Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

ChemComm

Trifluoromethyl Acting as Stopper in [2]Rotaxane

Suvankar Dasgupta,[a] Kuo-Wei Huang[b] and Jishan Wu*[a]

[a]*Department of Chemistry, National University of Singapore*
3 Science Drive 3, Singapore, 117543
Tel: (+65) 6516 2677, Fax: (+65) 6779-1691
E-mail: **chmwuj@nus.edu.sg**

[b]*King Abdullah University of Science and Technology (KAUST), Division of Chemical and Life Sciences and Engineering and KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia*

Electronic Supplementary Materials

Table of Contents

1. Experimental Section

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

1. Experimental Section

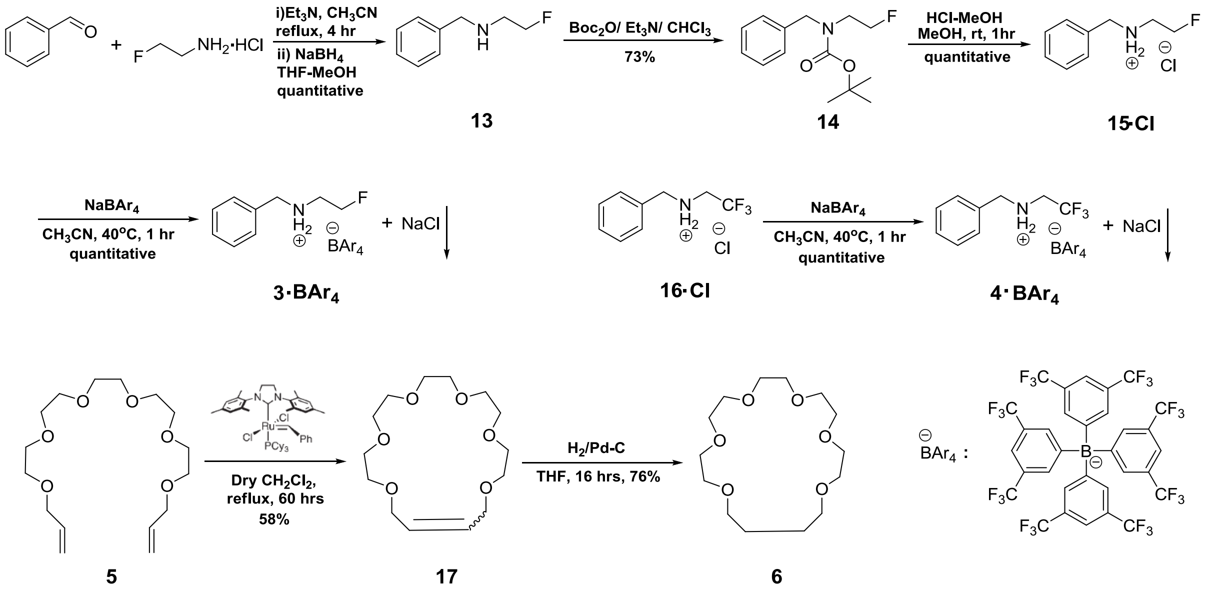
1.1 General

All reagents and starting materials were bought from commercial suppliers and used without further purification. Compound **16•Cl** was prepared according to literature (Dubowchik, G. M.; Michne, J. A.; Zuev, D. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3147-3149). Anhydrous dichloromethane (DCM) was obtained from dry distillation of its analytical grade by CaH_2. Anhydrous tetrahydrofuran (THF) was obtained by distilling its analytical grade with sodium-benzophenone. Always freshly distilled dry solvents were used. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). Deuterated solvents (Cambridge Isotope Laboratories) for NMR spectroscopic analyses were used as received. All NMR spectra were recorded on Bruker AMX500 at 500 MHz and Bruker ACF300 at 300 MHz spectrometers with tetramethylsilane (TMS) as the internal standard. The 2D NOESY NMR spectral data was recorded on Bruker AMX500 at 500 MHz. All chemical shifts are quoted in ppm with multiplicities being denoted by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Mass spectra were recorded on Finnigan LCQ quadrapole ion trap mass spectrometer and Shimadzu LCMS-IT-TOF, in ESI mode.

1.2 Schemes, synthetic procedures and characterization data

Scheme S1 outlines the synthetic routes for **3•BAr$_4$**, **4•BAr$_4$**, and **6**. Benzaldehyde was condensed with one equivalent of commercially available 2-fluoroethylamine hydrochloride in presence of one equivalent of triethylamine, which was subsequently reduced with sodium borohydride in quantitative yield. The missing peak for imine bond in ^{1}H NMR confirmed the formation of amine **13** which was treated with Boc_2O to give Boc-protected amine **14** in 73% yield. Compound **14** was purified and treated with HCl in MeOH to affect Boc deprotection and form chloride salt **15•Cl**, which was quantitatively converted to the compound **3•BAr$_4$** on treatment with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Likewise, the salt **16 Cl** was converted to the compound **4•BAr$_4$** in quantitative yield. When acyclic diolefin polyether **5** was treated with Grubbs' 2nd generation catalyst, compound **17** was obtained in 58% yield. Subsequent hydrogenation with palladium on charcoal, gave [20]crown ether **6** in 76% yield.

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012



Scheme S1. Synthetic route to **3 BAr₄**, **4 BAr₄**, and **6**.

Synthesis of 14: Benzaldehyde (428 mg, 4.03 mmol), 2-fluoroethylamine hydrochloride (401 mg, 4.03 mmol) and triethylamine (0.56 ml, 4.03 mmol) were mixed in CH_3CN (81 ml, 0.05 M) under nitrogen. The suspension was stirred for 45 minutes and then refluxed for another 4 hours. The reaction mixture was allowed to cool before removing the solvent under vacuum. The white residue was dissolved in THF (20 mL) and MeOH (20 mL) to which $NaBH_4$ (762 mg, 20.15 mmol) was added in portions. After stirring for overnight, the solvent was removed under vacuum leaving a residue which was extracted by $CHCl_3$. The organic layer was washed by brine, dried over anhydrous Na_2SO_4, and the solvent was then removed under vacuum leaving the crude product **13** in quantitative yield, which was dissolved in $CHCl_3$ (40 mL, 0.1 M) under nitrogen atmosphere. To this was added triethylamine (1.23 mL, 8.86 mmol) and stirred for 5 minutes. This was followed by addition of Boc_2O (1.75 g, 8.06 mmol) and stirring of the reaction mixture for 24 hours. The solvent was removed under vacuum leaving the crude residue which was purified by column chromatography (silica gel, EA/hexane = 1:9) to give compound **14** (740 mg, 73%). ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 7.34-7.31 (m, 2 H, ph), 7.27-7.23 (br, 3 H, ph), 4.60-4.41 (br, 4 H, CH_2), 3.53-3.39 (br, 2 H, CH_2), 1.52-1.44 (br, 9 H, Boc). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 155.6, 146.7, 128.5, 127.8, 127.2, 85.1, 80.2, 52.3, 28.3, 27.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm = 92.7. HR MS (ESI): m/z Calcd for $C_{14}H_{20}FNNaO_2$ $[M+Na]^+$: 276.1370, found 276.1383.

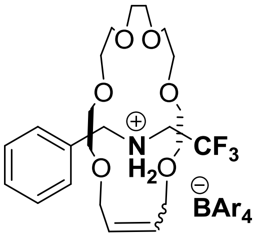
Synthesis of 3•BAr$_4$: Compound **14** (97 mg, 0.382 mmol) was dissolved in MeOH (10 mL, 0.04 M) under nitrogen. 6 mL of ~1.25 M HCl-MeOH was added under nitrogen and stirred for 1 hour. The excess reagent and solvent were removed under vacuum to get the compound **15•Cl** as white solid in quantitative yield. Compound **15•Cl** (18 mg, 0.098 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (101 mg, 0.114 mmol) were dissolved in CH_3CN (10 mL, 0.01 M) and heated for 1 hour. NaCl precipitate was filtered off and the solvent was concentrated under vacuum to leave the salt **3•BAr$_4$** in quantitative yield. ^{1}H NMR (500 MHz, CD_3CN): δ ppm = 7.70 (br, 8 H, BAr_4), 7.66 (s, 4 H, BAr_4), 7.49-7.44 (br, 5 H, ph), 4.75 (t, *J* = 4.4 Hz, 1 H, $C(H_2)F$), 4.65 (t, *J* = 4.4 Hz, 1 H, $C(H_2)F$), 4.24 (s, 2 H, CH_2), 3.39 (t, *J* = 5.0 Hz, 1 H, CH_2), 3.34 (t, *J* = 5.0 Hz, 1 H, CH_2). ^{13}C NMR (125 MHz, CD_3CN): δ ppm = 163.0, 162.6, 162.2, 161.8, 135.4, 130.99, 130.95, 130.6, 130.1, 129.94, 129.90, 129.88, 129.86, 129.67, 129.65, 129.63, 129.61, 129.38, 129.35, 128.5, 126.3, 124.2, 122.0, 80.4, 79.1, 52.5, 48.5, 48.3. ^{19}F NMR (282 MHz, CD_3CN): δ ppm = 13.0. HR MS (ESI): m/z Calcd for $C_9H_{13}FN$ $[M-BAr_4]^+$: 154.1027, found 154.1028.

Synthesis of 4•BAr$_4$: Compound **16 Cl** (40 mg, 0.18 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (200 mg, 0.225 mmol) were dissolved in CH_3CN (18 mL, 0.01 M) and heated for 1 hour. NaCl precipitate was filtered off and the solvent was concentrated under vacuum to leave the salt **4•BAr$_4$** in quantitative yield. ^{1}H NMR (500 MHz, CD_3CN): δ ppm = 7.68 (br, 8 H, BAr_4), 7.65 (s, 4 H, BAr_4), 7.50-7.47 (br, 5 H, ph), 4.30 (s, 2 H, CH_2), 3.86 (q, *J* = 8.8 Hz, 2 H, $C(H_2)CF_3$). ^{13}C NMR (125 MHz, CD_3CN): δ ppm = 163.0, 162.6, 162.2, 161.8, 135.4, 131.3, 130.9, 130.1, 129.97, 129.92, 129.89, 129.87, 129.64, 129.62, 129.5, 128.5, 126.3, 124.2, 122.0, 53.3, 48.1, 47.8. ^{19}F NMR (282 MHz, CD_3CN): δ ppm =13.0, 7.6. HR MS (ESI): m/z Calcd for $C_9H_{11}F_3N$ $[M- BAr_4]^+$: 190.0838, found 190.0841.

Synthesis of 17: Compound **5** (323 mg, 1.01 mmol) was dissolved in dry DCM (500 mL, 0.002 M) under nitrogen atmosphere. 2nd Generation Grubbs catalyst (85 mg, 0.1 mmol) was added and the resulting mixture was refluxed for 60 hours. The reaction mixture was cooled followed by quenching with ethyl vinyl ether. The excess solvent was removed in vacuum and the residue was subjected to column chromatography (silica gel, $MeOH/CHCl_3$ = 1:19 (v/v)) to give the desired product **17** (170 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm = 5.83 (br, 2 H, C(H)=C(H)), 4.04 (m, 4 H, CH_2), 3.68-3.60 (br, 20 H, OCH_2CH_2O). ^{13}C NMR

(125 MHz, $CDCl_3$): δ ppm = 129.3, 70.9, 70.7, 70.6, 70.5, 70.4, 69.1. HR MS (ESI): m/z Calcd for $C_{14}H_{27}O_6$ $[M+H]^+$: 291.1802, found 291.1812.

