N-Heterocyclic Carbene-Catalyzed Cross-Coupling of Aromatic Aldehydes with Activated Alkyl Halides

Mohan Padmanaban, Akkattu T. Biju, and Frank Glorius*

Westfälische Wilhelms-Universität, NRW Graduate School of Chemistry, Organisch-Chemisches Institut, Corrensstraße 40, 48149 Münster, Germany

glorius@uni-muenster.de

Supporting Information

1. General Information

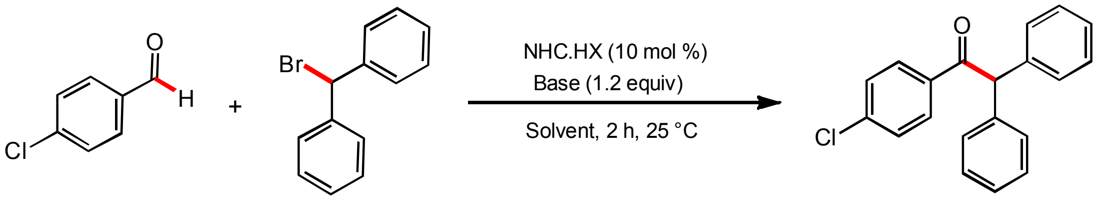
Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. THF was purified by distillation over Na-benzophenone and was transferred under argon. All aldehydes used in the present study were purchased either from Aldrich, Acros or Alfa Aesar and were purified either by distillation or washing with $NaHCO_3$ after dissolving in ether, prior to use. Benzhydryl bromide was purchased from Alfa Aesar, and recrystallized from CH_2Cl_2 before use. 9-Bromofluorene was purchased from Sigma-Aldrich, and recrystallized from hexane before use. Other benzhydryl bromides were synthesized following literature procedures. Ethyl 2-bromo-2-phenylacetate, methyl 2-bromo-2-phenylacetate and 2-bromo-1-phenylpropan-1-one were purchased from Alfa Aesar and used without further purification. Cs_2CO_3 (extra pure) was purchased from Alfa Aesar and stored in the glove box. K_2CO_3 was dried by heating at 110 °C for 12 h and left to cool under argon and stored in the glove box.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 300, or AV 400 MHz INOVA instruments in solvents as indicated. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta H = 7.26$ ppm, $\delta C = 77.16$ ppm).

Infra-red spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (υ) of recorded IR-signals are quoted in cm^{-1}. ESI mass spectra were recorded on a Bruker Daltonics MicroTof.

2. General Procedure for the Optimization of Reaction Conditions



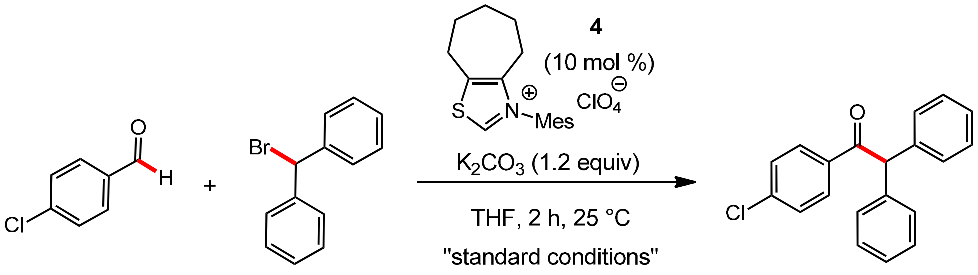
1a **2a** **3a**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the azolium salt (NHC·HX) (0.025 mmol, 0.1 equiv) and base (0.3 mmol, 1.2 equiv) in a glove box. To this mixture, (bromomethylene)dibenzene **2a** (61.7 mg, 0.25 mmol, 1.0 equiv), and 4-chlorobenzaldehyde **1a** (35.1 mg, 0.25 mmol, 1.0 equiv) were added outside the glove box under argon. The mixture was dissolved in 2.5 mL of solvent under argon. The resultant reaction mixture was stirred at 25 °C for 2 h. Then the mixture was diluted with EtOAc (2 mL) and filtered through a pad of silica gel and eluted with EtOAc (10 mL). The solvent was evaporated and the crude sample was analyzed by ^{1}H NMR analysis using CH_2Br_2 (43.4 mg, 18 μL, 0.25 mmol) as the internal standard.

3. Optimization Studies

Our optimization study commenced with the exposure of 4-chlorobenzaldehyde **1a** and (bromomethylene)dibenzene **2a** with thiazolium salt **4** and 1.2 equiv. of K_2CO_3 in THF. The reaction led to the formation of diphenylethanone derivative **3a** in 99% yield (based on ^1H NMR analysis of the crude product, Table 1, entry 1). Remarkably, in contrast to this NHC, other common NHCs derived from **5-8b** are less effective (entries 2-9). The use of bases such as DBU, Et_3N, KO*t*-Bu and Na_2CO_3furnished reduced yields of the product (entries 10-13), but Cs_2CO_3 afforded **3a** in 99% yield (entry 14). The use of other solvents such as 1,4-dioxane, DME, CH_3CN or Et_2O was not found to be beneficial (entries 15-18). Additionally, the reaction carried out using catalytic amounts of base considerably reduced the yield of product (entry 19) indicating that excess of base is needed for excellent conversion. Finally, reducing the catalyst loading to 5 mol % of **4** and 1.1 equiv of Cs_2CO_3 afforded the product **3a** in 93% isolated yield (entry 20).

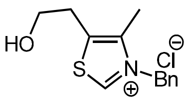
Table 1. Optimization of the Reaction Conditions



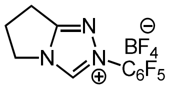
1a **2a** **3a**

entry	variation of the standard conditions[a]	yield of **3** (%)[b]
1	None	99
2	**5** instead of **4**	5
3	**6** instead of **4**	45
4	**6a** instead of **4**	3
5	**6b** instead of **4**	39
6	**7** instead of **4**	0
7	**8** instead of **4**	0
8	**8a** instead of **4**	8
9	**8b** instead of **4**	2
10	DBU instead of K_2CO_3	80
11	Et_3N instead of K_2CO_3	16
12	KO*t*-Bu instead of K_2CO_3	22
13	Na_2CO_3 instead of K_2CO_3	0
14	Cs_2CO_3 instead of K_2CO_3	99
15	1,4-dioxane instead of THF	52
16	DME instead of THF	87
17	CH_3CN instead of THF	46
18	Et_2O instead of THF	2
19	0.2 equiv K_2CO_3 instead of 1.2 equiv of K_2CO_3	28
20	**0.05 equiv 4 and 1.1 equiv of Cs_2CO_3**	**99 (93)**[c,d]

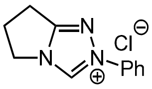
[a] Standard conditions: **1** (0.25 mmol), NHC·HX (10 mol%), K_2CO_3 (1.2equiv), THF (2.5 mL), rt and 2 h. [b]The yields were determined by ^{1}H NMR analysis of crude products using CH_2Br_2 as the internal standard. [c] Isolated yield in parentheses. [d] reaction carried out at rt for 3 h.



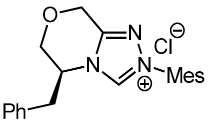
5



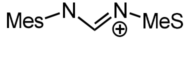
6



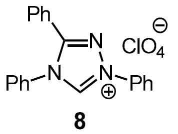
6a



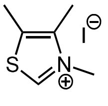
6b



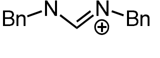
7



8

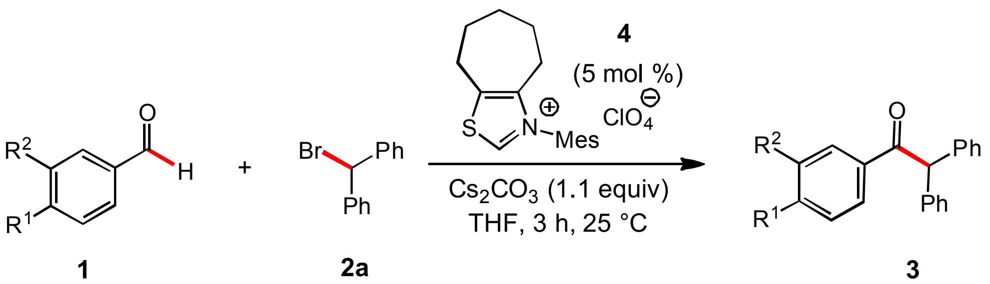


8a



8b

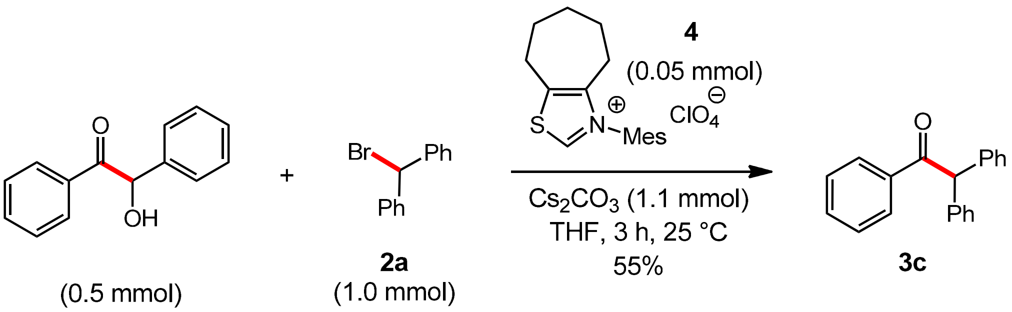
4. General Procedure for NHC-Catalyzed Cross-coupling of Aldehydes with Alkyl Halides



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the thiazolium salt **4** (18.6 mg, 0.05 mmol), Cs_2CO_3 (358.4 mg, 1.1 mmol), in a glove box. To this mixture was added the diaryl bromomethane **2** (1.0 mmol) outside the glove box under argon. The mixture was dissolved in THF (10 mL) and to this stirring solution was added the aldehyde **1** (1.0 mmol), (*solid* aldehydes were weighed in air and *liquid* aldehydes were transferred via syringe). The resultant reaction mixture was kept stirring at 25 °C for 3 h. Then the mixture was diluted with EtOAc (10 mL) and filtered through a pad of silica gel and eluted with EtOAc (20 mL). The solvent was evaporated and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography to afford the corresponding diaryl acetophenones **3**.

5. Employing a pre-formed benzoin as starting material

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the thiazolium salt **4** (18.6 mg, 0.05 mmol), Cs_2CO_3 (358.4 mg, 1.1 mmol), in a glove box. To this mixture was added the (bromomethylene)dibenzene **2a** (247.0 mg, 1.0 mmol) outside the glove box under argon. The mixture was dissolved in THF (10 mL) and to this stirring solution was added the benzoin (106.1 mg, 0.5 mmol). The resultant reaction mixture was kept stirring at 25 °C for 3 h. Then the mixture was diluted with EtOAc (10 mL) and filtered through a pad of silica gel and eluted with EtOAc (20 mL). The solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography to afford the corresponding 1,2,2-triphenylethanone **3c** as a white solid (150.0 mg, 55%)

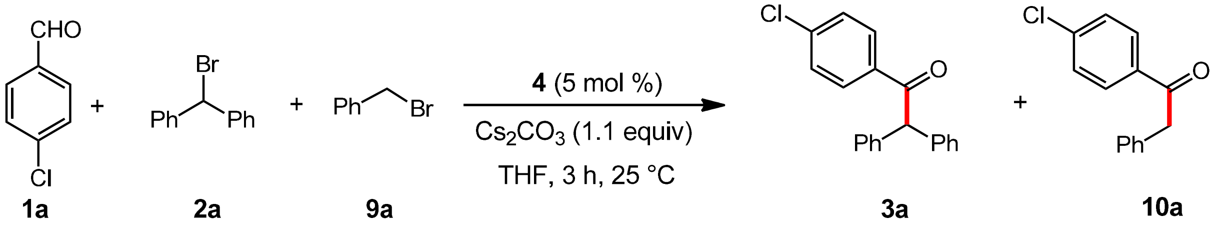


This experiment confirms the reversibility of the formation of Breslow intermediate under the present reaction conditions.

6. Electrophile Competition Experiment

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 4-chlorobenzaldehyde **1a** (35.1 mg, 0.25 mmol), the thiazolium salt **4** (4.7 mg, 0.0125 mmol) and Cs_2CO_3 (89.6 mg, 0.275) in a glove box. To this was added (bromomethylene)dibenzene **2a** (61.8 mg, 0.25 mmol) followed by benzyl bromide **9a** (42.7 mg, 30 µL, 0.25 mmol) outside the glove box. The mixture was dissolved in 2.5 mL of THF under argon. The resulting mixture was then stirred at 25 °C for 3h. After the reaction, the reaction mixture diluted with CH_2Cl_2 (1 mL) and filtered through a small pad of silica gel. It was further eluted with CH_2Cl_2 (5 mL). The solvent was evaporated to obtain the crude products yield was determined by ^1H NMR analysis using CH_2Br_2 (18 µL, 0.25 mmol) as the internal standard (Table 2, entry 3).

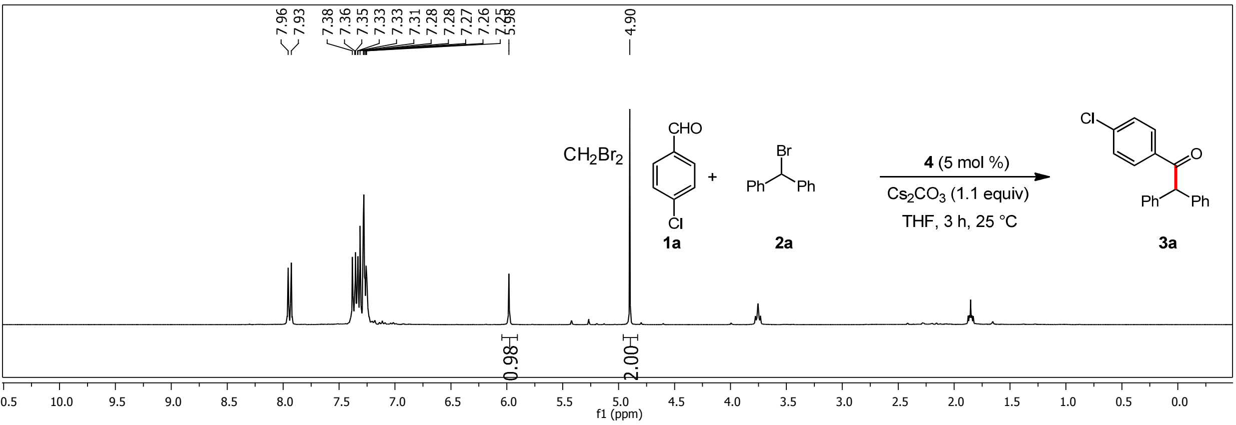
Table 2. Electrophile Competition Experiment



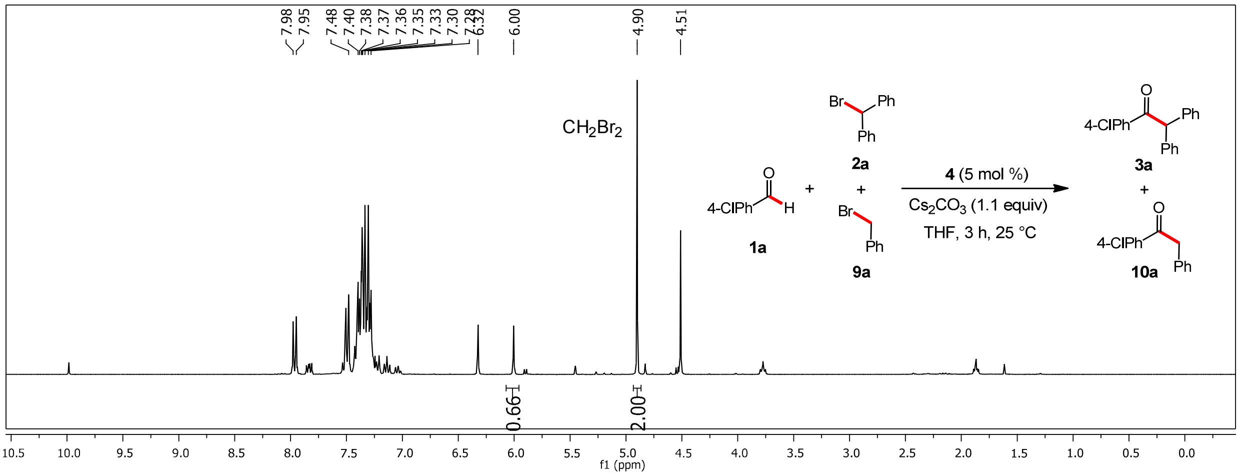
Entry	**2a** (equiv.)	**9a** (equiv.)	Yield of **3a** (%)[a]	Yield of **10a (%)**
1	1	0	98	0
2	0	1	0	0
3	1	1	66	0

[a]The yields were determined by ^1H NMR analysis of crude products using CH_2Br_2 as the internal standard.

^{1}H-NMR of the reaction mixture entry 1

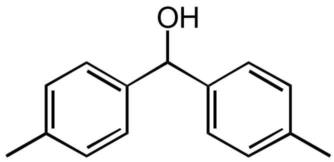


^{1}H-NMR of the reaction mixture entry 3



7. Synthesis and Characterization of Substrates (Benzhydrols)

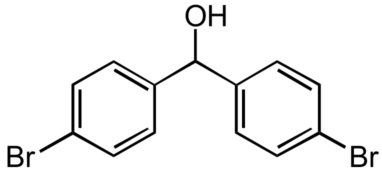
Di-*p*-tolylmethanol[1]



Following the known procedure[2] a flame- dried 100 mL flask was charged with 1-bromo-4-methylbenzene (1.71 g, 1.2 mL, 10 mmol) and THF (25 mL) under argon. The reaction mixture was cooled to −78°C, and *n*-BuLi (1.6M in hexane, 6.3 mL, 10 mmol) was added dropwise and the reaction mixture was stirred for 20 minutes. 4-methylbenzaldehyde (1.18 g, 1.3 mL, 10 mmol), as a solution in THF (25 mL) was added. The reaction mixture was stirred further for 20 minutes, after 20 minutes H_2O (50 mL) was added. The reaction mixture was extracted with CH_2Cl_2 (3 x 25 mL), the combined organic phases were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography to give di-*p*-tolylmethanol as a white solid (1.96 g, 93%). However, this compound was not completely pure and used for the bromination step without any further purification.

R*f* (EtOAc/pentane = 10/90): 0.35; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.31- 7.28 (m, 4H), 7.22-7.17 (m, 4H), 5.79 (s, 1H), 2.40 (s, 1H), 2.38 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 141.3, 137.2, 129.3, 126.6, 76.0, 21.2. **ESI-MS**: calculated $[M+Na]^+$ for $C_{15}H_{16}ONa$: 235.1093, found: 235.1090. **ATR-FTIR (cm^{-1})**: 3347, 3026, 2921, 1908, 1804, 1511, 1450, 1341, 1272, 1170, 1036, 1020, 946, 854, 807, 757, 610, 554.

Bis(4-bromophenyl)methanol[2]



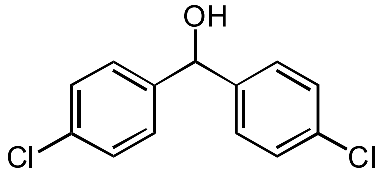
Following the known procedure[2] a flame- dried 100 mL flask was charged with 1,4-dibromobenzene (2.35 g, 10 mmol) and THF (25 mL) under argon. The reaction mixture was cooled to −78°C, and *n*-BuLi (1.6M in hexane, 6.3 mL, 10 mmol) was added dropwise and the reaction mixture was stirred for 20 minutes. 4-bromobenzaldehyde (1.85 g, 10 mmol), as a solution in THF (25 mL) was added. The reaction was stirred further for 20 minutes, after 20 minutes H_2O (50 mL) was added. The reaction mixture was extracted with CH_2Cl_2 (3 x 25 mL), the combined organic phases were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography to give bis (4-bromophenyl) methanol as a white solid (2.70 g, 79%).

---

[1] White, R. J.; Price, J.G.; Plucinski, K. P.; Frost, G. F.; *Tetrahedron Letters*, **2009**, *50*, 7365.
[2] Brown, A. R.; Kuo, W.-H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2010**, *132*, 9286.

R*f* (EtOAc/pentane = 10/90): 0.27; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.49- 7.44 (m, 4H), 7.24-7.20 (m, 4H), 5.75 (s, 1H), 2.16 (bs, 1H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 142.4, 131.9, 128.3, 121.9, 75.2. **ESI-MS**: calculated $[M\text{-}OH]^+$ for $C_{13}H_9Br_2$: 324.9045, found: 324.9053. **ATR-FTIR (cm^{-1})**: 3336, 2902, 1905, 1788, 1591, 1483, 1403, 1329, 1190, 1070, 1038, 1007, 944, 859, 791, 694, 645, 551.

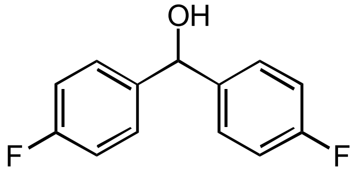
Bis(4-chlorophenyl)methanol[2]



Following the known procedure[3] sodium borohydride (0.76 g, 20 mmol) was added in portions to a stirred solution of bis(4-chlorophenyl)methanone (2.51g, 10 mmol) in a mixture of MeOH (20 mL) and THF (30 mL) at 0° C. The resulting mixture was warmed to room temperature and stirred for 1h. Excess of sodium borohydride was then quenched with acetone, THF and MeOH was removed in vacuo. The residue was diluted with EtOAc (100 mL). The organic phase was washed with water (2 x 25 mL) and brine (50 mL), dried over $MgSO_4$, filtered and concentrated in vacuo to yield bis(4-chlorophenyl)methanol as a white solid (2.33g, 92%).

R*f* (EtOAc/pentane = 10/90): 0.29; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.33 – 7.28 (m, 8H), 5.78 (s, 1H), 2.19 (s, 1H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 141.9, 133.8, 128.9, 128.0, 75.1. **ESI-MS**: calculated $[M\text{-}OH]^+$ for $C_{13}H_9Cl_2$: 235.0076, found: 235.0070; **ATR-FTIR (cm^{-1})**: 3340, 2904, 2662, 2288, 1905, 1597, 1487, 1407, 1330, 1191, 1088, 1038, 944, 857, 827, 796, 650, 517.

Bis(4-fluorophenyl)methanol[4]



Following the known procedure[2] a flame- dried 100 mL flask was charged with 1-bromo-4-fluorobenzene (1.74 g, 1.1 mL, 10 mmol) and THF (25 mL) under argon. The reaction mixture was cooled to −78° C, and *n*-BuLi (1.6M in hexane, 6.3 mL, 10 mmol) was added dropwise and the reaction mixture was stirred for 20 minutes. 4-fluorobenzaldehyde (1.85 g, 1.1 mL, 10 mmol), as a solution in THF (25 mL) was added. The reaction was stirred further for 20 minutes, to this H_2O (50 mL) was added. The reaction

---

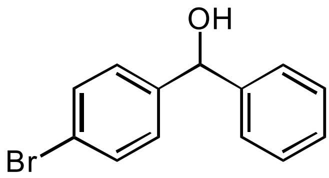
[3] Kharul, K. R.; Goswami, A.; Gite, A.; Godha, K. A.; Jain, M.; Patel, P. R.; *Synthetic communications*, **2008**, 38, *11*, 1703-1717.

[4] Forrat, J. V.; Diego J. R.; Yus, M.; *Tetrahedron: Asymmetry,* **2007**, *18*, 400.

mixture was extracted with CH_2Cl_2 (3 x 25 mL), the combined organic phases were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography to give bis(4-fluorophenyl)methanol as a white solid (1.66 g, 75%).

R*f* (EtOAc/pentane = 10/90): 0.22; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.34- 7.27 (m, 4H), 7.06-6.98 (m, 4H), 5.78 (s, 1H), 2.45 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.3, 139.5, 128.3, 115.5, 75.1. **ESI-MS**: calculated $[M-OH]^+$ for $C_{13}H_9F_2$: 203.0667, found: 203.0662; **ATR-FTIR (cm^{-1})**: 3254, 2891, 1897, 1603, 1506, 1415, 1327, 1219, 1146, 1184, 1156, 823, 781, 677, 596, 548, 530.

(4-bromophenyl)(phenyl)methanol[1]

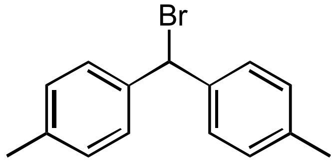


Following the known procedure[3] sodium borohydride (1.52 g, 40 mmol) was added in portions to a stirred solution of (4-bromophenyl)(phenyl)methanone (2.61 g, 10 mmol) in MeOH (40 mL) at 0° C. The resulting mixture was warmed to room temperature and stirred for 1h. Excess of sodium borohydride was then quenched with acetone and MeOH was removed in vacuo. The residue was diluted with EtOAc (100 mL). The organic phase was washed with water (2 x 25 mL) and brine (50 mL), dried over $MgSO_4$ filtered and concentrated in vacuo to yield (4-bromophenyl)(phenyl)methanol as a white solid (2.44 g, 93%).

R*f* (EtOAc/pentane = 10/90): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.47-7.44 (m, 2H), 7.37-7.31 (m, 4H), 7.28-7.24 (m, 3H), 5.79 (s, 1H), 2.07 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 143.5, 142.9, 131.7, 128.8, 128.4, 128.0, 126.7, 121.6, 75.8. **ESI-MS**: calculated $[M-OH]^+$ for $C_{13}H_{10}Br$: 244.9960, found: 244.9963. **ATR-FTIR (cm^{-1})**: 3349, 2904, 1589, 1482, 1453, 1399, 1345, 1287, 1192, 1109, 1070, 1035, 1007, 920, 846, 791, 758, 696, 616, 551.

8. Synthesis and Characterization of Substrates (Benzhydryl Bromides)

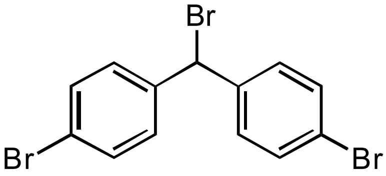
4,4'-(bromomethylene)bis(methylbenzene) (2o)[5]



Following the known procedure[2] a flame-dried 25 mL round-bottom flask was charged with di-*p*-tolylmethanol (1.06 g, 5.0 mmol) and benzene (15 mL) under argon. AcBr (1.7 mL, 22.3 mmol) was added, and the reaction was stirred at room temperature for 6 h. The reaction mixture was concentrated to give a yellowish residue; the residue was diluted with Et_2O (100 mL). The organic phase was washed with saturated $NaHCO_3$ solution (2 x 25 mL) and brine (50 mL), dried over $MgSO_4$, filtered and concentrated in vacuo to yield 4,4'-(bromomethylene)bis(methylbenzene) as a yellow oil (0.80 g, 58%). Attempts to further purify this compound failed due to decomposition.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.39 (m, 4H), 7.20-7.17 (m, 4H), 6.32 (s, 1H), 2.38 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 138.5, 137.9, 129.3, 128.4, 55.9, 21.2. **ESI-MS**: calculated $[M-Br]^+$ for $C_{15}H_{15}$: 195.1168, found: 195.1163. **ATR-FTIR (cm^{-1})**: 2922, 1905, 1612, 1511, 1449, 1379, 1182, 1117, 1021, 818, 669, 632, 543.

