

Protolytic defluorination of trifluoromethyl-substituted arenes.

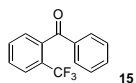
Anila Kethe, Adam F. Tracy, and Douglas A. Klumpp*

Department of Chemistry and Biochemistry
Northern Illinois University, DeKalb, IL 60115

Supporting Information:

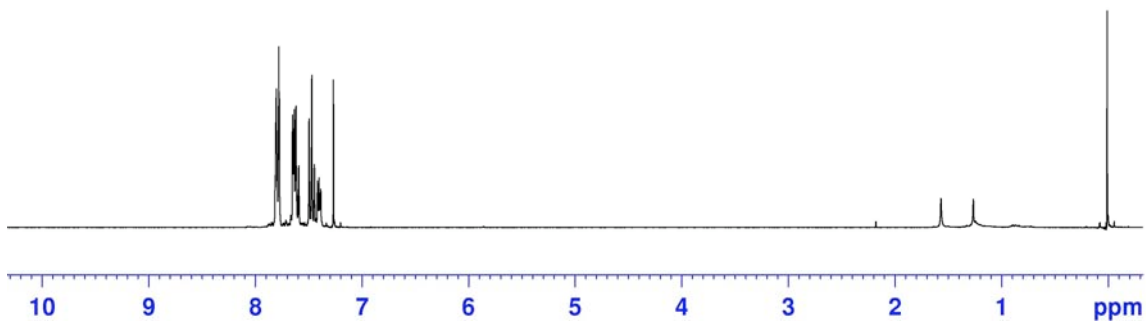
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Literature citations and NMR spectra for isolated known compounds:	Pages 2-14
Chromatograms of inseparable mixtures:	Pages 13-15
NMR spectra of new compounds:	Pages 16-21

Known compounds

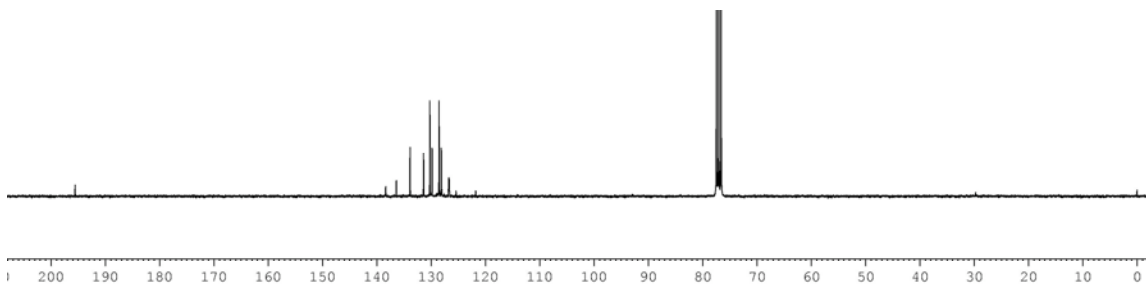


Gao, H.; Knochel, P. *Synlett*. **2009**, 8, 1321-1325.

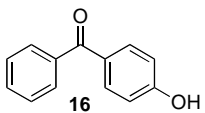
¹H NMR:



¹³C NMR:

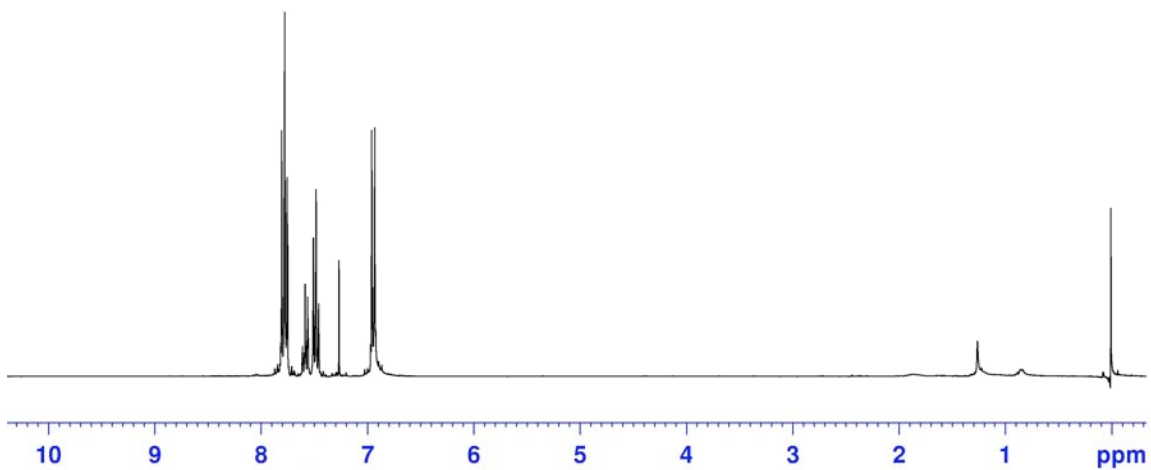


Low Resolution, EI MS: 250 (M⁺), 173, 145, 105, 77

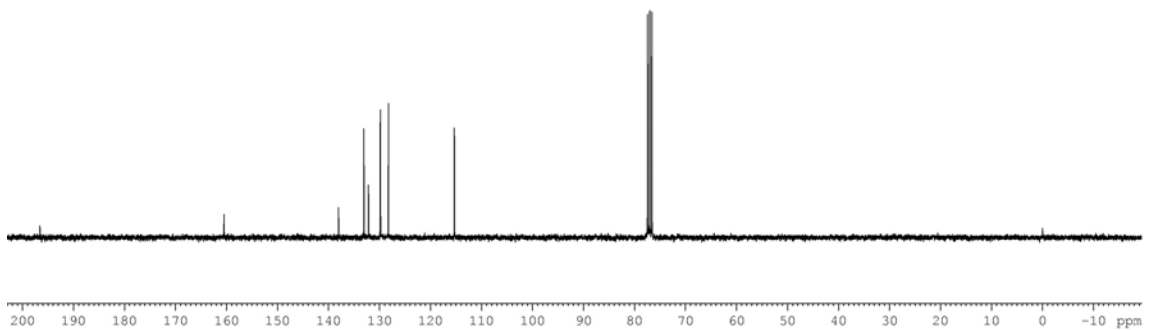


Olah, George A.; Arvanaghi, Massoud; Krishnamurthy, V. V. *J. Org. Chem.* **1983**, *48*, 3359.

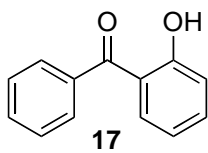
^1H NMR:



^{13}C NMR:

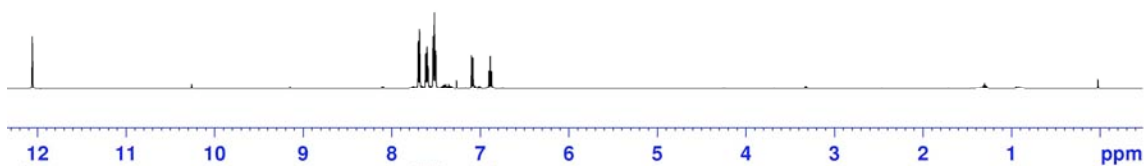


Low Resolution, EI MS: 198 (M^+), 121, 105, 77

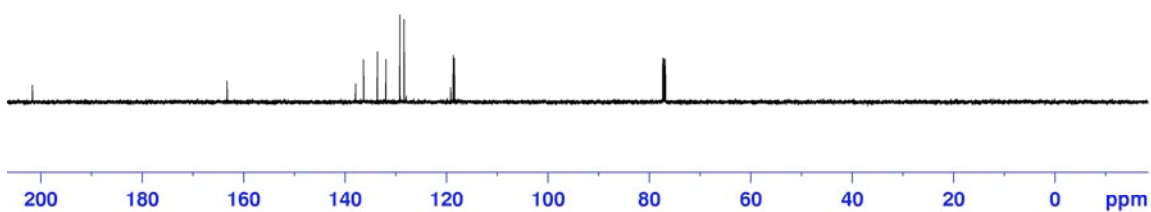


Weng, Fei; Wang, Chengming; Xu, Bin *Tetrahedron Lett.* **2010**, *51*, 2593.

