

Supporting Information

AgSCF₃-Mediated Trifluoromethylthiolation of α,α -Diaryl Allylic Alcohols via Radical Neophyl Rearrangement

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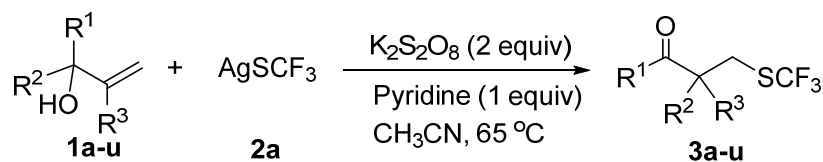
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1. General information

All manipulations were carried out in a sealed tube under a nitrogen atmosphere using standard Schlenk techniques. The solvents were distilled under nitrogen from sodium-benzophenone (THF, toluene, dioxane) or calcium hydride (DMF, MeCN, 1,2-DCE) before used. The α,α -diaryl allylic alcohols^[1] and AgSCF₃^[2] were prepared according to the literature methods. Other chemicals were obtained from commercial sources, and were used without further purification. Chemical shifts (δ , ppm) in the ¹H NMR spectra were recorded using TMS as internal standard. Chemical shifts in ¹³C{¹H} NMR spectra were internally referenced to CHCl₃ (δ = 77.16 ppm).

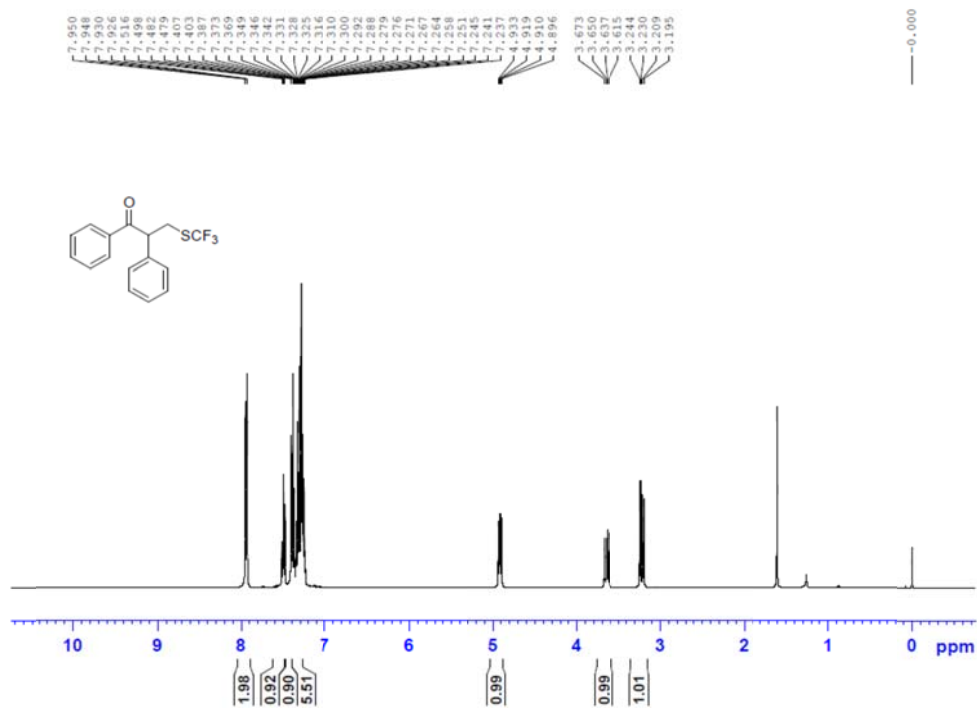
2. General procedure for the synthesis of α -aryl- β -trifluoromethylthiolated carbonyl ketones.



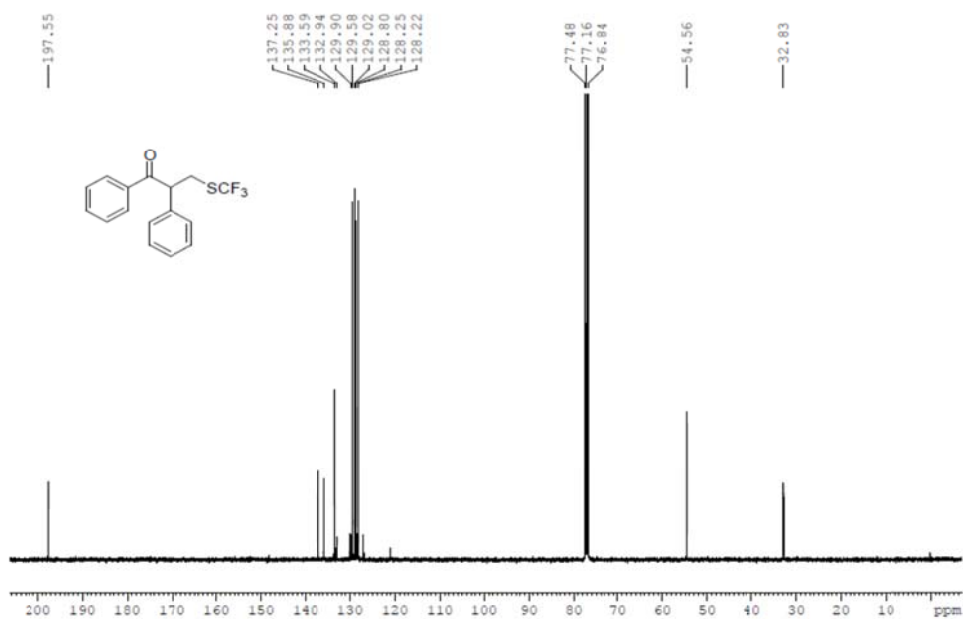
1a-u (0.2 mmol), **2a** (62.7 mg, 0.3 mmol), K₂S₂O₈ (81.1 mg, 0.3 mmol), pyridine (15.8 mg, 0.2 mmol), and CH₃CN (2 mL) were mixed in an oven-dried sealed tube under N₂. The tube was sealed and heated at 65 °C for 5h. The resulting mixture was cooled to room temperature and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel to afford the product **3a-u**.

3. Copies of the ^1H NMR, ^{13}C NMR and ^{19}F NMR for products 3a-u

^1H NMR (400 MHz, CDCl_3) of 1,2-diphenyl-3-((trifluoromethyl)thio)propan-1-one (3a)

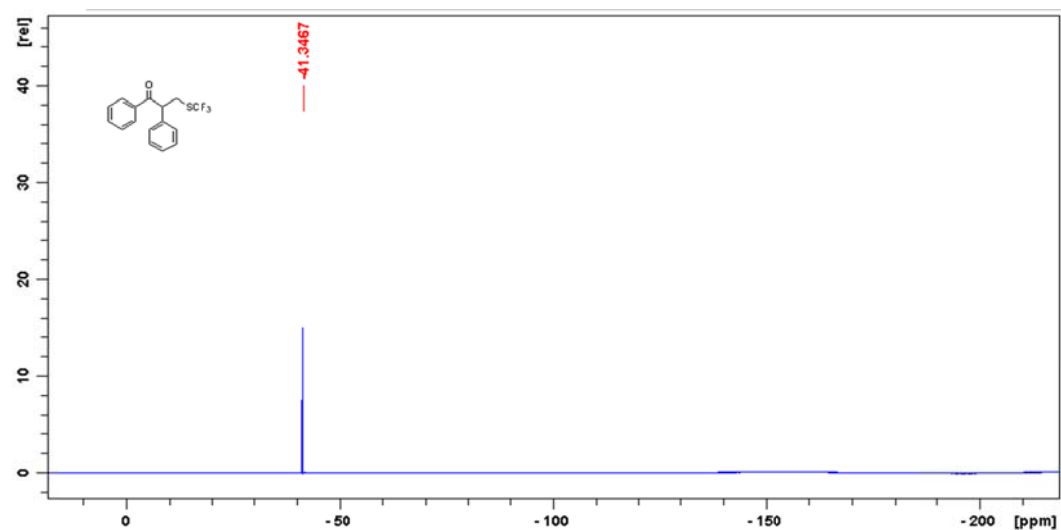


^{13}C NMR (100 MHz, CDCl_3) of 1,2-diphenyl-3-((trifluoromethyl)thio)propan-1-one (3a)



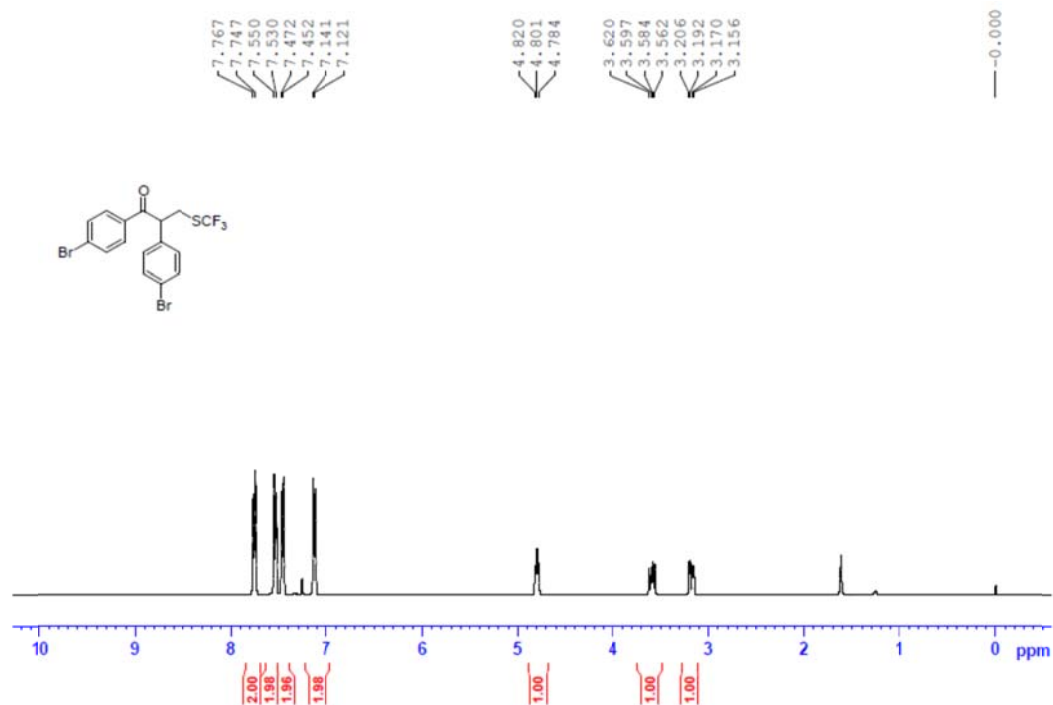
^{19}F NMR (376 MHz, CDCl_3) of 1,2-diphenyl-3-((trifluoromethyl)thio)-

propan-1-one (3a)

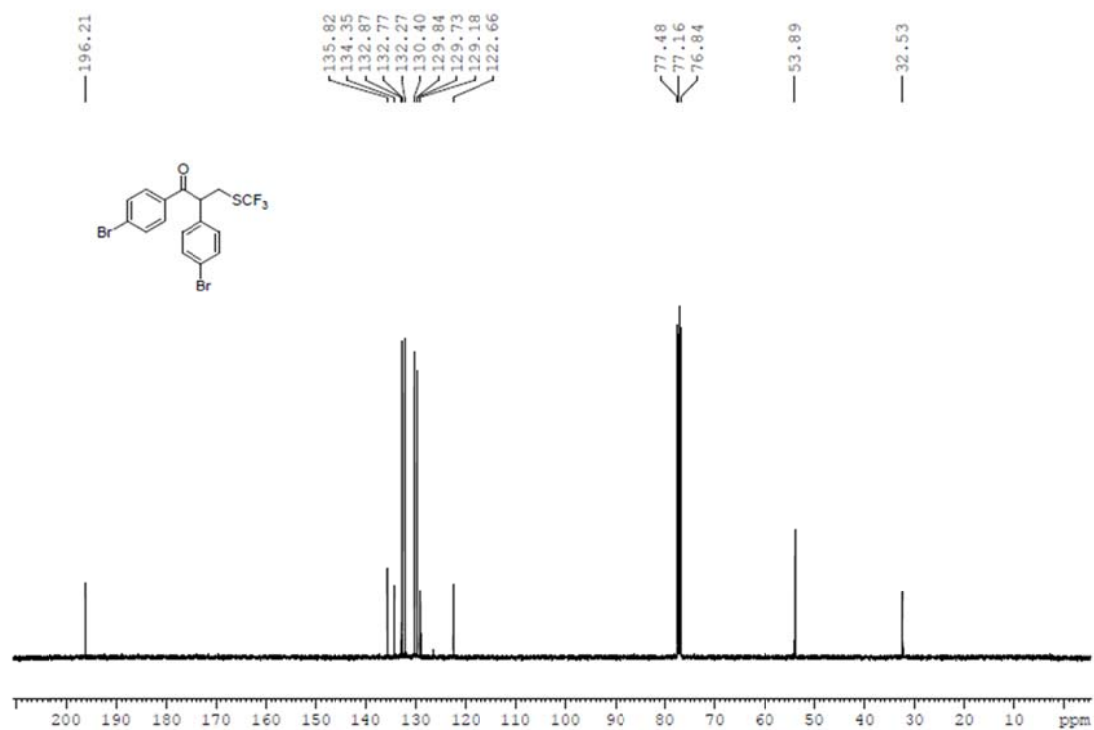


^1H NMR (400 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-3-((trifluoromethyl)thio)-

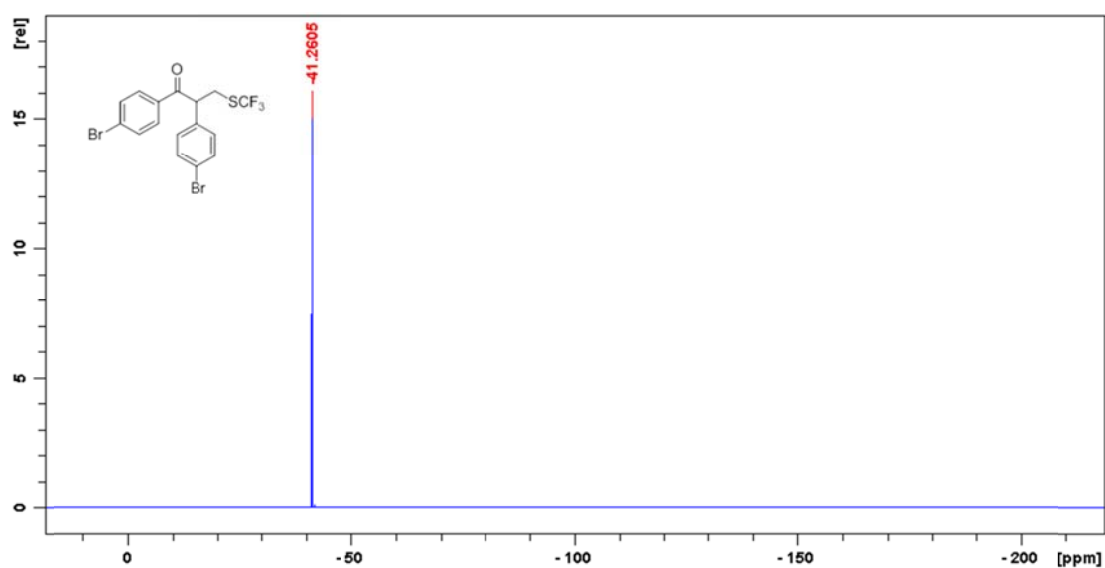
propan-1-one (3b)



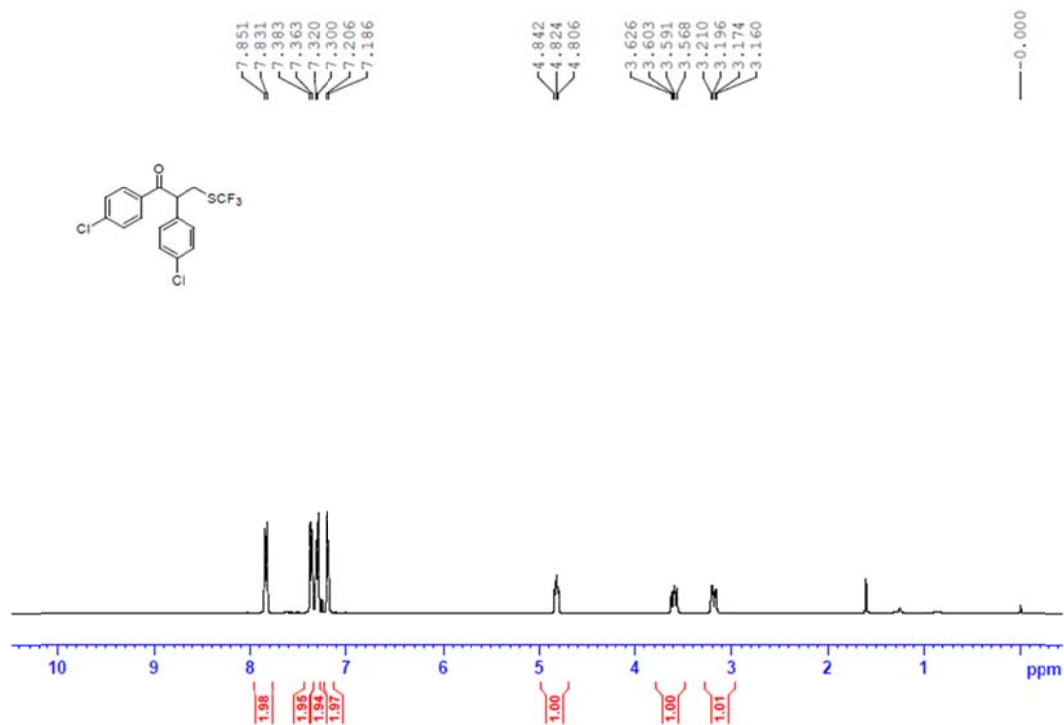
**^{13}C NMR (100 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-3-((trifluoromethyl)thio)
-propan-1-one (3b)**



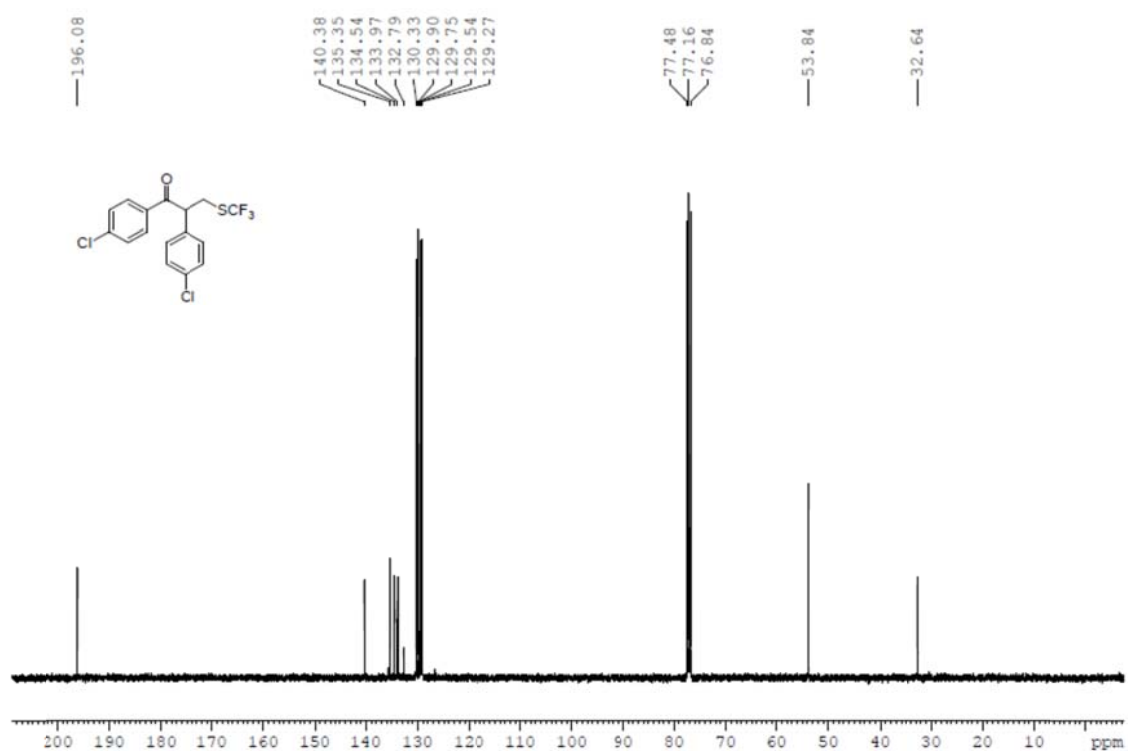
**^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-3-((trifluoromethyl)thio)
-propan-1-one (3b)**