4,4'-(bromomethylene)bis(bromobenzene) (2p)[2]



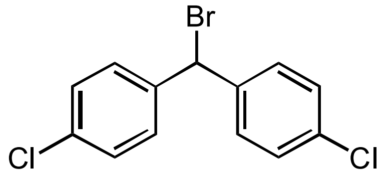
Following the known procedure[2] a flame-dried 25 mL round-bottom flask was charged with bis(4-bromophenyl)-methanol (1.71 g, 5.0 mmol) and benzene (15 mL) under argon. AcBr (1.7 mL, 22.3 mmol) was added, and the reaction was stirred at room temperature for 6 h. The reaction mixture was concentrated to give a yellowish residue; which was recrystallized from hexane to give 4,4'-(bromomethylene)bis(bromobenzene) as a white solid (1.36 g, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.45 (m, 4H), 7.32-7.28 (m, 4H), 6.16 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.7, 131.9, 130.1, 122.5, 53.3. **EI-MS**: calculated $[M-Br]^+$ for $C_{13}H_9Br_2$: 324.9051, found: 324.9048. **ATR-FTIR (cm^{-1})**: 1902, 1786, 1749, 1582, 1484, 1398, 1188, 1070, 1007, 852, 811, 786, 726, 696, 635, 614.

---

[5] Weber, E.; Seichter, W.; Goldberg, I.; *Chem. Ber.* **1990**, *123*, 811.

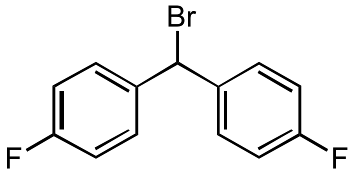
4, 4’-(bromomethylene)bis(chlorobenzene) (2q)[2]



Following the known procedure[2] a flame-dried 25 mL round-bottom flask was charged with 4, 4’-dichlorobenzhydrol (1.26 g, 5.0 mmol) and benzene (15 mL) under argon. AcBr (1.7 mL, 22.3 mmol) was added, and the reaction was stirred at room temperature for 6 h. The reaction mixture was concentrated to give an orange solid, which was recrystallized from hexane to give 4,4’-dichlorobenzhydryl bromide as a white solid (1.40 g, 74% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.30 (m, 8H), 6.20 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.3, 134.3, 129.9, 128.9, 53.3. **ESI-MS**: calculated $[M-Br]^+$ for $C_{13}H_9Cl_2$: 235.0076, found: 235.0092. **ATR-FTIR (cm^{-1})**: 3051, 2360, 1903, 1786, 1680, 1642, 1588, 1487, 1402, 1193, 1089, 1011, 856, 814, 791, 732, 660, 617, 528.

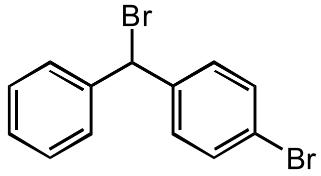
4,4'-(bromomethylene)bis(fluorobenzene) (2r)[2]



Following the known procedure[2] a flame-dried 25 mL round-bottom flask was charged with 4,4’-difluorobenzhydrol (1.10 g, 5.0 mmol) and benzene (15 mL) under argon. AcBr (1.7 mL, 22.3 mmol) was added, and the reaction was stirred at room temperature for 6h. The reaction mixture was concentrated to give a yellowish residue; the residue was diluted with Et_2O (100 mL). The organic phase was washed with saturated $NaHCO_3$ solution (2 x 25 mL) and brine (50 mL), dried over $MgSO_4$, filtered and concentrated in vacuo to yield 4,4'-bromomethylene)bis(fluorobenzene) as a yellow oil (1.00 g, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.39 (m, 4H), 7.07-6.99 (m, 4H), 6.26 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.4, 136.9, 130.3, 115.7, 53.6. **ESI-MS**: calculated $[M-Br]^+$ for $C_{13}H_9F_2$: 203.0667, found: 203.0668. **ATR-FTIR (cm^{-1})**: 1895, 1604, 1506, 1412, 1302, 1230, 1157, 1099, 1015, 834, 728, 634, 619, 569, 522.

1-bromo-4-(bromo(phenyl)methyl)benzene (2s)[5]

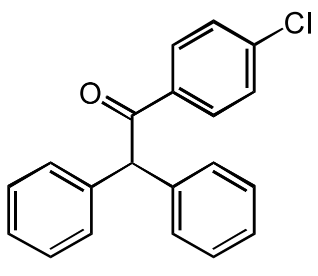


Following the known procedure[2] a flame-dried 25 mL round-bottom flask was charged with (4-bromophenyl)(phenyl)methanol (1.32 g, 5.0mmol) and benzene (15 mL) under argon. AcBr (1.7 mL, 22.3 mmol) was added, and the reaction was stirred at room temperature for 6 h. The reaction mixture was concentrated to give a yellowish residue; the residue was diluted with Et_2O (100 mL). The organic phase was washed with saturated $NaHCO_3$ solution (2 x 25 mL) and brine (50 mL), dried over $MgSO_4$, filtered and concentrated in vacuo to yield 1-bromo-4-(bromo(phenyl)methyl)benzene as a yellow oil (1.20 g, 73%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.41 (m, 4H), 7.38-7.29 (m, 5H), 6.23 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.5, 140.3, 131.8, 130.2, 128.8, 128.5, 128.4, 122.2, 54.4. **ESI-MS**: calculated $[M-Br]^+$ for $C_{13}H_{10}Br$: 244.9906, found: 245.0092. **ATR-FTIR (cm^{-1})**: 1901, 1742, 1588, 1486, 1451, 1403, 1339, 1289, 1231, 1183, 1155, 1072, 1072, 1010, 838, 696, 644, 616, 594.

9. Synthesis and Characterization of Products

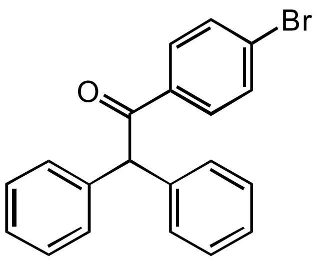
1-(4-Chlorophenyl)-2,2-diphenylethanone (3a)[6]



Following the general procedure, treatment of 4-chloro benzaldehyde **1a** (140.5 mg, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(4-chlorophenyl)-2,2-diphenylethanone **3a** as a white solid (285.0 mg, 93%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.50; **^{1}H NMR (300 MHz, $CDCl_3$)** δ7.92-7.90 (m, 2H), 7.36-7.29 (m, 6H), 7.24-7.22 (m, 6H), 5.95 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.1, 139.6, 138.9, 135.2, 130.5, 129.2, 129.1, 128.9, 127.4, 59.7. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{15}ClONa$: 329.0709, found: 329.0701. **ATR-FTIR (cm^{-1})**: 3028, 1677, 1588, 1573, 1493, 1453, 1400, 1359, 1278, 1208, 1174, 1092, 1079, 1031, 994, 862, 831, 814, 746, 697, 563.

1-(4-Bromophenyl)-2,2-diphenylethanone (3b)



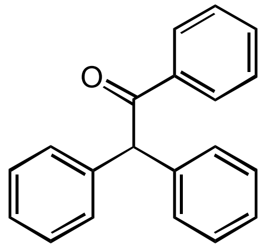
Following the general procedure, the treatment of 4-bromo-benzaldehyde **1b (**185.0 mg, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(4-bromophenyl)-2,2-diphenylethanone **3b** as a white solid (320.0 mg, 91%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.58; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.85-7.82 (m, 2H), 7.54-7.51 (m, 2H), 7.34-7.22 (m, 10H), 5.94 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.3, 138.8, 135.6, 132.1, 130.6, 129.2, 128.9, 128.4, 127.4, 59.7. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{15}BrONa$: 373.0204, found: 373.0198. **ATR-FTIR (cm^{-1})**: 3027, 2925, 2341, 1677, 1583, 1569, 1494, 1453, 1396, 1359, 1277, 1207, 1069, 1031, 993, 862, 830, 746, 97, 618, 563.

---

[6] Nilsson, P.; Larhed, M.; Hallberg, A. *J. Am. Chem. Soc.* **2001**, *123*, 8217.

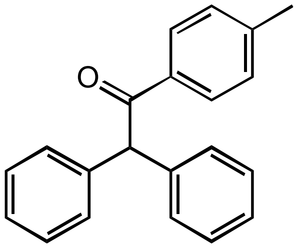
1,2,2-Triphenylethanone (3c)[6]



Following the general procedure, treatment of benzaldehyde **1c** (106.1 mg, 101 μL, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1,2,2-triphenylethanone **3c** as a white solid (190.0 mg, 70%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.40; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.08-8.04 (m, 2H), 7.55-7.47 (m, 1H), 7.49-7.25 (m, 12H), 6.10 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 198.3, 139.2, 136.9, 133.2, 129.3, 129.1, 128.8, 128.7, 127.2, 59.5. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{16}ONa$: 295.1093, found: 295.1081. **ATR-FTIR (cm^{-1})**: 3062, 3030, 1679, 1595, 1579, 1494, 1449, 1395, 1358, 1293, 1272, 1233, 1204, 1181, 1076, 1032, 1012, 998, 926.

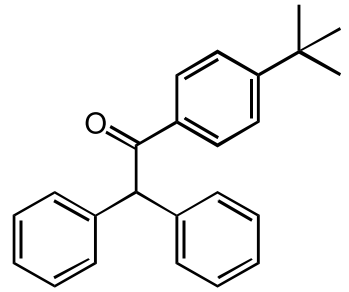
2,2-Diphenyl-1-(*p*-tolyl)ethanone (3d)[6]



Following the general procedure, treatment of 4-tolualdehyde **1d** (120.1 mg, 118 μL, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (74.4 mg, 0.20 mmol), and Cs_2CO_3 (456.1 mg, 1.4 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 2,2-diphenyl-1-(*p*-tolyl)ethanone **3d** as a white solid (177.0 mg, 62%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.41; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.39-7.23 (m, 12H), 6.07 (s, 1H), 2.40 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.9, 144.0, 139.4, 134.4, 129.4, 129.3, 129.2, 128.8, 127.2, 59.4, 21.7. **ESI-MS**: calculated $[M+Na]^+$ for $C_{21}H_{18}ONa$: 309.1250, found: 309.1257. **ATR-FTIR (cm^{-1})**: 3031. 2911, 1673, 1602, 1572, 1493, 1452, 1408, 1355, 1293, 1270, 1233, 1218, 1202, 1176, 1112, 1077, 1032, 1014, 999, 864.

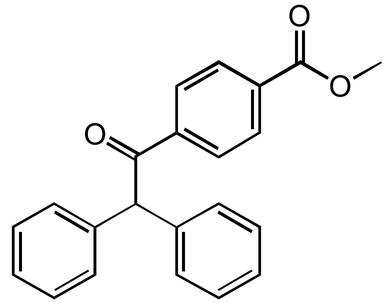
1-(4-(*tert*-Butyl)phenyl)-2,2-diphenylethanone (3e)[7]



Following the general procedure, treatment of 4-*tert*-butyl benzaldehyde **1e** (162.2 mg, 167 µL, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (74.4 mg, 0.20 mmol), and Cs_2CO_3 (456.1 mg, 1.4 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(4-(*tert*-butyl)phenyl)-2,2-diphenylethanone **3e** as a white solid (212.0 mg, 65%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.50; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.39-7.20 (m, 10H), 6.06 (s, 1H), 1.33 (s, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.9, 156.9, 139.4, 134.3, 129.3, 129.1, 128.8, 127.2, 125.7, 59.4, 35.2, 31.2. **ESI-MS**: calculated $[M+Na]^+$ for $C_{24}H_{24}ONa$: 351.1719, found: 351.1731. **ATR-FTIR (cm^{-1})**: 2964, 2869, 1698, 1675, 1601, 1564, 1493, 1454, 1406, 1364, 1337, 1287, 1269, 1227, 1211, 1198, 1181, 1108, 1081, 1034, 1010, 995, 874, 845.

Methyl 4-(2,2-diphenylacetyl)benzoate (3f)



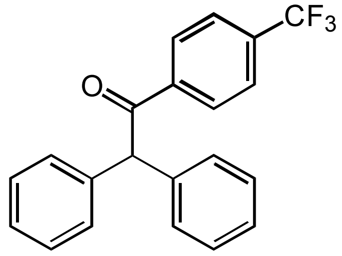
Following the general procedure, treatment of methyl 4-formylbenzoate **1f** (164.2 mg, 1.0 mmol) with (bromomethylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded methyl 4-(2,2-diphenyl-acetyl)benzoate **3f** as a white solid (296.0 mg, 90%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.21; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.10-8.04 (m, 4H), 7.40-7.28 (m, 10H), 6.05 (s, 1H), 3.93 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.9, 166.2, 140.1, 138.7, 133.8, 129.9, 129.2, 128.9, 128.9, 127.4, 59.9, 52.6. **ESI-MS**: calculated $[M+Na]^+$ for $C_{22}H_{18}O_3Na$: 353.1148, found: 353.1154. **ATR-FTIR (cm^{-1})**: 3056, 2954, 1724, 1677, 1596, 1570, 1495, 1453, 1434, 1406, 1276, 1202, 1110, 1032, 1006, 994, 959, 917, 889.

---

[7] Katritzky, R. A.; Wu, H.; Xie, L. *Tetrahedron Lett.* **1997**, *38*, 903.

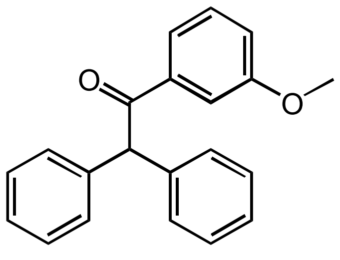
2,2-Diphenyl-1-(4-(trifluoromethyl)phenyl)ethanone (3g)[8]



Following the general procedure, treatment of 4-trifluoromethyl benzaldehyde **1g** (174.0 mg, 137 µL, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 2,2-diphenyl-1-(4-(trifluoromethyl)phenyl)ethanone **3g** as a white solid (309.0 mg, 91%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.62; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.38-7.26 (m, 10H), 6.01 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.4, 139.5, 138.5, 134.2, 129.4, 129.2, 129.0, 127.6, 125.8 (m), 60.0. **ESI-MS**: calculated $[M+Na]^+$ for $C_{21}H_{15}F_3ONa$: 363.0967, found: 363.0977. **ATR-FTIR (cm^{-1})**: 3072, 3032, 1686, 1599, 1582, 1495, 1453, 1408, 1325, 1235, 1204, 1183, 1162, 1122, 1065, 1032, 1012, 996, 966, 925.

1-(3-Methoxyphenyl)-2,2-diphenylethanone (3h)[9]



Following the general procedure, treatment of 3-methoxy benzaldehyde **1h** (136.2 mg, 122 µL, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(3-methoxyphenyl)-2,2-diphenylethanone **3h** as a white solid (239.0 mg, 79%).

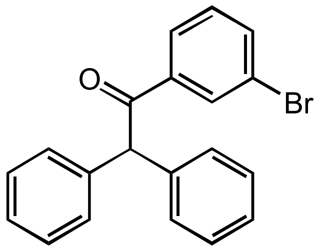
R*f* (CH_2Cl_2/pentane = 50/50): 0.29; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.60-7.54 (m, 2H), 7.36-7.24 (m, 11H), 7.07 (ddd, *J* = 8.2 Hz, 2.7 Hz, 0.9 Hz, 1H), 6.03 (s, 1H), 3.81 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 198.1, 159.9, 139.2, 138.3, 129.7, 129.2, 128.8, 127.3, 121.7, 119.6, 113.4, 59.6, 55.5. **ESI-MS**: calculated $[M+Na]^+$ for $C_{21}H_{18}O_2Na$: 325.1199, found: 325.1202. **ATR-FTIR (cm^{-1})**: 3026, 2950, 1675, 1600, 1582, 1487, 1433, 1326, 1293, 1273, 1254, 1193, 1157, 1075, 1057, 1020, 913, 882.

---

[8] Kuwano, R.; Utsunomiya, M.; Hartwig, F. J. *J. Org. Chem.* **2002**, *67*, 6479.

[9] Hong, P.; Yamazaki, H.; Sonogashira, K.; Hagihara, N. *Chem. Lett.* **1978**, *5*, 535.

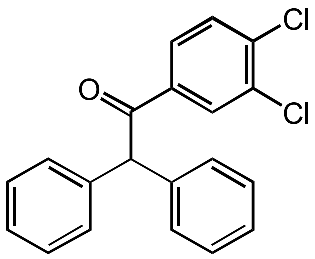
1-(3-Bromophenyl)-2,2-diphenylethanone (3i)



Following the general procedure, treatment of 3-bromobenzaldehyde **1i** (185.0 mg, 116 µL, 1.0 mmol) with (bromomethylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(3-bromophenyl)-2,2-diphenylethanone **3i** as a white solid (312.0 mg, 88%).

R_f (CH_2Cl_2/pentane = 50/50): 0.56; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.14 (t, *J* = 1.8 Hz, 1H), 7.90 (ddd, *J* = 7.8, 1.5, 1.0 Hz, 1H), 7.64 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.48 – 7.11 (m, 11H), 5.97 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.1, 138.8, 136.1, 132.1, 130.4, 129.3, 129.1, 127.7, 127.6, 123.2, 59.8. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{15}BrONa$: 373.0204, found: 373.0210. **ATR-FTIR (cm^{-1})**: 3087, 3068, 2925, 1682, 1567, 1494, 1453, 1419, 1270, 1205, 1190, 1076, 1034, 907, 862, 785, 745, 691, 613, 573.

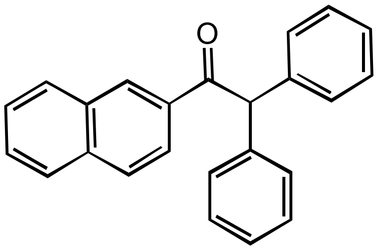
1-(3,4-Dichlorophenyl)-2,2-diphenylethanone (3j)



Following the general procedure, treatment of 3,4-dichloro benzaldehyde **1j** (175.0 mg, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(3,4-dichlorophenyl)-2,2-diphenylethanone **3j** as a white solid (199.0 mg, 58%).

R_f (CH_2Cl_2/pentane = 50/50): 0.58; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 2.1 Hz, 1H), 7.82 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.43-7.21 (m, 10H), 5.96 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.1, 138.4, 137.7, 136.3, 133.4, 130.9, 130.8, 129.1, 128.9, 128.1, 127.5, 59.7. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{14}Cl_2ONa$: 363.0314, found: 363.0317. **ATR-FTIR (cm^{-1})**: 3066, 3030, 1679, 1578, 1557, 1494, 1453, 1388, 1365, 1285, 1224, 1188, 1152, 1129, 1083, 1031, 1001, 911, 873, 837.

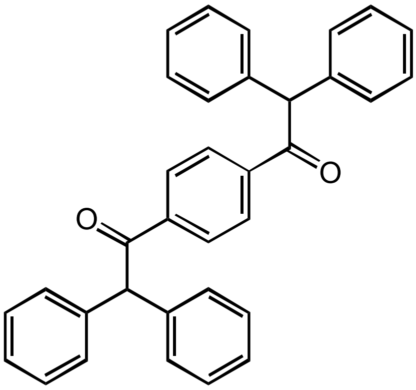
1-(Naphthalen-2-yl)-2,2-diphenylethanone (3k)



Following the general procedure, treatment of 2-naphthaldehyde **1k** (156.0 mg, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 24 h followed by column chromatography afforded 1-(naphthalen-2-yl)-2,2-diphenylethanone **3k** as a white solid (193.0 mg, 59%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.49; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.54 (d, *J* = 1.6 Hz, 1H), 8.06 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.85-7.82 (m, 3H), 7.56-7.52 (m, 2H), 7.34-7.24 (m, 10H), 6.21 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 198.3, 139.3, 135.6, 134.3, 132.6, 130.8, 129.8, 129.3, 128.9, 128.7, 128.6, 127.8, 127.3, 126.8, 124.7, 59.6. **ESI-MS**: calculated $[M+Na]^+$ for $C_{24}H_{18}ONa$: 345.1255, found: 345.1261. **ATR-FTIR (cm^{-1})**: 3059, 2926, 2361, 1659, 1625, 1596, 1495, 1453, 1352, 1279, 1212, 1177, 1121, 1079, 1033, 994, 958, 912, 863, 823, 736, 698, 594.

1,1'-(1,4-Phenylene)bis(2,2-diphenylethanone) (3l)[10]



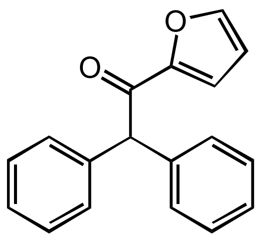
Following the general procedure, treatment of terephthalaldehyde **1l** (67.1 mg, 0.5 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1,1'-(1,4-phenylene)bis(2,2-diphenylethanone) **3l** as a white solid (148.0 mg, 63%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.16; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 (s, 4H), 7.35-7.21 (m, 20H), 5.97 (s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.7, 139.9, 138.6, 129.3, 129.2, 128.9, 127.5, 60.0. **ESI-MS**: calculated $[M+Na]^+$ for $C_{34}H_{26}O_2Na$: 489.1825, found: 489.1824. **ATR-FTIR (cm^{-1})**: 3029, 2912, 1681, 1598, 1493, 1452, 1401, 1355, 1308, 1270, 1233, 1207, 1191, 1113, 1077, 1032, 1010, 994, 920.

---

[10] Shi, D.; Chen, X. J.; Chai, Y. W.; Chen, X. W.; Kao, Y. T. *Tetrahedron Lett.* **1993**, *34*, 2963.

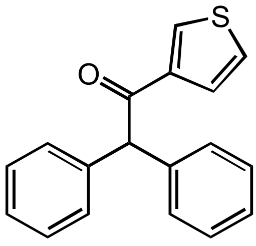
1-(Furan-2-yl)-2,2-diphenylethanone (3m)[11]



Following the general procedure, treatment of 2-furaldehyde **2m** (96.1 mg, 83 µL, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(furan-2-yl)-2,2-diphenyl-ethanone **3m** as a white solid (242.0 mg, 92%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.22; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.56-7.55 (m, 1H), 7.36 – 7.23 (m, 11H), 6.50 (dd, *J* = 3.6 Hz, 1.7 Hz, 1H), 5.89 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 187.3, 152.7, 146.8, 138.6, 129.2, 128.7, 127.3, 118.5, 112.6, 58.9. **ESI-MS**: calculated $[M+Na]^+$ for $C_{18}H_{14}O_2Na$: 285.0886, found: 285.0879. **ATR-FTIR (cm^{-1})**: 3120, 3092, 1659, 1597, 1558, 1495, 1459, 1393, 1350, 1313, 1290, 1248, 1162, 1088, 1048, 1034, 994, 930, 909.

2,2-Diphenyl-1-(thiophen-3-yl)ethanone (3n)



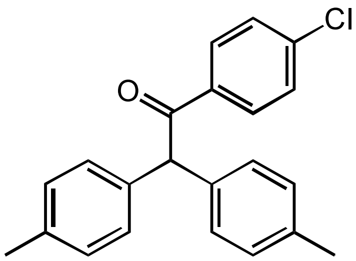
Following the general procedure, treatment of thiophene 3-carboxaldehyde **1n** (112.9 mg, 93 µL, 1.0 mmol) with (bromo methylene) dibenzene **2a** (247.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 12,2-Diphenyl-1-(thiophen-3-yl)ethanone **3n** as a white solid (215.0 mg, 77%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.34; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.07 (dd, *J* = 2.9 Hz, 1.2 Hz, 1H), 7.56 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 7.37 – 7.23 (m, 11H), 5.84 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 192.5, 142.1, 139.0, 133.2, 129.2, 128.8, 127.8, 127.3, 126.3, 61.2. **ESI-MS**: calculated $[M+Na]^+$ for $C_{18}H_{14}OSNa$: 301.0658, found: 301.0665. **ATR-FTIR (cm^{-1})**: 3107, 3029, 2921, 1670, 1599, 1495, m1451, 1403, 1350, 1300, 1270, 1241, 1223, 1166, 1088, 1076, 1032, 1003, 981, 928, 879, 851.

---

[11] Walter, A. L.; Springer, K. C.; Kenney, J.; Galen, K. S.; Sperber, N. *J. Med. Chem.* **1968**, *11*, 792.

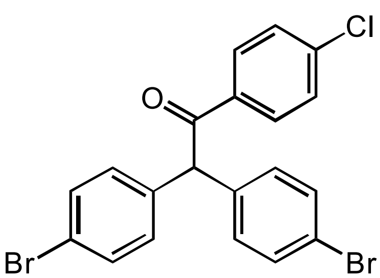
1-(4-Chlorophenyl)-2,2-di-*p*-tolylethanone (3o)



Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with 4,4'-(bromomethylene)bis(methylbenzene) **2o** (275.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(4-chlorophenyl)-2,2-di-*p*-tolylethanone **3o** as a white solid (245.0 mg, 74%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.60; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.14 (m, 8H), 5.90 (s, 1H), 2.32 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.4, 139.4, 137.0, 136.1, 135.2, 130.5, 129.6, 129.0, 129.0, 58.9, 21.2. **ESI-MS**: calculated $[M+Na]^+$ for $C_{22}H_{19}ClONa$: 357.1022, found: 357.1028. **ATR-FTIR (cm^{-1})**: 3092, 3060, 2919, 2857, 1932, 1906, 1799, 1683, 1585, 1573, 1512, 1451, 1400, 1271, 1204, 1088, 997, 873, 829, 764, 729, 661, 572, 534.

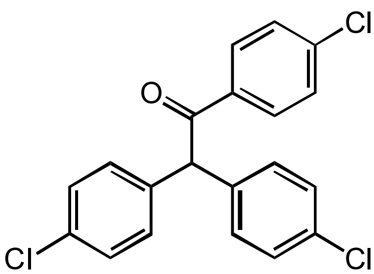
2,2-Bis(4-bromophenyl)-1-(4-chlorophenyl)ethanone (3p)



Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with 4,4'-(bromomethylene)bis(bromobenzene) **2p** (404.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 24 h followed by column chromatography afforded 2,2-bis(4-bromophenyl)-1-(4-chlorophenyl)ethanone **3p** as a white solid (393.0 mg, 85%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.67; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.91-7.88 (m, 2H), 7.48-7.44 (m, 4H), 7.41-7.38 (m, 2H), 7.11-7.08 (m, 4H), 5.87 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.2, 140.1, 137.4, 134.6, 132.2, 130.8, 130.5, 129.3, 121.8, 58.2. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{13}Br_2ClONa$: 484.8919, found: 484.8909. **ATR-FTIR (cm^{-1})**: 3749, 3088, 1931, 1908, 1688, 1586, 1487, 1401, 1286, 1209, 1090, 1072, 1010, 995, 870, 825, 794, 734, 650, 601.

