Supporting Information for:

Merging Visible Light Photocatalysis and Transition Metal Catalysis in the Copper-Catalyzed Trifluoromethylation of Boronic Acids with CF_3I

Yingda Ye and Melanie S. Sanford*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109

General Procedures

NMR spectra were obtained on a Varian MR400 (400 MHz for ^{1}H; 377 MHz for ^{19}F; 100 MHz for ^{13}C), a Varian vnmrs 500 (500MHz for ^{1}H), or a Varian vnmrs 700 (700MHz for ^{1}H; 175 MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR spectra are referenced based on the internal standard 1,3,5-trifluorobenzene, which appears at –107.40 ppm. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), doublet of triplets (dt) and multiplet (m). Kugelrohr distillations were performed on a Buchi Glass Oven B-580 Kugelrohr.

Materials and Methods

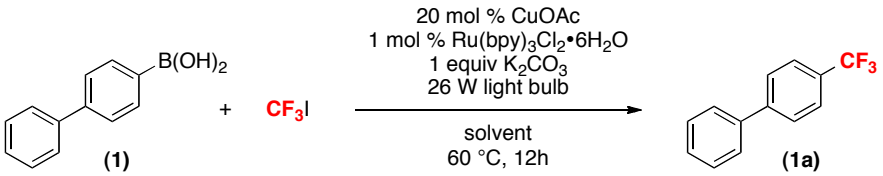
CuOAc was obtained from Strem Chemical. Aryl boronic acids were obtained from Frontier Scientific. 1,3,5-Trifluorobenzene, 4-(trifluoromethyl)benzonitrile, and iodobenzotrifluoride were obtained from Oakwood Products. 4-Fluorobenzotrifluoride and 4-(trifluoromethyl)pyridine were obtained from Matrix Scientific. Trifluorotoluene was obtained from Acros. Potassium carbonate was obtained from Fisher Scientific. CF_3SO_2Na, and 4-(trifluoromethyl)anisole were obtained from SynQuest Laboratories. $Ru(bpy)_3Cl_2•6H_2O$, $Ru(phen)_3Cl_2$, CF_3SO_2Cl, 1,4-bis(trifluoromethyl)benzene, 4-(trifluoromethyl)phenol, estrone and dry DMF, DMA, DMSO, 1,4-dioxane, diglyme and NMP were obtained from Sigma Aldrich. All syntheses were conducted using standard Schlenk techniques or in a nitrogen atmosphere glovebox unless otherwise stated.

Experimental Details

Preparation of CF_3I Stock Solution

DMF (20 mL) was added to a Schlenk graduated cylinder under nitrogen (see picture below for apparatus). The vessel and solvent were weighed. Next, CF_3I was bubbled through the DMF solution using a long needle until the total volume of the solution reached approximately 25 mL. The vessel was sealed weighed again. The concentration of the CF_3I stock solution was then calculated based on the mass of CF_3I added and the total volume of the solution.

Solvent Screening for Trifluoromethylation of Aryl Boronic Acids



In a glovebox, substrate **1** (9.9 mg, 0.05 mmol, 1 equiv), CuOAc (1.2 mg, 0.01 mmol, 0.2 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (0.37 mg, 0.0005 mmol, 0.01 equiv), and K_2CO_3 (6.9 mg, 0.05 mmol, 1 equiv) were weighed into a 4 mL vial. CF_3I (0.25 mmol, 5 equiv) was added to the reaction vial as a stock solution in reaction solvent. Additional solvent was added to make the total amount of solvent 0.3 mL. The vial was sealed with a Teflon-lined cap, removed from the glove box, and placed in an oil bath at 60 °C with two 26 W compact fluorescent light bulbs (one on either side of the vial approximately 5 cm away). The reaction mixture was allowed to stir for 12 h. The resulting red solution was cooled to room temperature and diluted with CH_2Cl_2 (2 mL). 1,3,5-trifluorobenzene and naphthalene (0.05 mmol, 1 equiv) were added as internal standards, and the reaction was analyzed by ^{19}F NMR spectroscopy and GC. The yields of **1a** are listed in **Table S1**.

Table S1. Solvent Screen for Reaction Between **1** and CF_3I

Entry	Solvent	Yield of 1a
1	1,4-Dioxane	7%
2	Diglyme	21%
3	NMP	65%
4	DMA	72%
5	DMSO	73%
6	DMF	76%

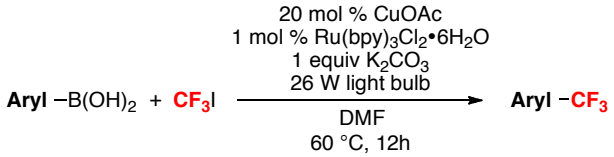
Reactivity of Aryl Boronic Acid under MacMillan's Reaction Conditions[1]

In a glovebox, substrate **1** (9.9 mg, 0.05 mmol, 1 equiv), $Ru(phen)_3Cl_2$ (0.36 mg, 0.0005 mmol, 0.01 equiv), and K_2HPO_4 (26.1 mg, 0.15 mmol, 3 equiv) were weighed into a 4 mL vial. MeCN (0.4 mL) was added. The vial was fitted with a screw cap containing a silicone septum and removed from the glove box. The CF_3SO_2Cl (10.64 µL, 2 equiv) was added by syringe, and the vial was sealed with parafilm and placed in a water bath at room temperature with two 26 W compact fluorescent light bulbs (one on either side of the vial approximately 5 cm away). The reaction mixture was allowed to stir for 24 h. The reaction was quenched with water (1 mL) and extracted with ethyl acetate (2 x 1 mL) and CH_2Cl_2 (1 x 1 mL). The combined organic layers were dried over $MgSO_4$. 1,3,5-trifluorobenzene and naphthalene (0.05 mmol, 1 equiv) were added as internal standards, and the reaction was analyzed by ^1H NMR and ^{19}F NMR spectroscopy. The starting material **1** was recovered in nearly quantitative yield, and trifluoromethylated product **1a** was formed in less than 2% yield.

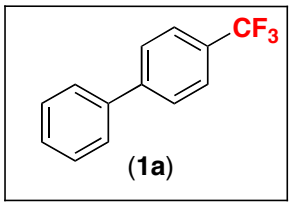
Reactivity of Aryl Boronic Acid under Baran's Reaction Conditions[2]

To a solution of substrate **1** (49.5 mg, 0.25 mmol, 1.0 equiv) and sodium trifluoromethylsulfinate (117 mg, 0.75 mmol, 3.0 equiv) in dichloromethane (1 mL) and water (0.4 mL) at 0 °C was slowly added tert-butylhydroperoxide (70% solution in water, 0.17 mL, 1.25 mmol, 5.0 equiv) with vigorous stirring. The reaction was warmed to room temperature and stirred for 24 h. The resulting solution was partitioned between dichloromethane (2 mL) and saturated sodium bicarbonate (2 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 2 mL). The combined organic layers were dried over $MgSO_4$. 1,3,5-trifluorobenzene and naphthalene (0.25 mmol, 1 equiv) were added as internal standards, and the reaction was analyzed by ^{19}F NMR spectroscopy and GCMS. No trifluoromethylated product was observed. 4-Hydroxybiphenyl was formed in 75% yield.

Standard Procedure for Trifluoromethylation of Aryl Boronic Acids



In a glovebox, the boronic acid substrate **1** (0.25 mmol, 1 equiv), CuOAc (6 mg, 0.05 mmol, 0.2 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (1.85 mg, 0.0025 mmol, 0.01 equiv), and K_2CO_3 (35 mg, 0.25 mmol, 1 equiv) were weighed into a 20 mL vial. CF_3I (1.25 mmol, 5 equiv) was added to the reaction vial as a stock solution in DMF. Additional DMF was added to make the total volume 1.5 mL. The vial was sealed with a Teflon-lined cap, removed from the glove box, and placed in an oil bath at 60 °C with two 26 W compact fluorescent light bulbs (one on either side of the vial approximately 5 cm away). The reaction mixture was allowed to stir for 12 h. The resulting red solution was cooled to room temperature. 1,3,5-Trifluorobenzene (0.25 mmol, 1 equiv) was added as an internal standard, and the reaction was analyzed by ^{19}F NMR spectroscopy. GCMS analysis was performed on a Shimadzu GCMS-QP2010 plus gas chromatograph mass spectrometer. The products were separated on a 30 m length by 0.25 mm id, RESTEK XTI-5 column coated with a 0.25 µm film. Helium was employed as the carrier gas, with a constant column flow of 1.5 mL/min. The injector temperature was held constant at 250 ºC. The GC oven temperature program was as follows: 40 ºC hold 6 min, ramp 15 ºC/min to 250 ºC, and hold for 3 min.

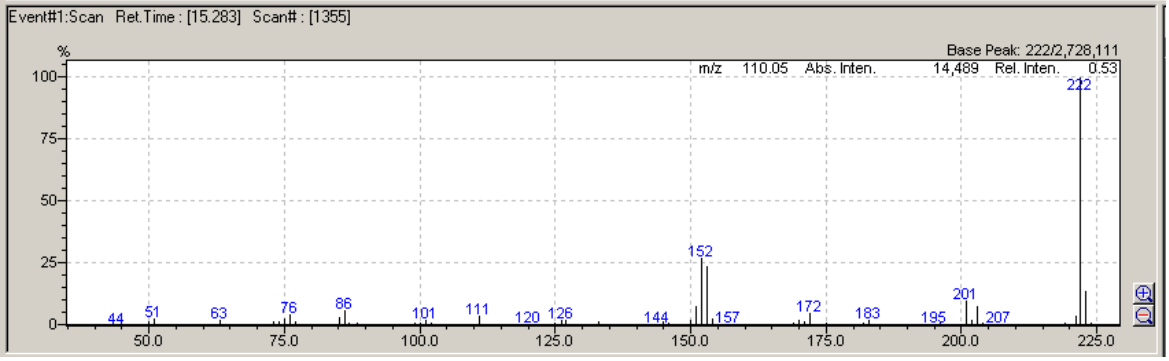


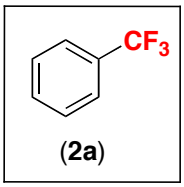
(**1a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The trifluoromethylated product **1a** was formed in 80% yield. The product showed a ^{19}F NMR signal at –62.4 ppm in DCE (lit. –62.4 ppm in $CDCl_3$).[3] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 15.28 min.

This reaction of substrate **1** was also conducted on a 5 mmol scale. For the 5 mmol scale reaction, substrate **1** (0.99 g, 5 mmol, 1 equiv), CuOAc (122 mg, 1 mmol, 0.2 equiv), K_2CO_3 (0.69 g, 5 mmol, 1 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (37.4 mg, 0.05 mmol, 0.01 equiv), CF_3I (25 mmol, 5 equiv) and DMF (30 mL) were used. The reaction was conducted in a 250 mL round bottom flask, and the yield was determined to be 82% by ^{19}F NMR spectroscopy. The reaction mixture was then diluted with Et_2O (50 mL), and the resulting mixture was washed with water (3 x 50 mL) and brine (1 x 50 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the product was purified by column chromatography on silica gel using pentane as the eluent. Compound **1a** was obtained as white crystalline solid (776 mg, 70% yield, mp = 64.0-64.4 ºC). The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[3]

Mass spectrum of product peak (15.28 min) from GCMS of Cu/Ru-catalyzed reaction between [1,1'-biphenyl]-4-ylboronic acid and CF_3I

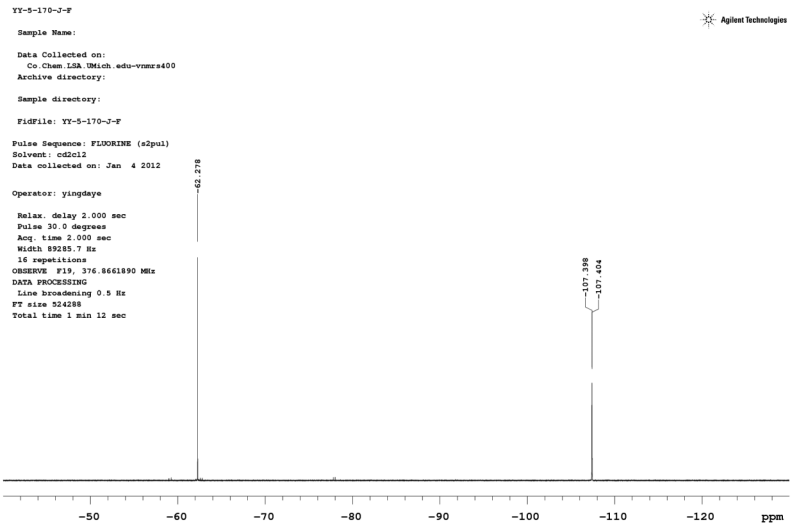




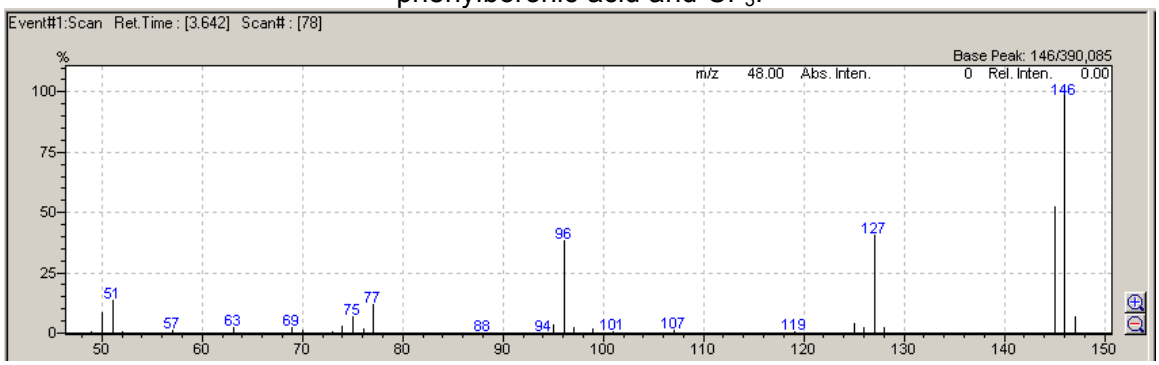
(**2a**)

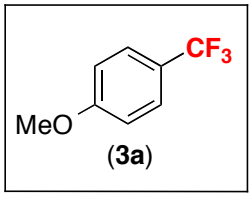
The reaction was performed on a 0.25 mmol scale using the standard procedure. The ^{19}F NMR spectral data for **2a** matched that of an authentic sample (Acros, s, –62.3 ppm). The trifluoromethylated product was formed in 70% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 3.64 min.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of phenylboronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (3.64 min) from GCMS of Cu/Ru-catalyzed reaction between phenylboronic acid and CF_3I

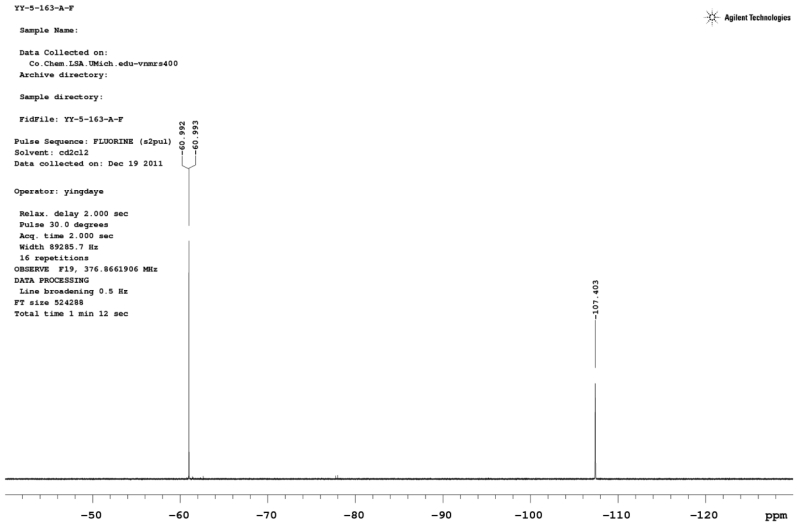




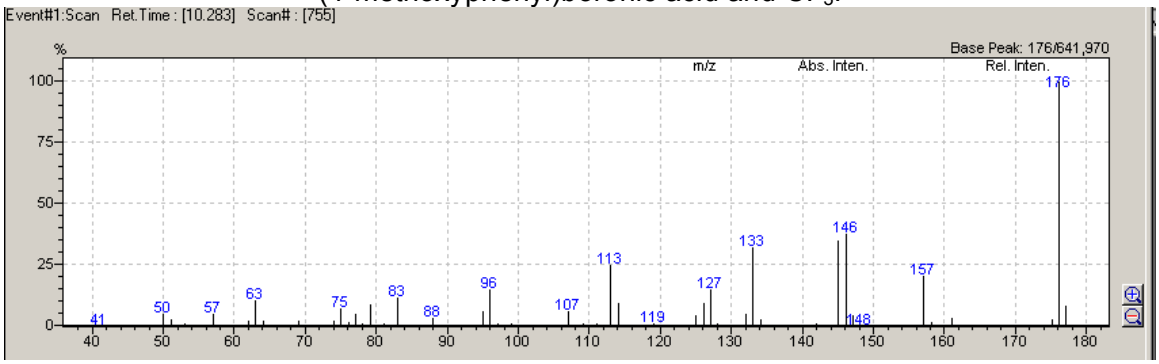
(**3a**)

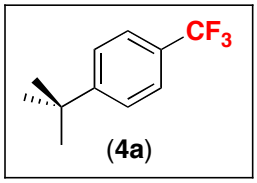
The reaction was performed on a 0.25 mmol scale using the standard procedure. The ^{19}F NMR spectral data for **3a** matched that of an authentic sample (SynQuest Labs, s, –61.0 ppm). The trifluoromethylated product was formed in 84% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 10.28 min.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of (4-methoxyphenyl)boronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (10.28 min) from GCMS of Cu/Ru-catalyzed reaction between (4-methoxyphenyl)boronic acid and CF_3I



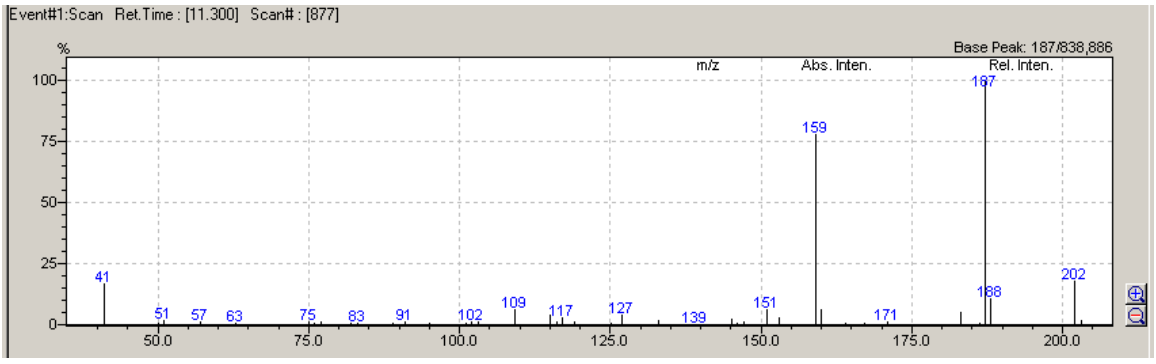


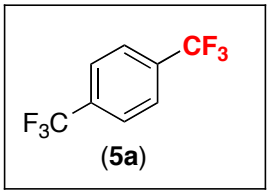
(**4a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The trifluoromethylated product **4a** was formed in 86% yield. The product showed a ^{19}F NMR signal at –61.8 ppm in DCE (lit. –62.2 ppm in $CDCl_3$).[4] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 11.30 min.

This reaction of substrate **4** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **4** (178 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 80 ºC at 10 mm Hg. The isolated product **4a** (145 mg, 72% yield) was 96% pure, and contained traces (4%) of the corresponding protodeboronation byproduct *tert*-butylbenzene, which was not easily separable by chromatography on silica gel. The ^1H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[4]

Mass spectrum of product peak (11.30 min) from GCMS of Cu/Ru-catalyzed reaction between (4-(*tert*-butyl)phenyl)boronic acid and CF_3I

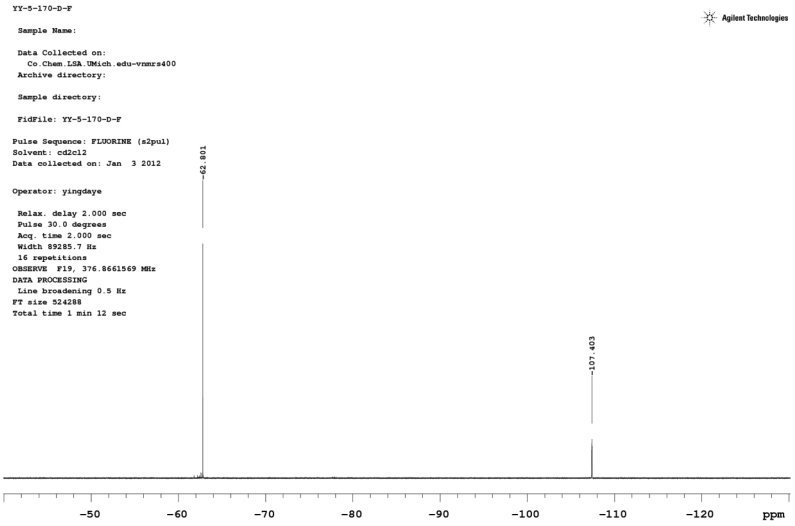




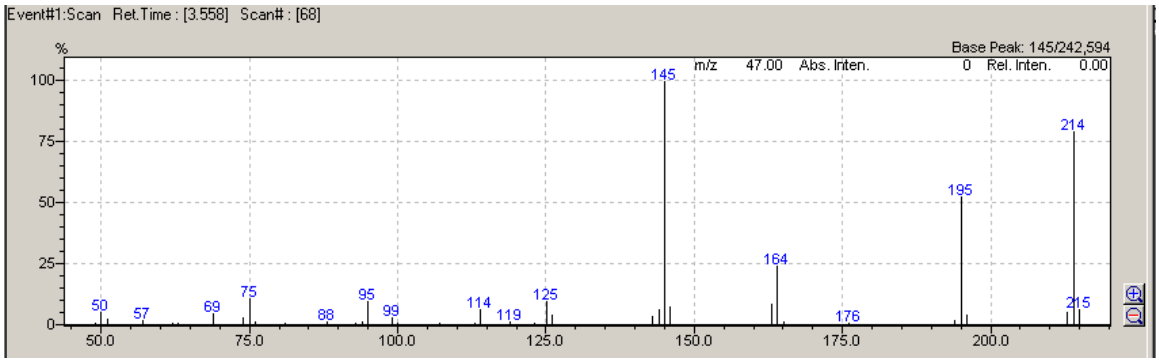
(**5a**)

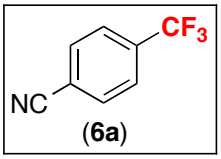
The reaction was performed on a 0.25 mmol scale using 50 mol % of CuOAc (15 mg, 0.125 mmol, 0.5 equiv) under otherwise identical conditions to the standard procedure. The ^{19}F NMR spectral data for **5a** matched that of an authentic sample (Aldrich, s, –62.8 ppm). The trifluoromethylated product was formed in 64% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 3.56 min.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of (4-(trifluoromethyl)phenyl)boronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (3.56 min) from GCMS of Cu/Ru-catalyzed reaction between (4-(trifluoromethyl)phenyl)boronic acid and CF_3I



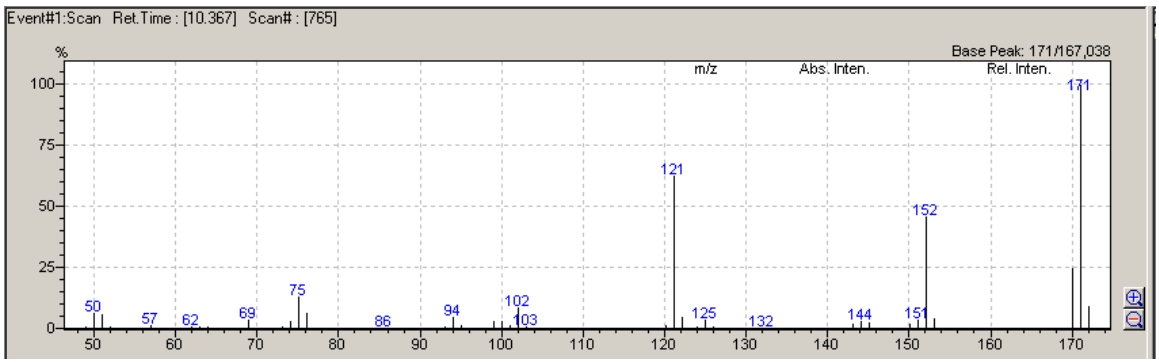


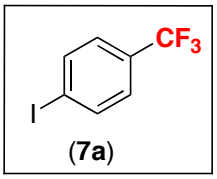
(**6a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The ^{19}F NMR spectral data for **6a** matched that of an authentic sample (Oakwood, s, –63.1 ppm). The trifluoromethylated product was formed in 84% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 10.37 min.

This reaction of substrate **6** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **6** (147 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 90 ºC at 10 mm Hg. The isolated product **6a** (112 mg, 65% yield) was 97% pure, and contained traces (3%) of the corresponding protodeboronation byproduct benzonitrile. If necessary, the protodeboronation product can be completely removed by subsequent column chromatographic purification on silica gel using 2% diethyl ether in pentane as the eluent. After this second purification, compound **6a** was obtained as a white solid (89 mg, 52% yield). The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to the authentic sample.

Mass spectrum of product peak (10.37 min) from GCMS of Cu/Ru-catalyzed reaction between (4-(cyano)phenyl)boronic acid and CF_3I



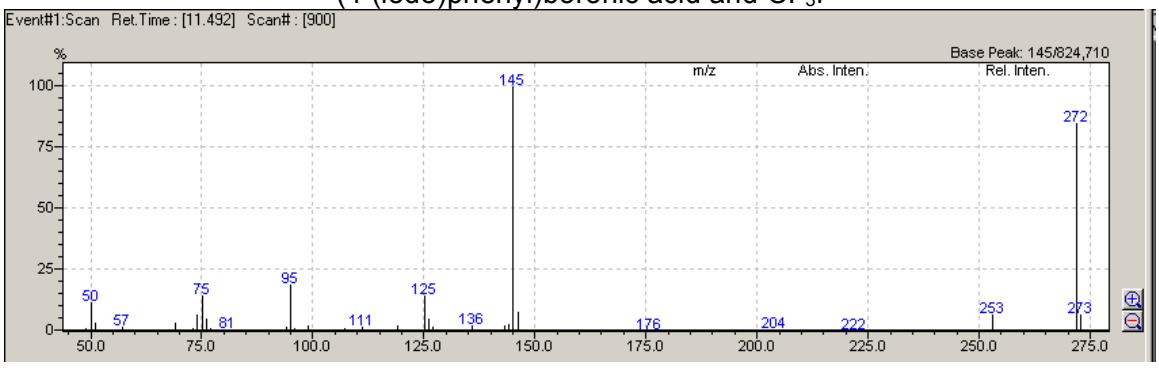


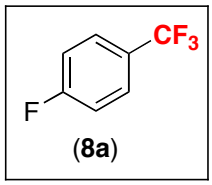
(**7a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The ^{19}F NMR spectral data for **7a** matched that of an authentic sample (Oakwood, s, –62.5 ppm). The trifluoromethylated product was formed in 73% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 11.49 min.

This reaction of substrate **7** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **7** (248 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 100 ºC at 10 mm Hg. The isolated product **7a** (174 mg, 64% yield) was 96% pure, and contained traces (4%) of the corresponding protodeboronation byproduct iodobenzene, which was not easily separable by chromatography on silica gel. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to the authentic sample.

Mass spectrum of product peak (11.49 min) from GCMS of Cu/Ru-catalyzed reaction between (4-(iodo)phenyl)boronic acid and CF_3I

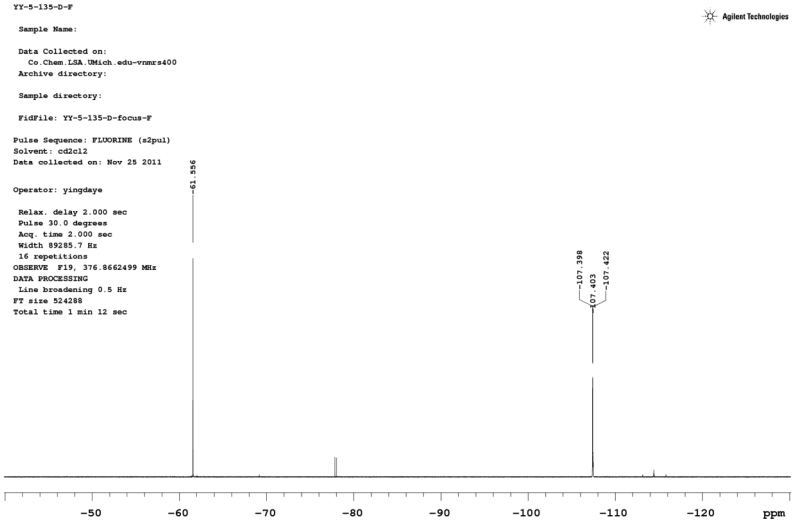




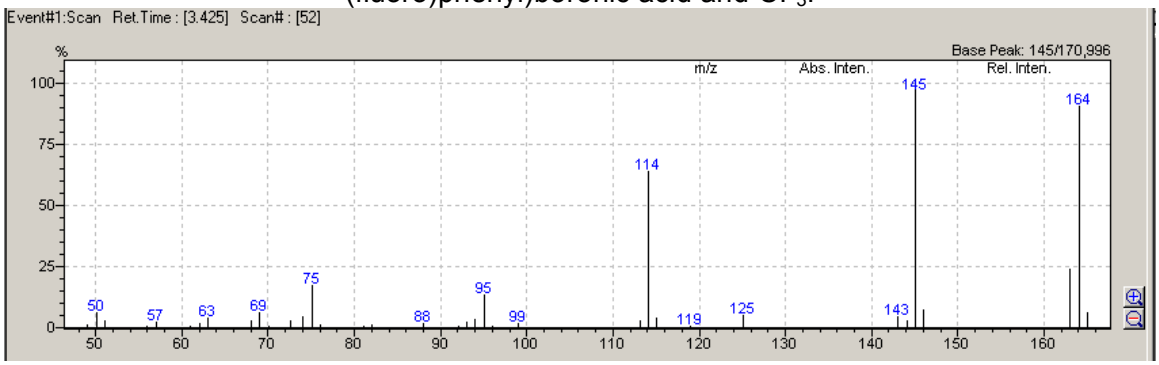
(**8a**)

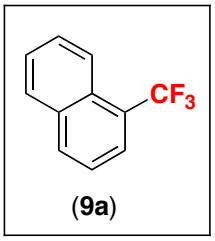
The reaction was performed on a 0.25 mmol scale using the standard procedure. The ^{19}F NMR spectral data for **8a** matched that of an authentic sample (Matrix Scientific, s, 3F, –61.6 ppm; m, 1F, –107.5 ppm). The trifluoromethylated product was formed in 93% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 3.42 min.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of (4-(fluoro)phenyl)boronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (3.42 min) from GCMS of Cu/Ru-catalyzed reaction between (4-(fluoro)phenyl)boronic acid and CF_3I



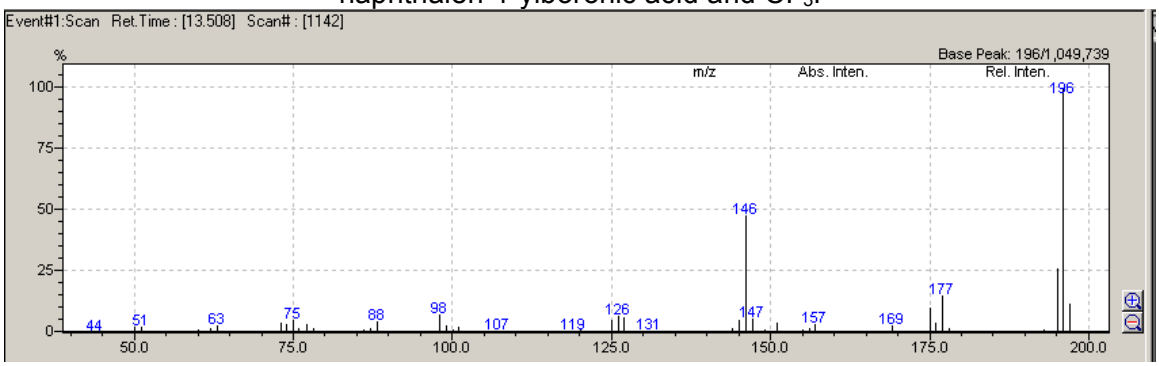


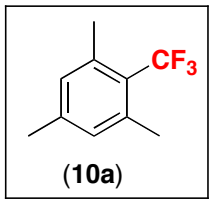
(**9a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The trifluoromethylated product **9a** was formed in 57% yield. The product showed a ^{19}F NMR signal at –59.3 ppm in DCE (lit. –59.72 ppm in $CDCl_3$).[3] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 13.51 min.

This reaction of substrate **9** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **9** (172 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 120 ºC at 10 mm Hg. Compound **9a** was obtained as a 5:1 mixture with the protodeboronation product naphthalene (103 mg in total, 46% yield for **9a**). Subsequent purification of this sample by column chromatography on silica gel using pentane as the eluent afforded **9a** was obtained as a pure clear liquid (79 mg, 40% yield). The ^1H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[3]

Mass spectrum of product peak (13.51 min) from GCMS of Cu/Ru-catalyzed reaction between naphthalen-1-ylboronic acid and CF_3I



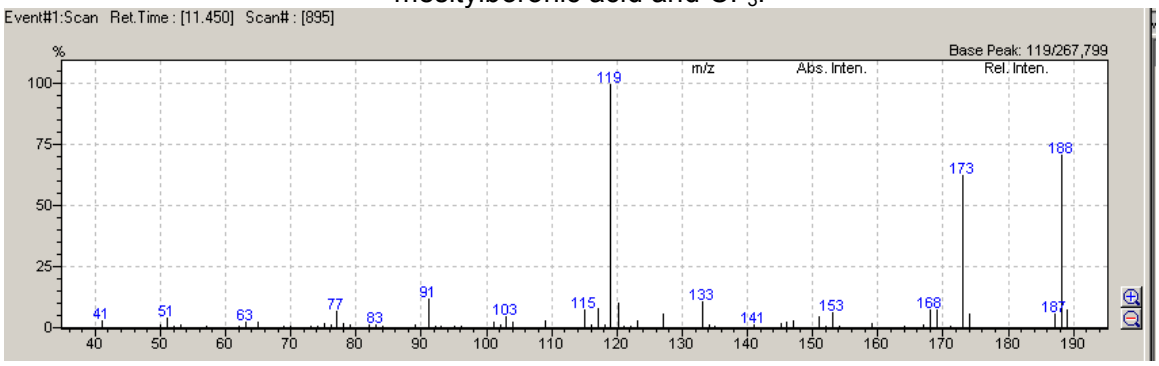


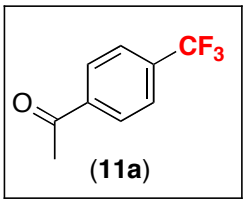
(**10a**)

The reaction was performed on a 0.25 mmol scale using 50 mol % of CuOAc (15 mg, 0.125 mmol, 0.5 equiv) under otherwise identical conditions to the standard procedure. The trifluoromethylated product **10a** was formed in 45% yield. The product showed a ^{19}F NMR signal at –53.2 ppm in DCE (lit. –55.0 ppm in $CDCl_3$).[5a] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 11.45 min.

This reaction of substrate **10** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **10** (164 mg, 1 mmol, 1 equiv), CuOAc (60 mg, 0.5 mmol, 0.5 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 90 ºC at 10 mm Hg. Compound **10a** was obtained as a 1:1 mixture with the inseparable protodeboronation product mesitylene as a clear liquid (119 mg in total, 39% yield for **10a**). The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[5b]

Mass spectrum of product peak (11.45 min) from GCMS of Cu/Ru-catalyzed reaction between mesitylboronic acid and CF_3I



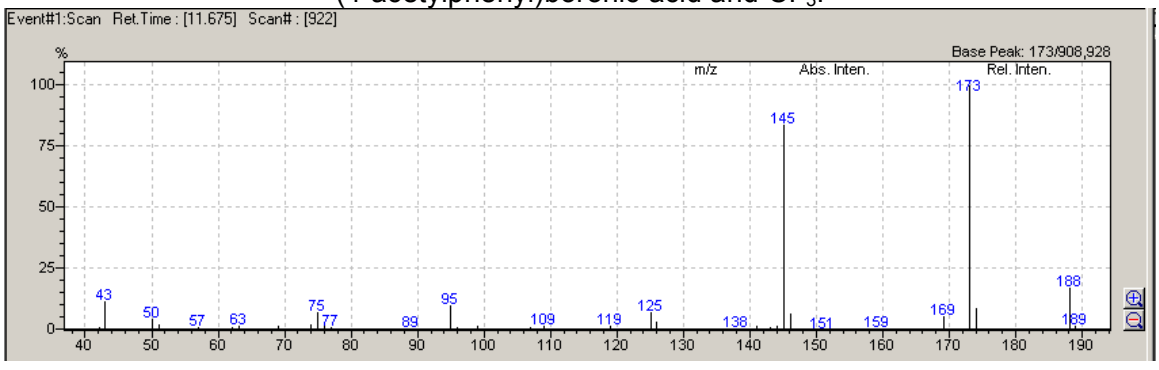


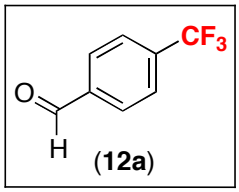
(**11a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The trifluoromethylated product **11a** was formed in 70% yield. The product showed a ^{19}F NMR signal at –62.7 ppm in DCE (lit. –63.0 ppm in $CDCl_3$).[4] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 11.68 min.