Synthesis of 6: Compound **17** (170 mg, 0.58 mmol) was dissolved in dry THF (24 mL, 0.02 M) under nitrogen atmosphere. A pinch of Pd/C (cat.) was added and the resulting suspension was stirred under an atmosphere of hydrogen for 16 hours. The reaction mixture was filtered through celite to remove Pd/C and concentrated in vacuum. The crude residue was purified by column chromatography (silica gel, $MeOH/CHCl_3$ = 1:19 (v/v)) to give the desired product **6** (130 mg, 76%). ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 3.70-3.58 (br, 20 H, OCH_2CH_2O), 3.51 (t, *J* = 5.6 Hz, 4 H, CH_2), 1.67 (p, *J* = 3.1 Hz, 4 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 71.0, 70.8, 70.6, 70.5, 70.1, 26.2. HR MS (ESI): m/z Calcd for $C_{14}H_{28}O_6Na$ $[M+Na]^+$: 315.1778, found 315.1789.



12·BAr₄

Synthesis of 12•BAr₄: Compound **4•BAr₄** (191 mg, 0.181 mmol) and compound **5** (116 mg, 0.364 mmol) were dissolved in the mixed solvent (40 mL, $CHCl_3/CH_3CN$ = 3:1 (v/v)). The solution was stirred for 24 hours and the solvent was then removed under vacuum without heating and then the residue (**9•BAr₄**) was dissolved in dry DCM (360 mL, 0.001 M) under nitrogen atmosphere. 2nd Generation Grubbs catalyst (31 mg, 0.036 mmol) was added and the resulting mixture was refluxed for 60 hours. The reaction mixture was cooled followed by quenching with ethyl vinyl ether. The excess solvent was removed in vacuum and the residue was subjected to column chromatography (silica gel, $MeOH/CHCl_3$ = 1:9 (v/v)) to give the desired product **12•BAr₄** (130 mg, 54%). ^1H NMR (500 MHz, $CDCl_3$): δ ppm = 8.48 (br, 2 H, NH_2^+), 7.70 (br, 8 H, BAr_4), 7.51 (s, 4 H, BAr_4), 7.43-7.36 (br, 5 H, ph), 5.94-5.92 (br, 2 H, C(H)=C(H)), 4.42-4.34 (m, 4 H, $NH_2^+C(H_2)CF_3$), 4.27-4.24 (m, 4 H, $NH_2^+C(H_2)$ph), 3.96-3.95 (br, 4 H, CH_2), 3.63-3.29 (br, 20 H, OCH_2CH_2O). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 162.2, 161.8, 161.4, 161.0, 134.7, 132.7, 130.8, 130.4, 130.1, 129.0, 128.8, 128.7, 127.7, 125.6, 123.4, 121.2, 117.4, 71.0, 70.9, 70.7, 70.4, 70.2, 69.7, 51.5, 46.6, 46.3. ^{19}F NMR (282

MHz, $CDCl_3$): δ ppm = 13.5, 6.8. HR MS (ESI): m/z Calcd for $C_{23}H_{37}F_3NO_6$ $[M\text{-}BAr_4]^+$: 480.2567, found 480.2573.

2. Nominal ESI-MS of 10•PF_6 and 11•BAr_4

a) **10•PF_6**:

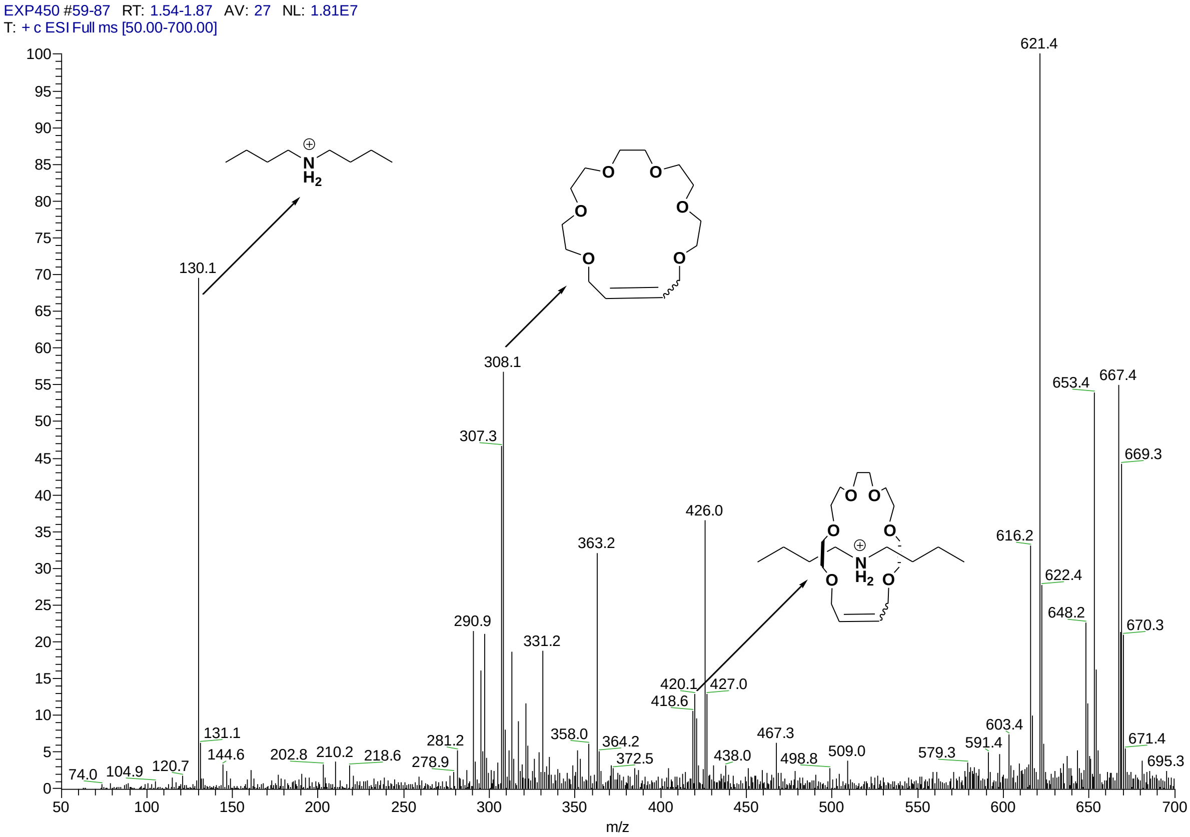


Figure S1. ESI mass spectrum of the reaction mixture in CH_2Cl_2 displayed base peak at m/z 130.1 which corresponds to dumbbell **2.** Strong peak corresponding to [20]crown ether was observed at 308.1 [M + H_2O]. Very weak intensity peaks for **10** (420.1) indicated the formation of **10•PF_6**.

b) **11•BAr$_4$**:

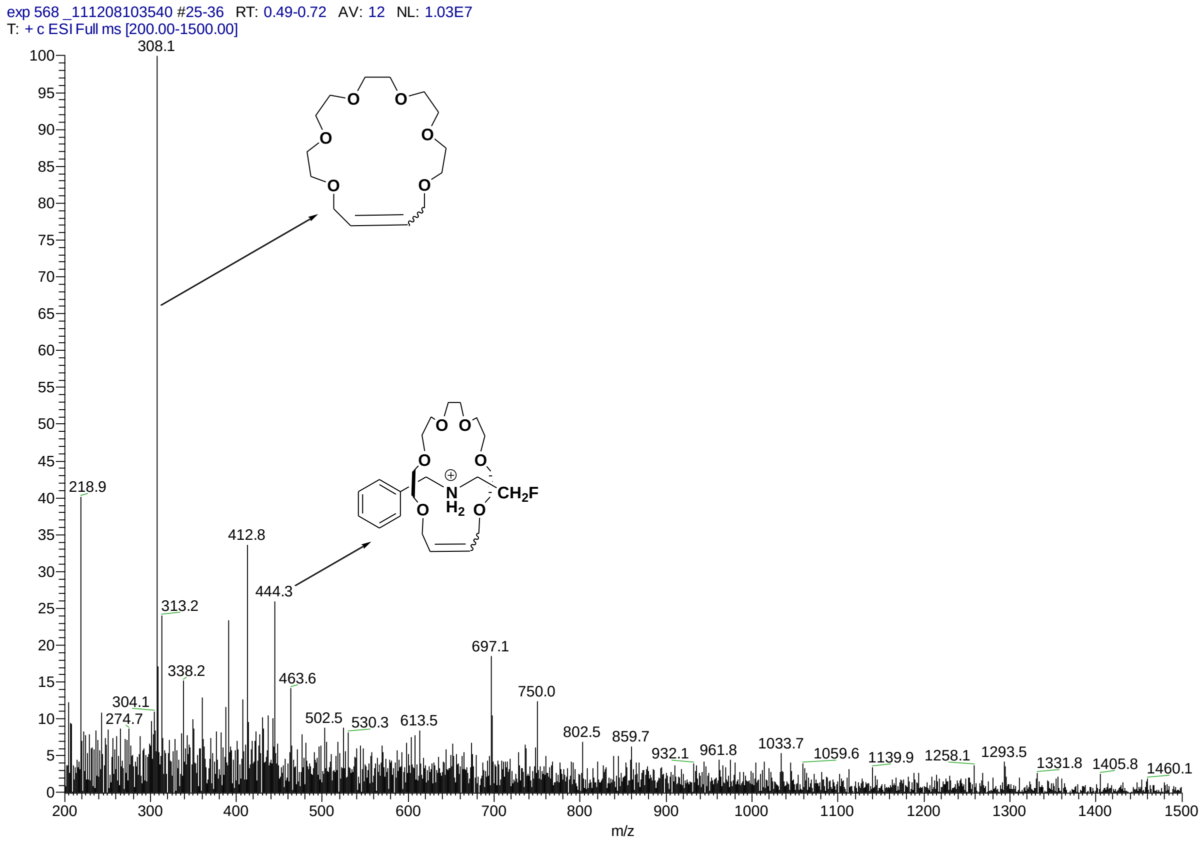
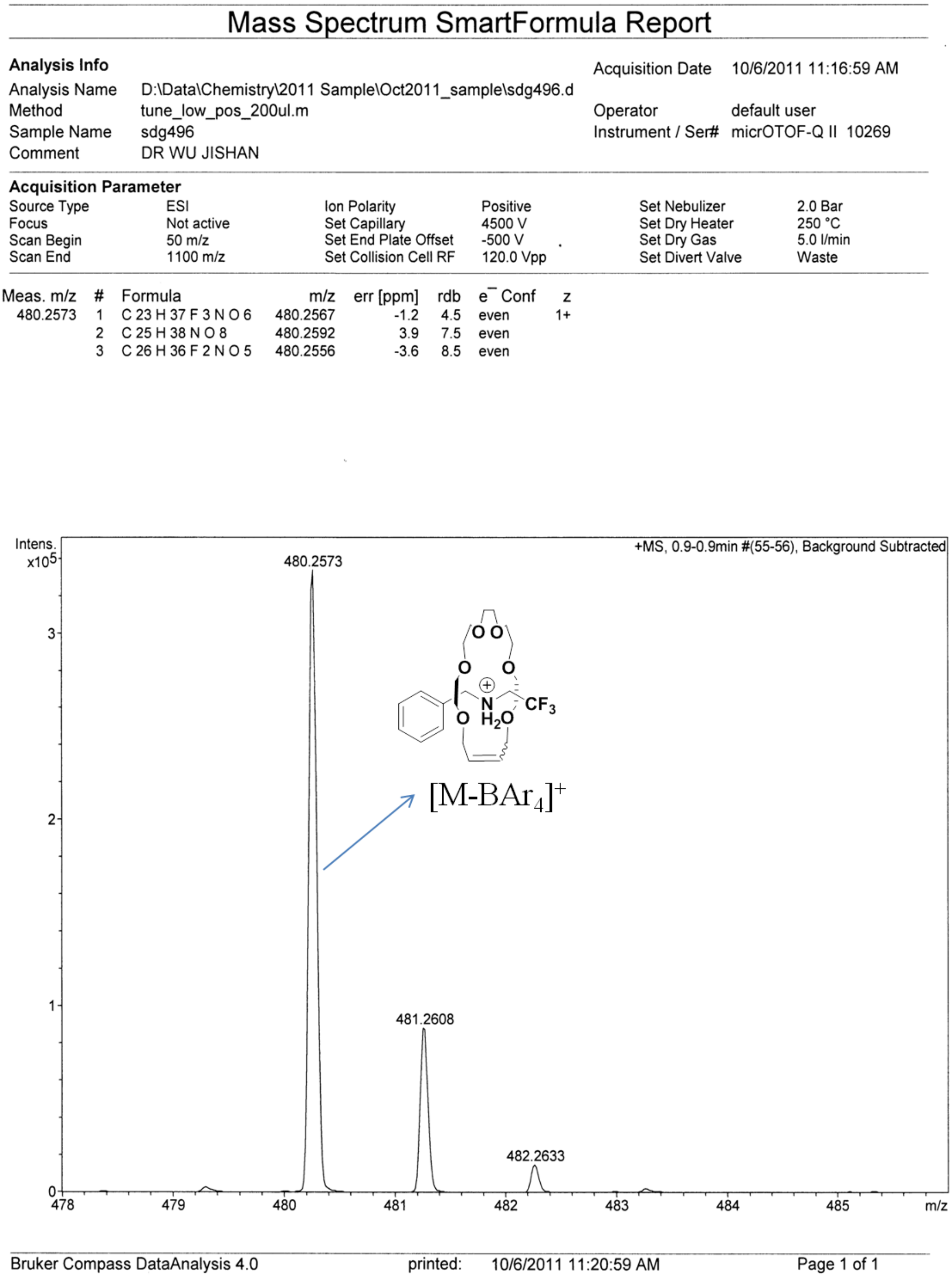