1,2,2-Tris(4-chlorophenyl)ethanone (3q)[6]

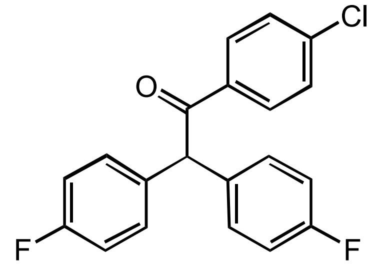


Following the general procedure, treatment of 4-cholrobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with 4,4'-(bromomethylene)bis(chlorobenzene) **2q** (316.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 24 h followed by column chromatography afforded 1,2,2-tris(4-chlorophenyl)ethanone **3q** as a white solid (326.0 mg, 87%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.67; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.92-7.87 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.29 (m, 4H), 7.17-7.14 (m, 4H), 5.90 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.4, 140.1, 136.9, 134.6, 133.7, 130.8, 130.4, 129.2, 128.8 58.1.

ESI-MS: calculated $[M+Na]^+$ for $C_{20}H_{13}Cl_3ONa$: 396.9930, found: 396.9939. **ATR-FTIR (cm^{-1})**: 3090, 2920, 1688, 1586, 1571, 1491, 1400, 1290, 1264, 1207, 1088, 1014, 995, 872, 797, 727, 667, 614, 522.

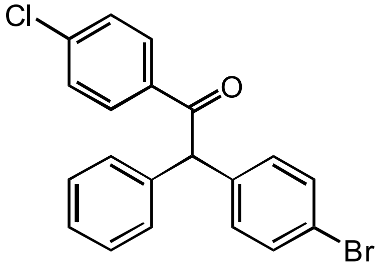
1-(4-Chlorophenyl)-2,2-bis(4-fluorophenyl)ethanone (3r)



Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with 4,4'-(bromomethylene)bis(fluorobenzene) **2r** (283.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(4-chlorophenyl)-2,2-bis(4-fluorophenyl)-ethanone **3r** as a white solid (319.0 mg, 93%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.59; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.93-7.89 (m, 2H), 7.41-7.38 (m, 2H), 7.19-7.17 (m, 4H), 7.05-6.99 (m, 4H), 5.93 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.9, 162.2, 139.9, 134.8, 134.5, 134.5, 130.7, 130.6, 130.5, 129.2, 115.9, 57.8. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{13}ClF_2ONa$: 365.0521, found: 365.0515. **ATR-FTIR (cm^{-1})**: 2360, 1683, 1589, 1573, 1504, 1400, 1333, 1298, 1275, 1223, 1207, 1157, 1095, 997, 872, 817, 797, 663, 571, 525.

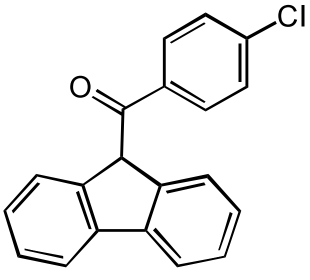
2-(4-Bromophenyl)-1-(4-chlorophenyl)-2-phenylethanone (3s)



Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with 1-bromo-4-(bromo(phenyl)methyl)benzene **2a** (326.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 24 h followed by column chromatography afforded 2-(4-bromophenyl)-1-(4-chlorophenyl)-2-phenylethanone **3s** as a white solid (308.0 mg, 80%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.64; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.92-7.88 (m, 2H), 7.45-7.42 (m, 2H), 7.38-7.23 (m, 7H), 7.12-7.09 (m, 2H) 5.90 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.6, 139.9, 138.3, 137.9, 134.9, 131.9, 130.9, 130.5, 129.2, 129.2, 129.1, 127.7, 121.6, 58.9. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{14}BrClONa$: 406.9814, found: 406.9808. **ATR-FTIR (cm^{-1})**: 3063, 3029, 2924, 1901, 1684, 1587, 1487, 1399, 1290, 1207, 1094, 1009, 908, 818, 795, 700, 633, 576, 537.

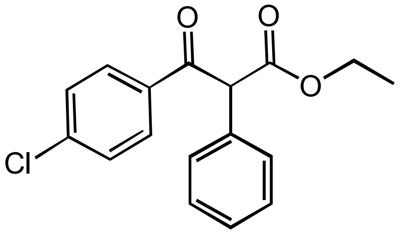
(4-Chlorophenyl)(9H-fluoren-9-yl)methanone (3t)



Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with 9-bromo-9H-fluorene (245.0 mg, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h afforded (4-chlorophenyl)(9H-fluoren-9-yl)methanone **3t** (60%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.41; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.87-7.85 (m, 2H), 7.57-7.55 (m, 2H), 7.48-7.38 (m, 4H), 7.31-7.28 (m, 4H), 5.49 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.1, 142.2, 141.6, 139.7, 134.6, 130.6, 128.9, 128.4, 127.8, 125.2, 120.8, 59.7. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{13}ClONa$: 327.0553, found: 327.0542. **ATR-FTIR (cm^{-1})**: 3059, 2925, 1919, 1677, 1587, 1446, 1399, 1314, 1270, 1204, 1091, 1028, 999, 887, 822, 739, 695, 622, 536.

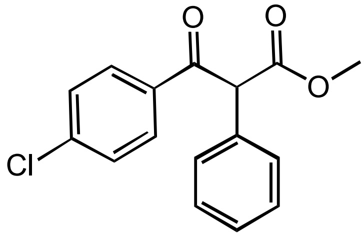
Ethyl 3-(4-chlorophenyl)-3-oxo-2-phenylpropanoate (12a)[12]



Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with ethyl 2-bromo-2-phenylacetate (243.0 mg, 175 µL, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded ethyl 3-(4-chlorophenyl)-3-oxo-2-phenylpropanoate **12a** as a white solid (265.0 mg, 88%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.28; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.91-7.88 (m, 2H), 7.41-7.34 (m, 7H), 5.54 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 192.3, 168.7, 140.2, 134.1, 132.8, 130.4, 129.6, 129.2, 129.1, 128.4, 62.0, 60.7, 14.2. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{15}ClO_3Na$: 325.0607, found: 325.0602. **ATR-FTIR (cm^{-1})**: 2980, 2935, 1747, 1675, 1587, 1493, 1454, 1400, 1366, 1323, 1296, 1260, 1224, 1183, 1165, 1091, 1009, 951, 895, 816, 711, 679, 625, 579, 532.

Methyl 3-(4-chlorophenyl)-3-oxo-2-phenylpropanoate (12b)[12]



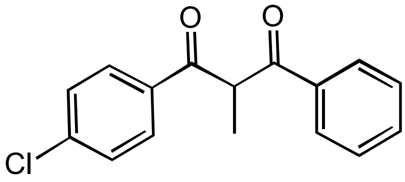
Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with methyl 2-bromo-2-phenylacetate (229.0 mg, 157 µL, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded methyl 3-(4-chlorophenyl)-3-oxo-2-phenylpropanoate **12b** as a white solid (158.0 mg, 55%).

R*f* (CH_2Cl_2/pentane = 50/50): 0.22; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.90-7.87 (m, 2H), 7.40-7.36 m, 7H), 5.57 (s, 1H), 3.76 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 192.2, 169.2, 140.2, 133.9, 132.7, 130.4, 129.6, 129.2, 129.1, 128.5, 60.6, 52.9. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{13}ClO_3Na$: 311.0451, found: 311.0445. **ATR-FTIR (cm^{-1})**: 2398, 2289, 1754, 1679, 1588, 1489, 1453, 1434, 1399, 1318, 1260, 1222, 1192, 1152, 1094, 1011, 981, 863, 839, 817, 746, 714, 680, 578.

---

[12] Campbell, M. M.; Fox, L. J.; Sainsbury, M. *Tetrahedron* **1989**, *45*, 4551.(The ^{1}H NMR of the β-ketoesters recorded in CDCl3 shows it to exist as enol isomer ~ 9%).

1-(4-Chlorophenyl)-2-methyl-3-phenylpropane-1,3-dione (12c)[13]



Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (140.5 mg, 1.0 mmol) with 2-bromo-1-phenylpropan-1-one (213.0 mg, 152 μL, 1.0 mmol) in the presence of thiazolium salt **4** (18.6 mg, 0.05 mmol), and Cs_2CO_3 (358.4 mg, 1.1 mmol) in THF (10 mL) at rt for 3 h followed by column chromatography afforded 1-(4-chlorophenyl)-2-methyl-3-phenylpropane-1,3-dione **12c** as a yellow solid (108.0 mg, 40%).

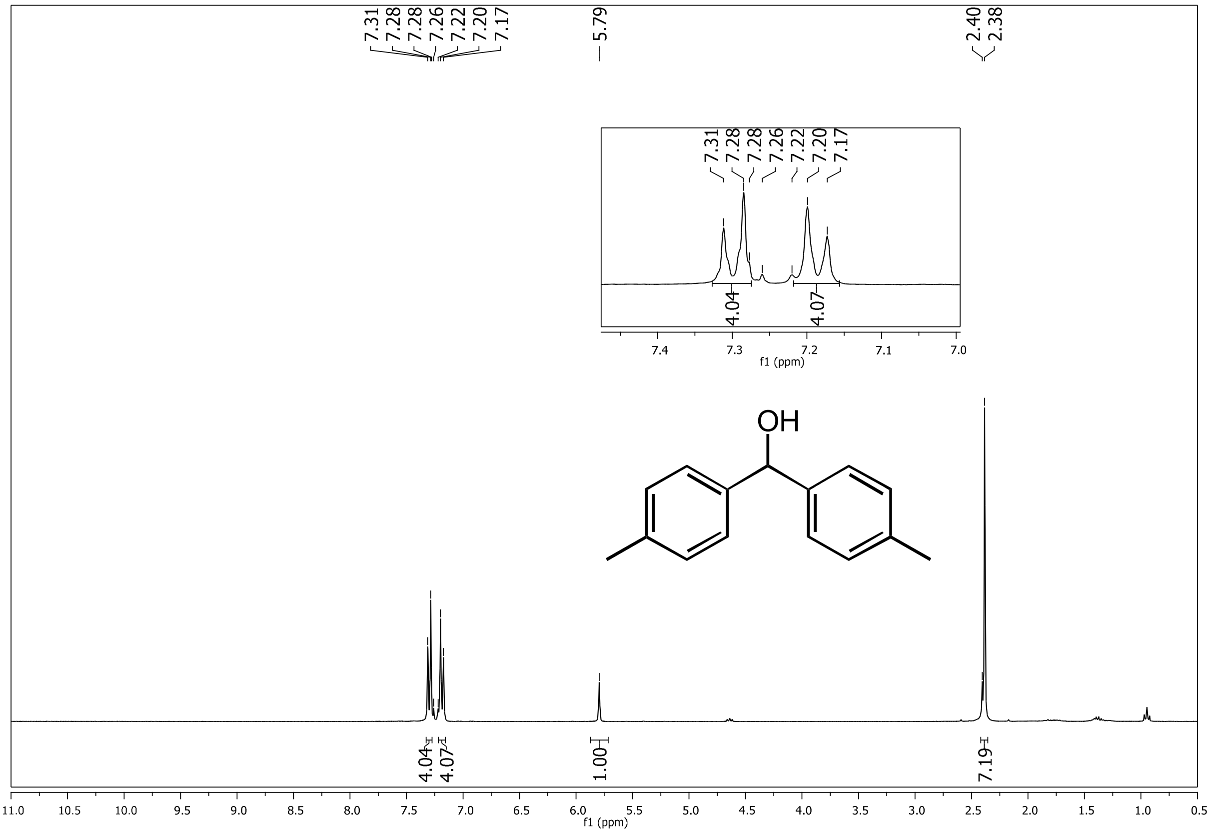
R*f* (CH_2Cl_2/pentane = 50/50): 0.26; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.97-7.86 (m, 4H), 7.59-7.56 (m, 1H), 7.49-7.40 (m, 4H), 5.20 (q, *J* = 7.0 Hz, 1H) 1.60 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.2, 196.1, 140.1, 135.6, 134.2, 133.8, 130.1, 129.3, 129.1, 128.7, 51.3, 14.5. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{13}ClO_2Na$: 295.0502, found: 295.0496. **ATR-FTIR (cm^{-1})**: 3064, 2953, 2931, 2361, 1695, 1668, 1585, 1455, 1399, 1379, 1337, 1285, 1227, 1200, 1090, 969, 941, 838, 752, 723, 691, 651, 601.

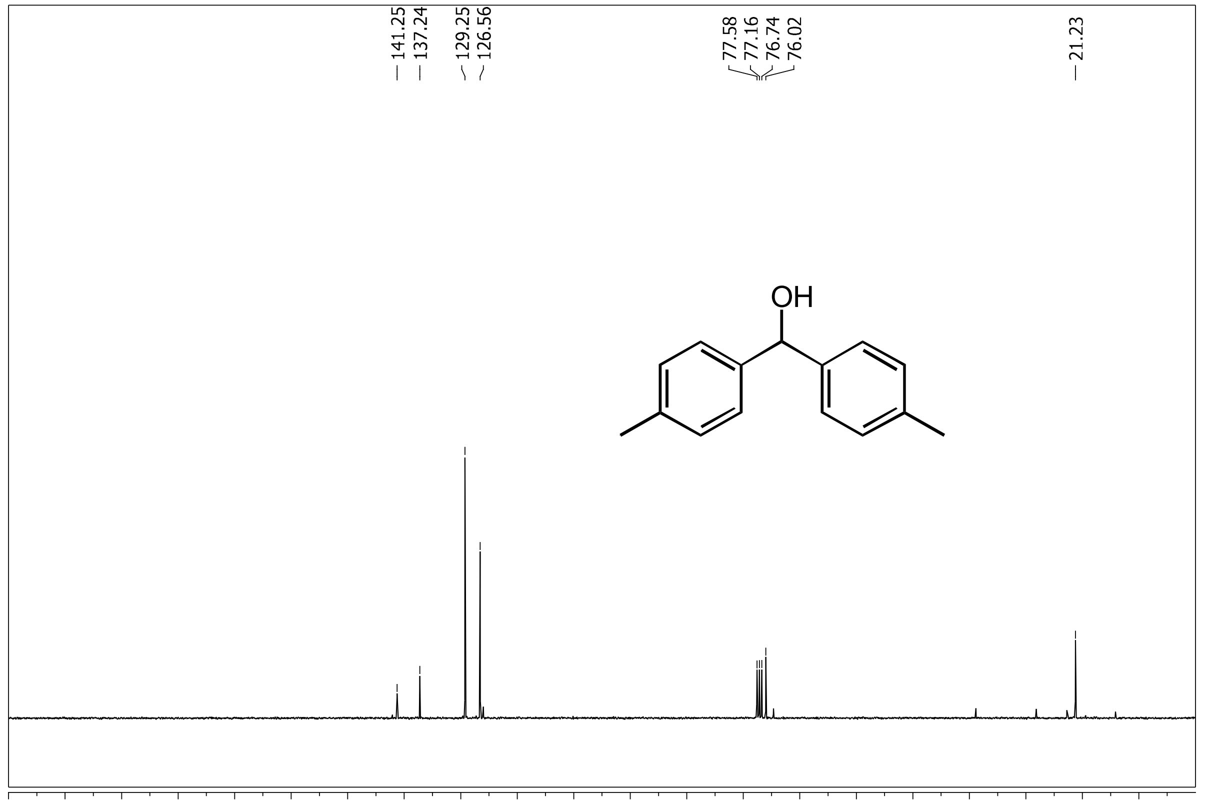
---

[13] Bickel, L.C. *J. Am. Chem. Soc.* **1945**, *67*, 2204.

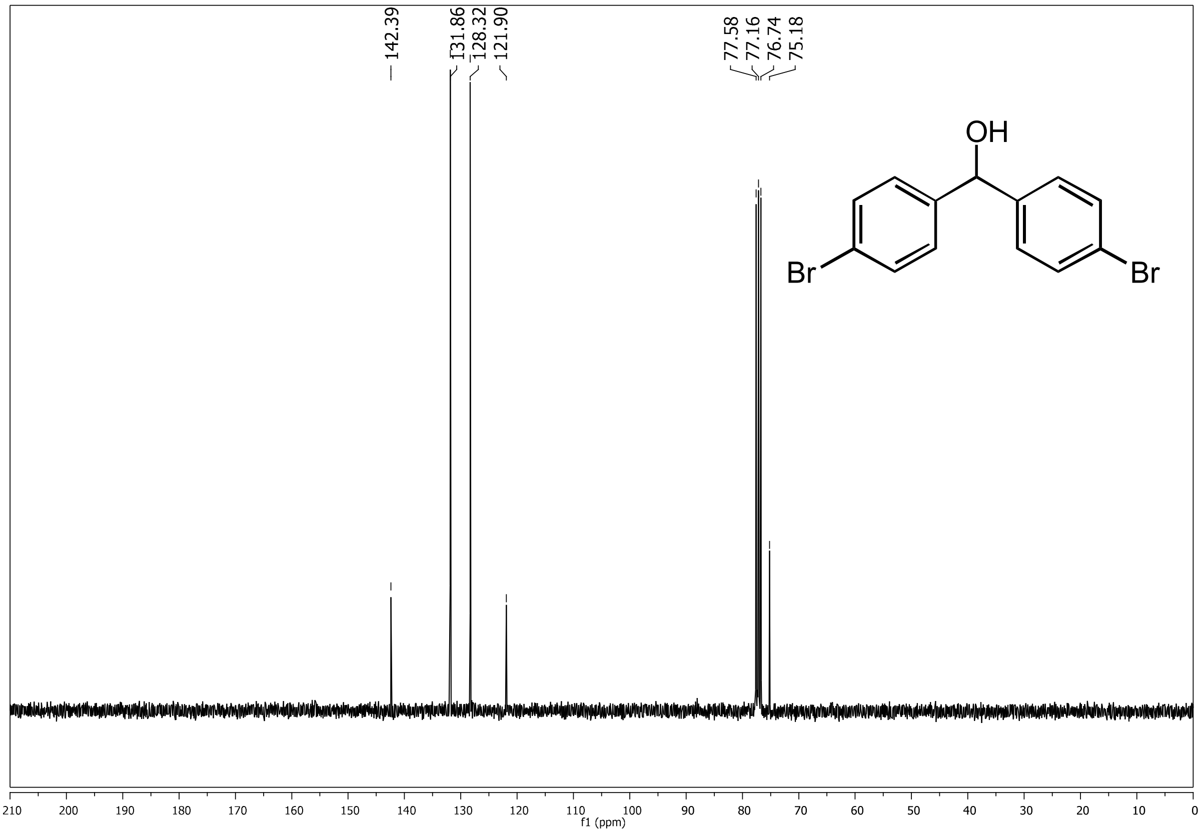
10. ^{1}H and ^{13}C NMR Spectra of Substrates (Benzhydrols)