This reaction of substrate **11** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **11** (164 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 100 ºC at 10 mm Hg. The isolated product **11a** (120.0 mg, 64% yield) was 95% pure, and contained traces (5%) of the corresponding protodeboronation byproduct acetophenone, which was not easily separable by chromatography on silica gel. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[4]

Mass spectrum of product peak (11.68 min) from GCMS of Cu/Ru-catalyzed reaction between (4-acetylphenyl)boronic acid and CF_3I



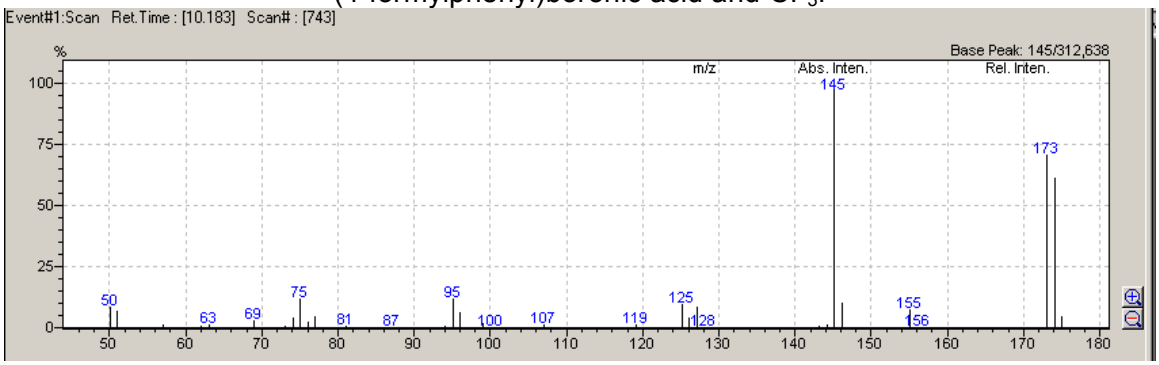


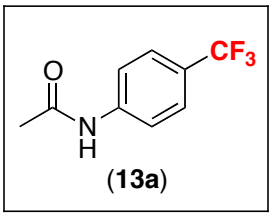
(**12a**)

The reaction was performed on a 0.25 mmol scale using 50 mol % of CuOAc (15 mg, 0.125 mmol, 0.5 equiv) under otherwise identical conditions. The trifluoromethylated product **12a** was formed in 74% yield. The product showed a ^{19}F NMR signal at –62.8 ppm in DCE (lit. –62.7 ppm in $CDCl_3$).[6] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 10.18 min.

This reaction of substrate **12** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **12** (150 mg, 1 mmol, 1 equiv), CuOAc (60 mg, 0.5 mmol, 0.5 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 100 ºC at 10 mm Hg. The isolated product **12a** (110.0 mg, 63% yield) was 95% pure, and contained traces (5%) of the corresponding protodeboronation byproduct benzaldehyde, which was not easily separable by chromatography on silica gel. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[6]

Mass spectrum of product peak (10.18 min) from GCMS of Cu/Ru-catalyzed reaction between (4-formylphenyl)boronic acid and CF_3I



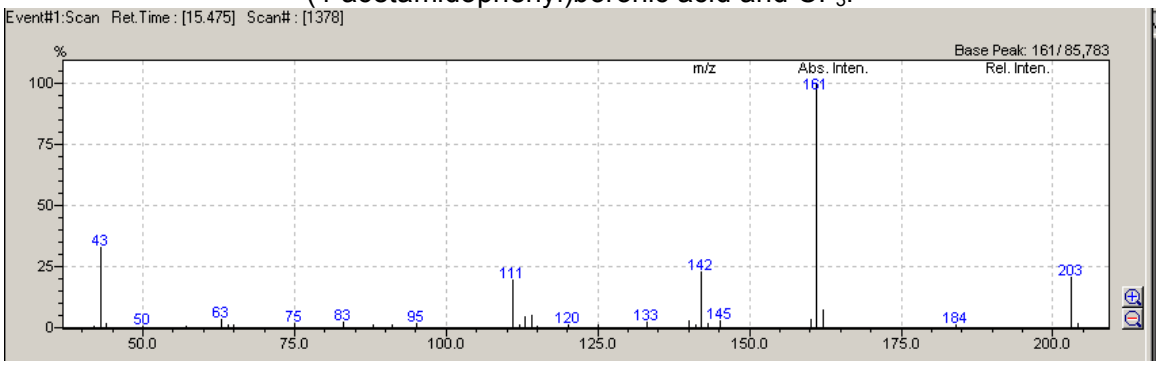


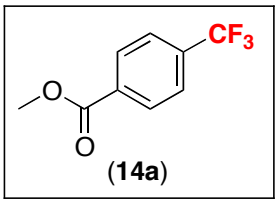
(**13a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The trifluoromethylated product **13a** was formed in 67% yield. The product showed a ^{19}F NMR signal at –63.5 ppm in DCE (lit. –62.3 ppm in $CDCl_3$).[7] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 15.48 min.

This reaction of substrate **13** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **13** (179 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 150 ºC at 10 mm Hg. The isolated product **13a** (121.0 mg, 60% yield) was 95% pure, and contained traces (5%) of the corresponding protodeboronation byproduct *N*-phenylacetamide, which was not easily separable by chromatography on silica gel. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[7]

Mass spectrum of product peak (15.48 min) from GCMS of Cu/Ru-catalyzed reaction between (4-acetamidophenyl)boronic acid and CF_3I



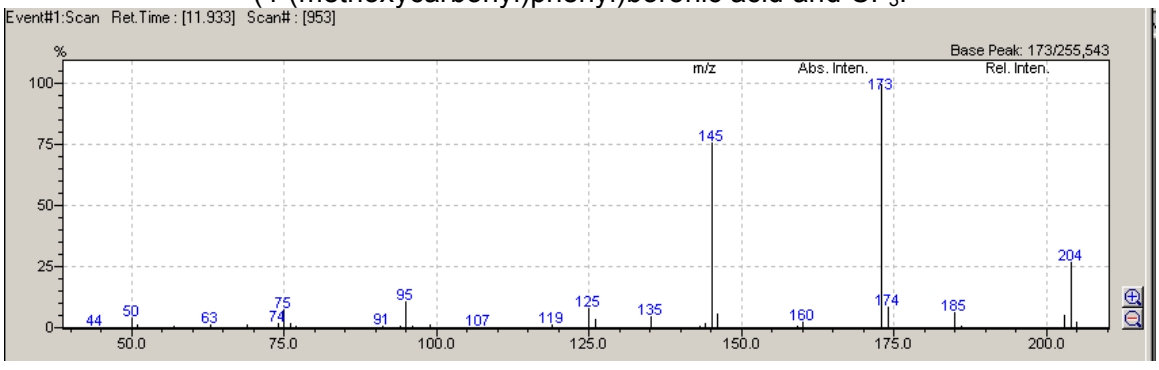


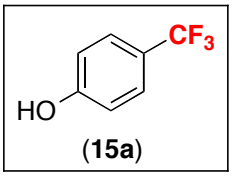
(**14a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The trifluoromethylated product **14a** was formed in 86% yield. The product showed a ^{19}F NMR signal at –62.7 ppm in DCE (lit. –62.9 ppm in $CDCl_3$).[4] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 11.93 min.

This reaction of substrate 1**4** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **14** (180 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 100 ºC at 10 mm Hg. The isolated product **14a** (139.0 mg, 68% yield) was 95% pure, and contained traces (5%) of the corresponding protodeboronation byproduct methyl benzoate, which was not easily separable by chromatography on silica gel. The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[4]

Mass spectrum of product peak (11.93 min) from GCMS of Cu/Ru-catalyzed reaction between (4-(methoxycarbonyl)phenyl)boronic acid and CF_3I



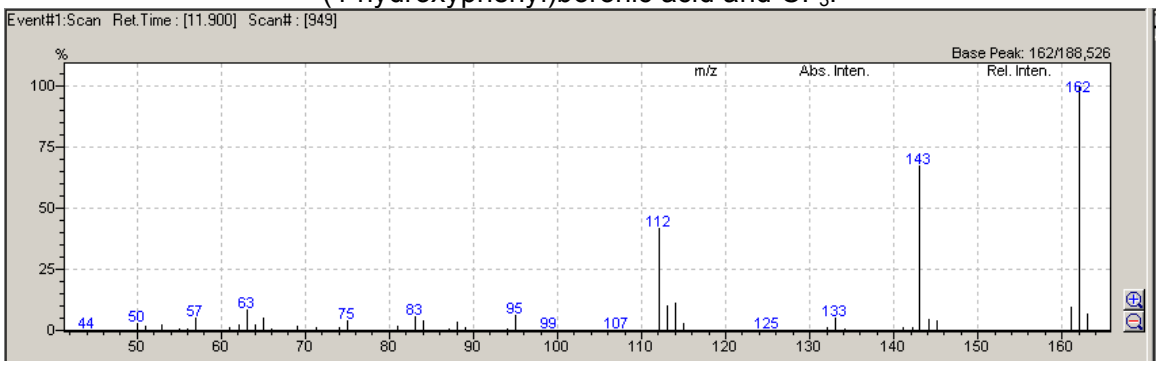


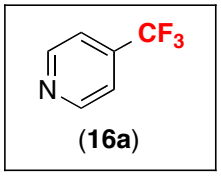
(**15a**)

The reaction was performed on a 0.25 mmol scale using 10 mol % of CuOAc (3 mg, 0.025 mmol, 0.1 equiv) under otherwise identical conditions. The ^{19}F NMR spectral data for **15a** matched that of an authentic sample (Matrix Scientific, s, –60.7 ppm). The trifluoromethylated product was formed in 50% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 11.90 min.

This reaction of substrate **15** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **15** (138 mg, 1 mmol, 1 equiv), CuOAc (12 mg, 0.1 mmol, 0.1 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 110 ºC at 10 mm Hg. Compound **15a** was obtained as a 10:1 mixture with the inseparable protodeboronation product phenol as a clear liquid (69.0 mg in total, 40% yield for **15a**). The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to the authentic sample.

Mass spectrum of product peak (11.90 min) from GCMS of Cu/Ru-catalyzed reaction between (4-hydroxyphenyl)boronic acid and CF_3I

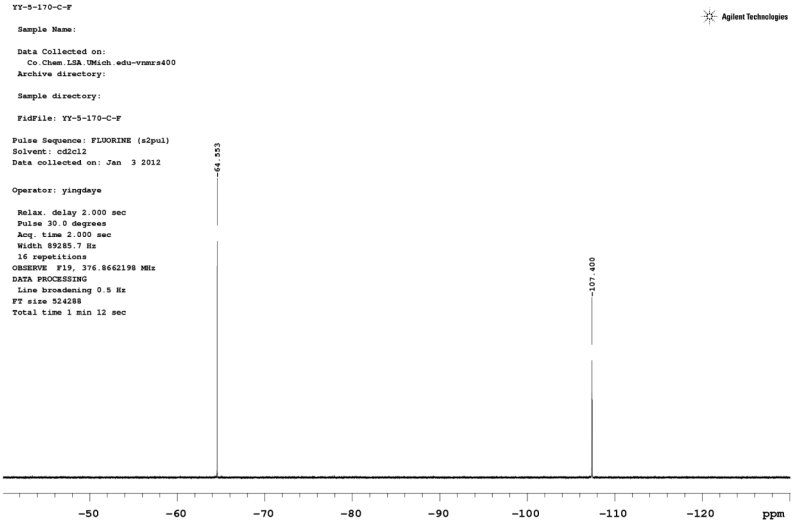




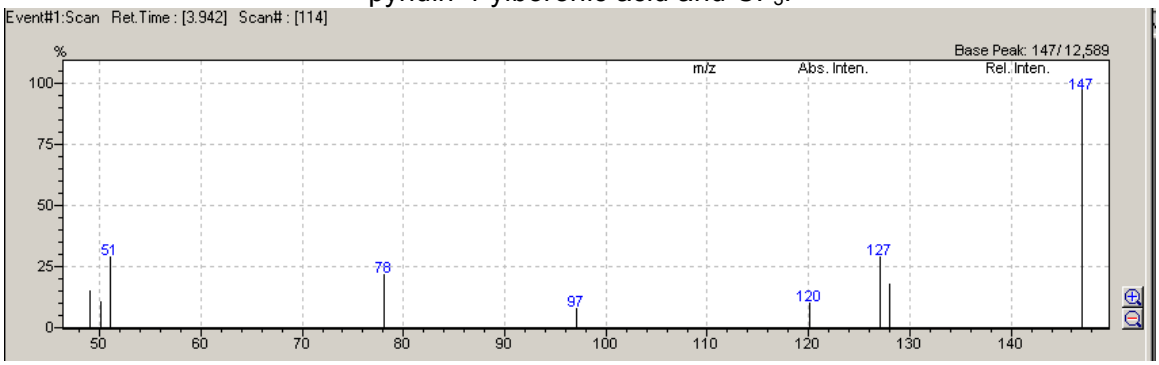
(**16a**)

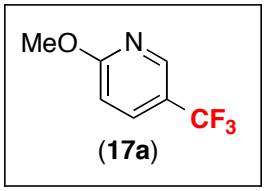
The reaction was performed on a 0.25 mmol scale using 50 mol % of CuOAc (15 mg, 0.125 mmol, 0.5 equiv) and 3 equivalent of CF_3I (0.75 mmol, 3 equiv) under otherwise identical conditions. The ^{19}F NMR spectral data for **16a** matched that of an authentic sample (Matrix Scientific, s, –64.6 ppm). The trifluoromethylated product was formed in 64% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 3.94 min. The mass spectrum of the product is provided in the spectral data below.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of pyridin-4-ylboronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (3.94 min) from GCMS of Cu/Ru-catalyzed reaction between pyridin-4-ylboronic acid and CF_3I

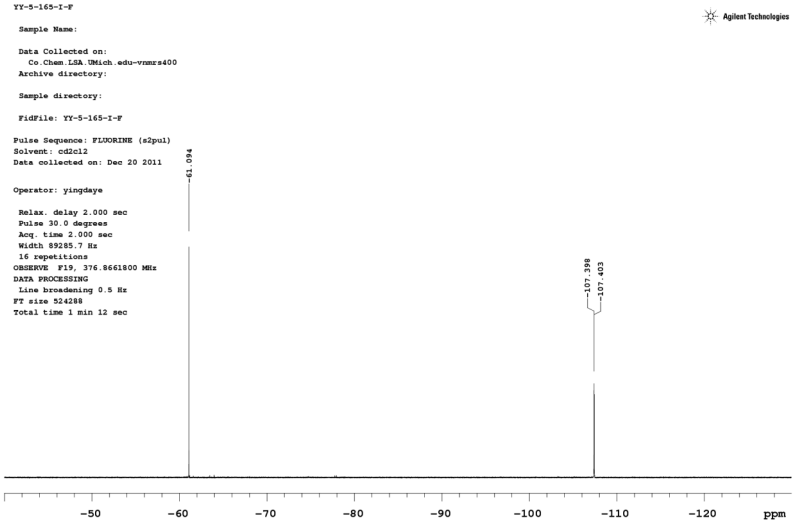




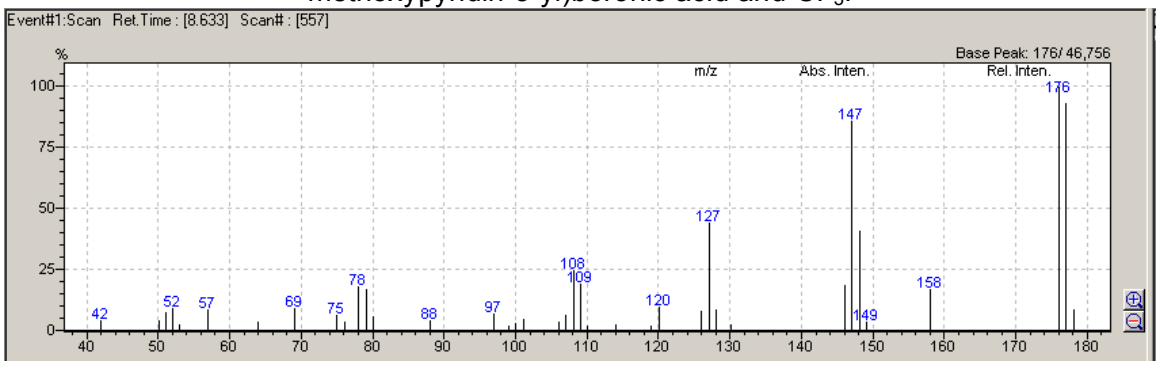
(**17a**)

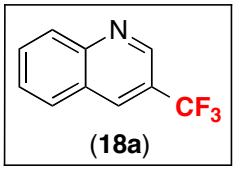
The reaction was performed on a 0.25 mmol scale using the standard procedure. The ^{19}F NMR spectral data for **17a** matched that of an authentic sample (Matrix Scientific, s, –61.1 ppm). The trifluoromethylated product was formed in 66% yield. The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 8.63 min. The mass spectrum of the product is provided in the spectral data below.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of (6-methoxypyridin-3-yl)boronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (8.63 min) from GCMS of Cu/Ru-catalyzed reaction between (6-methoxypyridin-3-yl)boronic acid and CF_3I



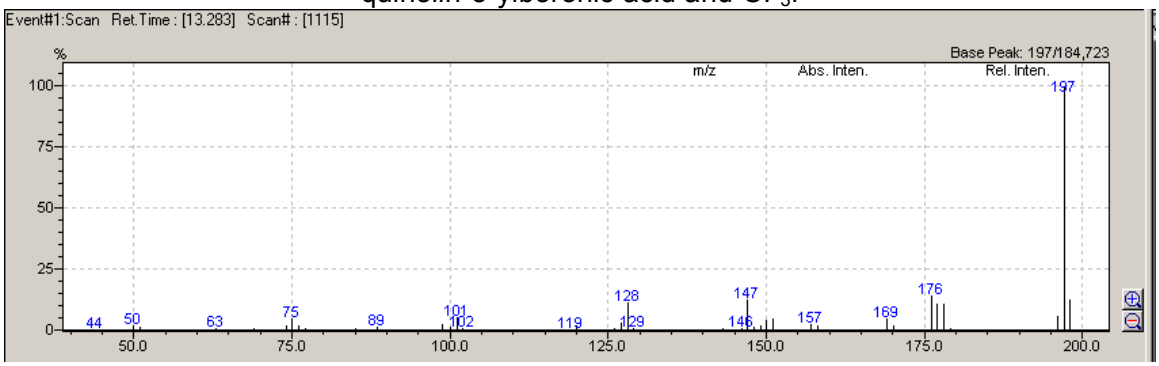


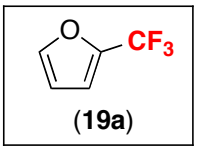
(**18a**)

The reaction was performed on a 0.25 mmol scale using the standard procedure. The trifluoromethylated product **18a** was formed in 70% yield. The product showed a ^{19}F NMR signal at –61.4 ppm in DCE (lit. –61.4 ppm in $CDCl_3$).[6] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 13.28 min. The mass spectrum of the product is provided in the spectral data below.

This reaction of substrate **18** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **18** (173 mg, 1 mmol, 1 equiv), CuOAc (24 mg, 0.2 mmol, 0.2 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 25 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by Kugelrohr distillation at 130 ºC at 10 mm Hg. The isolated product **18a** (132.0 mg, 67% yield) was 96% pure, and contained traces (4%) of the corresponding protodeboronation byproduct quinoline. Subsequent purification of this sample by column chromatography on silica gel using 2% diethyl ether in pentane as the eluent afforded **18a** as a white solid (108 mg, 55% yield). The ^1H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[6]

Mass spectrum of product peak (13.28 min) from GCMS of Cu/Ru-catalyzed reaction between quinolin-3-ylboronic acid and CF_3I

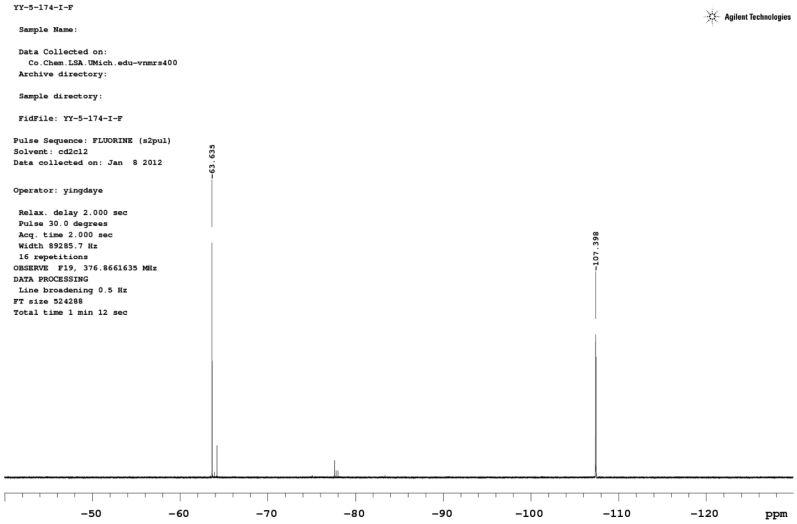




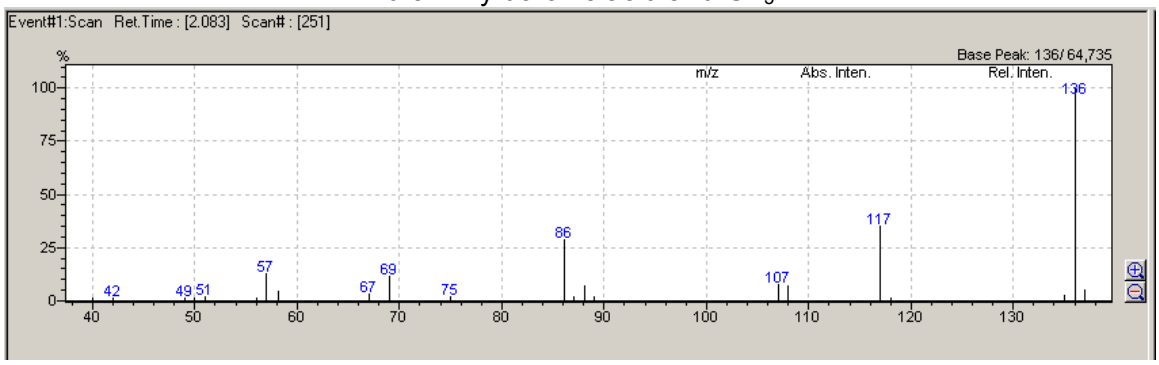
(**19a**)

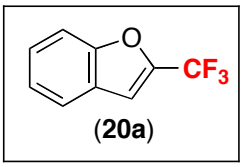
The reaction was performed on a 0.25 mmol scale using 50 mol % of CuOAc (15 mg, 0.125 mmol, 0.5 equiv) at 70 ˚C under otherwise identical conditions. The trifluoromethylated product **19a** was formed in 44% yield. The product showed a ^{19}F NMR signal at –63.6 ppm in DCE (lit. –64.8 ppm in CD_3CN).[8] The identity of the product was further confirmed by GCMS analysis. The GC oven temperature program was as follows: 30 ºC hold 6 min, ramp 20 ºC/min to 250 ºC, and hold for 3 min. The product peak was observed at 2.08 min. The mass spectrum of the product is provided in the spectral data below.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of furan-2-ylboronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (2.08 min) from GCMS of Cu/Ru-catalyzed reaction between furan-2-ylboronic acid and CF_3I



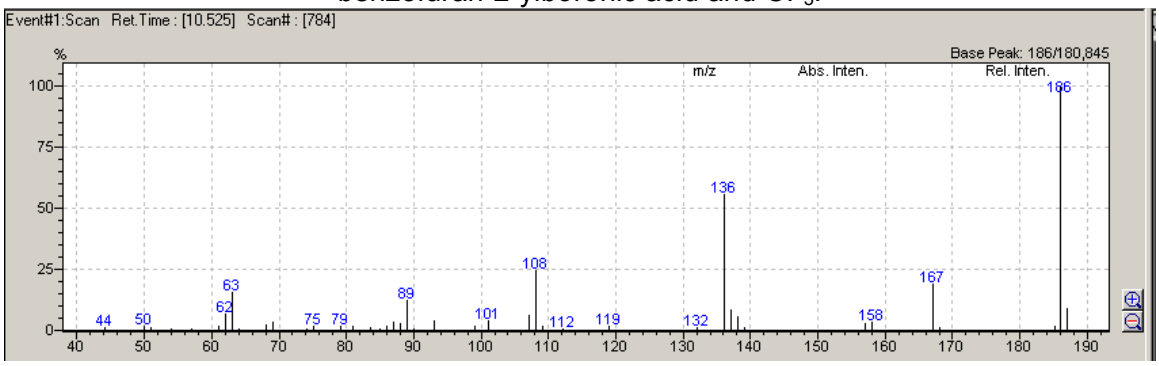


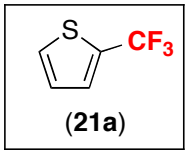
(**20a**)

The reaction was performed on a 0.25 mmol scale using 10 mol % of CuOAc (3 mg, 0.025 mmol, 0.1 equiv) at 40 ˚C under otherwise identical conditions. The trifluoromethylated product **20a** was formed in 72% yield. The product showed a ^{19}F NMR signal at –64.4 ppm in DCE (lit. –64.8 ppm in $CDCl_3$).[4] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 10.52 min. The mass spectrum of the product is provided in the spectral data below.

This reaction of substrate **20** was also conducted on a 1 mmol scale. For the 1 mmol scale reaction, substrate **20** (162 mg, 1 mmol, 1 equiv), CuOAc (12 mg, 0.1 mmol, 0.1 equiv), K_2CO_3 (138 mg, 1 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (7.4 mg, 0.01 mmol, 0.01 equiv), CF_3I (5 mmol, 5 equiv) and DMF (6 mL) were used. The reaction was conducted in a 100 mL round bottom flask. The reaction mixture was then diluted with Et_2O (40 mL), and the resulting mixture was washed with water (2 x 40 mL), saturated aqueous $CaCl_2$ (1 x 40 mL), and brine (1 x 40 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation at 0 ºC, and the product was purified by column chromatography on aluminum oxide using pentane as the eluent. Compound **20a** was isolated as a clear liquid (104.0 mg, 56% yield). The ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data were identical to that reported previously in the literature.[4]

Mass spectrum of product peak (10.52 min) from GCMS of Cu/Ru-catalyzed reaction between benzofuran-2-ylboronic acid and CF_3I

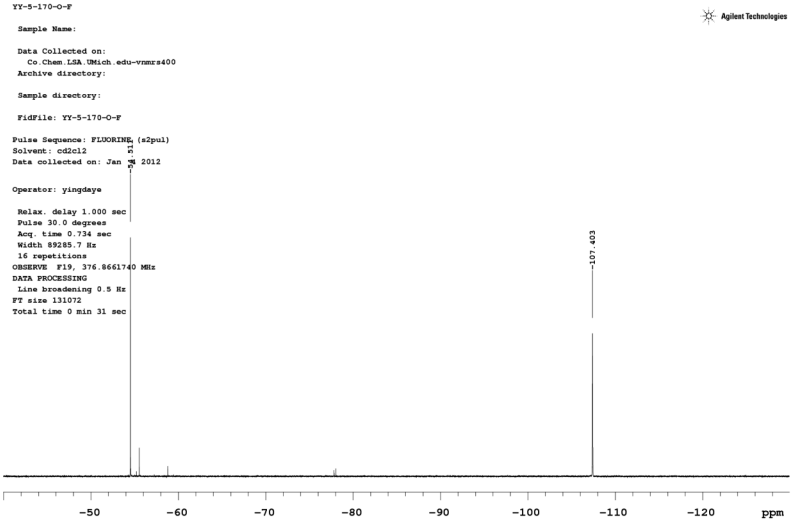




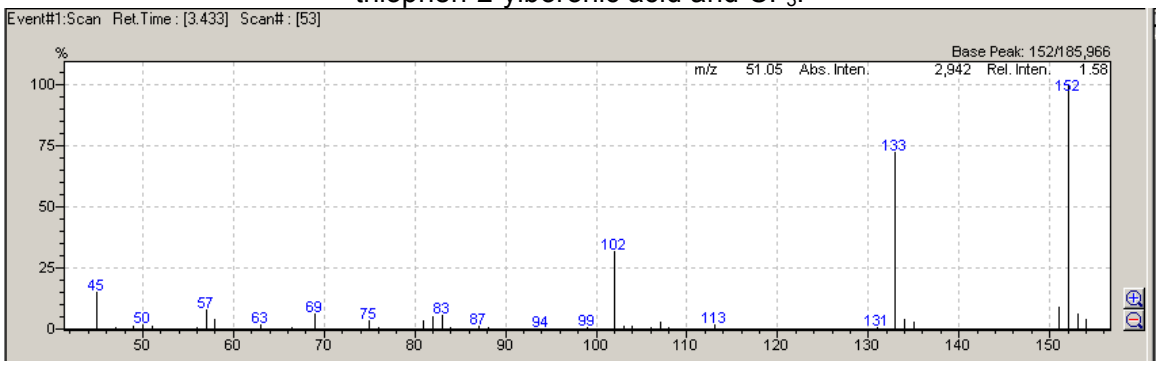
(**21a**)

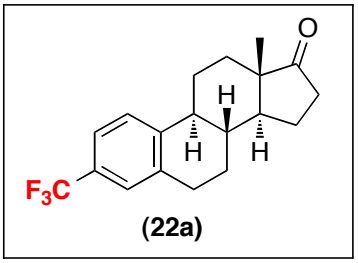
The reaction was performed on a 0.25 mmol scale using 5 mol % of CuOAc (1.5 mg, 0.0125 mmol, 0.05 equiv) under otherwise identical conditions. The trifluoromethylated product **21a** was formed in 54% yield. The product showed a ^{19}F NMR signal at –54.5 ppm in DCE (lit. –55.1 ppm in $CDCl_3$).[9] The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 3.43 min. The mass spectrum of the product is provided in the spectral data below.

^{19}F NMR spectrum of crude reaction mixture for Cu/Ru-catalyzed reaction of thiophen-2-ylboronic acid with CF_3I (internal standard = 1,3,5-trifluorobenzene at –107.4 ppm)



Mass spectrum of product peak (3.43 min) from GCMS of Cu/Ru-catalyzed reaction between thiophen-2-ylboronic acid and CF_3I





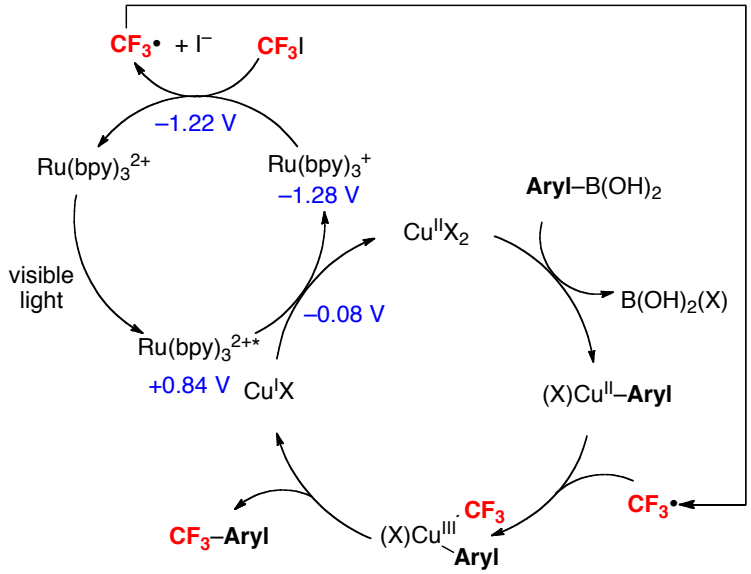
(22a)

Estrone boronic acid was prepared according to literature procedure.[10,11] The reaction was performed on a 0.25 mmol scale using 50 mol % of CuOAc (6 mg, 0.125 mmol, 0.5 equiv) under otherwise identical conditions. The trifluoromethylated product **22a** was formed in 87% yield by ^{19}F NMR spectroscopy. The reaction mixture was then diluted with ethyl acetate (20 mL), and the resulting mixture was washed with brine (3 x 30 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the product was purified by column chromatography on silica gel using ethyl acetate/hexane 1:9 as the eluent. Compound **22a** was obtained as white crystalline solid (65.0 mg, 80% yield, mp = 146.4-147.8 ºC). ^1H NMR ($CDCl_3$, 25 °C): δ 7.40-7.38 (m, 2H), 7.36-7.33 (m, 1H), 2.98-2.93 (m, 2H), 2.52 (dd, *J* = 19.1, 9.0 Hz, 1H), 2.47-2.42 (m, 1H), 2.37-2.30 (m, 1H), 2.20-1.96 (m, 4H), 1.70-1.44 (m, 6H), 0.92 (s, 3H). ^{13}C NMR (^1H decoupled, $CDCl_3$, 25 °C): δ 220.59, 143.86, 137.39, 128.24 (q, *J* = 31.8 Hz), 125.92, 125.86 (q, *J* = 4.1 Hz), 124.48 (q, *J* = 272.3 Hz), 122.59 (q, *J* = 3.6 Hz), 50.63, 48.02, 44.58, 37.96, 35.95, 31.66, 29.43, 26.34, 25.76, 21.72, 13.94. ^{19}F NMR ($CDCl_3$, 25 °C): δ –62.46 (s, 3F). HRMS EI (m/z): $[M]^+$ calcd for $C_{19}H_{21}F_3O$, 322.1545; measured, 322.1542.

Possible Mechanism for Cu/Ru-Catalyzed Trifluoromethylation with Redox Values

Although the redox values of the Cu and Ru species under our exact reaction conditions are not available, the proposed mechanism is consistent with the redox values reported in the literature.

Figure S1. Redox potentials for proposed catalytic intermediates

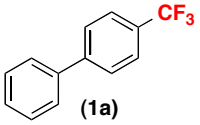
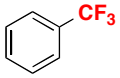
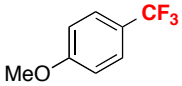
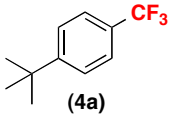
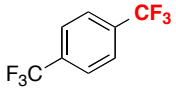
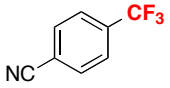
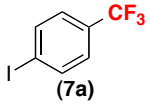
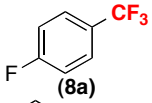
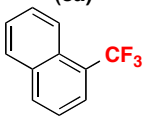
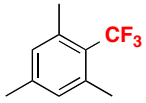
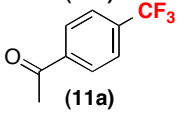
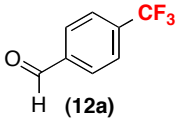


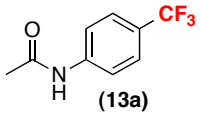
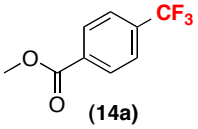
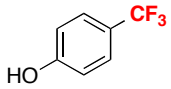
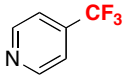
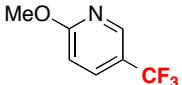
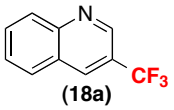
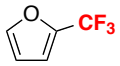
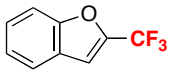
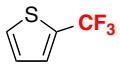
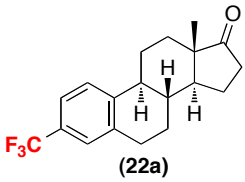
Reported potentials of Ru and Cu are in aqueous solution vs SCE.[12,13]

Reported potential of CF_3I is in DMF vs SCE.[14]

Control Reactions of Trifluoromethylation of Aryl Boronic Acids[a]

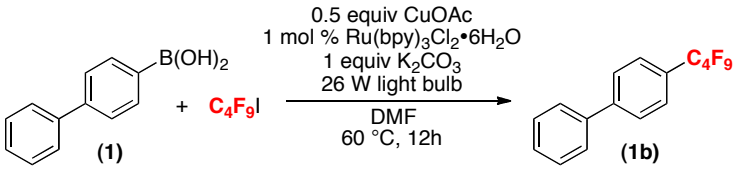
The control reactions were performed on 0.05 mmol scale under otherwise identical conditions.

Entry	Product	Yield	Without Cu cat	Without Ru cat	Without light
1	 (1a)	80%	3%	3%	1%
2	 (2a)	70%	5%	0%	0%
3	 (3a)	84%	5%	1%	0%
4	 (4a)	86%	2%	1%	3%
5[b]	 (5a)	64%	2%	11%	2%
6	 (6a)	84%	1%	22%	2%
7	 (7a)	73%	2%	13%	8%
8	 (8a)	93%	1%	20%	4%
9	 (9a)	57%	6%	2%	0%
10[b]	 (10a)	45%	4%	4%	0%
11	 (11a)	70%	4%	14%	0%
12[b]	 (12a)	74%	4%	5%	2%

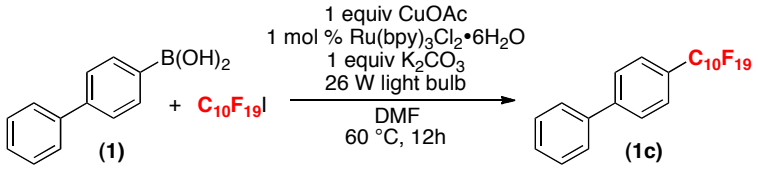
Entry	Product	Yield	Without Cu cat	Without Ru cat	Without light
13	 (13a)	67%	4%	5%	1%
14	 (14a)	86%	4%	15%	2%
15[c]	 (15a)	50%	3%	1%	0%
16[b,d]	 (16a)	64%	2%	21%	3%
17	 (17a)	66%	2%	10%	1%
18	 (18a)	70%	5%	34%	13%
19[c,e]	 (19a)	48%	7%	2%	0%
20[c,f]	 (20a)	72%	23%	15%	1%
21[g]	 (21a)	54%	17%	7%	0%
22[b]	 (22a)	87%	0%	29%	1%

[a] General conditions: substrate (0.05 mmol, 1 equiv), CF_3I (5 equiv), [Cu] (0.2 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (0.01 equiv), K_2CO_3 (1 equiv), DMF (0.17 M in substrate), 60 °C, 12 h, 26 W compact fluorescent light bulb. ^{19}F NMR yield. [b] 0.5 equiv of CuOAc. [c] 0.1 equiv of CuOAc. [d] 3 equiv of CF_3I. [e] Reaction run at 70 °C. [f] Reaction run at 40 °C. [g] 0.05 equiv of CuOAc.