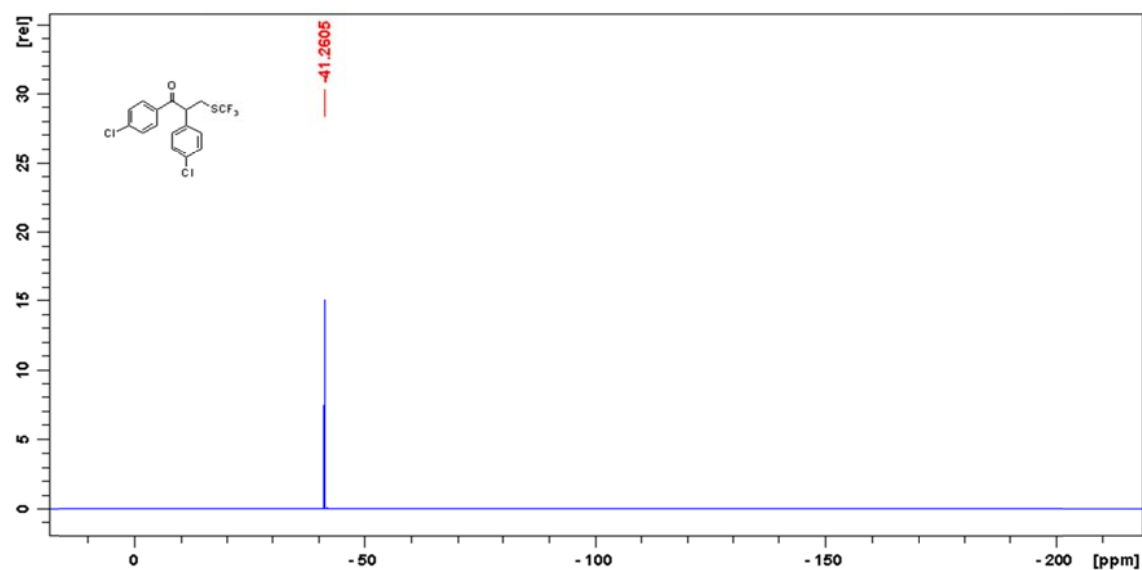
^1H NMR (400 MHz, CDCl_3) of 1,2-bis(4-chlorophenyl)-3-((trifluoromethyl)thio)propan-1-one (3c)



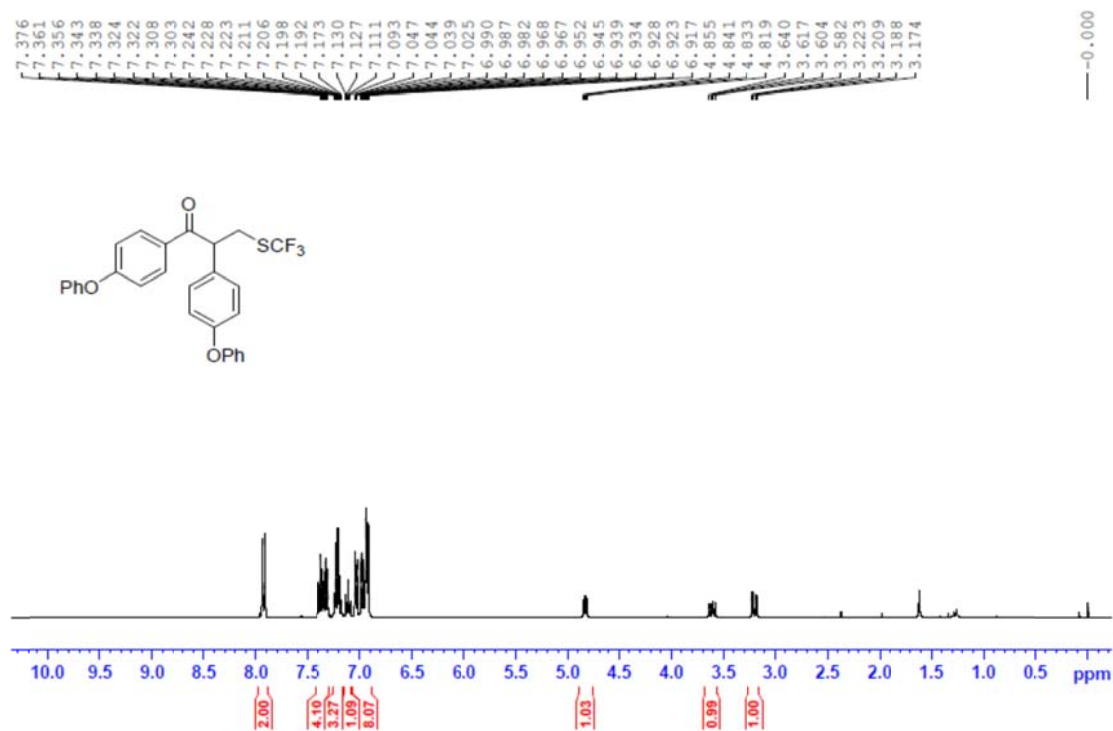
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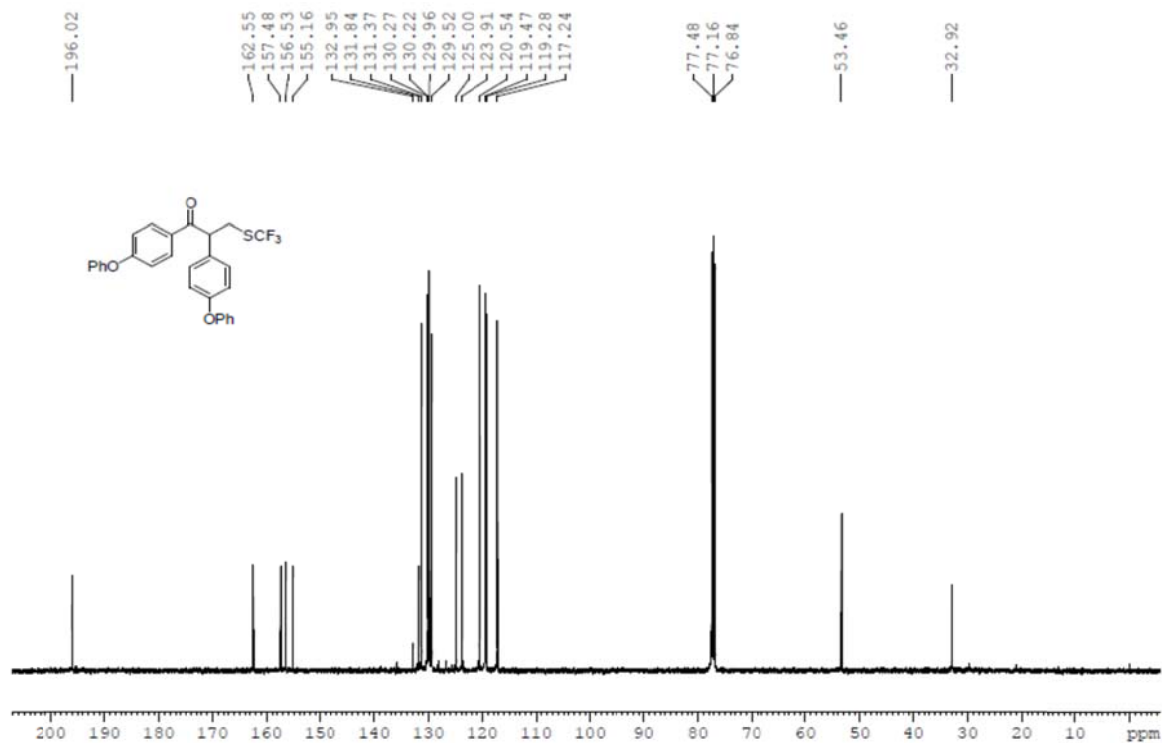
^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(4-chlorophenyl)-3-((trifluoromethyl)thio)propan-1-one (3c)



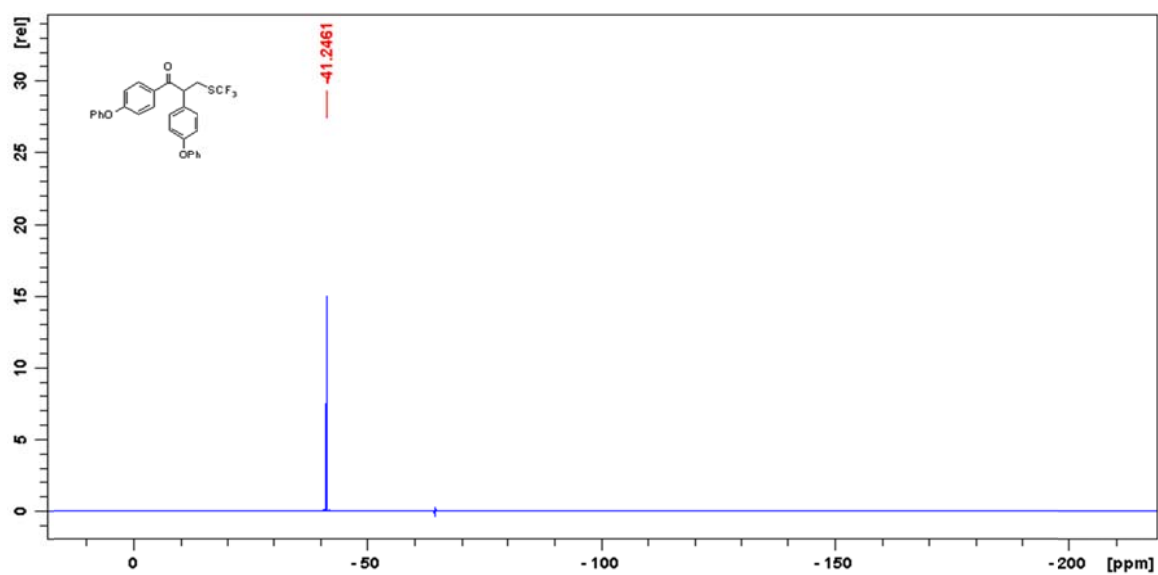
^1H NMR (400 MHz, CDCl_3) of 1,2-bis(4-phenoxyphenyl)-3-((trifluoromethyl)thio)propan-1-one (3d)



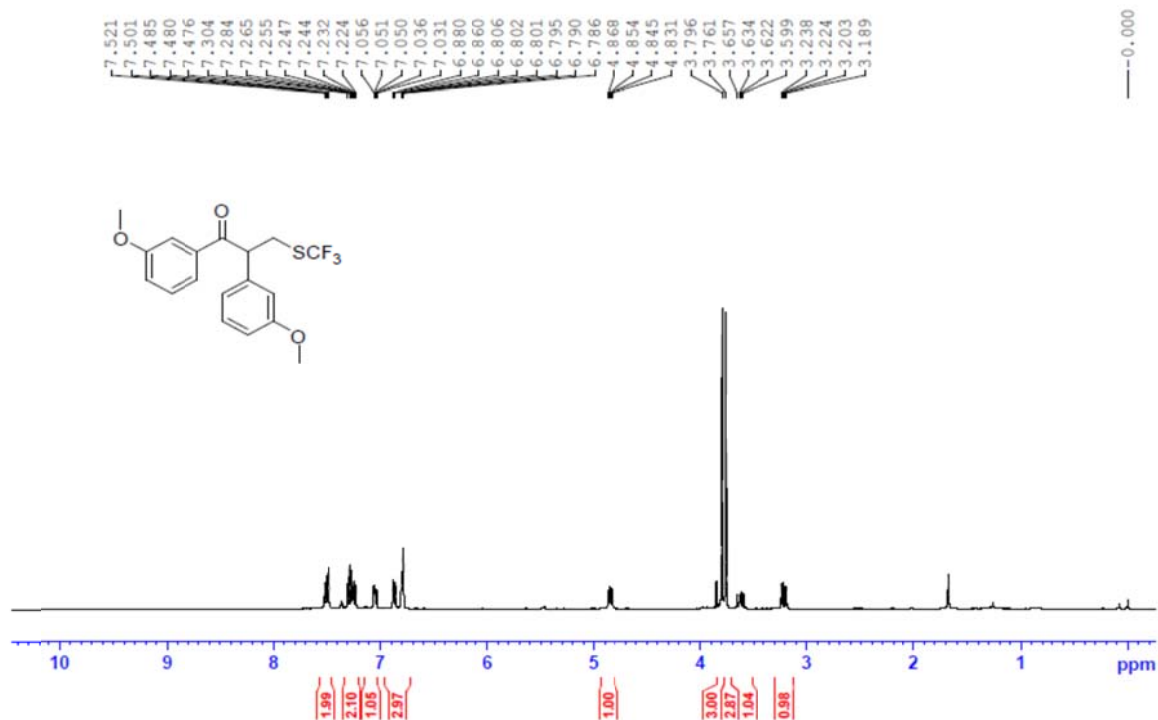
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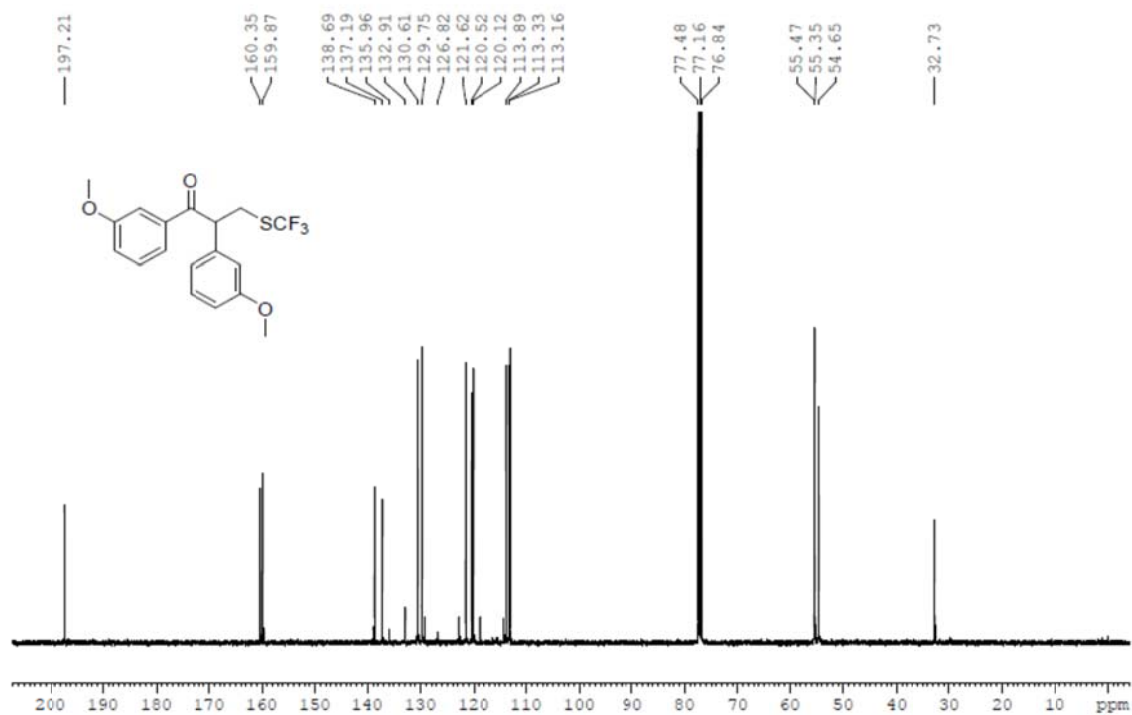
^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(4-phenoxyphenyl)-3-((trifluoromethyl)-thio)propan-1-one (3d)



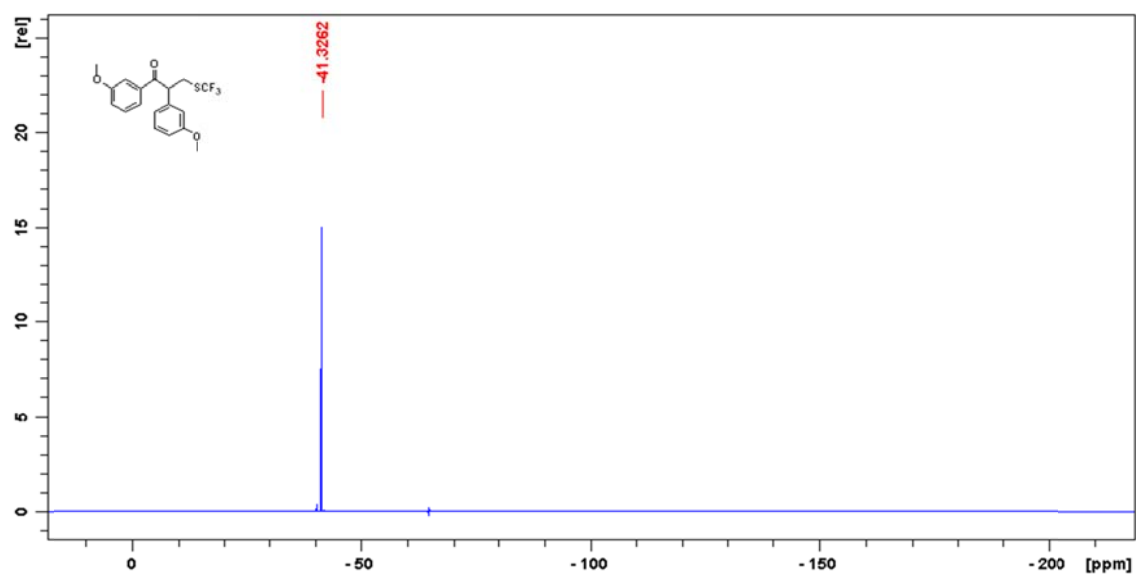
^1H NMR (400 MHz, CDCl_3) of 1,2-bis(3-methoxyphenyl)-3-((trifluoromethyl)-thio)propan-1-one (3e)