Di-*p*-tolylmethanol

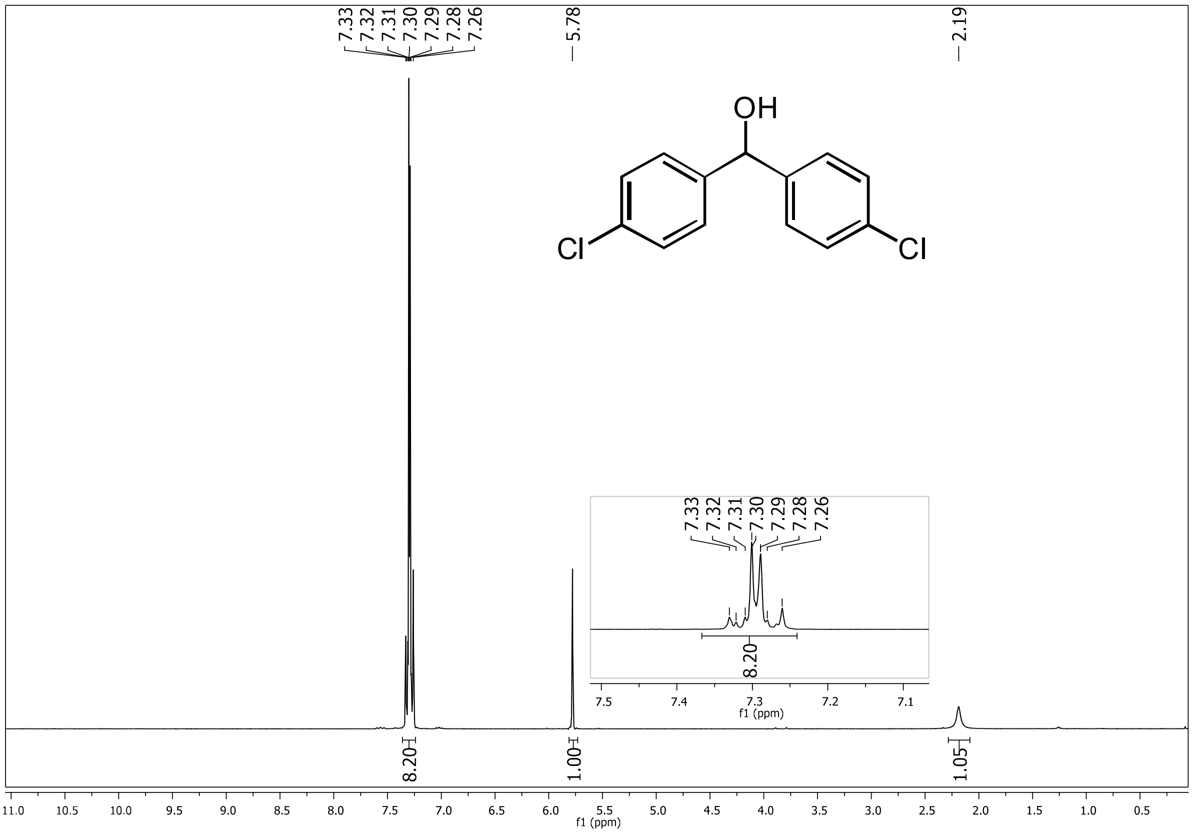


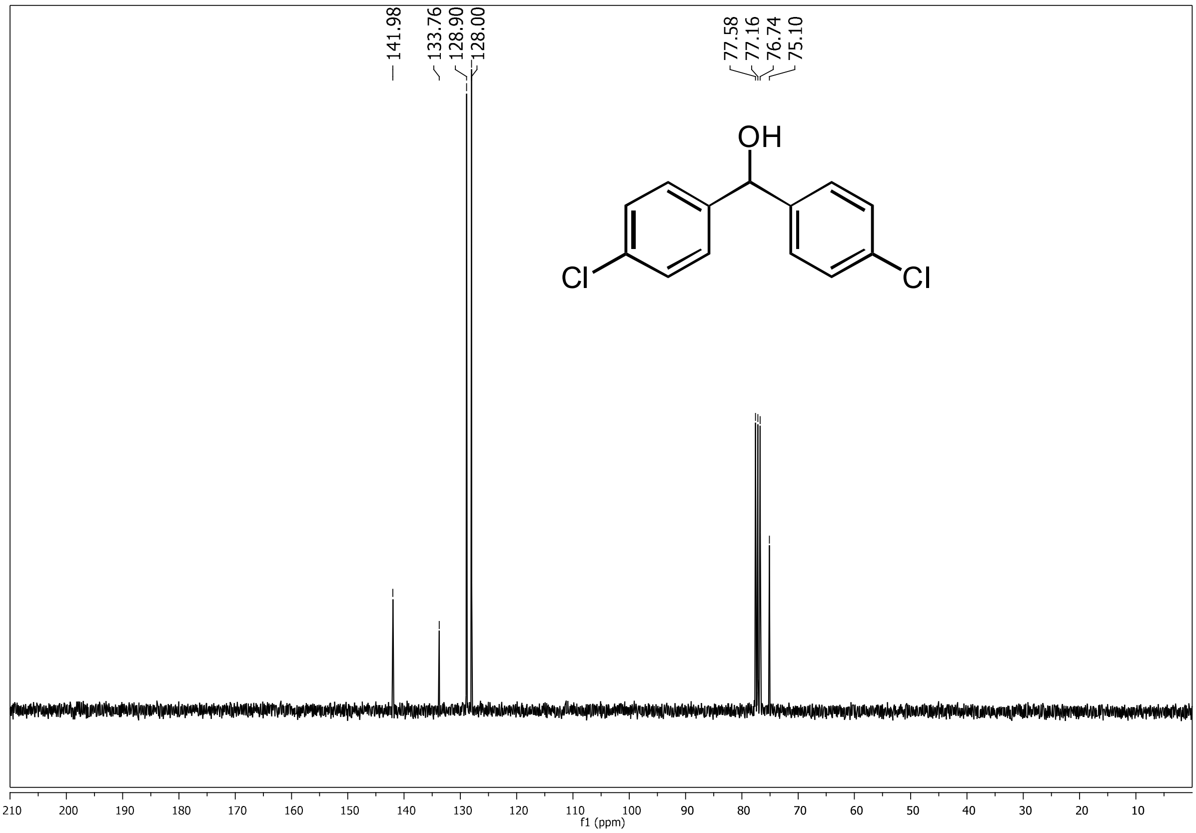


Bis(4-bromophenyl)methanol

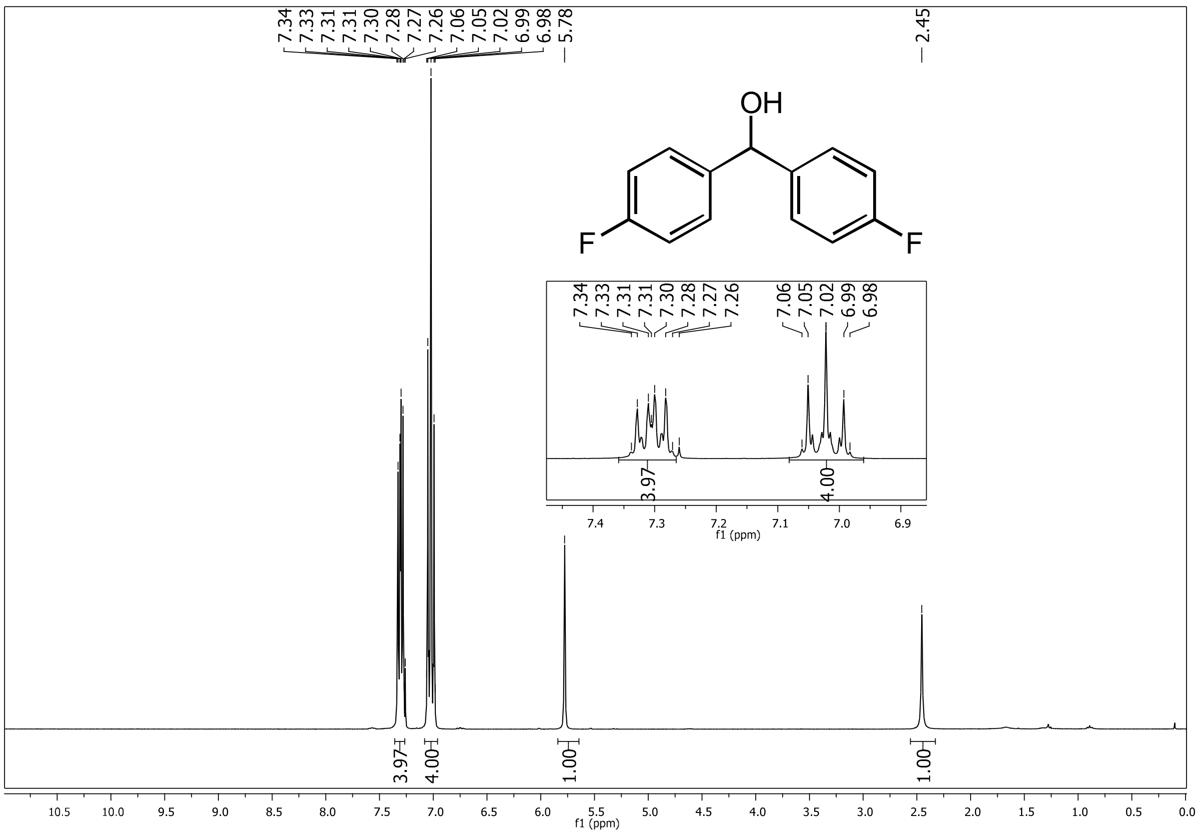


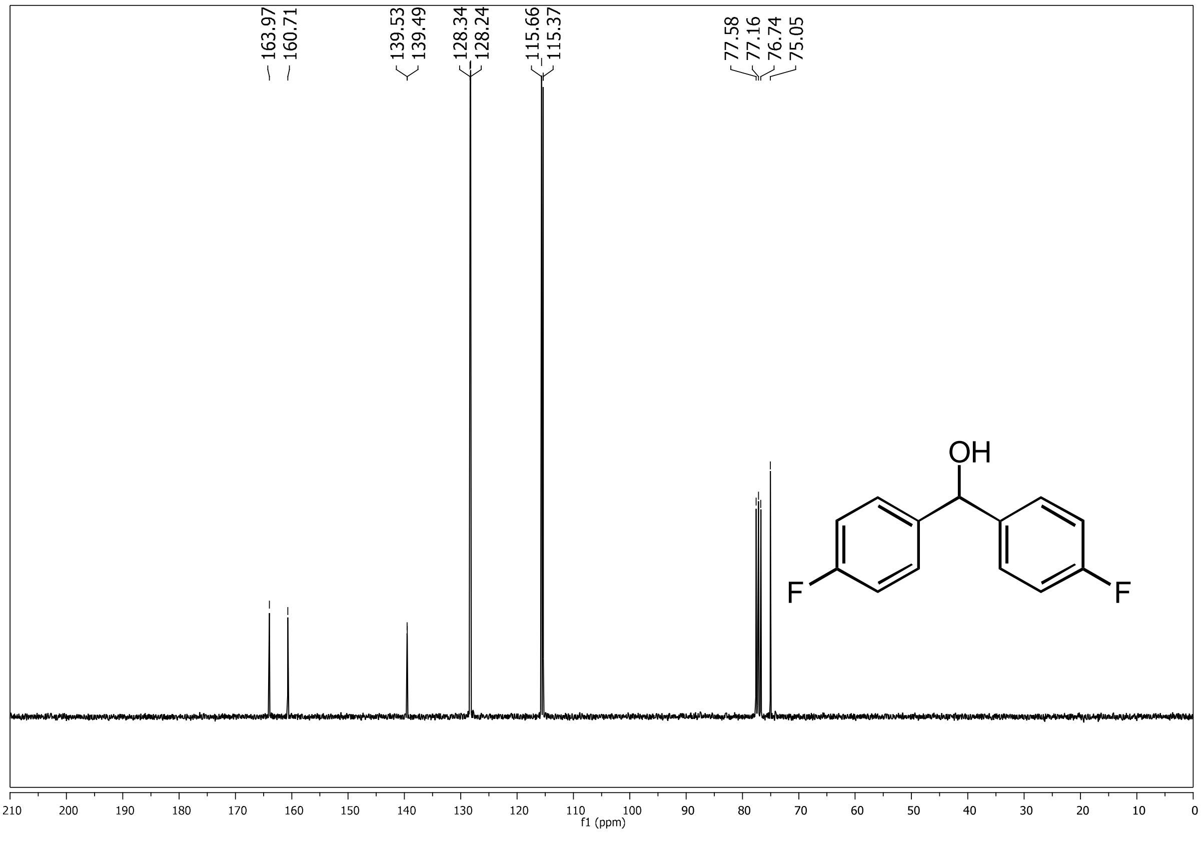
Bis(4-chlorophenyl)methanol



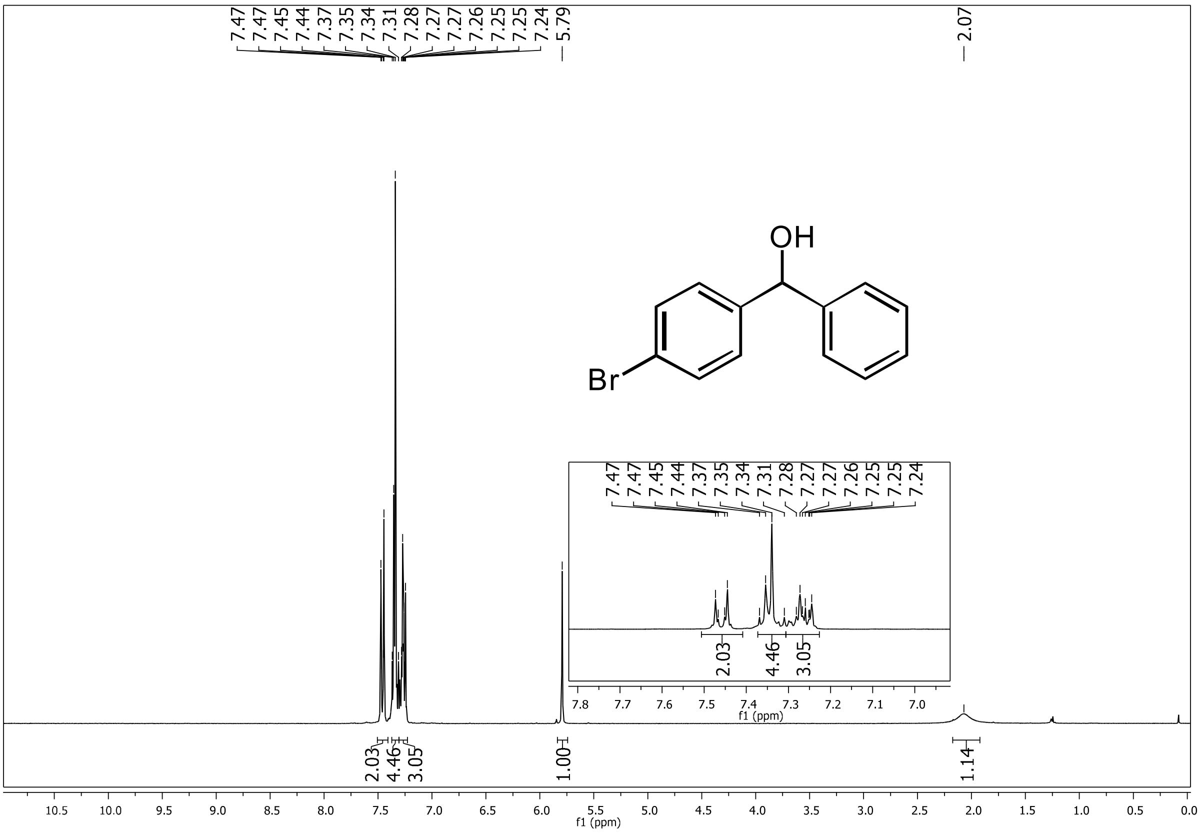


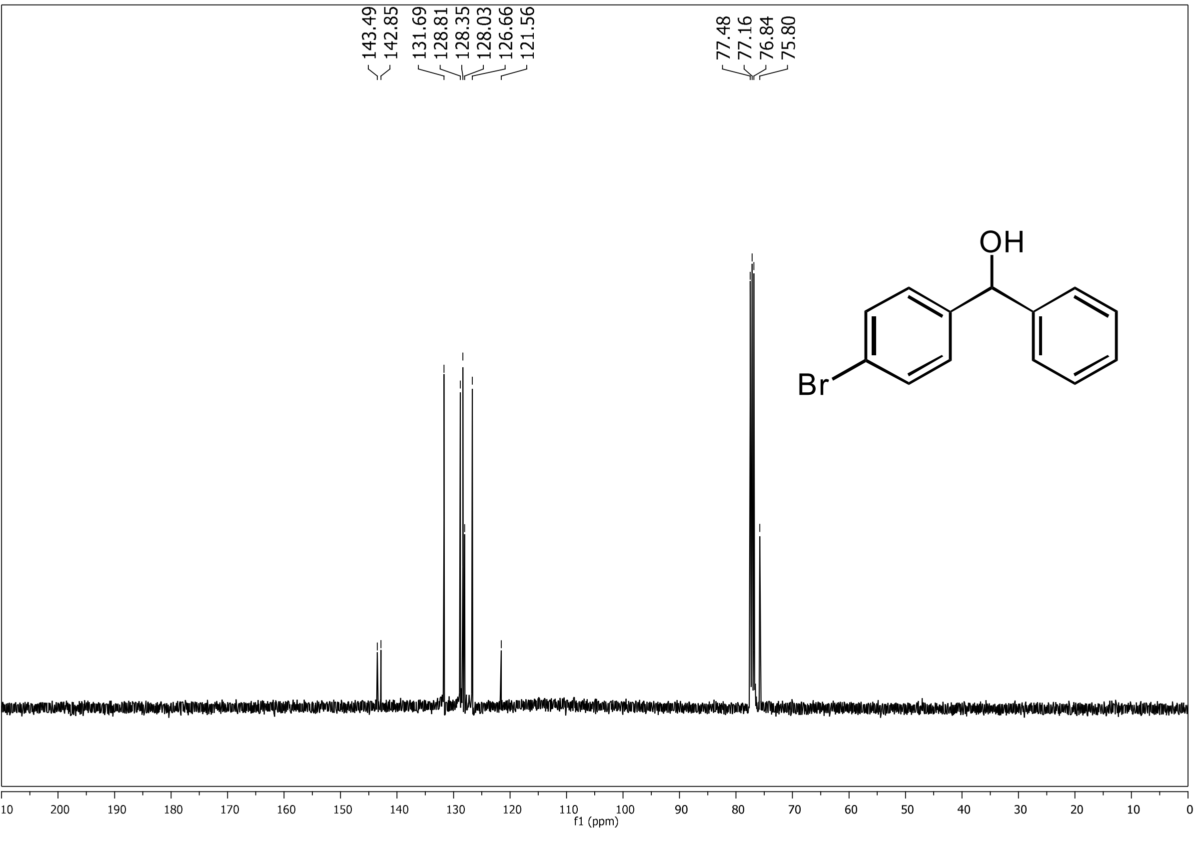
Bis(4-fluorophenyl)methanol





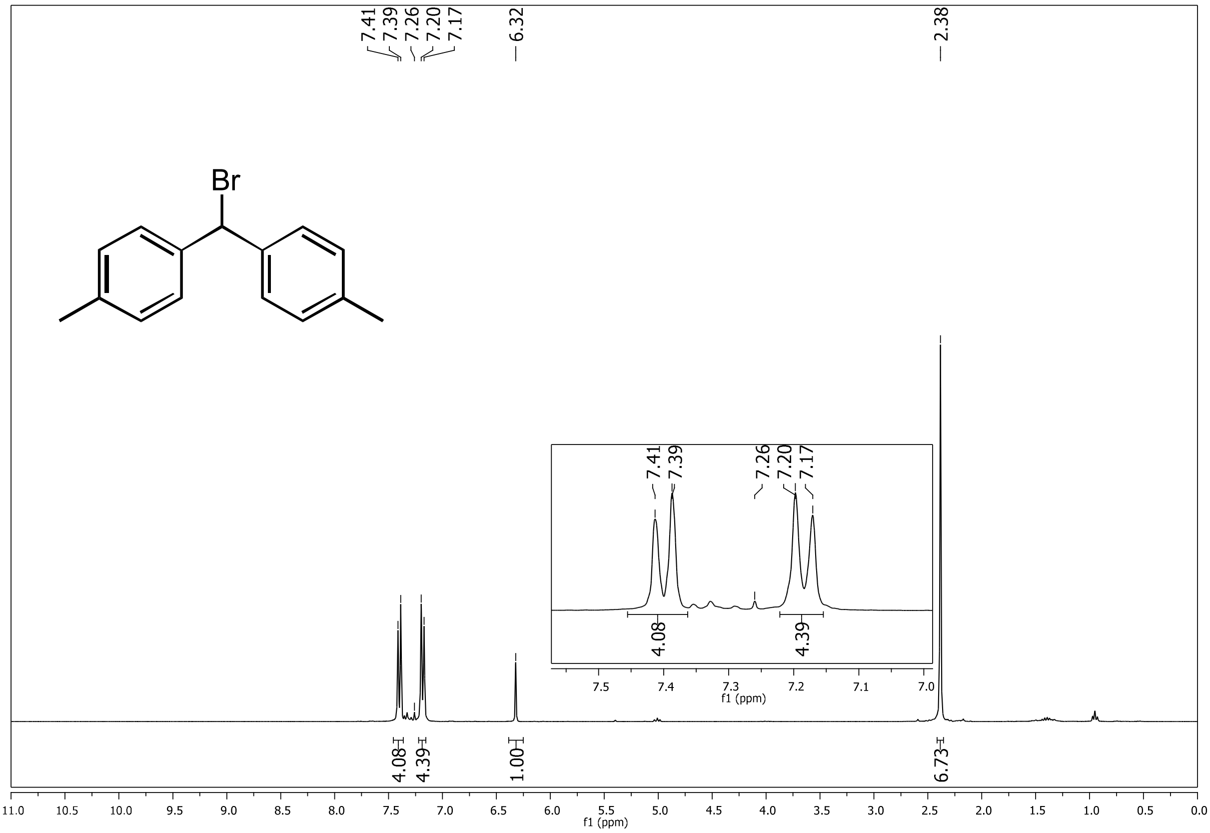
(4-Bromophenyl)(phenyl)methanol

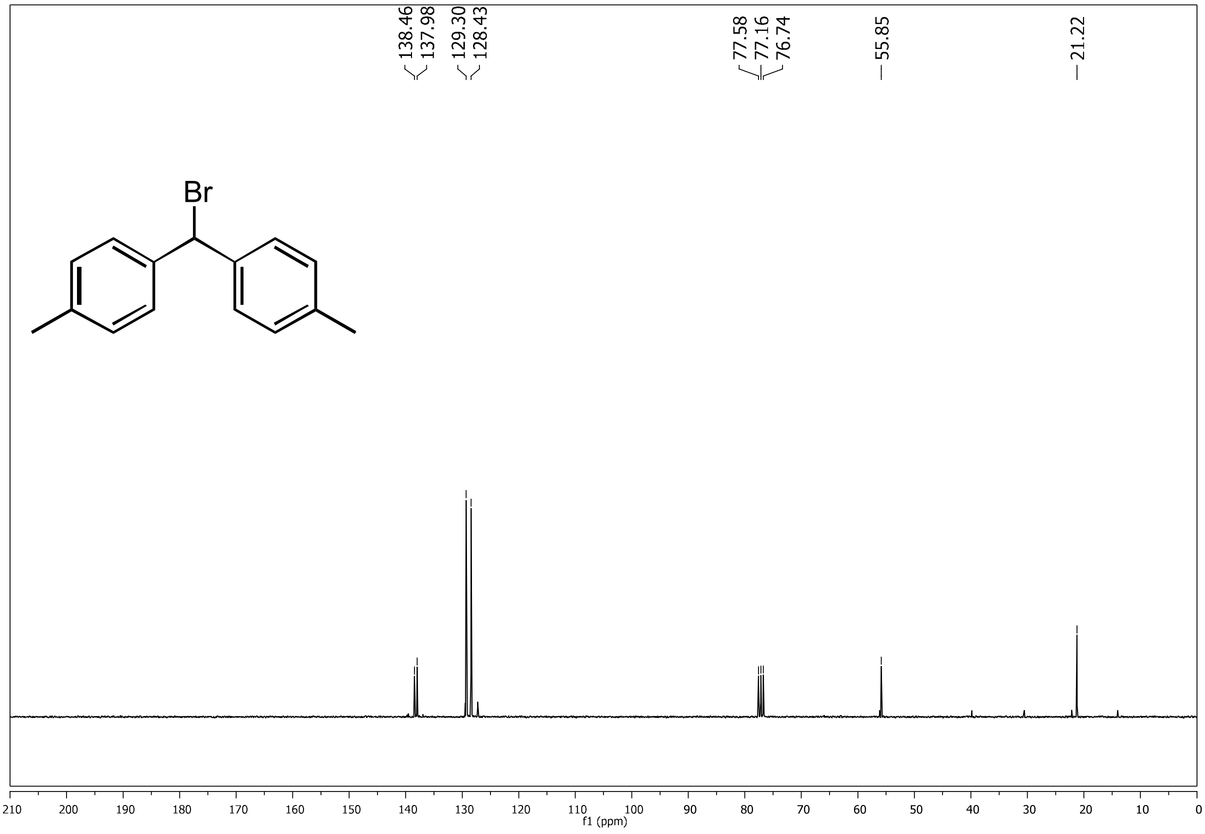




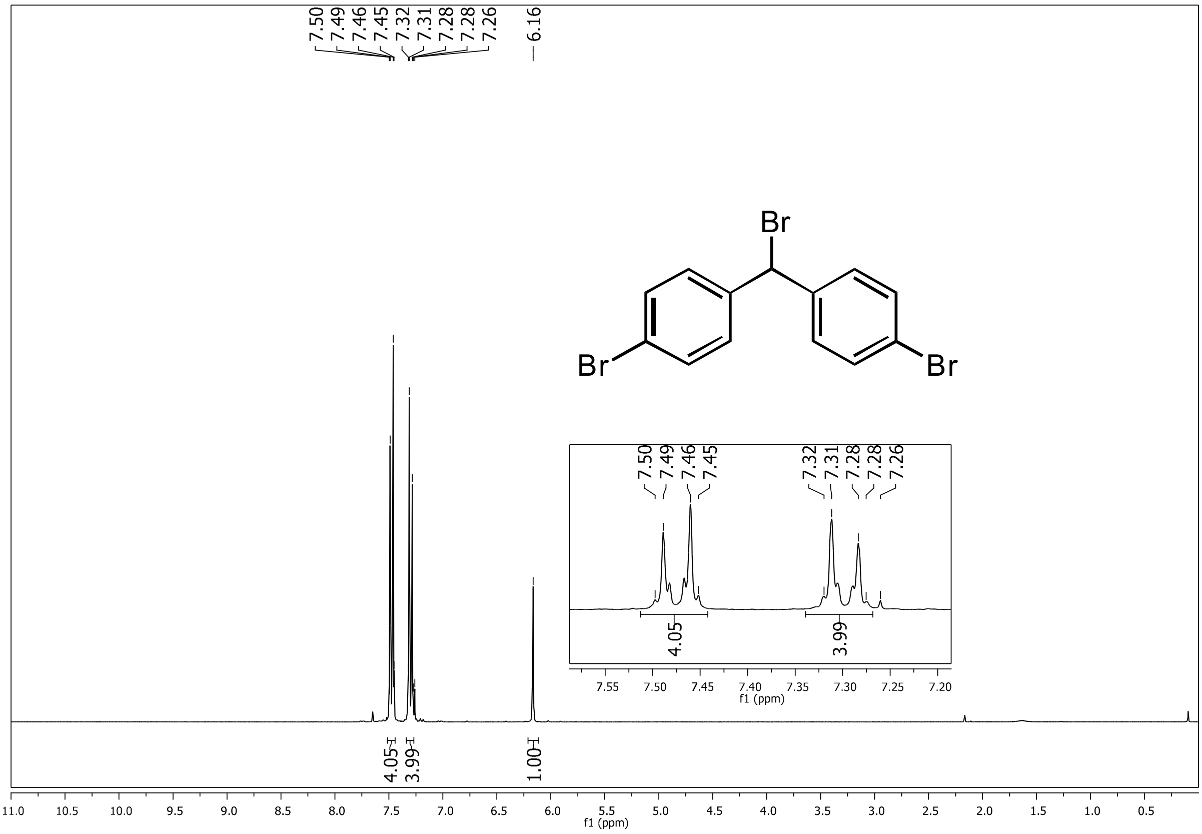
11. ^{1}H and ^{13}C NMR Spectra of Substrates (Benzhydryl bromides)

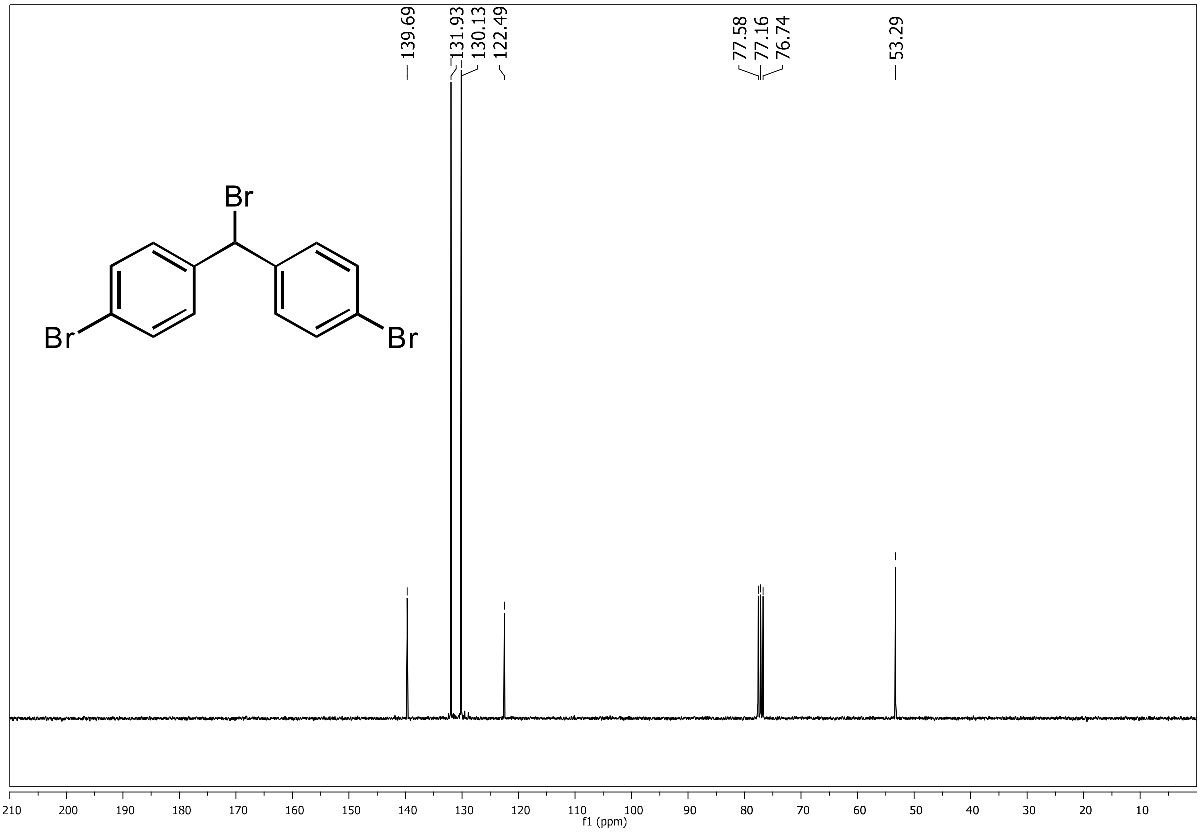
4,4'-(Bromomethylene)bis(methylbenzene) (2o)



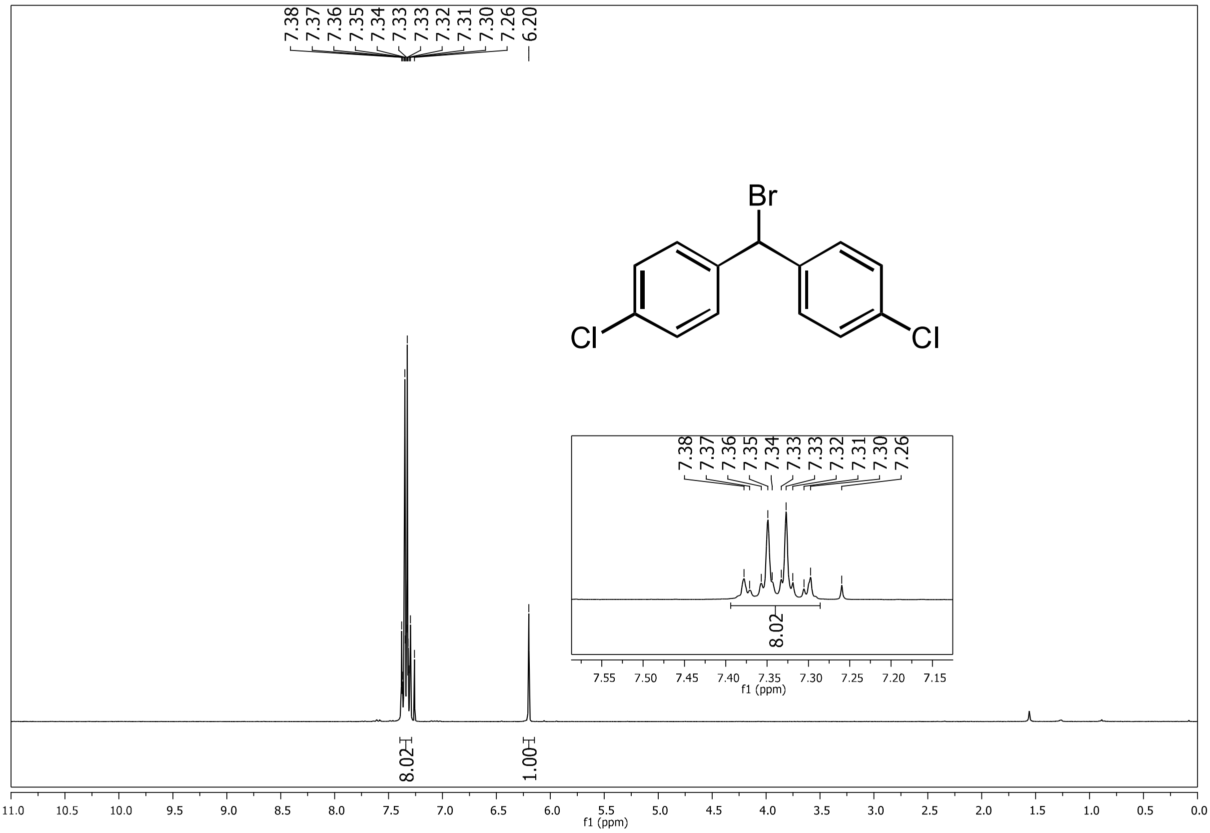


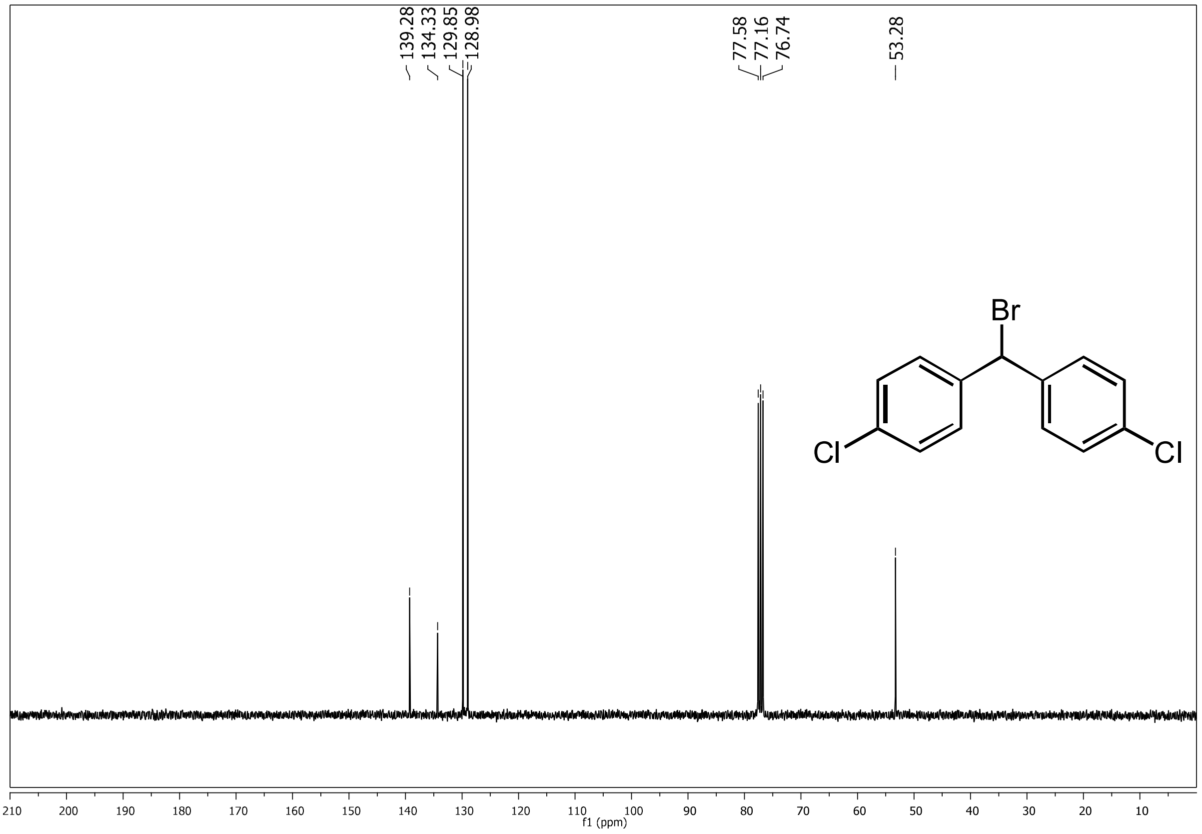
4,4'-(Bromomethylene)bis(bromobenzene) (2p)