Perfluoroalkylation of Aryl Boronic Acids

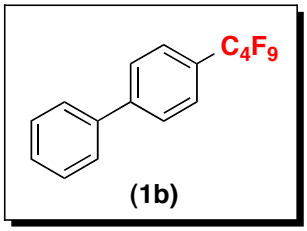


In a glovebox, substrate **1** (49.5 mg, 0.25 mmol, 1 equiv), CuOAc (15.3 mg, 0.125 mmol, 0.5 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (1.85 mg, 0.0025 mmol, 0.01 equiv) and K_2CO_3 (35 mg, 0.25 mmol, 1 equiv) were weighed into a 20 mL vial. DMF (1.5 mL) and then C_4F_9I (215 µL, 1.25 mmol, 5 equiv) were added. The vial was sealed with a Teflon-lined cap, removed from the glove box and placed in a clear oil bath at 60 °C with two 26 W compact fluorescent light bulbs (one on either side of the vial about 5 cm away). The reaction mixture was allowed to stir for 12 h. The resulting red reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (2 mL). 1,3,5-Trifluorobenzene (0.25 mmol, 1 equiv) was added as an internal standard, and the yield was determined to be 82% by ^{19}F NMR spectroscopy. The reaction mixture was then diluted with Et_2O (20 mL), and the resulting mixture was washed with water (3 x 20 mL) and brine (1 x 20 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the product was purified by column chromatography on silica gel using hexane as the eluent. Compound **1b** was obtained as white crystalline solid (62.0 mg, 67% yield, mp = 50.8-51.6 ºC). ^1H NMR ($CDCl_3$, 25 °C): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (^1H decoupled, $CDCl_3$, 25 °C): δ 145.07, 139.79, 129.15, 128.41, 127.70 (t, *J* = 24.7 Hz), 127.47 (2 carbons), 127.45, 127.40, 118-109 (multiple peaks, perfluoroalkyl chain). ^{13}C NMR (^{19}F decoupled, $CDCl_3$, 25 °C): δ 145.07 (m), 139.79 (m), 129.15 (dd, *J* = 161.8, 7.6 Hz), 128.42 (dt, *J* = 160.8, 7.8 Hz), 127.72 (t, *J* = 7.8 Hz), 128-126 (multiple overlapping peaks), 117.67, 116.06 (m), 110.51, 109.15.^{19}F NMR ($CDCl_3$, 25 °C): δ –81.03 (t, *J* = 9.4 Hz, 3F), –110.82 (t, *J* = 13.2 Hz, 2F), –122.70 (m, 2F), –125.57 (m, 2F). HRMS EI (m/z): $[M]^+$ calcd for $C_{16}H_9F_9$, 372.0561; measured, 372.0551.



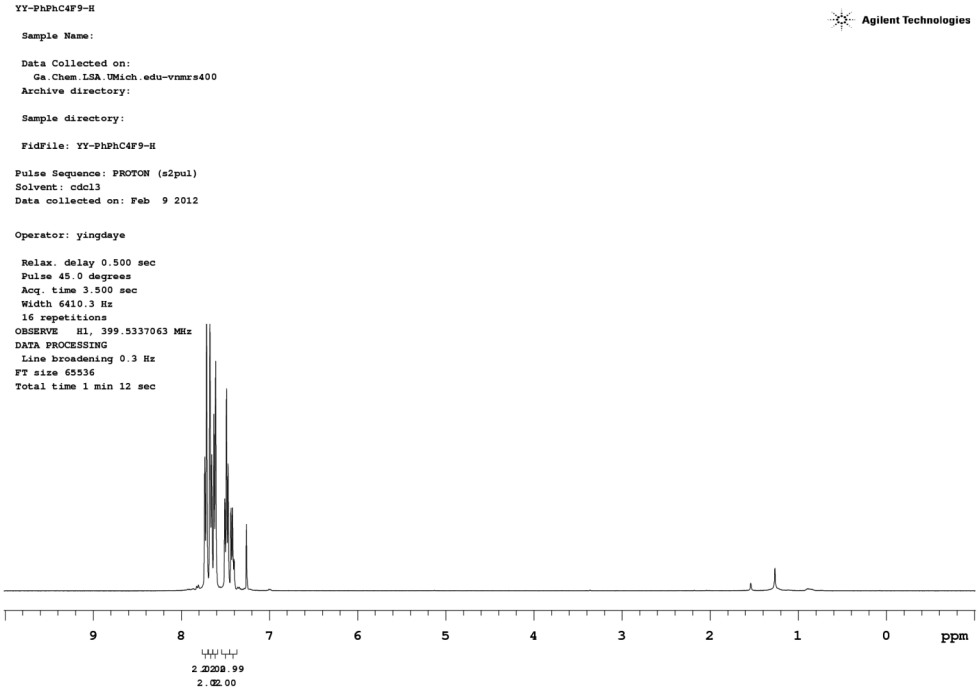
In a glovebox, substrate **1** (49.5 mg, 0.25 mmol, 1 equiv), CuOAc (30.6 mg, 0.25 mmol, 1 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (1.85 mg, 0.0025 mmol, 0.01 equiv) and K_2CO_3 (35 mg, 0.25 mmol, 1 equiv) and $C_{10}F_{21}I$ (193.8 mg, 0.3 mmol, 1.2 equiv) were weighed into a 20 mL vial. DMF (1.5 mL) was added. The vial was sealed with a Teflon-lined cap, removed from the glove box, and placed in a clear oil bath at 60 °C with two 26 W compact fluorescent light bulbs (one on either side of the vial about 5 cm away). The reaction mixture was allowed to stir for 12 h. The resulting red reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (2 mL). 1,3,5-Trifluorobenzene (0.25 mmol, 1 equiv) was added as an internal standard, and the yield was determined to be 80% by ^{19}F NMR spectroscopy. The reaction mixture was then diluted with Et_2O (20 mL), and the resulting mixture was washed with water (3 x 20 mL) and brine (1 x 20 mL) and then dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the product was purified by column chromatography on silica gel using hexane as the eluent. Compound **1c** was obtained as white crystalline solid (119.0 mg, 71% yield, mp = 91.4-94.8 ºC). ^1H NMR ($CDCl_3$, 25 °C): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (^1H decoupled, $CDCl_3$, 25 °C): δ 145.08, 139.82, 129.15, 128.41, 127.87 (t, *J* = 24.8 Hz), 127.52, 127.46 (2 carbons), 127.42, 118-108 (multiple peaks, perfluoroalkyl chain). ^{13}C NMR (^{19}F decoupled, $CDCl_3$, 25 °C): δ 145.08 (m), 139.82 (m), 129.15 (dd, *J* = 161.8, 7.8 Hz), 128.41 (dt, *J* = 160.8, 7.3 Hz), 127.86 (t, *J* = 7.9 Hz), 128-126 (multiple overlapping peaks), 117.29, 116.21, 111.57, 111.08, 111.04, 110.96, 110.86, 110.34, 108.55. ^{19}F NMR ($CDCl_3$, 25 °C): δ –80.88 (t, *J* = 9.4 Hz, 3F), –110.61 (t, *J* = 14.1 Hz, 2F), –121.25 (m, 2F), –121.80 (m, 8F), –121.96 (m, 2F), –122.76 (m, 2F), –126.19 (m, 2F). HRMS EI (m/z): $[M]^+$ calcd for $C_{22}H_9F_{21}$, 672.0369; found, 672.0361.

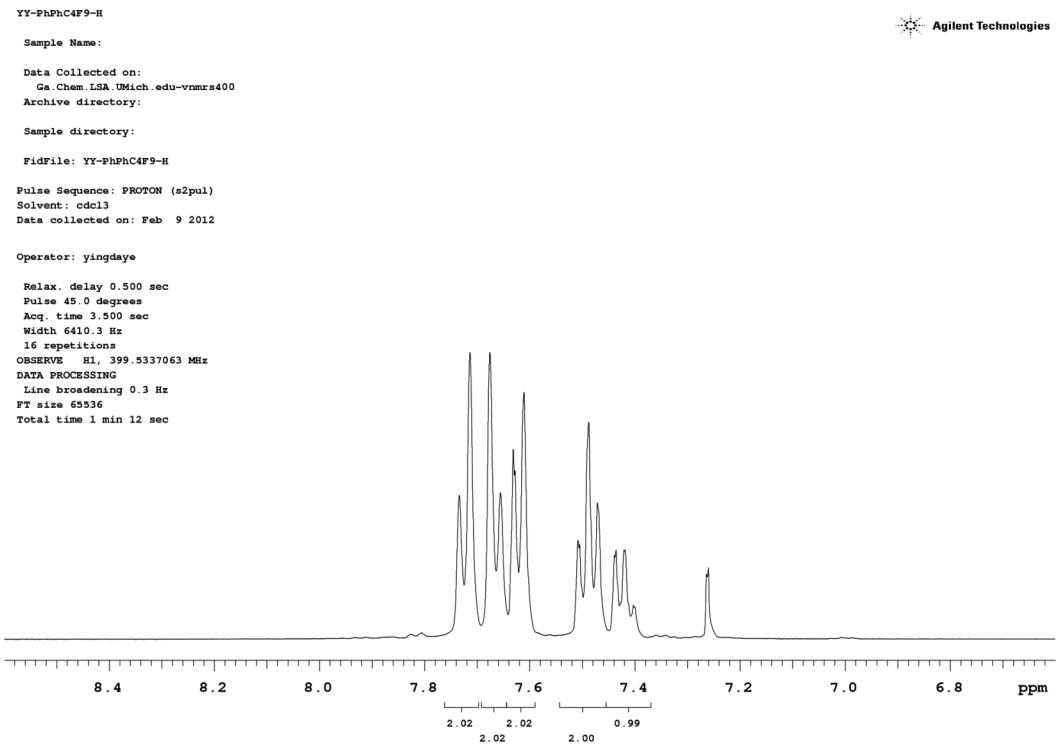
NMR Spectra of New Compounds



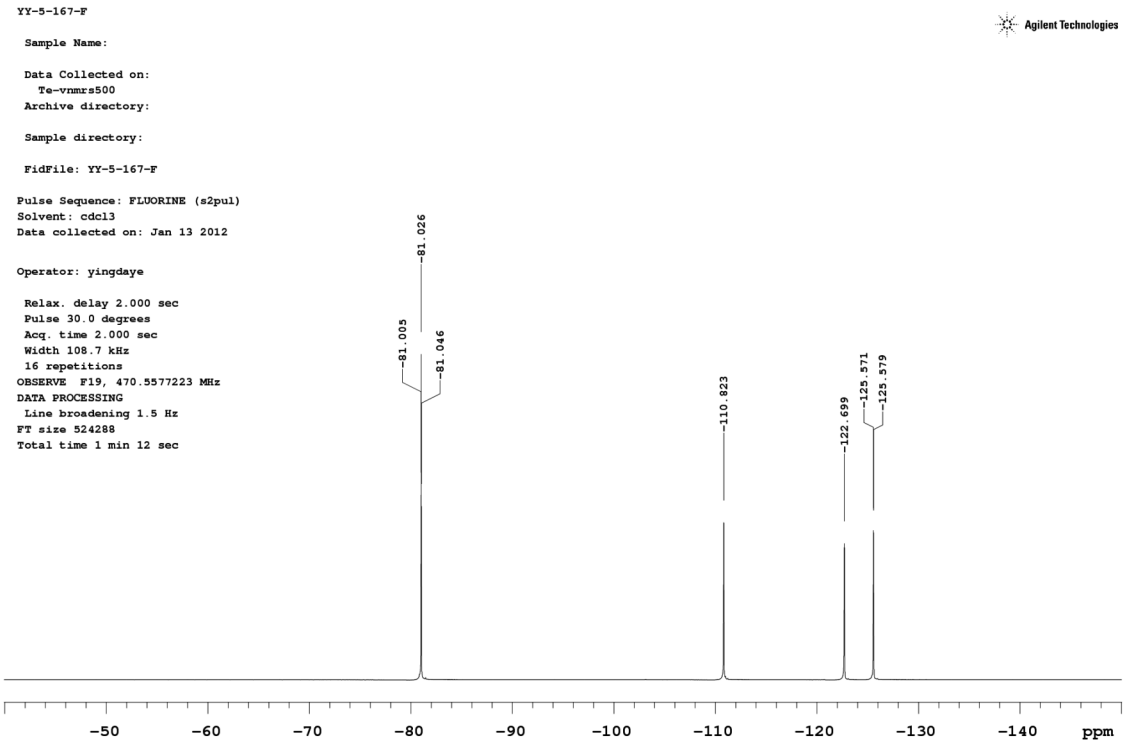
(1b)

^{1}H NMR

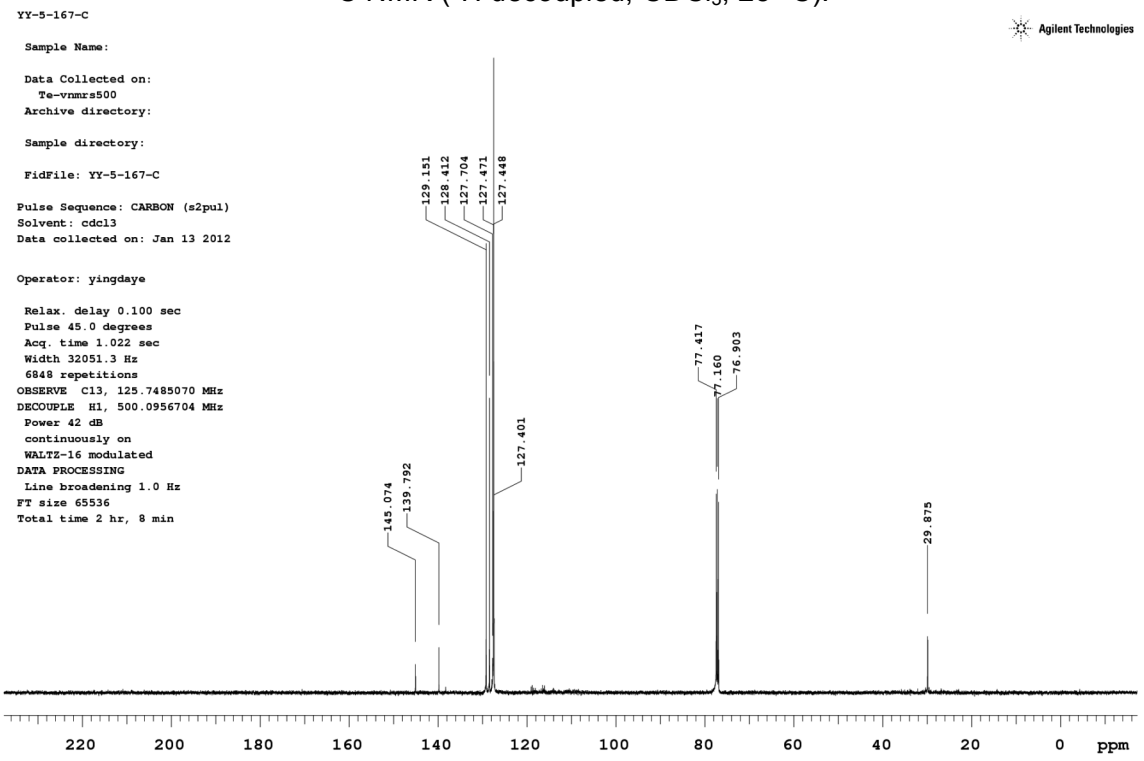


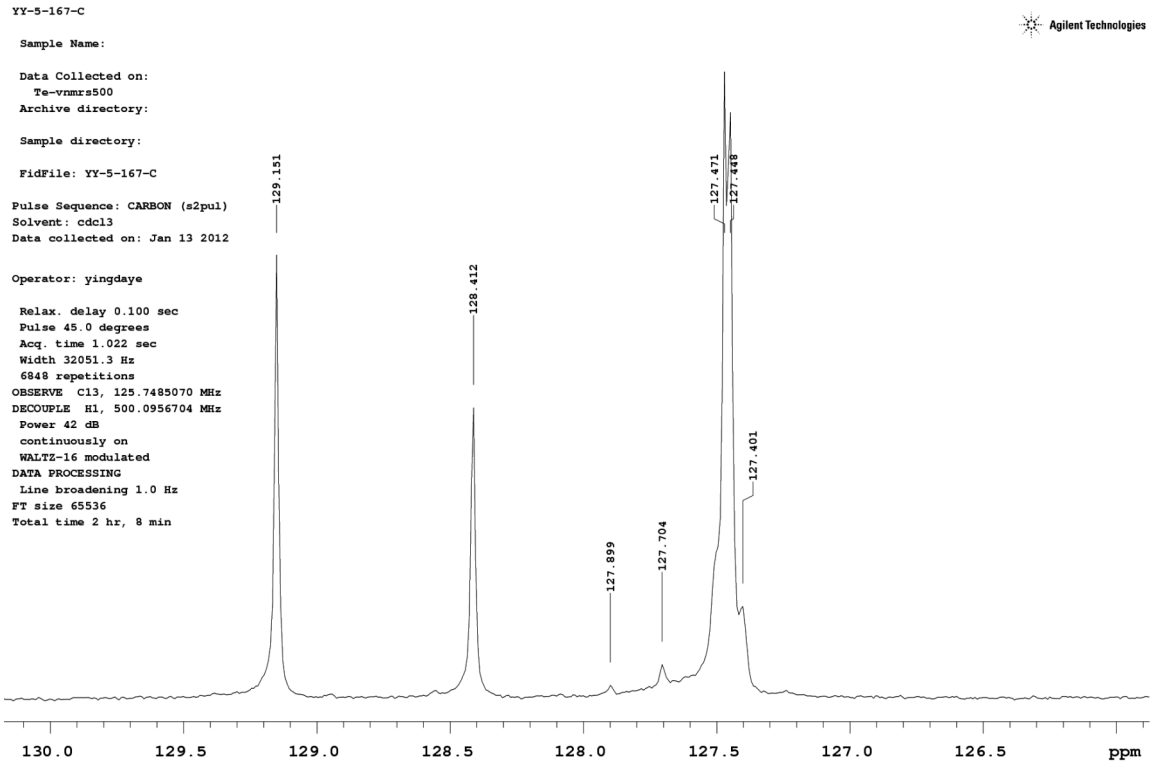

YY-PhPhC4F9-H
Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-PhPhC4F9-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 9 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.5337063 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
ppm
2.02
2.02
0.99
2.02
2.00

^{19}F NMR

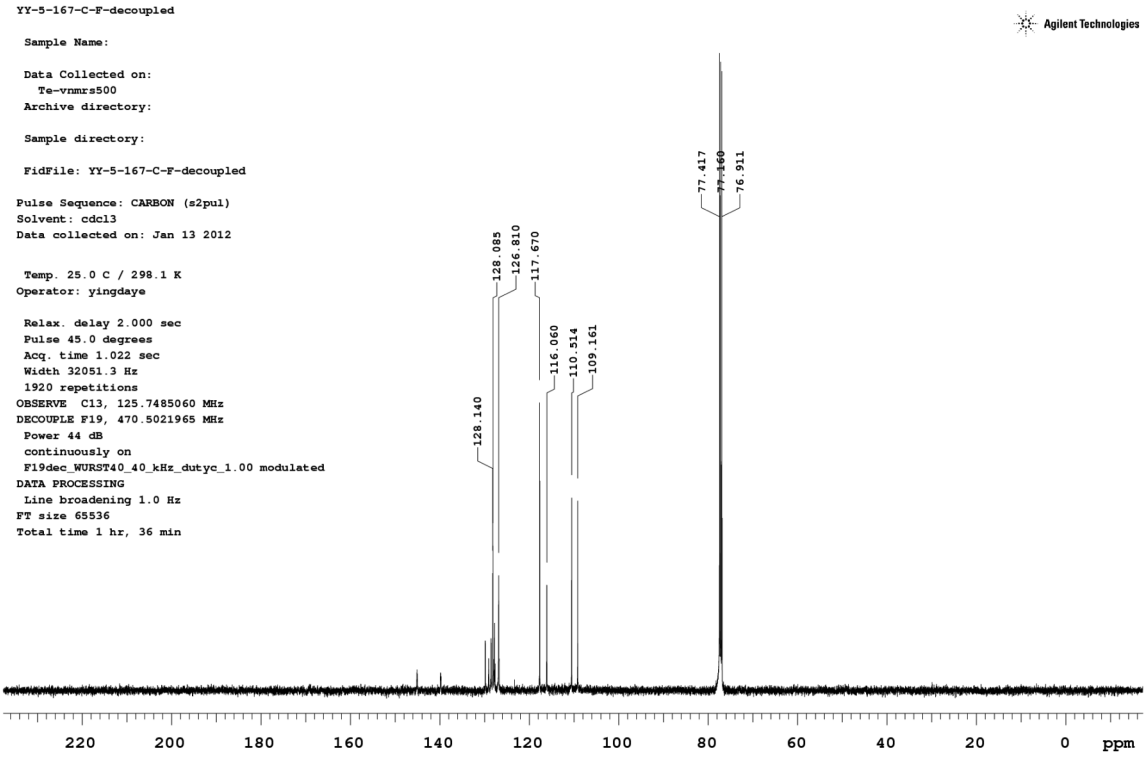

YY-5-167-F
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-167-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Jan 13 2012
Operator: yingdaye
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.000 sec
Width 108.7 kHz
16 repetitions
OBSERVE F19, 470.5577223 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 524288
Total time 1 min 12 sec
Agilent Technologies
-81.005
-81.026
-81.046
-110.823
-122.699
-125.571
-125.579
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm

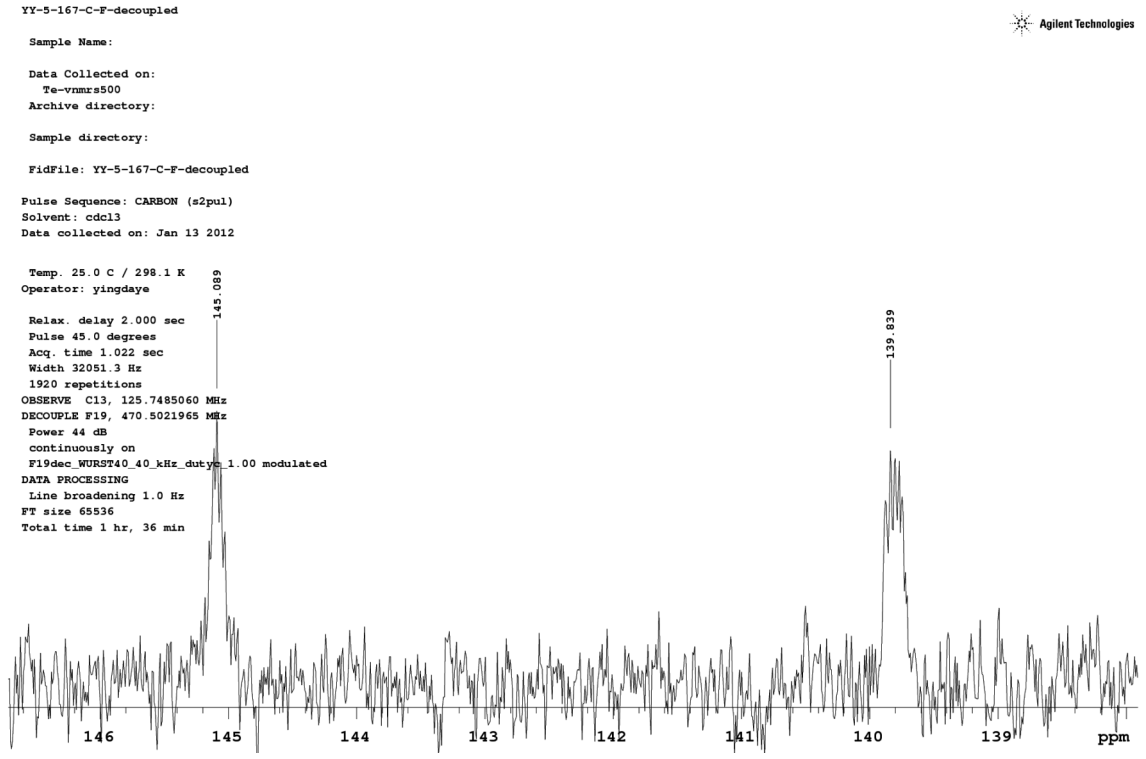
^{13}C NMR (^{1}H decoupled, $CDCl_3$, 25 °C):

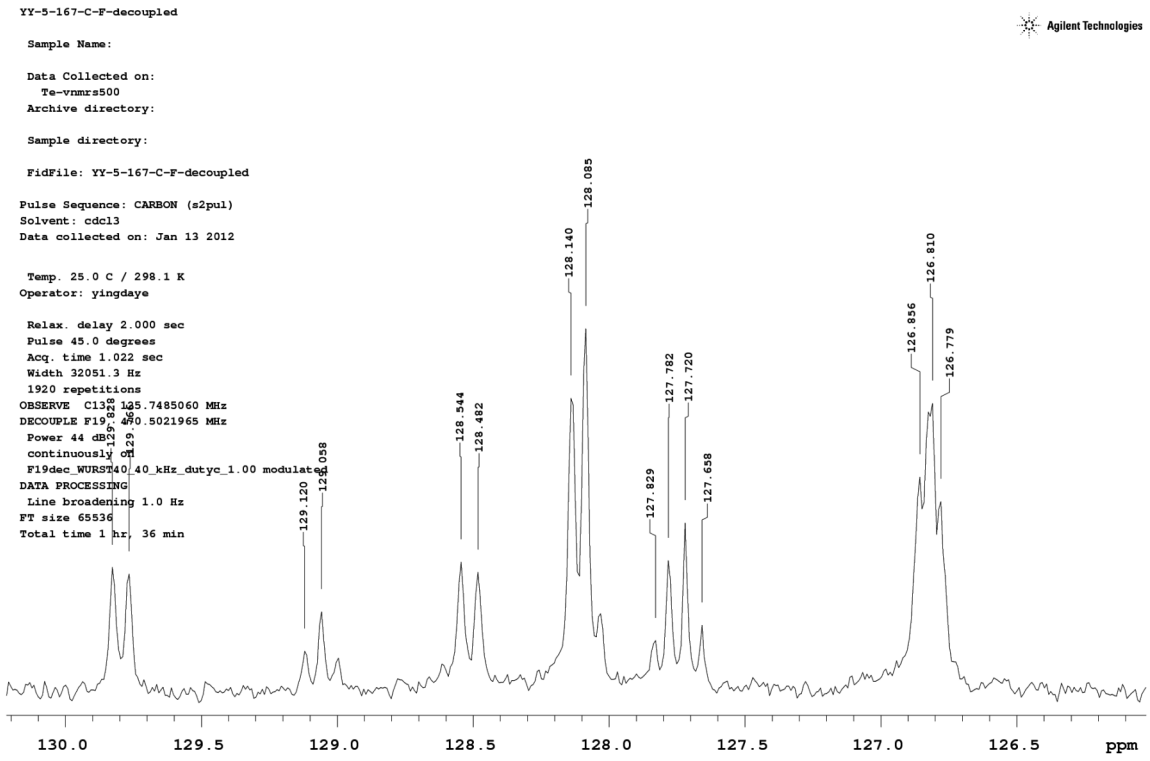


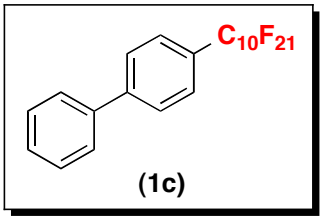


^{13}C NMR (^{19}F decoupled, $CDCl_3$, 25 °C):



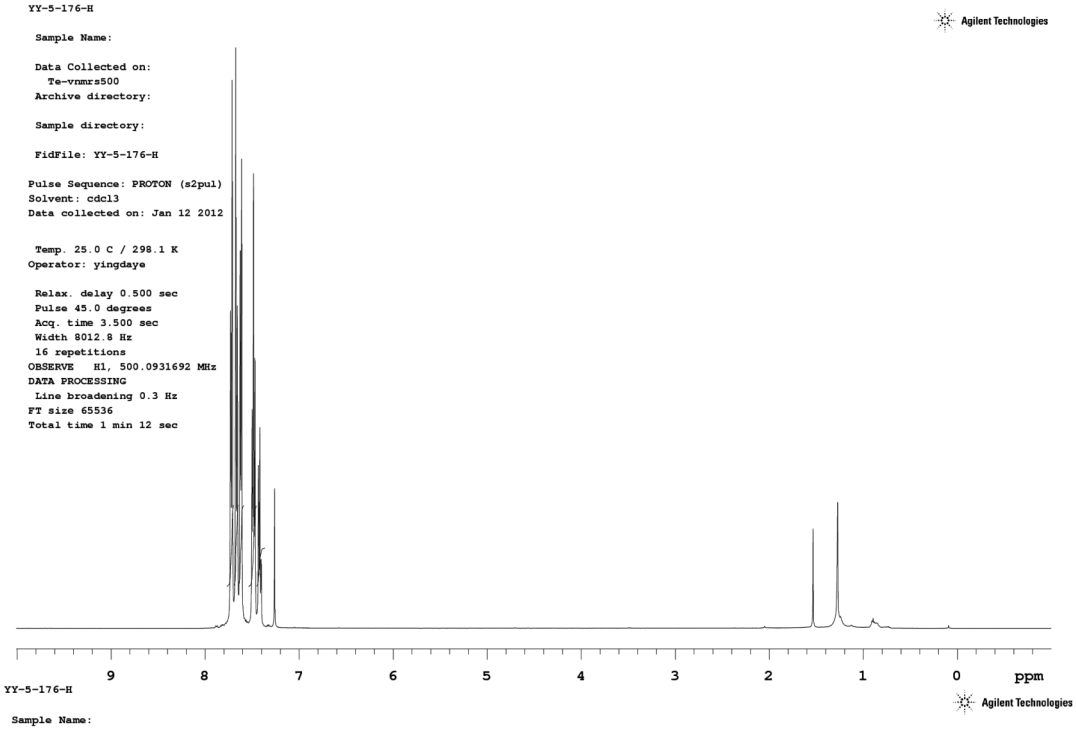


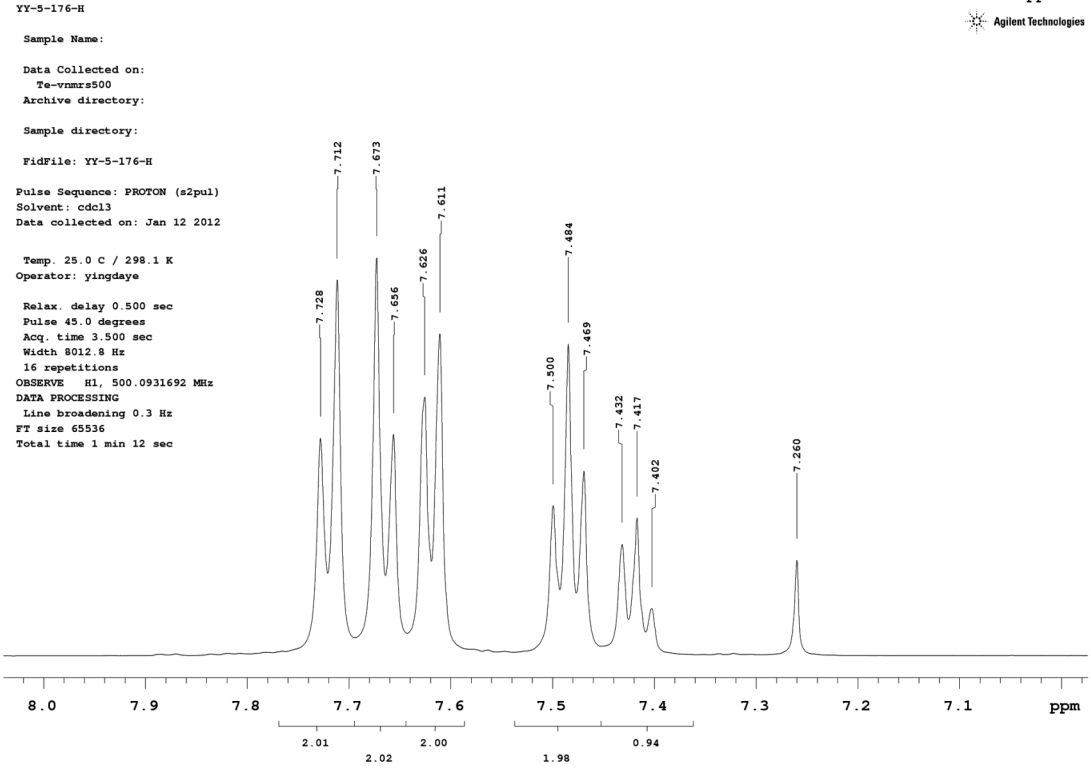

YY-5-167-C-F-decoupled
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-167-C-F-decoupled
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 13 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
1920 repetitions
OBSERVE C13, 125.7485060 MHz
DECOUPLE F19, 470.5021965 MHz
Power 44 dB
continuously on
F19dec_WURST40_40_kHz_dutyc_1.00 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 36 min
Agilent Technologies
129.120
129.058
128.544
128.482
128.140
128.085
127.829
127.782
127.720
127.658
126.856
126.810
126.779
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
ppm


$C_{10}F_{21}$

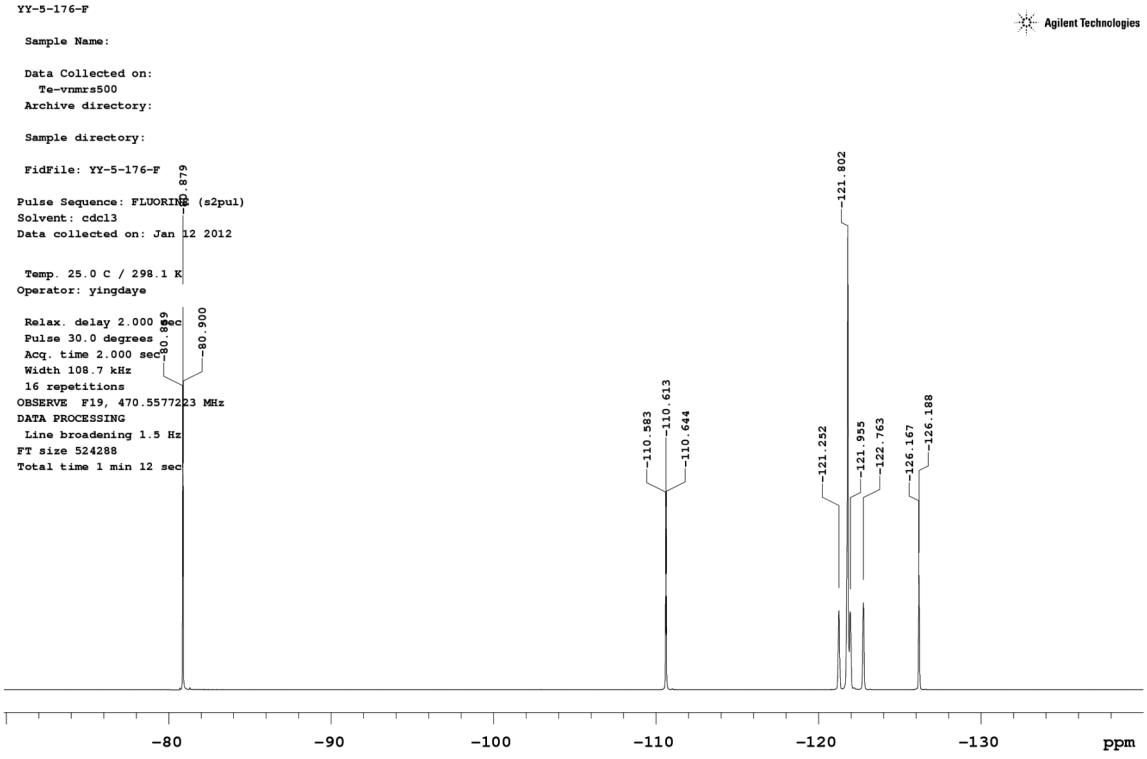
(1c)

^{1}H NMR

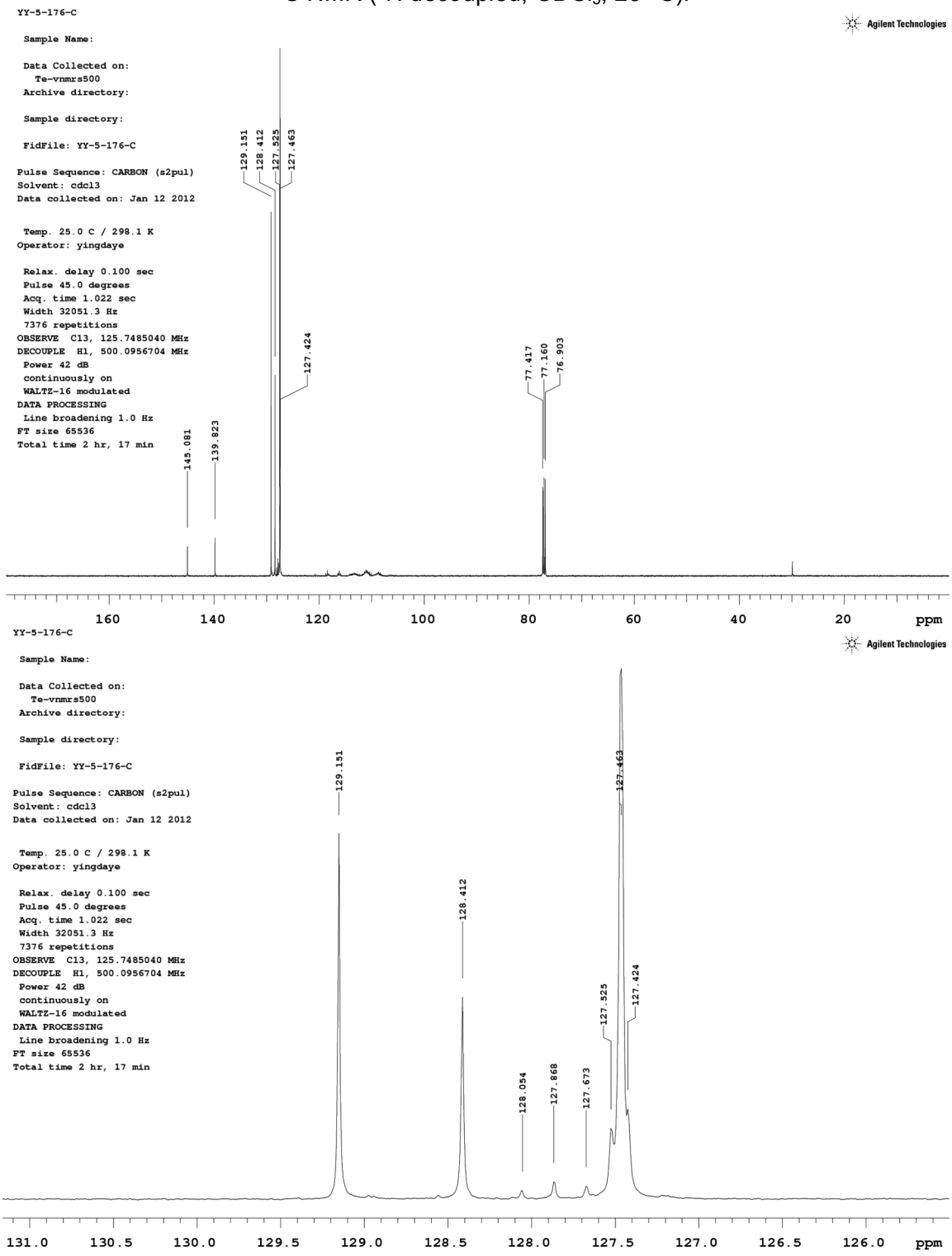

YY-5-176-H
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-176-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 12 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931692 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
9
8
7
6
5
4
3
2
1
0
ppm