Figure S2. ESI mass spectrum of the reaction mixture in CH_2Cl_2 displayed base peak at m/z 308.1 [M + H_2O] which corresponds to the [20]crown ether. Very weak intensity peaks for **11** (444.3) indicated the formation of **11•BAr$_4$**.

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

3. High Resolution ESI-MS spectrum of 12•BAr$_4$



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Chemistry\2011 Sample\Oct2011_sample\sdg496.d	Acquisition Date	10/6/2011 11:16:59 AM
Method	tune_low_pos_200ul.m	Operator	default user
Sample Name	sdg496	Instrument / Ser#	micrOTOF-Q II 10269
Comment	DR WU JISHAN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	1100 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	z
480.2573	1	C 23 H 37 F 3 N O 6	480.2567	-1.2	4.5	even	1+
	2	C 25 H 38 N O 8	480.2592	3.9	7.5	even	
	3	C 26 H 36 F 2 N O 5	480.2556	-3.6	8.5	even	

Bruker Compass DataAnalysis 4.0 printed: 10/6/2011 11:20:59 AM Page 1 of 1

Figure S3. HR ESI-MS spectrum of the [2]rotaxane **12•BAr$_4$**.

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

4. 2D NOESY NMR spectrum of 12•BAr$_4$

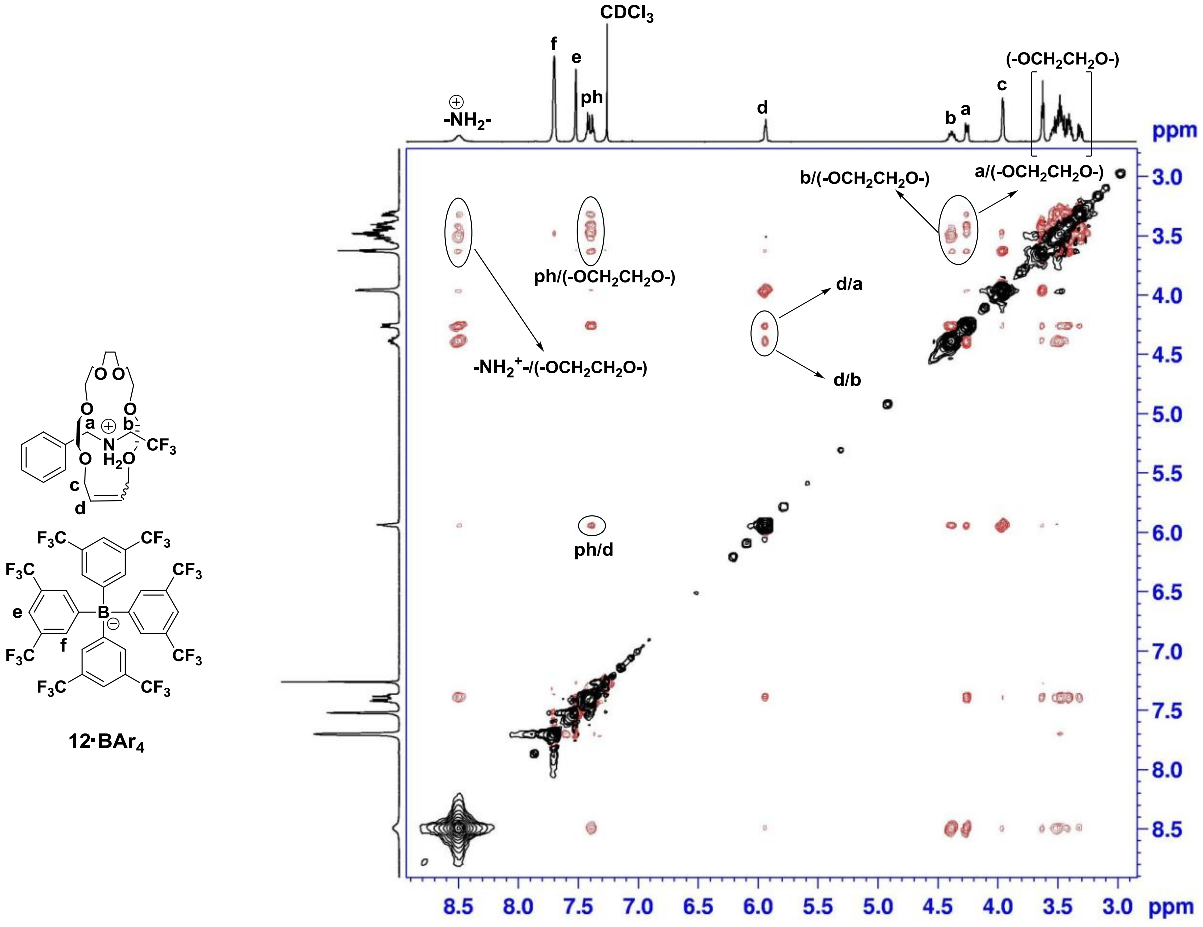


Figure S4. 2D NOESY ^{1}H NMR spectrum (500 MHz) of **12•BAr$_4$** in CDCl$_3$. NOESY spectra correlates protons not separated by more than 5 Angstroms through space. In our case, we noticed a strong correlation of (-**OCH$_2$CH$_2$O**-) protons of [20]crown ether with the protons of dumbbell (referred as **a, b -NH$_2$$^+$**-, and **ph**), decisively proving that [20]crown ether indeed clipped onto the dumbbell. Moreover, there exists some correlation between olefinic protons "**d**" of [20]crown ether with methylene protons (**a** and **b**) and phenyl protons of the dumbbell, further supporting our argument.

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

5. Time based decay study of 12•BAr$_4$ in DMSO-d$_6$

a) **Stacked ^{1}H NMR spectra**:

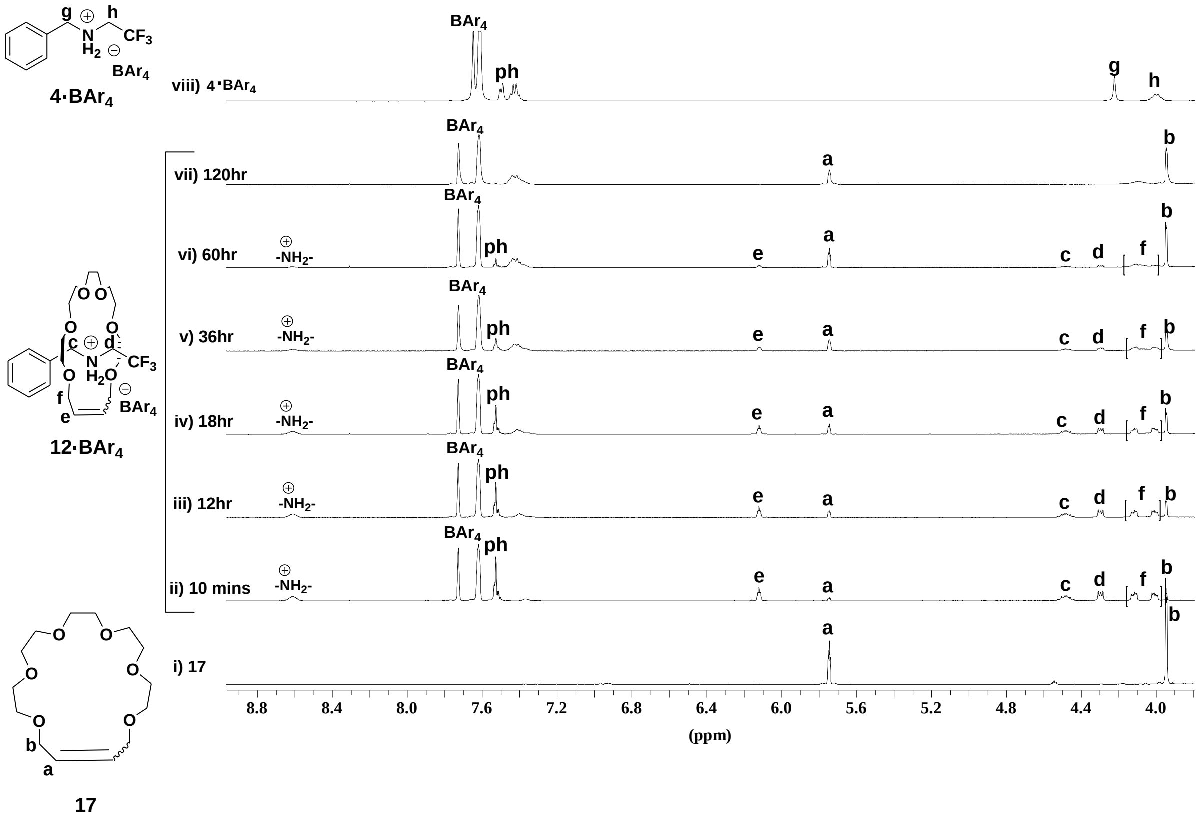
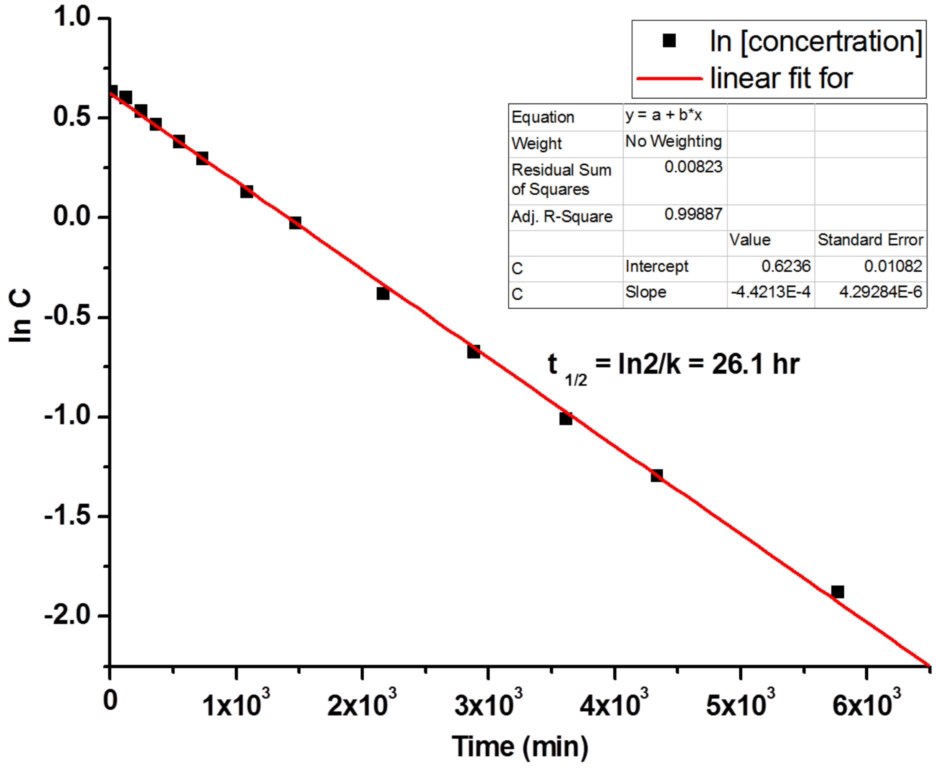


Figure S5. Stacked ^{1}H NMR spectra (500 MHz, DMSO-d$_6$) showing the decay of **12•BAr$_4$** with time. i) the ^{1}H NMR of pure compound **17** is stacked for reference to appreciate the formation of **17** from **12•BAr$_4$** with time. 2.1mg of **12•BAr$_4$** was dissolved in 0.75 ml DMSO-d$_6$ and the ^{1}H NMR (ii→vii) was recorded till 120 hrs when the species **12•BAr$_4$** completely decayed. Surprisingly, the completely decayed ^{1}H NMR (vii) did not indicate the presence of salt **4•BAr$_4$** (viii), suggesting decay of the dumbbell in polar solvent is not by dethreading.

