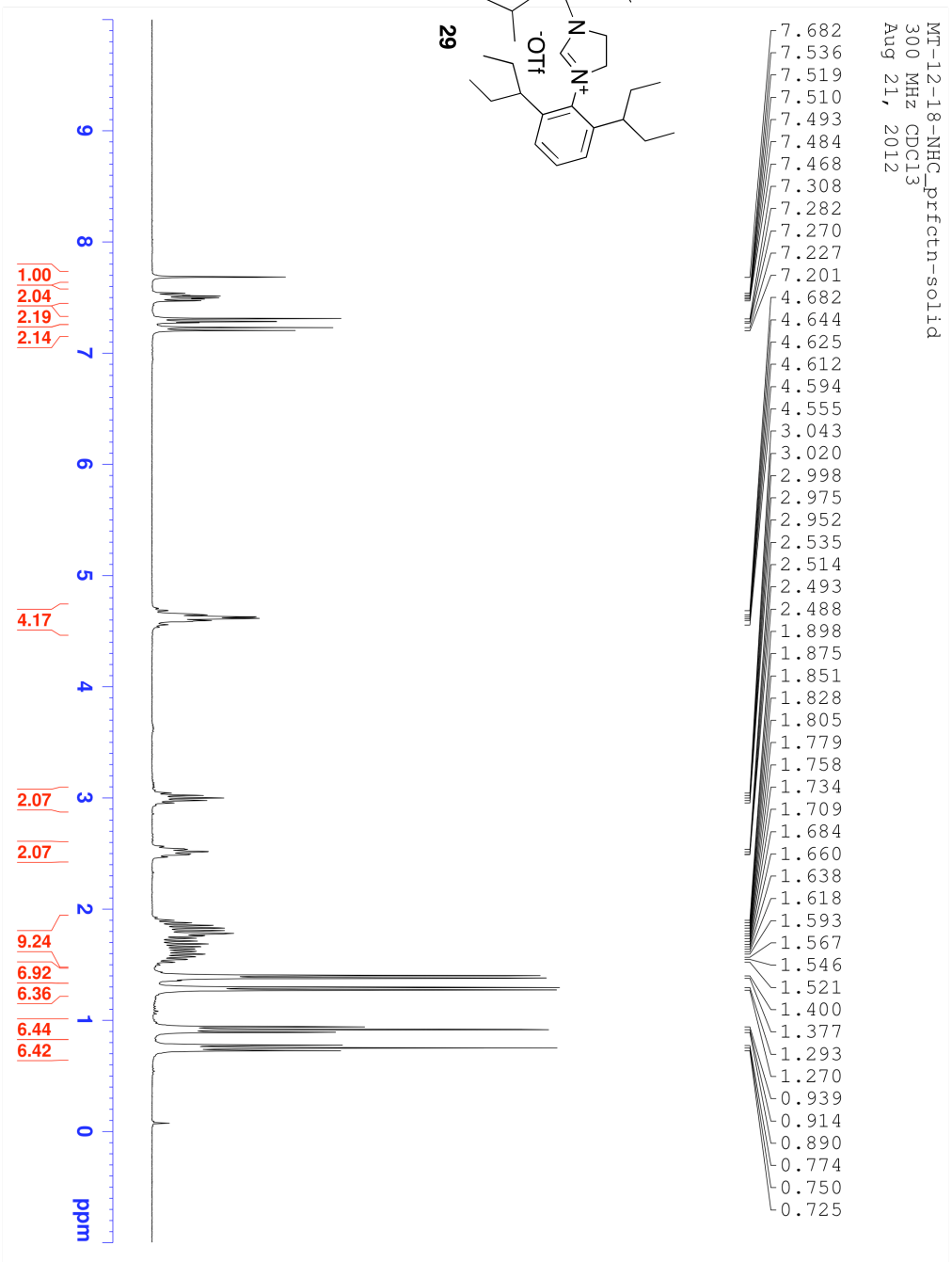

MT-TMO-I-57-column-fi6-24-13C
75 MHz CDCl3
26
N
O
HN
163.53
149.70
147.58
143.42
142.58
135.60
129.40
124.39
115.33
77.43
77.00
76.58
53.52
49.81
48.48
48.27
43.12
32.73
31.35
28.29
25.44
23.42
9.04
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