YY-5-176-H
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-176-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 12 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931692 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
7.728
7.712
7.673
7.656
7.626
7.611
7.500
7.484
7.469
7.432
7.417
7.402
7.260
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm
2.01
2.00
0.94
2.02
1.98

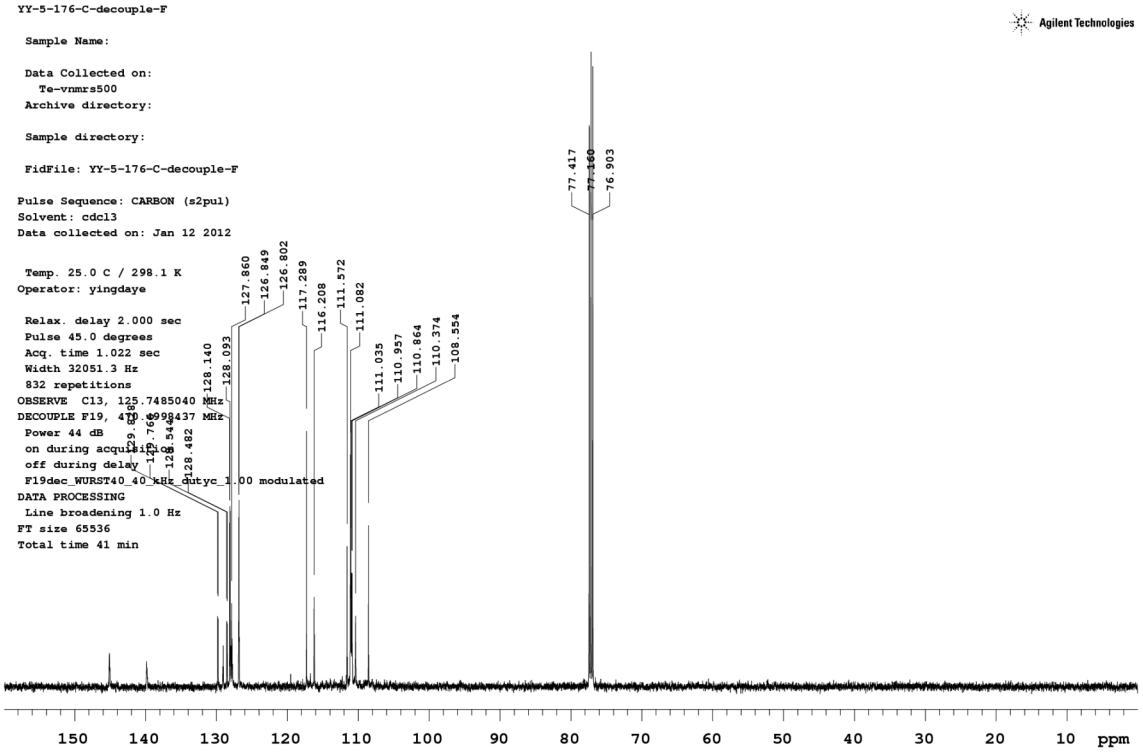
^{19}F NMR

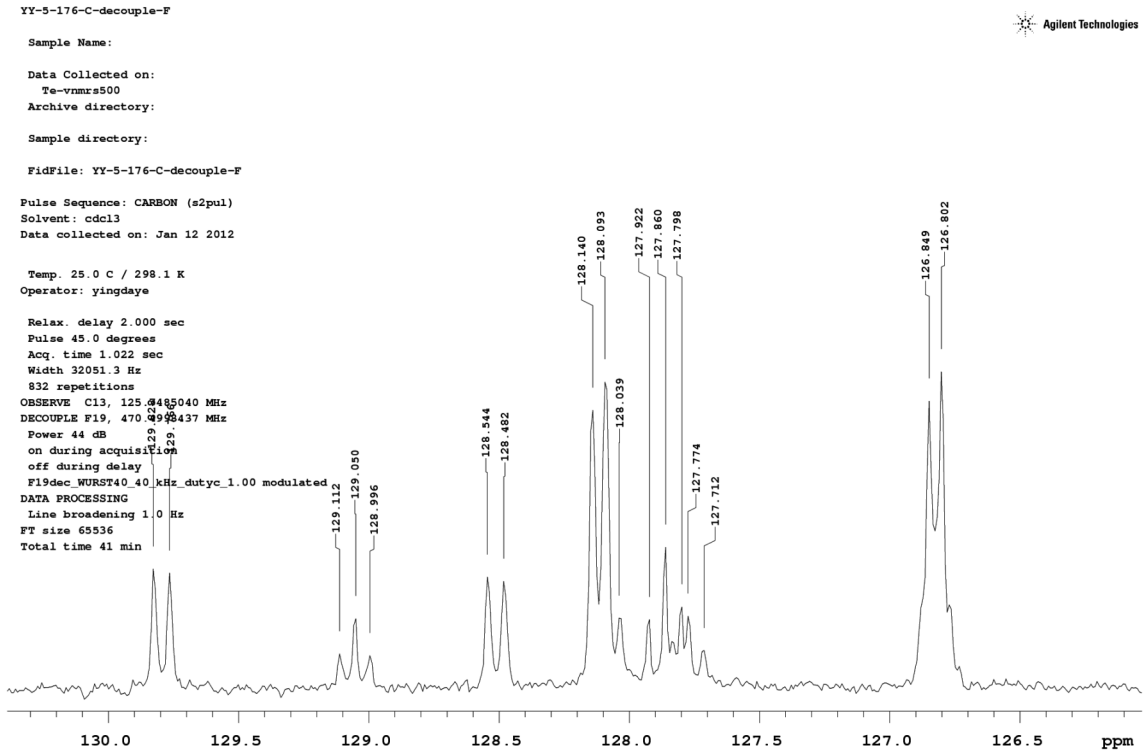

YY-5-176-F
Agilent Technologies
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-176-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Jan 12 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.000 sec
Width 108.7 kHz
16 repetitions
OBSERVE F19, 470.5577223 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 524288
Total time 1 min 12 sec
-80.879
-80.889
-80.900
-110.583
-110.613
-110.644
-121.252
-121.802
-121.955
-122.763
-126.167
-126.188
-80
-90
-100
-110
-120
-130
ppm

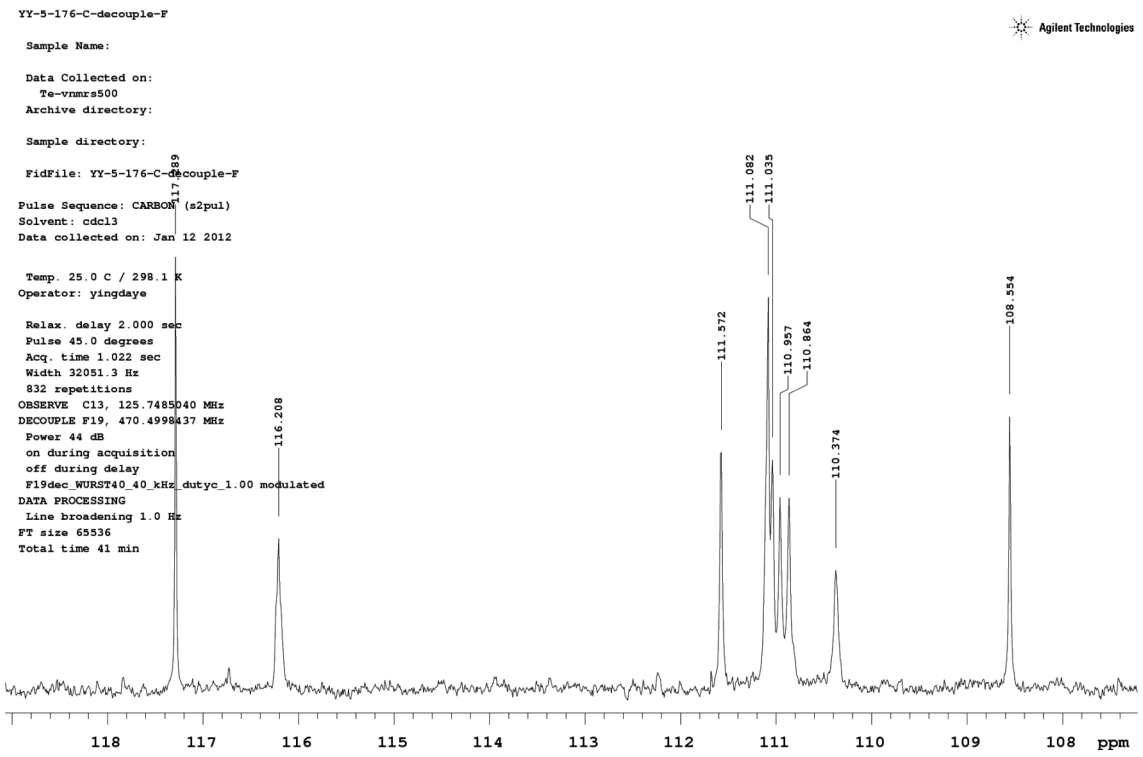
^{13}C NMR (^{1}H decoupled, $CDCl_3$, 25 °C):



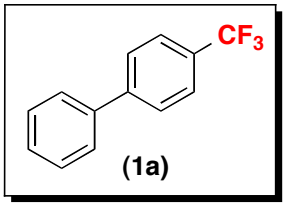
^{13}C NMR (^{19}F decoupled, $CDCl_3$, 25 °C):





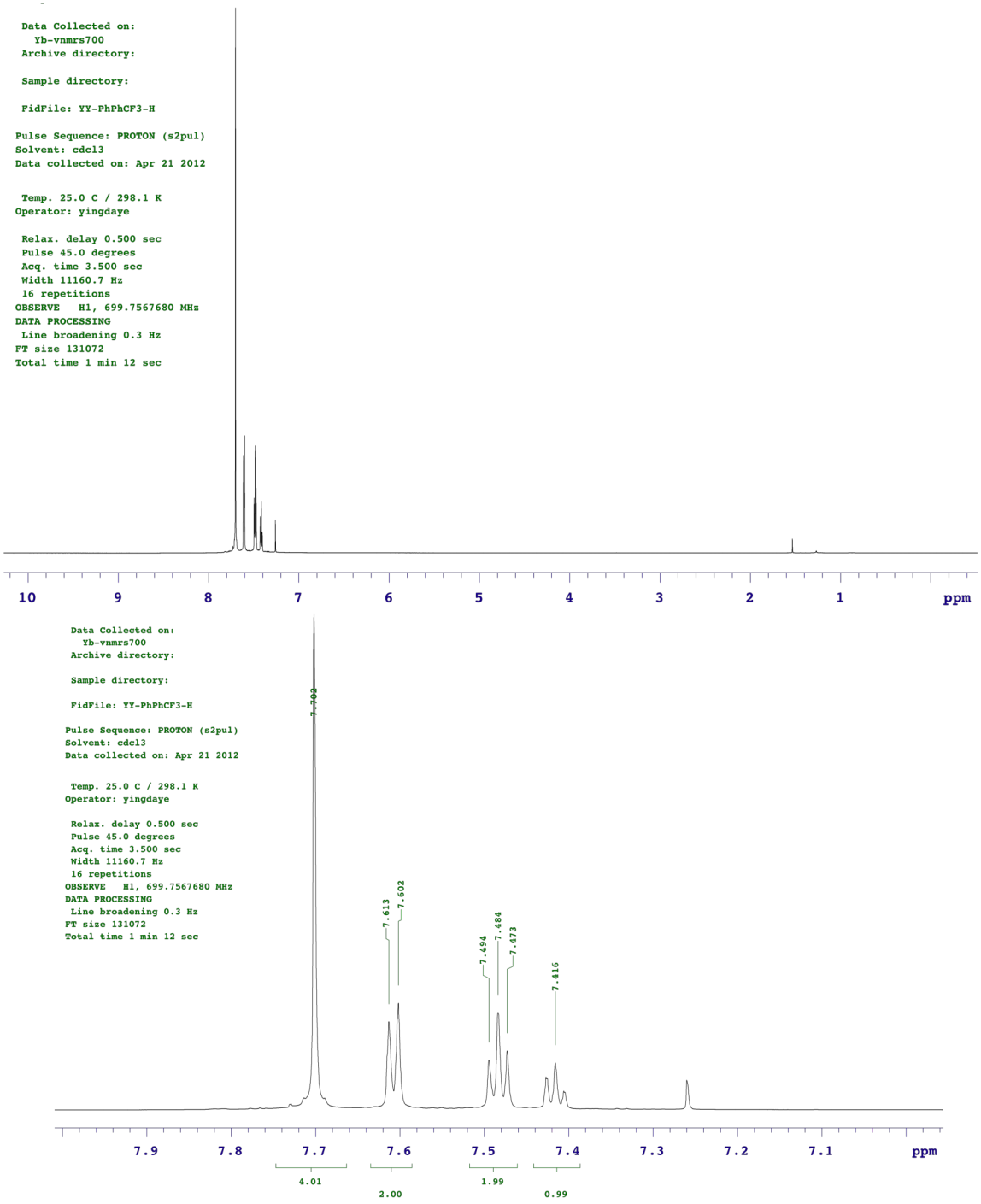

YY-5-176-C-decouple-F
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-176-C-decouple-F
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 12 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
832 repetitions
OBSERVE C13, 125.7485040 MHz
DECOUPLE F19, 470.4998437 MHz
Power 44 dB
on during acquisition
off during delay
F19dec_WURST40_40_kHz_dutyc_1.00 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 41 min
Agilent Technologies
117.089
116.208
111.572
111.082
111.035
110.957
110.864
110.374
108.554
118
117
116
115
114
113
112
111
110
109
108
ppm

NMR Spectra of Isolated Products (Previously Reported Compounds)

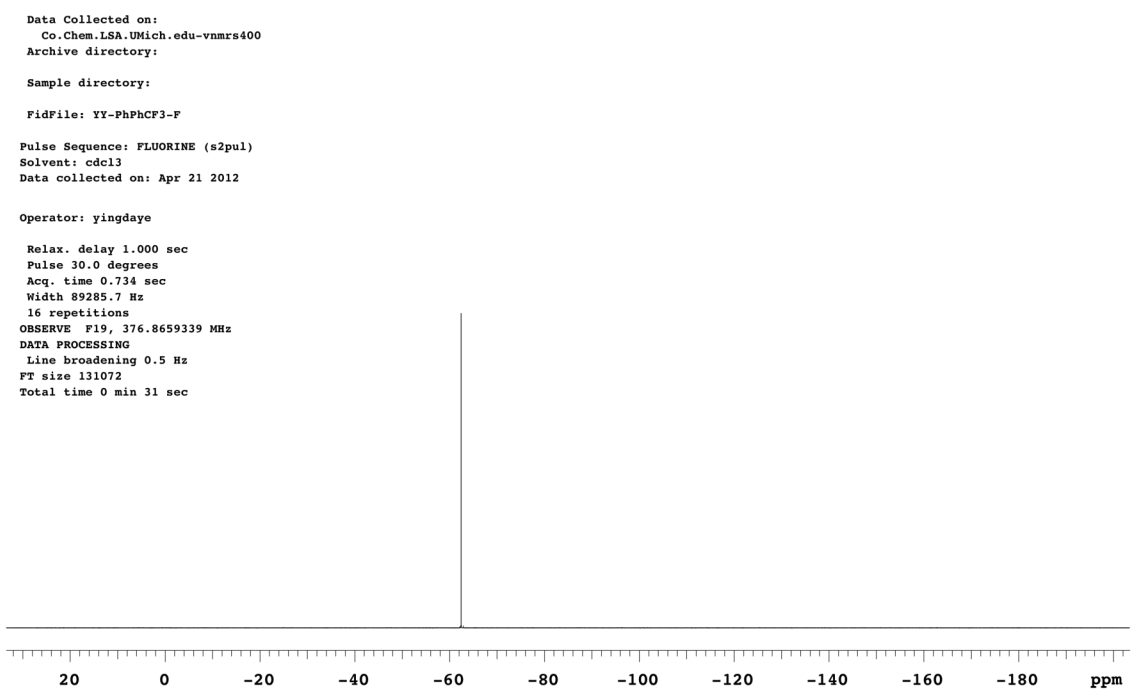


(1a)

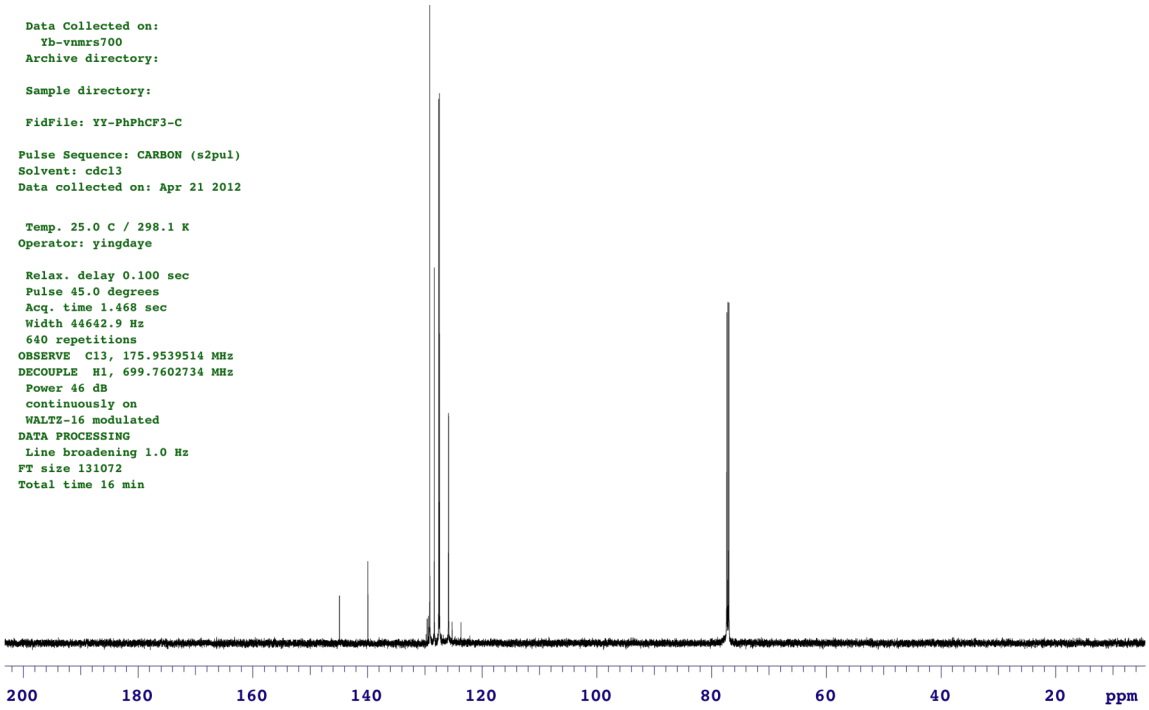
^{1}H NMR

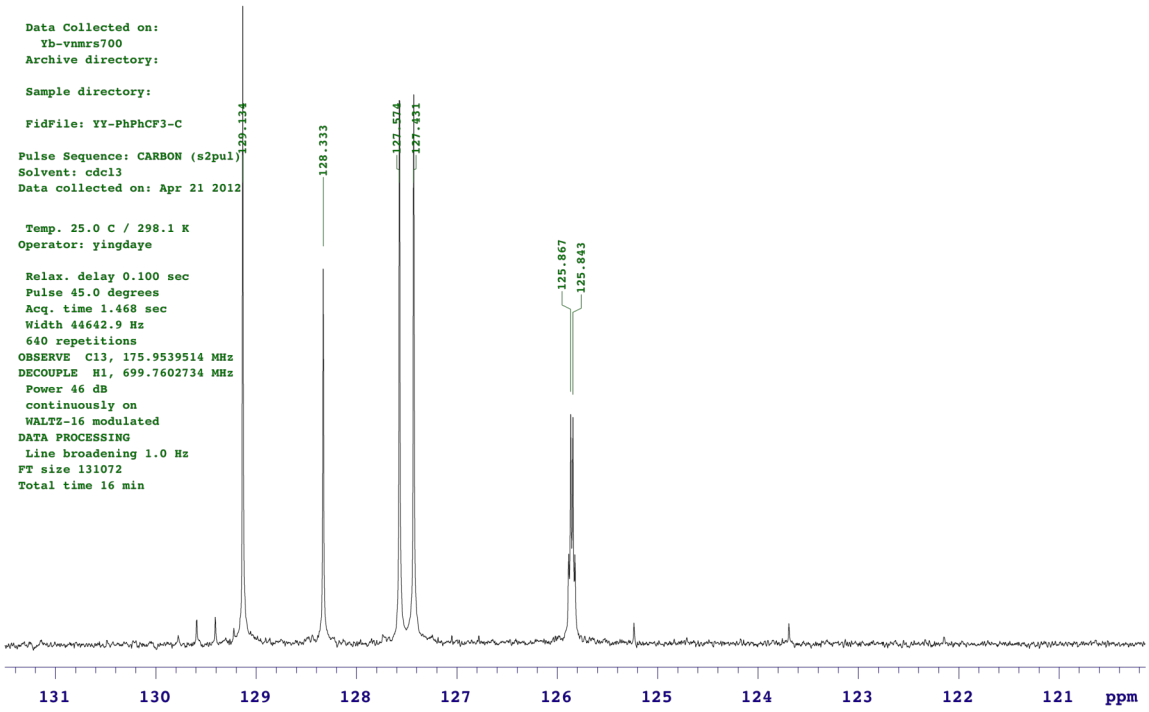


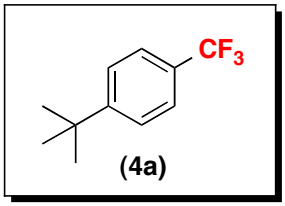
^{19}F NMR


Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-PhPhCF3-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 21 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8659339 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR

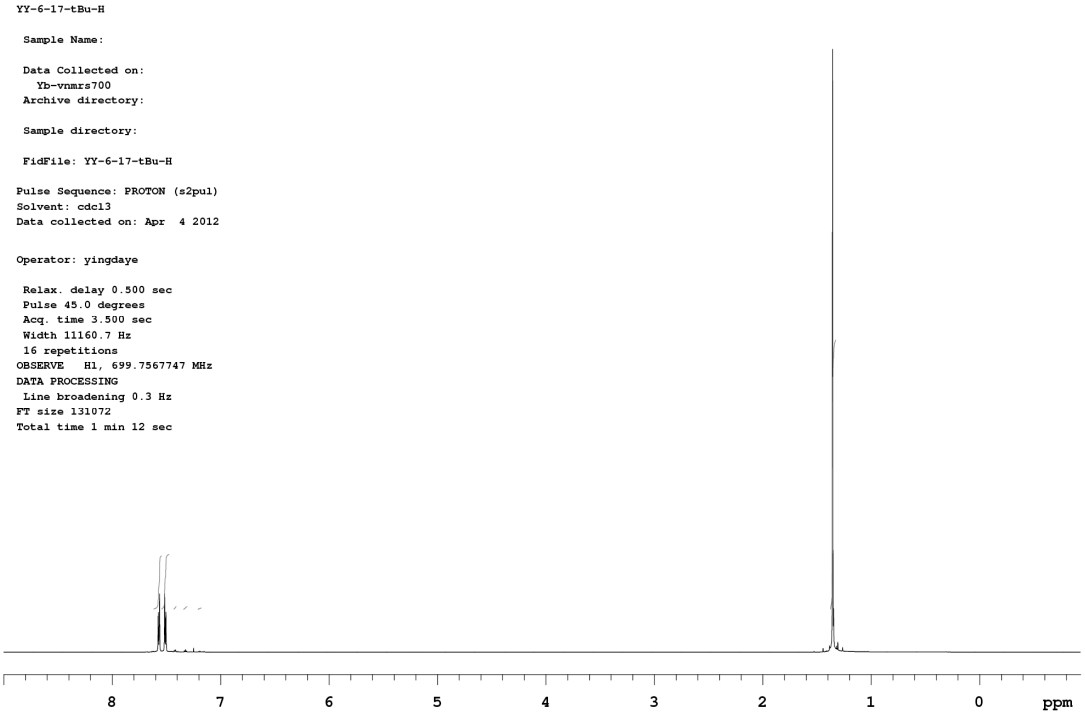

Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-PhPhCF3-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 21 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
640 repetitions
OBSERVE C13, 175.9539514 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 16 min
200
180
160
140
120
100
80
60
40
20
ppm

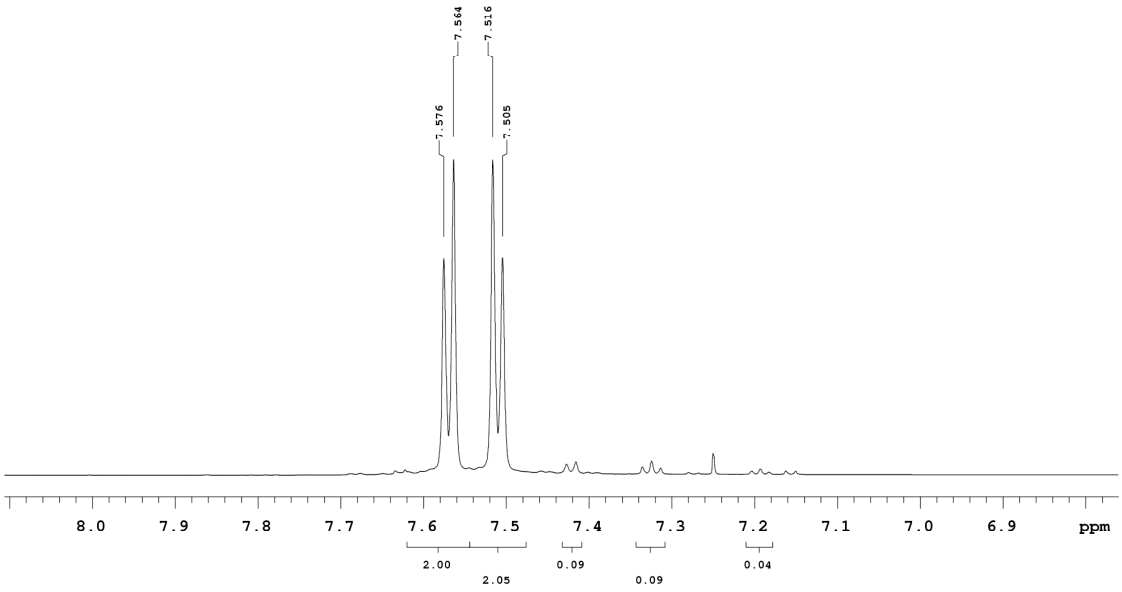

Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-PhPhCF3-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 21 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
640 repetitions
OBSERVE C13, 175.9539514 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 16 min
129.134
128.333
127.574
127.431
125.867
125.843
131
130
129
128
127
126
125
124
123
122
121
ppm


CF3

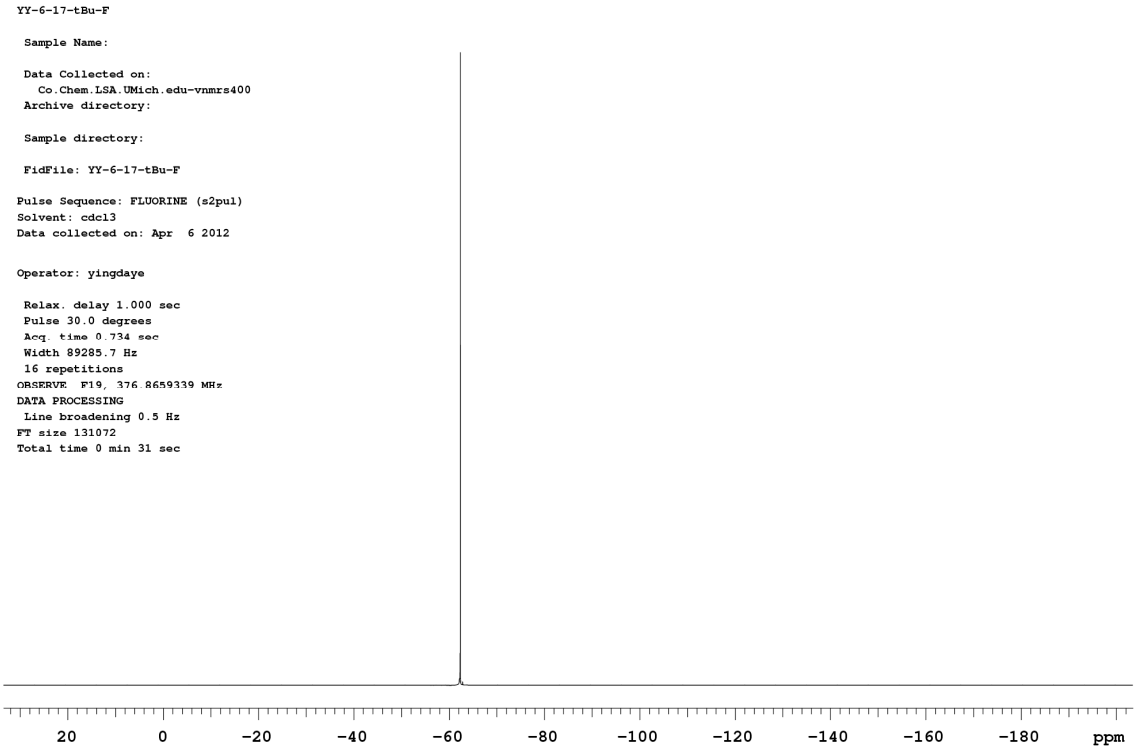
(4a)

^{1}H NMR

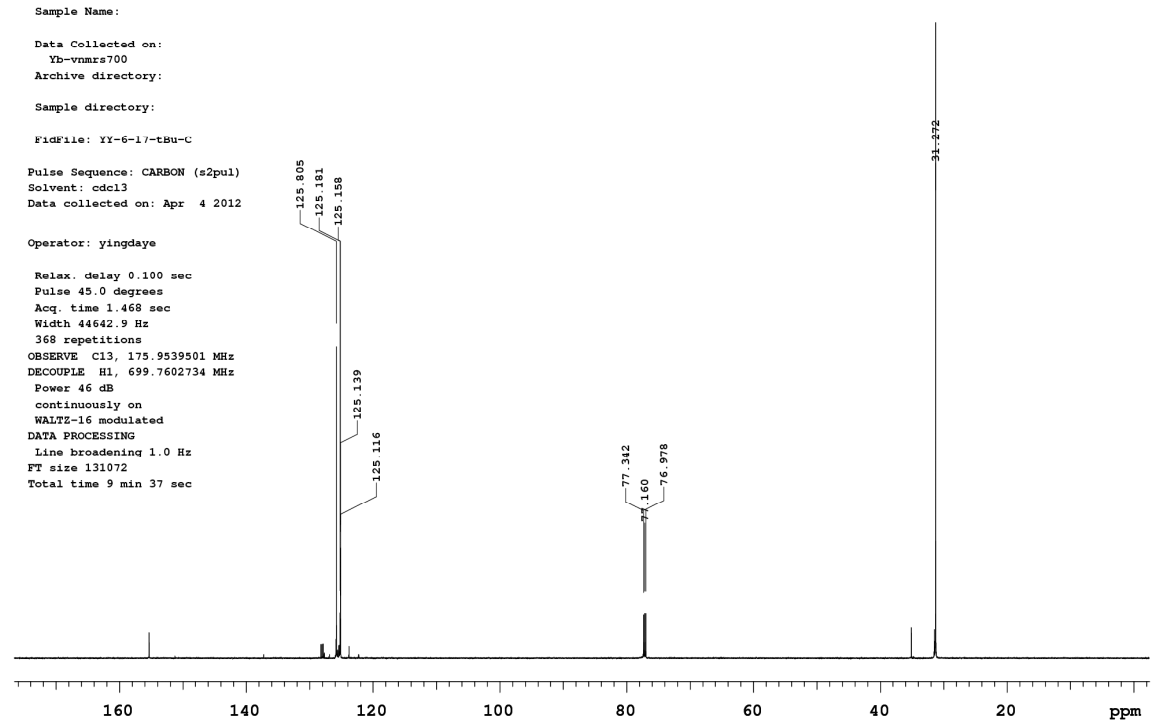

YY-6-17-tBu-H
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-tBu-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11160.7 Hz
16 repetitions
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
8
7
6
5
4
3
2
1
0
ppm

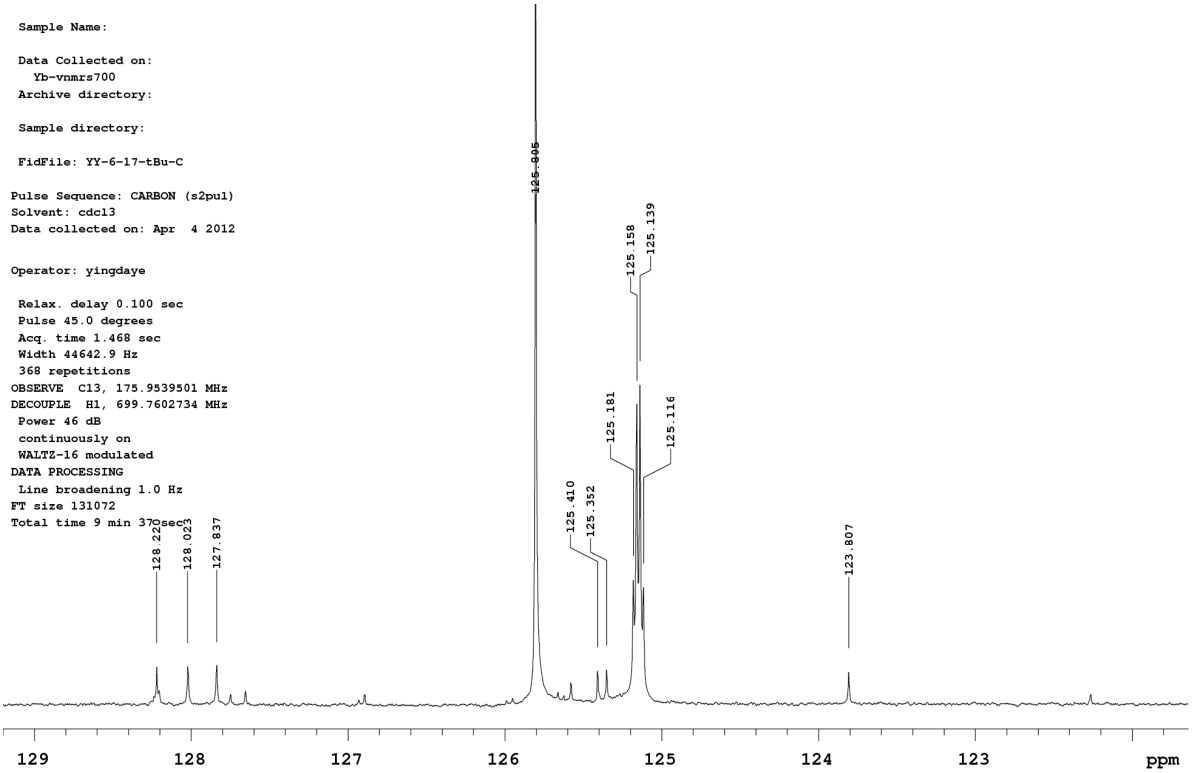

7.576
7.564
7.516
7.505
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm
2.00
2.05
0.09
0.09
0.04

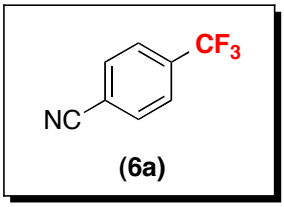
^{19}F NMR


YY-6-17-tBu-F
Sample Name:
Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-tBu-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8659339 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR

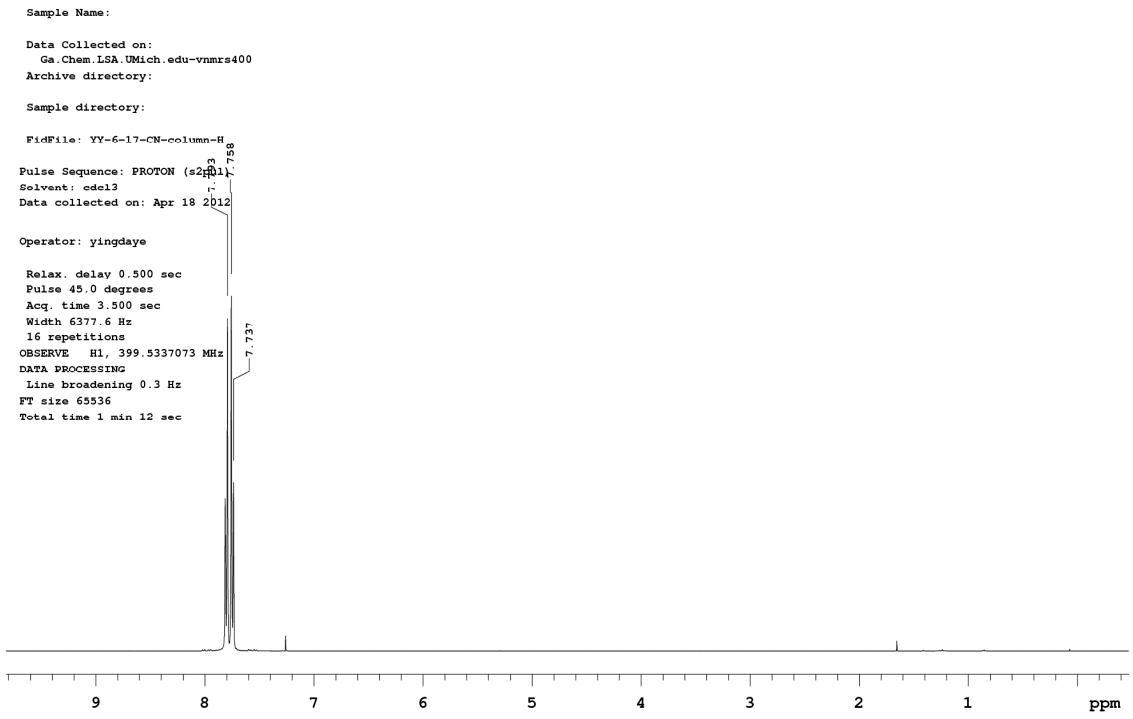

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-tBu-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
368 repetitions
OBSERVE C13, 175.9539501 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 min 37 sec
125.805
125.181
125.158
125.139
125.116
77.342
77.160
76.978
31.272
160
140
120
100
80
60
40
20
ppm