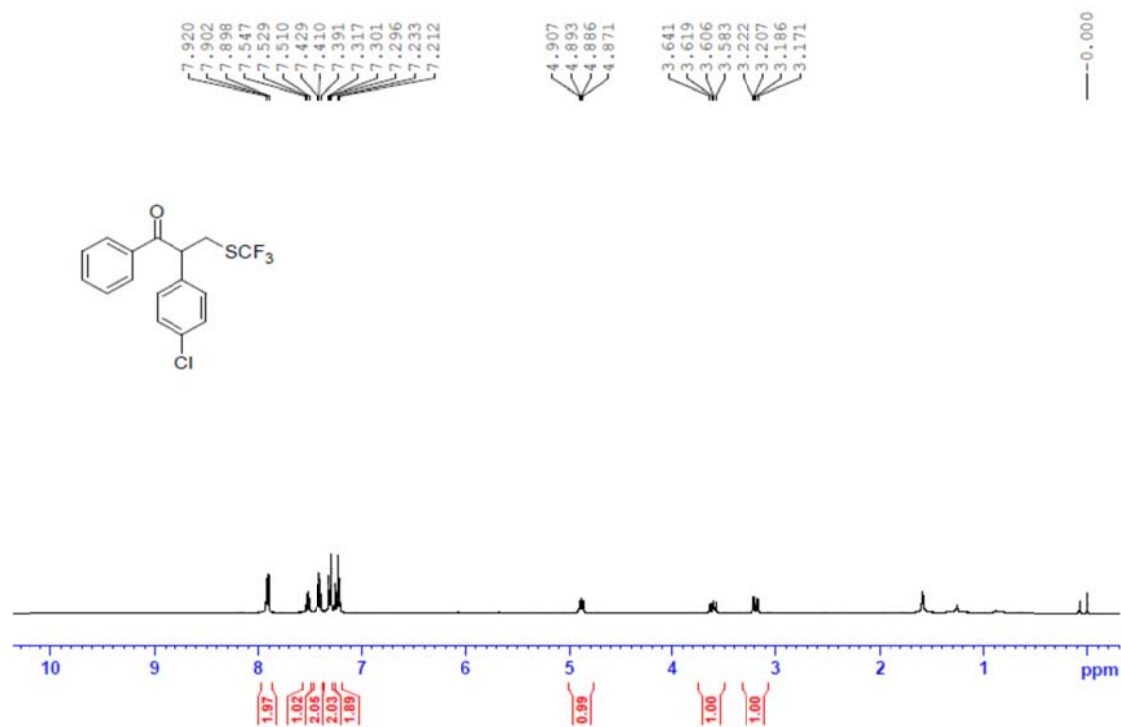
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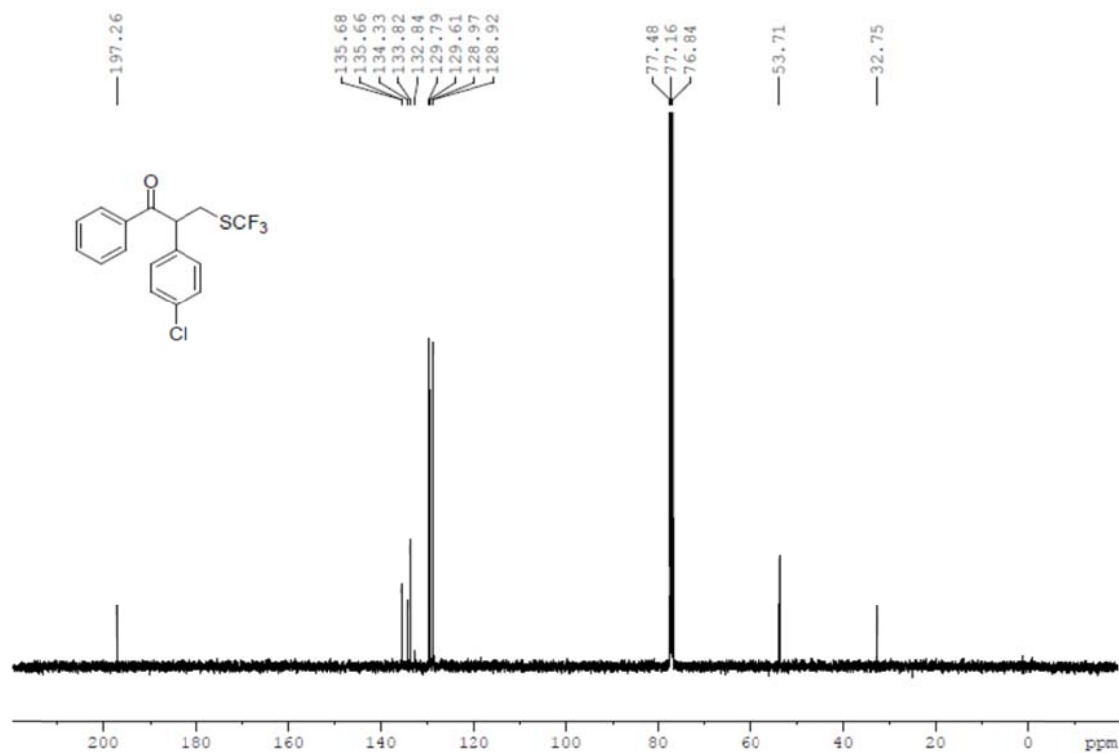
^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(3-methoxyphenyl)-3-((trifluoromethyl)-thio)propan-1-one (3e)



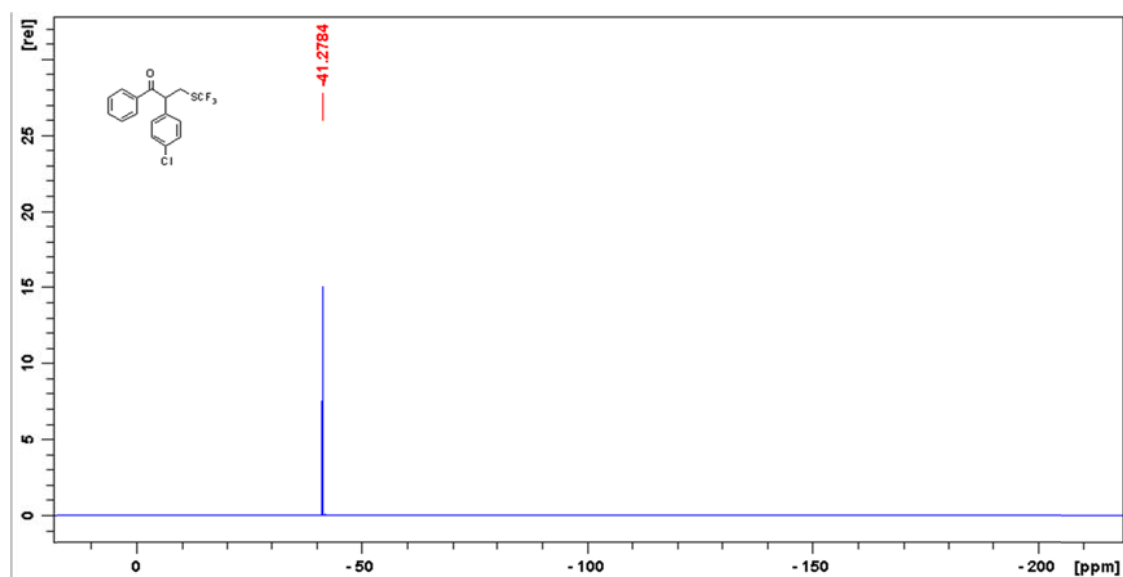
^1H NMR (400 MHz, CDCl_3) of 2-(4-chlorophenyl)-1-phenyl-3-((trifluoromethyl)-thio)propan-1-one (3f)



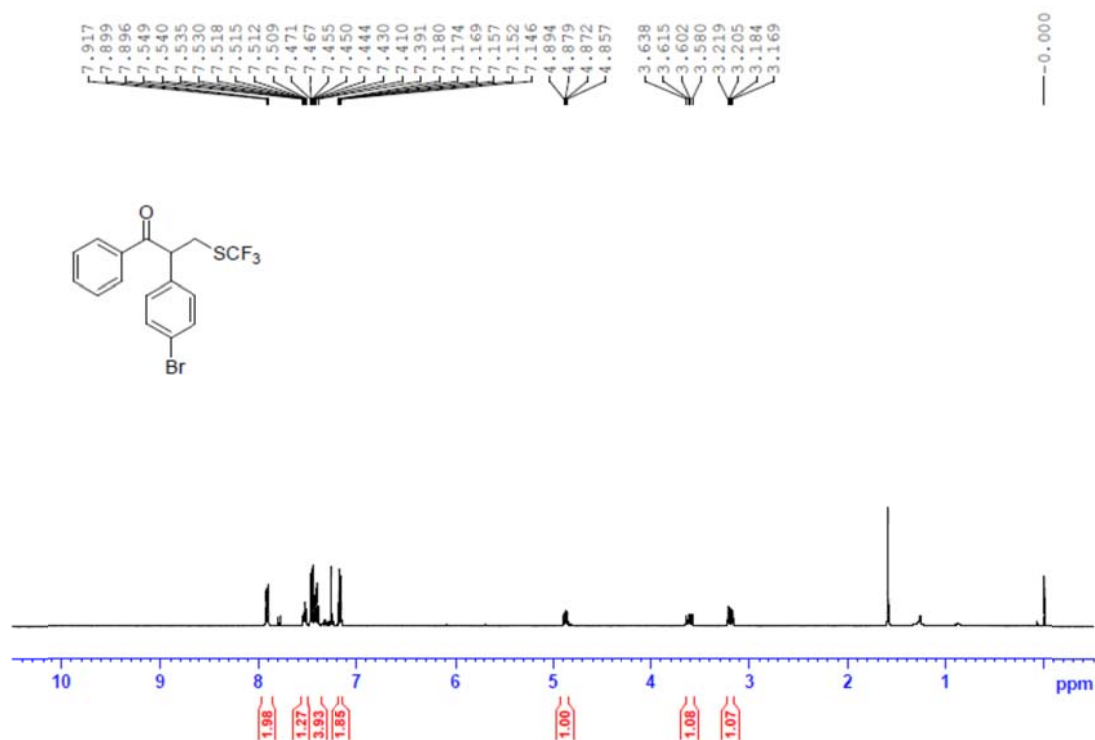
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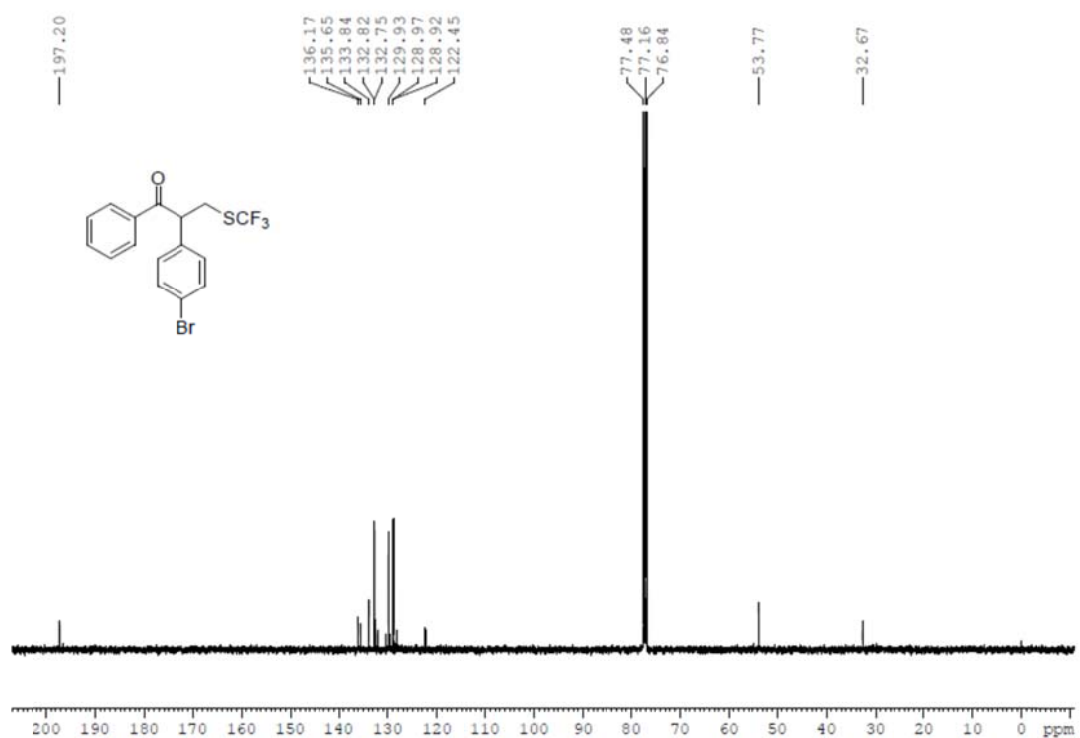
^{19}F NMR (376 MHz, CDCl_3) of 2-(4-chlorophenyl)-1-phenyl-3-((trifluoromethyl)-thio)propan-1-one (3f)



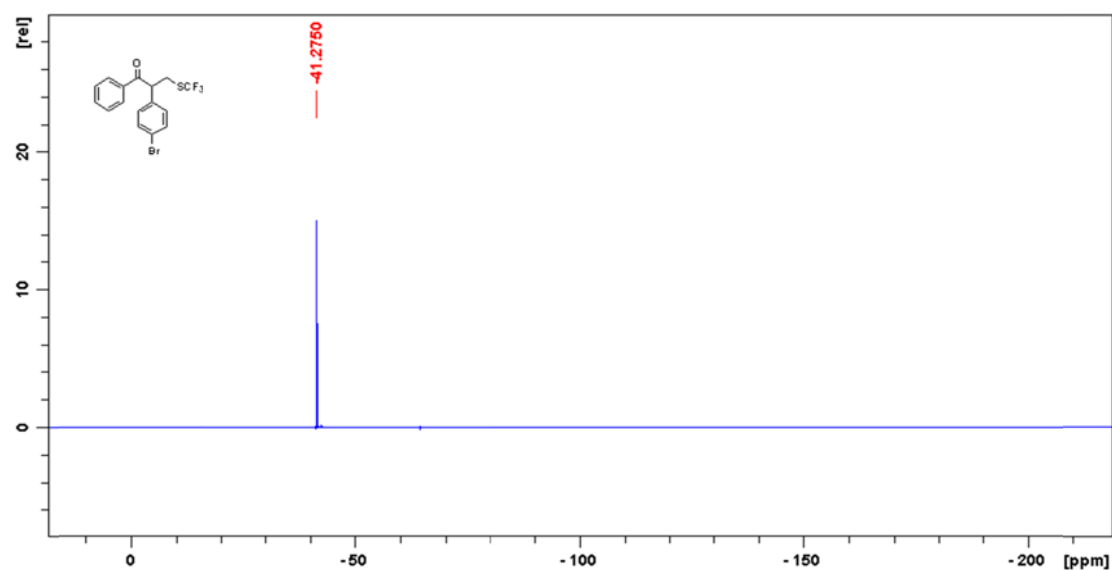
^1H NMR (400 MHz, CDCl_3) of 2-(4-bromophenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3g)