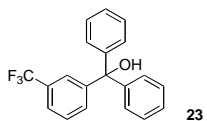
^1H NMR:



^{13}C NMR:

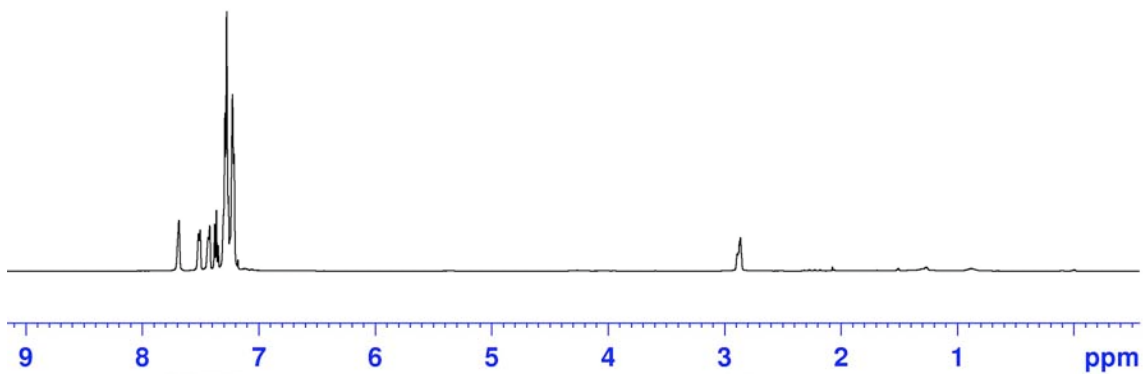


Low Resolution, EI MS: 198 (M^+), 121, 105, 77

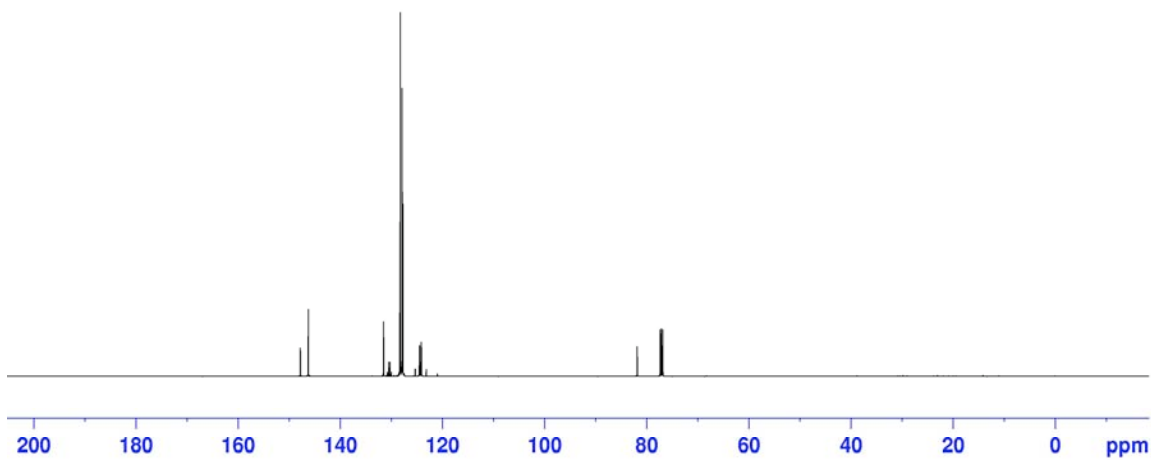


Benkeser, R. A.; Schroeder, W. *J. Am. Chem. Soc.* **1958**, *80*, 3314-22.

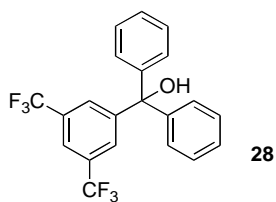
^1H NMR:



^{13}C NMR:

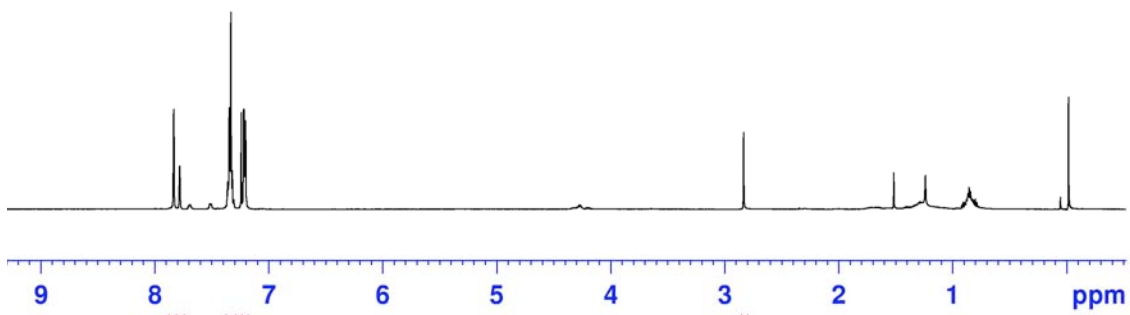


Low Resolution, EI MS: 328 (M^+), 312, 251, 173, 105, 77

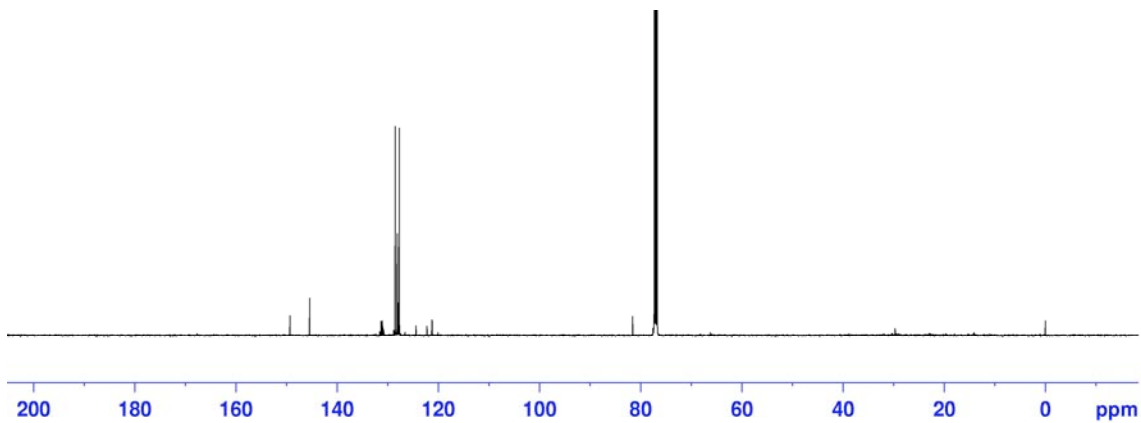


Porwisiak, Jacek.; Schlosser, Manfred. *Chem. Ber.* **1996**, *129*, 2, 233-235

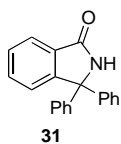
^1H NMR



^{13}C NMR

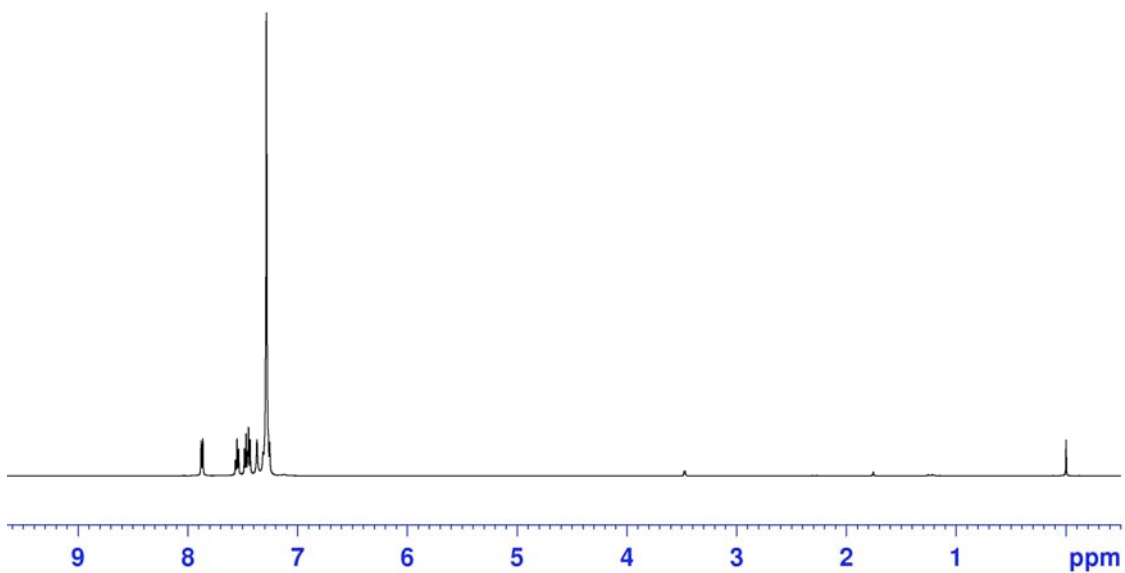


Low Resolution, EI MS: 396 (M^+), 377, 319, 241, 213, 183, 105, 77.

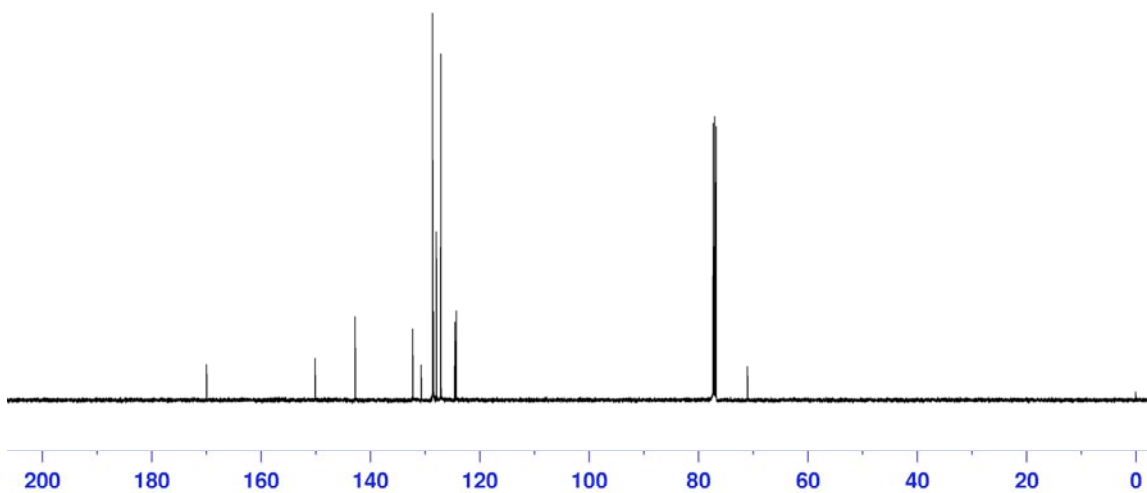


Koltunov, K. Yu.; Prakash, G. K. S.; Rasul, G.; Olah, G. A. *Eur. J. Org. Chem.*, **2006**, 4861-4866.

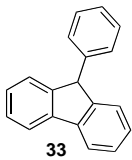
^1H NMR



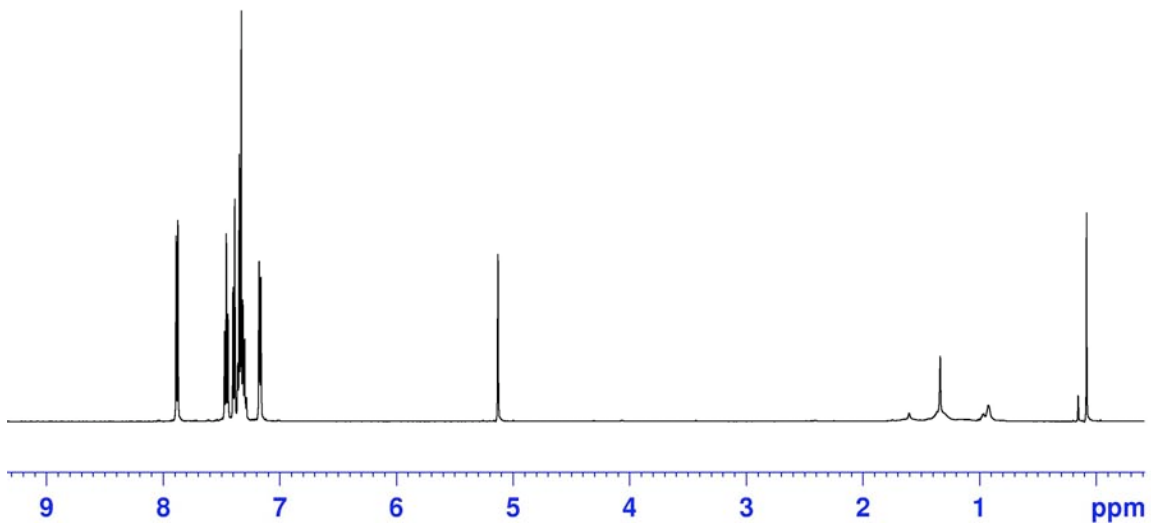
^{13}C NMR



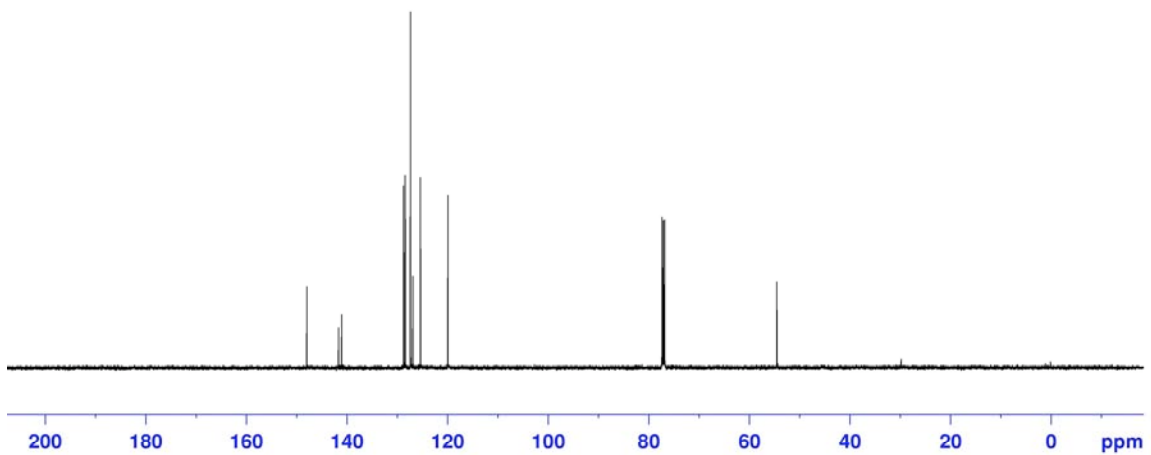
Low Resolution, EI MS: 285 (M^+), 208, 130, 102, 77.