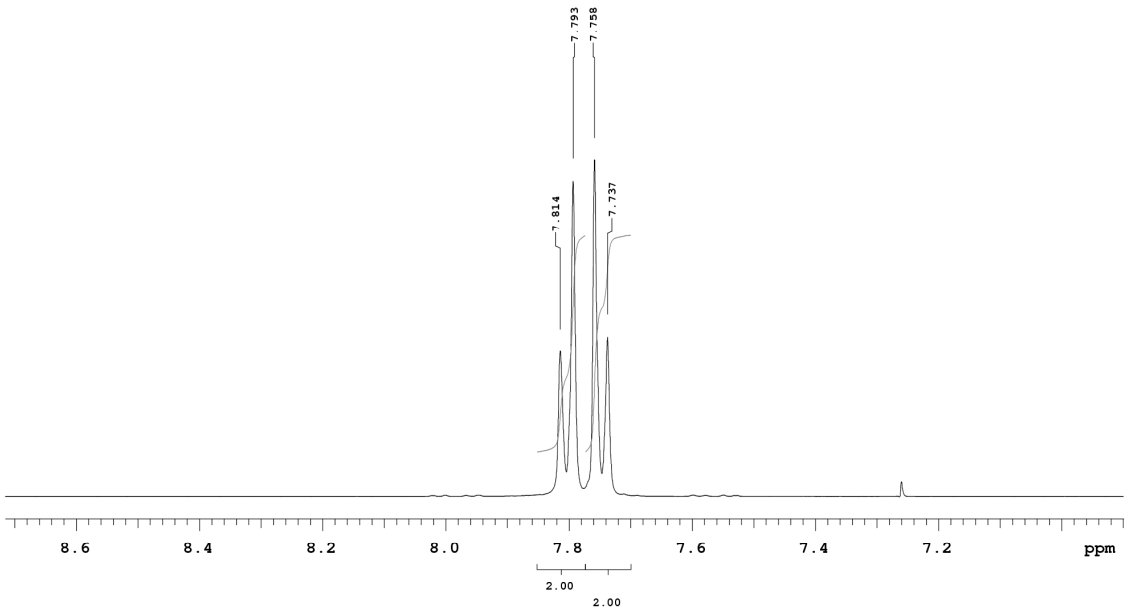

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-tBu-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
368 repetitions
OBSERVE C13, 175.9539501 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 min 37 sec
128.220
128.023
127.837
125.805
125.410
125.352
125.158
125.139
125.181
125.116
123.807
129
128
127
126
125
124
123
ppm


CF3
NC

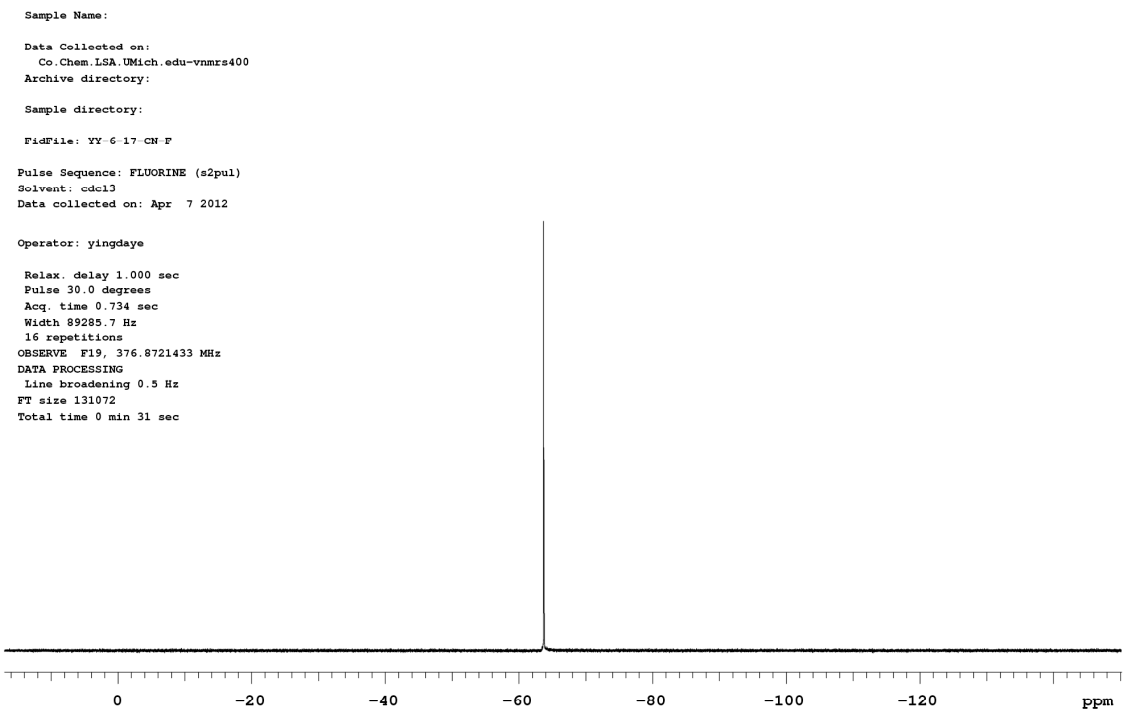
(6a)

^{1}H NMR

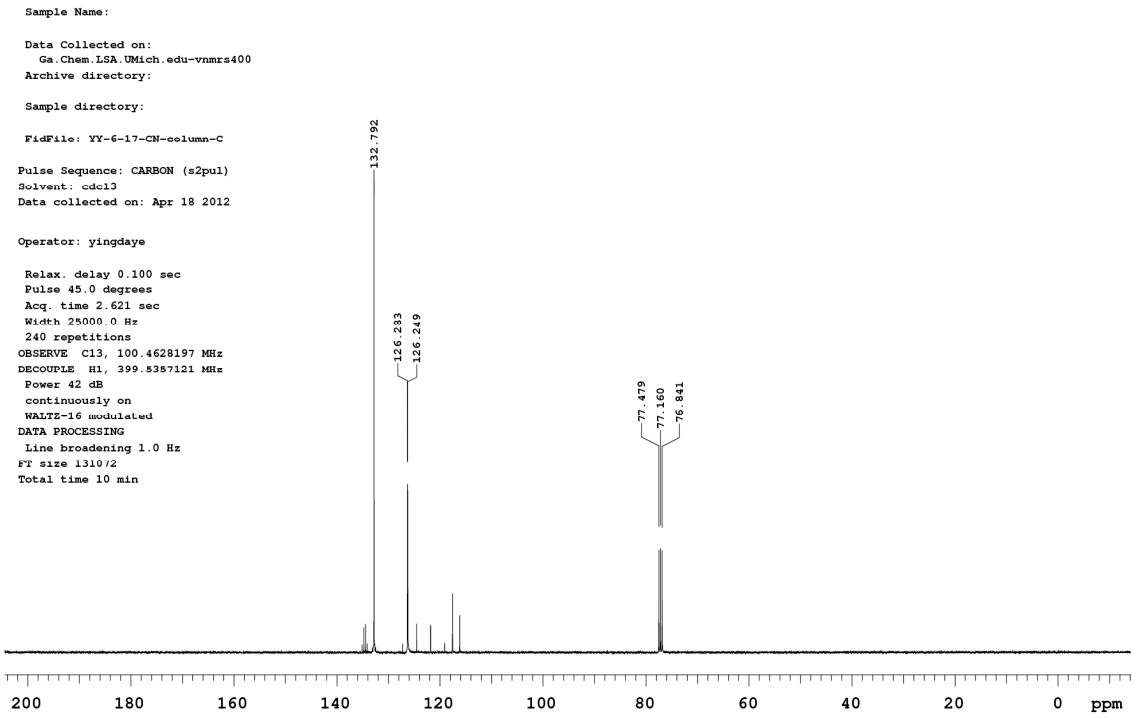

Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-CN-column-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 18 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6377.6 Hz
16 repetitions
OBSERVE H1, 399.5337073 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
7.758
7.737
9
8
7
6
5
4
3
2
1
ppm

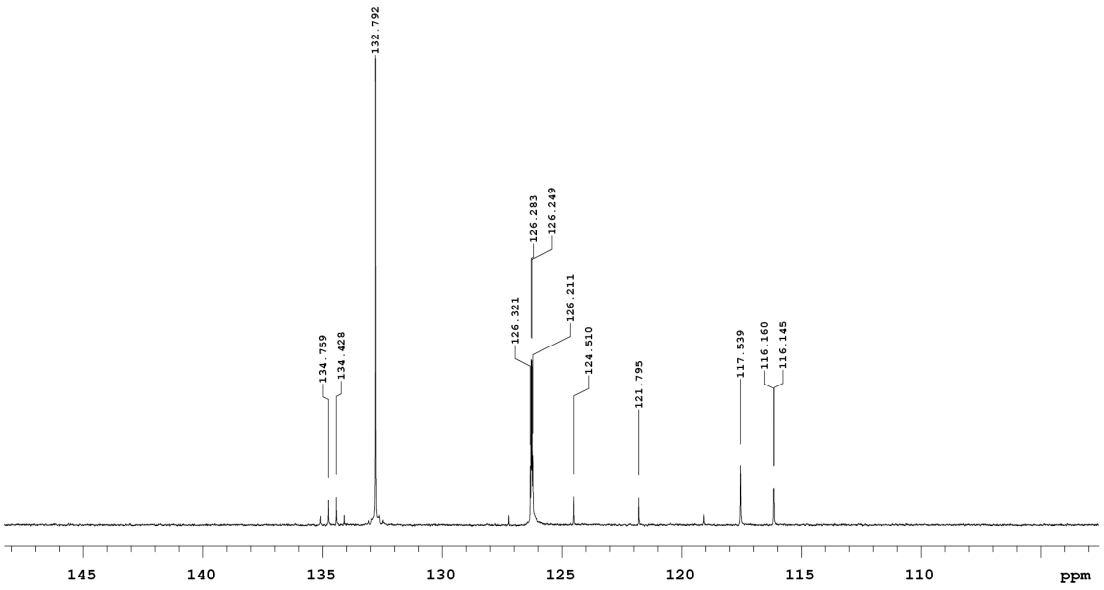

7.793
7.758
7.814
7.737
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
2.00
2.00

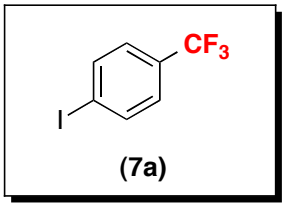
^{19}F NMR


Sample Name:
Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-CN-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 7 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8721433 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
0
-20
-40
-60
-80
-100
-120
ppm

^{13}C NMR


Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-CN-column-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 18 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.621 sec
Width 25000.0 Hz
240 repetitions
OBSERVE C13, 100.4628197 MHz
DECOUPLE H1, 399.5357121 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 10 min
132.792
126.283
126.249
77.479
77.160
76.841
200
180
160
140
120
100
80
60
40
20
0
ppm

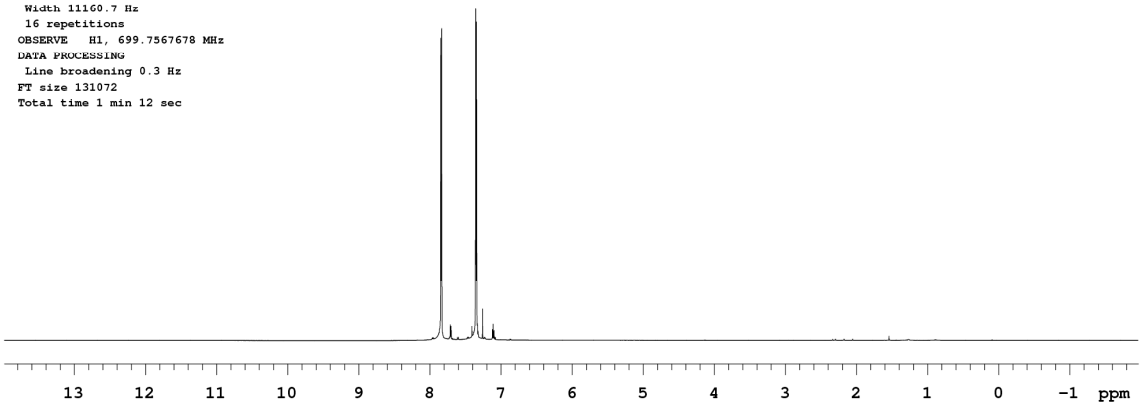

132.792
126.283
126.249
126.321
126.211
124.510
134.759
134.428
121.795
117.539
116.160
116.145
145
140
135
130
125
120
115
110
ppm

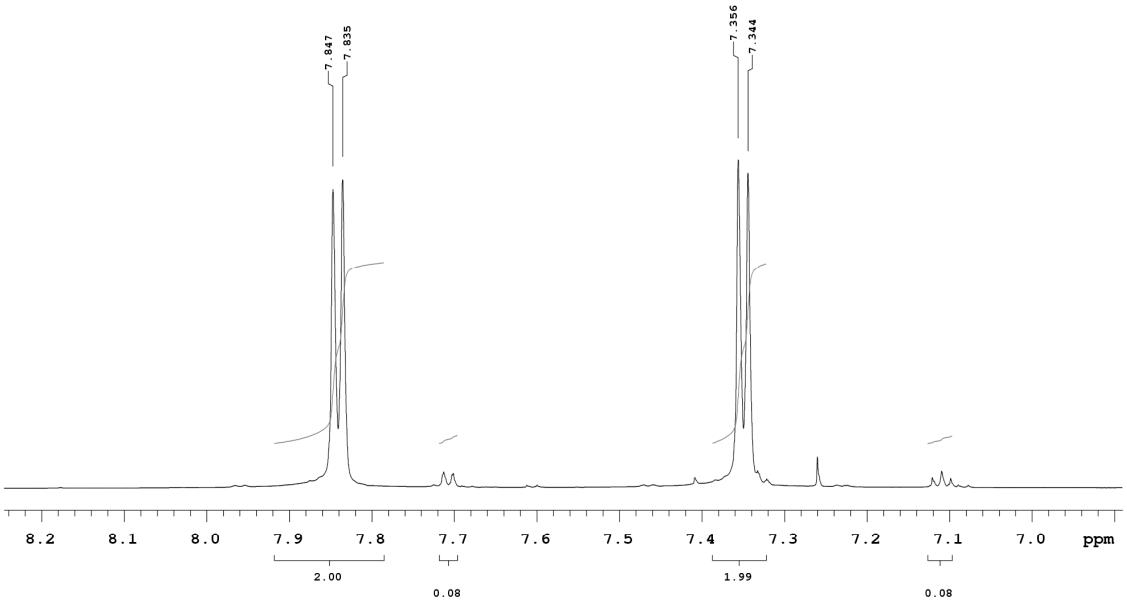


(7a)

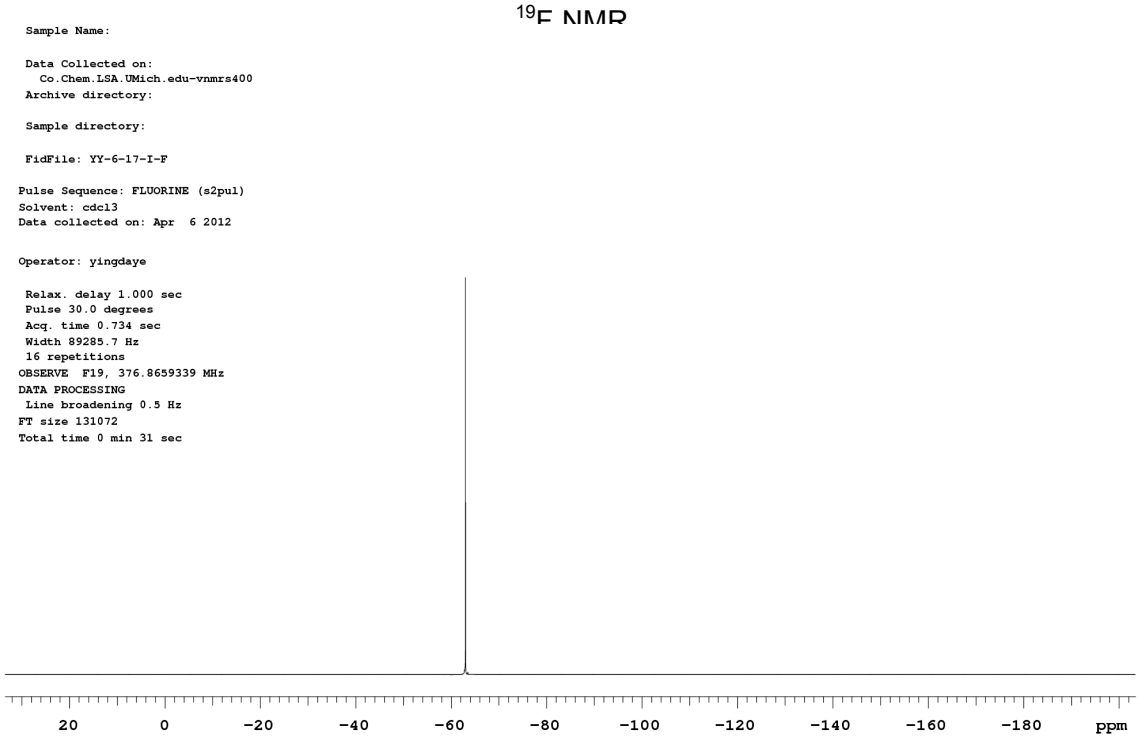
^{1}H NMR

```
Sample Name:

Data Collected on:
  Yb-vnmrs700
Archive directory:

Sample directory:

FidFile: YY-6-17-I-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr  4 2012

Operator: yingdaye

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 11160.7 Hz
 16 repetitions
OBSERVE   H1, 699.7567678 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
```

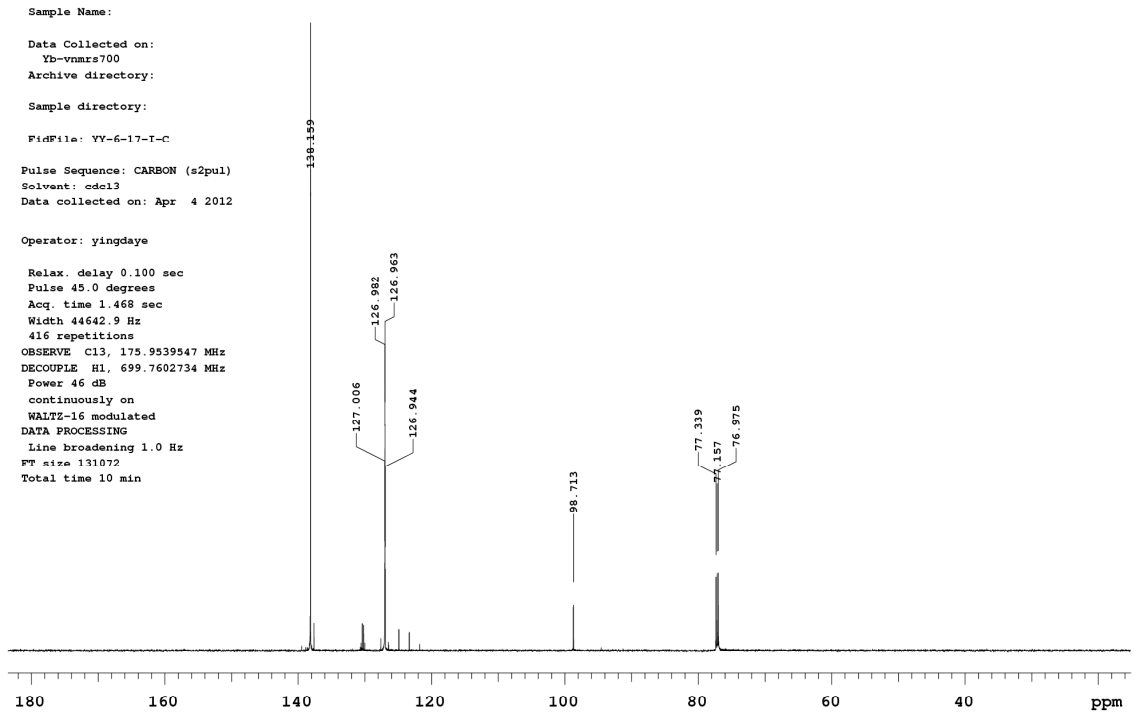


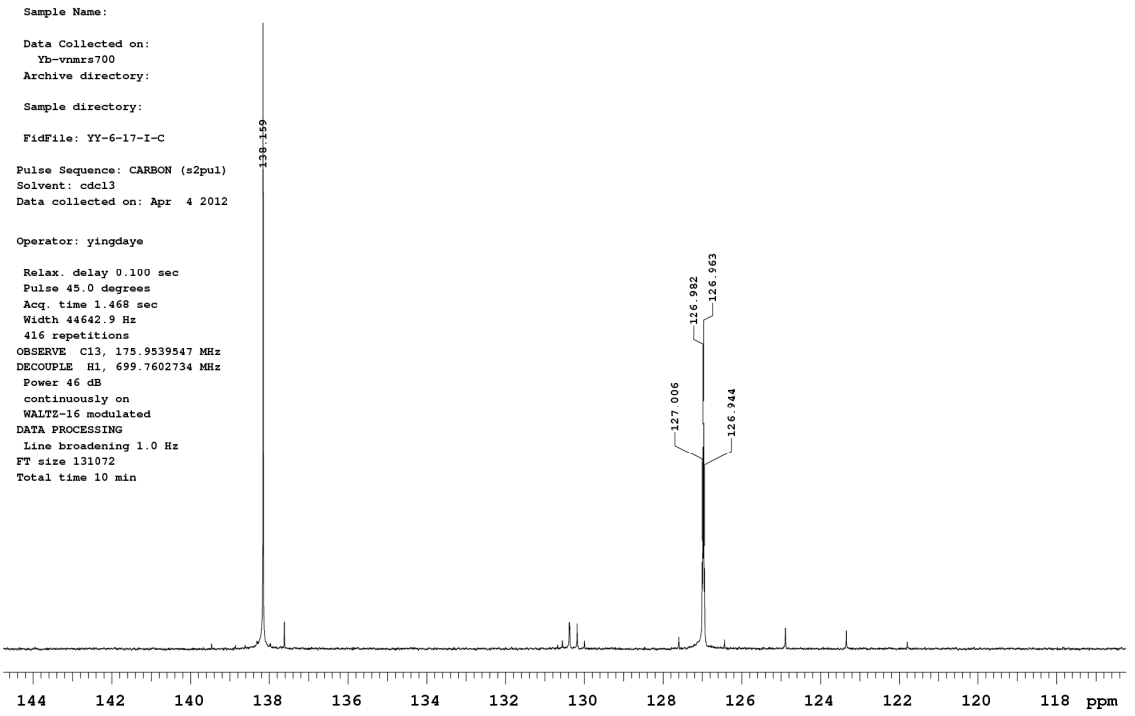


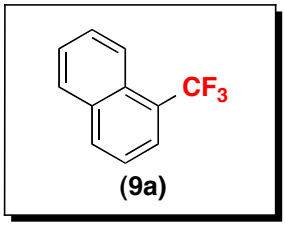
^{19}F NMR


Sample Name:
Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-I-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8659339 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR

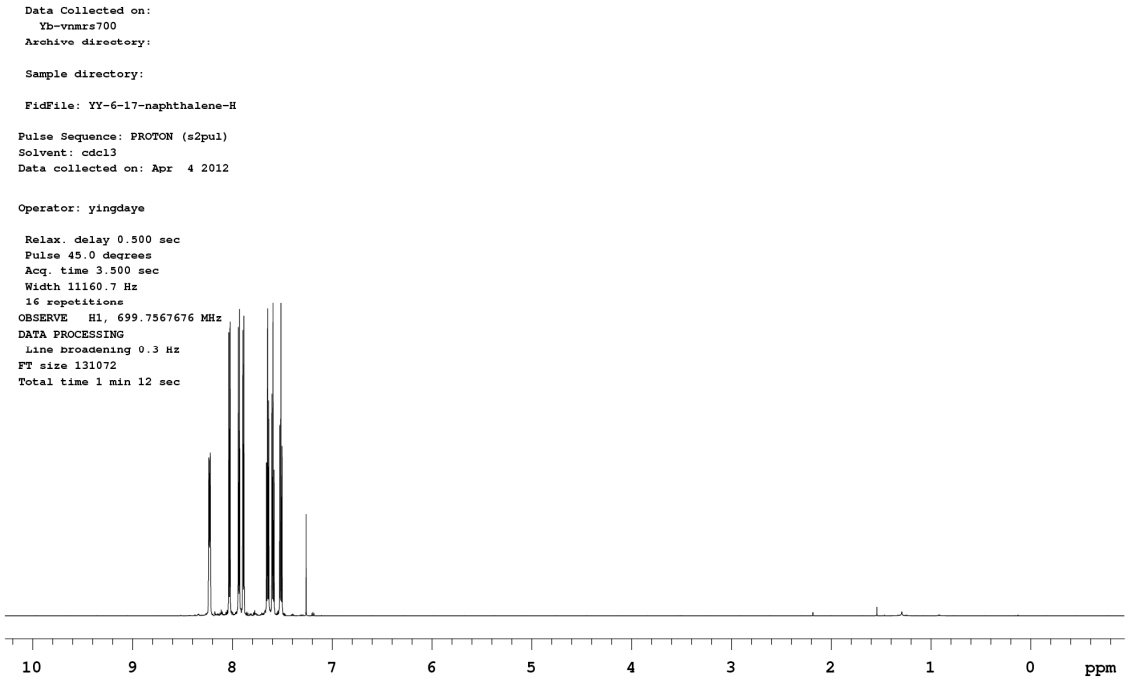

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-I-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
416 repetitions
OBSERVE C13, 175.9539547 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 10 min
138.159
126.982
126.963
127.006
126.944
98.713
77.339
77.157
76.975
180
160
140
120
100
80
60
40
ppm

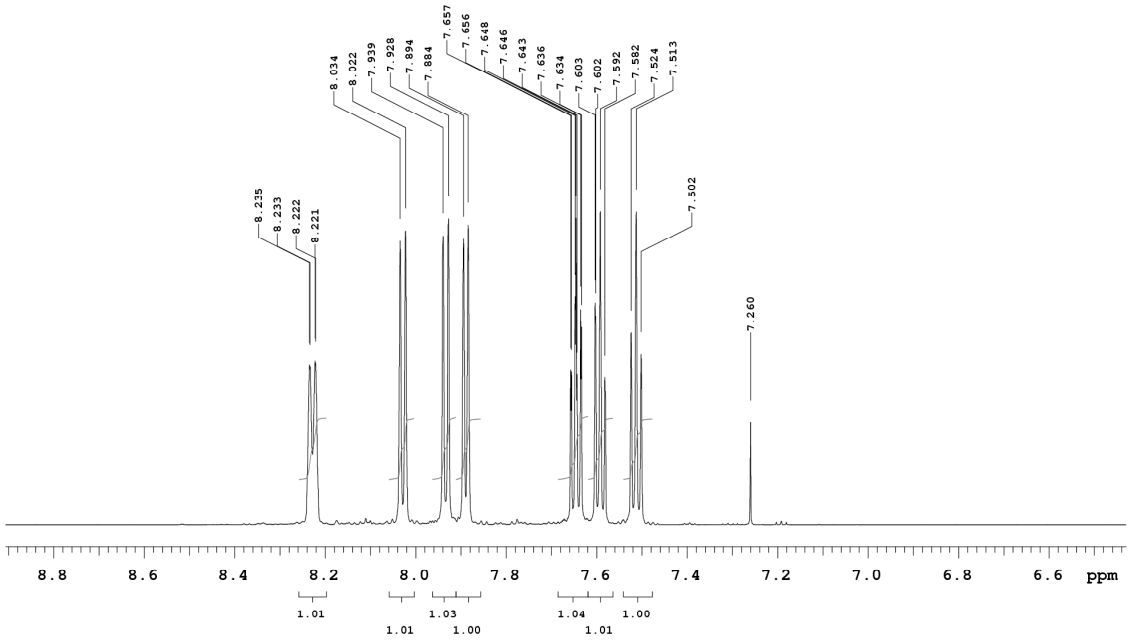

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-I-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
416 repetitions
OBSERVE C13, 175.9539547 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 10 min
138.159
126.982
126.963
127.006
126.944
144
142
140
138
136
134
132
130
128
126
124
122
120
118
ppm


CF3

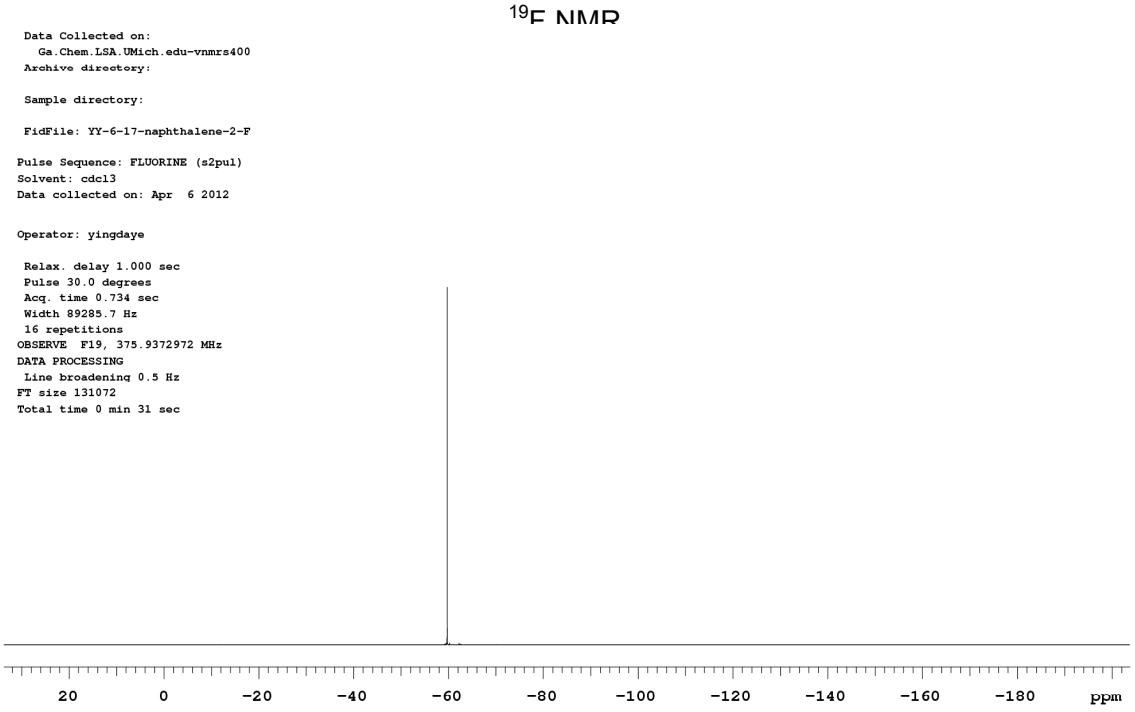
(9a)

^{1}H NMR

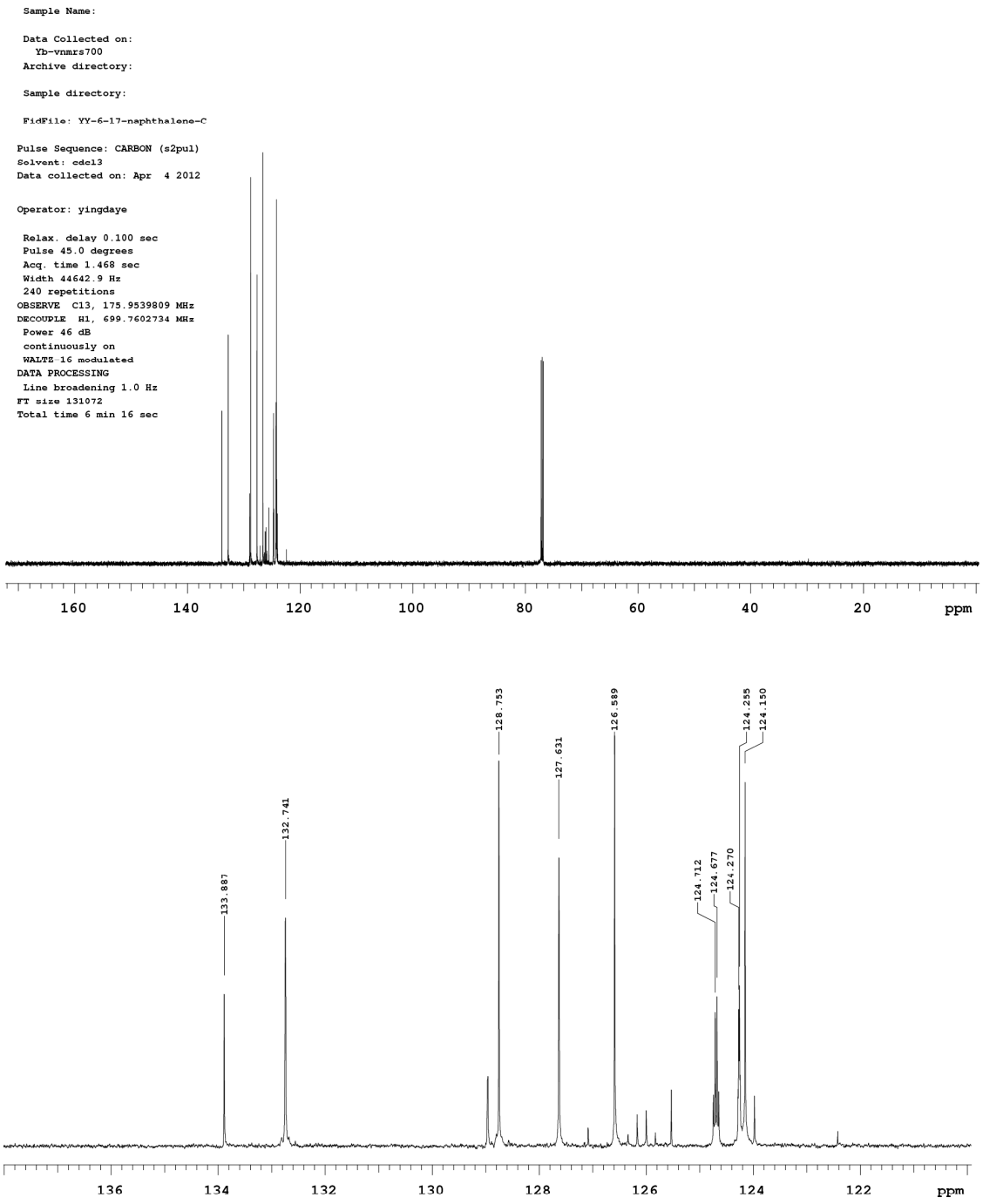

Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-naphthalene-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11160.7 Hz
16 repetitions
OBSERVE H1, 699.7567676 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
10
9
8
7
6
5
4
3
2
1
0
ppm

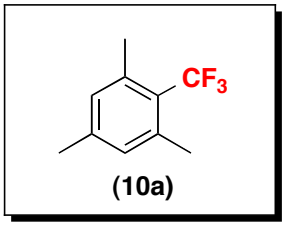

8.235
8.233
8.222
8.221
8.034
8.032
7.939
7.928
7.894
7.884
7.657
7.656
7.648
7.646
7.643
7.636
7.634
7.603
7.602
7.592
7.582
7.524
7.513
7.502
7.260
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm
1.01
1.01
1.03
1.00
1.04
1.01
1.00

^{19}F NMR


Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-naphthalene-2-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 375.9372972 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

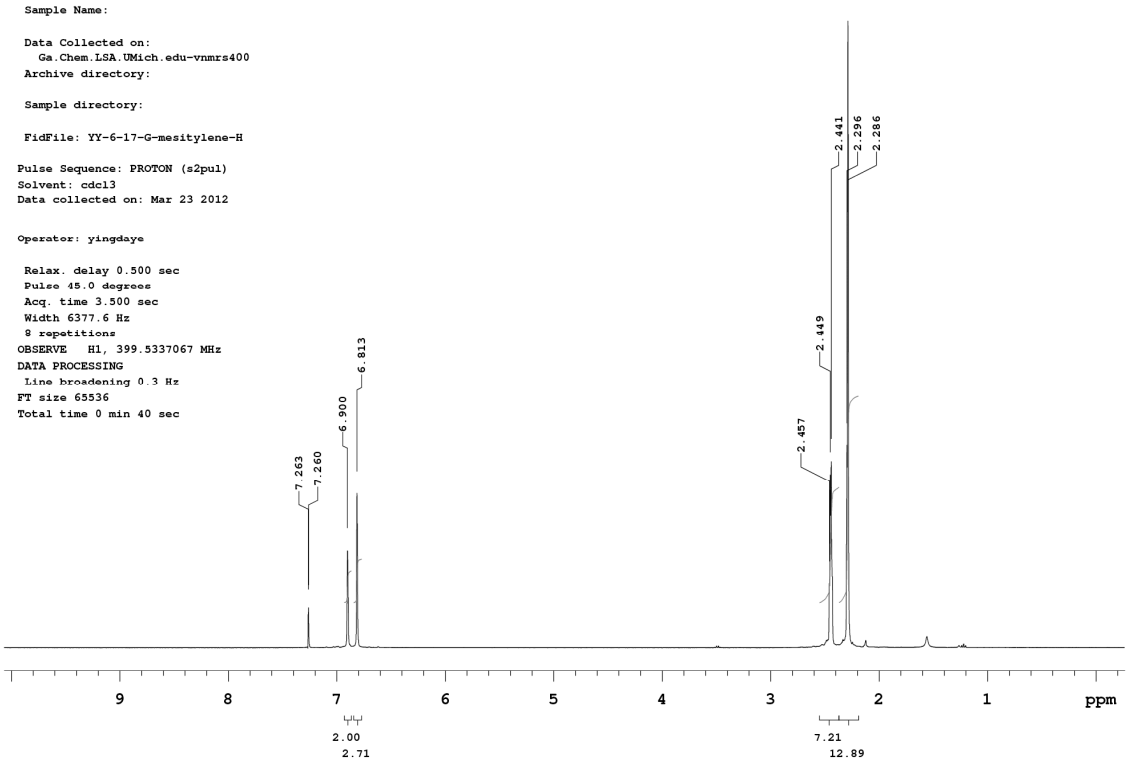
^{13}C NMR


Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-naphthalene-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
240 repetitions
OBSERVE C13, 175.9539809 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 min 16 sec
160
140
120
100
80
60
40
20
ppm
133.887
132.741
128.753
127.631
126.589
124.712
124.677
124.270
124.255
124.150
136
134
132
130
128
126
124
122
ppm