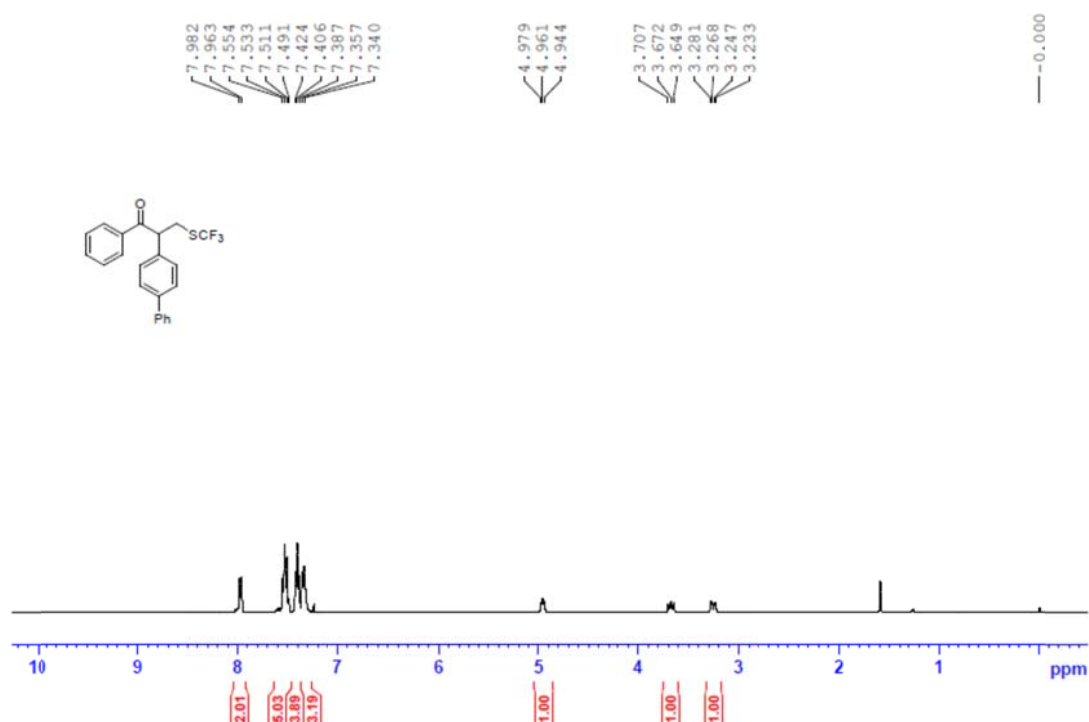
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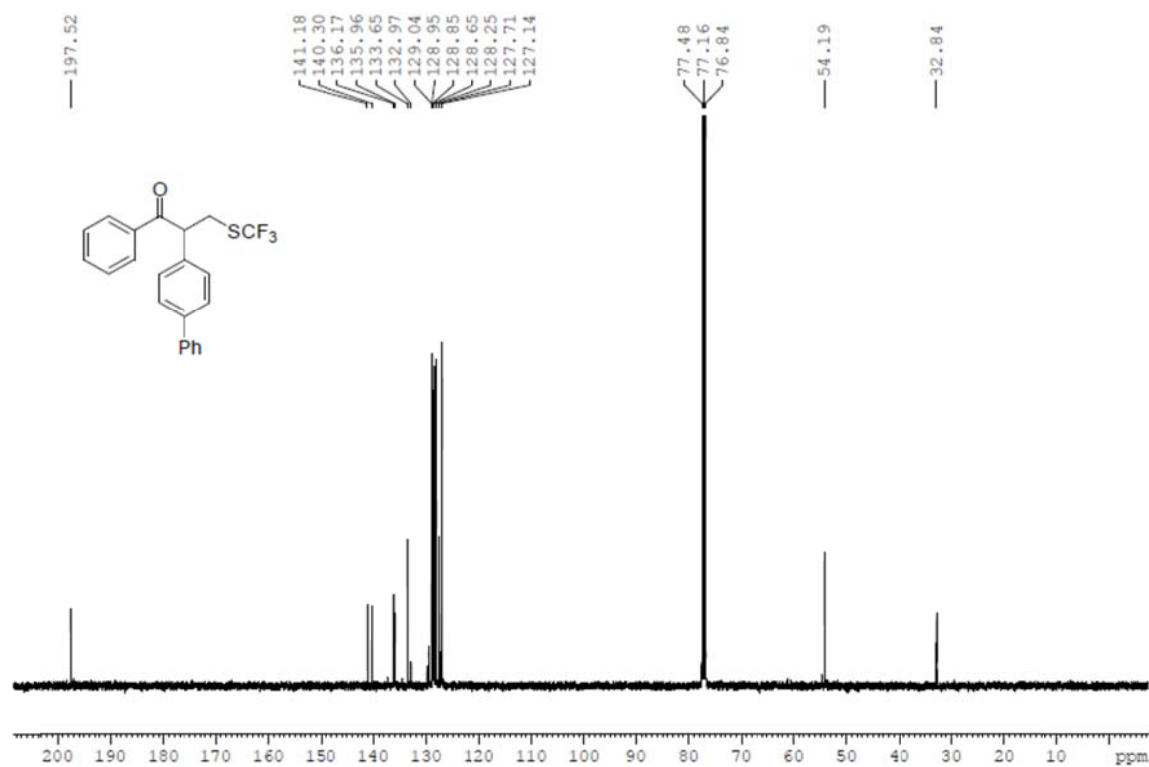
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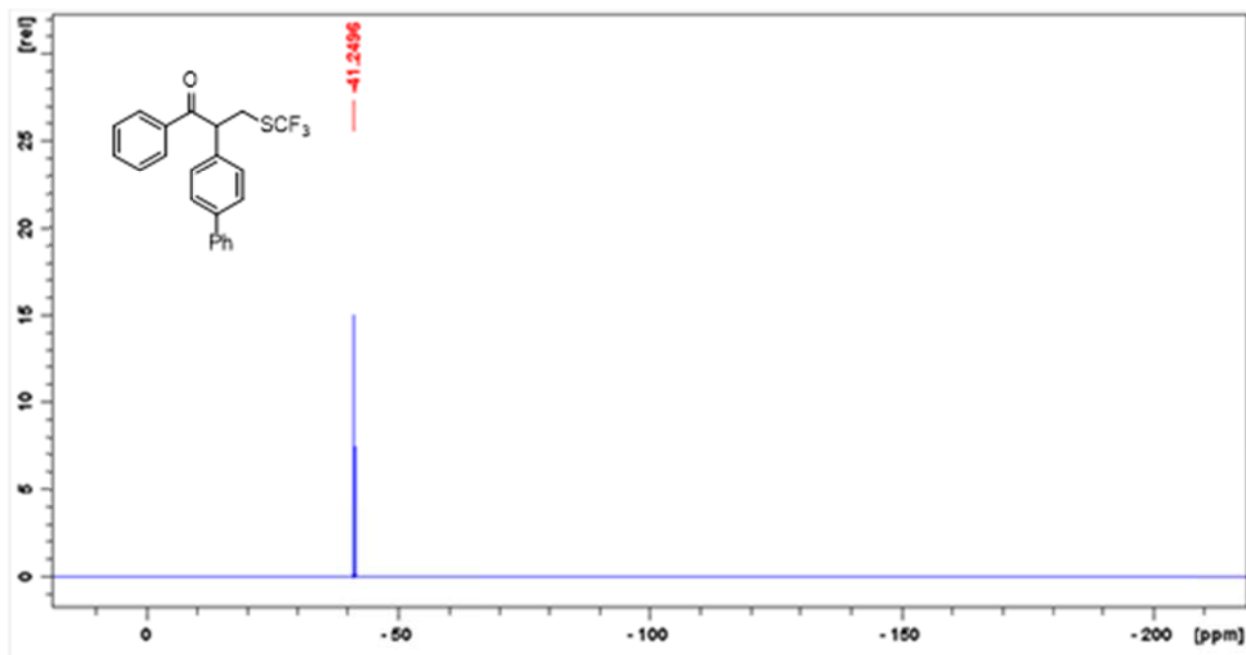
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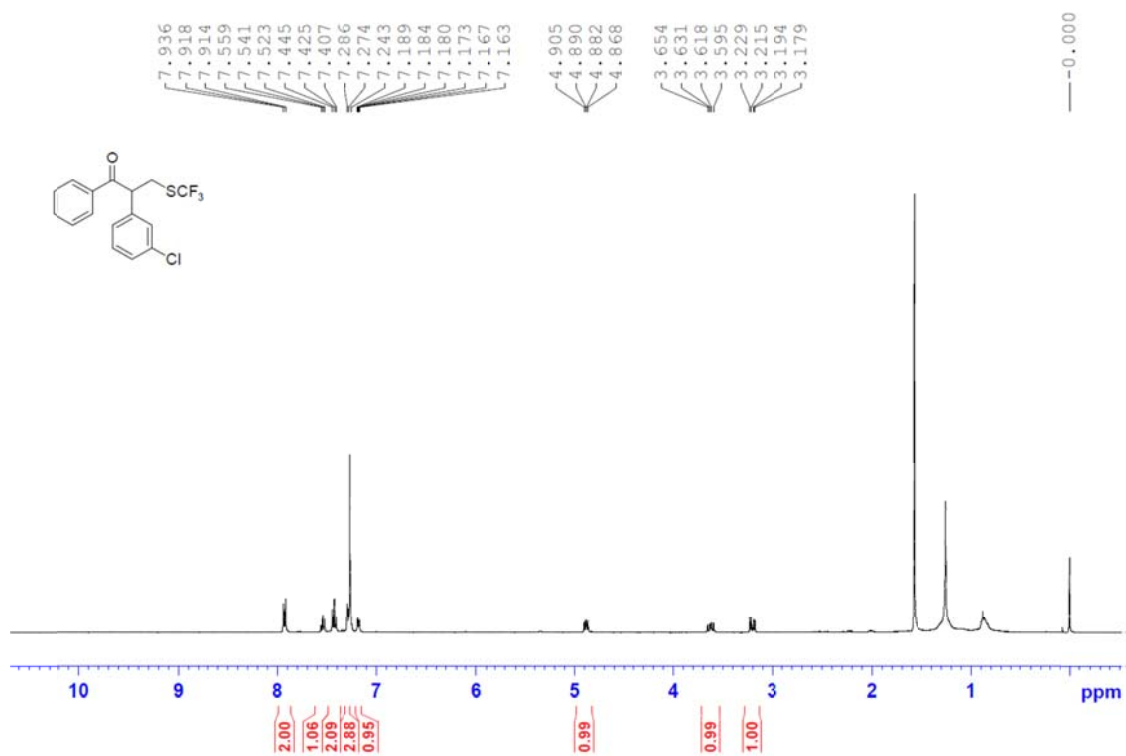
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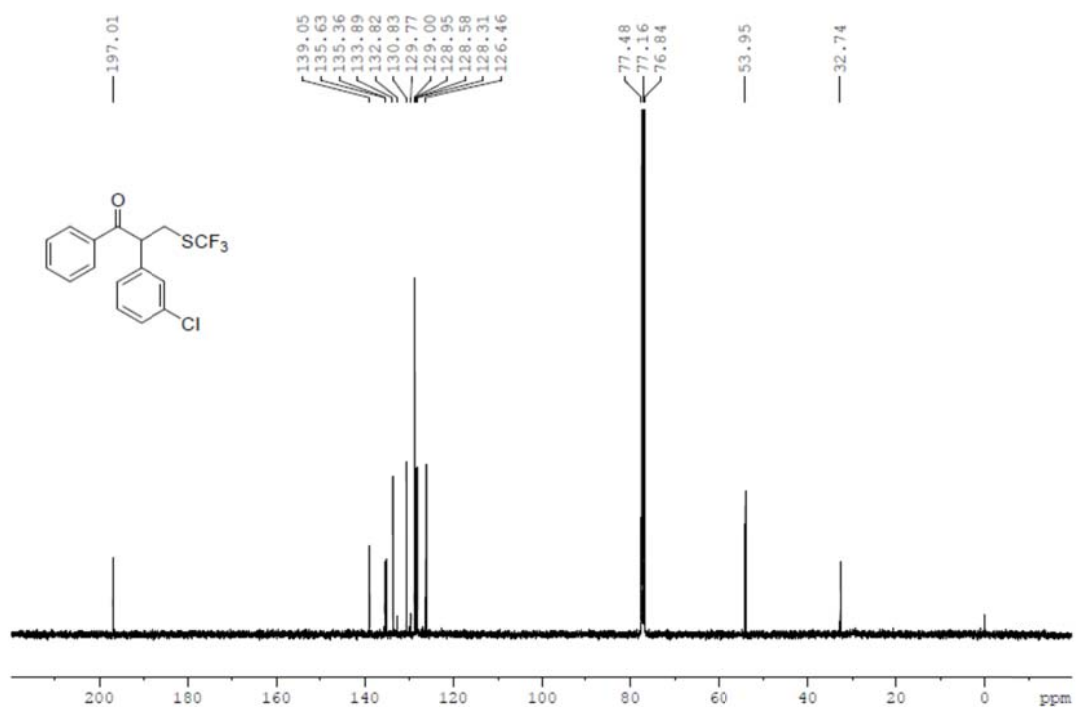
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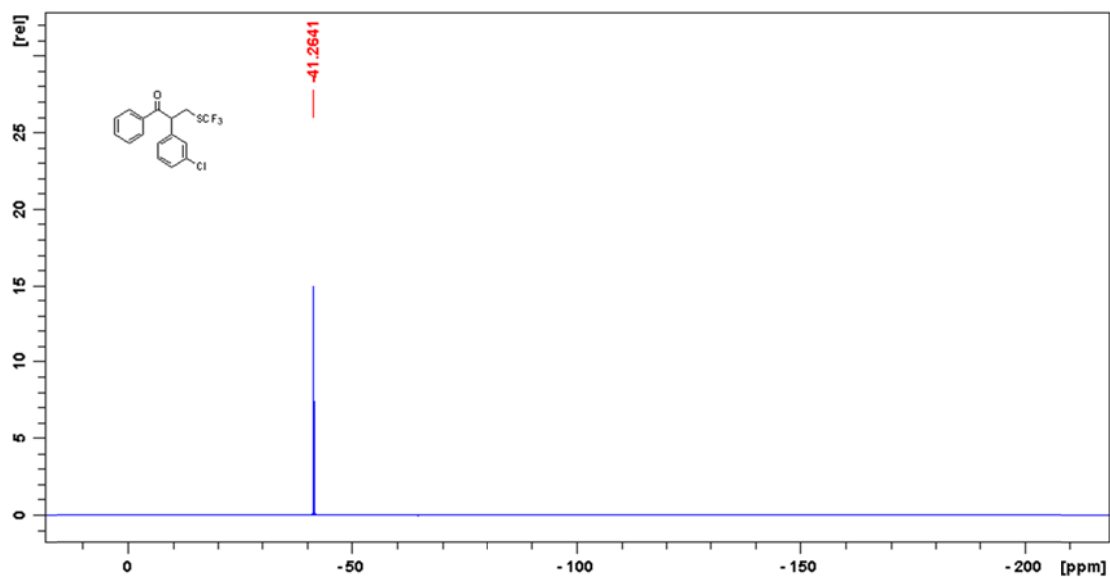
^1H NMR (400 MHz, CDCl_3) of 2-(3-chlorophenyl)-1-phenyl-3-((trifluoromethyl)-thio)propan-1-one (3i)



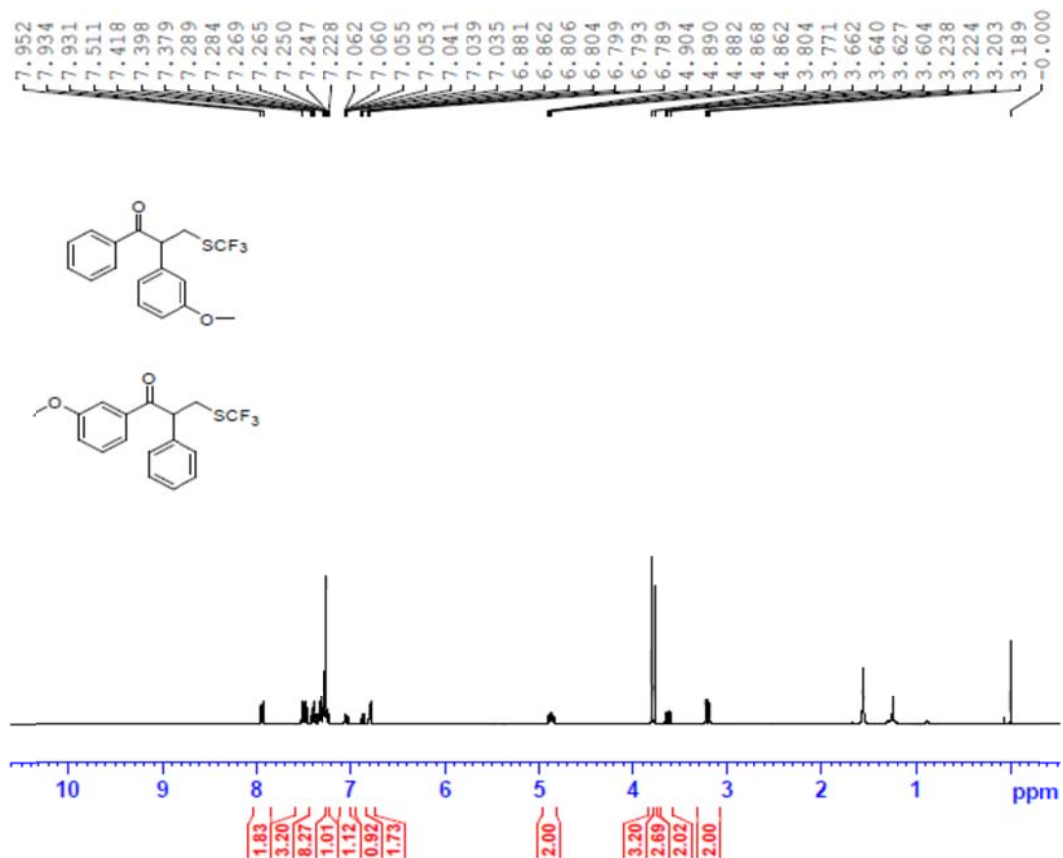
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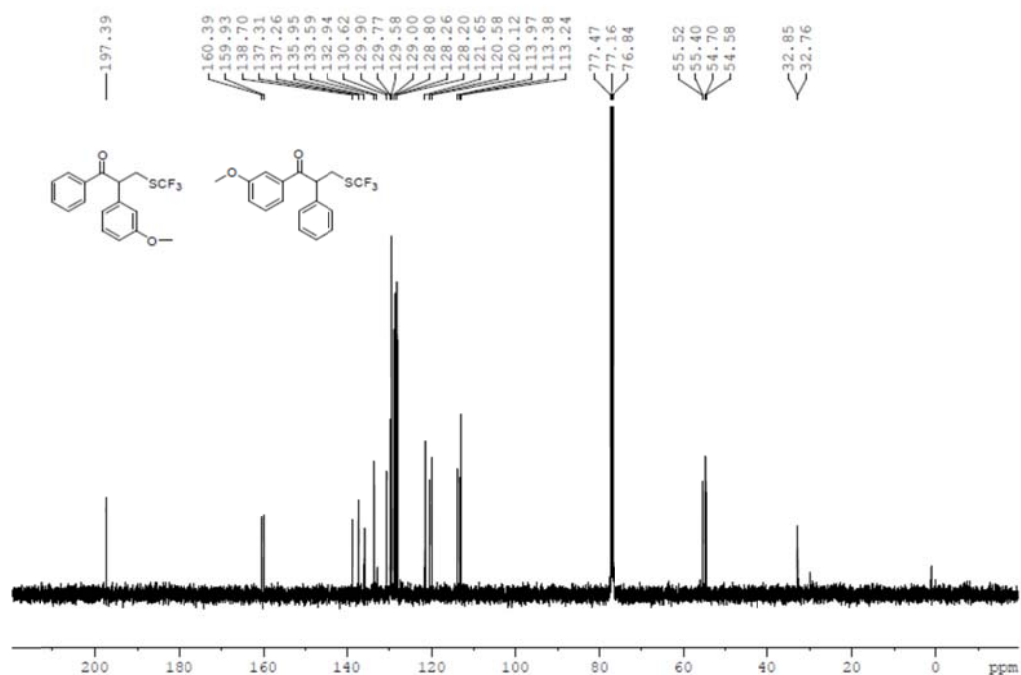
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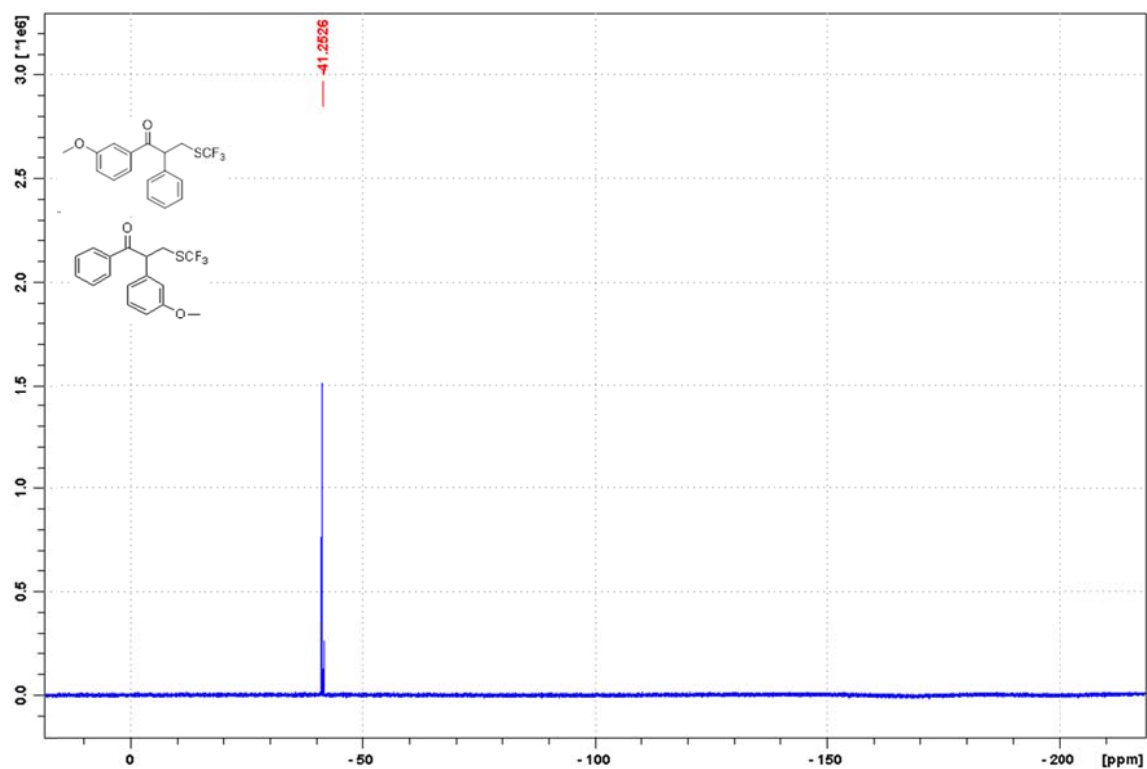
^1H NMR (400 MHz, CDCl_3) of the mixture of 1-(3-methoxyphenyl)-2-phenyl-3-((trifluoromethyl)thio)propan-1-one (3j) and 2-(3-methoxyphenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3j')