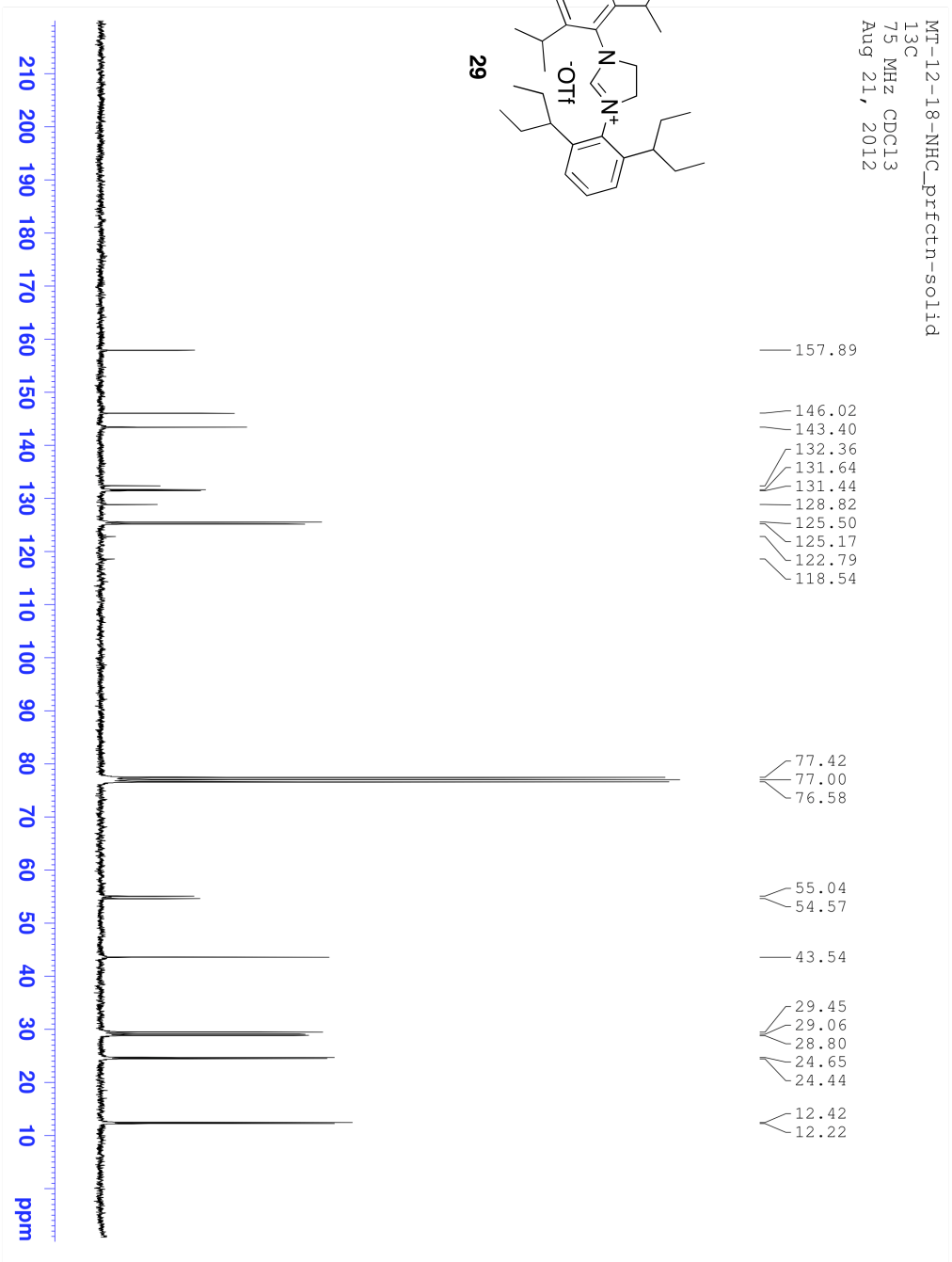

MT-TMO-II-9-reduction-column-f7-10
300 CDC13
Feb 2, 2012
8.065
7.292
7.279
7.269
7.265
7.244
7.236
7.215
7.200
7.190
6.671
3.751
3.730
3.708
3.688
3.671
3.575
3.561
3.544
2.780
2.761
2.748
2.675
2.657
2.641
2.624
1.810
1.782
1.761
1.692
1.667
1.644
1.621
1.618
1.607
1.581
1.555
1.544
1.530
1.520
1.504
1.496
1.473
1.449
1.349
1.327
1.238
1.220
1.191
0.783
0.759
0.742
0.737
0.718
27
N
O
HN
0.99
5.16
0.99
2.05
1.03
1.00
1.00
4.67
9.67
3.55
12.70
12.66
ppm