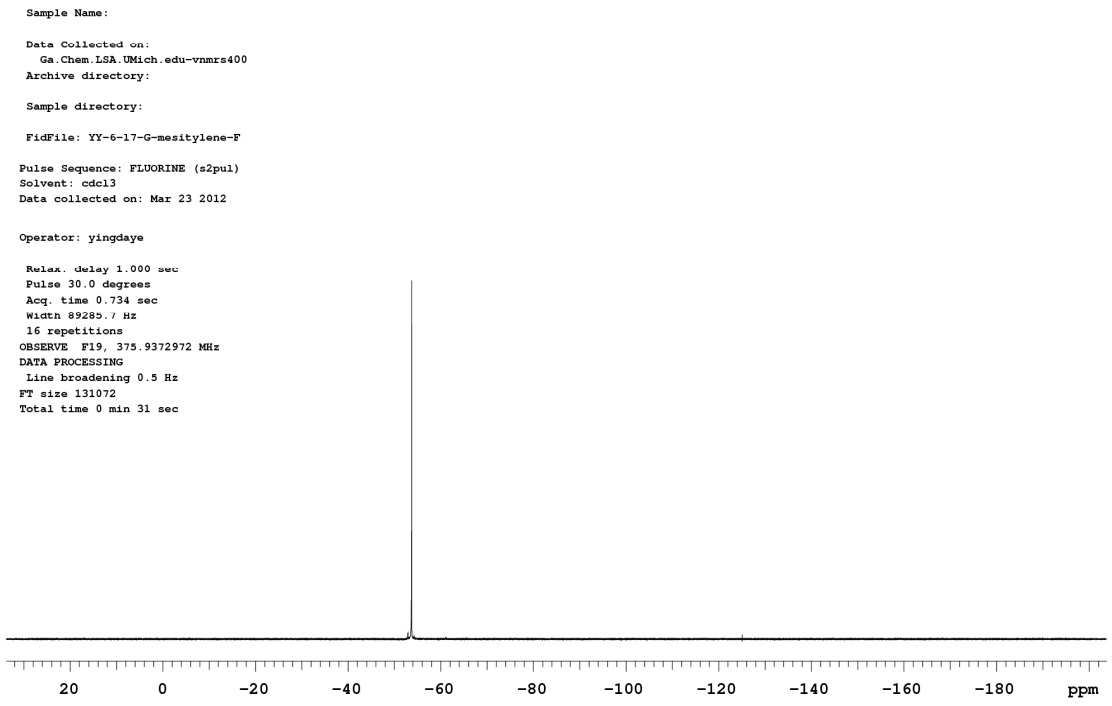

CF3

(10a)

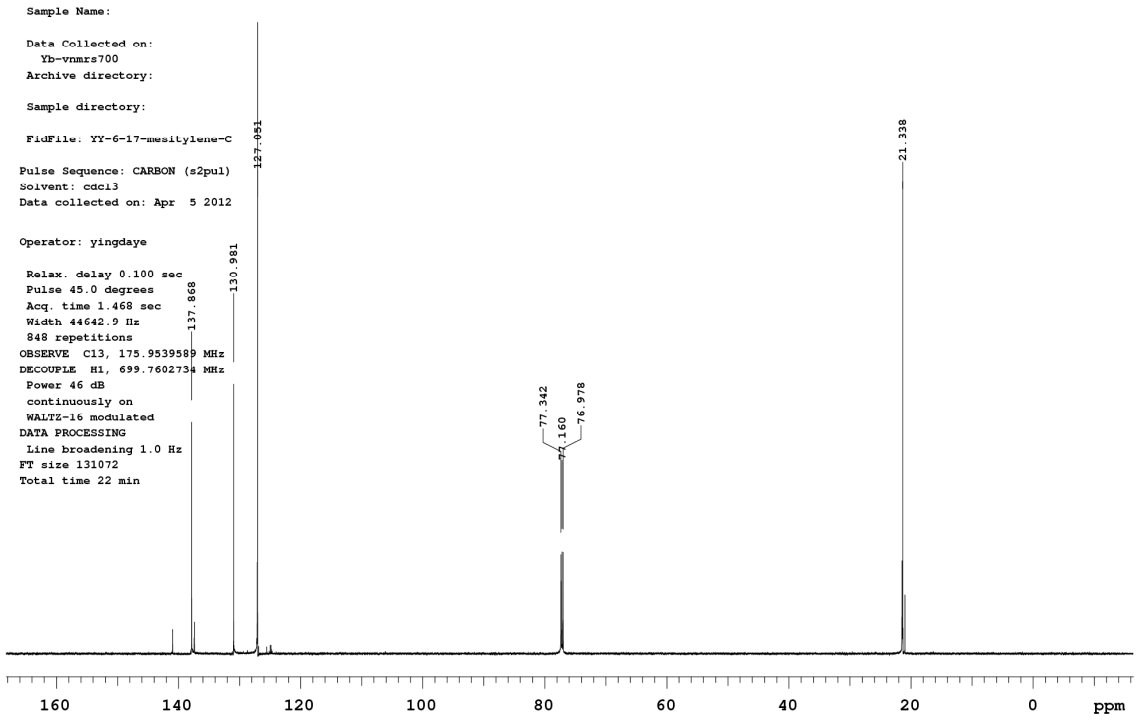
^{1}H NMR

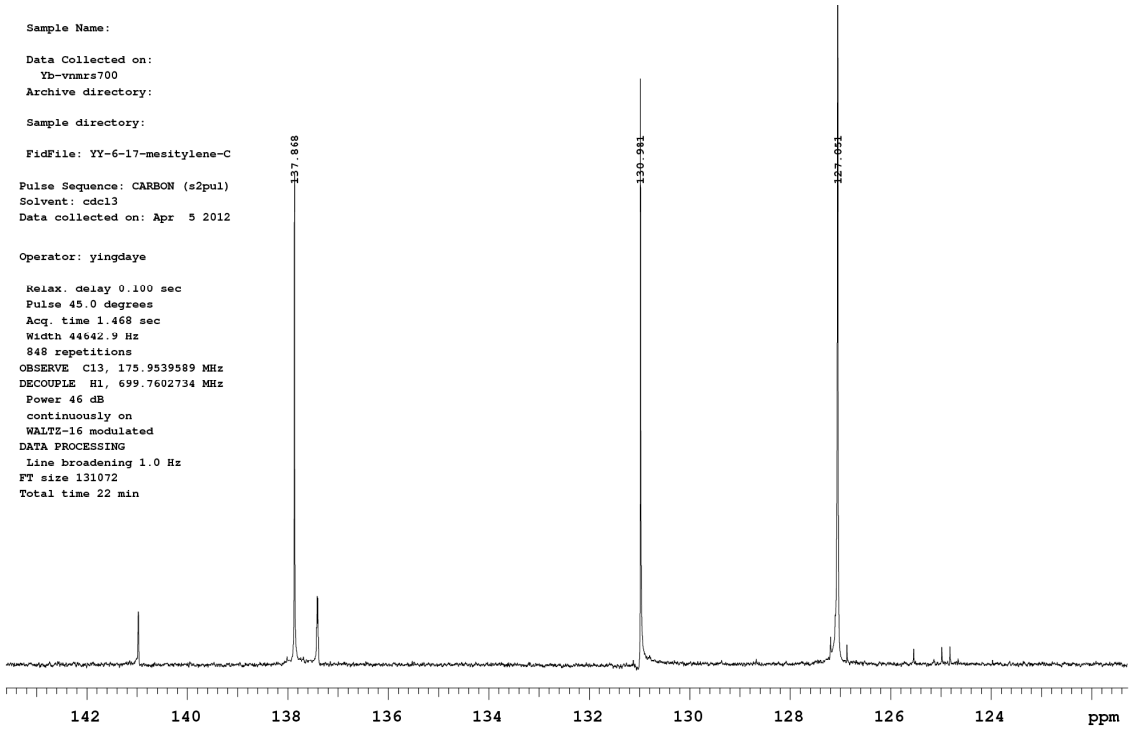

Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-G-mesitylene-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 23 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6377.6 Hz
8 repetitions
OBSERVE H1, 399.5337067 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 40 sec
7.263
7.260
6.900
6.813
2.457
2.449
2.441
2.296
2.286
9
8
7
6
5
4
3
2
1
ppm
2.00
2.71
7.21
12.89

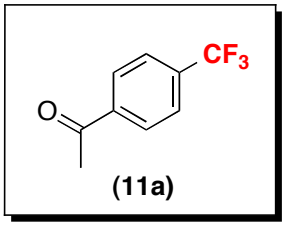
^{19}F NMR


Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-G-mesitylene-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Mar 23 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 375.9372972 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR

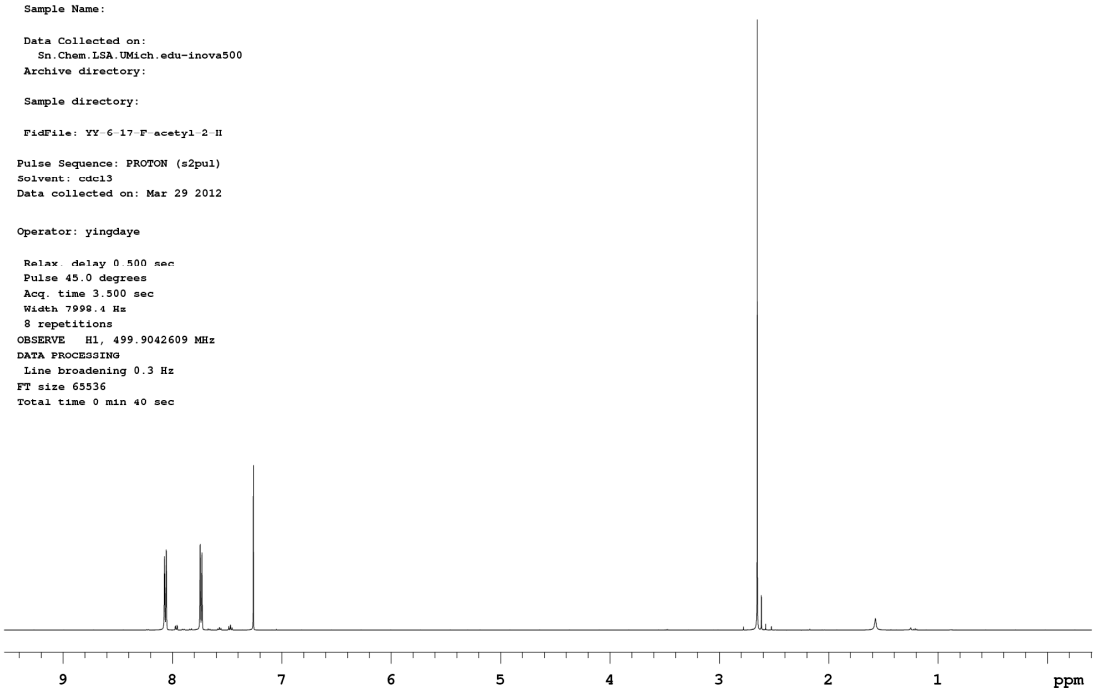

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-mesitylene-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
848 repetitions
OBSERVE C13, 175.9539589 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 22 min
137.868
130.981
127.951
77.342
77.160
76.978
21.338
160
140
120
100
80
60
40
20
0
ppm

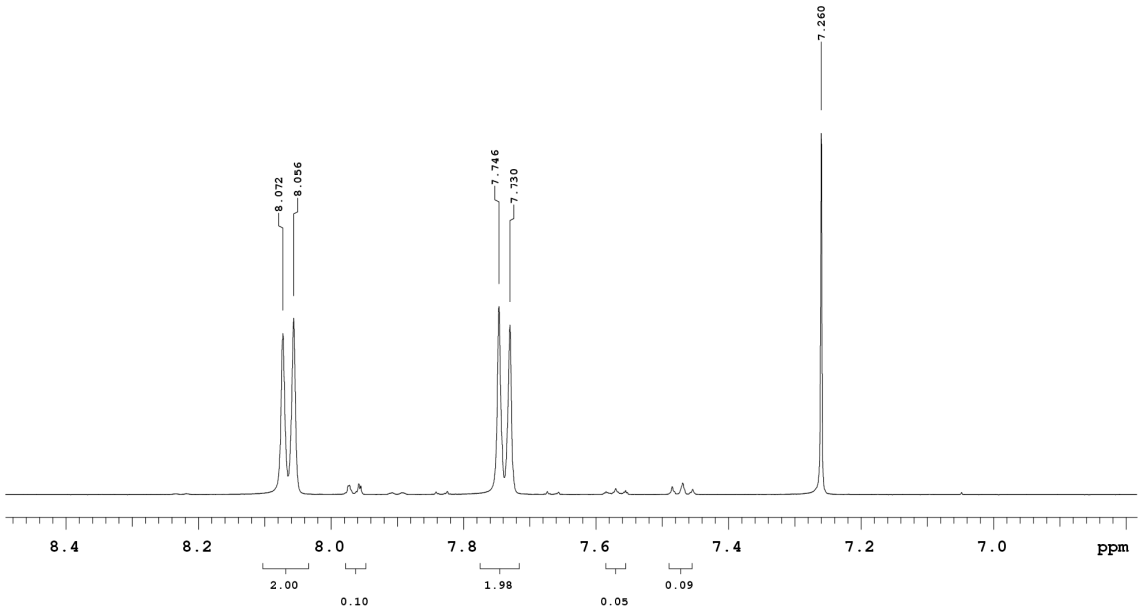

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-mesitylene-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
848 repetitions
OBSERVE C13, 175.9539589 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 22 min
137.868
130.981
127.951
142
140
138
136
134
132
130
128
126
124
ppm


CF3
O

(11a)

^{1}H NMR


Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: YY-6-17-F-acetyl-2-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 29 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7999.4 Hz
8 repetitions
OBSERVE H1, 499.9042609 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min 40 sec
9
8
7
6
5
4
3
2
1
ppm


8.072
8.056
7.746
7.730
7.260
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
2.00
0.10
1.98
0.05
0.09

^{19}F NMR

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

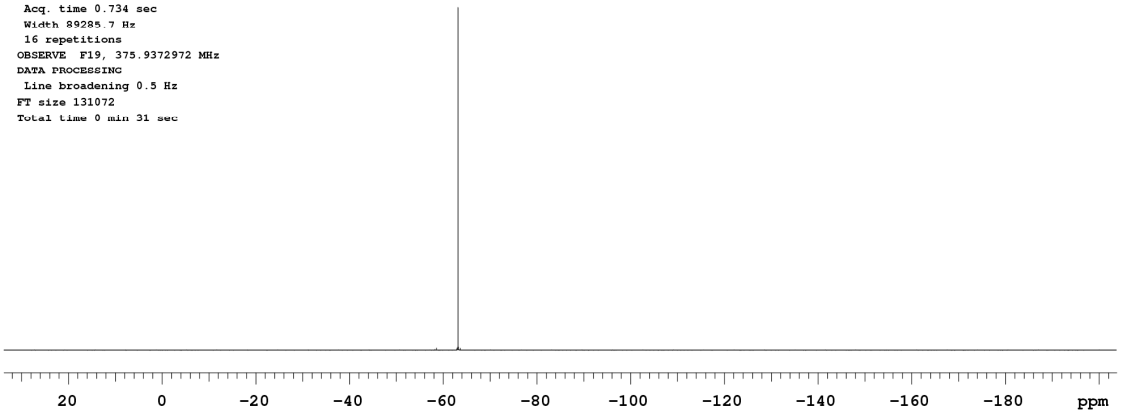
Sample directory:

FidFile: YY-6-17-F-acetyl-F

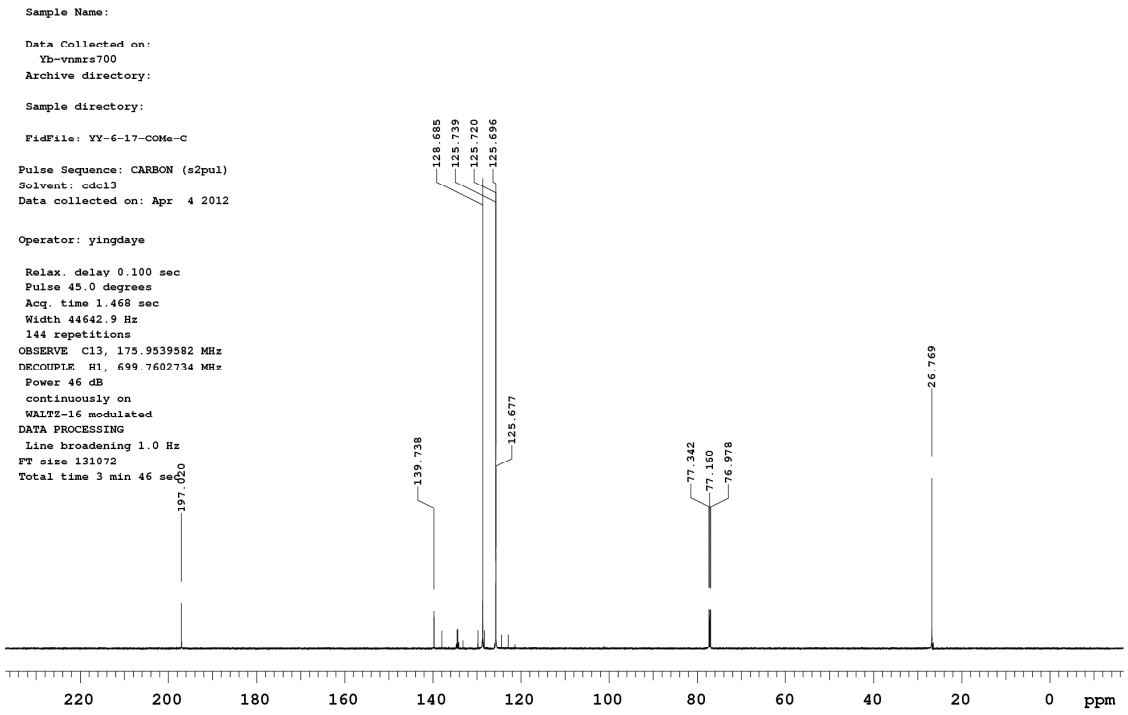
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Mar 22 2012

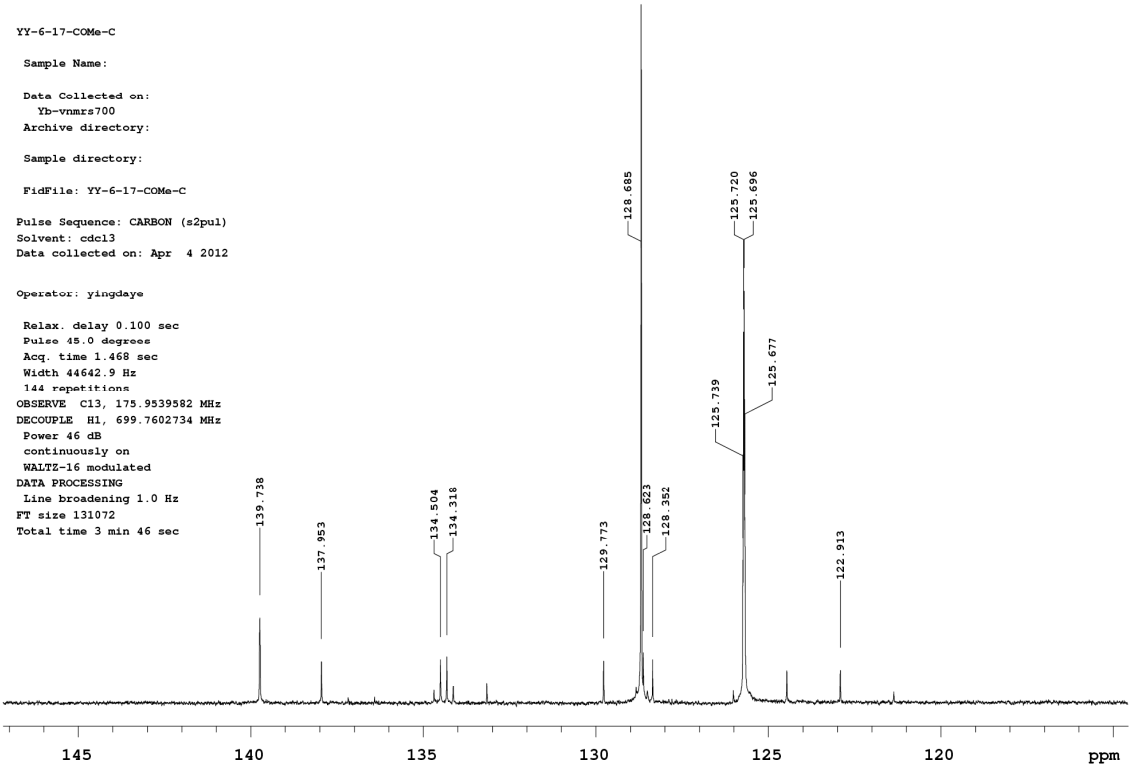
Operator: yingdaye

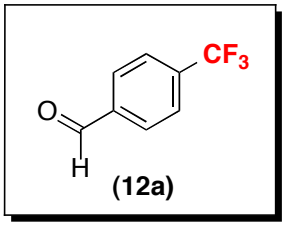
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 375.9372972 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec



^{13}C NMR

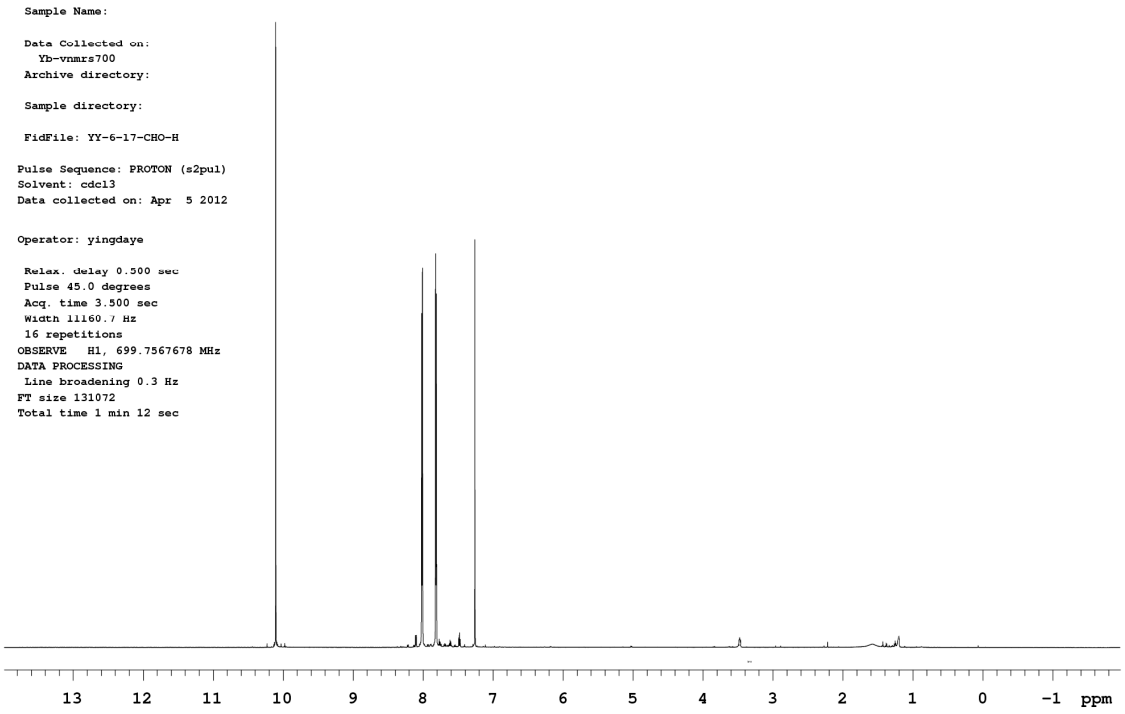

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-COMe-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
144 repetitions
OBSERVE C13, 175.9539582 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 min 46 sec
197.020
139.738
128.685
125.739
125.720
125.696
125.677
77.342
77.160
76.978
26.769
220
200
180
160
140
120
100
80
60
40
20
0
ppm

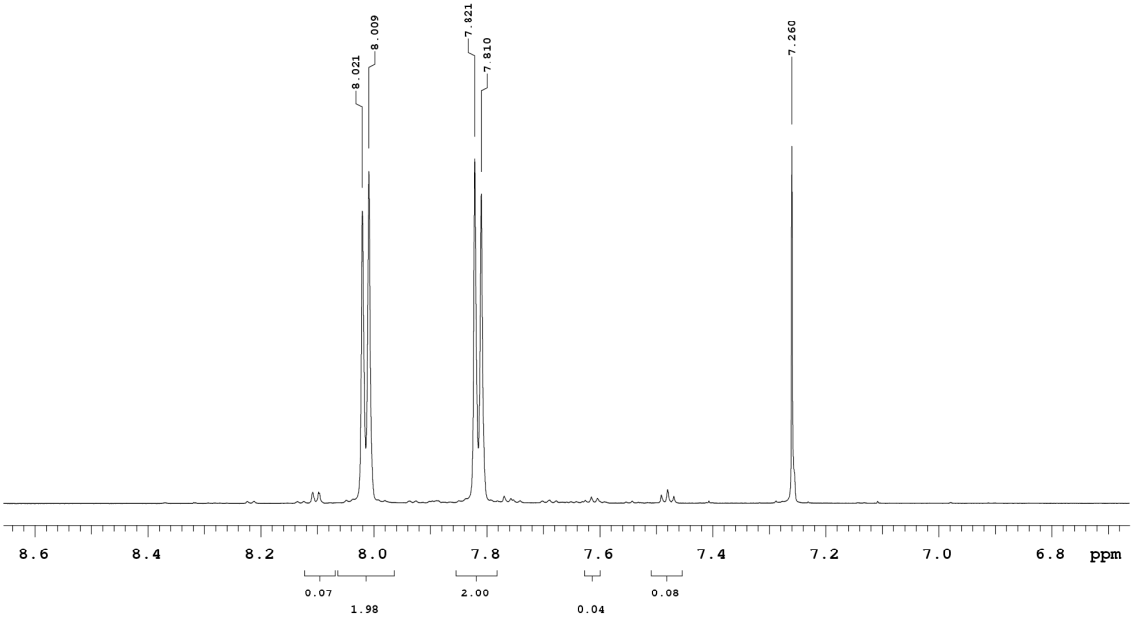

YY-6-17-COMe-C
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-COMe-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
144 repetitions
OBSERVE C13, 175.9539582 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 min 46 sec
139.738
137.953
134.504
134.318
129.773
128.685
128.623
128.352
125.739
125.720
125.696
125.677
122.913
145
140
135
130
125
120
ppm


CF3
O
H

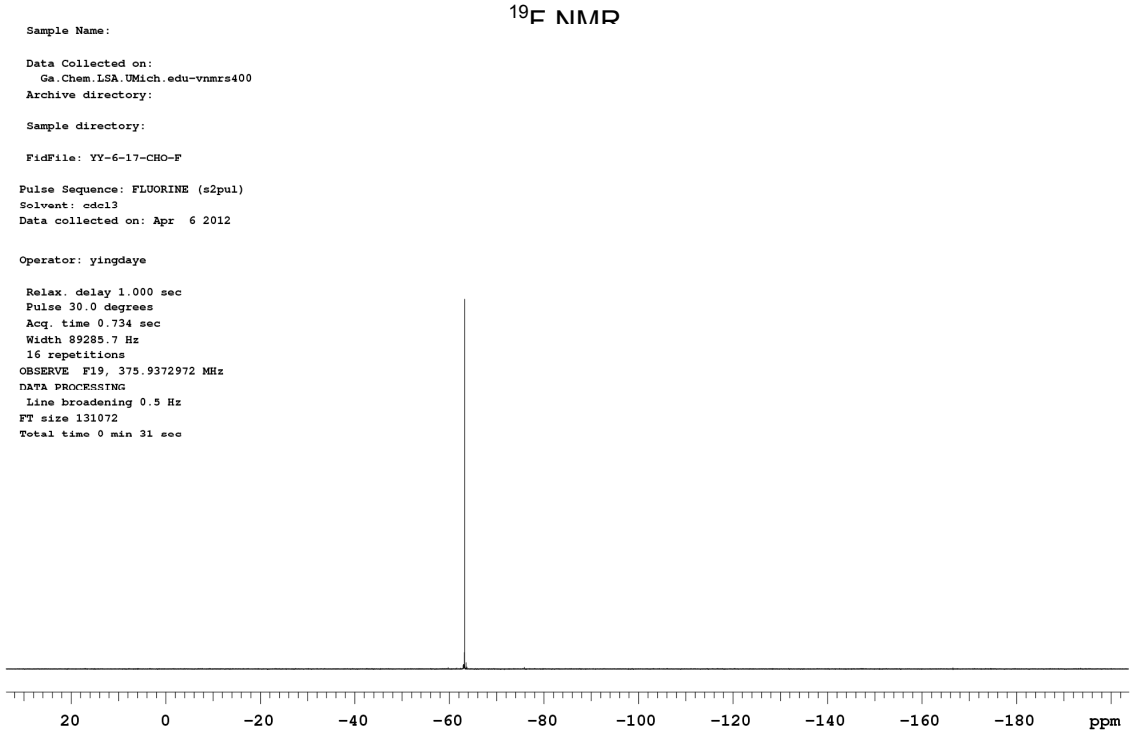
(12a)

^{1}H NMR

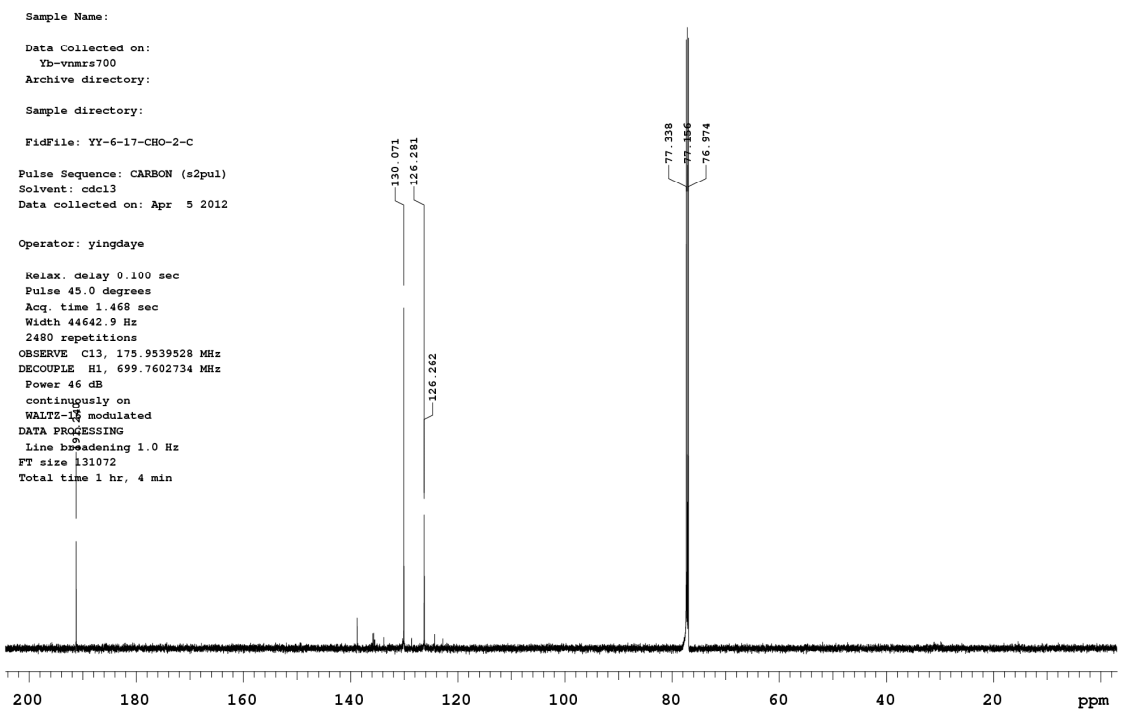

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-CHO-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11160.7 Hz
16 repetitions
OBSERVE H1, 699.7567678 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm

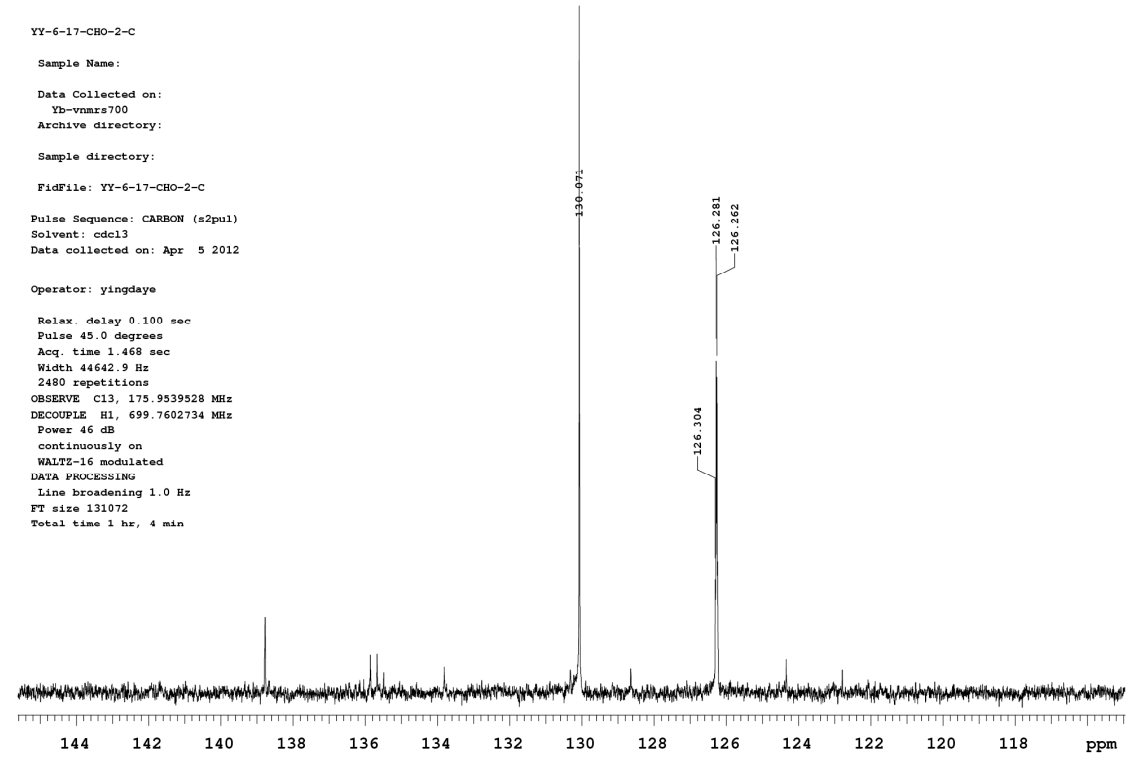

8.021
8.009
7.821
7.810
7.260
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
0.07
1.98
2.00
0.04
0.08

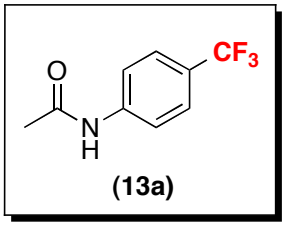
^{19}F NMR


Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-CHO-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 375.9372972 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR

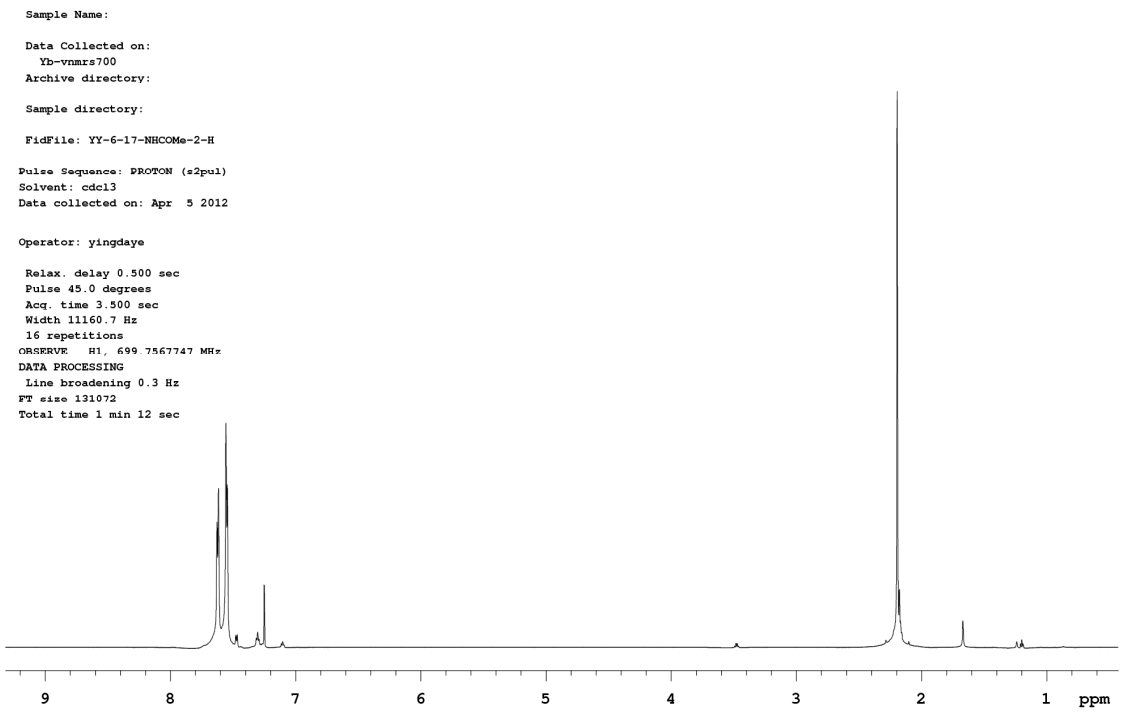

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-CHO-2-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
2480 repetitions
OBSERVE C13, 175.9539528 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 4 min
130.071
126.281
126.262
77.338
77.166
76.974
200
180
160
140
120
100
80
60
40
20
ppm

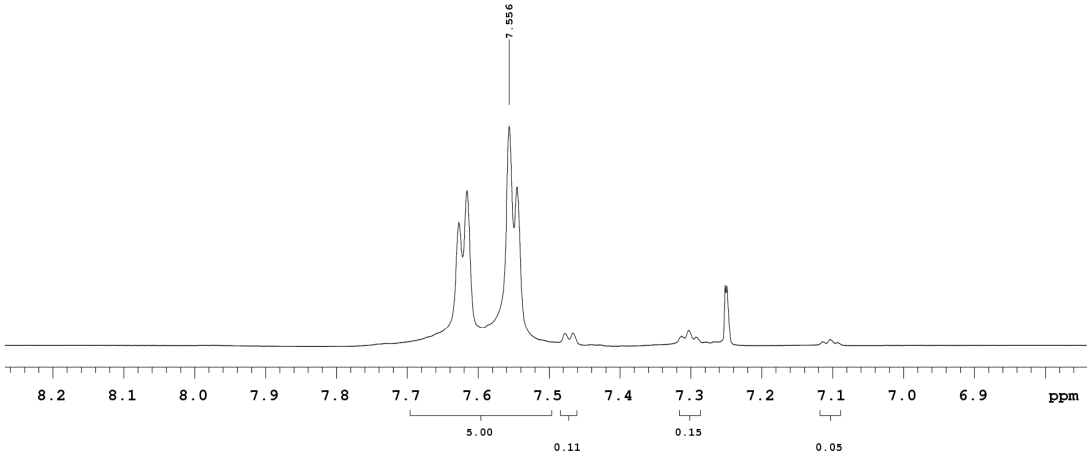

YY-6-17-CHO-2-C
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-CHO-2-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
2480 repetitions
OBSERVE C13, 175.9539528 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 4 min
130.071
126.281
126.262
126.304
144
142
140
138
136
134
132
130
128
126
124
122
120
118
ppm