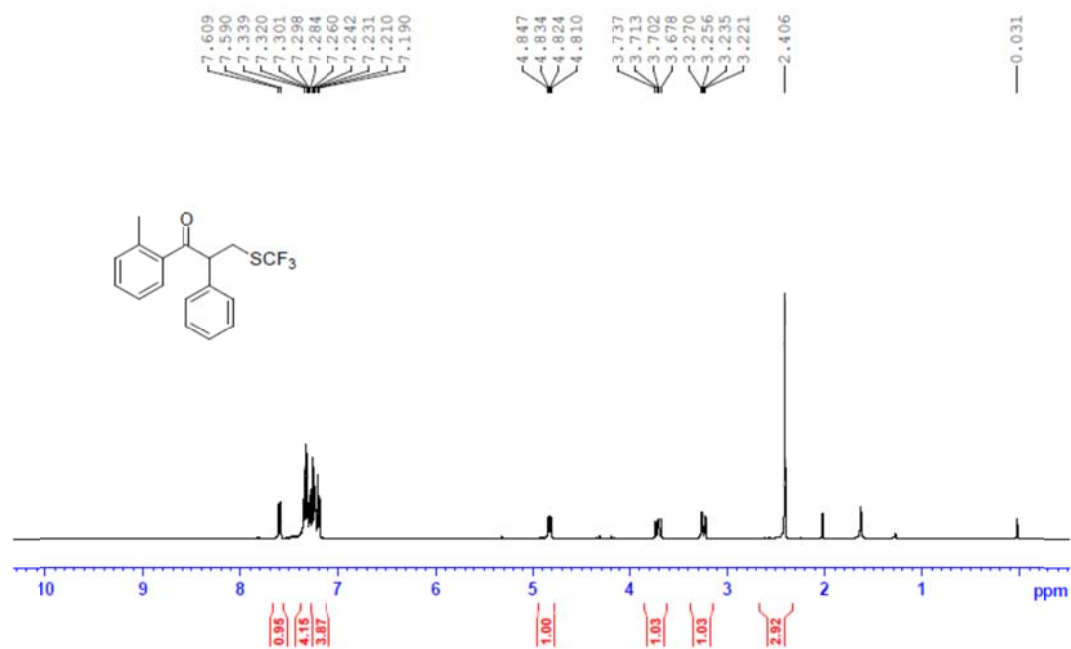
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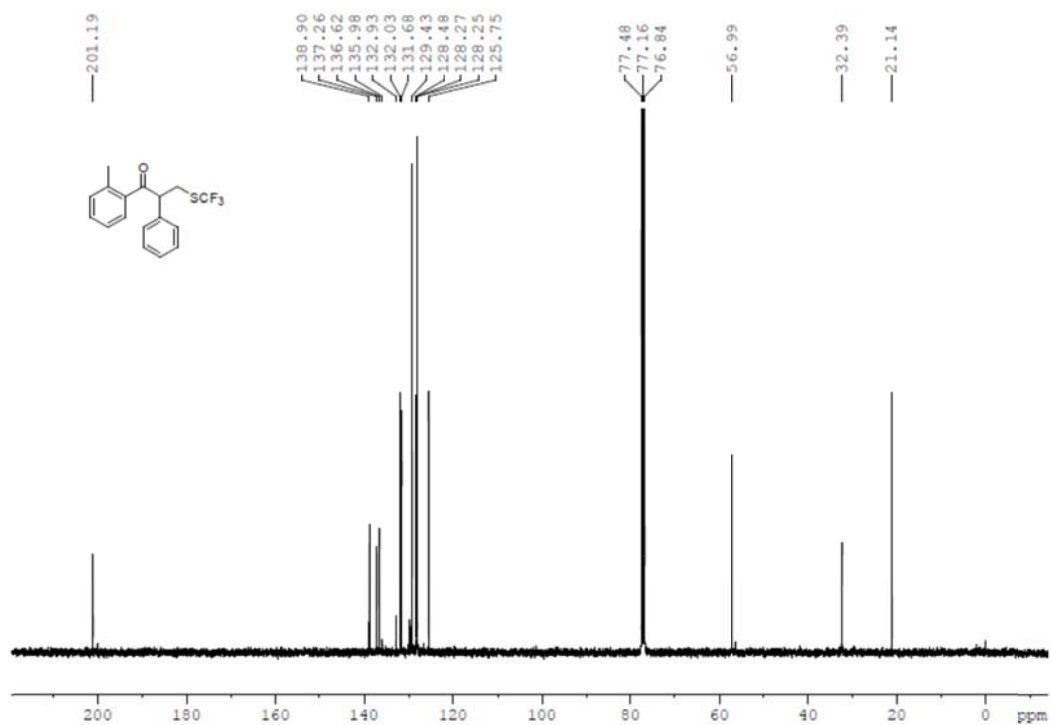
^{19}F NMR (376 MHz, CDCl_3) of the mixture of 1-(3-methoxyphenyl)-2-phenyl-3-((trifluoromethyl)thio)propan-1-one (3j) and 2-(3-methoxyphenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3j')



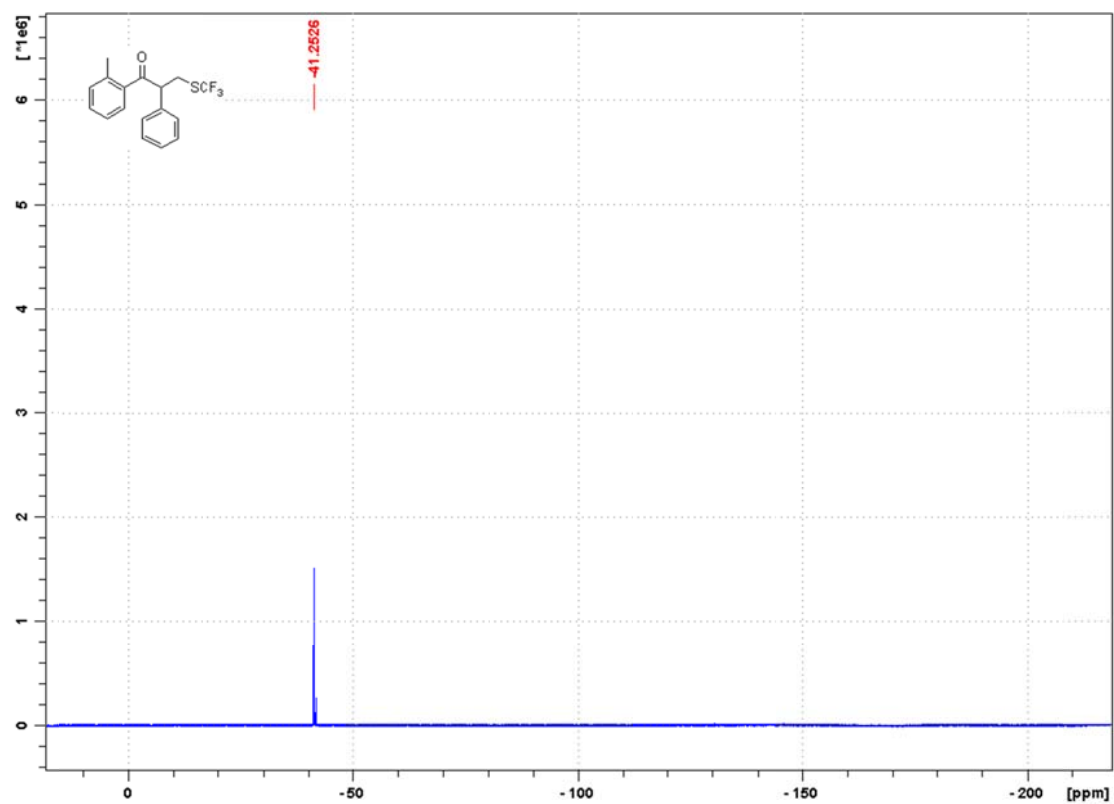
¹H NMR (400 MHz, CDCl₃) of 2-phenyl-1-(o-tolyl)-3-((trifluoromethyl)-thio)propan-1-one (3k)



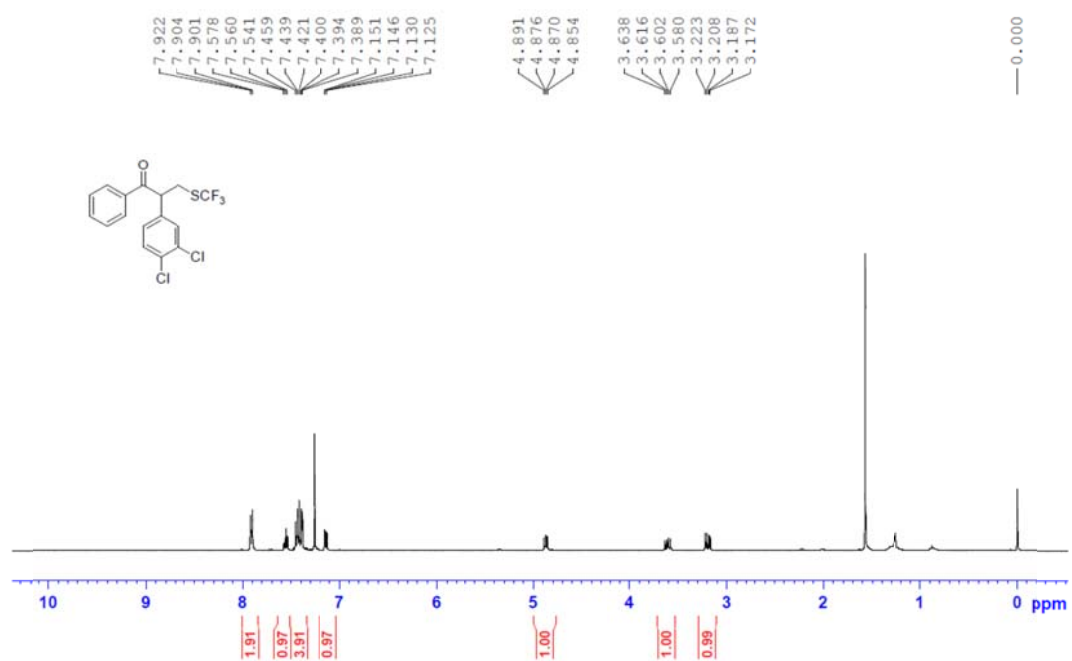
¹³C NMR (100 MHz, CDCl₃) 2-phenyl-1-(o-tolyl)-3-((trifluoromethyl)-thio)propan-1-one (3k)



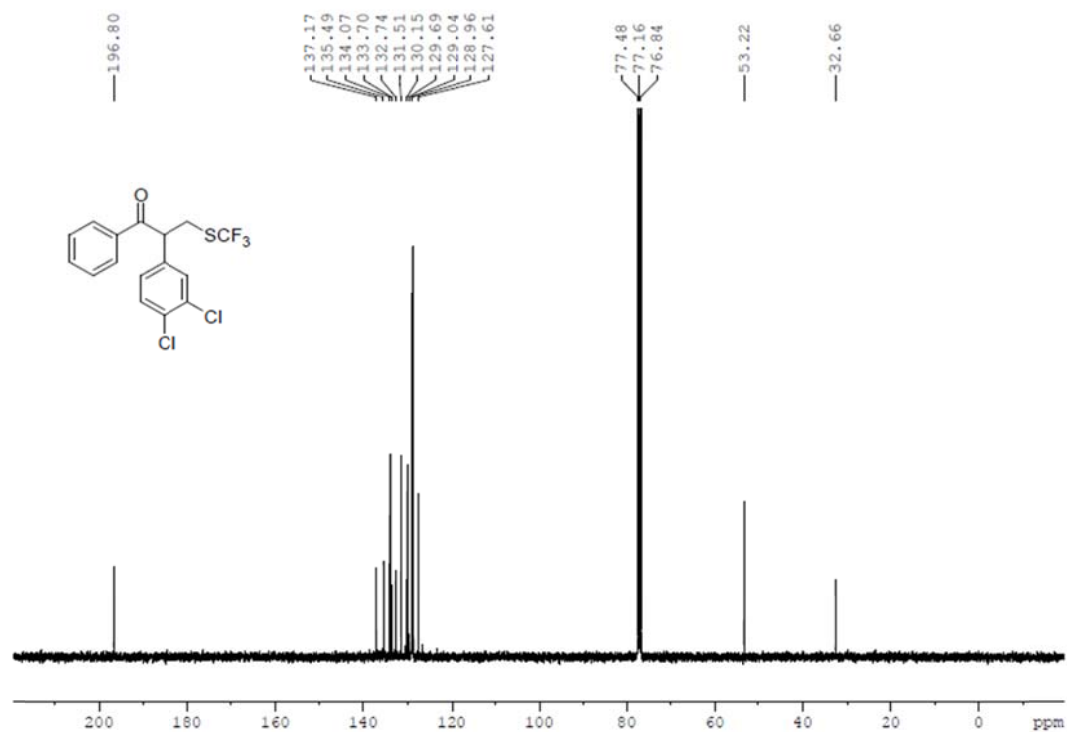
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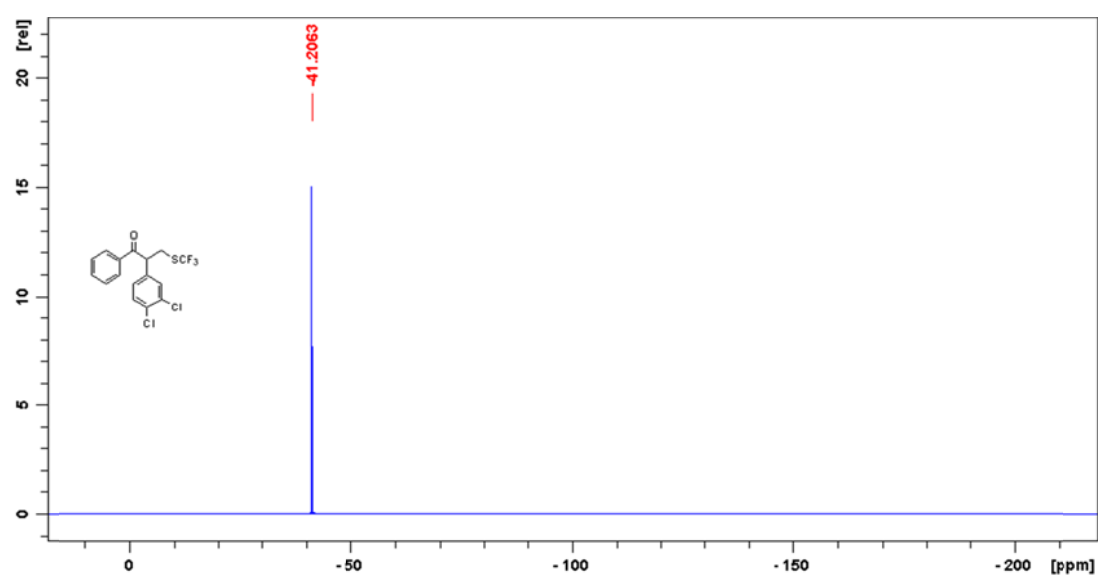
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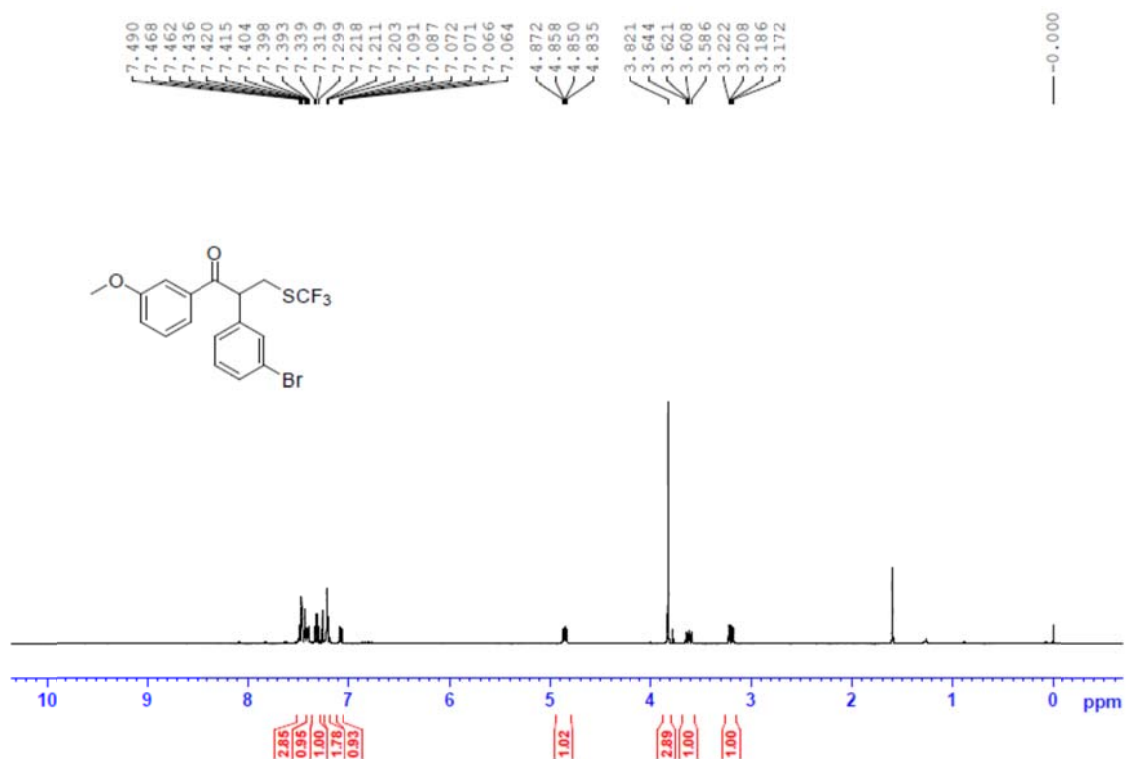
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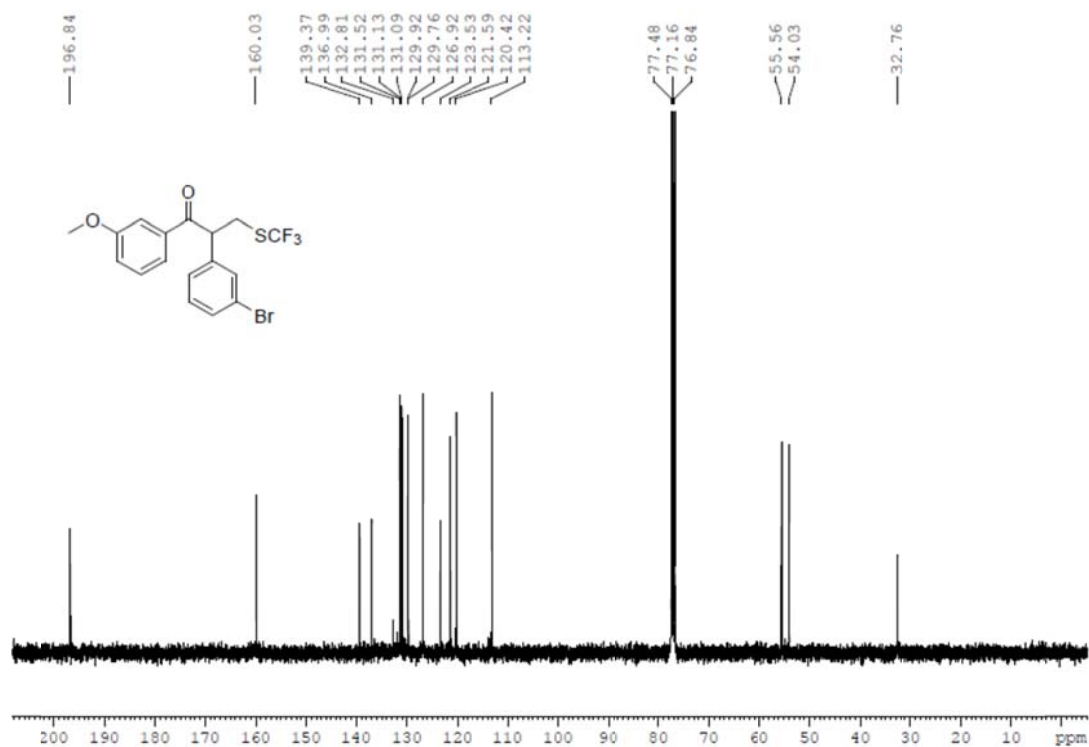
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^1H NMR (400 MHz, CDCl_3) of 2-(3-bromophenyl)-1-(3-methoxyphenyl)-3-((trifluoromethyl)thio)propan-1-one (3m)