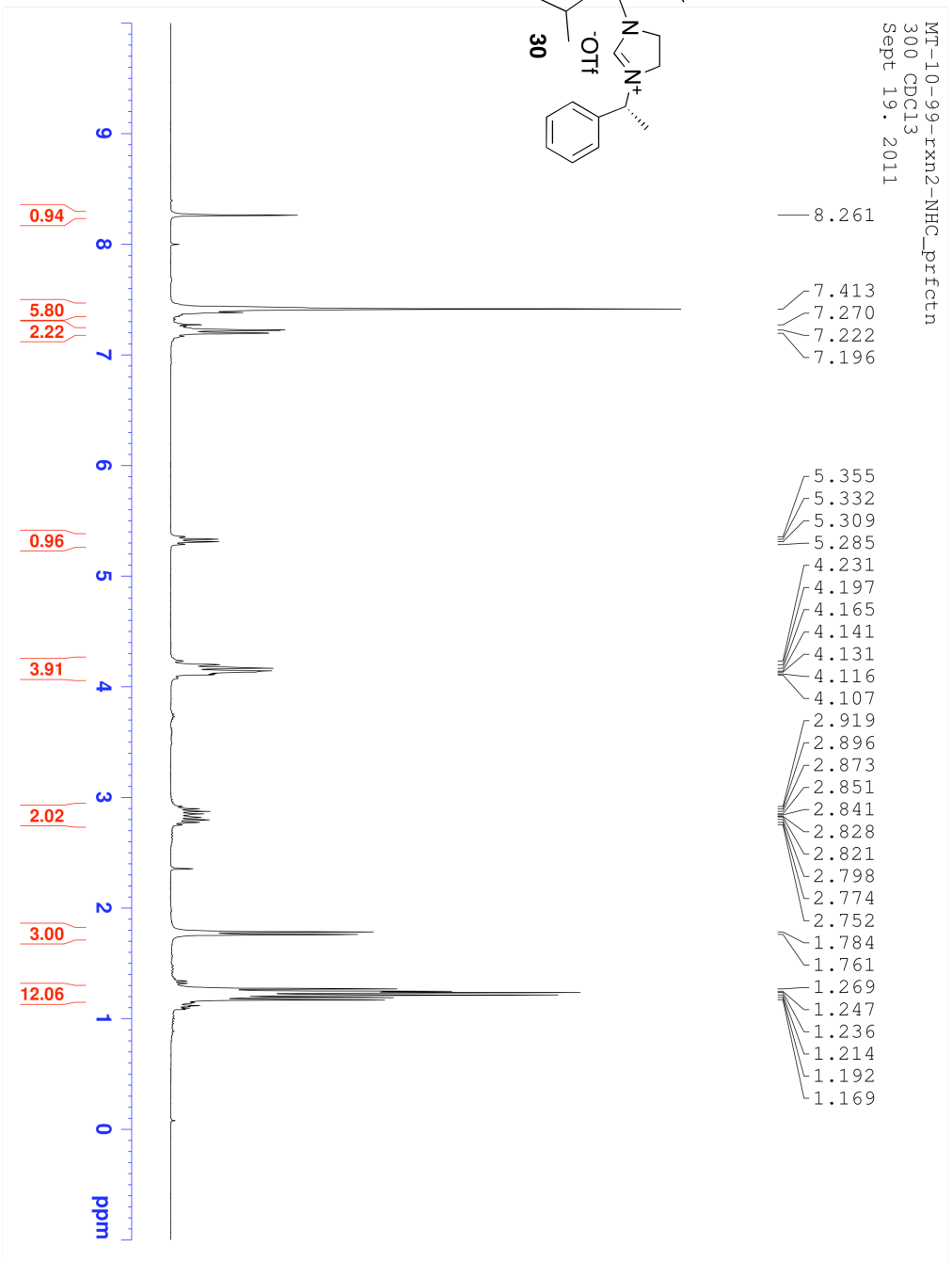

MT-TMO-II-9-reduction-column-f7-10
13C
75 CDCl3
Feb 2, 2012
27
N
O
HN
165.05
150.41
150.27
147.68
147.61
145.22
132.91
128.29
126.82
126.46
120.75
77.42
77.00
76.57
58.12
52.89
52.68
50.07
48.07
47.99
44.39
43.53
43.46
32.98
32.88
32.39
32.06
31.69
31.52
30.54
24.22
8.97
8.92
8.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