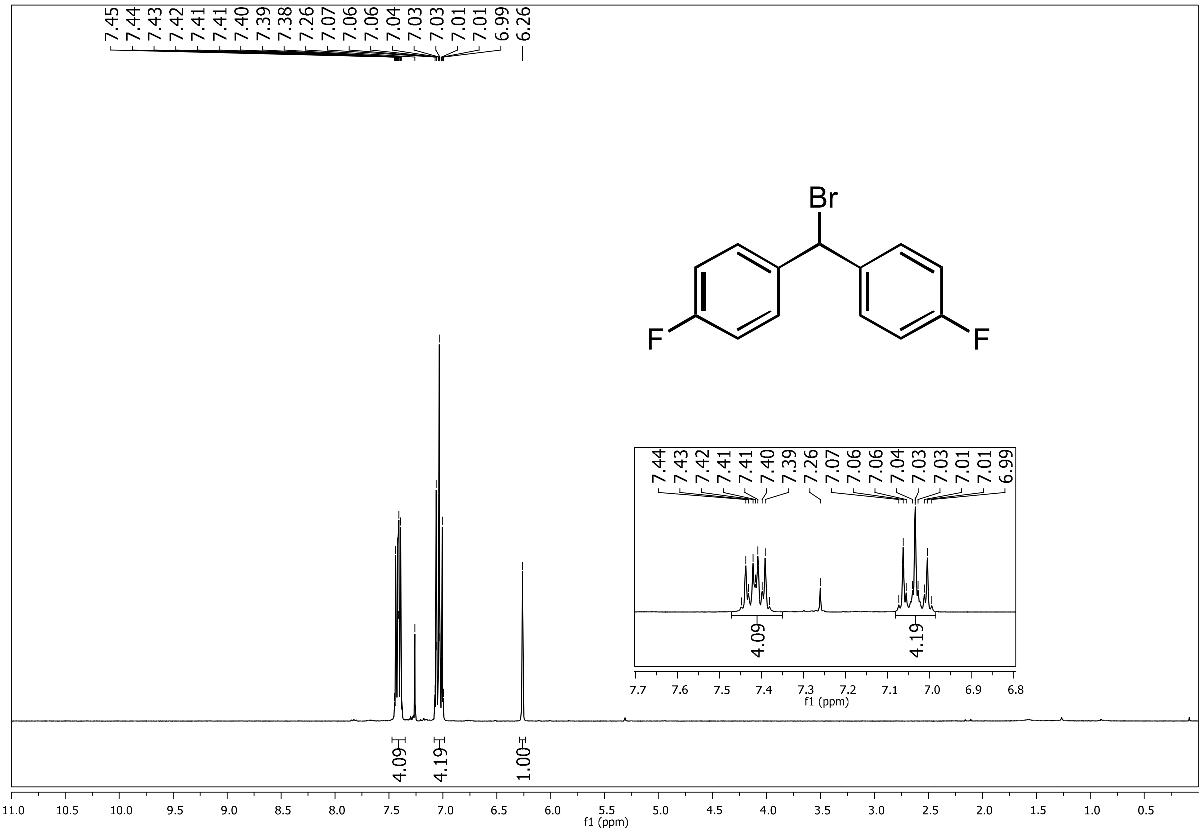


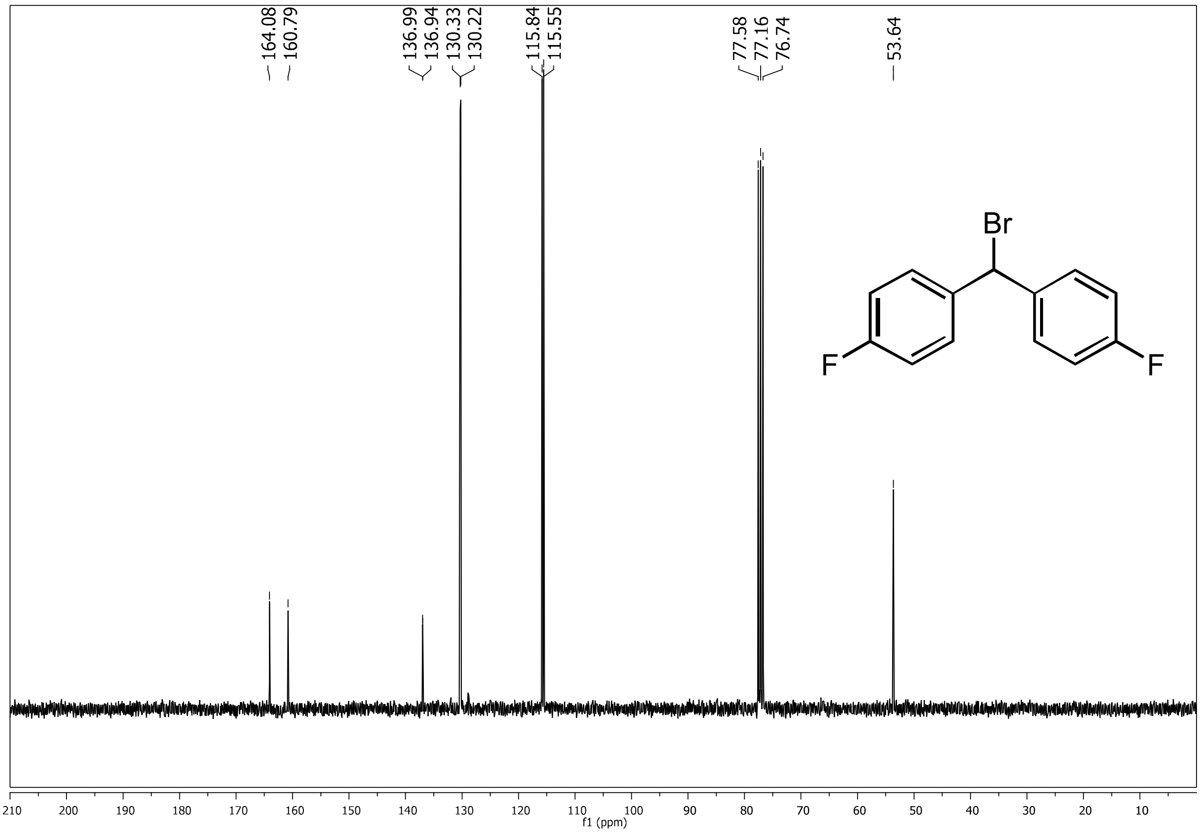
4, 4’-(Bromomethylene)bis(chlorobenzene) (2q)



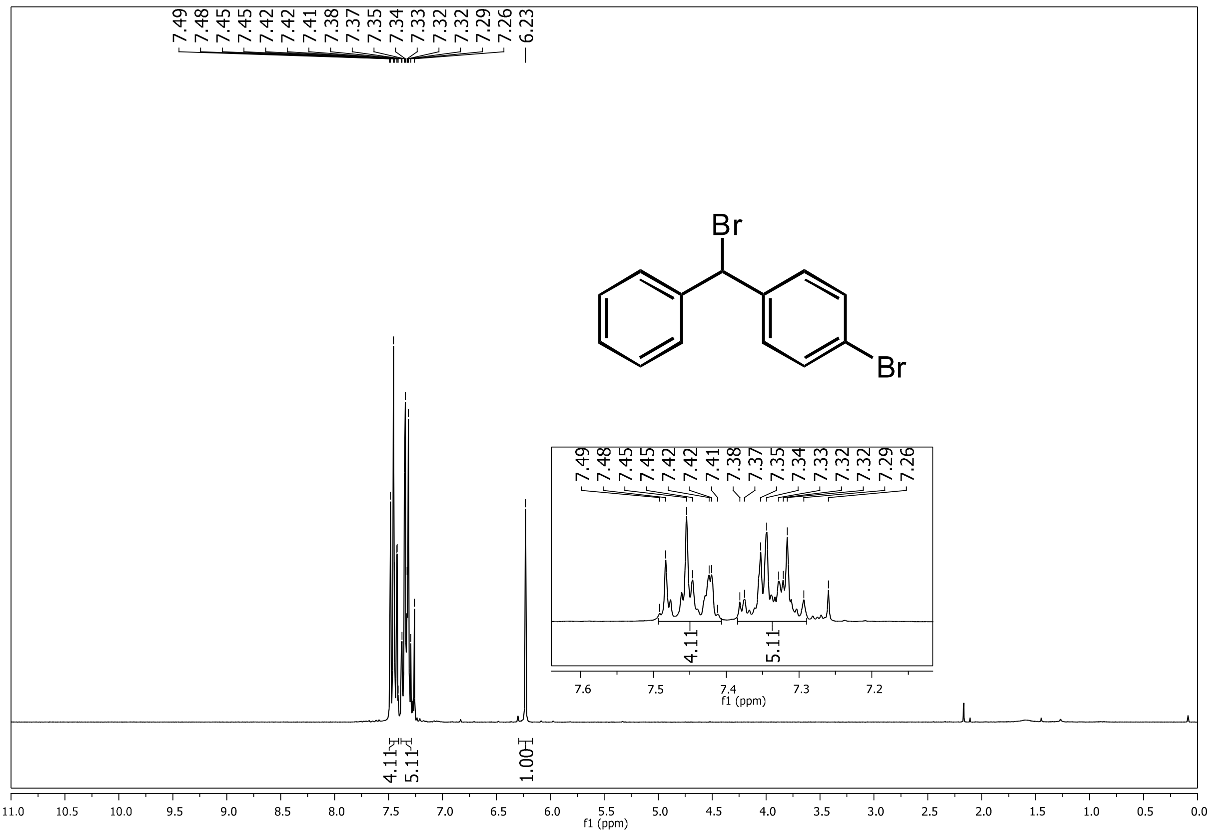


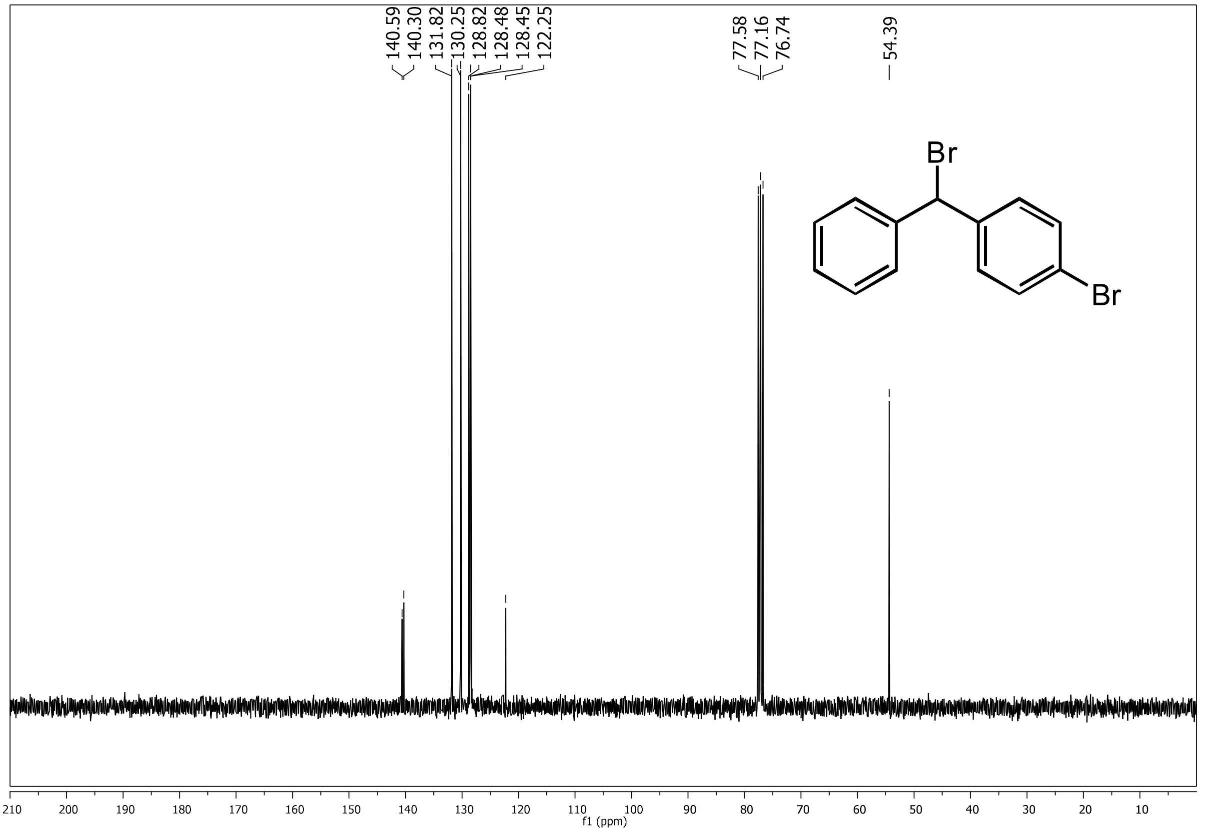
4,4'-(Bromomethylene)bis(fluorobenzene) (2r)





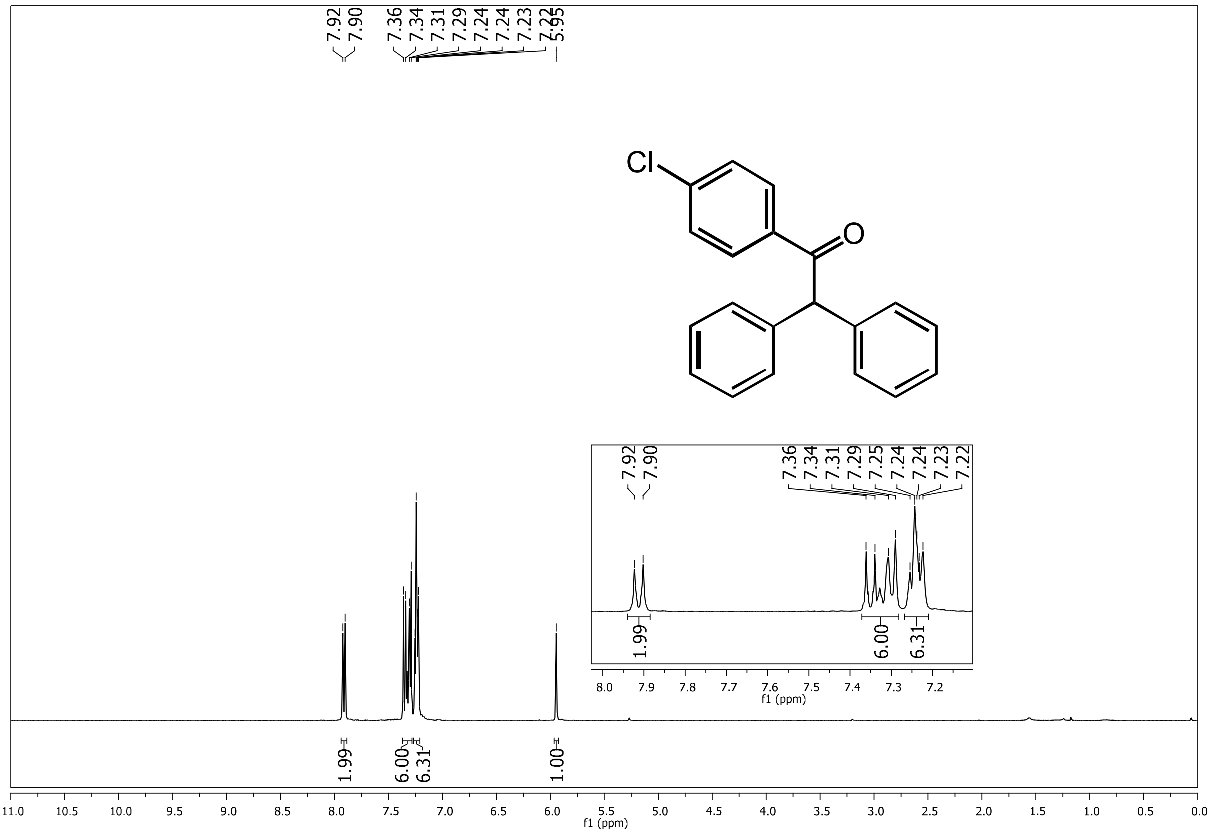
1-Bromo-4-(bromo(phenyl)methyl)benzene (2s)

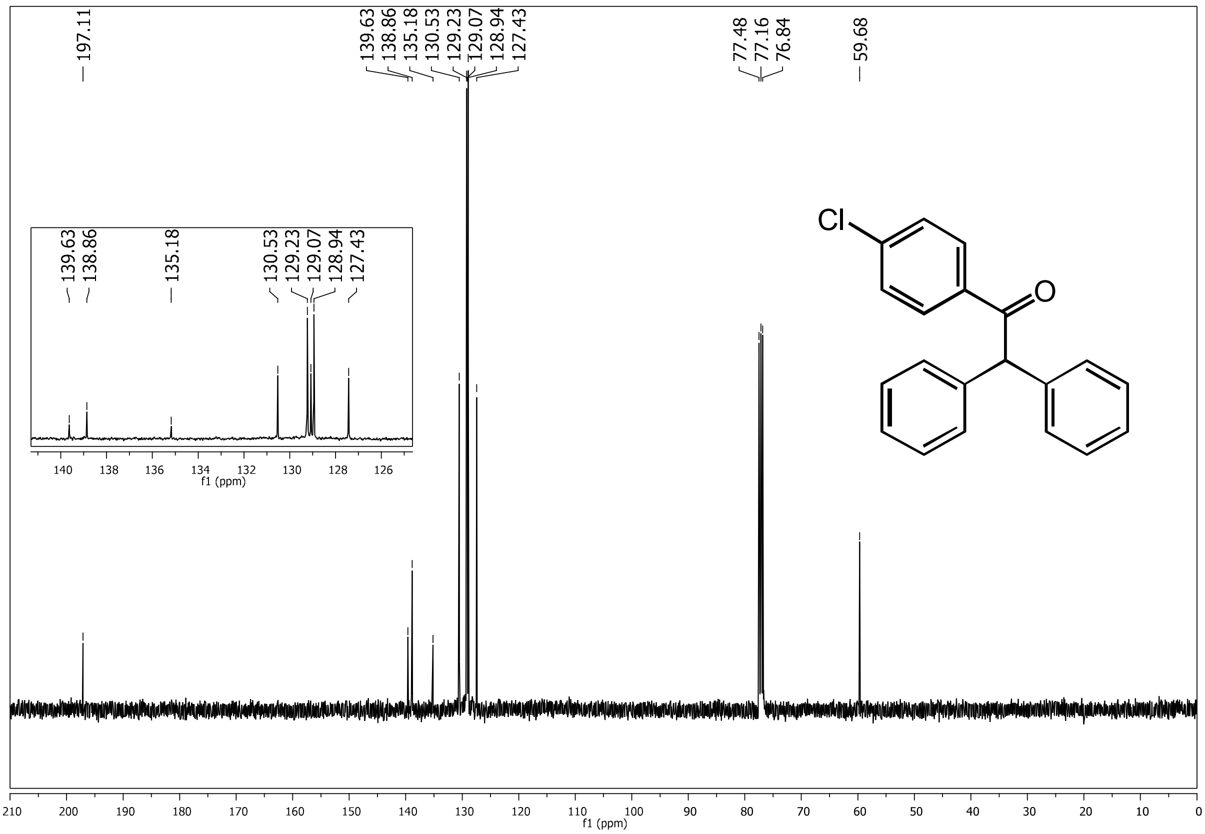




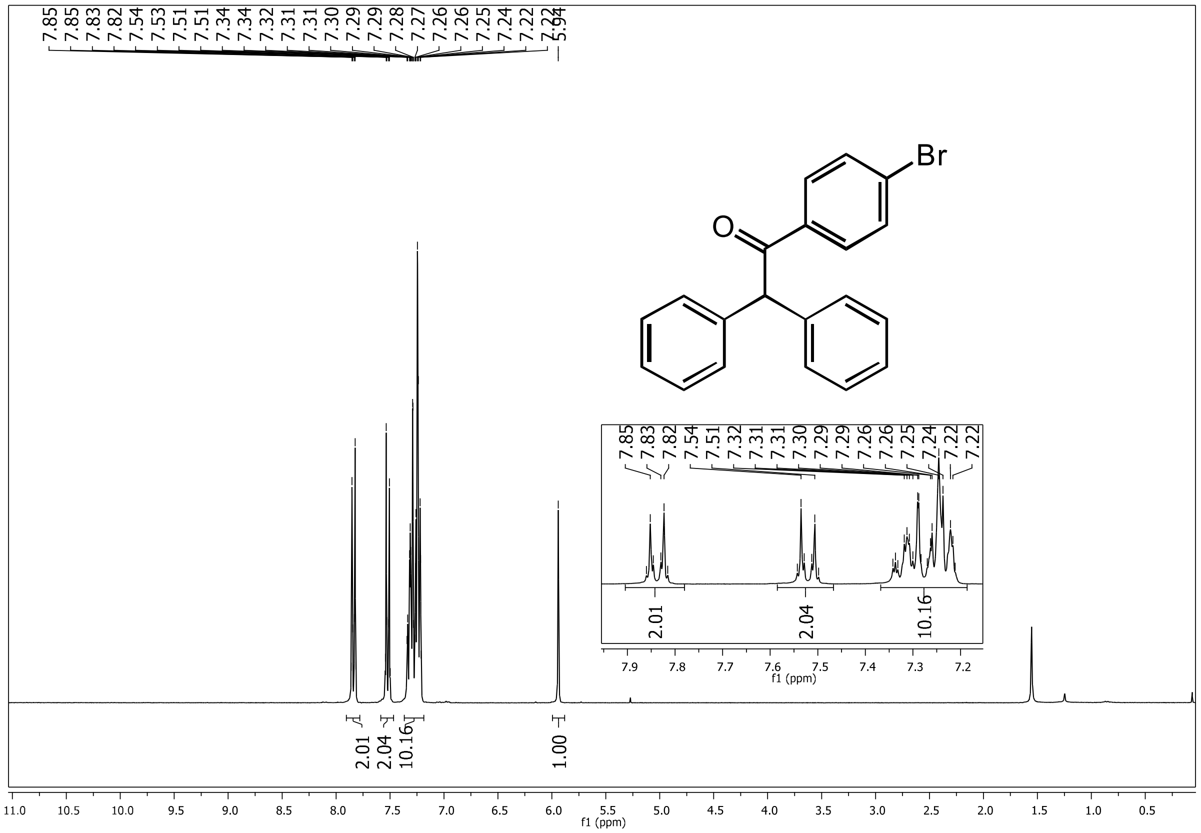
12. ^{1}H and ^{13}C NMR Spectra of Products

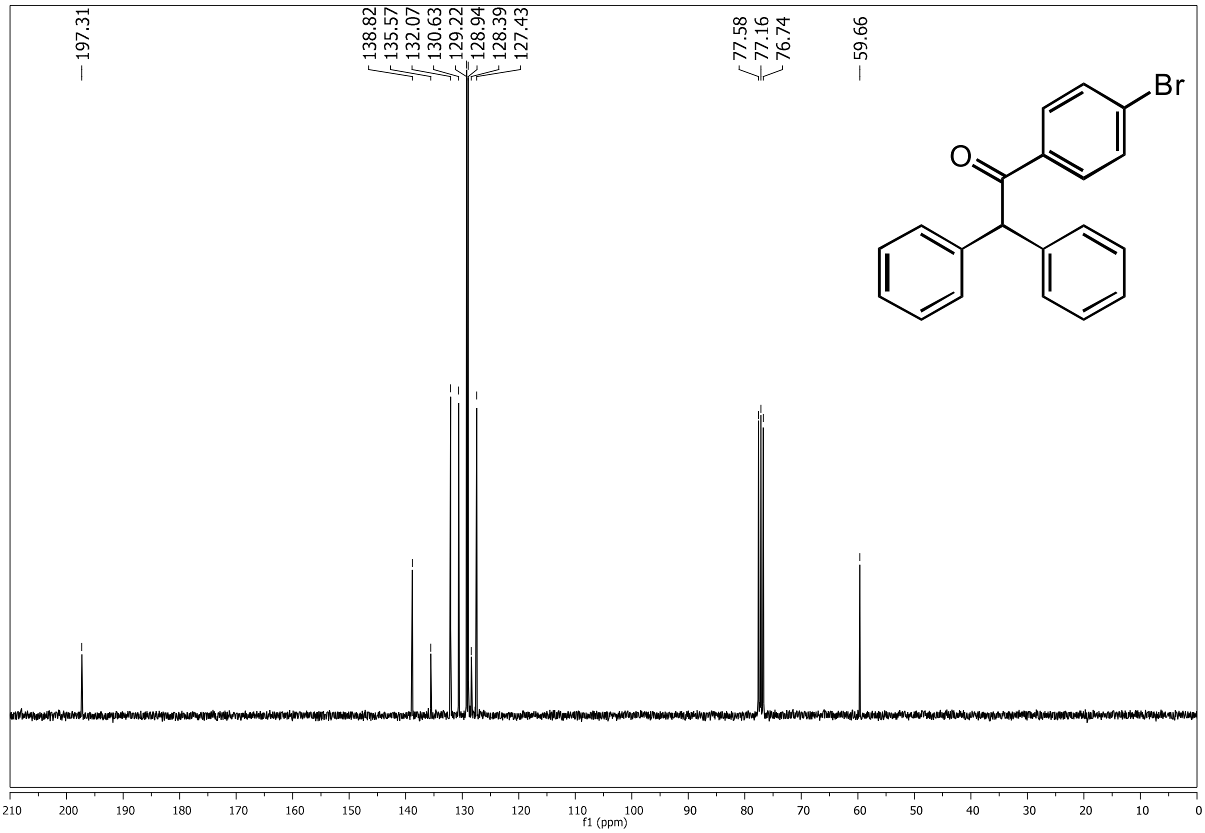
1-(4-Chlorophenyl)-2,2-diphenylethanone (3a)