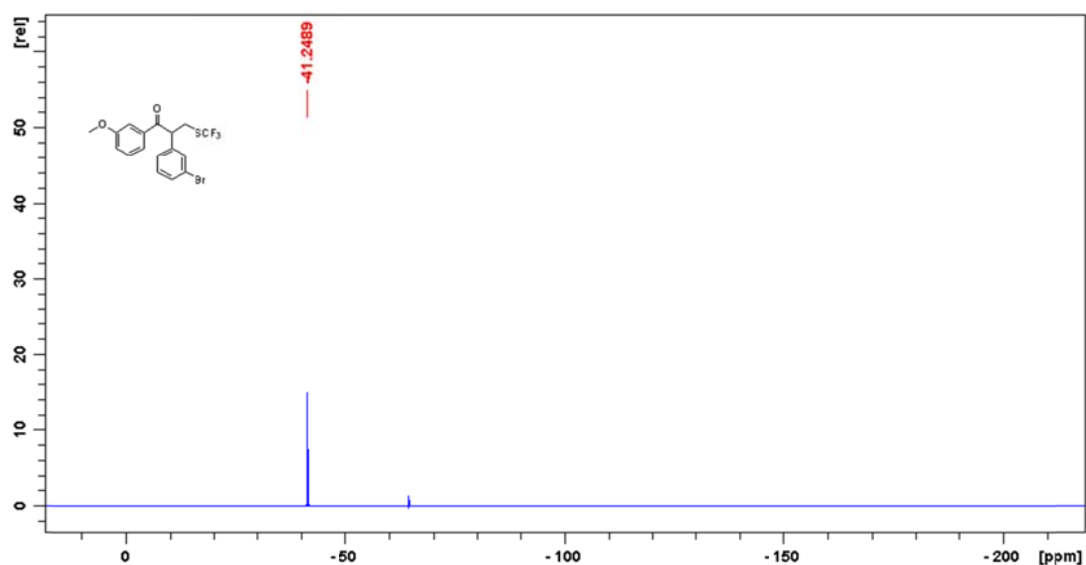


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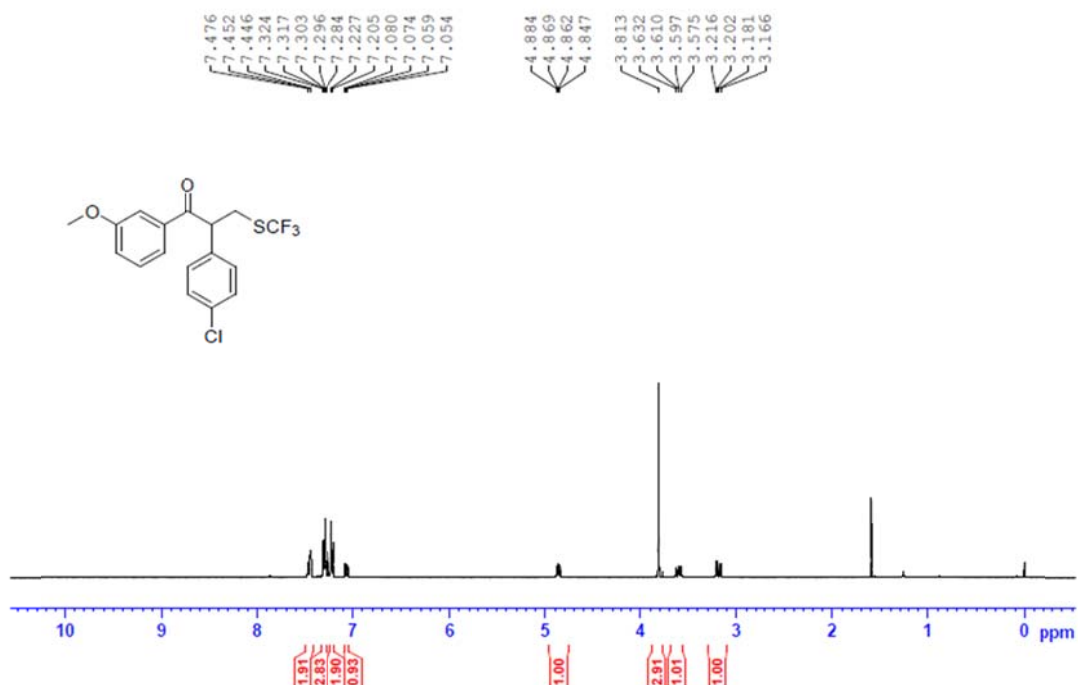
^{19}F NMR (376 MHz, CDCl_3) of 2-(3-bromophenyl)-1-(3-methoxyphenyl)-3-((trifluoromethyl)thio)propan-1-one (3m)

-3-((trifluoromethyl)thio)propan-1-one (3m)



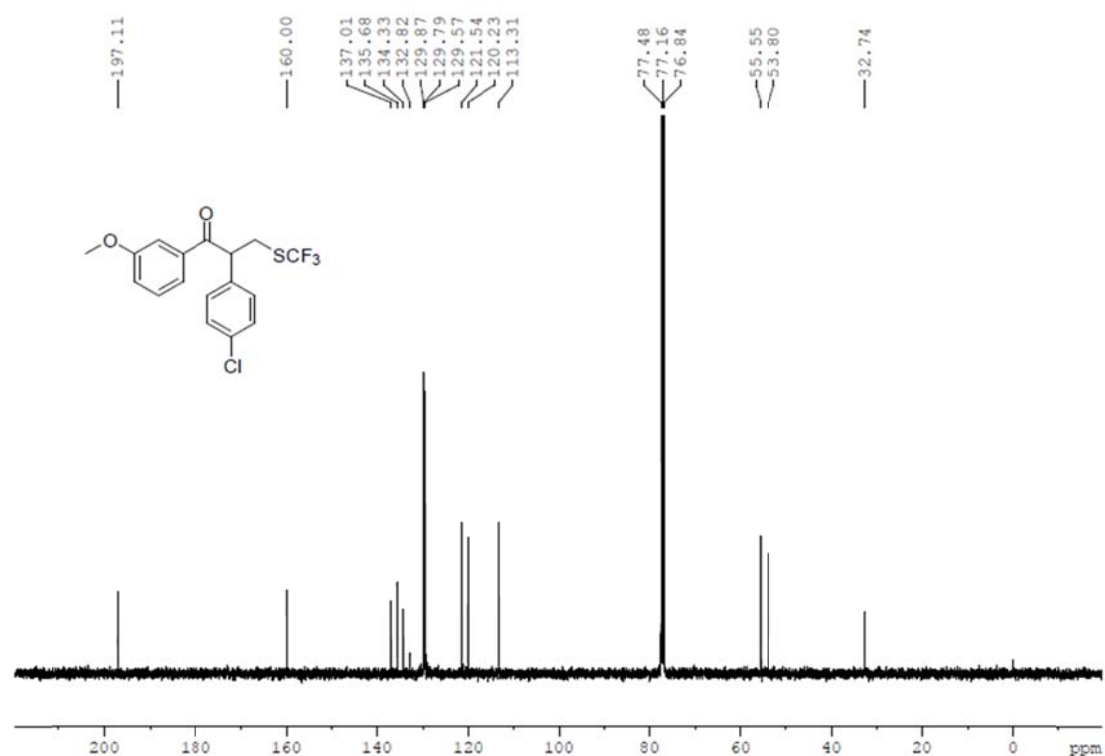
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-3-((trifluoromethyl)thio)propan-1-one (3n)



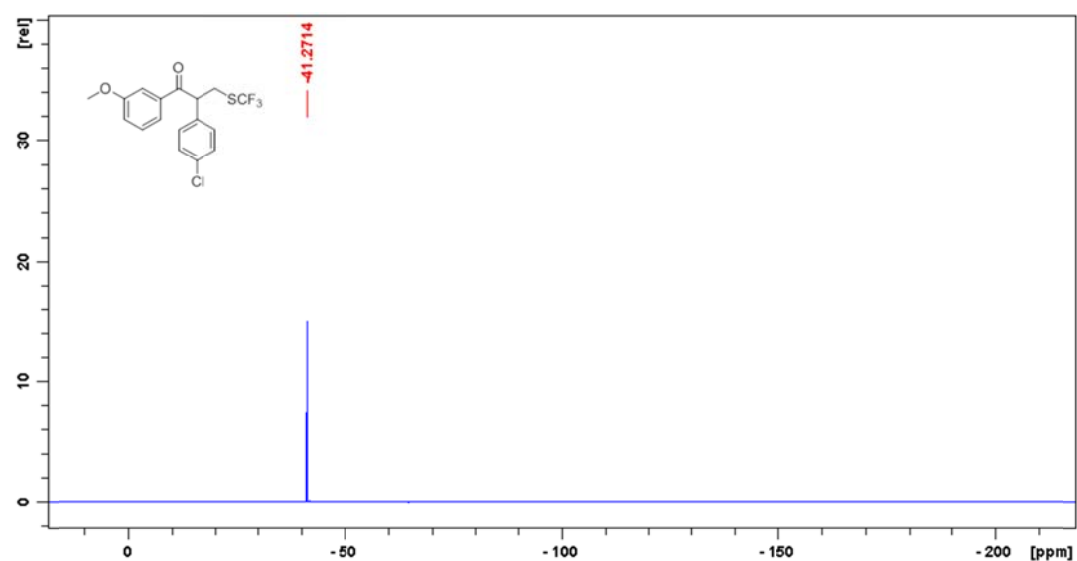
^{13}C NMR (100 MHz, CDCl_3) of 2-(4-chlorophenyl)-1-(3-methoxyphenyl)

-3-((trifluoromethyl)thio)propan-1-one (3n)

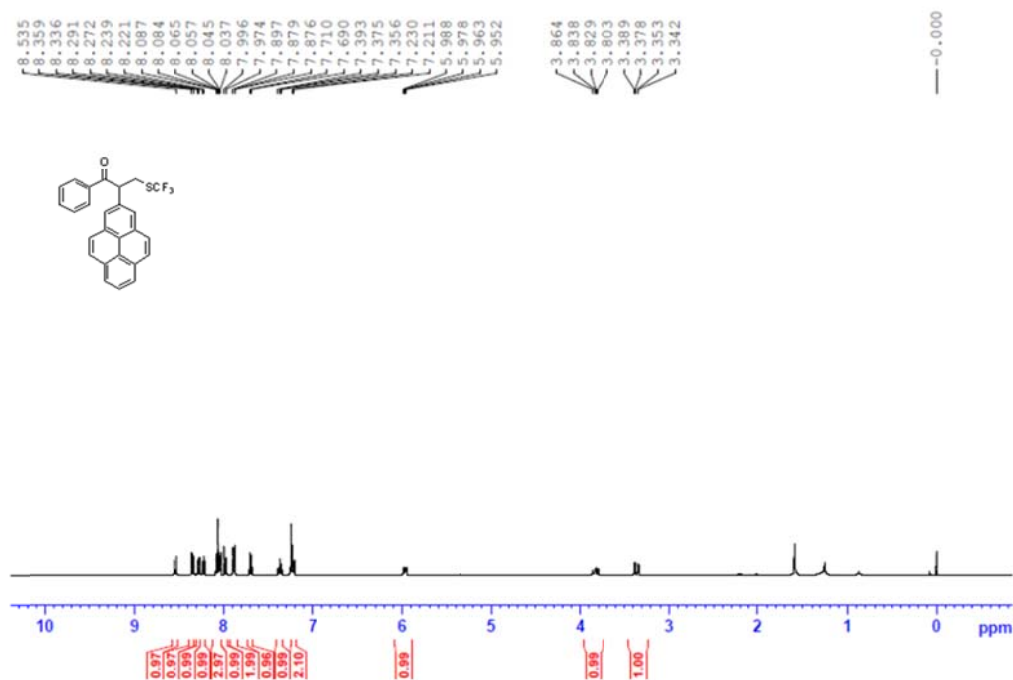


^{19}F NMR (376 MHz, CDCl_3) of 2-(4-chlorophenyl)-1-(3-methoxyphenyl)

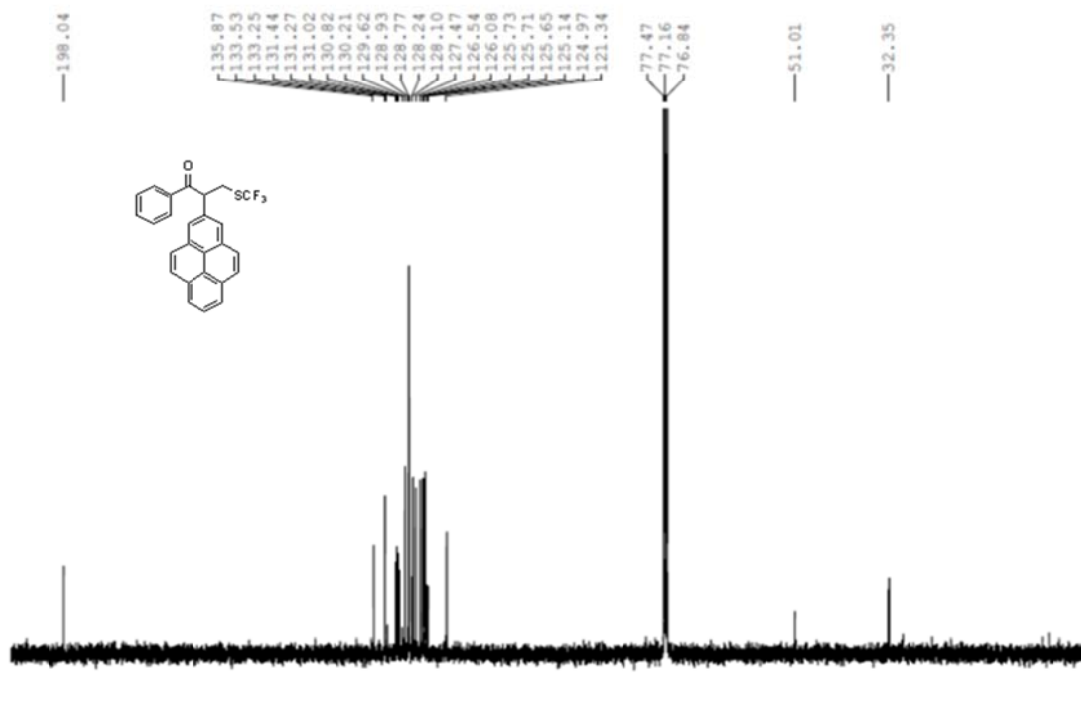
-3-((trifluoromethyl)thio)propan-1-one (3n)



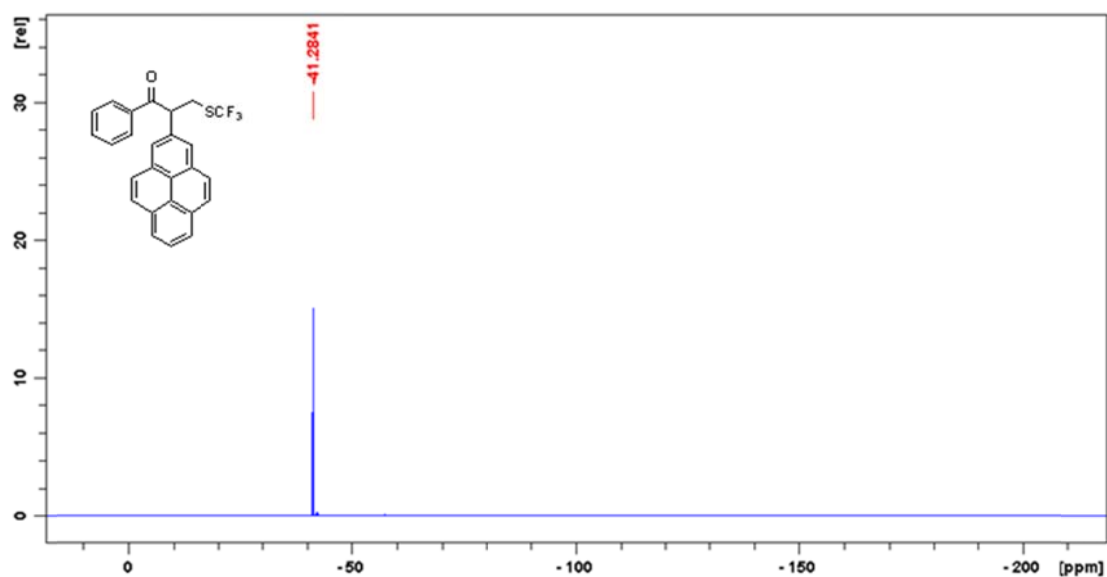
^1H NMR (400 MHz, CDCl_3) of 1-phenyl-2-(pyren-2-yl)-3-((trifluoromethyl)-thio)propan-1-one (3o)



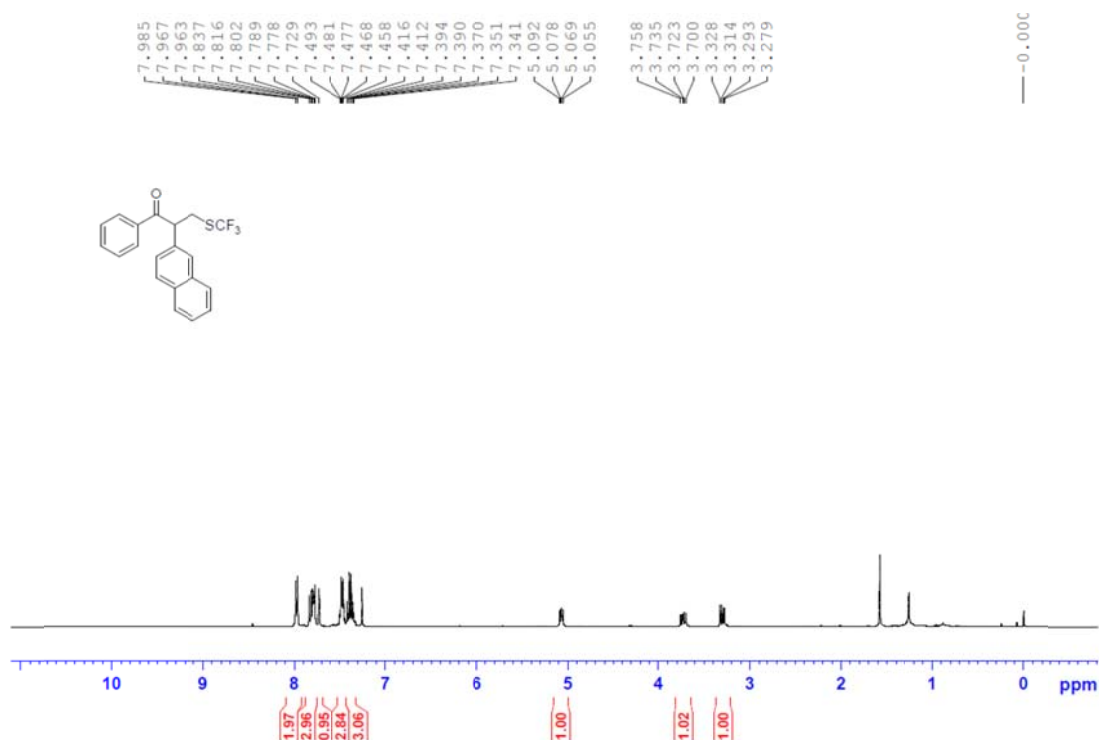
^{13}C NMR (100 MHz, CDCl_3) of 1-phenyl-2-(pyren-2-yl)-3-((trifluoromethyl)-thio)propan-1-one (3o)