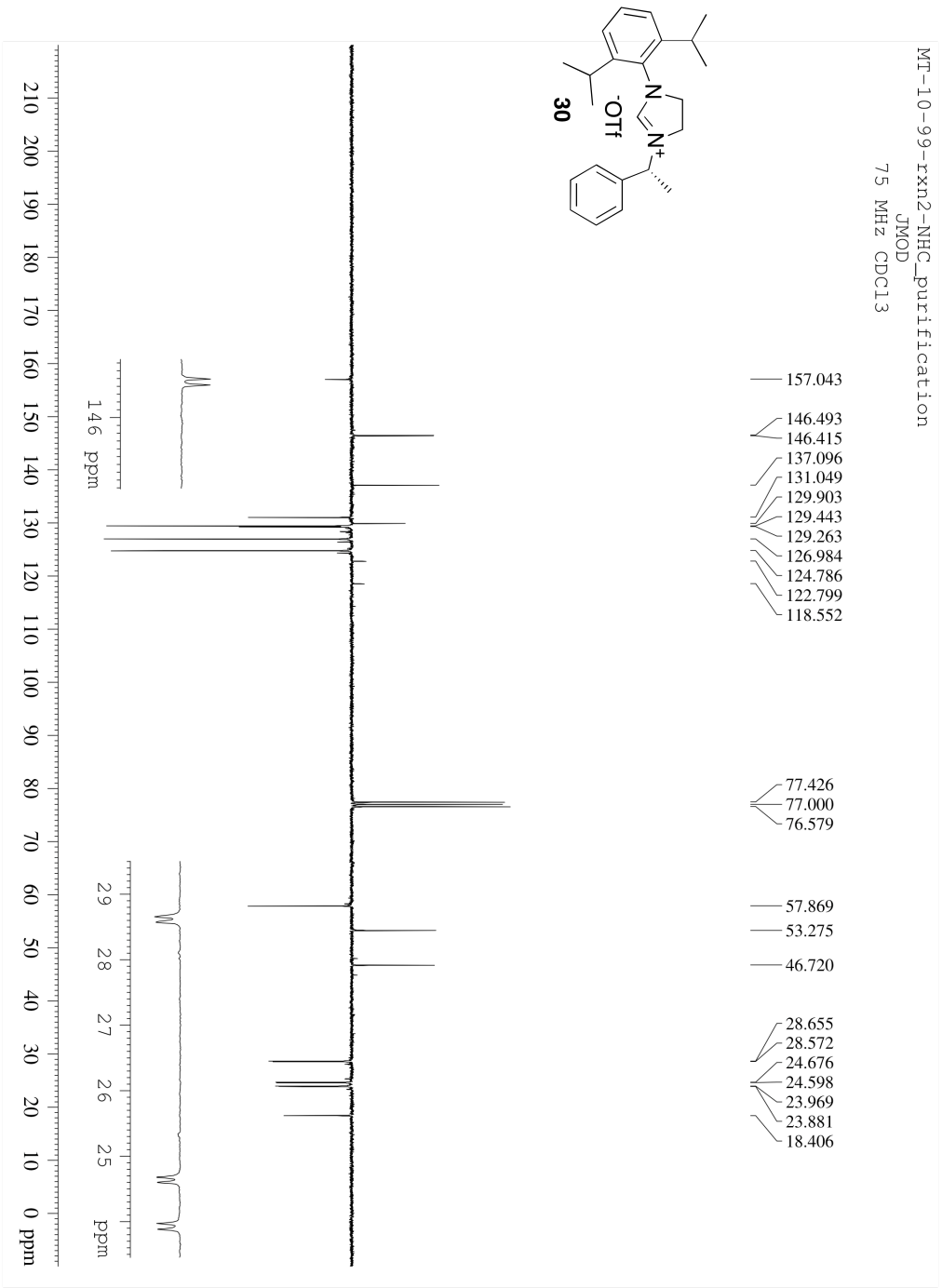

MT-11-100-NHC_prfctn-trituration-Et2O
300 MHz CDCl3
Aug 21, 2012
28
-OTf
8.027
7.513
7.487
7.461
7.420
7.395
7.370
7.302
7.275
7.270
7.218
7.192
4.601
3.034
3.011
2.989
2.966
2.944
2.627
2.602
2.579
2.555
2.529
2.503
2.481
2.455
2.000
1.977
1.954
1.932
1.910
1.887
1.865
1.390
1.367
1.287
1.265
0.988
0.966
1.00
1.05
1.07
2.33
2.05
4.17
2.03
4.27
2.11
6.27
6.35
12.93
ppm