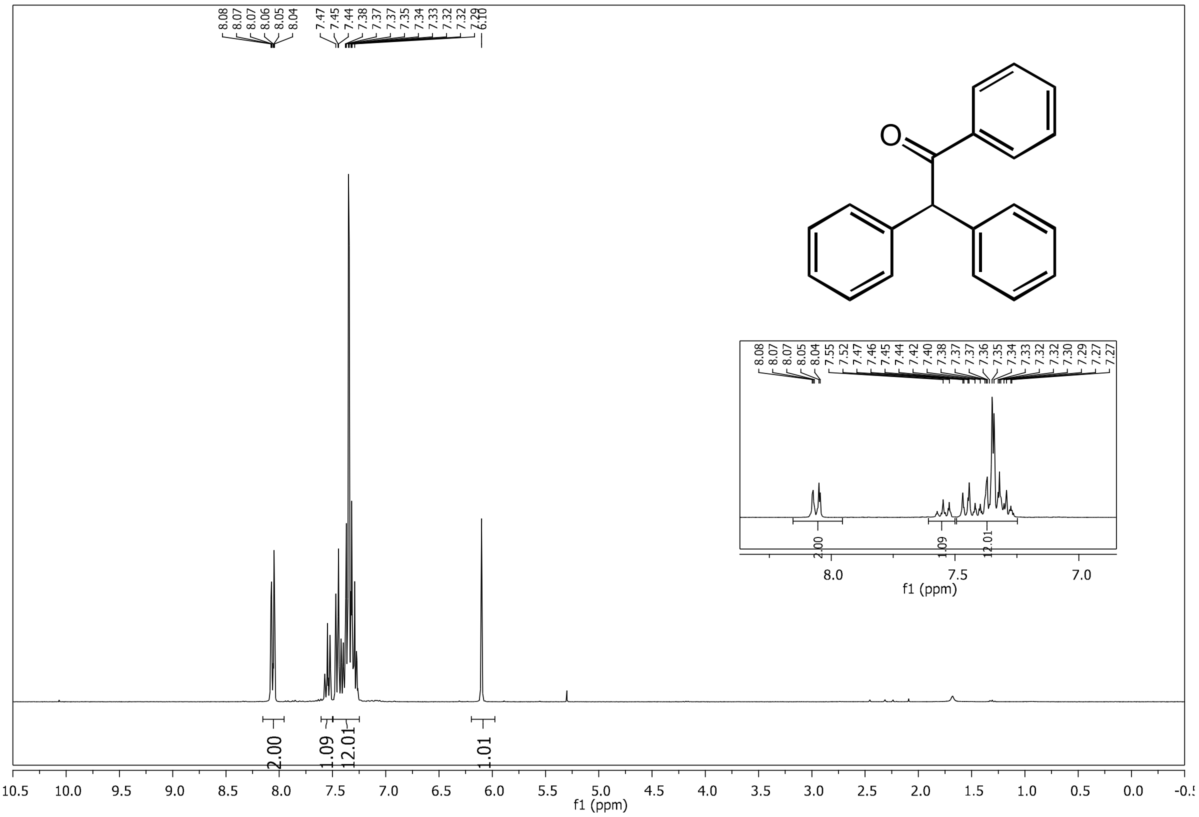


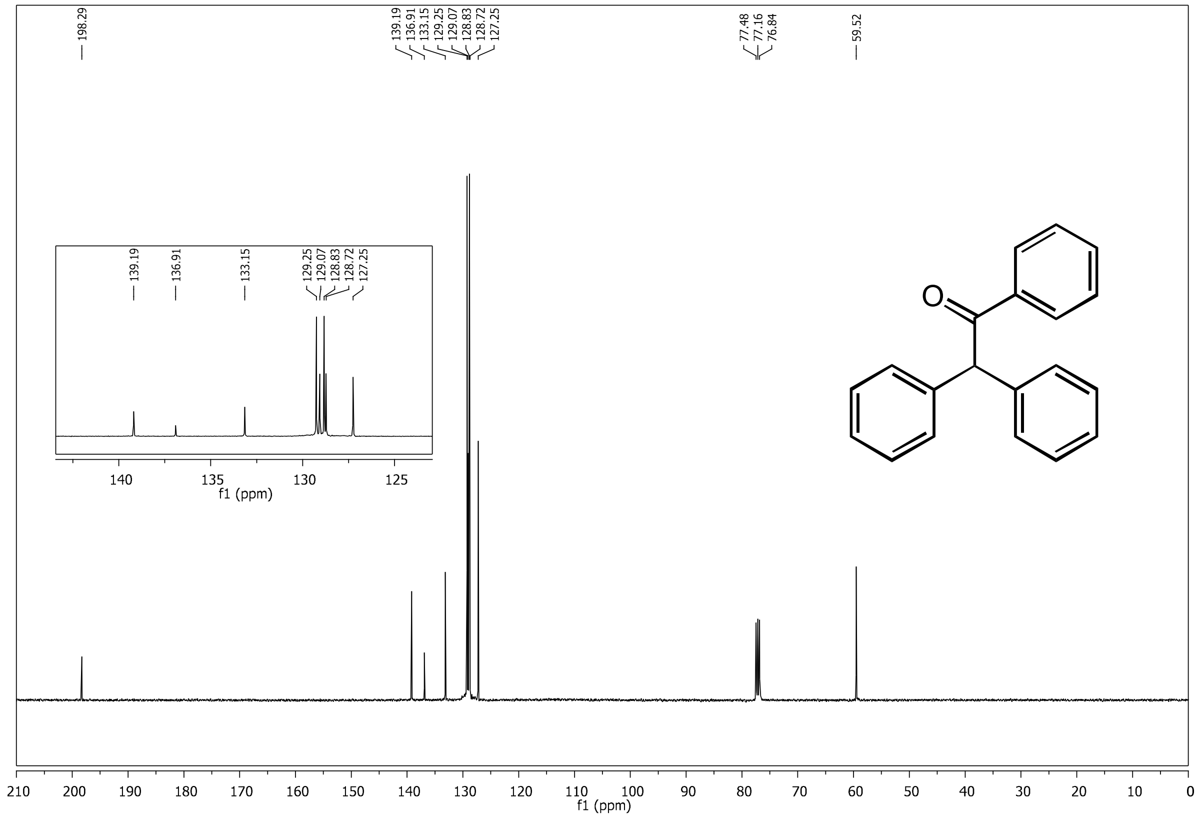
1-(4-Bromophenyl)-2,2-diphenylethanone (3b)



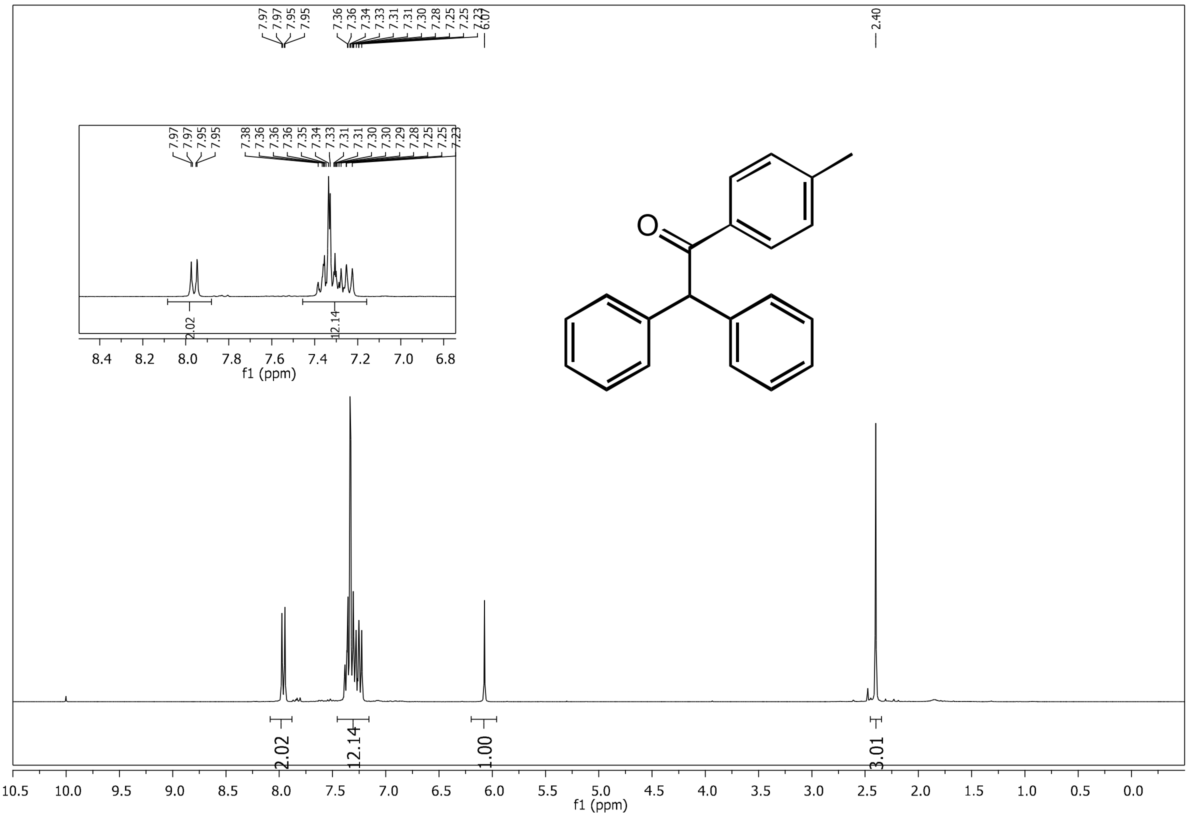


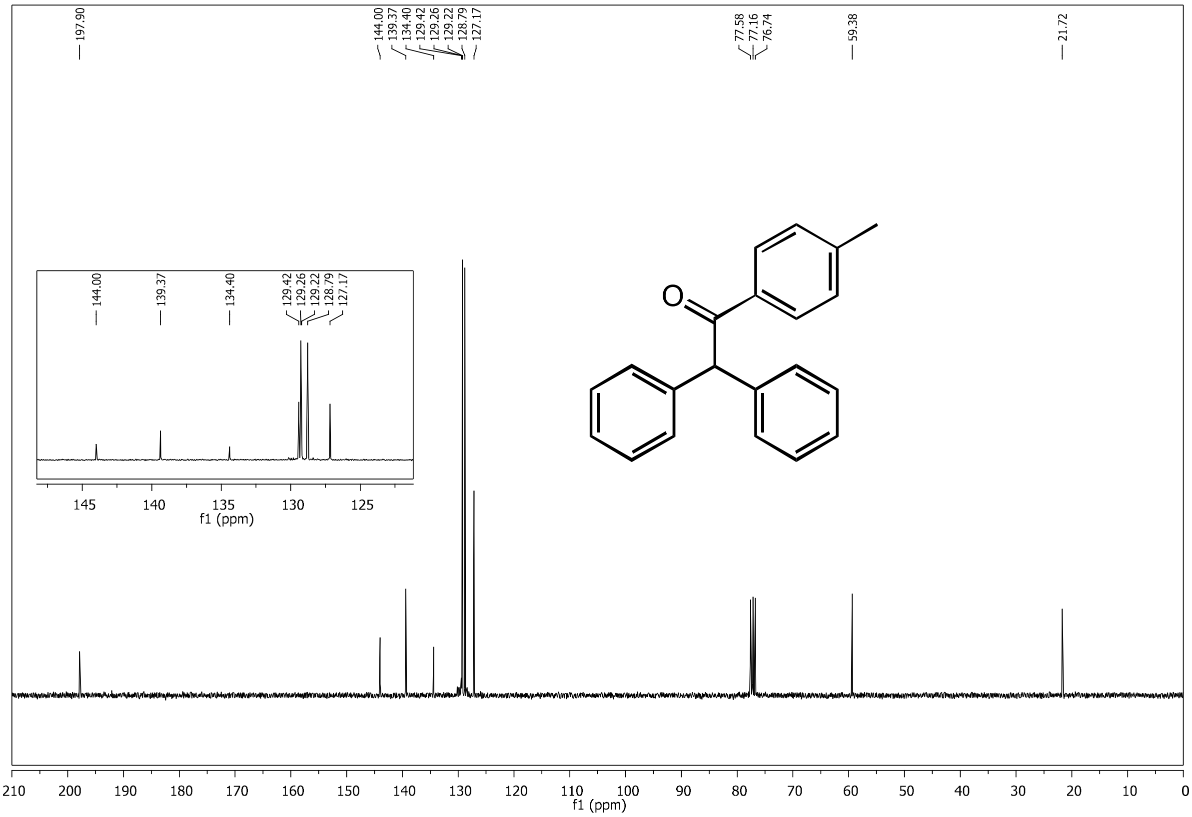
1,2,2-Triphenylethanone (3c)



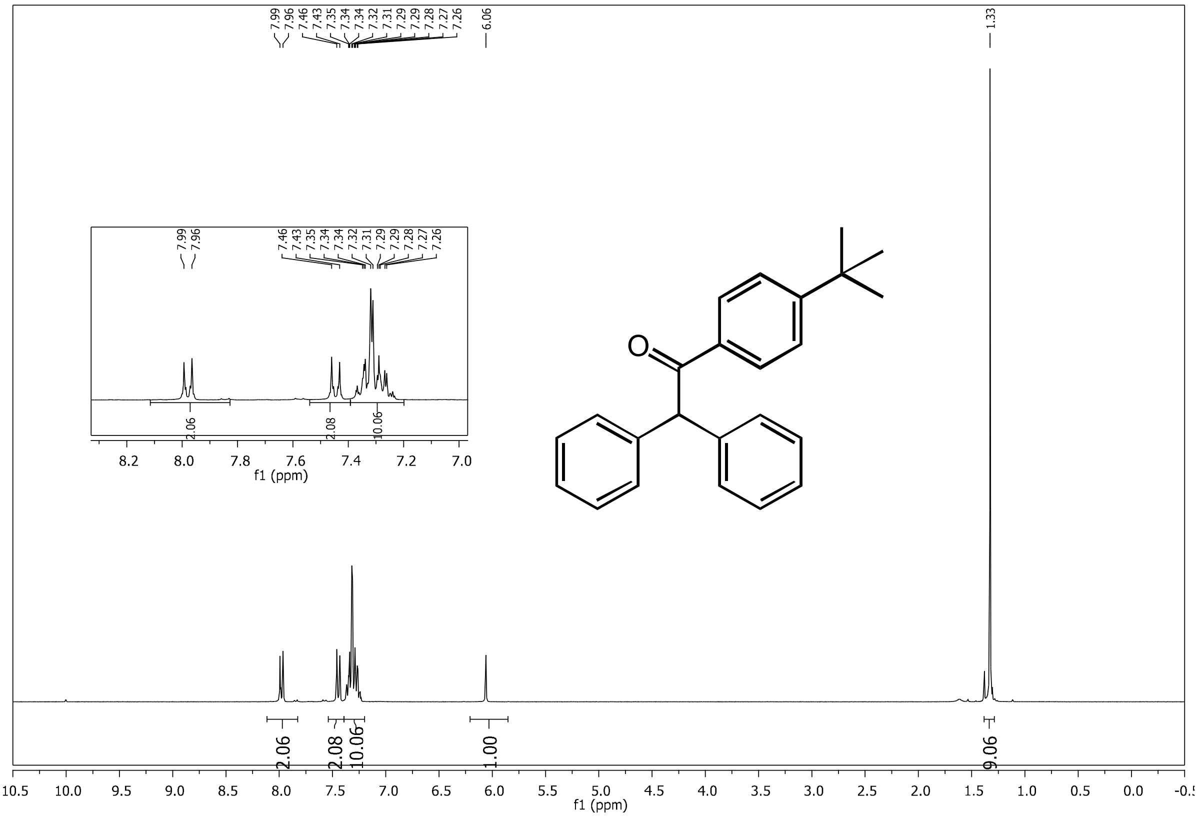


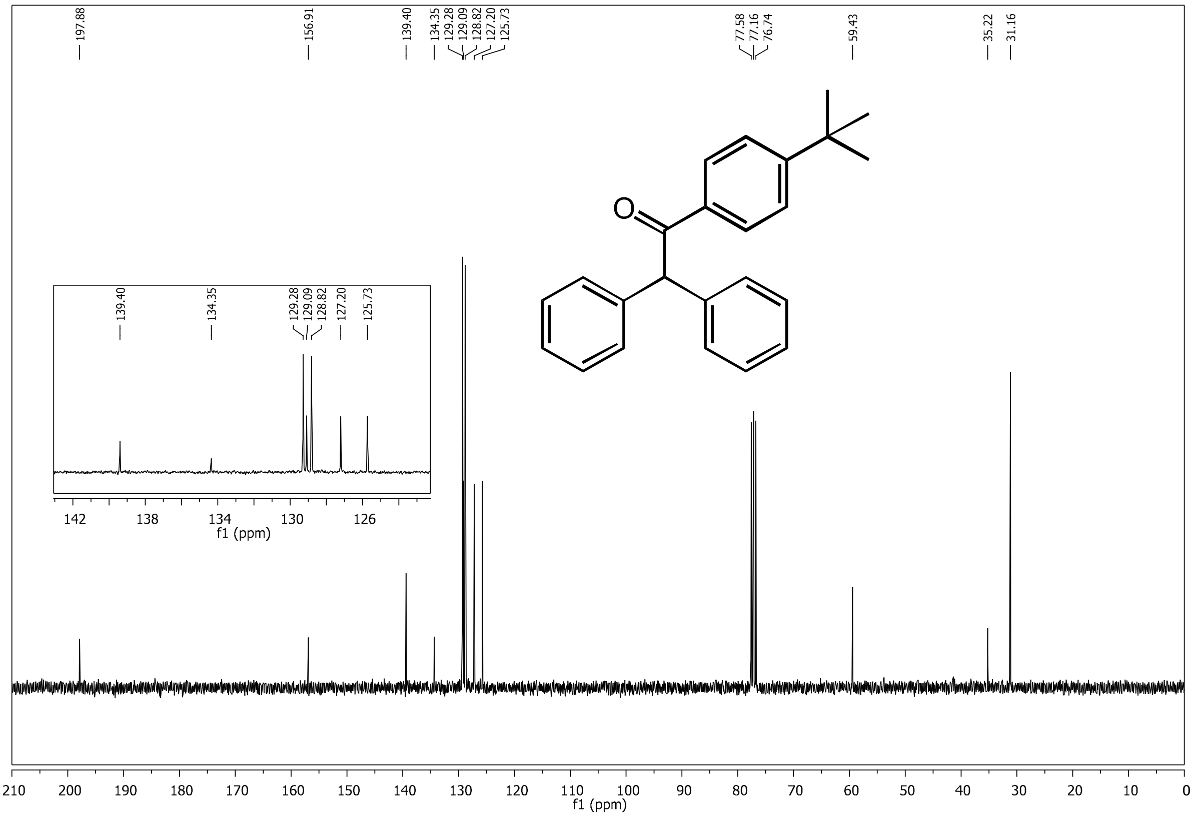
2,2-Diphenyl-1-(p-tolyl)ethanone (3d)



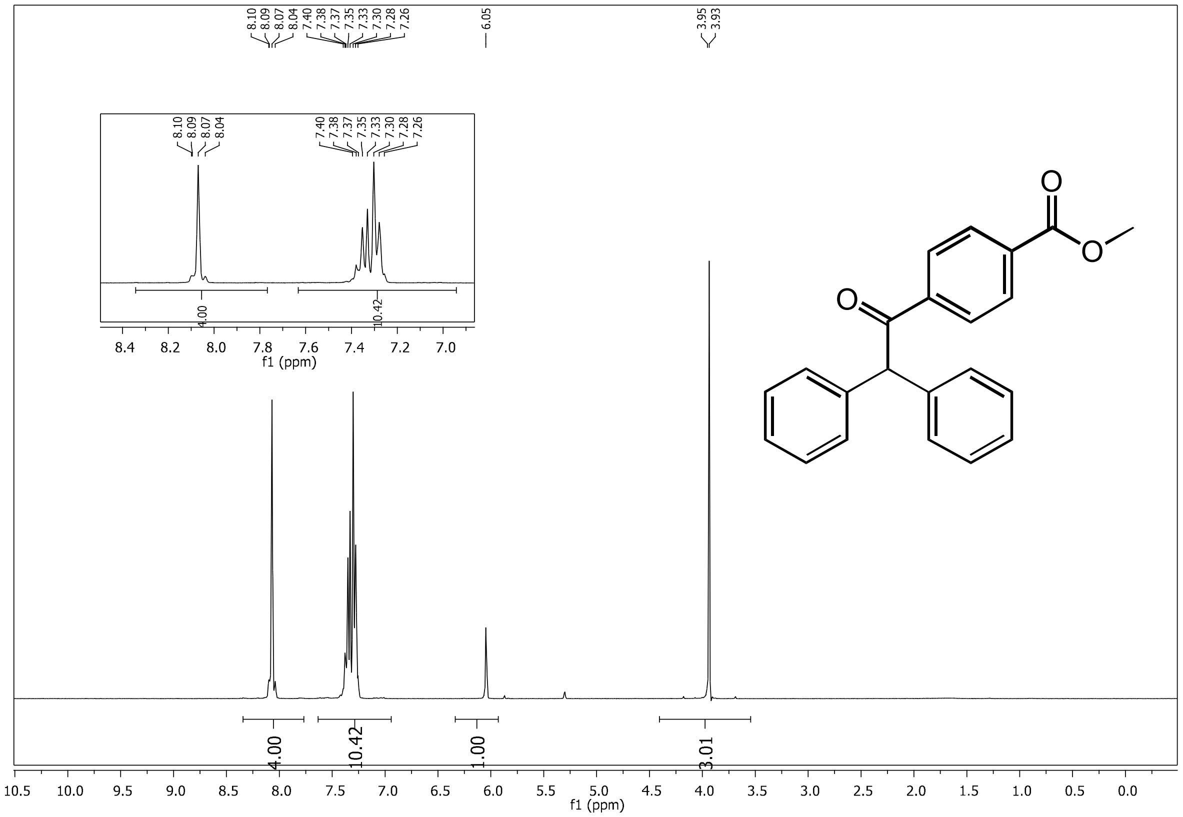


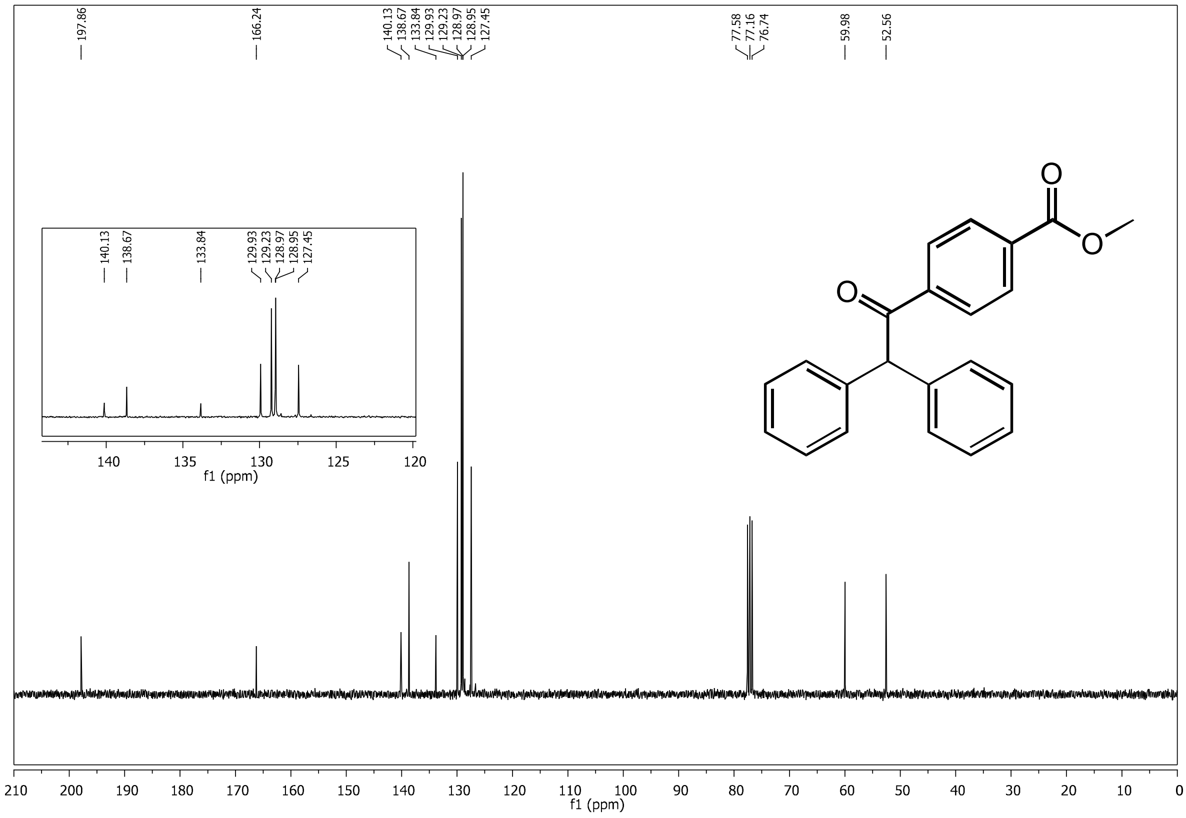
1-(4-(*tert*-Butyl)phenyl)-2,2-diphenylethanone (3e)