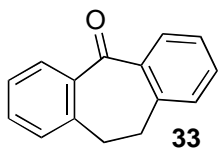
^1H NMR



^{13}C NMR

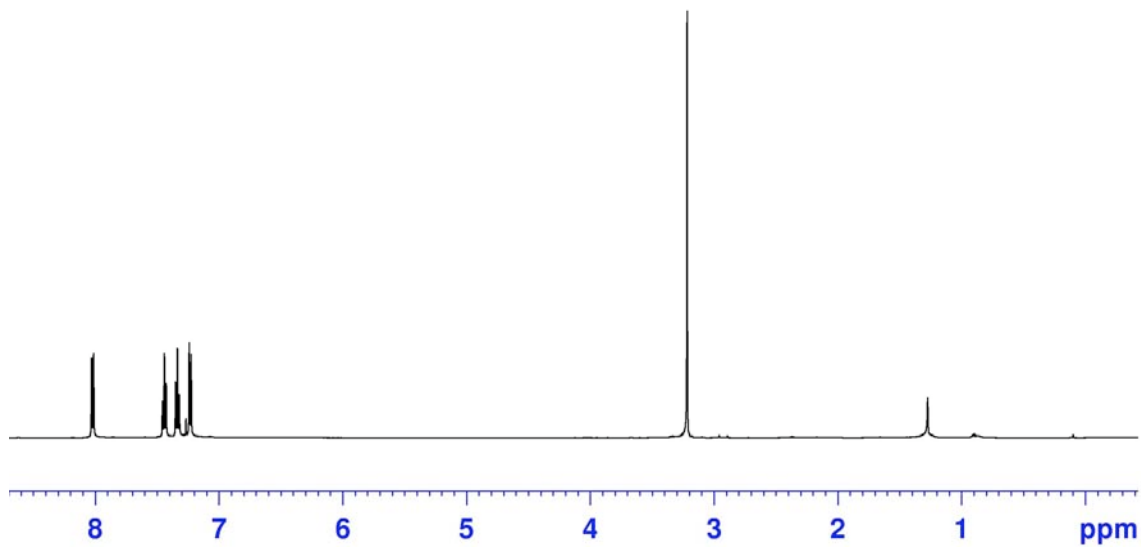


Low Resolution, EI MS: 242 (M^+), 241, 165, 119.

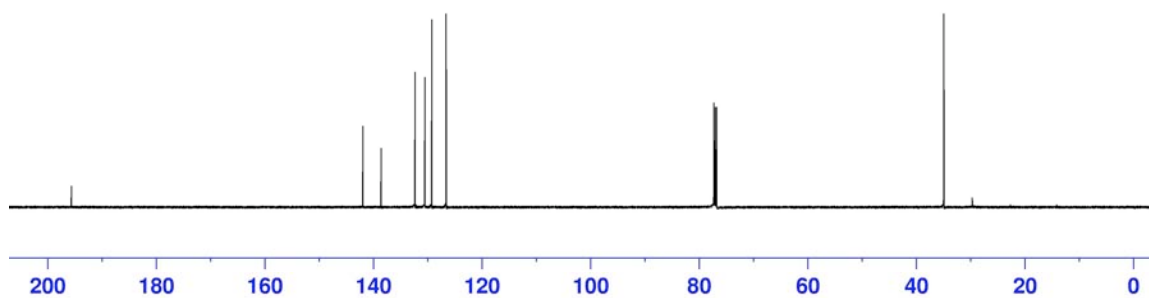


Guram, Anil S.; Bei, Xiaohong; Turner, Howard W. *Org. Lett.* **2003**, *5*, 2485.

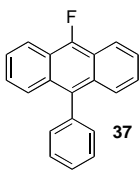
^1H NMR



^{13}C NMR

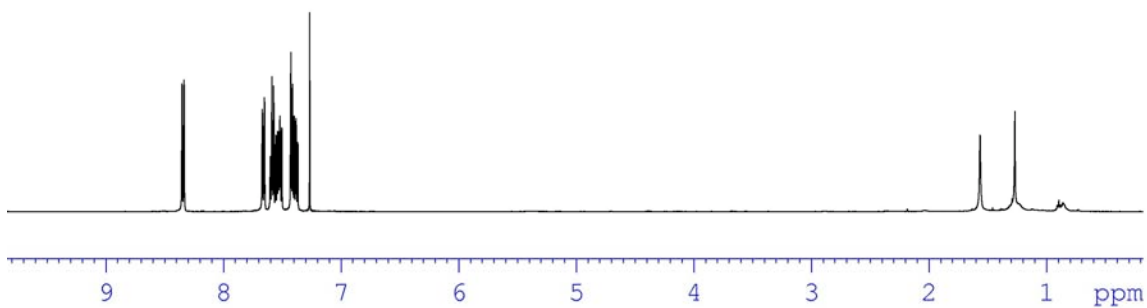


Low Resolution, EI MS: 208 (M^+), 180, 179, 178, 152, 89.