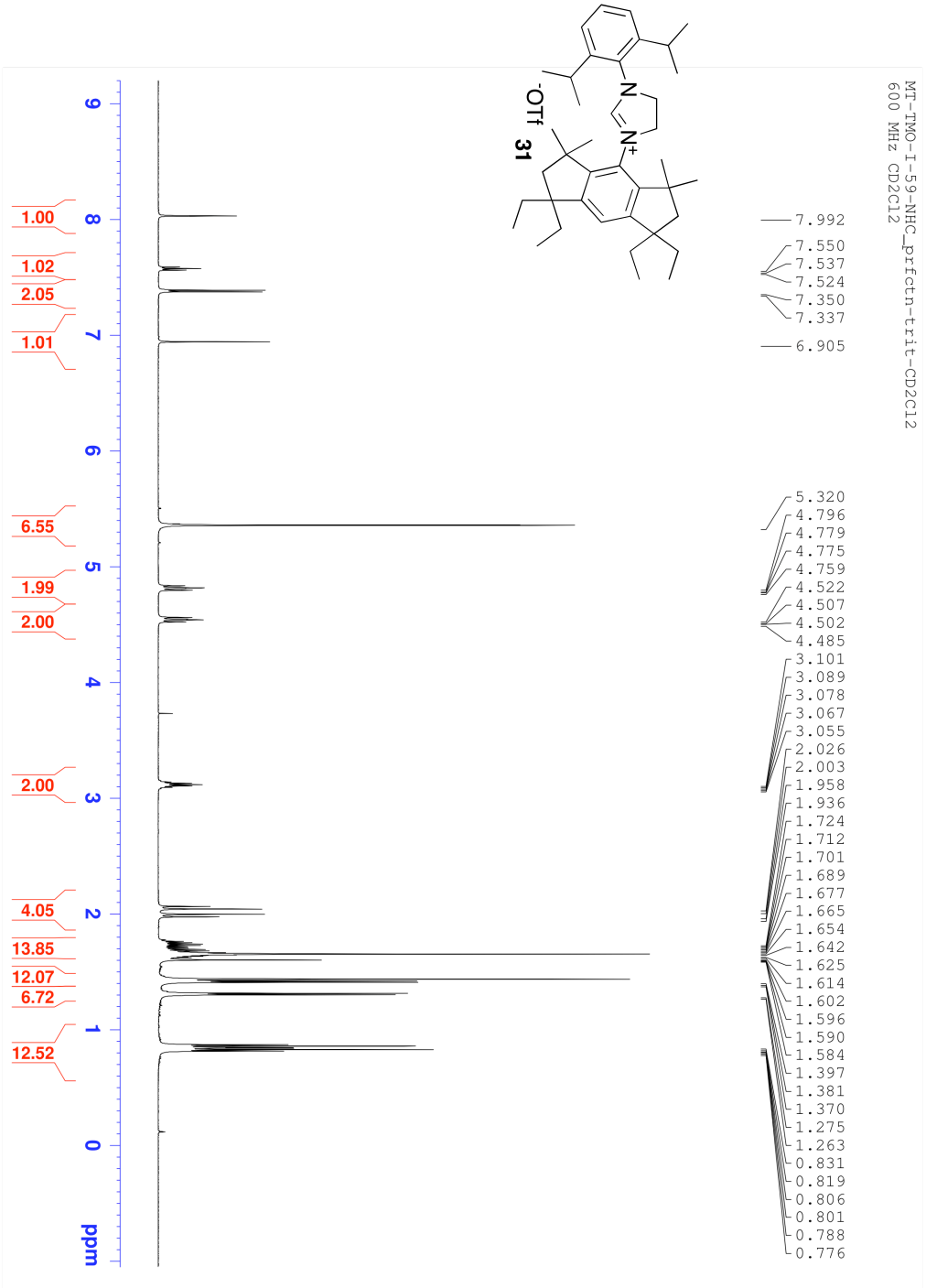

MT-11-100-NHC_prfctn-trituration-Et2O
75 MHz CDCl3
Aug 21, 2012
28
-OTf
158.48
146.02
138.78
132.05
131.58
130.52
128.96
125.10
122.74
118.49
77.42
77.00
76.56
54.49
53.61
40.38
29.41
29.05
24.99
24.20
22.78
22.36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