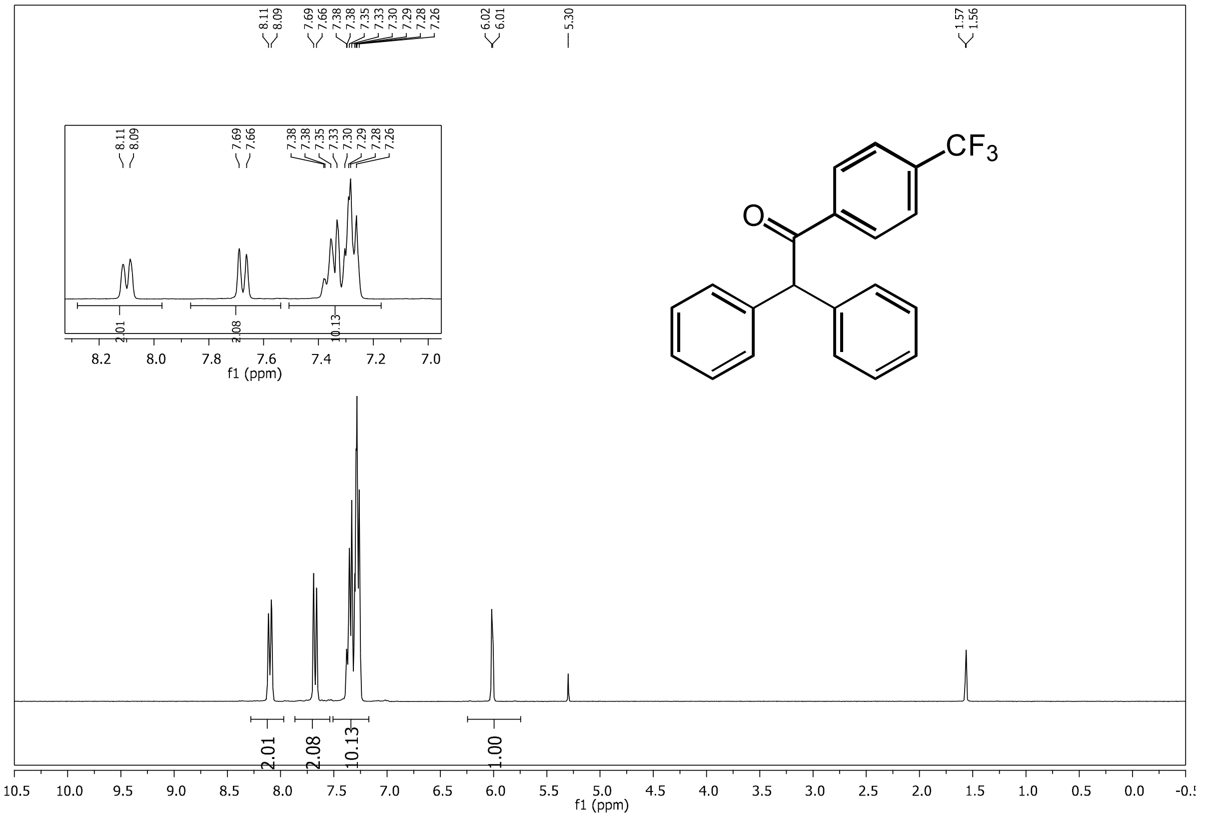


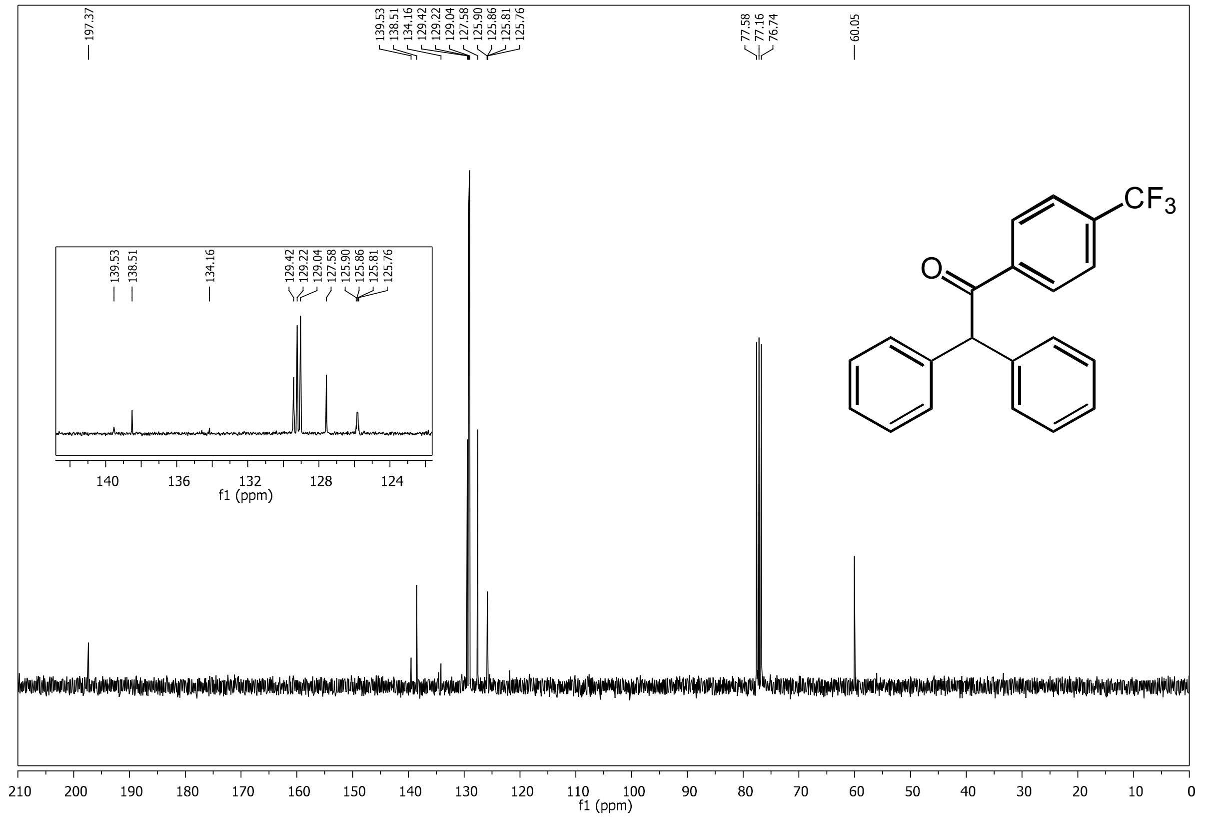
Methyl 4-(2,2-diphenylacetyl)benzoate (3f)



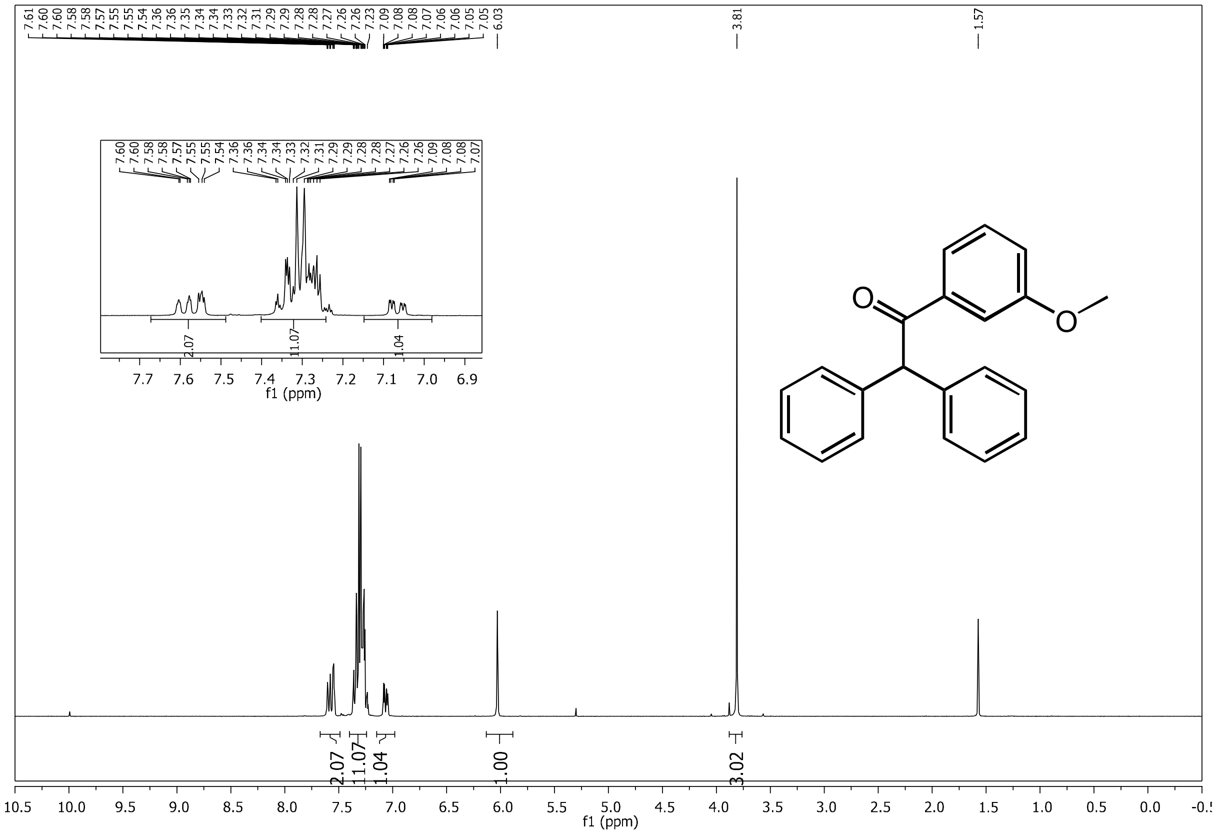


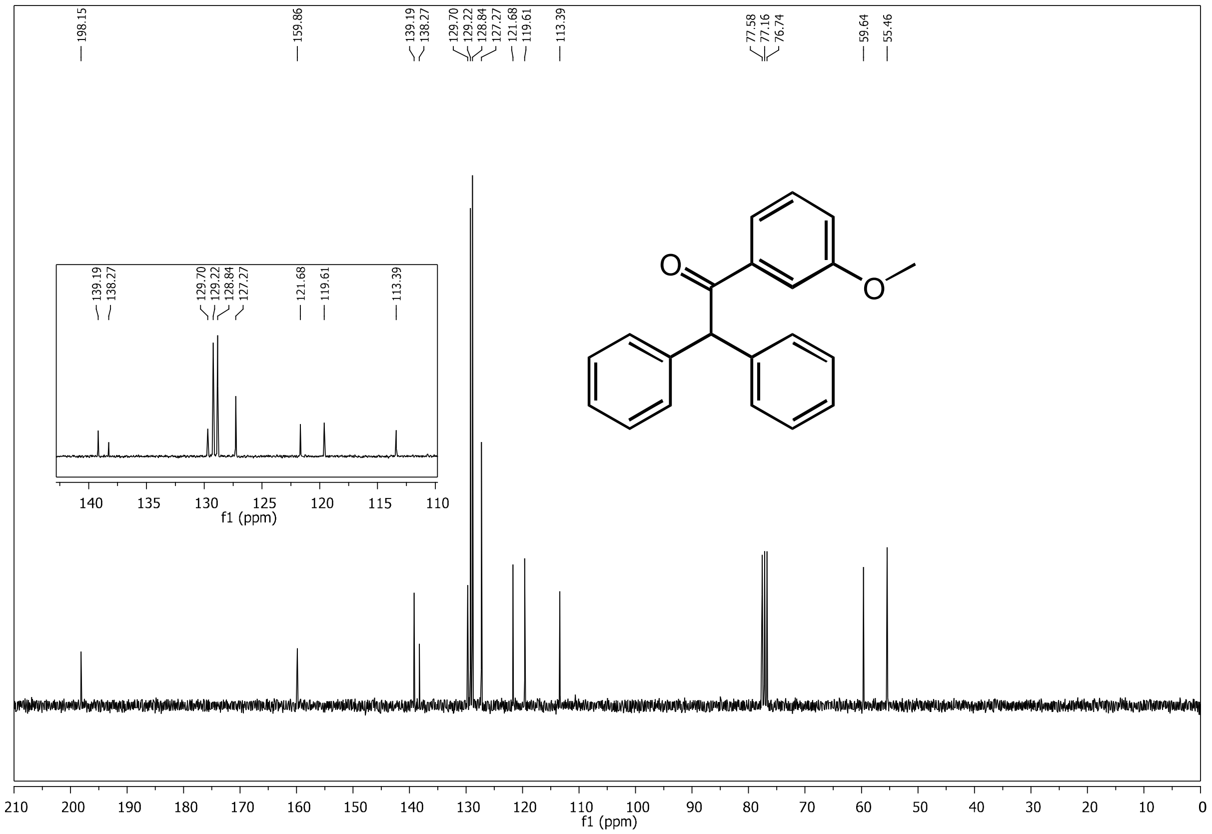
2,2-Diphenyl-1-(4-(trifluoromethyl)phenyl)ethanone (3g)



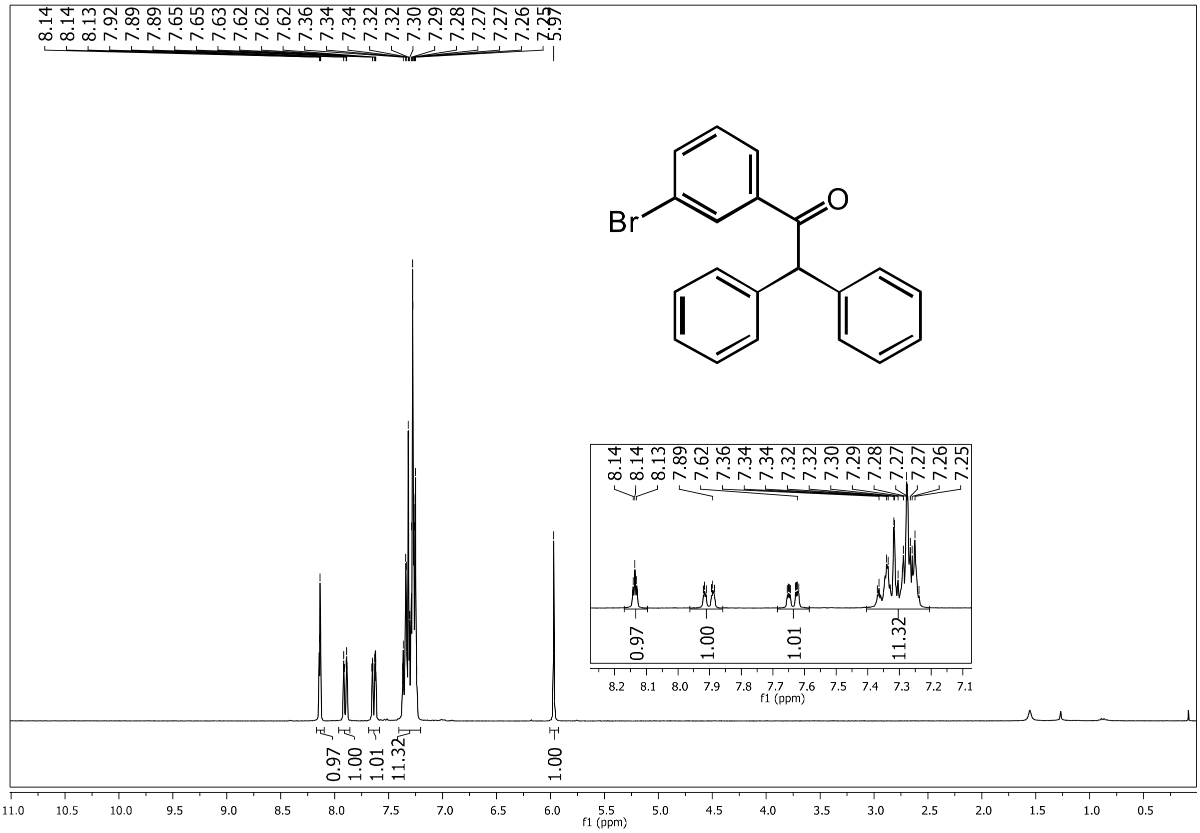


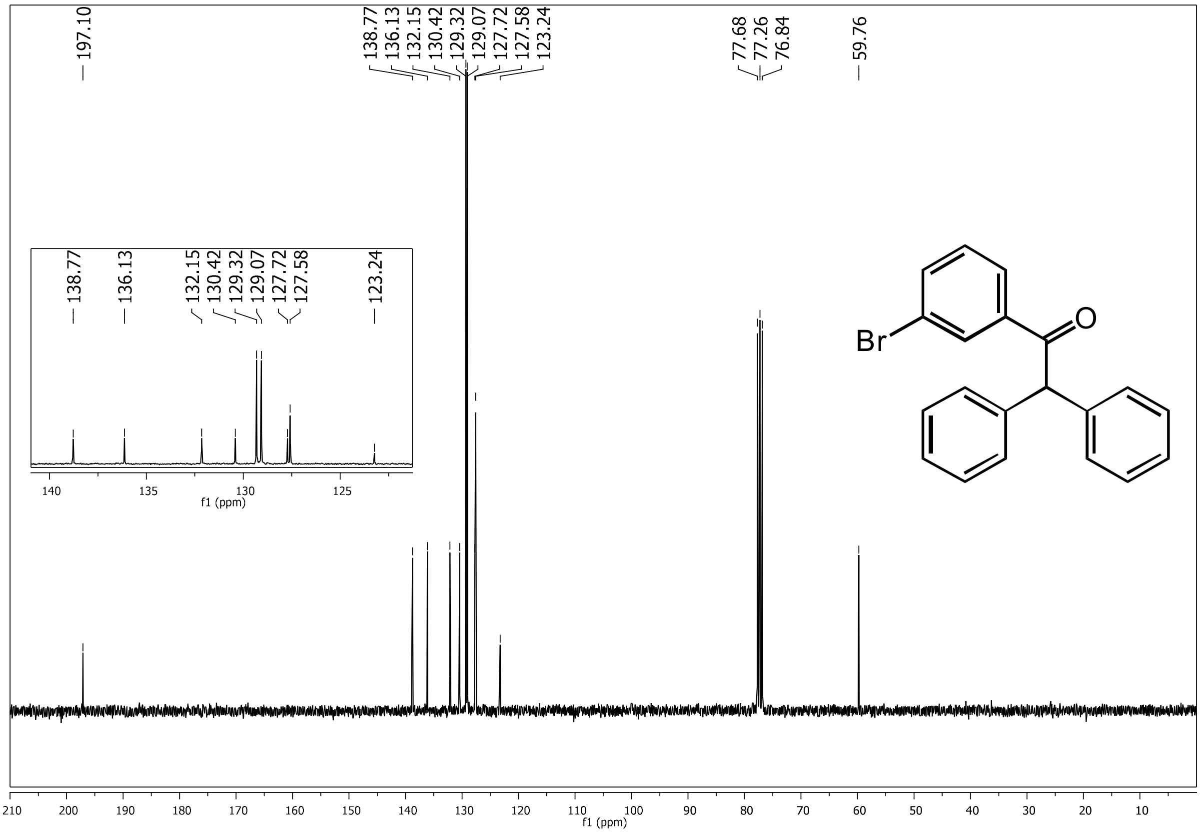
1-(3-Methoxyphenyl)-2,2-diphenylethanone (3h)



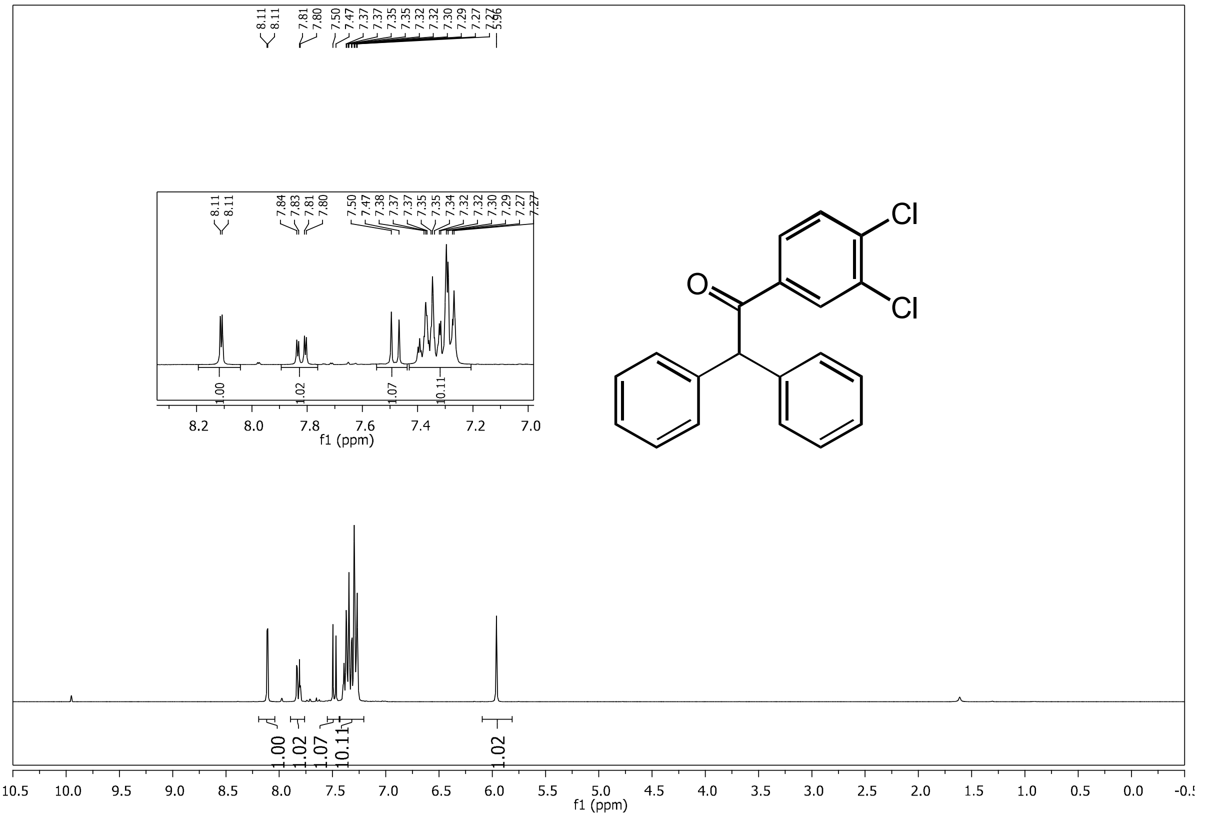


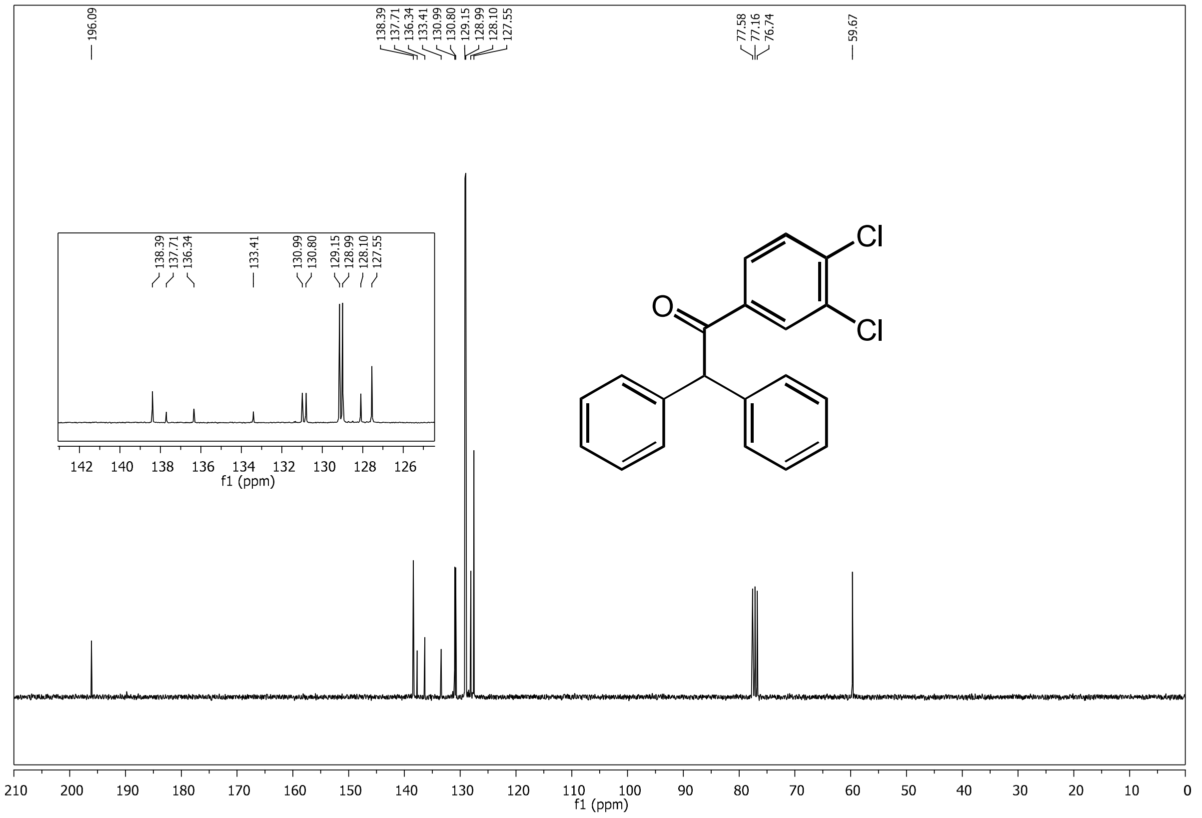
1-(3-Bromophenyl)-2,2-diphenylethanone (3i)