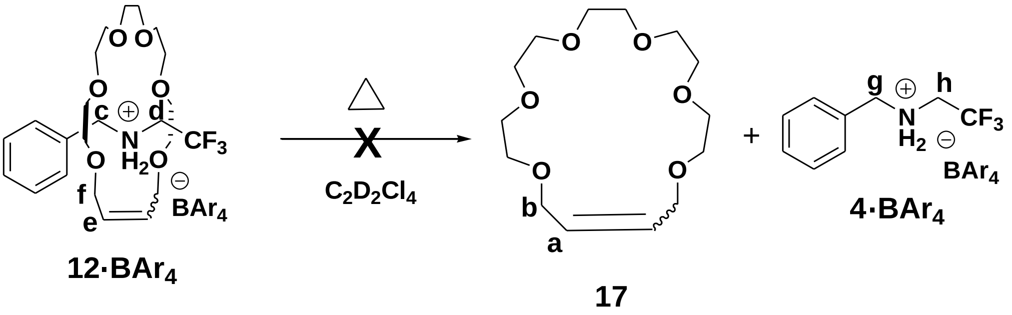
b) **Decay curve**:



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00823		
Adj. R-Square	0.99887		
		Value	Standard Error
C	Intercept	0.6236	0.01082
C	Slope	-4.4213E-4	4.29284E-6

Figure S6. Plot of logarithmic concentration value (lnC) of **12•BAr$_4$** in DMSO-d$_6$ with time. 2.1 mg of **12•BAr$_4$** was dissolved in 0.75 mL DMSO-d$_6$. The linear plot reveals a first order decay of **12•BAr$_4$** with a slope equal to 4.42x10^{-4} min^{-1}. The half-life of this species was calculated to be 26.1 hour.

6. Varied temperature ^{1}H NMR spectra of 12•BAr$_4$ in $C_2D_2Cl_4$



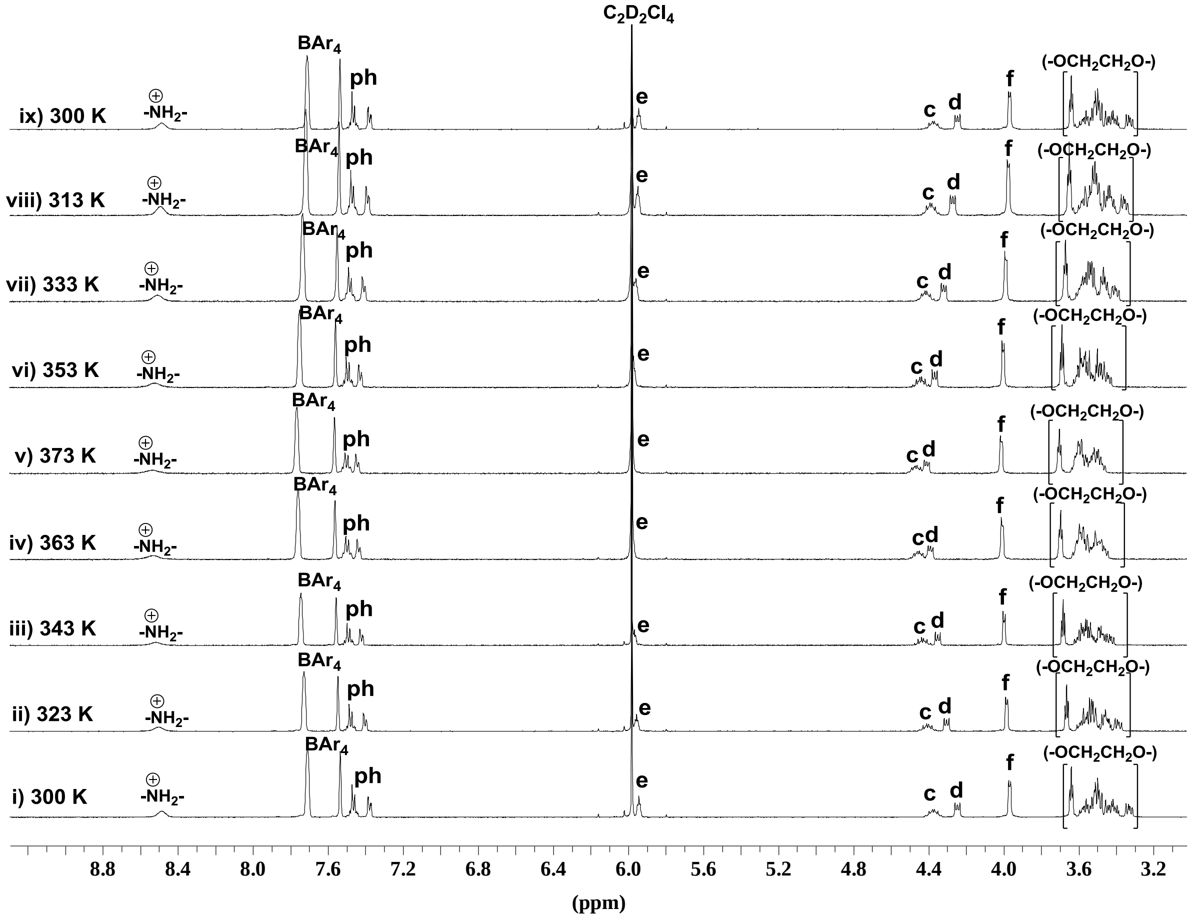


Figure S7. Stacked ^{1}H NMR spectra (500 MHz, $C_2D_2Cl_4$) showing the effect of temperature on **12•BAr$_4$**. On increasing the temperature from 300 k→373 k, there is a very small downfield shift of all the peaks which leads to overlapping of peak **e** with $C_2D_2Cl_4$ peak, however no peak (**a**, **b**, **g**, **h**) corresponding to **17** or **4•BAr$_4$** could be found suggesting a strongly stable interlocked structure in chlorinated solvents. On reducing the temperature from 373 k→300 k, the peaks display slight upfield shift and comes back to the original peak value.

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

7. Computational Details

DFT calculations were conducted with the Gaussian 09 program.[1] The B3LYP[2] method with 6-31+G(d,p) all electron basis set for all atoms.[3] was employed. The geometries were optimized in gas phase using the default convergence criteria without any constraints. Frequency calculations were performed to characterize the stationary points as minima.

Cartesian Coordinates of Computed Structures:

[2]Rotaxane 8b cation (*Chem. Sci.* 2012, 3, 425-432), in which the dumbbell is dibenzylammonium and the macrocycle is 20C6.

Sum of electronic and zero-point Energies= -1597.529521
Sum of electronic and thermal Energies= -1597.493447
Sum of electronic and thermal Enthalpies= -1597.492503
Sum of electronic and thermal Free Energies= -1597.599221

	X	Y	Z
O	2.88916500	-0.23040300	2.40346700
O	3.63331500	-0.05309000	-0.43064200
O	1.64422800	-0.47541200	-2.61294000
O	-1.29321100	-0.04577200	-2.51701600
O	-3.04004700	-0.05815800	-0.08768200
O	-1.95422600	0.49268200	2.46069100
C	4.16135700	0.19099200	1.92410800
H	4.94797300	-0.05755400	2.65331000
H	4.17070200	1.28019800	1.76628800
C	4.47423300	-0.52743600	0.62277700
H	5.52899200	-0.34377800	0.36671000
H	4.33659800	-1.61046900	0.75814300
C	3.88320100	-0.69075800	-1.67917400
H	3.69821900	-1.77337000	-1.60201200
H	4.93567400	-0.54843000	-1.97018600
C	3.01369900	-0.09325000	-2.77138000
H	3.10732100	1.00298700	-2.76445700
H	3.38617700	-0.45908000	-3.74024300
C	0.82672900	-0.05054800	-3.70410500
H	1.26466500	-0.39607500	-4.65310200
H	0.76844300	1.04699600	-3.73437800
C	-0.56787800	-0.63893500	-3.60057600
H	-1.09556900	-0.43093400	-4.54253700
H	-0.51544000	-1.72725900	-3.46585400

C	-2.65605400	-0.49210300	-2.44083200
H	-2.68825400	-1.56216400	-2.19528600
H	-3.13427600	-0.34207900	-3.41908600
C	-3.43148800	0.30919400	-1.41125500
H	-3.27225600	1.38529500	-1.57152100
H	-4.50122000	0.09266100	-1.55267100
C	-3.80170000	0.59446800	0.92625200
H	-4.86825500	0.34324200	0.82256200
H	-3.69457400	1.68491200	0.83554700
C	-3.32812400	0.13346400	2.29301400
H	-3.94524600	0.62050400	3.06195200
H	-3.44697500	-0.95486500	2.39058000
C	-1.43053800	0.24836800	3.78374100
H	-1.49642200	-0.82244500	4.02347300
H	-2.03797300	0.80234600	4.51408200
C	-0.00387900	0.71726000	3.78315700
H	0.14046100	1.78876600	3.64317900
C	1.05819900	-0.09170100	3.86076100
H	0.91601300	-1.16357400	4.00063900
C	2.48019100	0.35404300	3.64703900
H	2.54233800	1.45139300	3.59611800
H	3.14088000	0.01066300	4.45754600
N	-0.12265900	0.04173700	0.05872300
H	-0.97441800	0.12346300	0.63269700
H	-0.45076400	-0.00304300	-0.92503400
C	-0.23059500	-2.48255600	0.14148100
C	0.01258900	-3.25911700	-1.00070900
H	0.77966200	-2.94526200	-1.70276100
C	-0.70889700	-4.43359200	-1.23202100
H	-0.50137800	-5.03114500	-2.11493000
C	-1.68308200	-4.84780100	-0.32039300
H	-2.23920100	-5.76392100	-0.49448400
C	-1.92631600	-4.08701600	0.82698400
H	-2.67010900	-4.41350800	1.54775300
C	-1.20159500	-2.91638200	1.05576800
H	-1.38372200	-2.33912100	1.95777700
C	0.59389600	-1.24569200	0.40882300
H	0.87478300	-1.16389400	1.45635000
H	1.50718800	-1.24277600	-0.18021800
C	0.73167000	1.27582300	0.25267400
H	1.67062200	1.08353000	-0.26244800
H	0.94324900	1.32478400	1.31953100
C	0.07176500	2.54140600	-0.24423400
C	0.54147400	3.16603700	-1.40758700
H	1.36973700	2.72418900	-1.95421700
C	-0.02538100	4.36053200	-1.85878600
H	0.35687600	4.83575900	-2.75719800
C	-1.07441700	4.94737900	-1.14763600
H	-1.51314400	5.87891200	-1.49202400

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

C	-1.54576800	4.33832500	0.01933300
H	-2.34855700	4.80094400	0.58627700
C	-0.97446900	3.14617300	0.46996700
H	-1.33695100	2.68280100	1.38288700

[2]rotaxane 12 Cation.