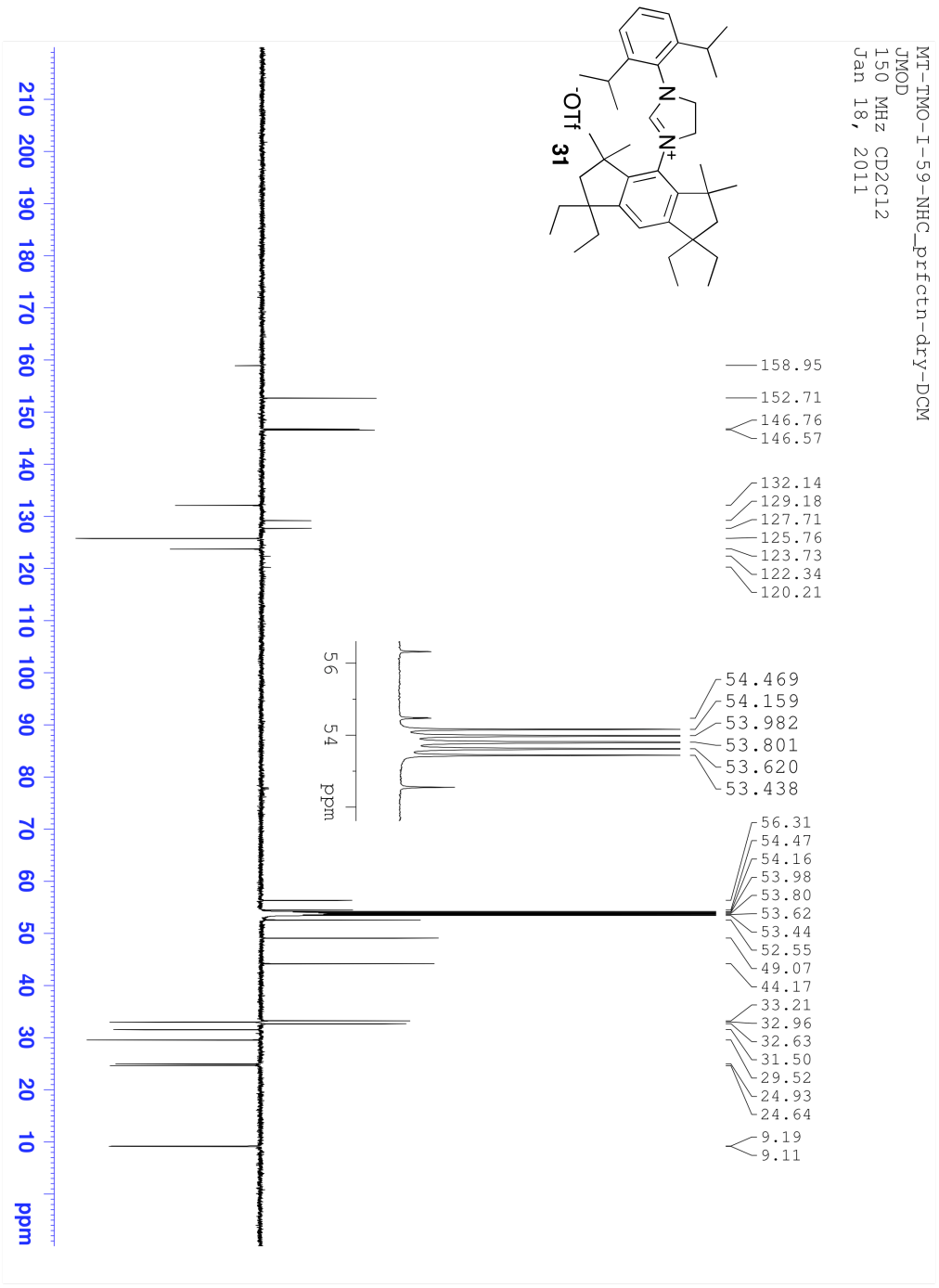

29
-OTf
MT-12-18-NHC_prfctn-solid
300 MHz CDCl3
Aug 21, 2012
7.682
7.536
7.519
7.510
7.493
7.484
7.468
7.308
7.282
7.270
7.227
7.201
4.682
4.644
4.625
4.612
4.594
4.555
3.043
3.020
2.998
2.975
2.952
2.535
2.514
2.493
2.488
1.898
1.875
1.851
1.828
1.805
1.779
1.758
1.734
1.709
1.684
1.660
1.638
1.618
1.593
1.567
1.546
1.521
1.400
1.377
1.293
1.270
0.939
0.914
0.890
0.774
0.750
0.725
1.00
2.04
2.19
2.14
4.17
2.07
2.07
9.24
6.92
6.36
6.44
6.42
ppm