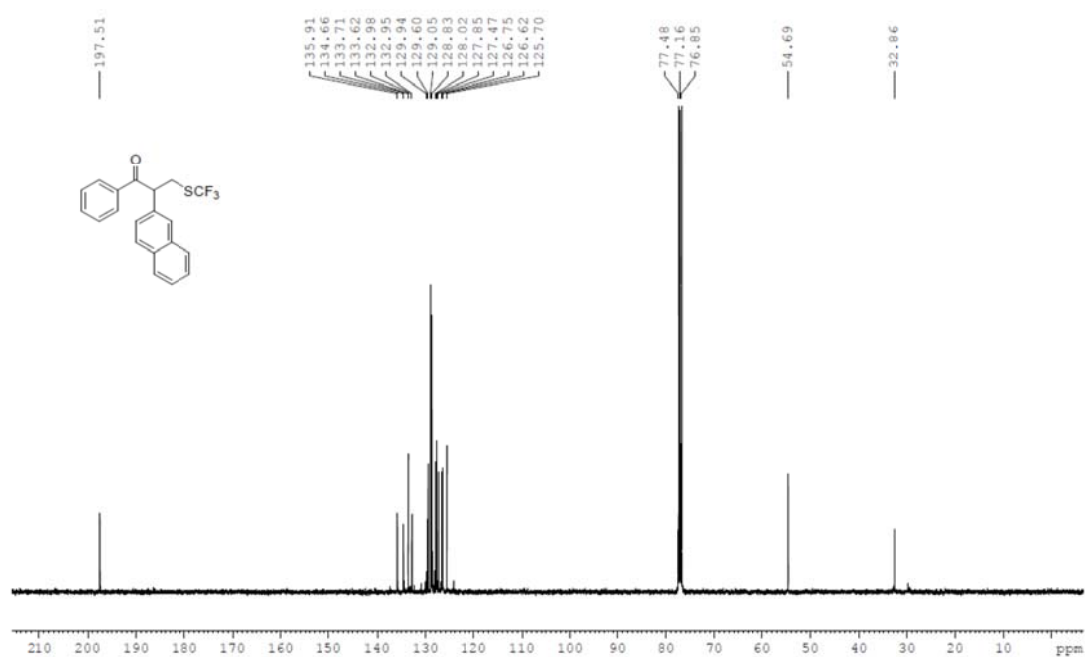
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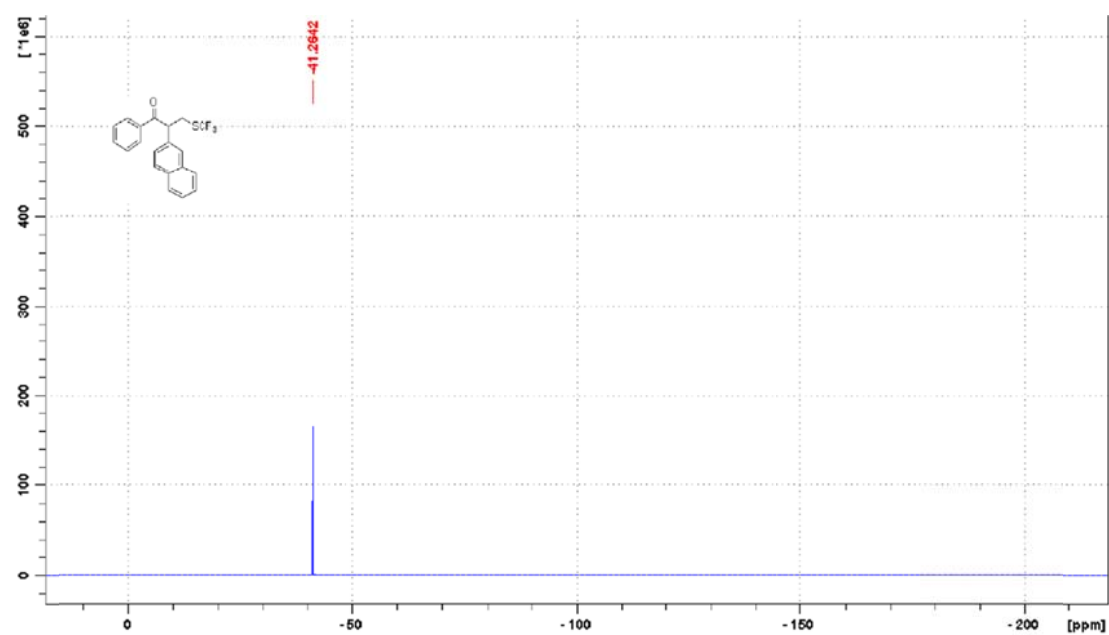
^1H NMR (400 MHz, CDCl_3) of 2-(naphthalen-2-yl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3p)



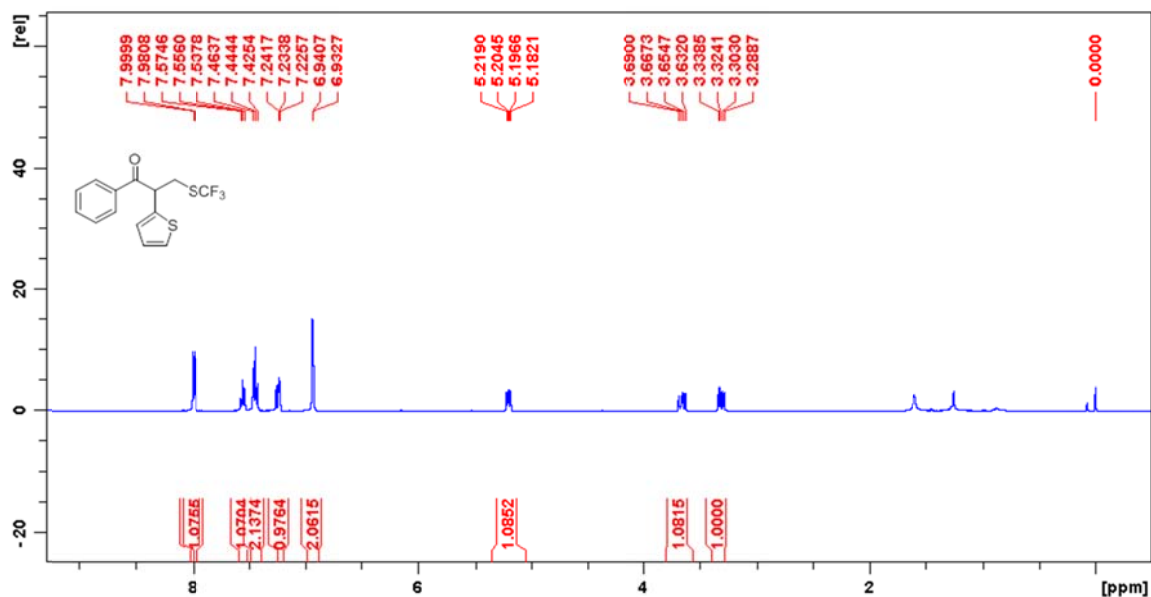
^{13}C NMR (100 MHz, CDCl_3) of 2-(naphthalen-2-yl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3p)



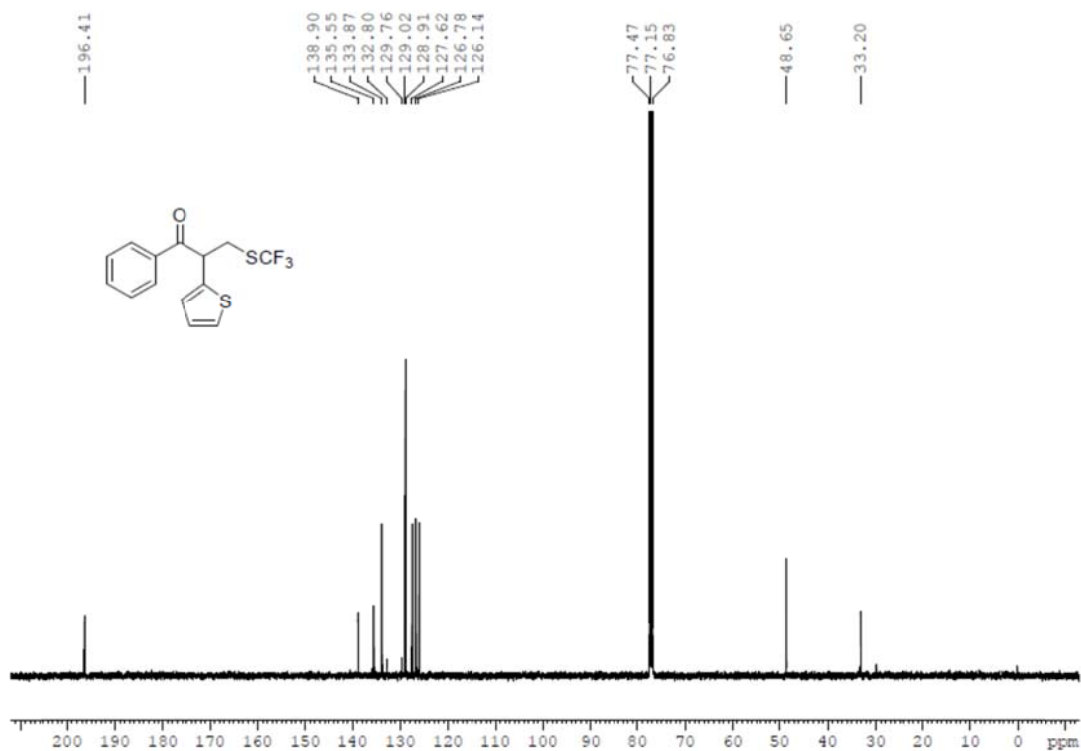
^{19}F NMR (376 MHz, CDCl_3) of 2-(naphthalen-2-yl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3p)



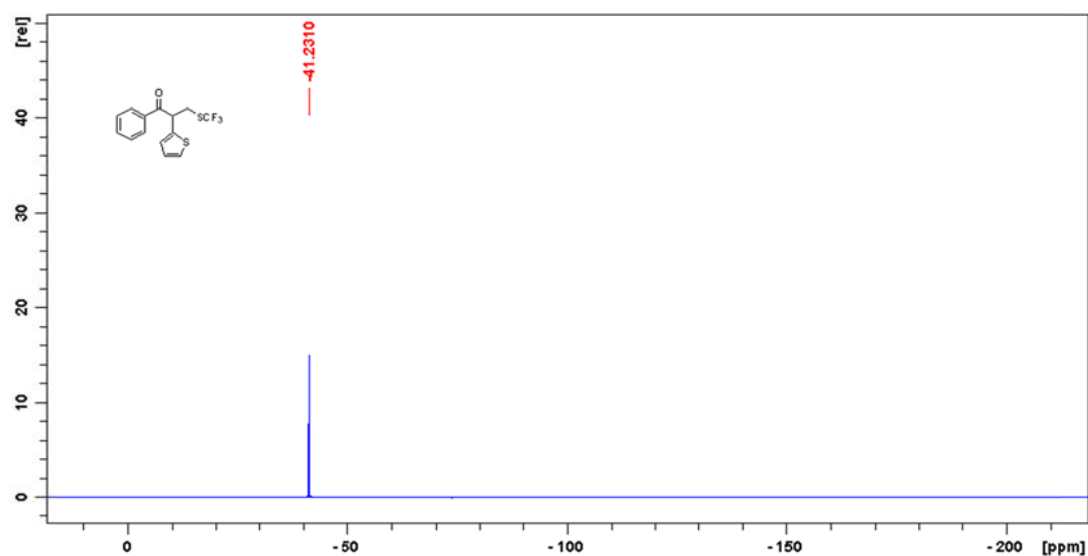
^1H NMR (400 MHz, CDCl_3) of 1-phenyl-2-(thiophen-2-yl)-3-((trifluoromethyl)-thio)propan-1-one (3q)



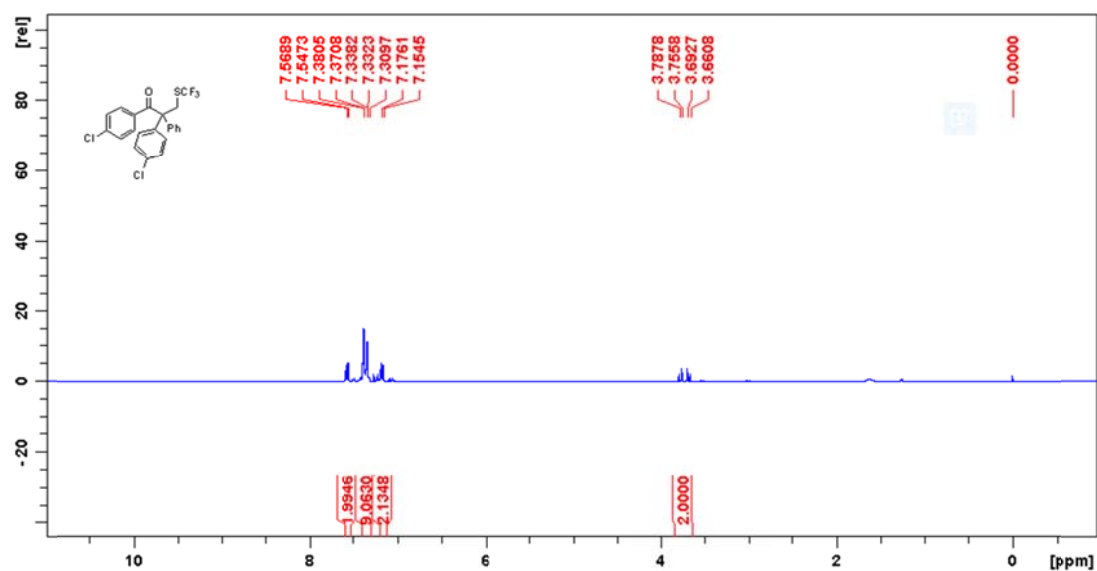
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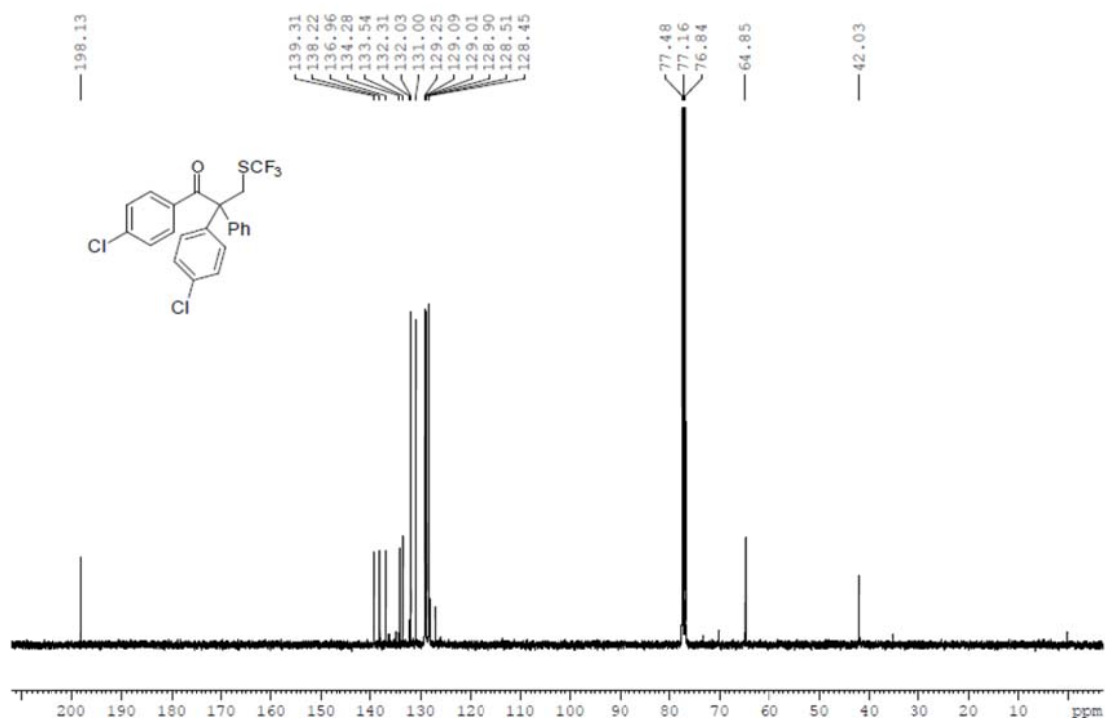
^{19}F NMR (376 MHz, CDCl_3) of 1-phenyl-2-(thiophen-2-yl)-3-((trifluoromethyl)-thio)propan-1-one (3q)