Sum of electronic and zero-point Energies= -1703.594392
Sum of electronic and thermal Energies= -1703.559618
Sum of electronic and thermal Enthalpies= -1703.558674
Sum of electronic and thermal Free Energies= -1703.662170

	X	Y	Z
O	-3.10910300	1.74847000	0.85494900
O	-3.34466000	-1.15364100	0.76856300
O	-1.37379200	-2.79821800	-0.67971100
O	1.51877500	-2.19388500	-1.20776300
O	2.85106500	0.42331400	-1.28638600
O	1.65847900	2.64408400	0.03360600
C	-4.07650600	1.00442500	1.59094800
H	-4.98767900	1.60355200	1.73815400
H	-3.67721300	0.73420900	2.57995300
C	-4.44580100	-0.24496500	0.81319800
H	-5.30496000	-0.72318700	1.30822400
H	-4.74842000	0.03187100	-0.20765100
C	-3.64372300	-2.34592600	0.04863000
H	-3.89655500	-2.10924300	-0.99638300
H	-4.51061300	-2.85282600	0.50031100
C	-2.46829700	-3.30439700	0.09006300
H	-2.15475800	-3.47387700	1.13089700
H	-2.79869700	-4.26675200	-0.32819000
C	-0.32675700	-3.75081600	-0.85863500
H	-0.73939700	-4.67503000	-1.29082500
H	0.13396000	-4.00273800	0.10761100
C	0.72797100	-3.22745700	-1.81424100
H	1.38538200	-4.06727100	-2.07922500
H	0.25971200	-2.85095700	-2.73363600
C	2.69105000	-1.87678600	-1.97658700
H	2.39864000	-1.51257400	-2.96994700
H	3.29553300	-2.78644100	-2.09700200
C	3.52702500	-0.83244300	-1.26442100
H	3.72497700	-1.14154500	-0.22764600
H	4.48963100	-0.75105100	-1.79153600
C	3.62209100	1.49432400	-0.74558200
H	4.54278100	1.63320500	-1.33215400
H	3.90400700	1.27159600	0.29355300
C	2.81234000	2.77456200	-0.80674500

H	3.43785300	3.60717500	-0.45514100
H	2.49843900	2.98086700	-1.83877200
C	0.87301500	3.85213200	0.13895200
H	0.53845400	4.16803400	-0.85752600
H	1.50420600	4.64526500	0.56444400
C	-0.29455600	3.53941500	1.02881100
H	-0.05350000	3.28776400	2.06190700
C	-1.56432200	3.49246600	0.61235200
H	-1.80655200	3.74770900	-0.41934400
C	-2.70913500	2.99232800	1.44956100
H	-2.39429700	2.83474700	2.49167400
H	-3.55613400	3.69419200	1.44748300
N	0.17153000	0.10714200	-0.20348100
H	0.79007100	0.94044900	-0.22929700
H	0.72150800	-0.70008200	-0.56398200
C	-1.02533400	0.30658100	-1.07453900
H	-1.69407700	1.02687900	-0.60362800
H	-1.53389400	-0.65261400	-1.15245100
C	-0.21951500	-0.16649800	1.24244600
H	-0.99513600	-0.92865600	1.20873300
H	-0.67345800	0.75662000	1.60181700
C	0.95010600	-0.59416200	2.09668500
C	1.07058300	-1.93261000	2.49596100
H	0.33197500	-2.65844900	2.16816000
C	2.11823000	-2.33999800	3.32480800
H	2.19255700	-3.37882000	3.63165000
C	3.06111400	-1.40897300	3.76667100
H	3.87249500	-1.72153100	4.41684200
C	2.94771500	-0.07021900	3.37988600
H	3.66947000	0.66031400	3.73318900
C	1.89729000	0.33538400	2.55398800
H	1.81550700	1.37718500	2.25973300
C	-0.68197500	0.78110200	-2.47398600
F	-0.05339300	1.98219700	-2.48061700
F	0.11532300	-0.08828300	-3.14001400
F	-1.82240700	0.91455400	-3.18170600

References:

1. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai,T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,

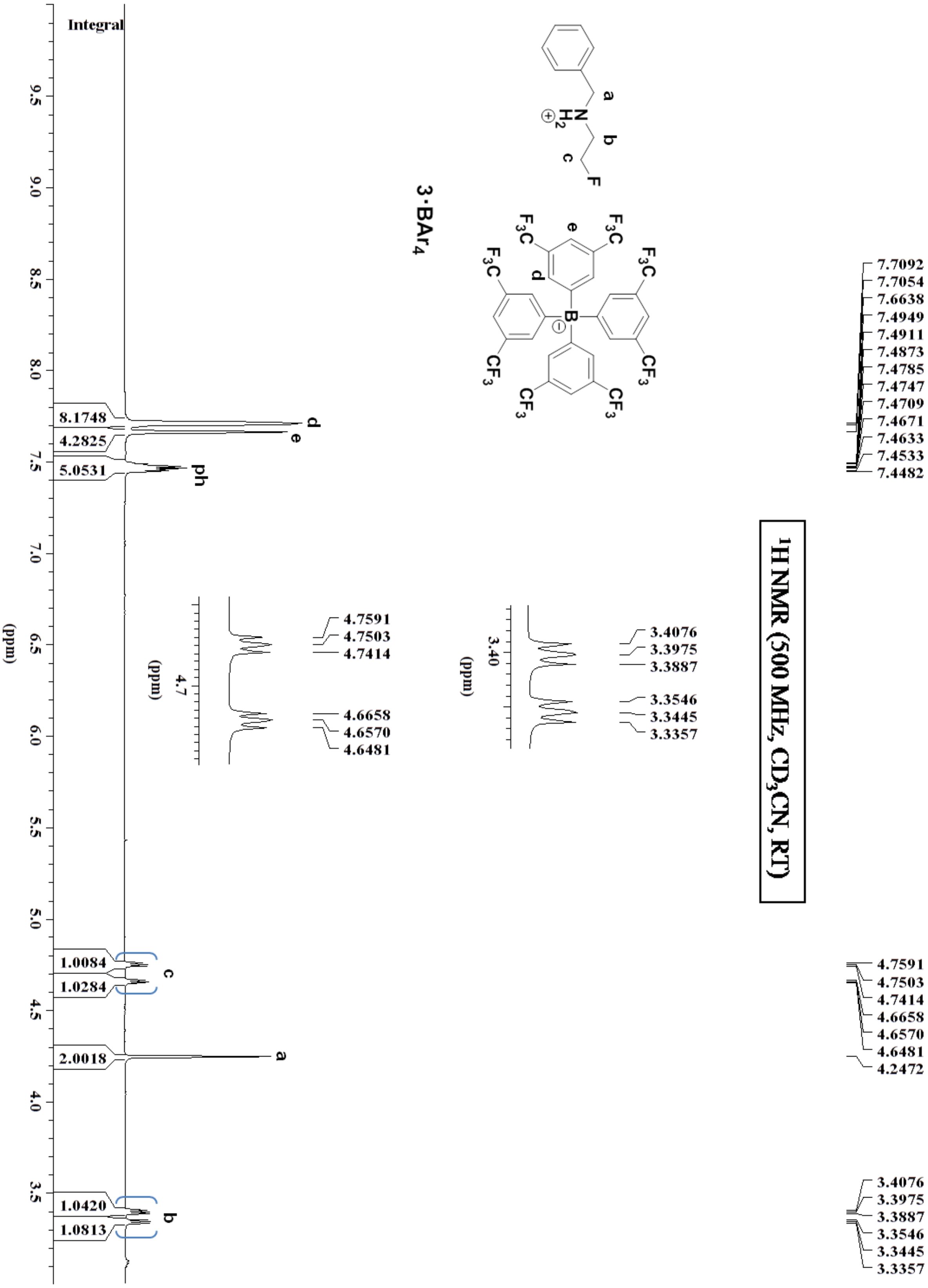
Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

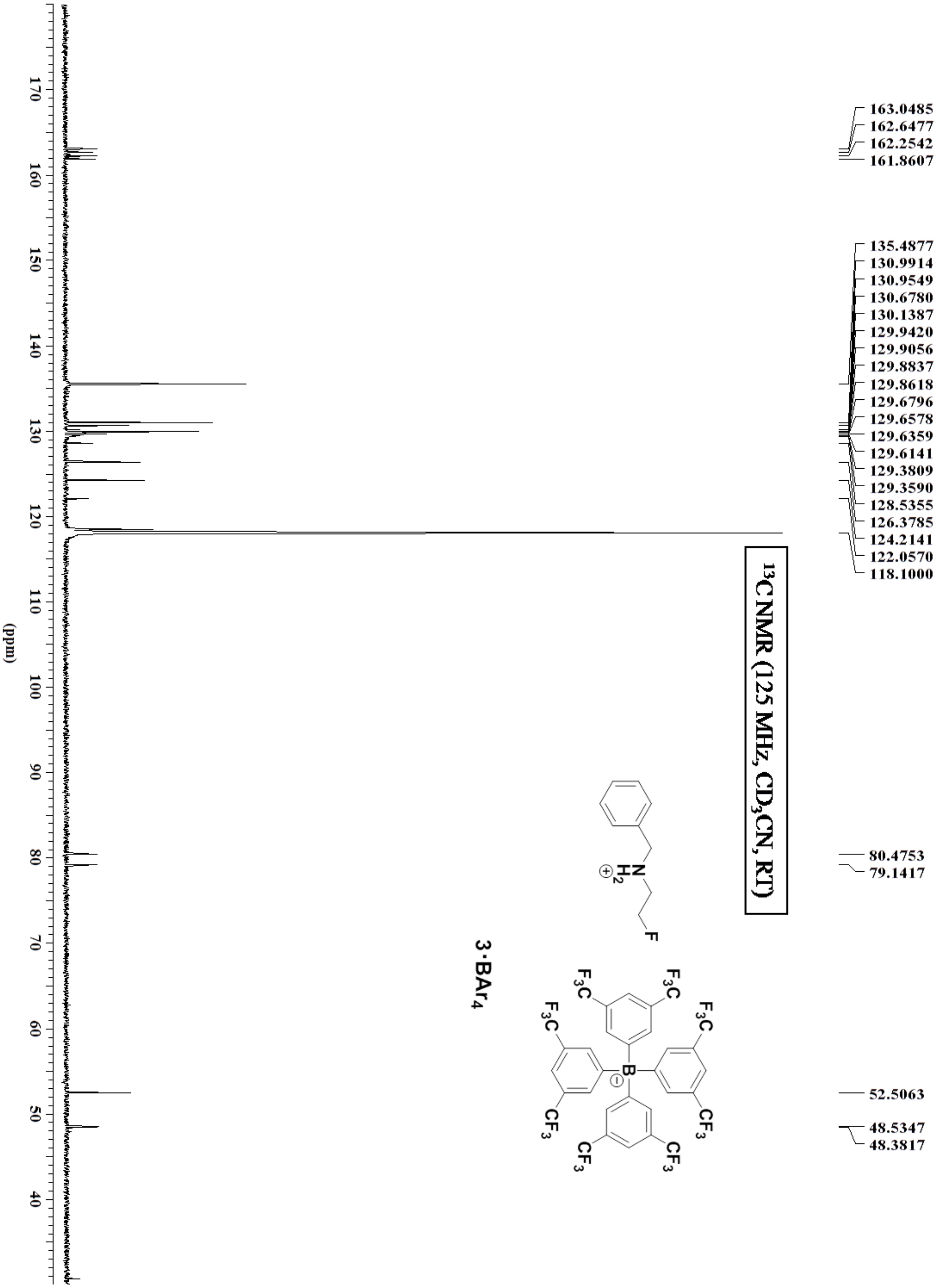
2. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