O
N
H
CF3

(13a)

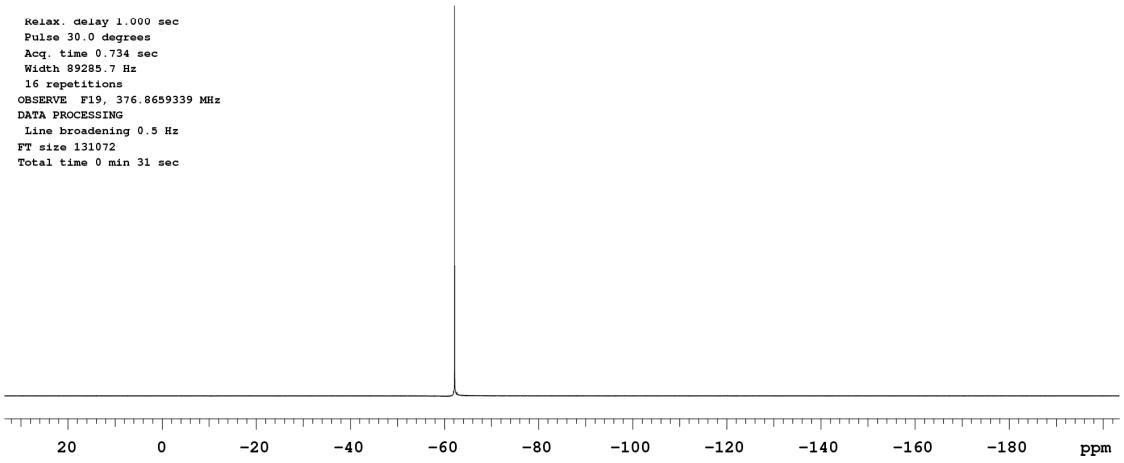
^{1}H NMR


Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-NHCOMe-2-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11160.7 Hz
16 repetitions
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
9
8
7
6
5
4
3
2
1
ppm

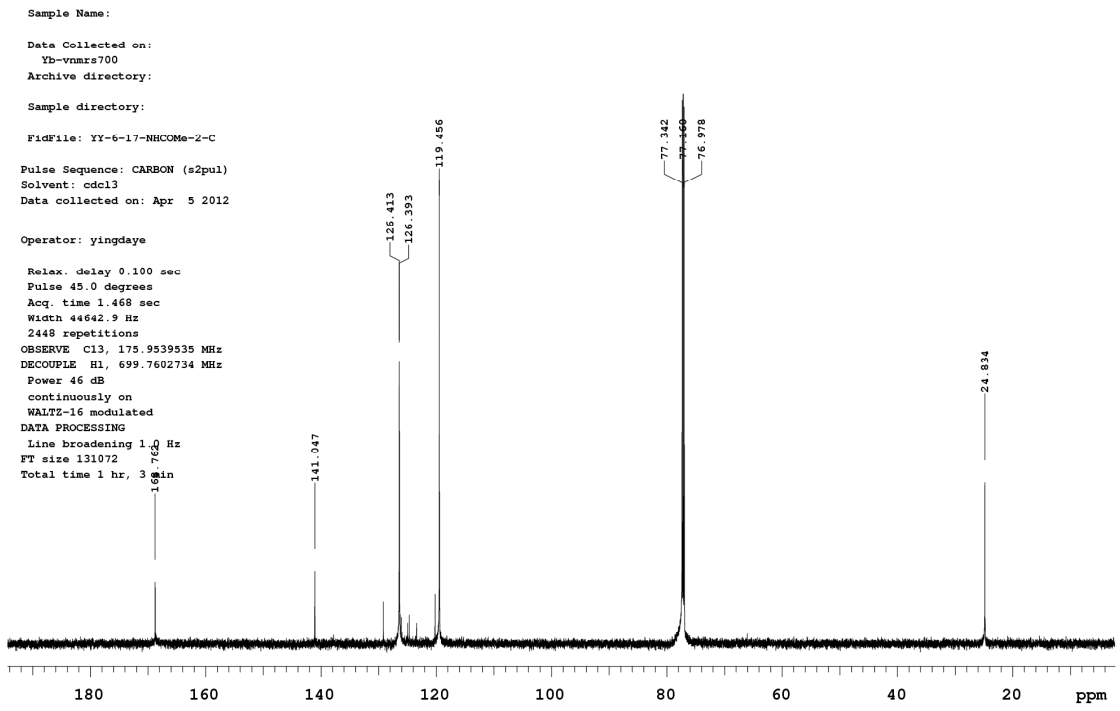

7.556
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm
5.00
0.11
0.15
0.05

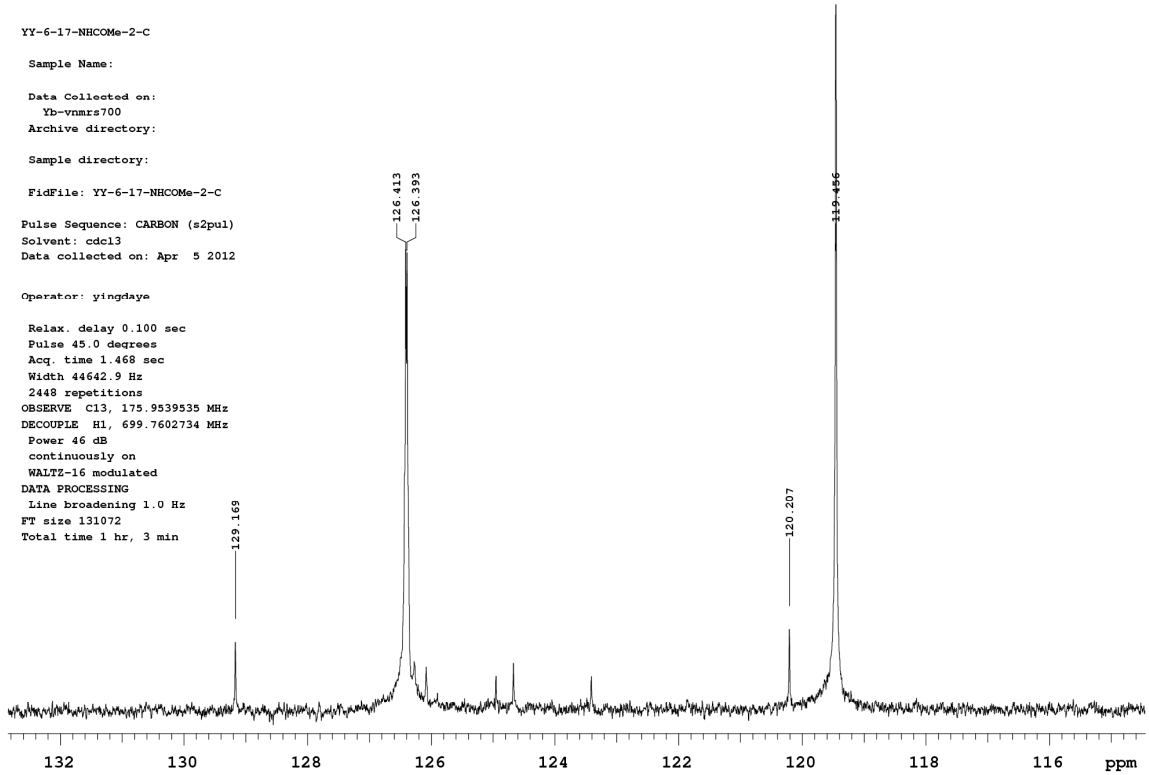
^{19}F NMR

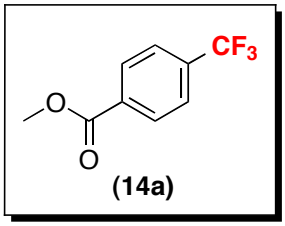
```
 Sample Name:

 Data Collected on:
   Co.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

 Sample directory:

 FidFile: YY-6-17-NHCOMe-F

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr  6 2012

Operator: yingdaye

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 0.734 sec
 Width 89285.7 Hz
 16 repetitions
OBSERVE  F19, 376.8659339 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
```



^{13}C NMR


Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-NHCOMe-2-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
2448 repetitions
OBSERVE C13, 175.9539535 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 3 min
169.762
141.047
126.413
126.393
119.456
77.342
77.160
76.978
24.834
180
160
140
120
100
80
60
40
20
ppm


YY-6-17-NHCOMe-2-C
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-NHCOMe-2-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
2448 repetitions
OBSERVE C13, 175.9539535 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 3 min
129.169
126.413
126.393
120.207
119.456
132
130
128
126
124
122
120
118
116
ppm



(14a)

^{1}H NMR

Sample Name:

Data Collected on:
Yb-vnmrs700
Archive directory:

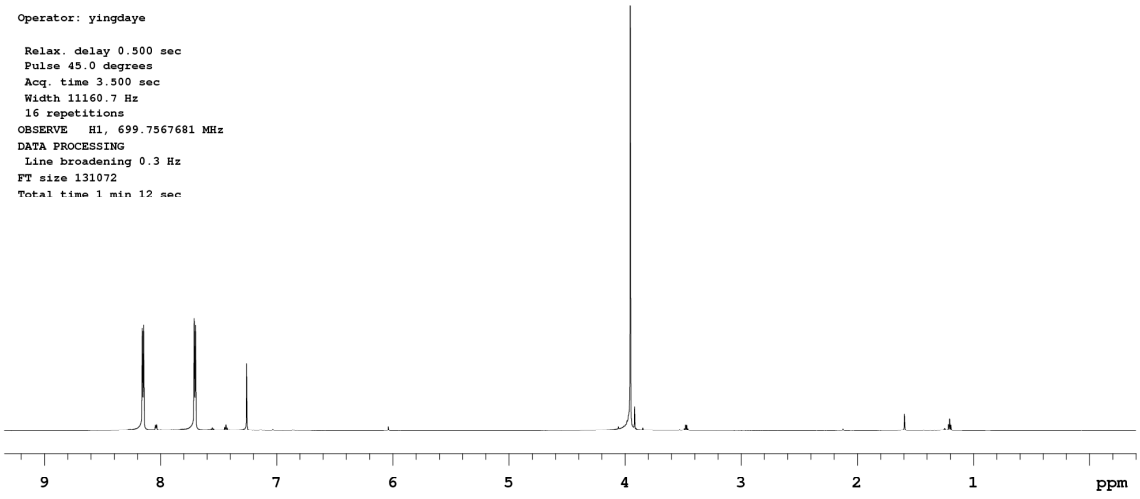
Sample directory:

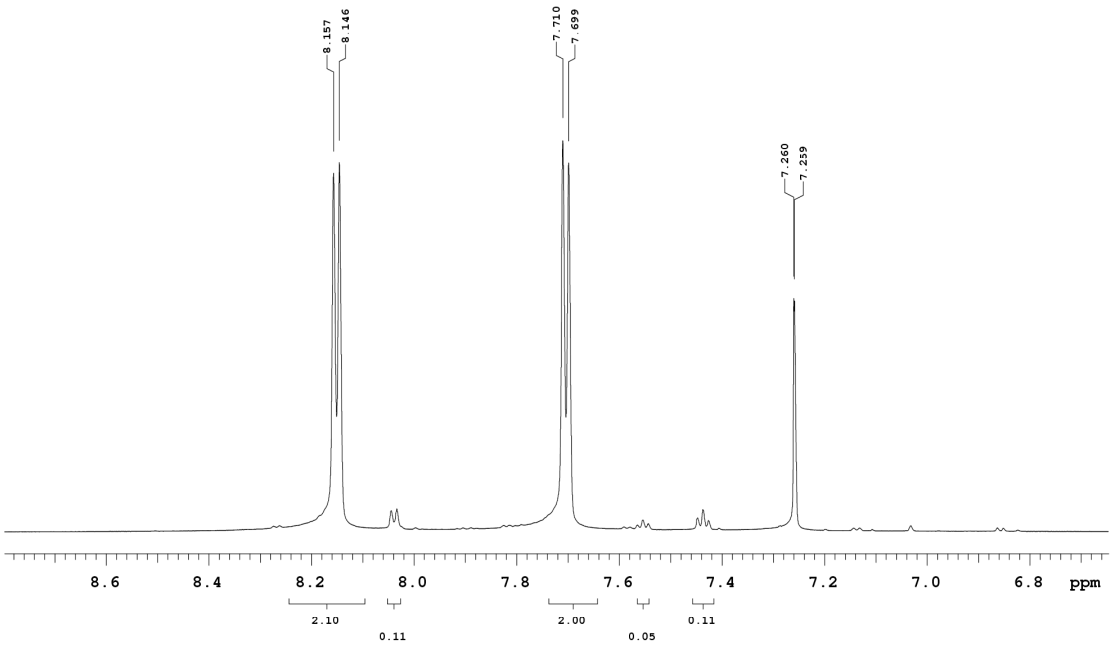
FidFile: YY-6-17-COOMe-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012

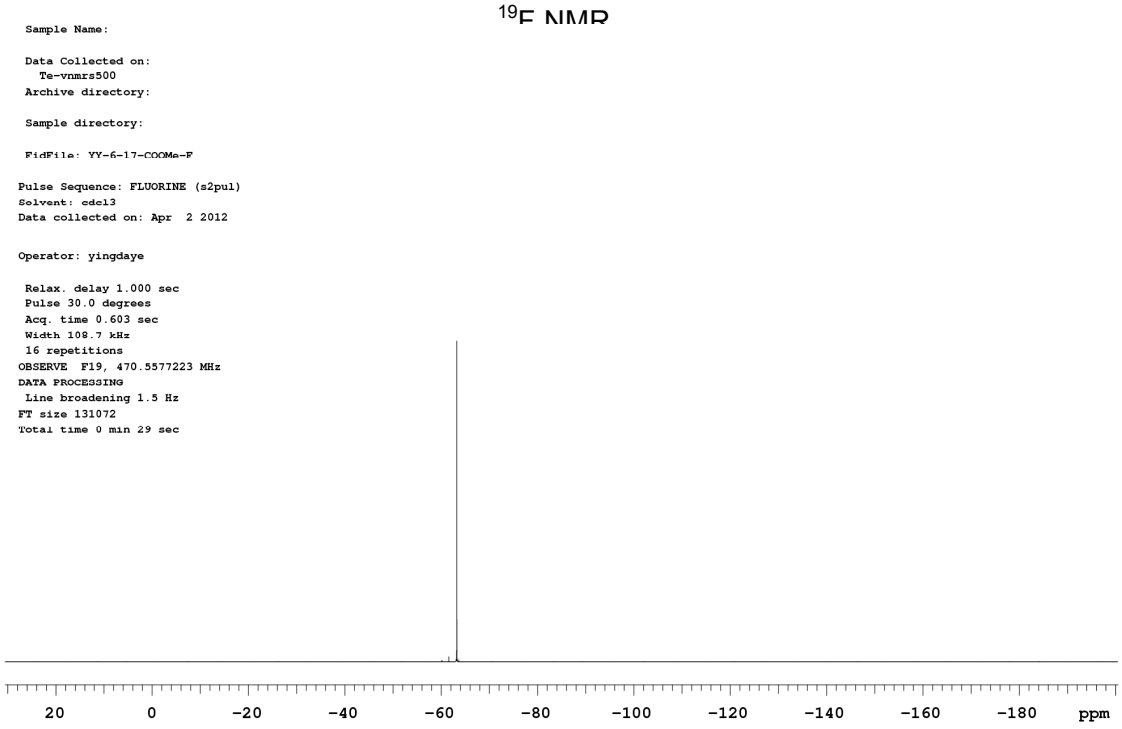
Operator: yingdaye

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11160.7 Hz
16 repetitions
OBSERVE H1, 699.7567681 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec

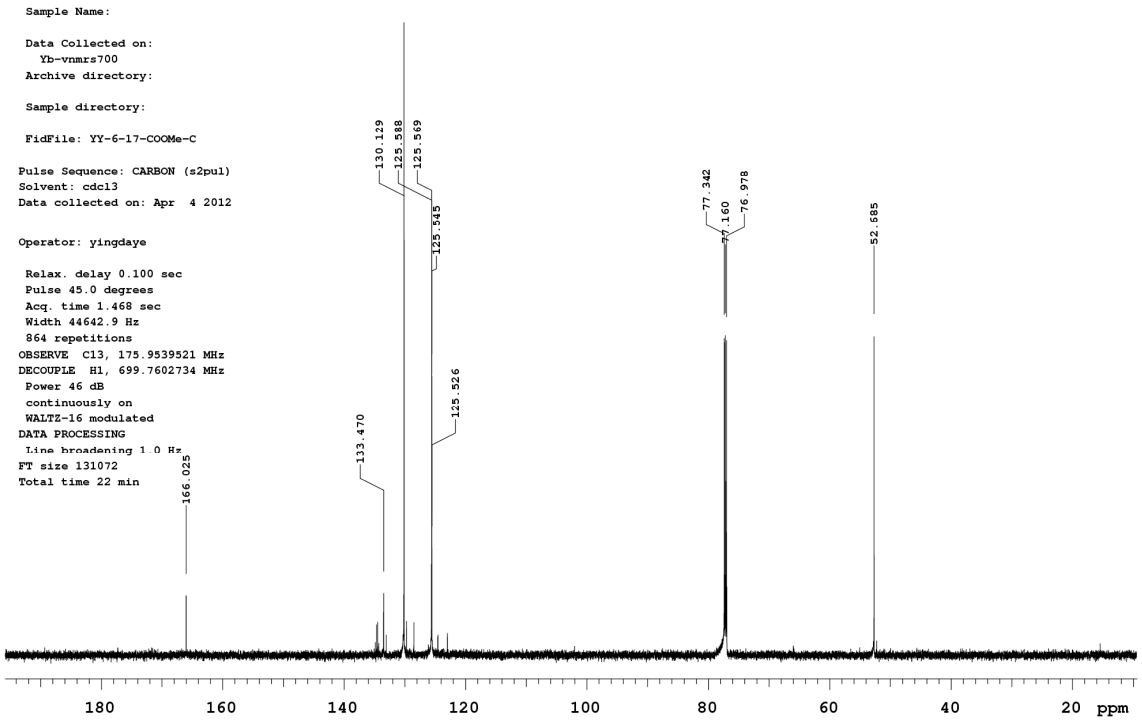


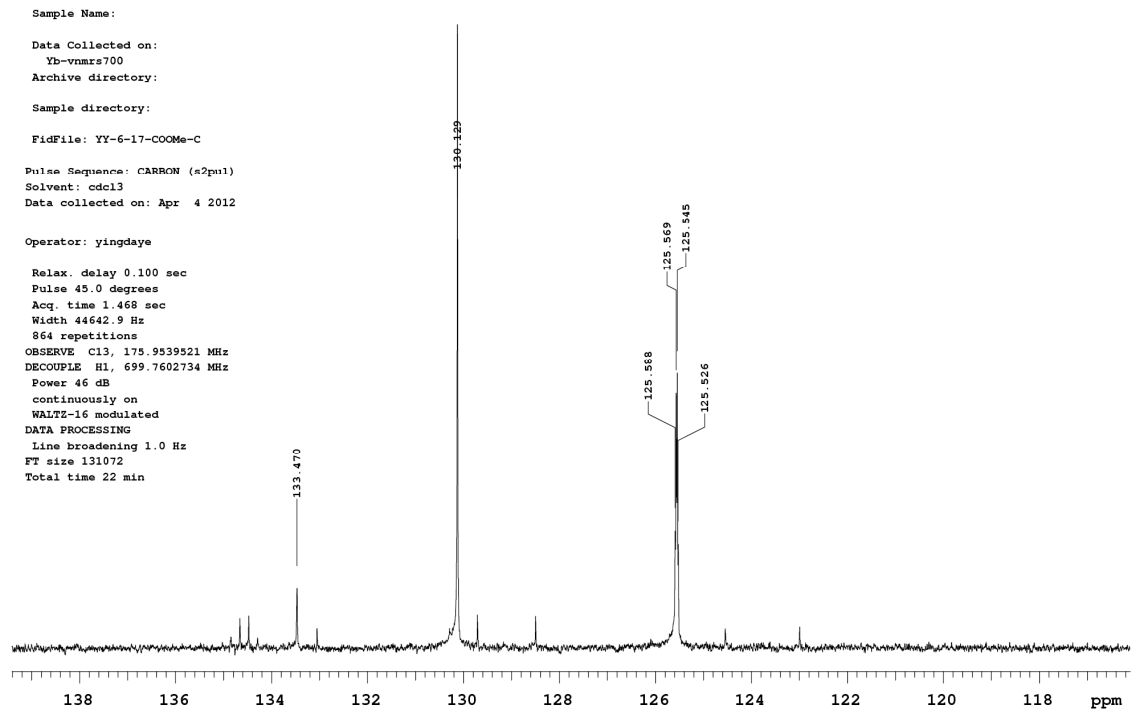


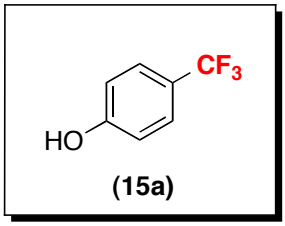
^{19}F NMR


Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-6-17-COOMe-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 2 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.603 sec
Width 108.7 kHz
16 repetitions
OBSERVE F19, 470.5577223 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 0 min 29 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR

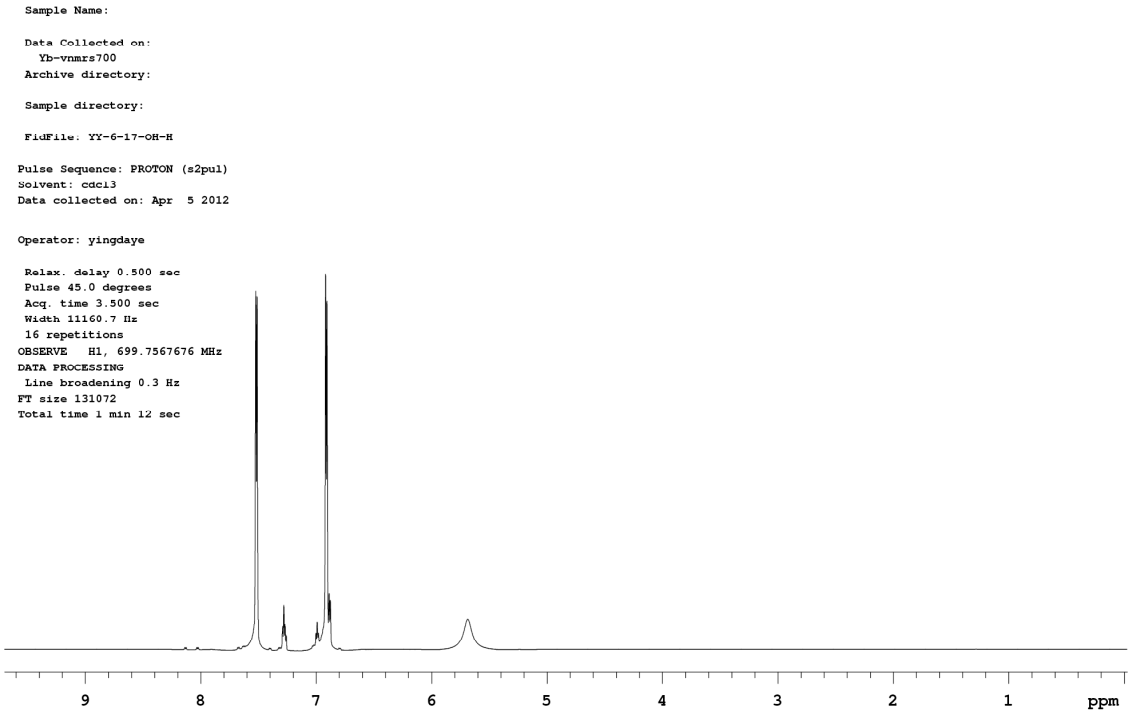

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-COOMe-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
864 repetitions
OBSERVE C13, 175.9539521 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 22 min
166.025
133.470
130.129
125.588
125.569
125.545
125.526
77.342
77.160
76.978
52.685
180
160
140
120
100
80
60
40
20
ppm

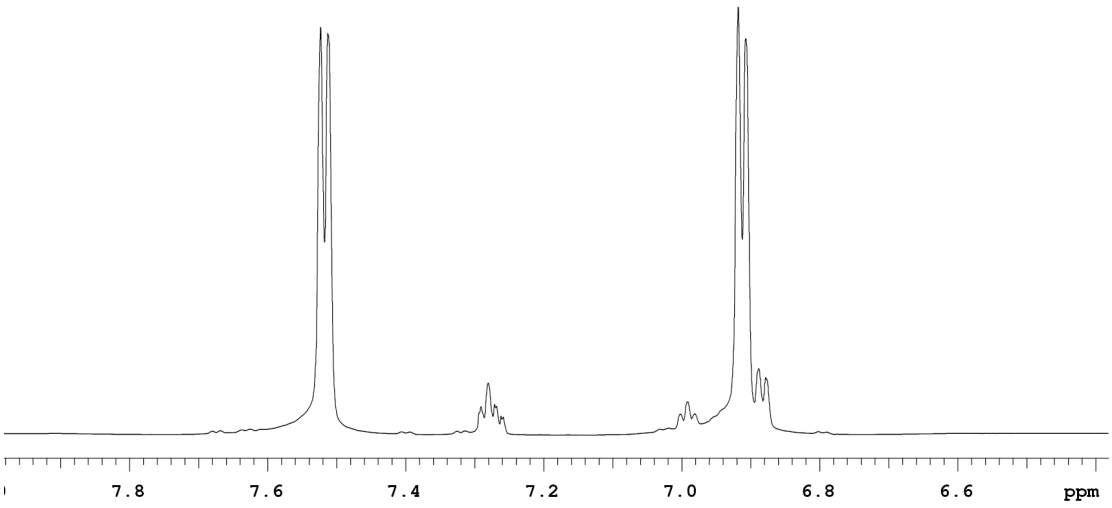

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-COOMe-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
864 repetitions
OBSERVE C13, 175.9539521 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 22 min
133.470
130.129
125.569
125.545
125.568
125.526
138
136
134
132
130
128
126
124
122
120
118
ppm


CF3
HO

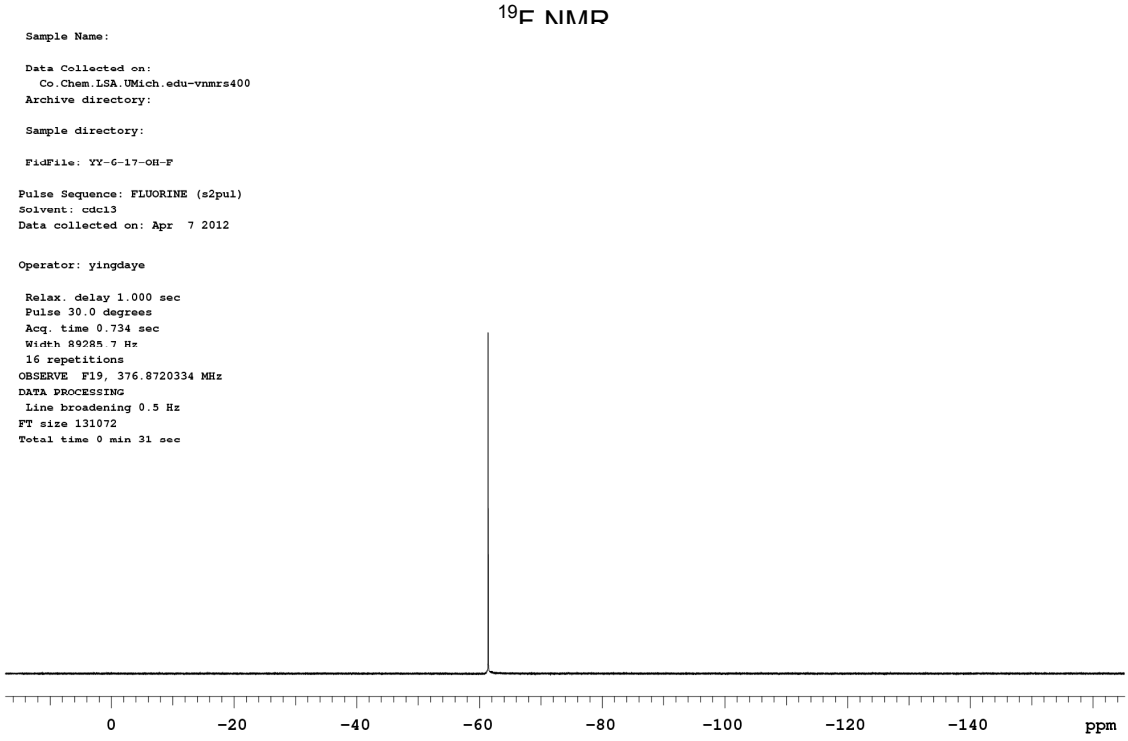
(15a)

^{1}H NMR

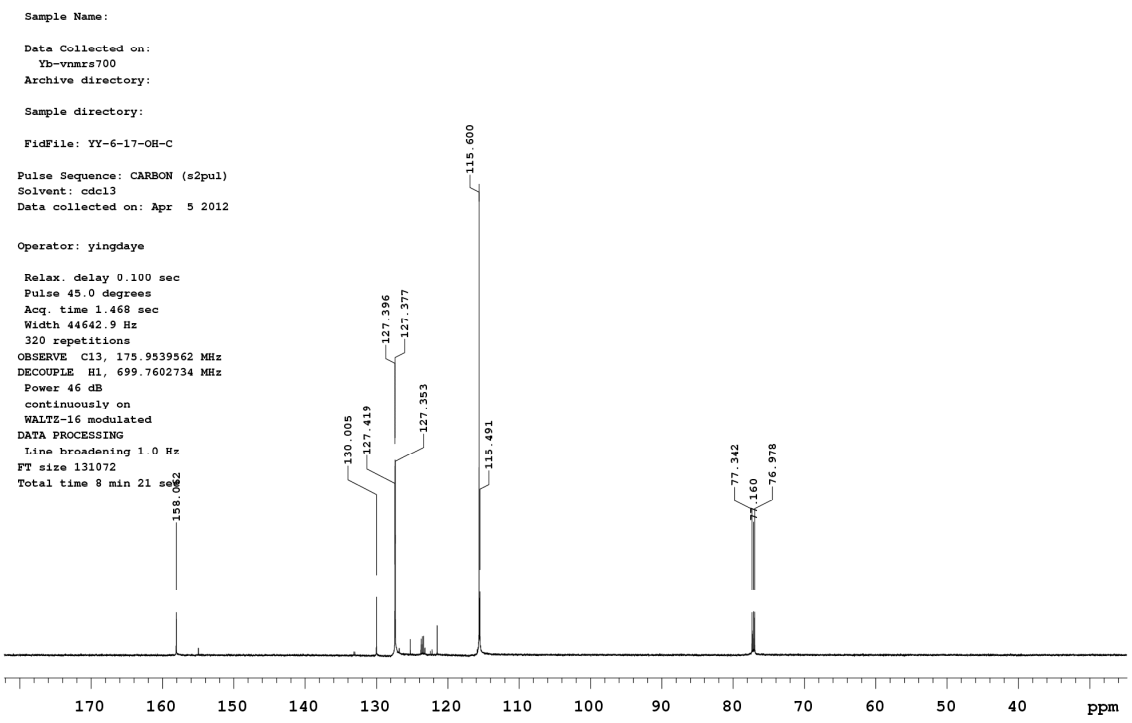

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-OH-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11160.7 Hz
16 repetitions
OBSERVE H1, 699.7567676 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
9
8
7
6
5
4
3
2
1
ppm

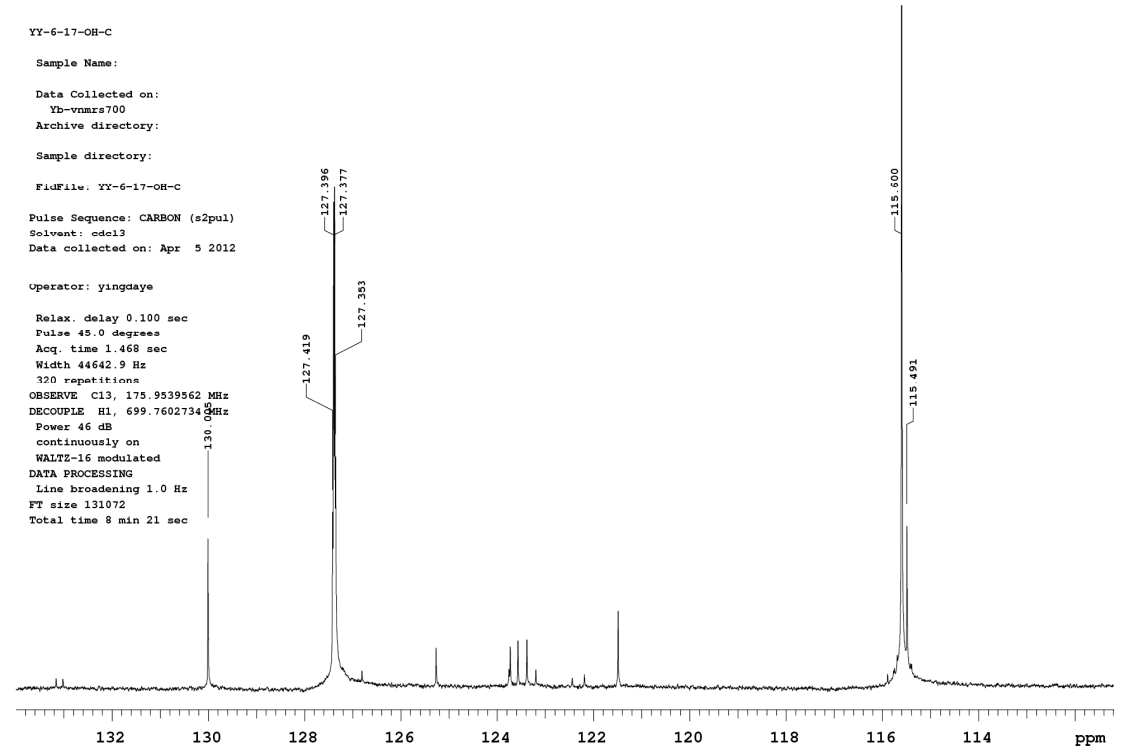

7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm

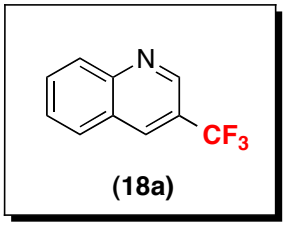
^{19}F NMR


Sample Name:
Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-G-17-OH-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 7 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8720334 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
0
-20
-40
-60
-80
-100
-120
-140
ppm

^{13}C NMR

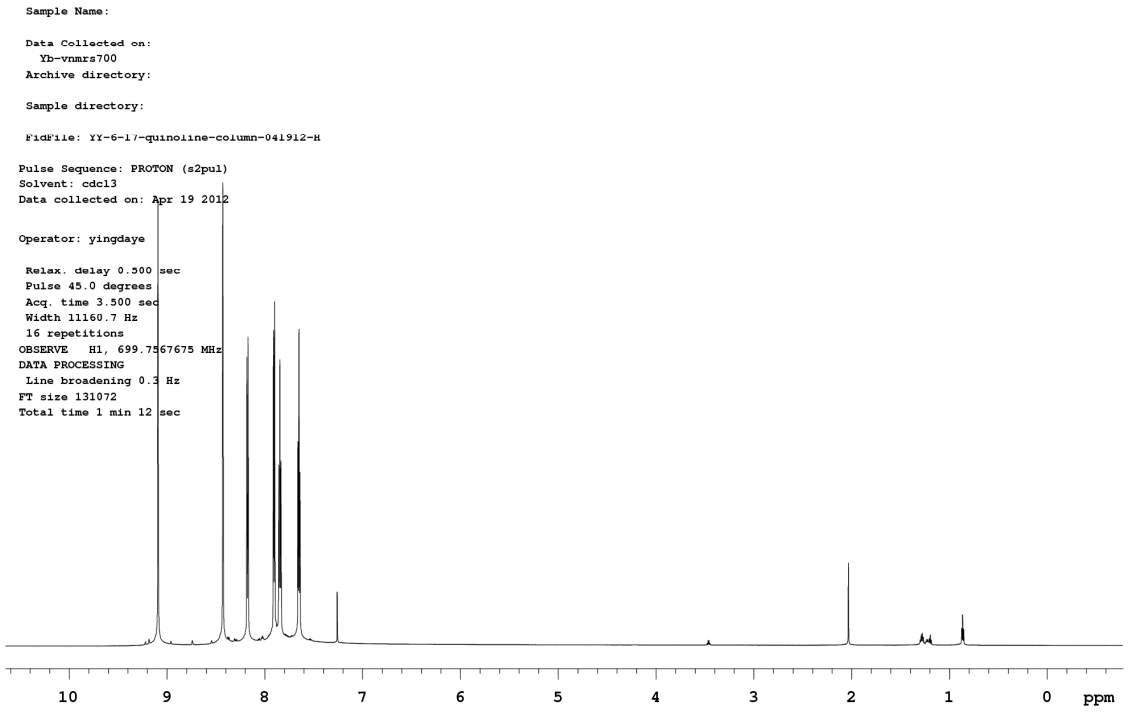

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-OH-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
320 repetitions
OBSERVE C13, 175.9539562 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 8 min 21 sec
158.062
130.005
127.419
127.396
127.377
127.353
115.600
115.491
77.342
77.160
76.978
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