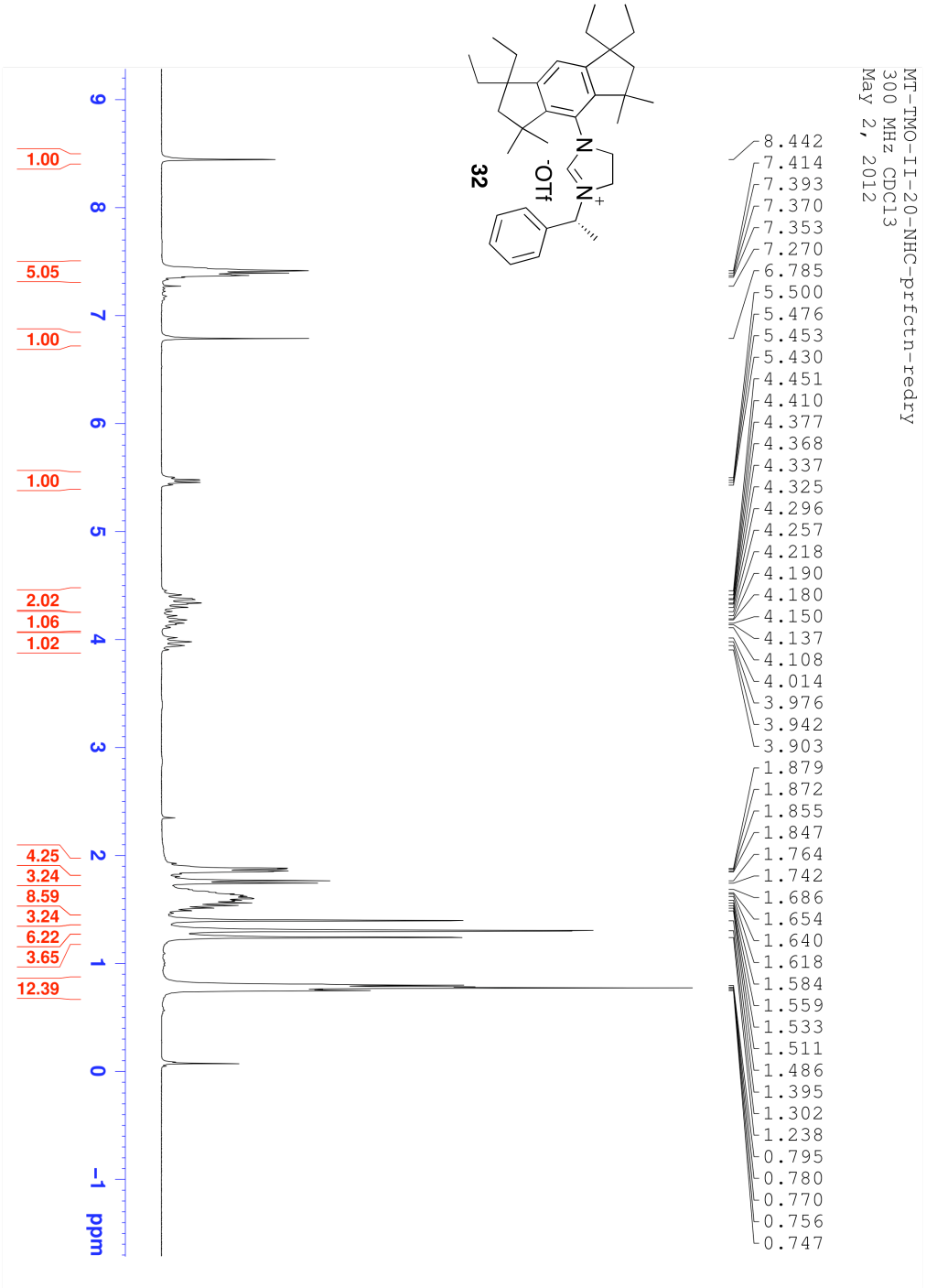

MT-12-18-NHC_prfctn-solid
13C
75 MHz CDCl3
Aug 21, 2012
29
-OTf
157.89
146.02
143.40
132.36
131.64
131.44
128.82
125.50
125.17
122.79
118.54
77.42
77.00
76.58
55.04
54.57
43.54
29.45
29.06
28.80
24.65
24.44
12.42
12.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