3. (a) Ditchfie, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfie, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Harihara, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

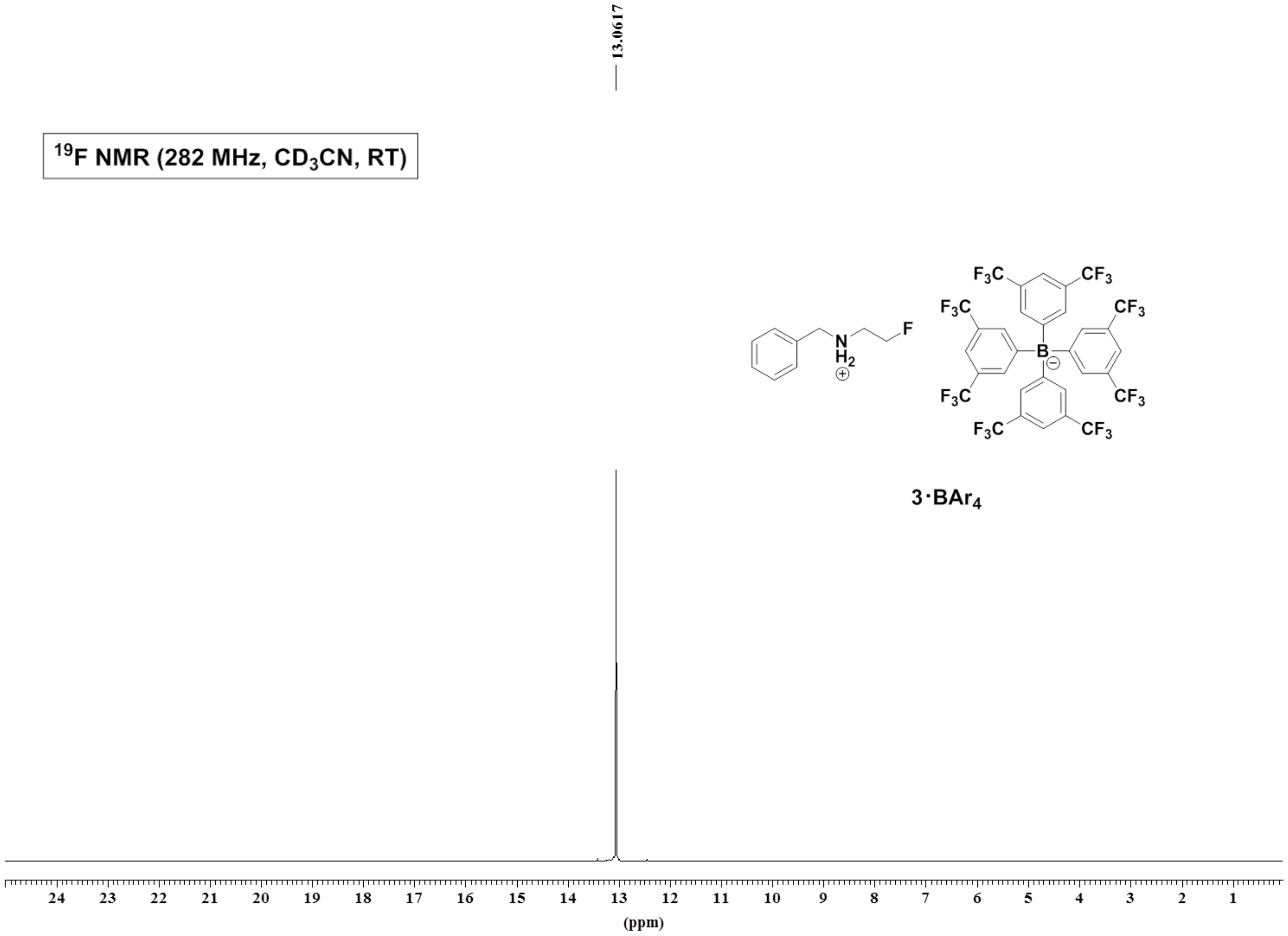
8. ^{1}H NMR and ^{13}C NMR spectra of key compounds



Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012



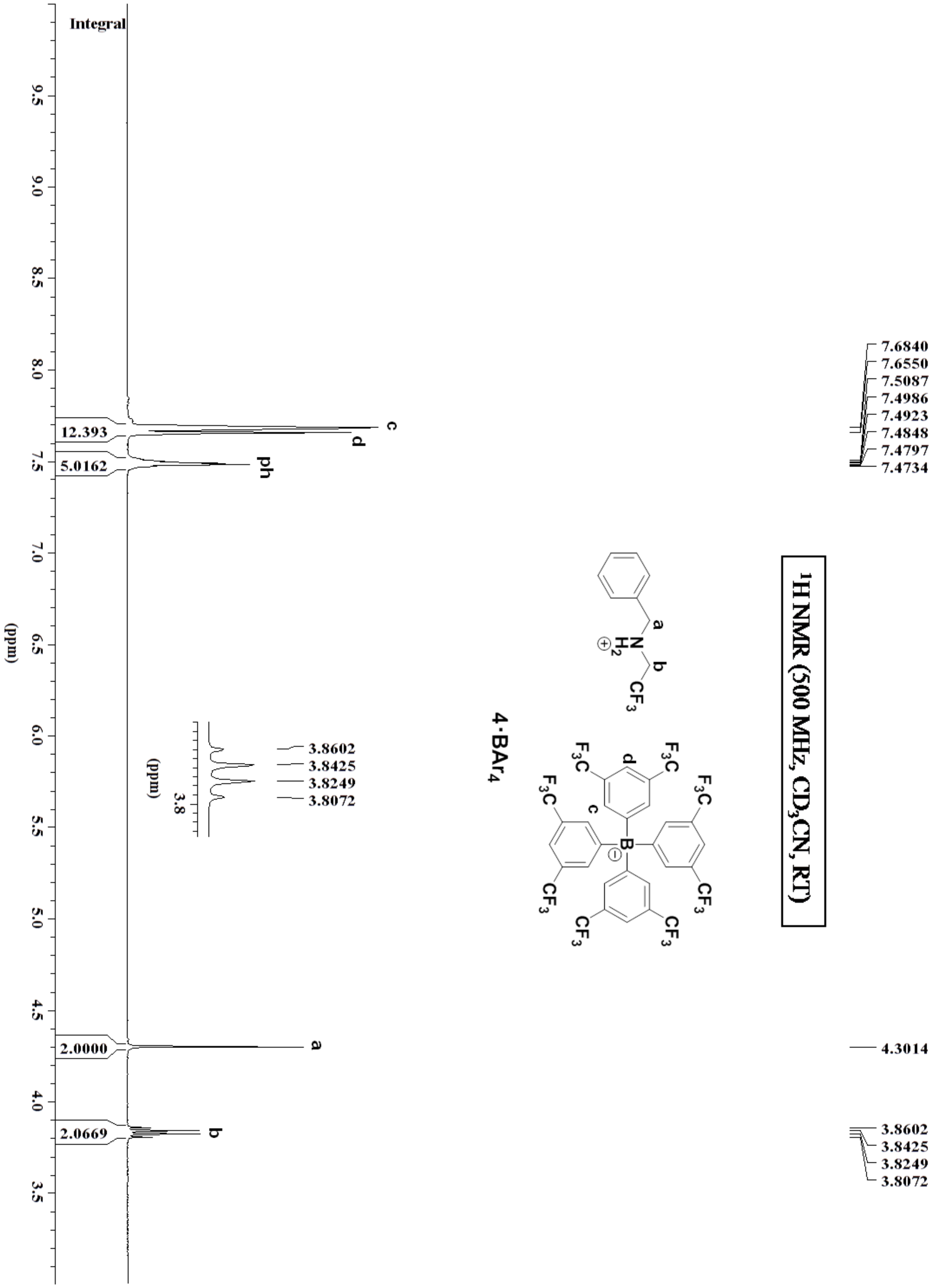
Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012



^{19}F NMR (282 MHz, CD_3CN, RT)

3·BAr$_4$

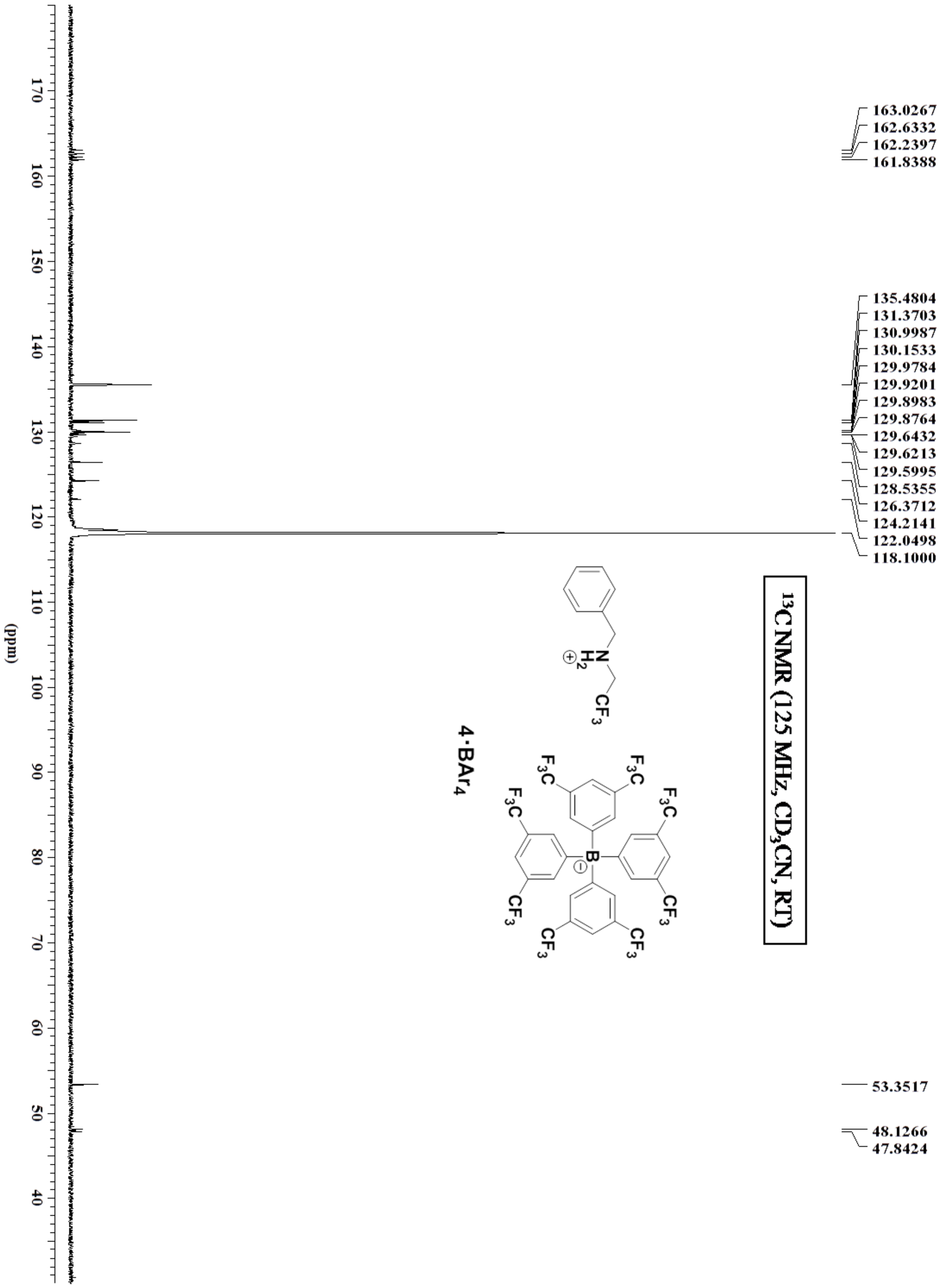
Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012