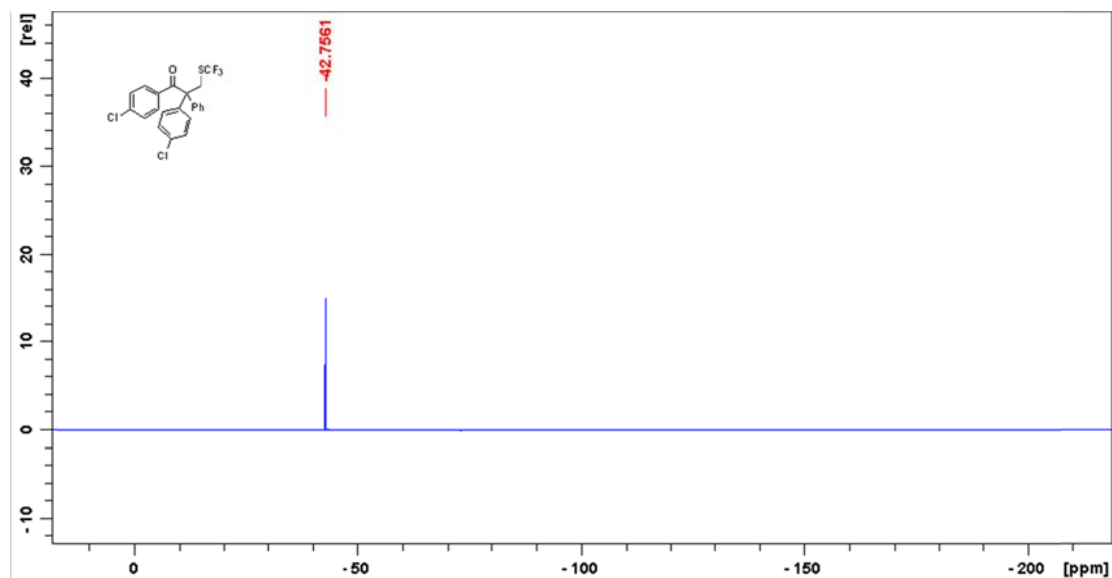
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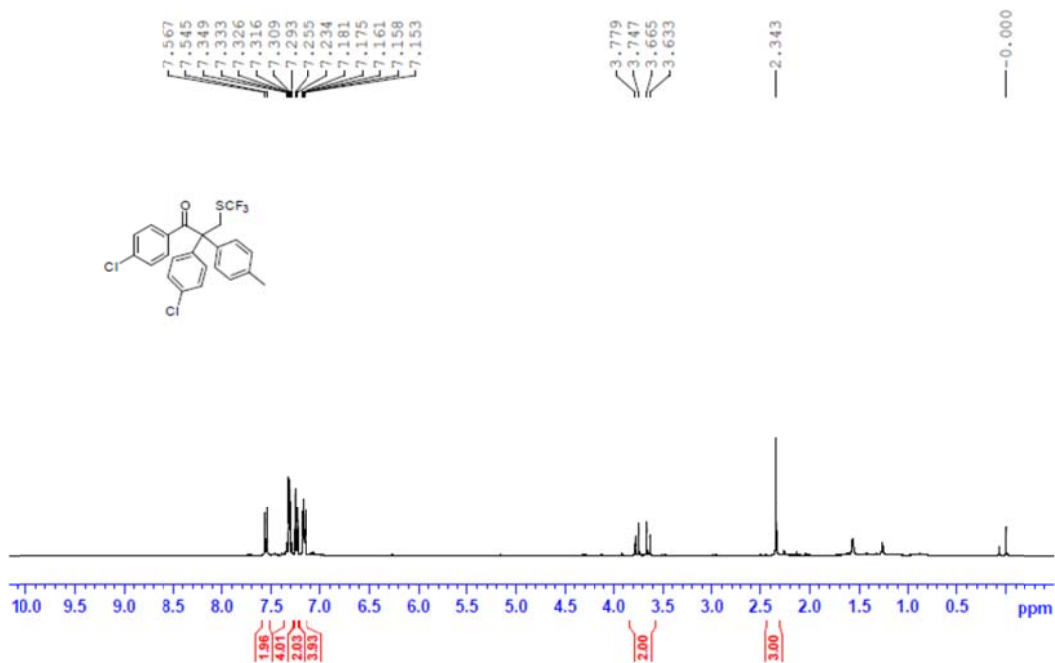
^{13}C NMR (100 MHz, CDCl_3) of 1,2-bis(4-chlorophenyl)-2-phenyl-3-((trifluoromethyl)thio)propan-1-one (3r)



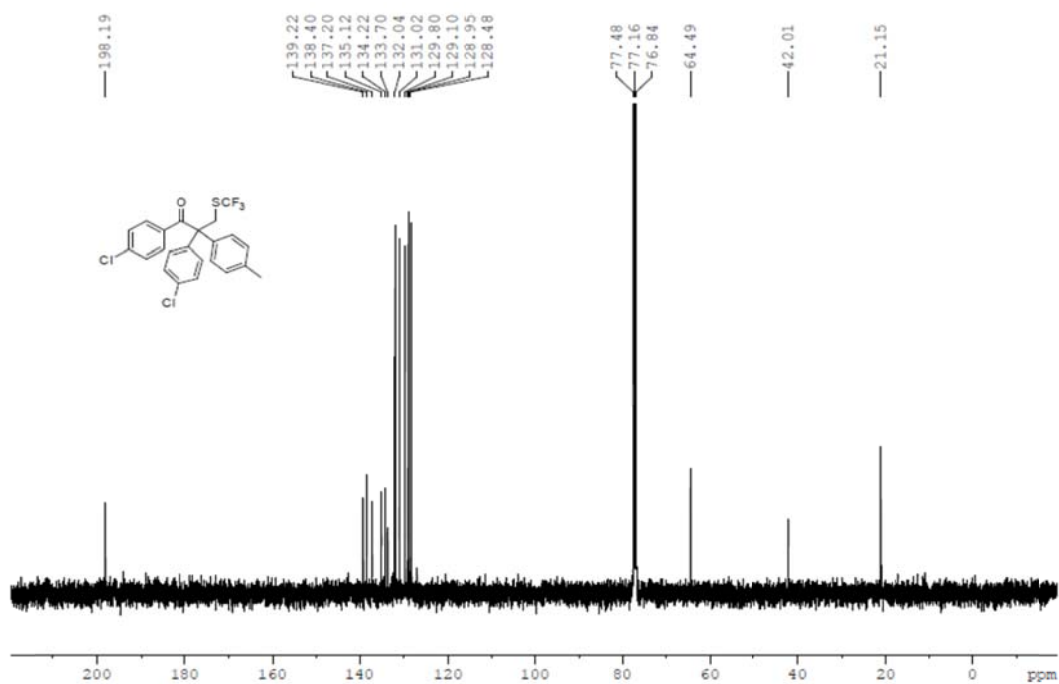
^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(4-chlorophenyl)-2-phenyl-3-((trifluoromethyl)thio)propan-1-one(3r)



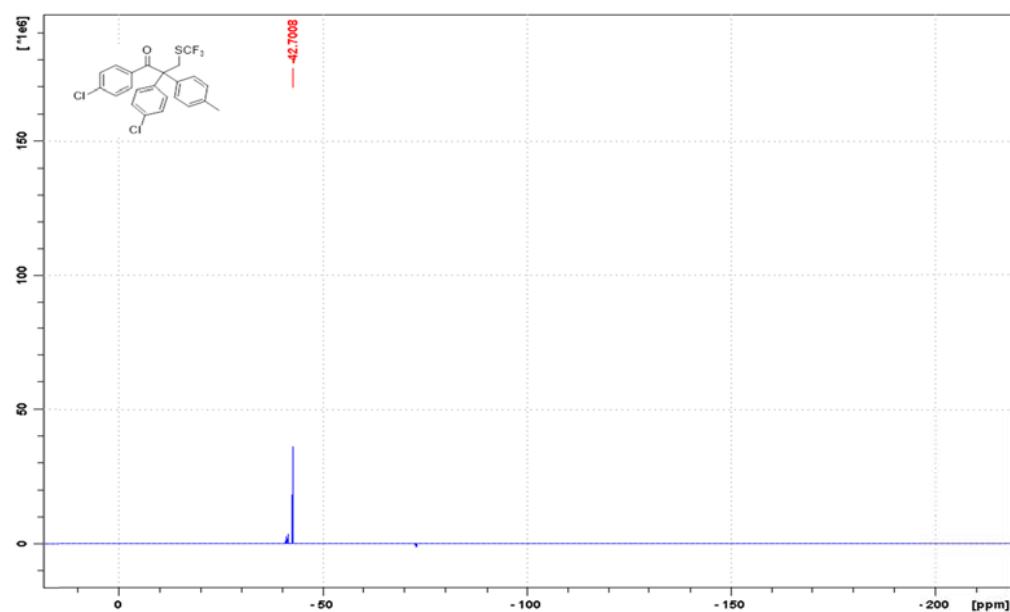
^1H NMR (400 MHz, CDCl_3) of 1,2-bis(4-chlorophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)propan-1-one (3s)



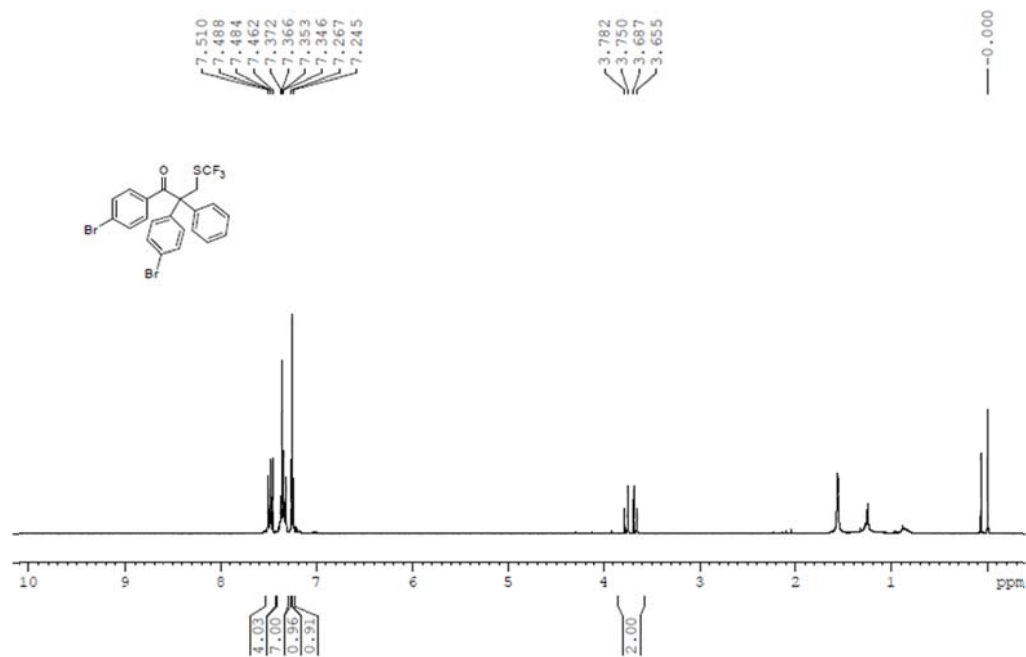
^{13}C NMR (100 MHz, CDCl_3) of 1,2-bis(4-chlorophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)propan-1-one (3s)



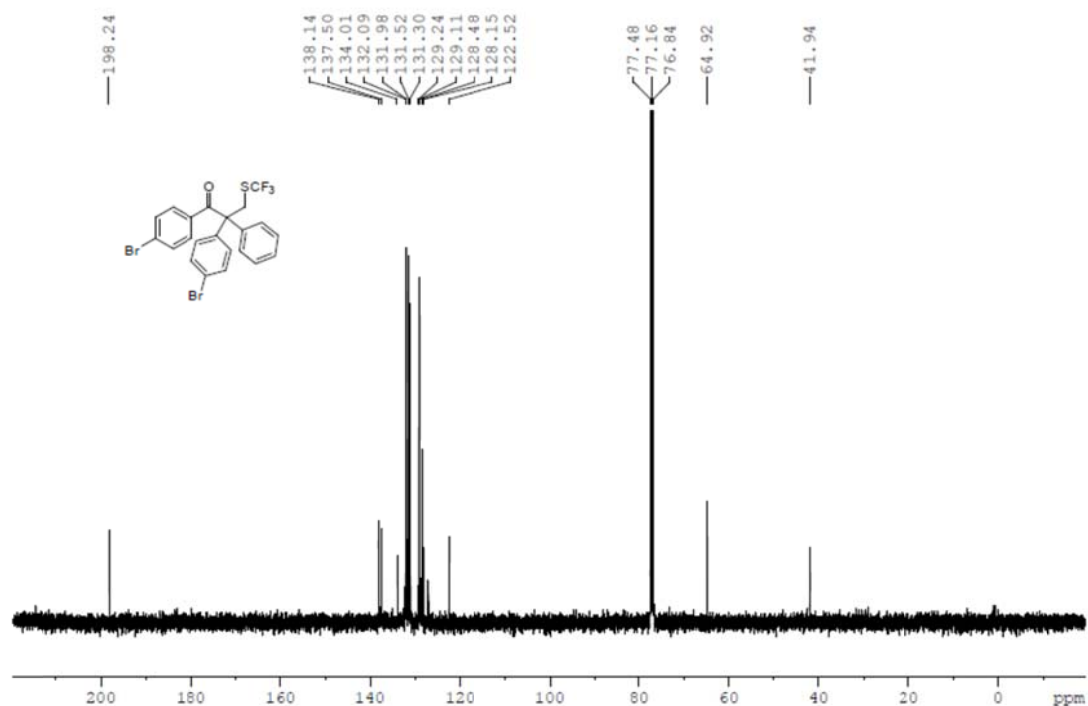
^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(4-chlorophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)propan-1-one (3s)



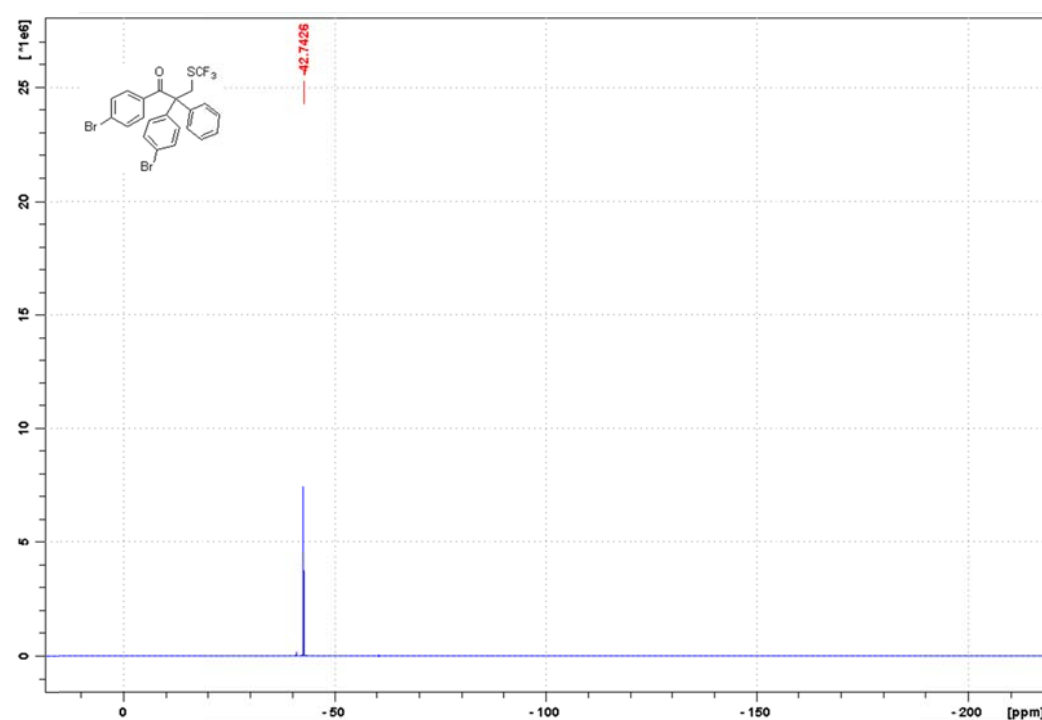
^1H NMR (400 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-2-phenyl-3-((trifluoromethyl)thio)propan-1-one (3t)



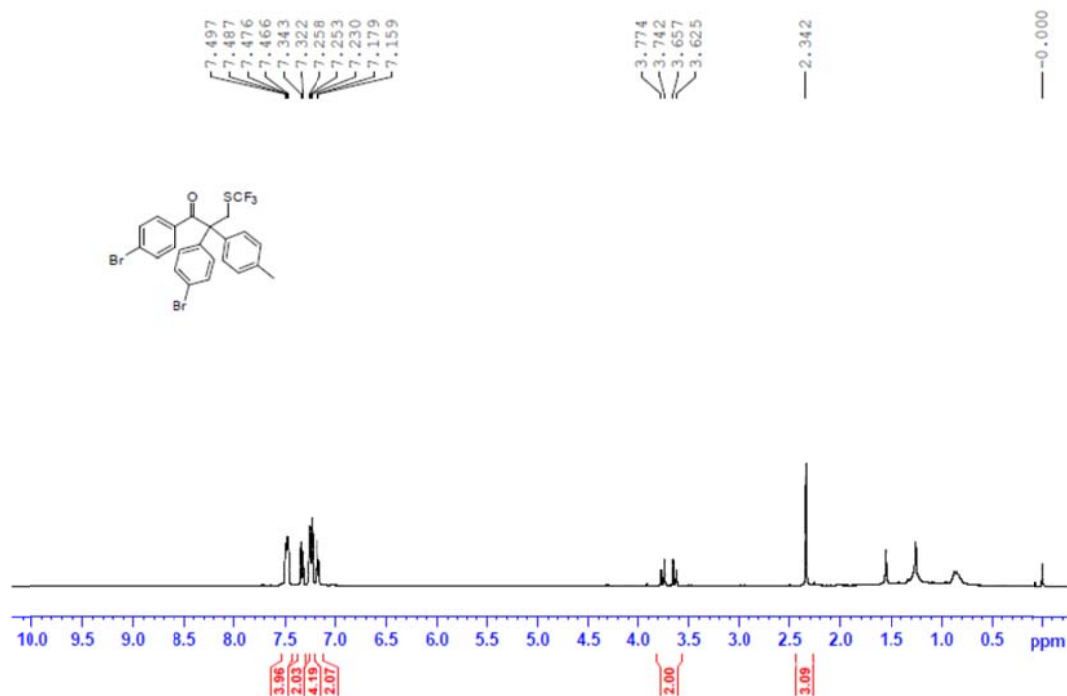
^{13}C NMR (100 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-2-phenyl-3-((trifluoromethyl)thio)propan-1-one (3t)



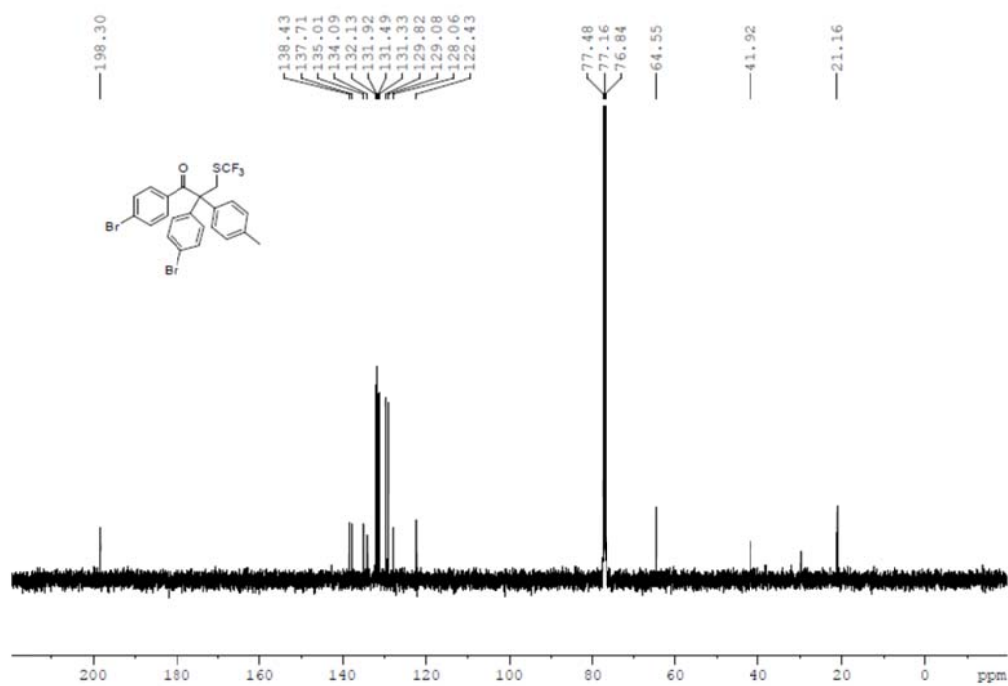
^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)propan-1-one (3t)



^1H NMR (400 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)propan-1-one (3u)



^{13}C NMR (100 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)propan-1-one (3u)



^{19}F NMR (376 MHz, CDCl_3) of 1,2-bis(4-bromophenyl)-2-(p-tolyl)-3-((trifluoromethylthio)propan-1-one (3u)