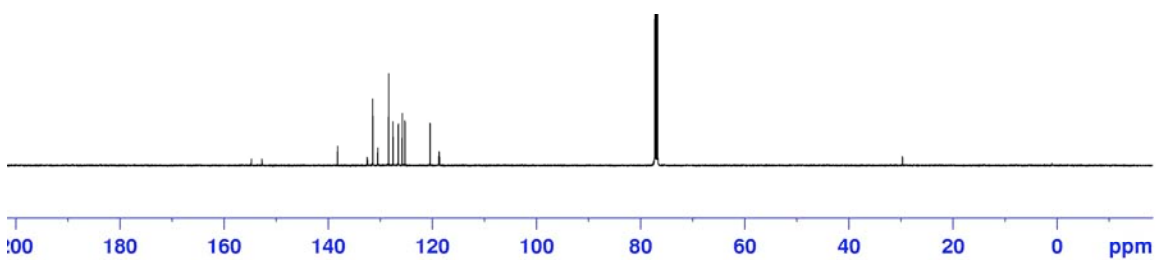


Norrzell, F.; Handoo, K. L.; Parker, V. D. *J. Org. Chem.* **1993**, *58*, 4929

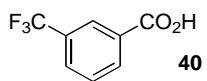
^1H NMR



^{13}C NMR

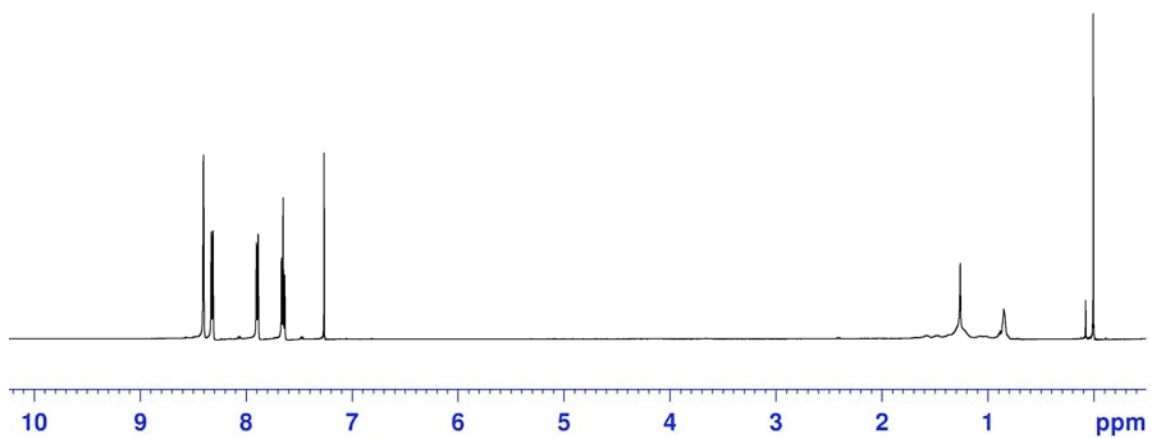


Low Resolution, EI MS: 272 (M^+), 271, 270, 252, 135.

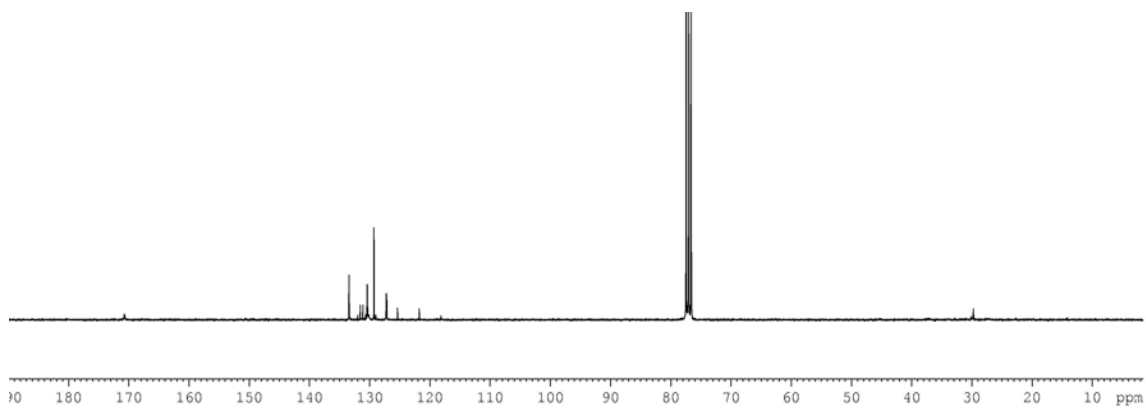


Soloski, Edward J.; Tamborski, Christ *Journal of Organometallic Chemistry* **1978**, *157*, 373.

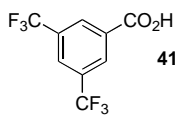
^1H NMR



^{13}C NMR

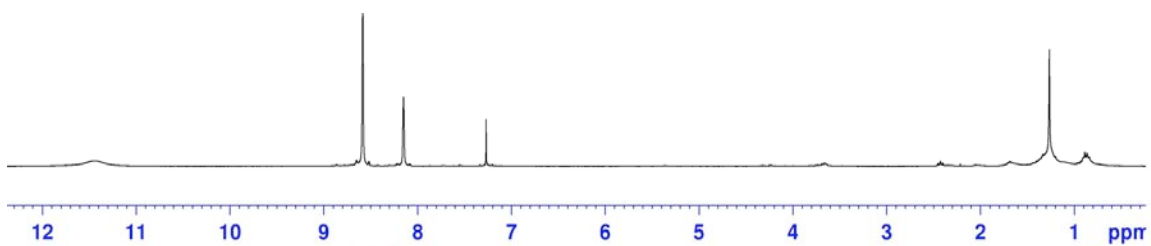


Low Resolution, EI MS: 190 (M⁺), 173, 145, 125, 95, 75.

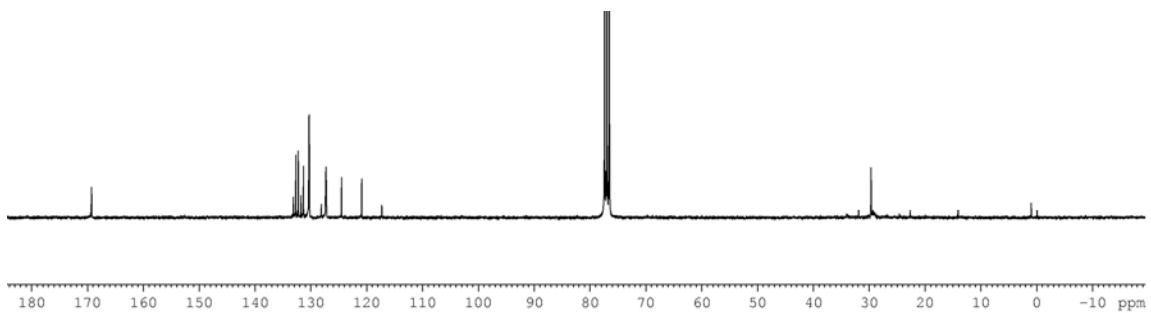


Leazer, Johnnie L., Jr.; Cvetovich, Raymond; Tsay, Fuh-Rong; Dolling, Ulf; Vickery, Thomas; Bachert, Donald *J. Org. Chem.* **2003**, *68*, 3695.

^1H NMR



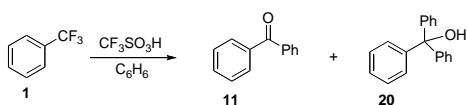
^{13}C NMR



Low Resolution, EI MS: 258 (M^+), 241, 213, 163, 143, 75.

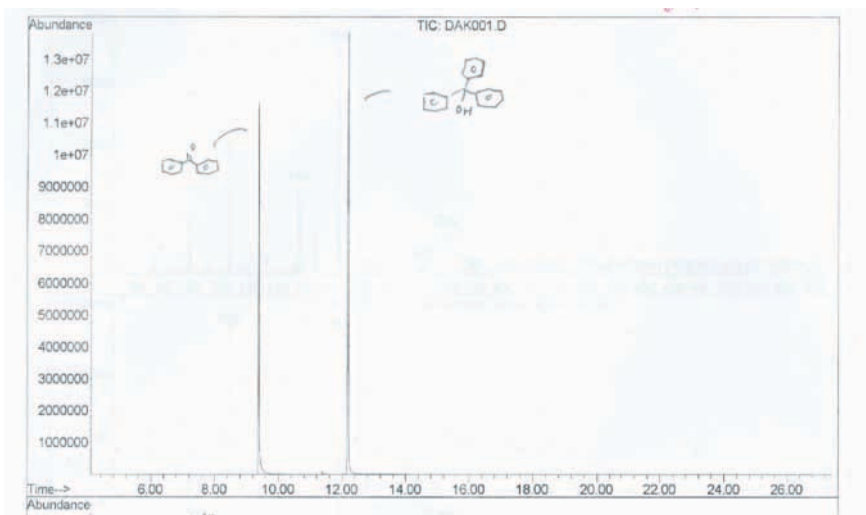
Method for calculating relative yields: A sample of biphenyl (0.1g) was mixed with genuine benzophenone (0.1 g) and dissolved in CHCl_3 (5 mL). This mixture was injected onto the GC-FID and a relative response factor was calculated for the standard biphenyl and benzophenone. A similar analysis was done with biphenyl and triphenylmethanol. Both benzophenone and triphenylmethanol had similar FID response factors to the standard (1.0 ± 0.05), so calculations of relative yields assumed relative response factors of 1.0 for the diaryl ketone products (**11-13**) and the triarylmethanol products (**20-22**). Follow the superacid catalyzed reactions, a sample of biphenyl (0.1g) was added to each crude product mixture. The mixtures were then analyzed by GC-FID and relative yields were calculated from peak integrations, including the peak area for the biphenyl standard.