$4\cdot BAr_4$

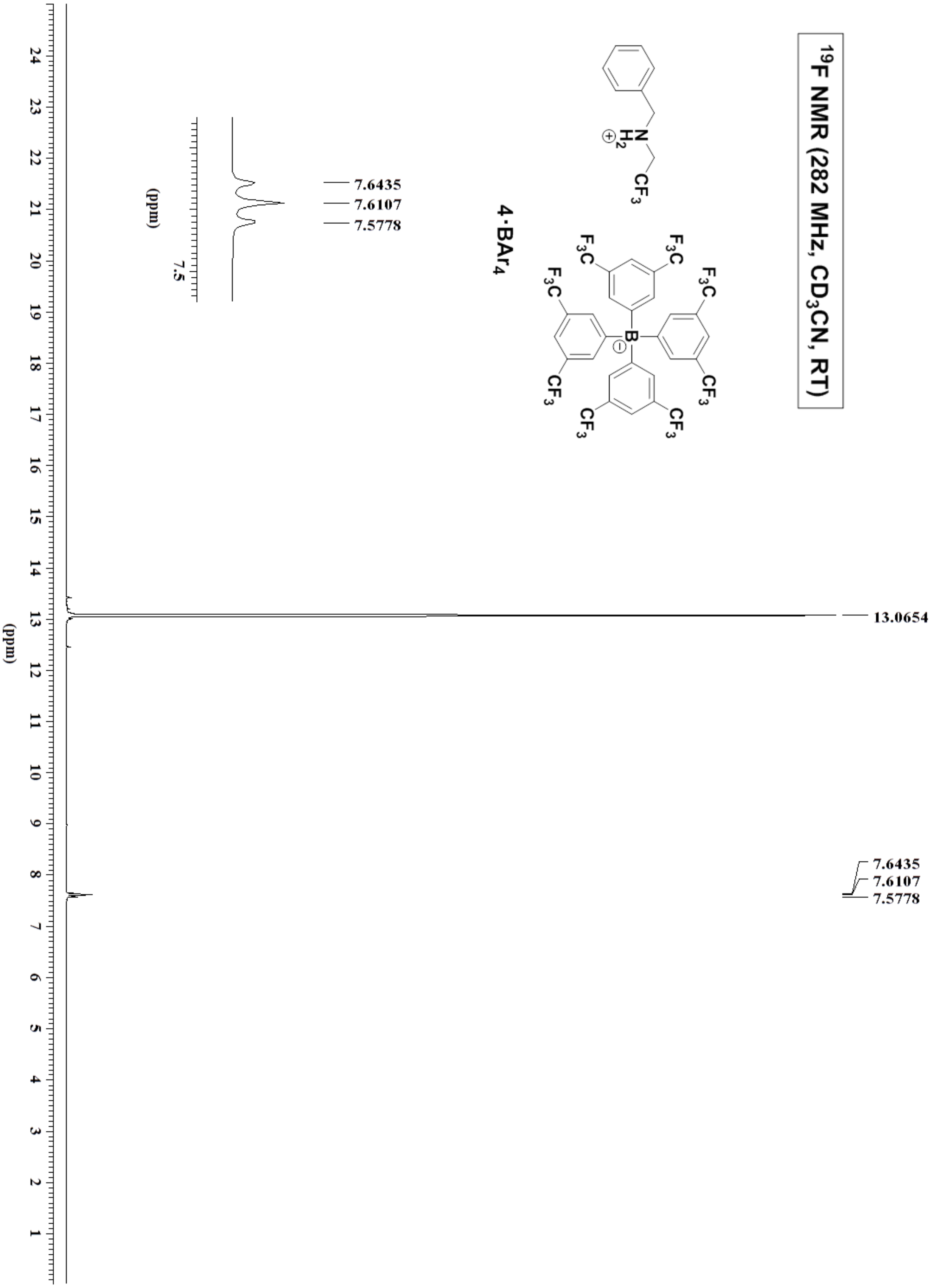
^1H NMR (500 MHz, CD_3CN, RT)