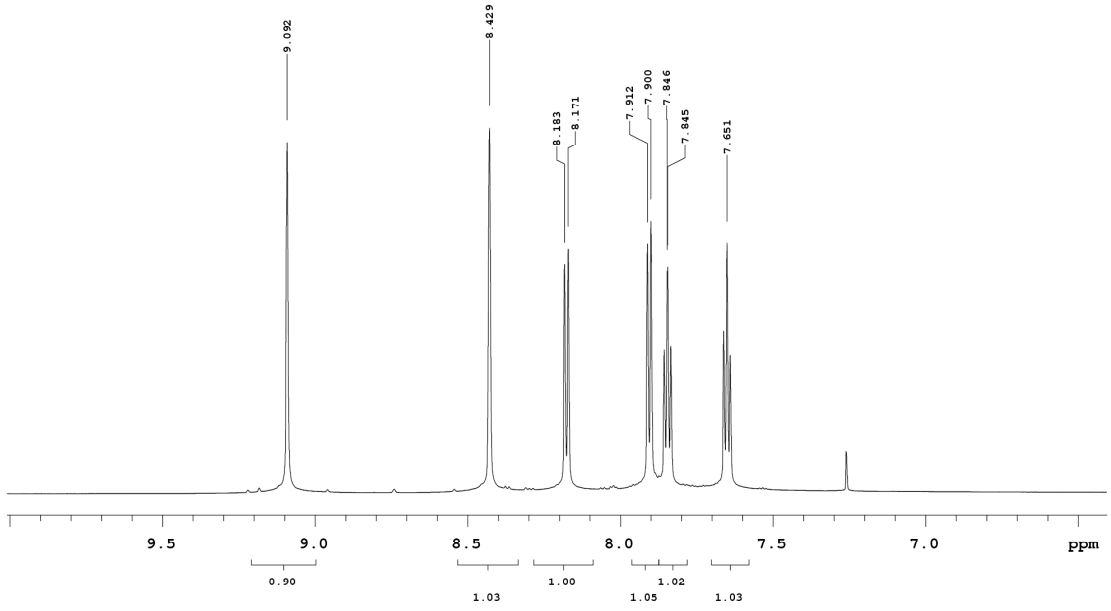

YY-6-17-OH-C
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-OH-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
320 repetitions
OBSERVE C13, 175.9539562 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 8 min 21 sec
130.005
127.419
127.396
127.377
127.353
115.600
115.491
132
130
128
126
124
122
120
118
116
114
ppm


N
CF3

(18a)

^{1}H NMR


Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-quinoline-column-041912-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 19 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 11160.7 Hz
16 repetitions
OBSERVE H1, 699.7567675 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min 12 sec
10
9
8
7
6
5
4
3
2
1
0
ppm


9.092
8.429
8.183
8.171
7.912
7.900
7.846
7.845
7.651
9.5
9.0
8.5
8.0
7.5
7.0
ppm
0.90
1.03
1.00
1.05
1.02
1.03

^{19}F NMR

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

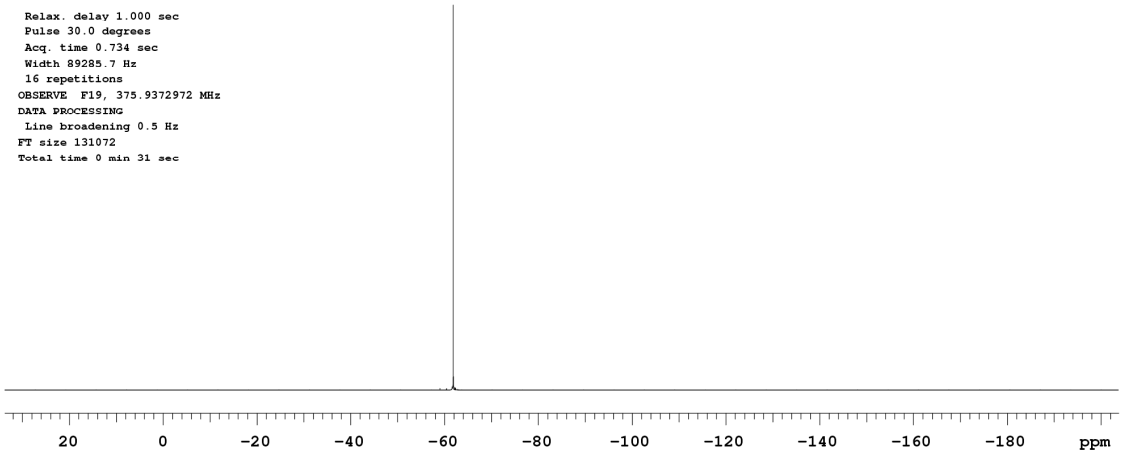
Sample directory:

FidFile: YY-6-17-quinoline-F

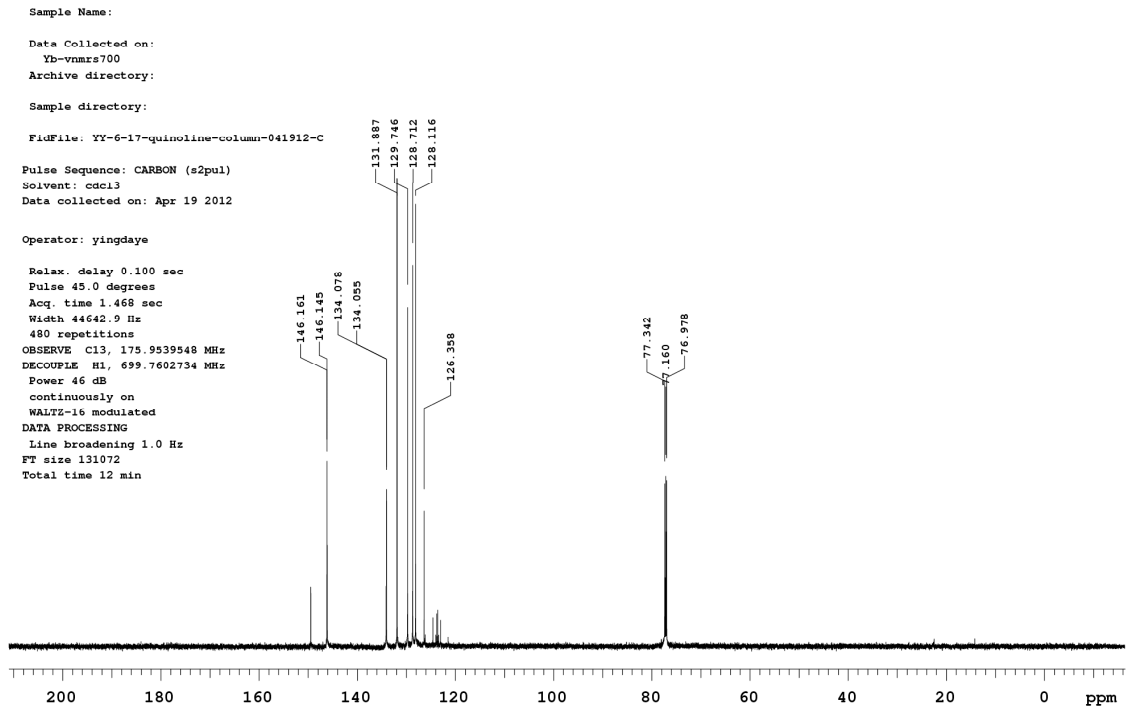
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2012

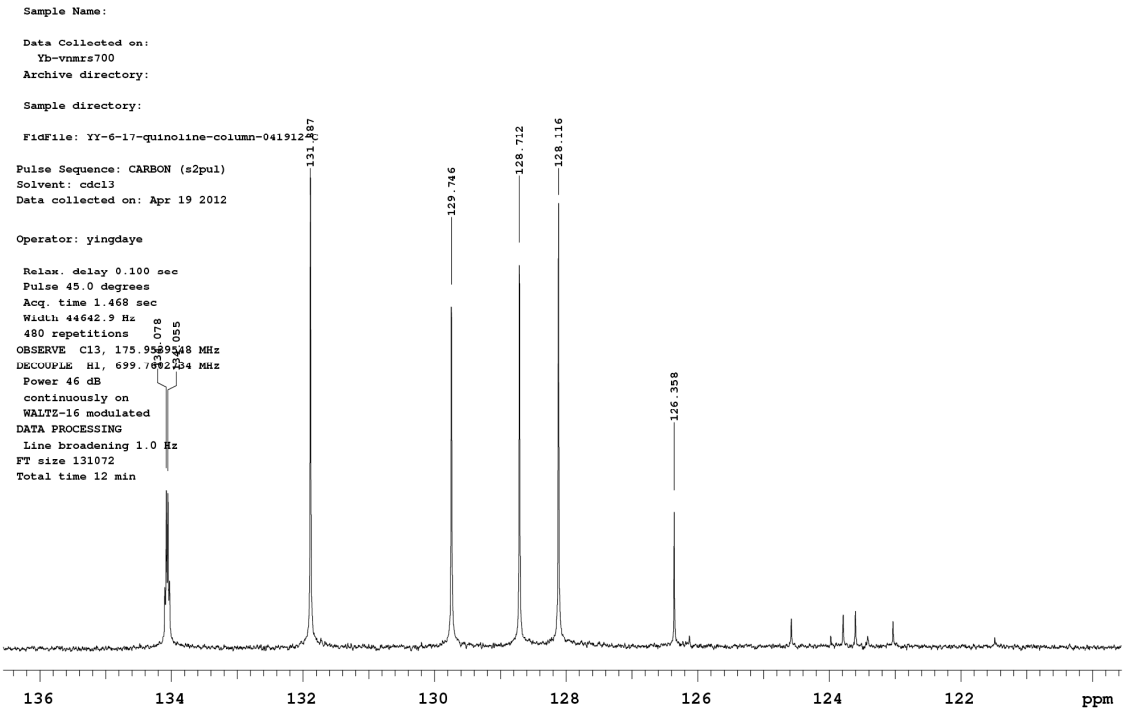
Operator: yingdaye

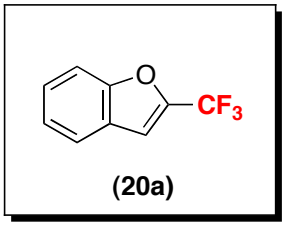
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 375.9372972 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec



^{13}C NMR

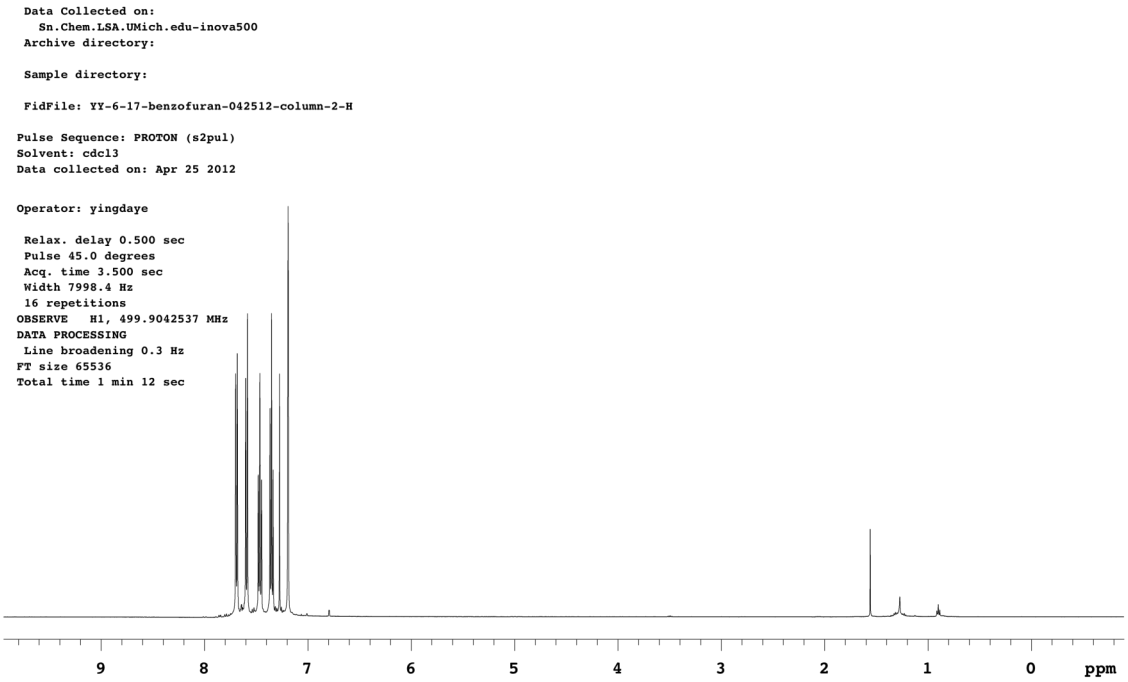

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-quinoline-column-041912-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 19 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
480 repetitions
OBSERVE C13, 175.9539548 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min
131.887
129.746
128.712
128.116
146.161
146.145
134.078
134.055
126.358
77.342
77.160
76.978
200
180
160
140
120
100
80
60
40
20
0
ppm

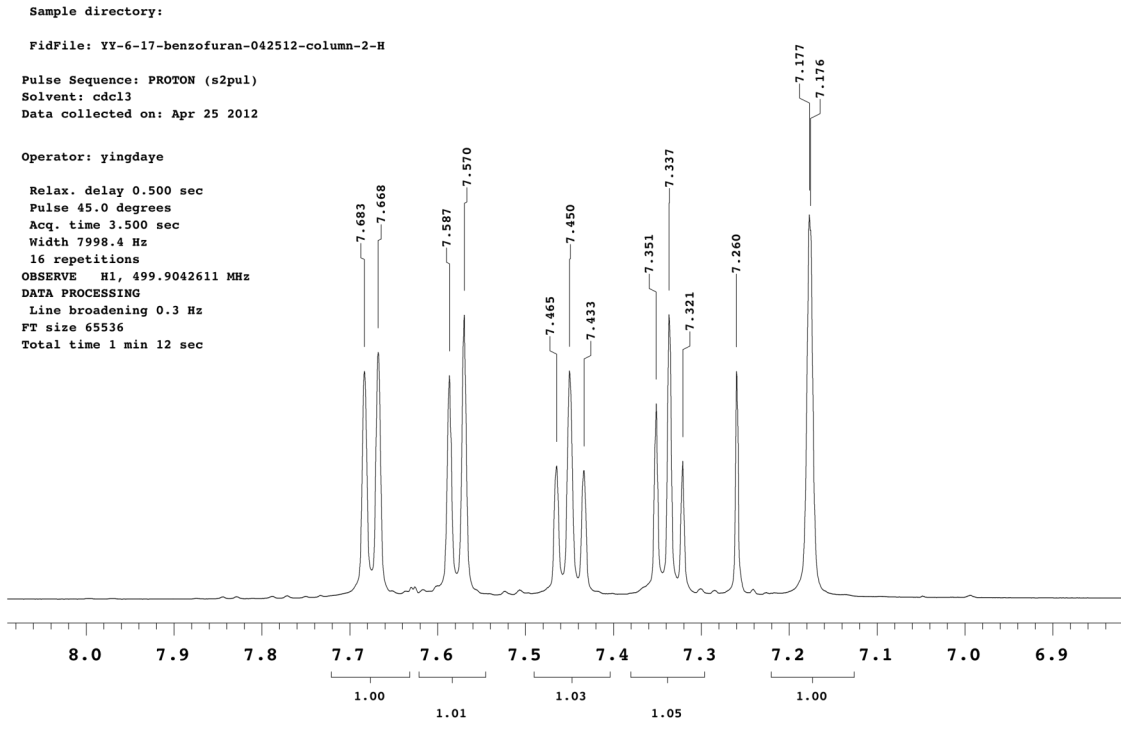

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-quinoline-column-041912-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 19 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
480 repetitions
OBSERVE C13, 175.9539548 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min
131.887
129.746
128.712
128.116
134.078
134.055
126.358
136
134
132
130
128
126
124
122
ppm


O
CF3

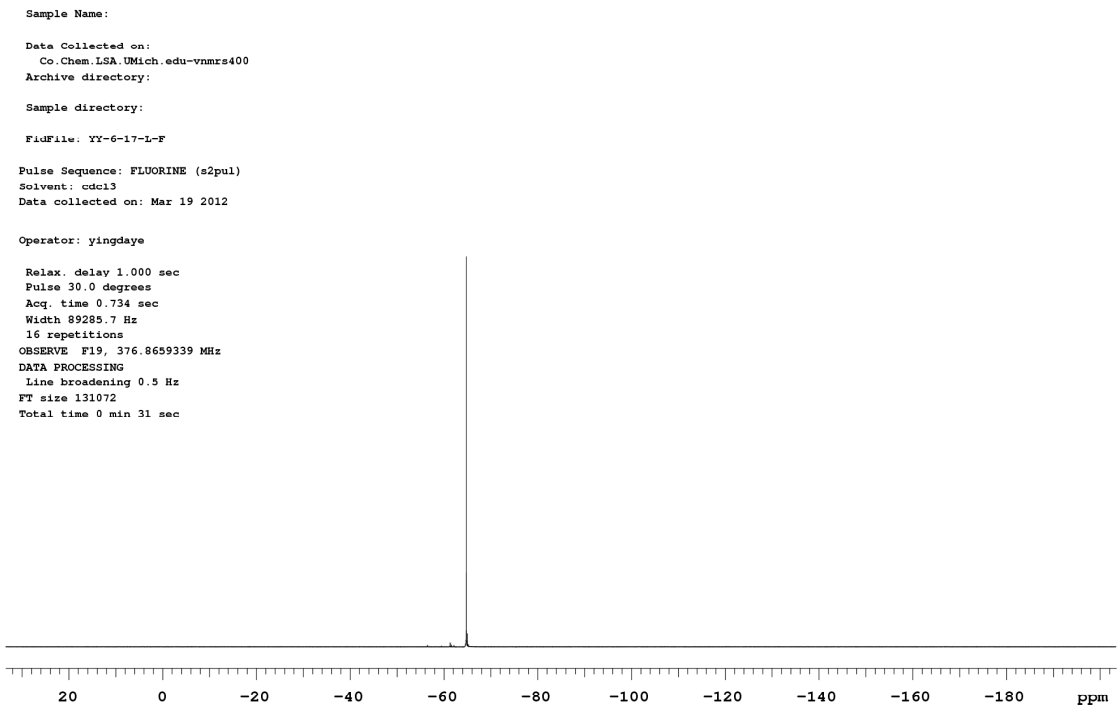
(20a)

^{1}H NMR

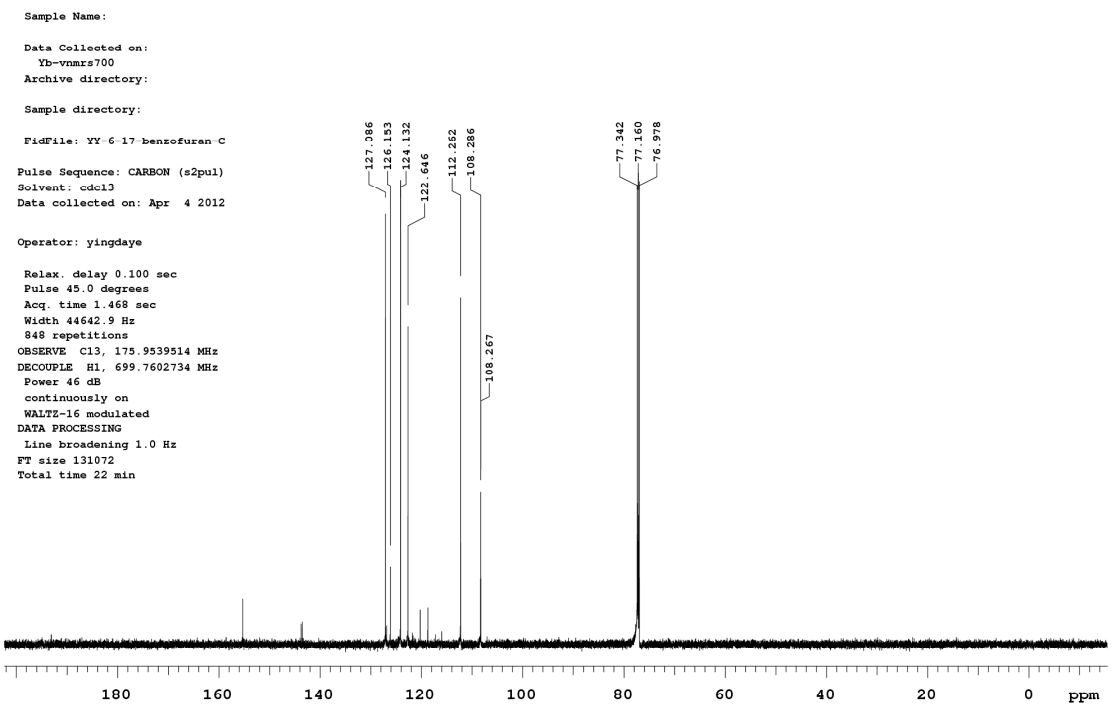

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: YY-6-17-benzofuran-042512-column-2-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 25 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9042537 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
9
8
7
6
5
4
3
2
1
0
ppm

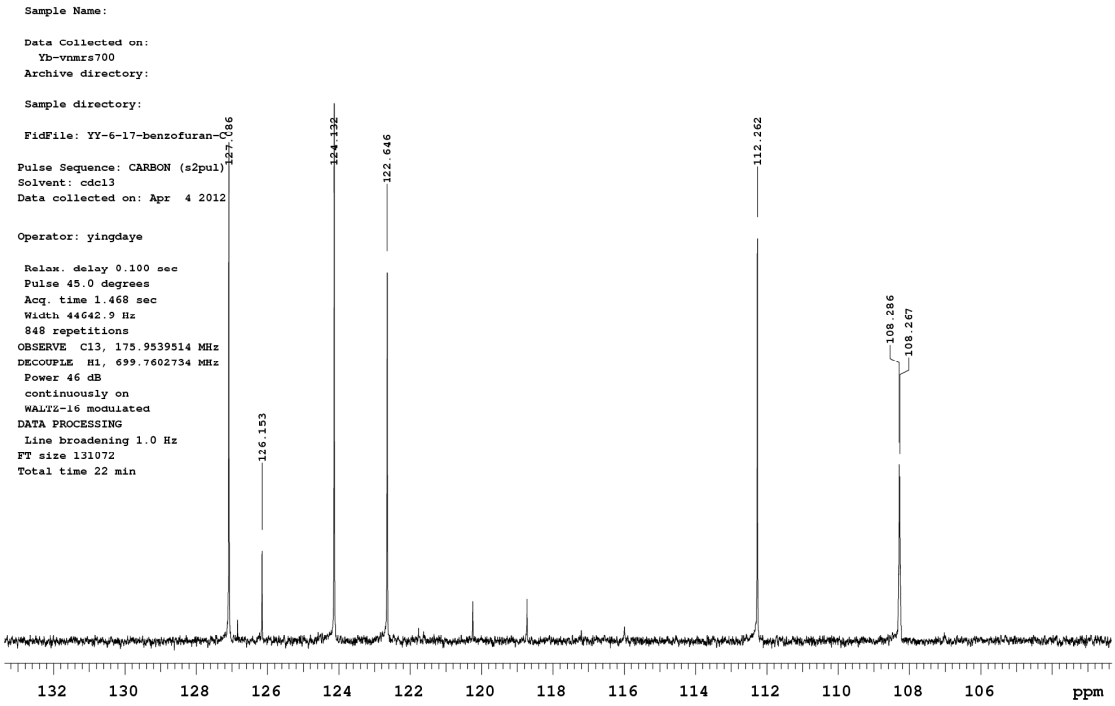

Sample directory:
FidFile: YY-6-17-benzofuran-042512-column-2-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 25 2012
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9042611 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
7.683
7.668
7.587
7.570
7.465
7.450
7.433
7.351
7.337
7.321
7.260
7.177
7.176
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
1.00
1.01
1.03
1.05
1.00

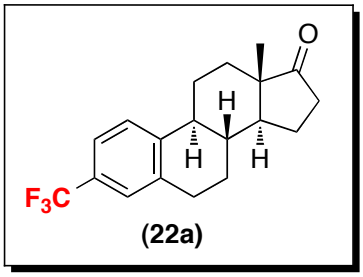
^{19}F NMR


Sample Name:
Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: YY-6-17-L-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Mar 19 2012
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
16 repetitions
OBSERVE F19, 376.8659339 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR

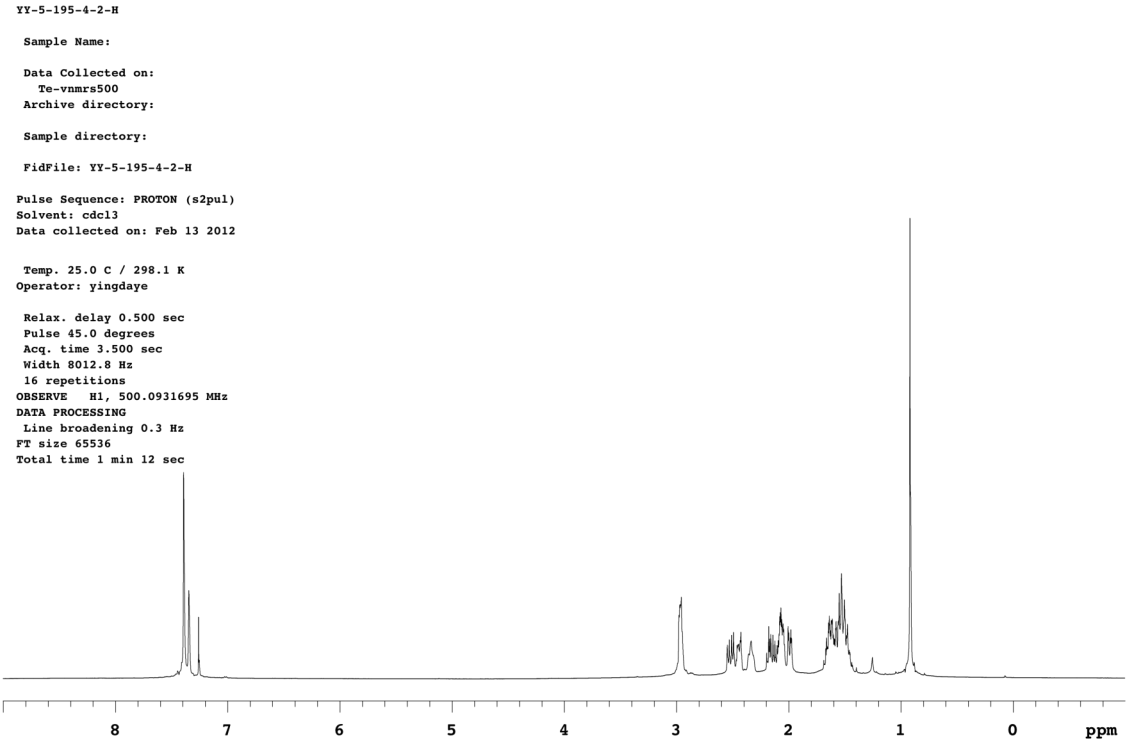

Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-benzofuran-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
848 repetitions
OBSERVE C13, 175.9539514 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 22 min
127.086
126.153
124.132
122.646
112.262
108.286
108.267
77.342
77.160
76.978
180
160
140
120
100
80
60
40
20
0
ppm


Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
FidFile: YY-6-17-benzofuran-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2012
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.468 sec
Width 44642.9 Hz
848 repetitions
OBSERVE C13, 175.9539514 MHz
DECOUPLE H1, 699.7602734 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 22 min
127.086
126.153
124.132
122.646
112.262
108.286
108.267
132
130
128
126
124
122
120
118
116
114
112
110
108
106
ppm

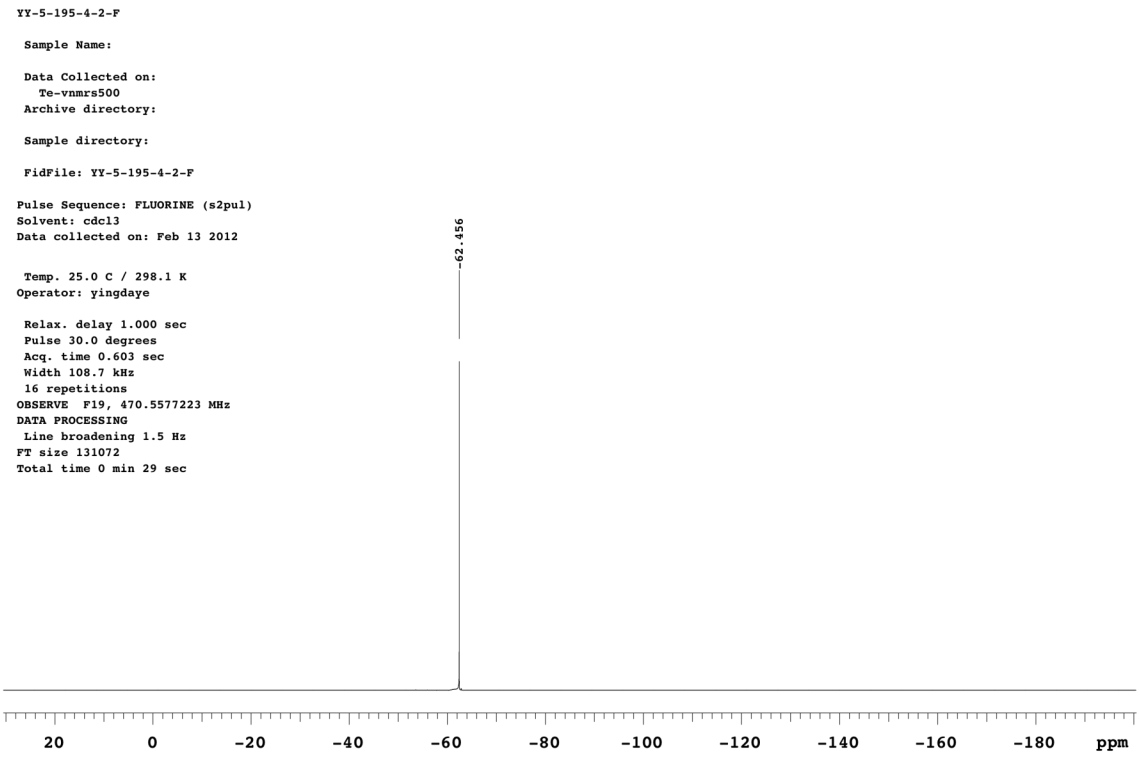

O
H
H
H
F3C

(22a)

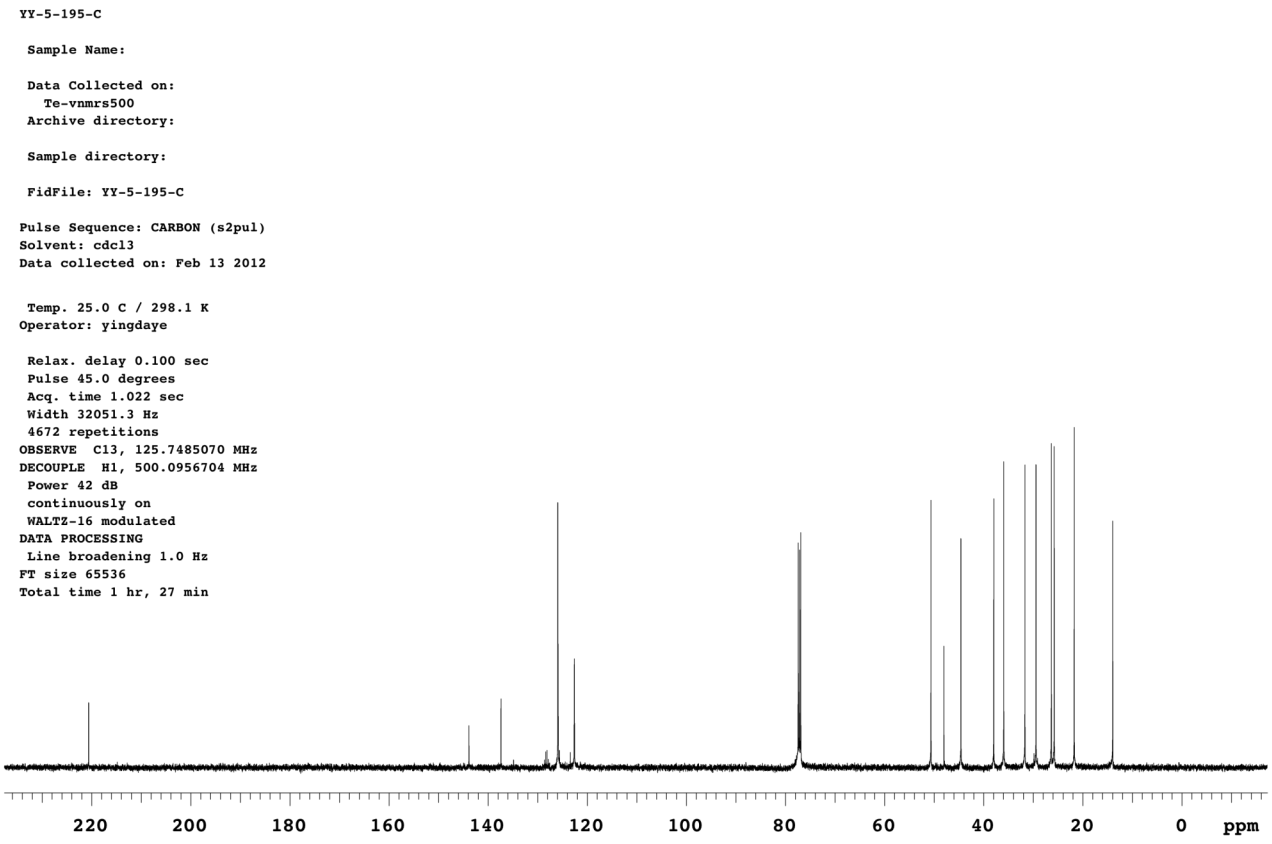
^{1}H NMR

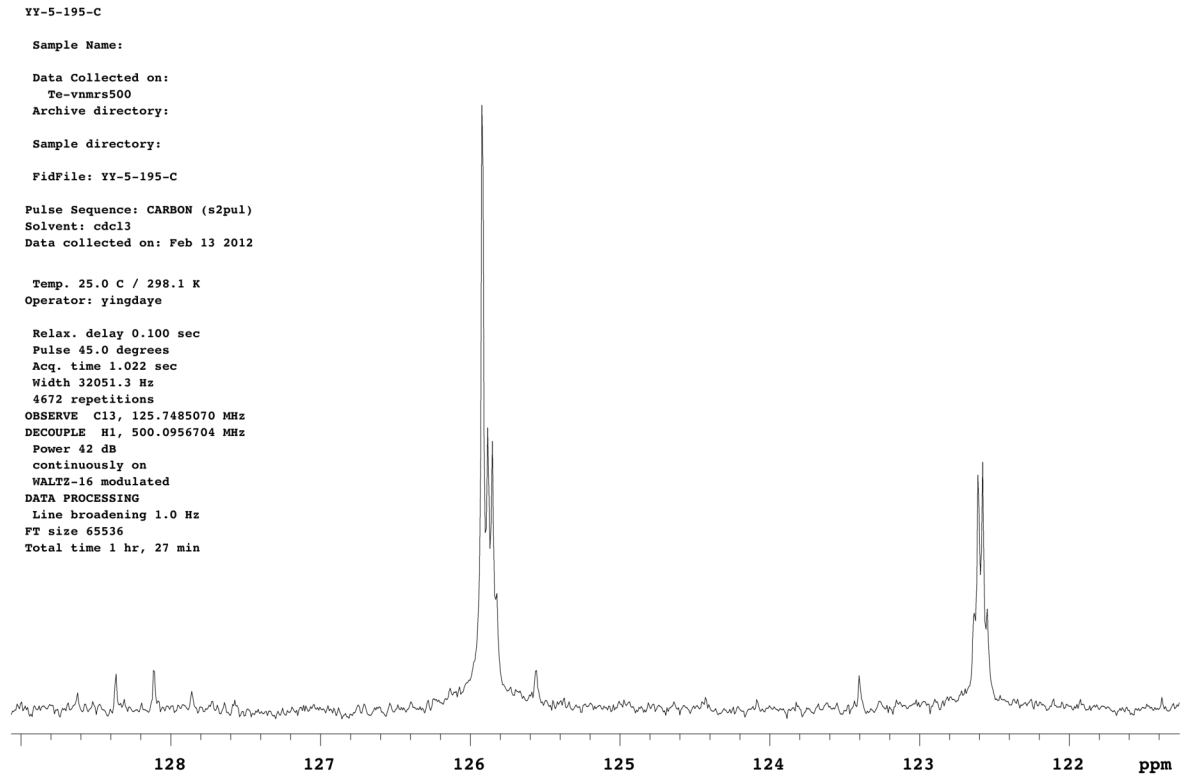

YY-5-195-4-2-H
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-195-4-2-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 13 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931695 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
8
7
6
5
4
3
2
1
0
ppm

^{19}F NMR


YY-5-195-4-2-F
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-195-4-2-F
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Feb 13 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.603 sec
Width 108.7 kHz
16 repetitions
OBSERVE F19, 470.5577223 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 0 min 29 sec
-62.456
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{13}C NMR


YY-5-195-C
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-195-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 13 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
4672 repetitions
OBSERVE C13, 125.7485070 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 27 min
220
200
180
160
140
120
100
80
60
40
20
0
ppm


YY-5-195-C
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: YY-5-195-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 13 2012
Temp. 25.0 C / 298.1 K
Operator: yingdaye
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
4672 repetitions
OBSERVE C13, 125.7485070 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 27 min
128
127
126
125
124
123
122
ppm

References

(1) Nagib, D. A.; MacMillan, D. W. C. *Nature* **2011**, *480*, 224.
(2) Ji, Y.; Brueckl, T.; Baxter, R. D.; Fujiwara, Y.; Seiple, I. B.; Su, S.; Blackmond, D. G.; Baran, P. S. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 14411.
(3) Xu, J.; Luo, D. F.; Xiao, B.; Liu, J.; Gong, T. J.; Fu, Y.; Liu, L. *Chem. Commun.* **2011**, *47*, 4300.
(4) Chu, L.; Qing, F. L. *Org. Lett.* **2010**, *12*, 5060.
(5) (a) Stavber, S.; Zupan, M. *J. Org. Chem.* **1983**, *48*, 2223. (b)Li, Y.; Chen, T.; Wang, H.; Zhang, R.; Jin, K.; Wang, X.; Duan, C. *Synlett* **2011**, *12*, 1713.
(6) Zhang, C.-P.; Cai, J.; Zhou, C.-B.; Wang, X.-P.; Zheng, X.; Gu, Y.-C.; Xiao, J.-C. *Chem. Commun.* **2011**, *47*, 9516.
(7) Morimoto, H.; Tsubogo, T.; Litvinas, N. D.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 3793.
(8) Naumann, D.; Kischkewitz, J. *J. Fluorine Chem.* **1990**, *46*, 265.
(9) Knauber, T.; Arikan, F.; Röschenthaler, G.-V.; Gooßen, L. J. *Chem. Eur. J.* **2011**, *17*, 2689.
(10) Furuya, T.; Strom, A. E.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 1662.
(11) Ahmed, V.; Liu, Y.; Silvestro, C.; Taylor, S. D. *Bioorg. Med. Chem.* **2006**, *14*, 8564.
(12) Campagna, S.; Puntoriero, F.; Nastasi, F.; Bergamini, G.; Balzani, V. *Top. Curr. Chem.* **2007**, *280*, 117.
(13) *Inorganic Chemistry, 3rd ed.;* Housecroft, C. E.; Sharpe, A. G.; Pearson Education: Harlow, England, 2008.
(14) (a) Andrieux, C. P.; Gelis, L.; Médebielle, M.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 3509. (b) Bonesi, S. M; Erra-Balsells, R. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1583.