Data on inseparable mixture from compound 1:



Crude mixture, GC-MS trace:

Peaks: 9.4 min, compound **11**; 12.2 min, compound **20**. Identities confirmed by NIST mass spectral database.



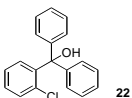
Compound **11**, low resolution EI MS: 182 (M^+), 105, 77, 51.

Compound **20**, low resolution EI MS: 260 (M^+), 183, 154, 105, 77, 51.

Data on inseparable mixture from compound 4:



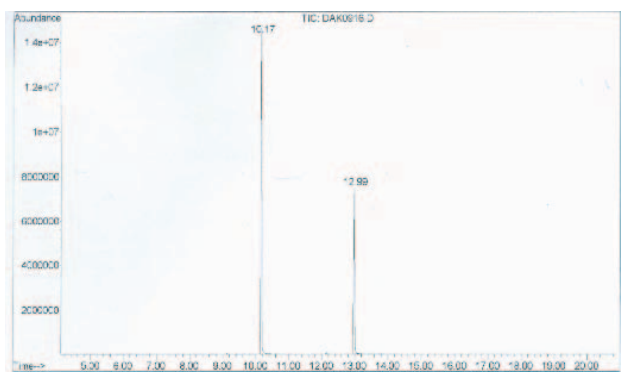
Metzger, A.; Bernhardt, S.; Manolikakes, G.; Knochel, P. *Angew. Chem. Int. Ed.* **2010**, *49*, 4665.



McNaughton-Smith, G. A.; Burns, J. F.; Stocker, J. W.; Rigdon, G. C.; Creech, C.; Arrington, S.; Shelton, T.; de Franceschi, L. *J. Med. Chem.*, **2008**, *51*, 976-982

Crude mixture, GC-MS trace:

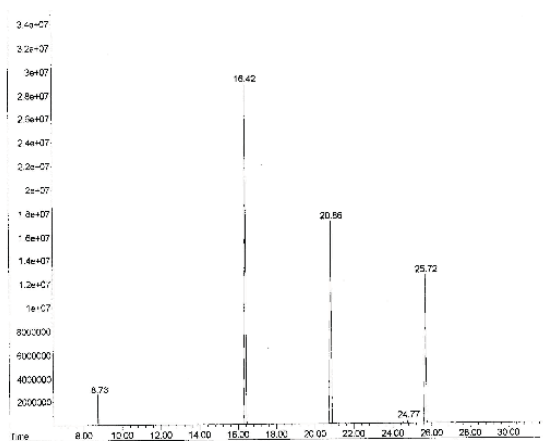
Peaks: 10.2 min, compound **13**; 13.0 min, compound **22**. Identities confirmed by NIST mass spectral database.



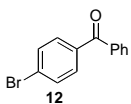
Compound **13**, low resolution EI MS: 218/216 (M⁺), 181, 141/139, 105, 77.

Compound **22**, low resolution EI MS: 296/294 (M⁺), 239, 219/217, 183, 141/139, 105, 77.

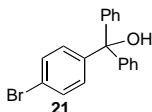
Crude mixture, GC-FID trace with added standard (biphenyl, at 16.42 min):



Data on inseparable mixture from compound 3:



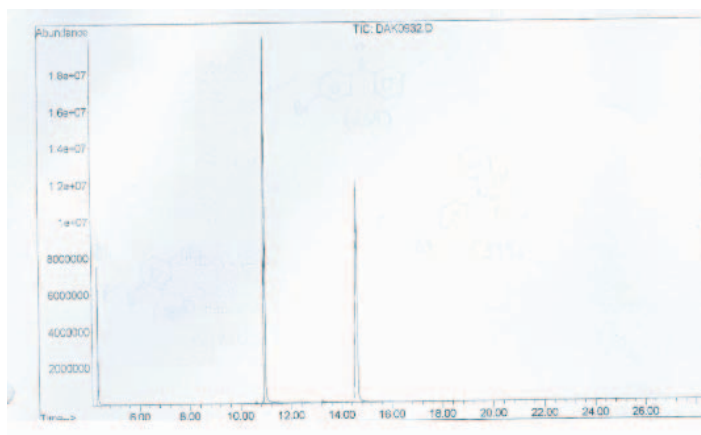
Cai, Mingzhong; Zheng, Guomin; Zha, Lingfang; Peng, Jian *Eur. J. Org. Chem.* **2009**, 1585-1591.



Theodorou, Vassiliki; Skobridis, Konstantinos; Karkatsoulis, Aris *Tetrahedron* **2007**, 63, 4284-4289.

Crude mixture, GC-MS trace:

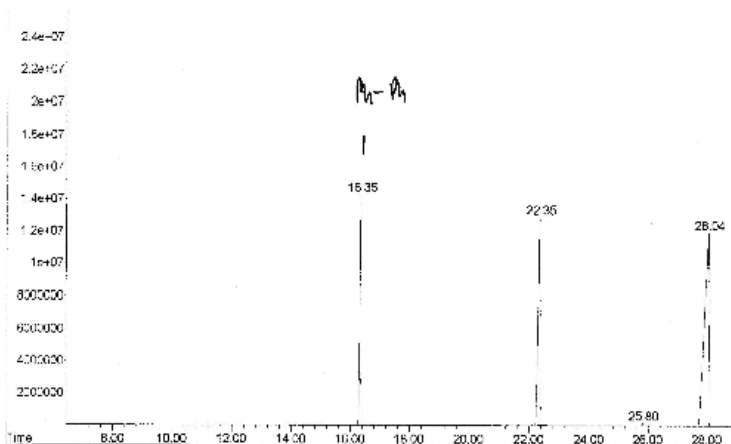
Peaks: 10.9 min, compound **12**; 14.5 min, compound **21**. Identities confirmed by NIST mass spectral database.



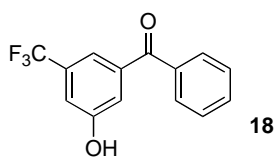
Compound **12**, low resolution EI MS: 262/260 (M⁺), 185/183, 157/155, 105, 77.

Compound **21**, low resolution EI MS: 340/338 (M⁺), 263/261, 183, 105, 77.