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012



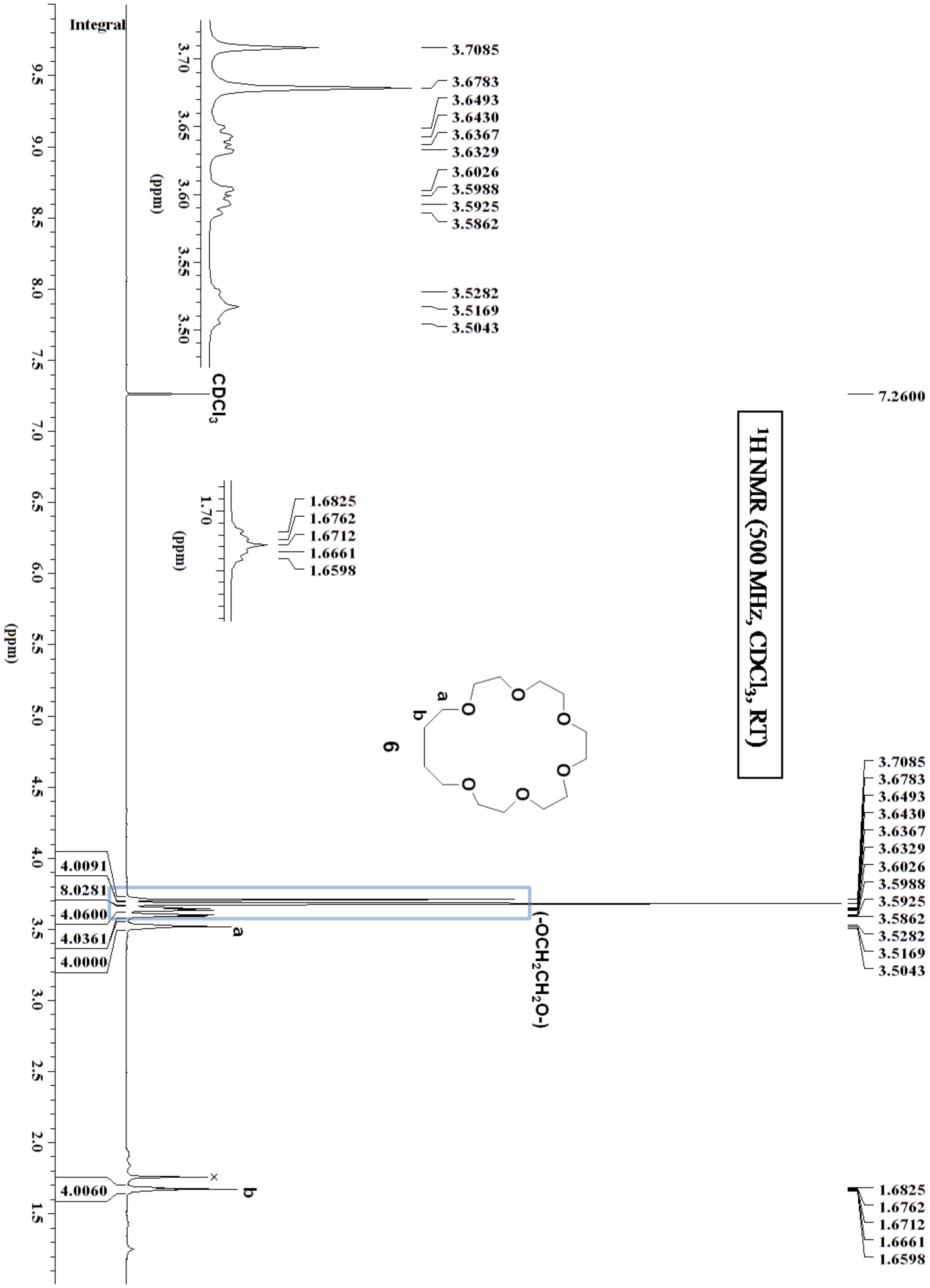
4·BAr$_4$

Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

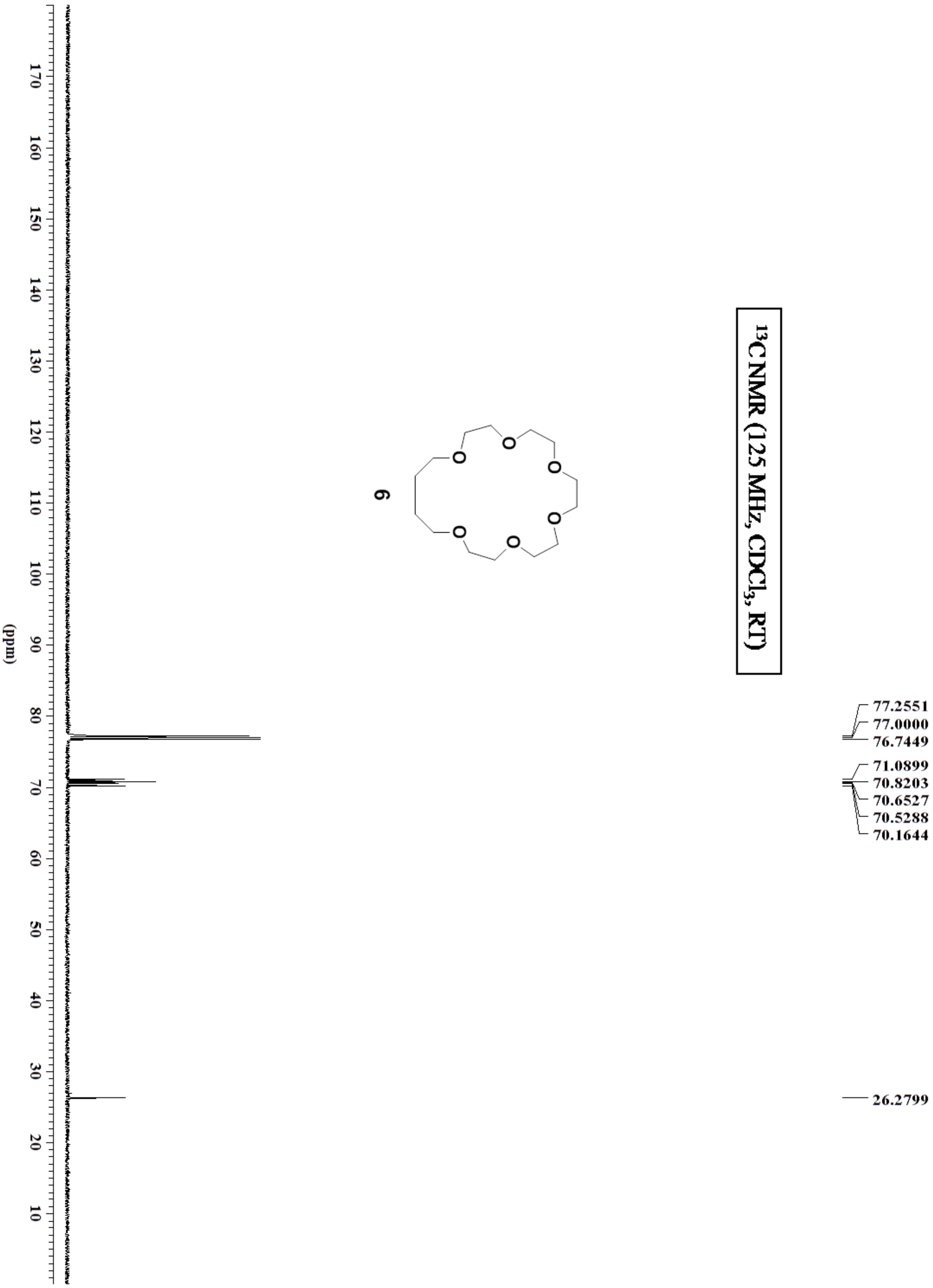


4·BAr$_4$

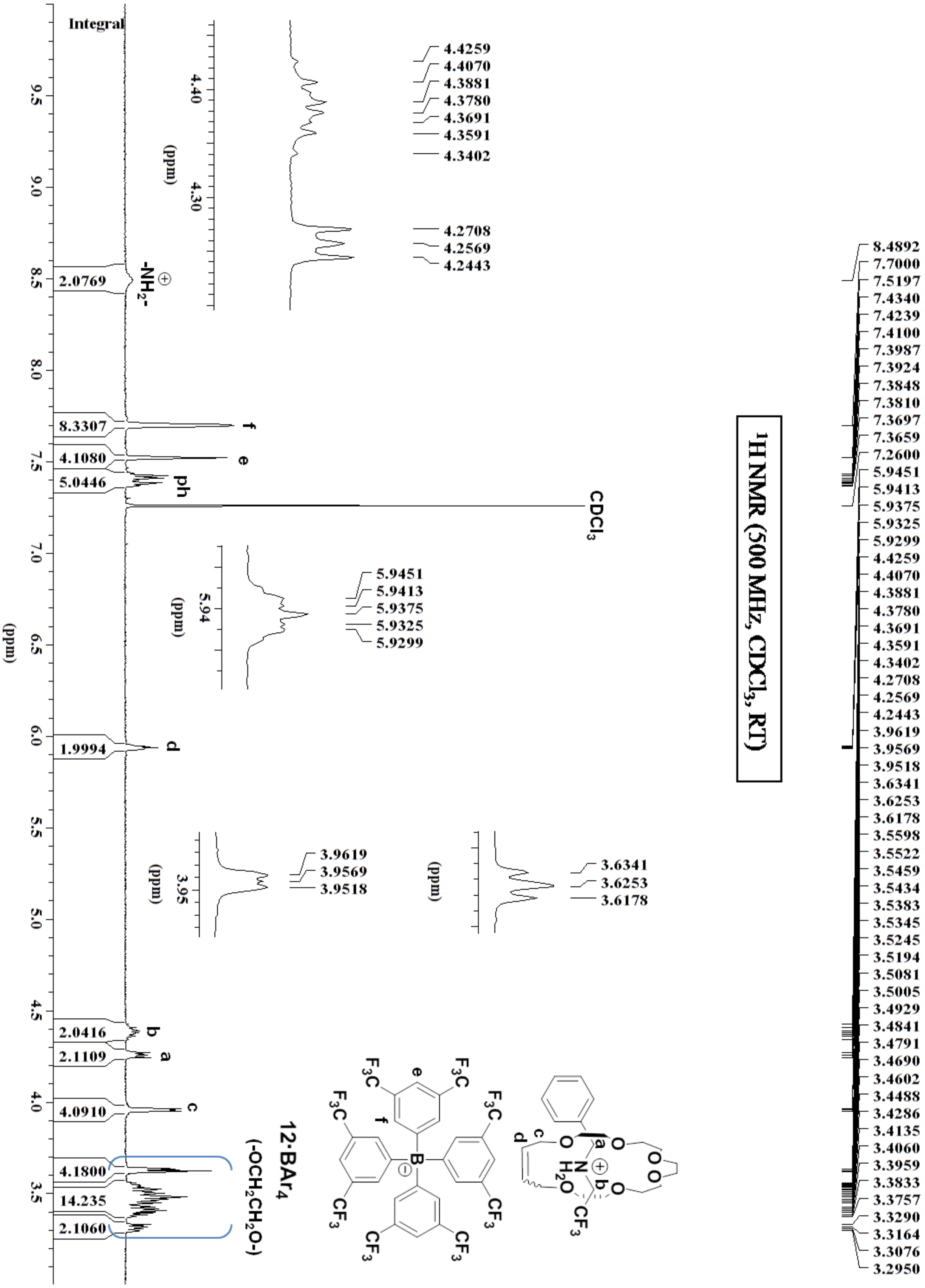
Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012



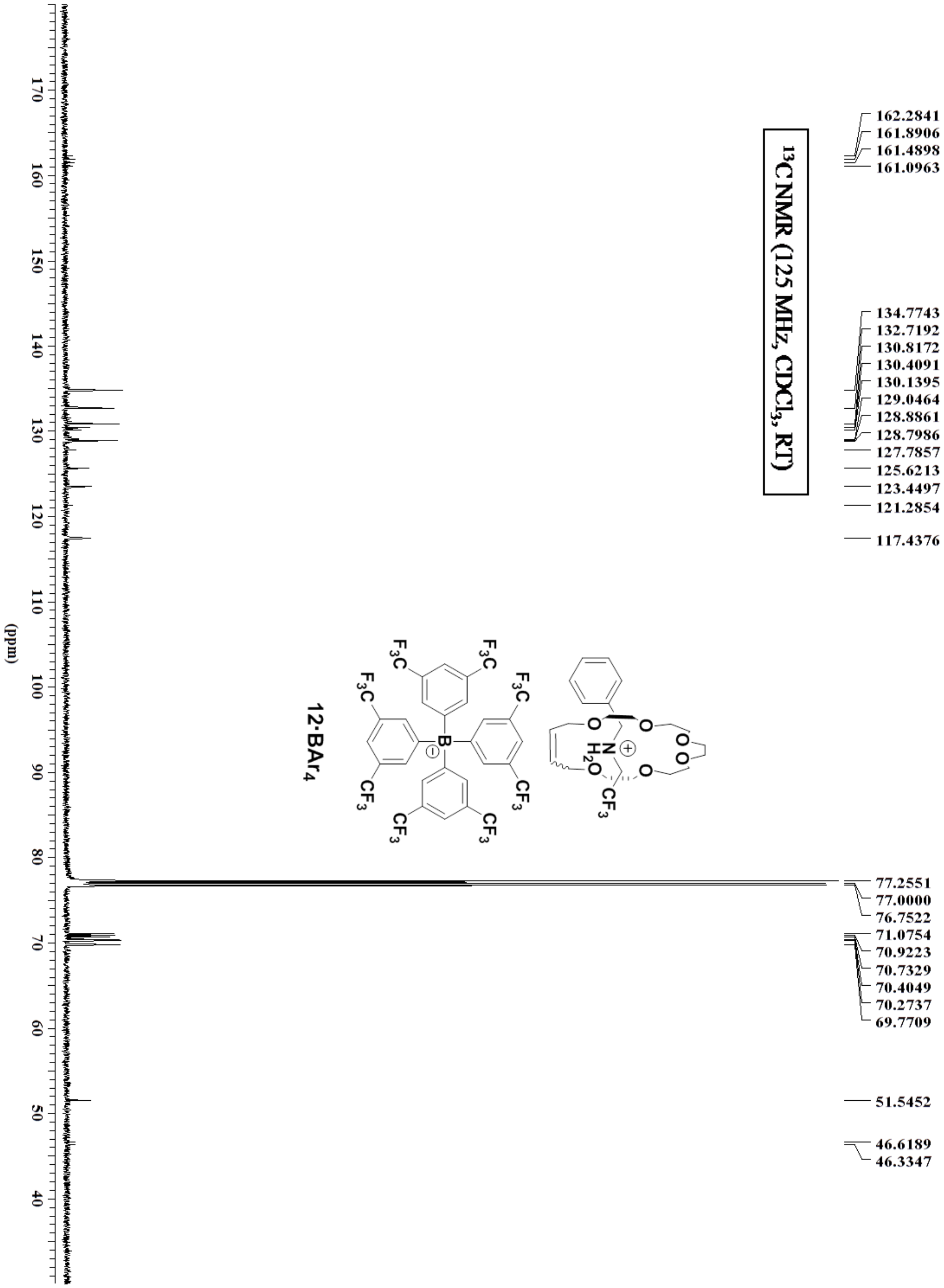
Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012

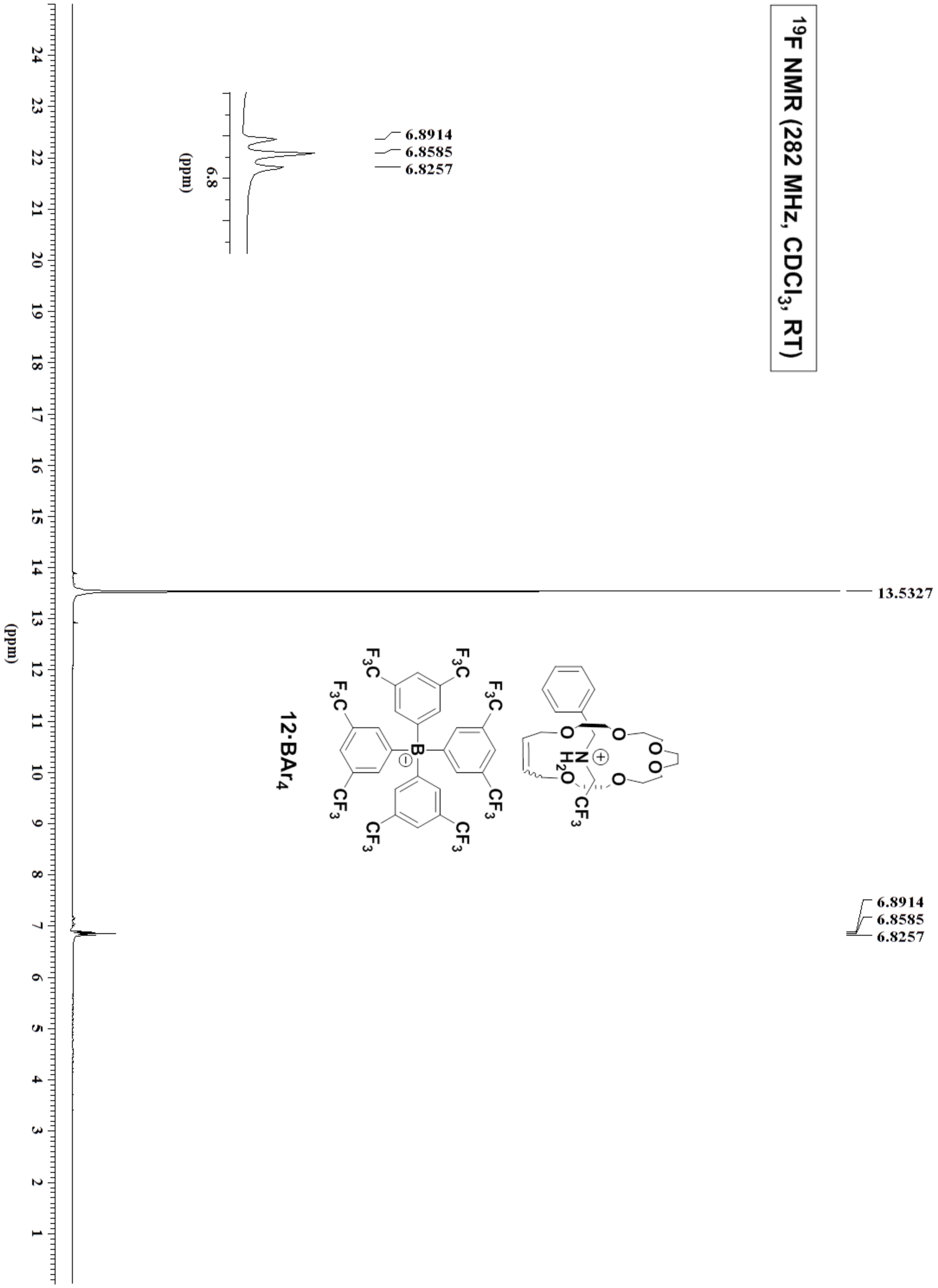


Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012



Electronic Supplementary Material (ESI) for Chemical Communications
This Journal is © The Royal Society of Chemistry 2012




^{19}F NMR (282 MHz, CDCl$_3$, RT)
12·BAr$_4$
13.5327
6.8914
6.8585
6.8257
6.8
(ppm)
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
(ppm)
F$_3$C
CF$_3$
B
O
N
H$_2$O