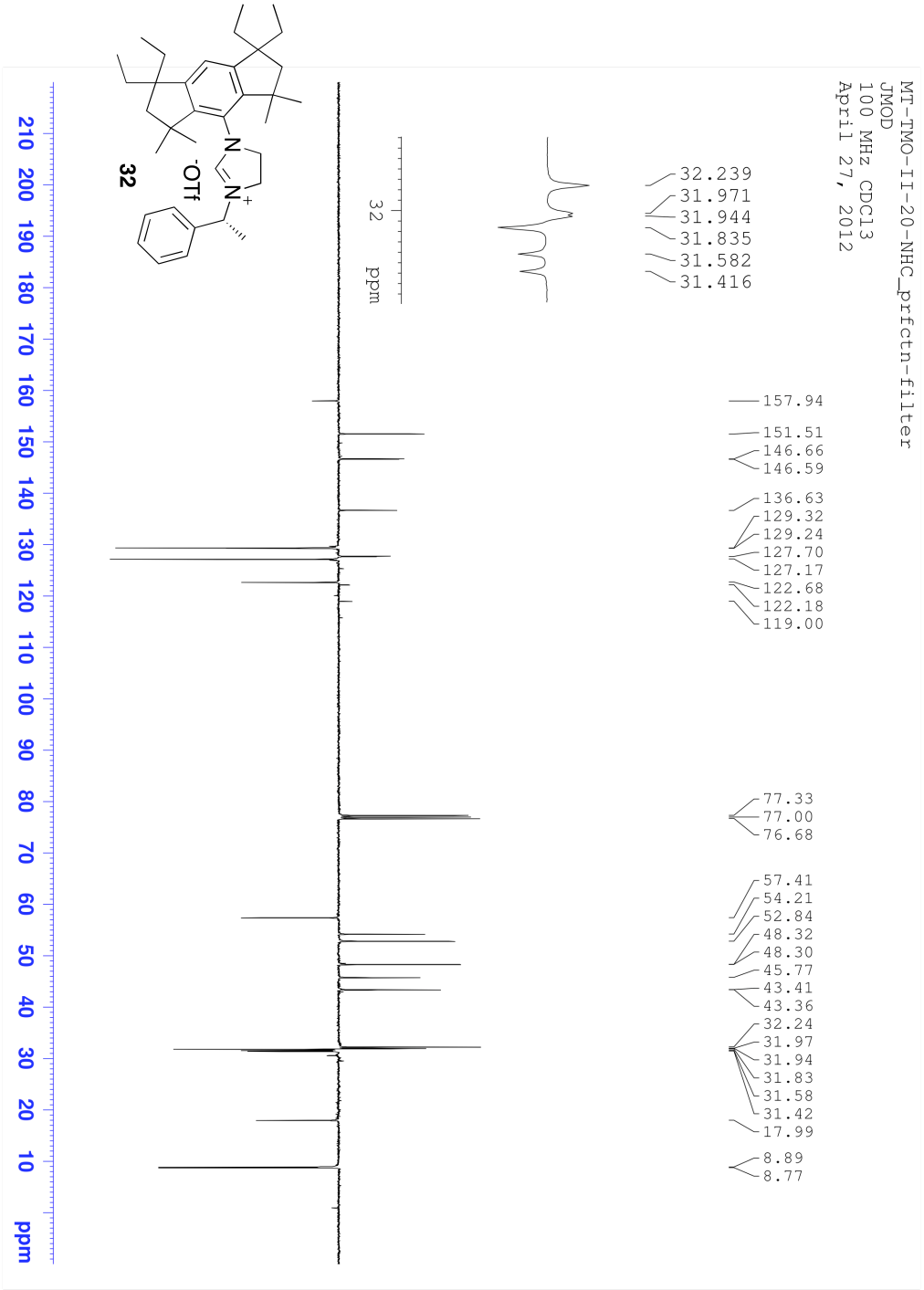

30
-OTf
MT-10-99-rxn2-NHC_prfctn
300 CDCl3
Sept 19. 2011
8.261
7.413
7.270
7.222
7.196
5.355
5.332
5.309
5.285
4.231
4.197
4.165
4.141
4.131
4.116
4.107
2.919
2.896
2.873
2.851
2.841
2.828
2.821
2.798
2.774
2.752
1.784
1.761
1.269
1.247
1.236
1.214
1.192
1.169
0.94
5.80
2.22
0.96
3.91
2.02
3.00
12.06
ppm


MT-10-99-rxn2-NHC_purification
JMOD
75 MHz CDCl3
30
-OTf
157.043
146.493
146.415
137.096
131.049
129.903
129.443
129.263
126.984
124.786
122.799
118.552
77.426
77.000
76.579
57.869
53.275
46.720
28.655
28.572
24.676
24.598
23.969
23.881
18.406
146 ppm
29 28 27 26 25 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


31
-OTf
MT-TMO-I-59-NHC_prfctn-trit-CD2Cl2
600 MHz CD2Cl2
1.00
1.02
2.05
1.01
6.55
1.99
2.00
2.00
4.05
13.85
12.07
6.72
12.52
ppm
7.992
7.550
7.537
7.524
7.350
7.337
6.905
5.320
4.796
4.779
4.775
4.759
4.522
4.507
4.502
4.485
3.101
3.089
3.078
3.067
3.055
2.026
2.003
1.958
1.936
1.724
1.712
1.701
1.689
1.677
1.665
1.654
1.642
1.625
1.614
1.602
1.596
1.590
1.584
1.397
1.381
1.370
1.275
1.263
0.831
0.819
0.806
0.801
0.788
0.776


MT-TMO-I-59-NHC_prfctn-dry-DCM
JMOD
150 MHz CD2C12
Jan 18, 2011
-OTf
31
158.95
152.71
146.76
146.57
132.14
129.18
127.71
125.76
123.73
122.34
120.21
54.469
54.159
53.982
53.801
53.620
53.438
56.31
54.47
54.16
53.98
53.80
53.62
53.44
52.55
49.07
44.17
33.21
32.96
32.63
31.50
29.52
24.93
24.64
9.19
9.11
56
54
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


MT-TMO-II-20-NHC-prfctn-redry
300 MHz CDCl3
May 2, 2012
32
OTf
8.442
7.414
7.393
7.370
7.353
7.270
6.785
5.500
5.476
5.453
5.430
4.451
4.410
4.377
4.368
4.337
4.325
4.296
4.257
4.218
4.190
4.180
4.150
4.137
4.108
4.014
3.976
3.942
3.903
1.879
1.872
1.855
1.847
1.764
1.742
1.686
1.654
1.640
1.618
1.584
1.559
1.533
1.511
1.486
1.395
1.302
1.238
0.795
0.780
0.770
0.756
0.747
1.00
5.05
1.00
1.00
2.02
1.06
1.02
4.25
3.24
8.59
3.24
6.22
3.65
12.39
ppm


MT-TMO-II-20-NHC_prfctn-filter
JMOD
100 MHz CDCl3
April 27, 2012
32.239
31.971
31.944
31.835
31.582
31.416
157.94
151.51
146.66
146.59
136.63
129.32
129.24
127.70
127.17
122.68
122.18
119.00
77.33
77.00
76.68
57.41
54.21
52.84
48.32
48.30
45.77
43.41
43.36
32.24
31.97
31.94
31.83
31.58
31.42
17.99
8.89
8.77
32 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
32
-OTf

References

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2. A. Fürstner, M. Alcarazo, V. Cèsar, C. W. Lehmann, *Chem. Commun.* 2006, **20**, 2176.

3. T. Matsuo, K. Suzuki, T. Fukawa, B. Li, M. Ito, Y. Shoji, T. Otani, L. Li, M. Kobayashi, M. Hachiya, Y. Tahara, D. Hashizume, T. Fukunaga, A. Fukazawa, Y. Li, H. Tsuji and K. Tamao *Bull. Chem. Soc. Jpn.*, 2011, **84**, 1178.