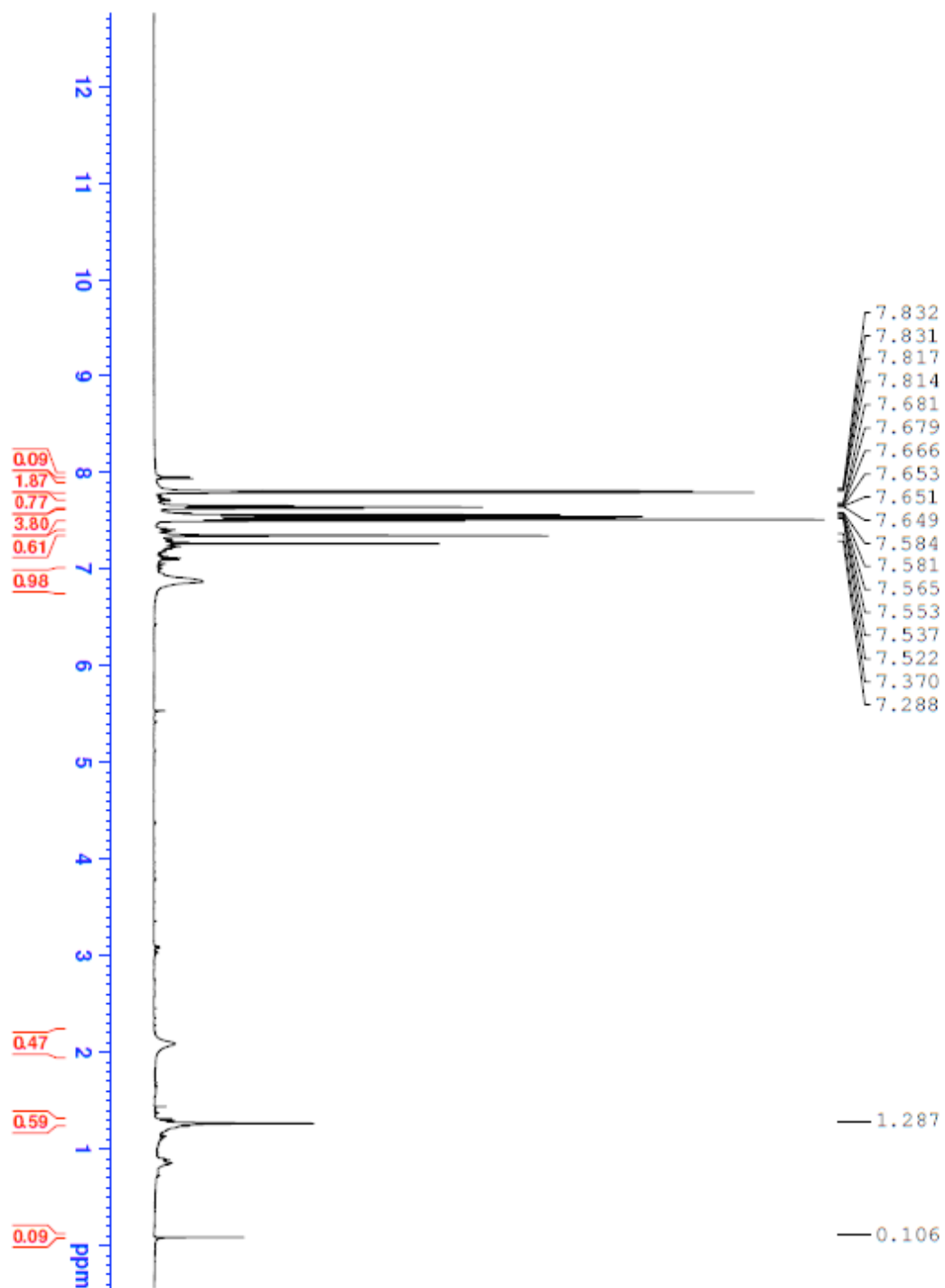
Crude mixture, GC-FID trace with added standard (biphenyl, at 16.35 min):



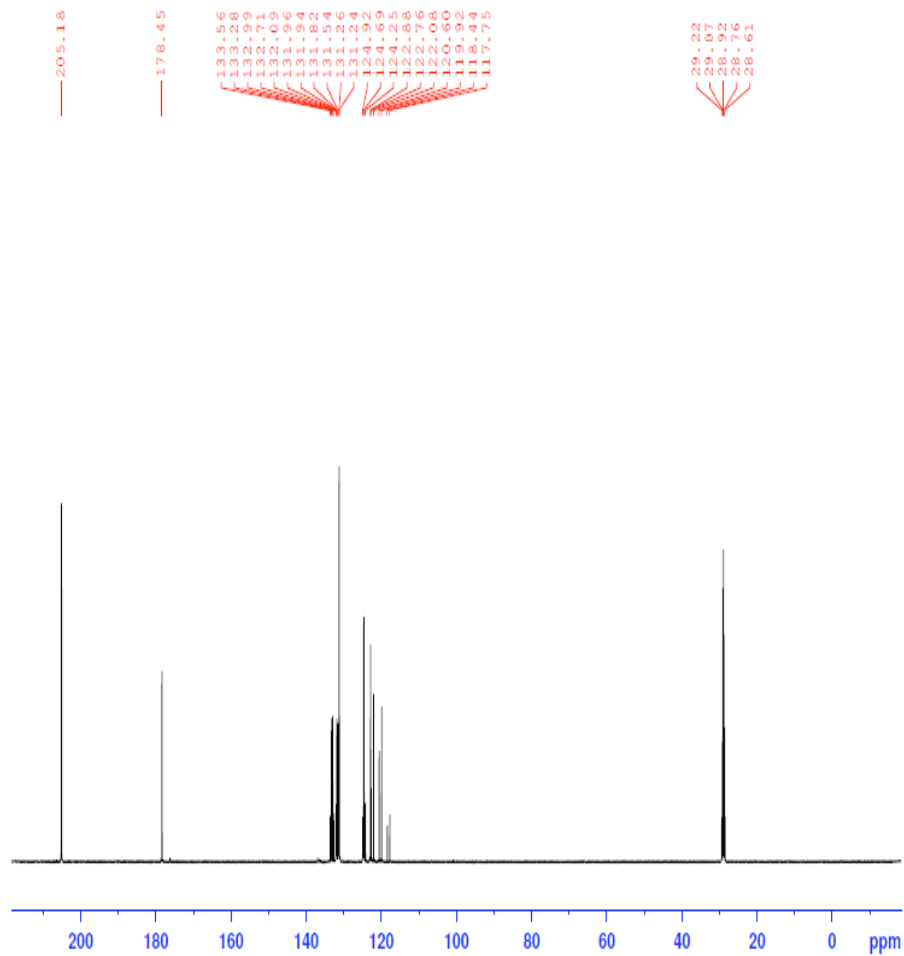
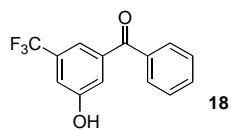
New Compounds:



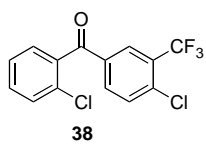
¹H NMR:



¹³C NMR:

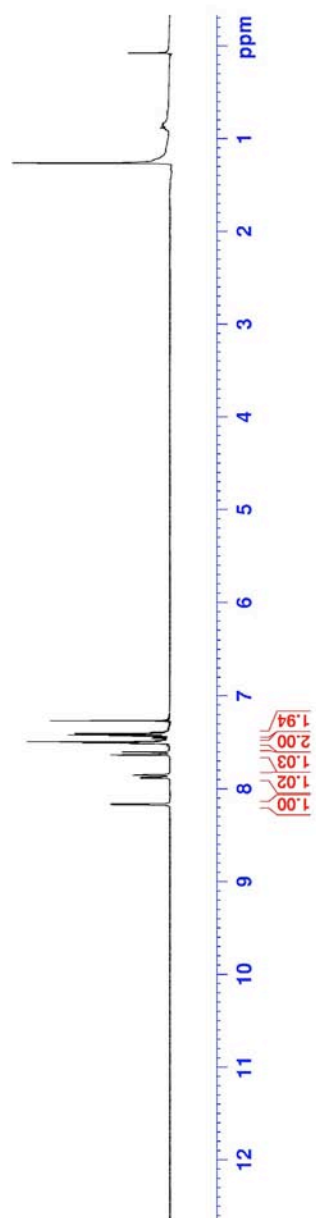


¹H NMR

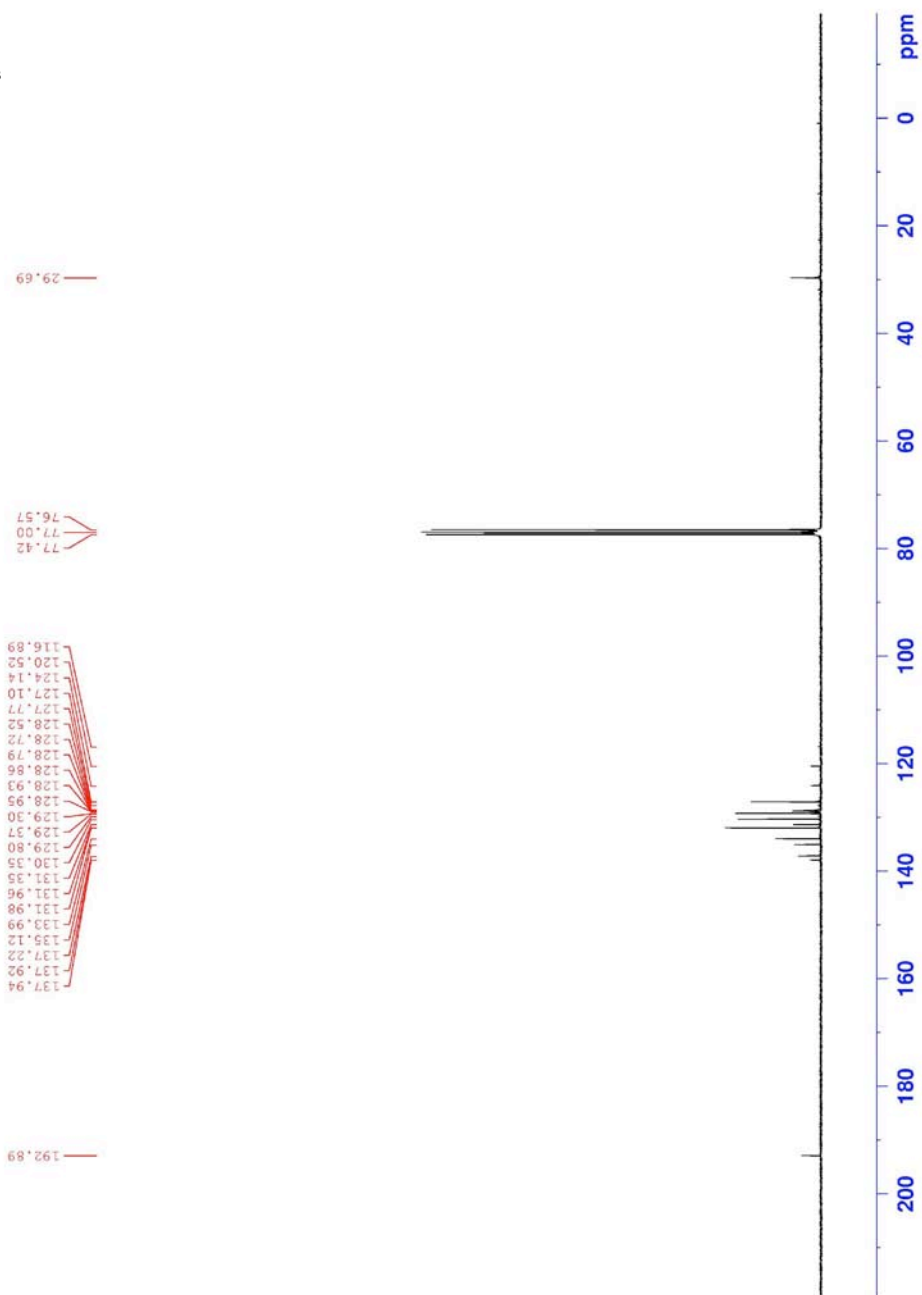
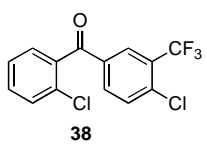


1.265

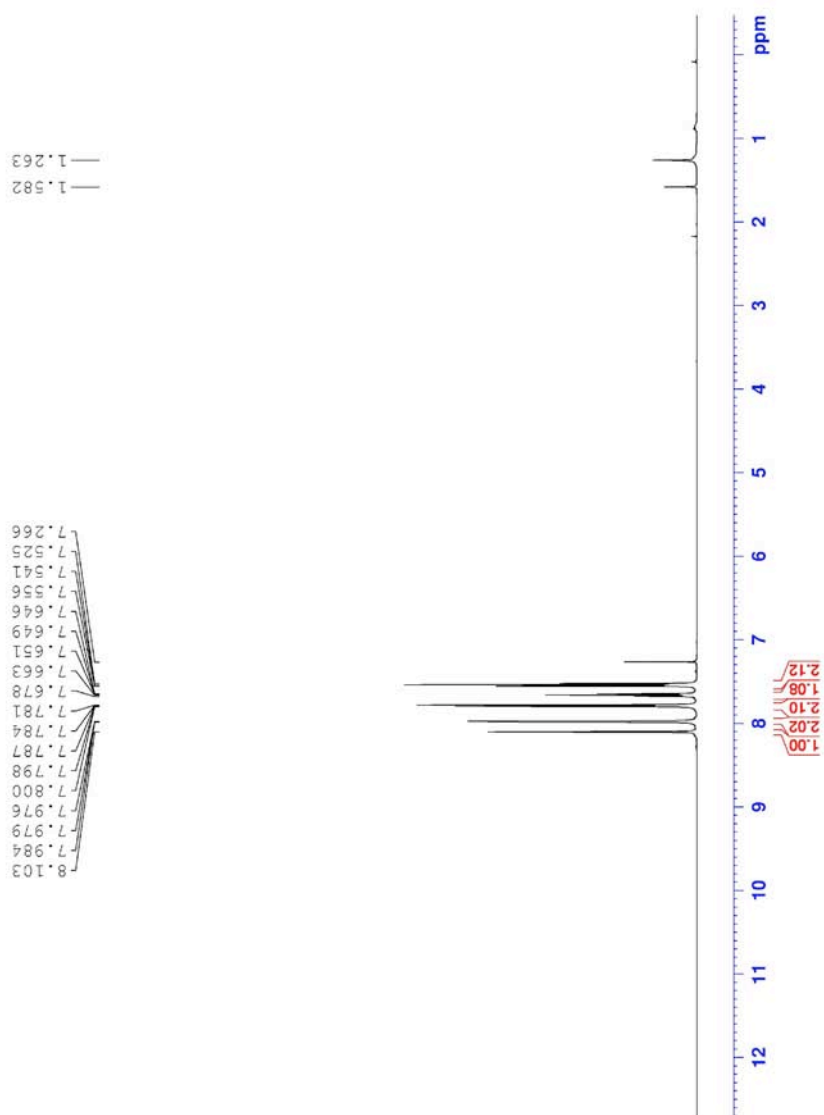
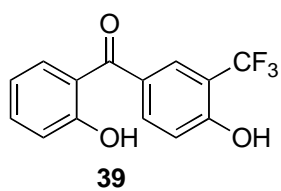
8.174
8.168
8.185
7.879
7.858
7.851
7.636
7.608
7.517
7.508
7.503
7.500
7.496
7.433
7.420
7.416
7.408
7.269



¹³C NMR:



¹H NMR



¹³C NMR