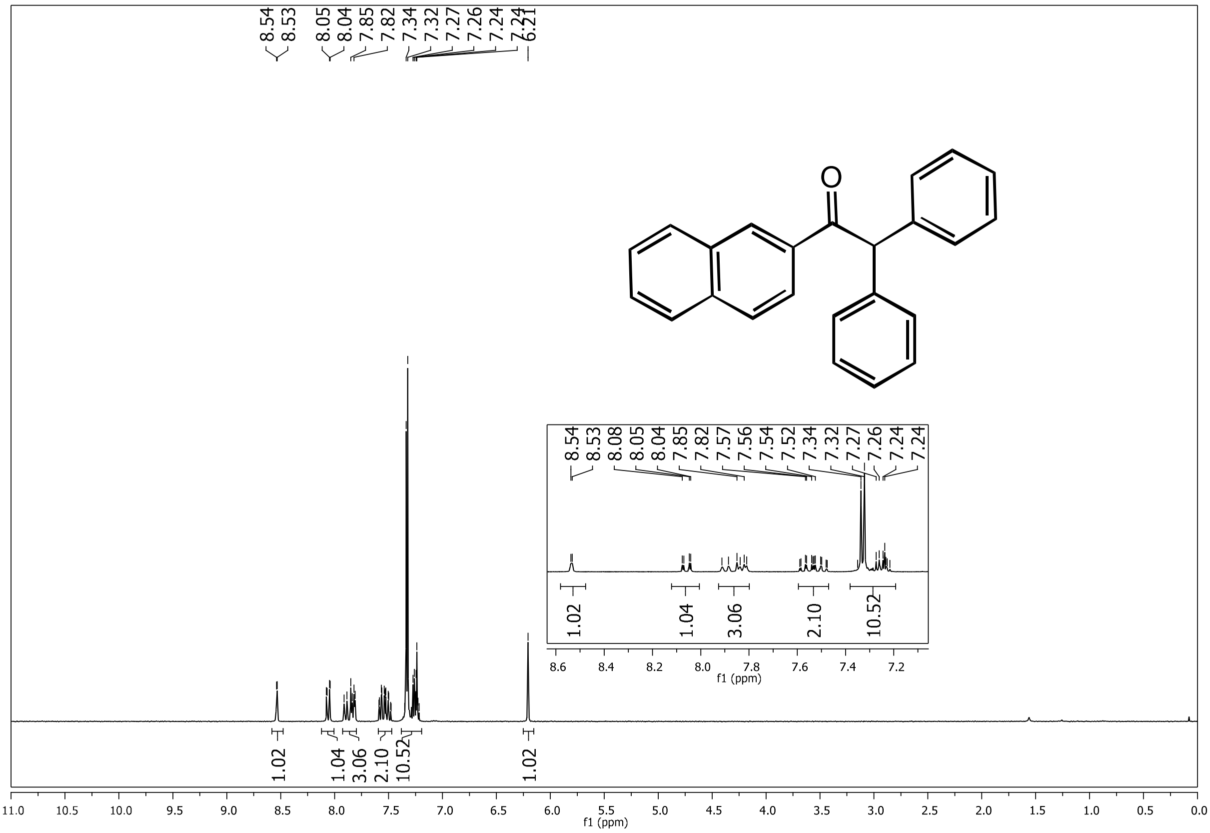


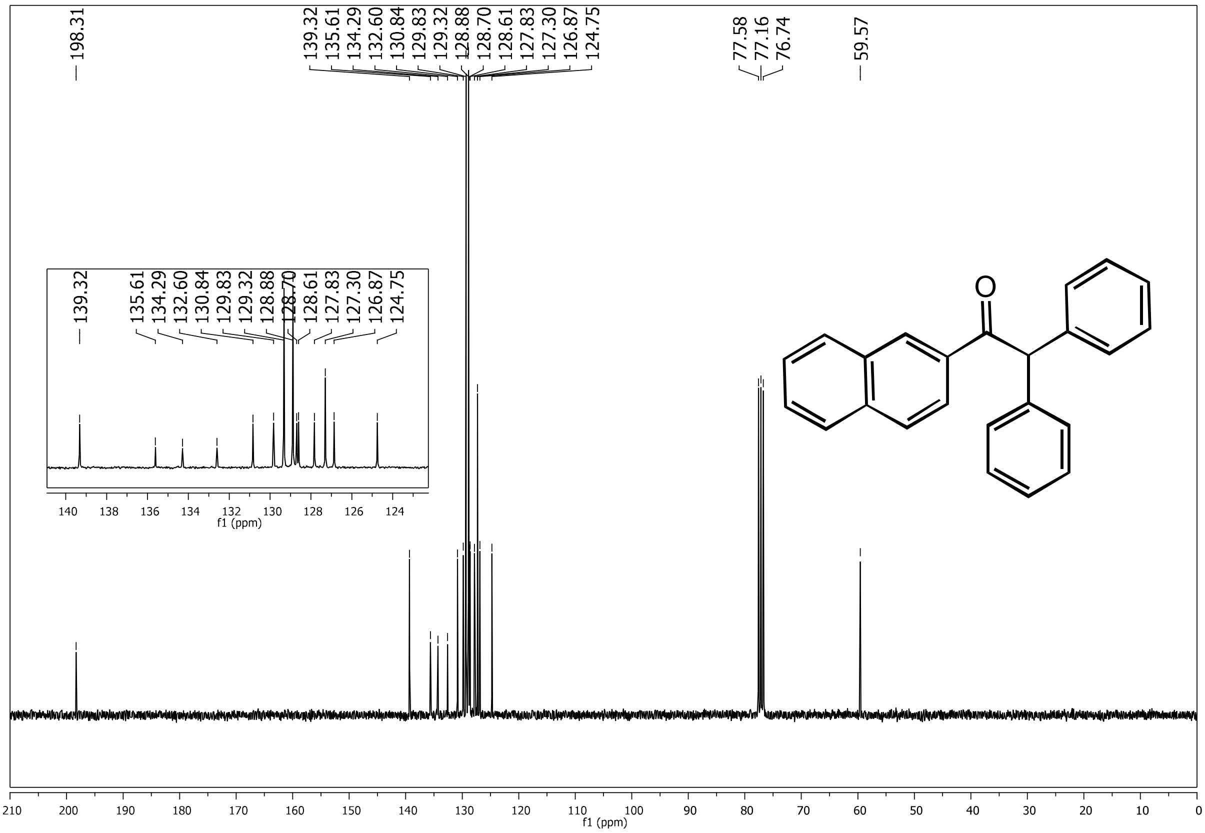
1-(3,4-Dichlorophenyl)-2,2-diphenylethanone (3j)



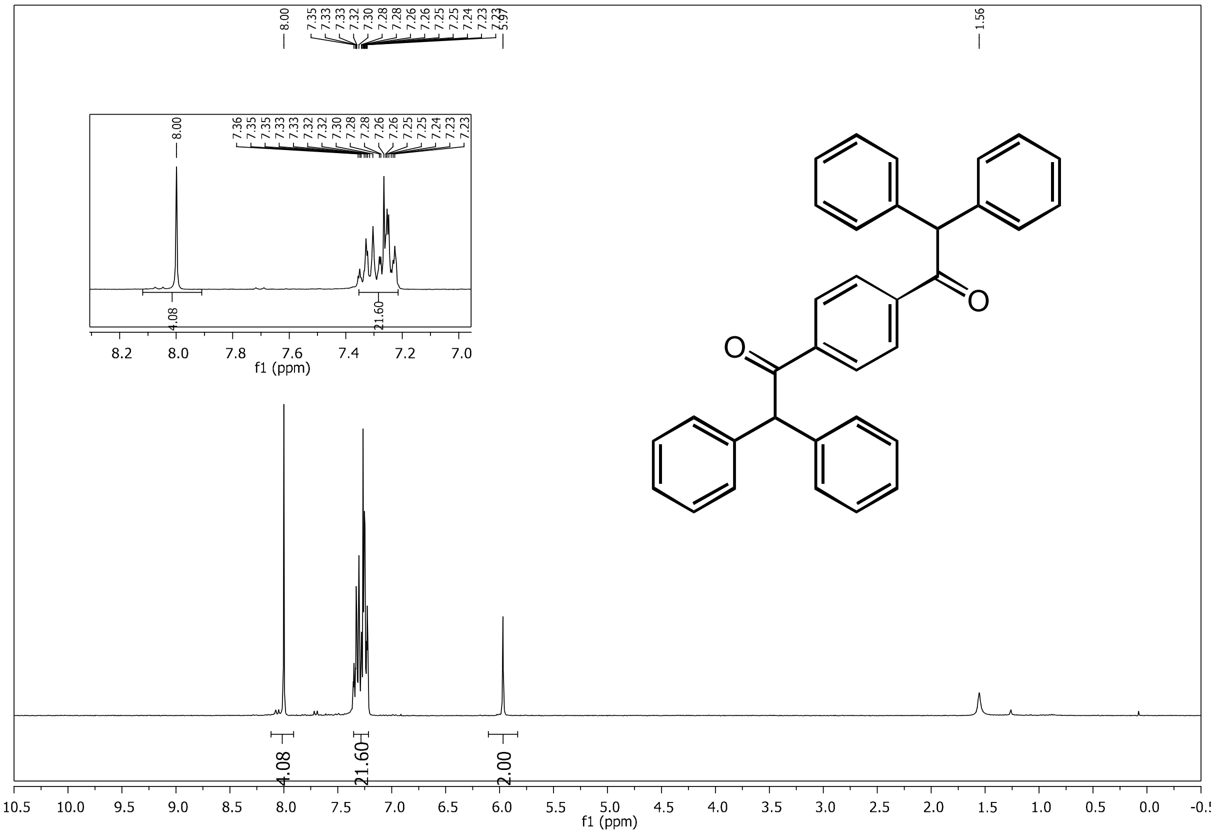


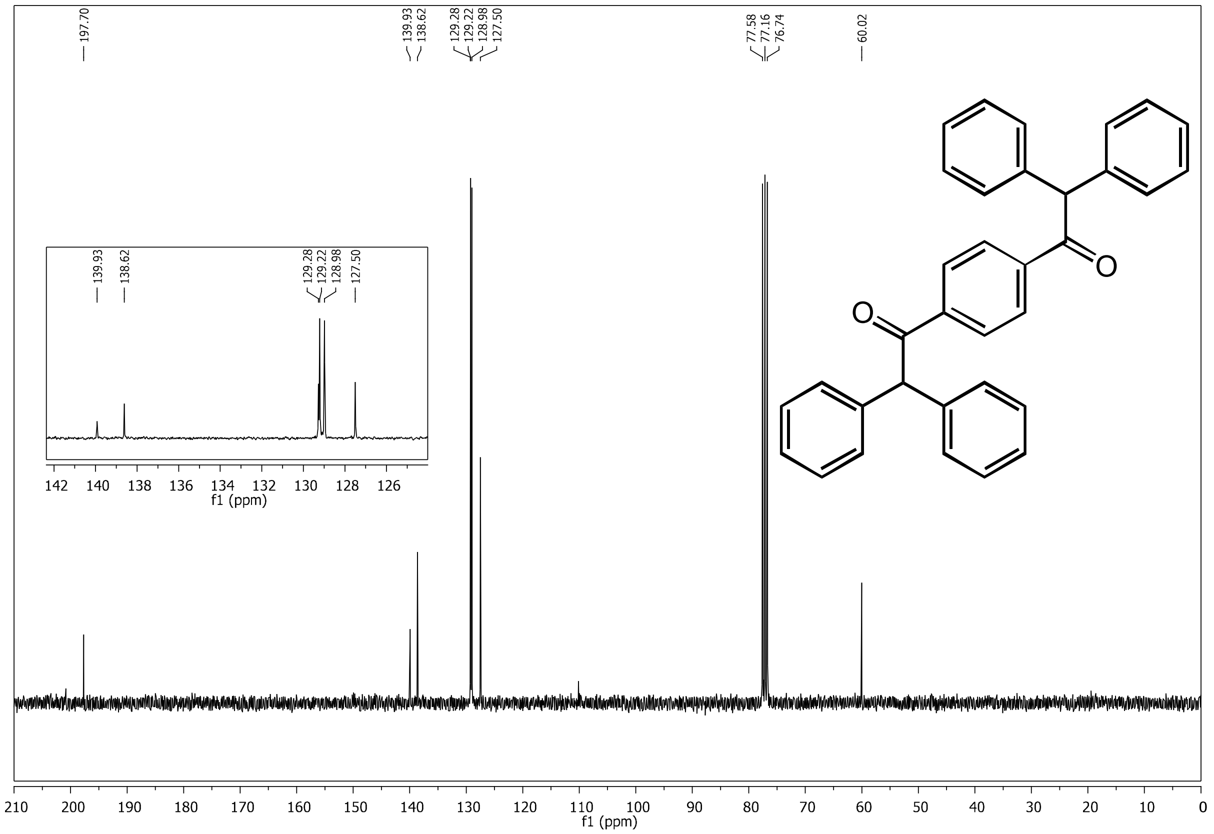
1-(Naphthalen-2-yl)-2,2-diphenylethanone (3k)



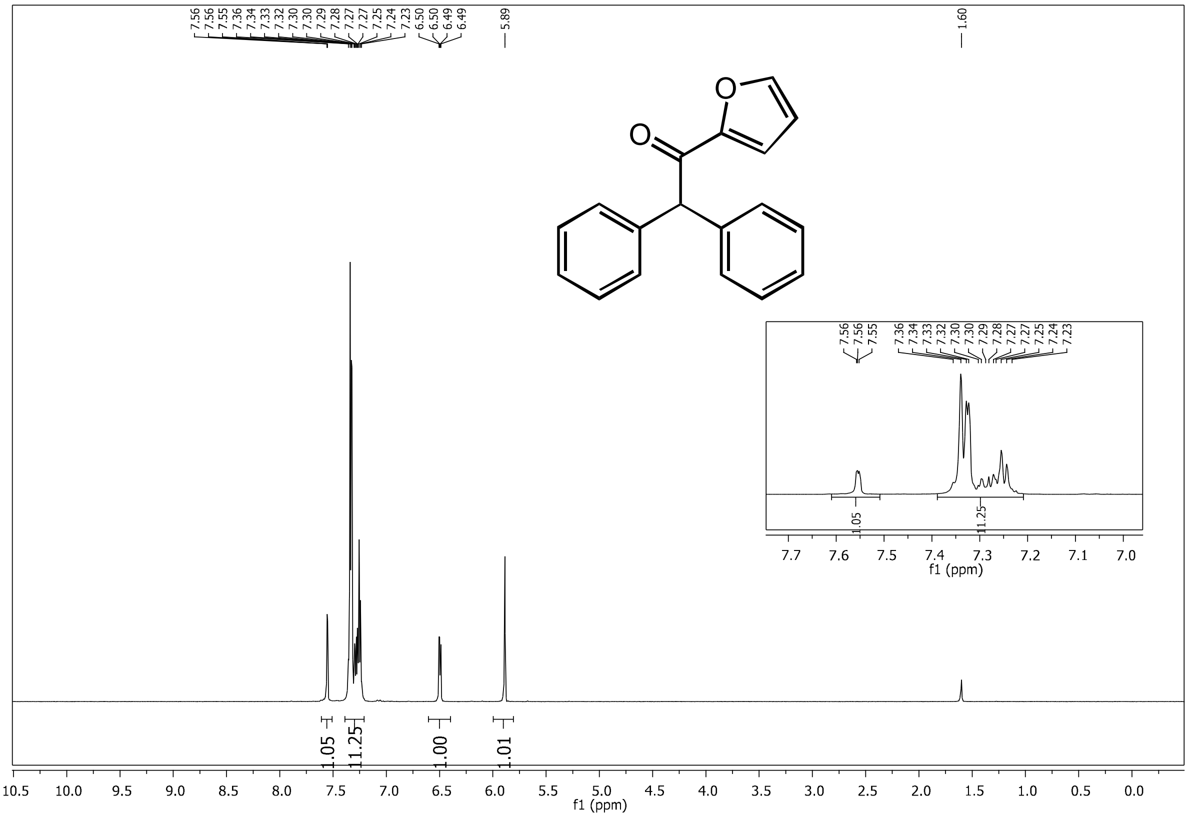


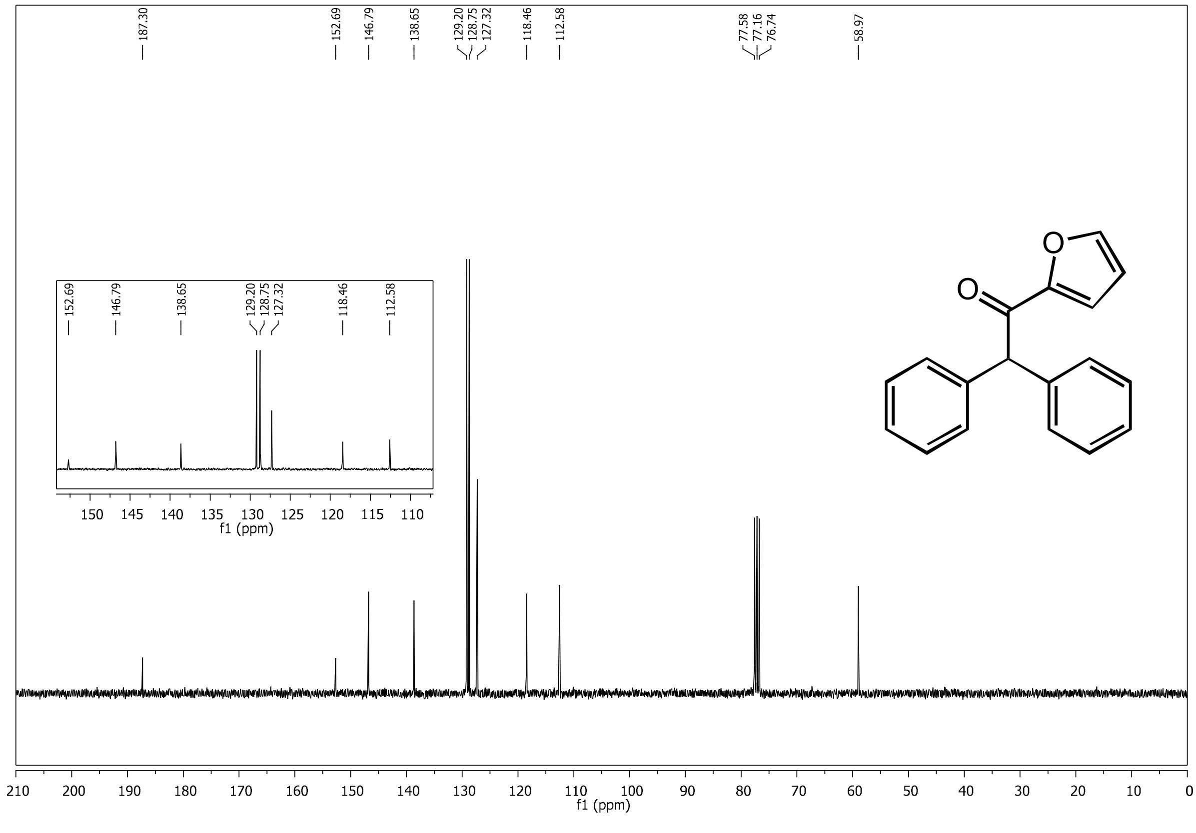
1,1'-(1,4-Phenylene)bis(2,2-diphenylethanone) (3l)



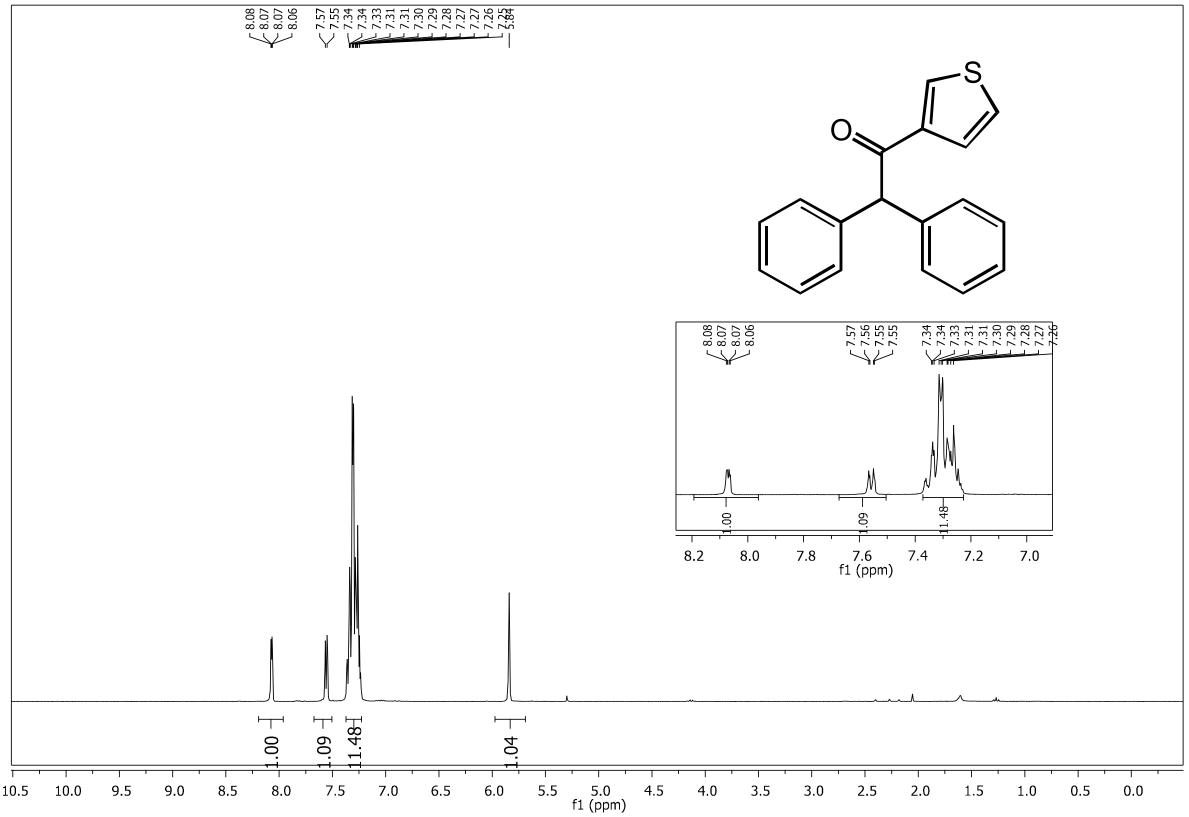


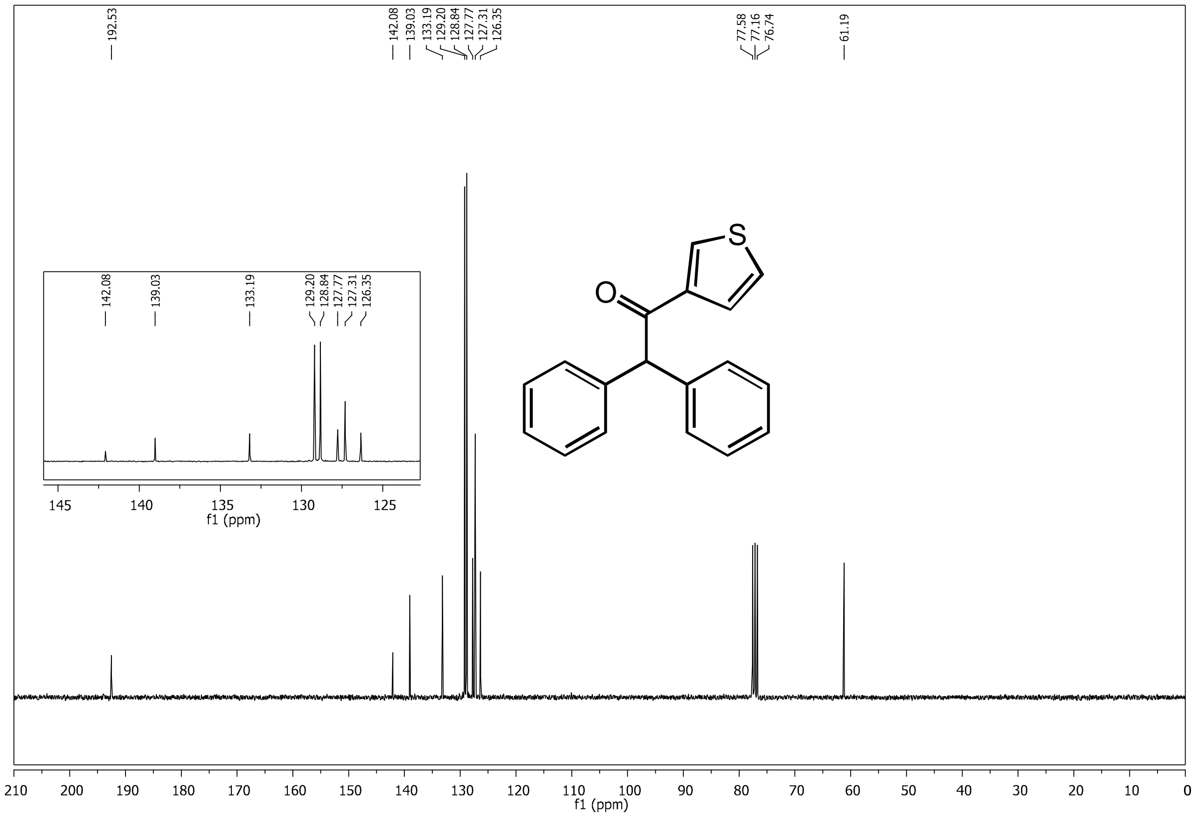
1-(Furan-2-yl)-2,2-diphenylethanone (3m)



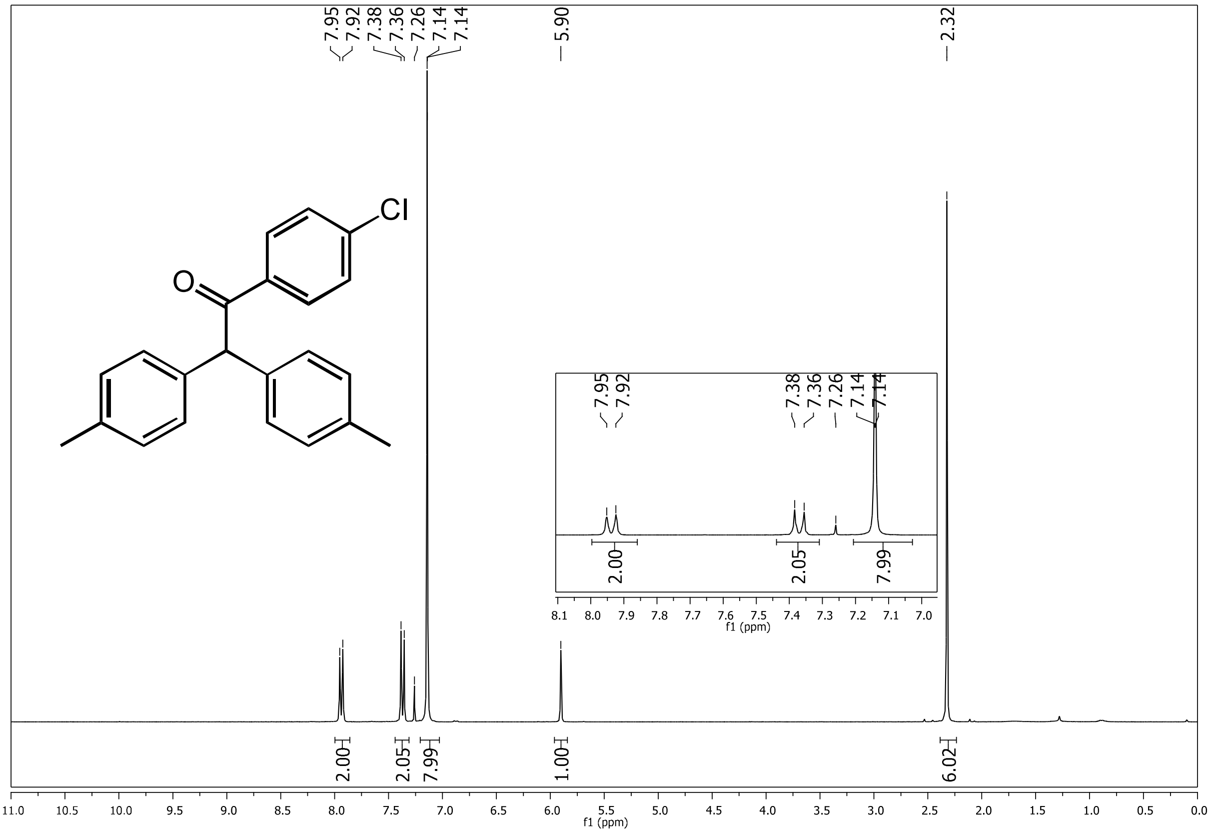


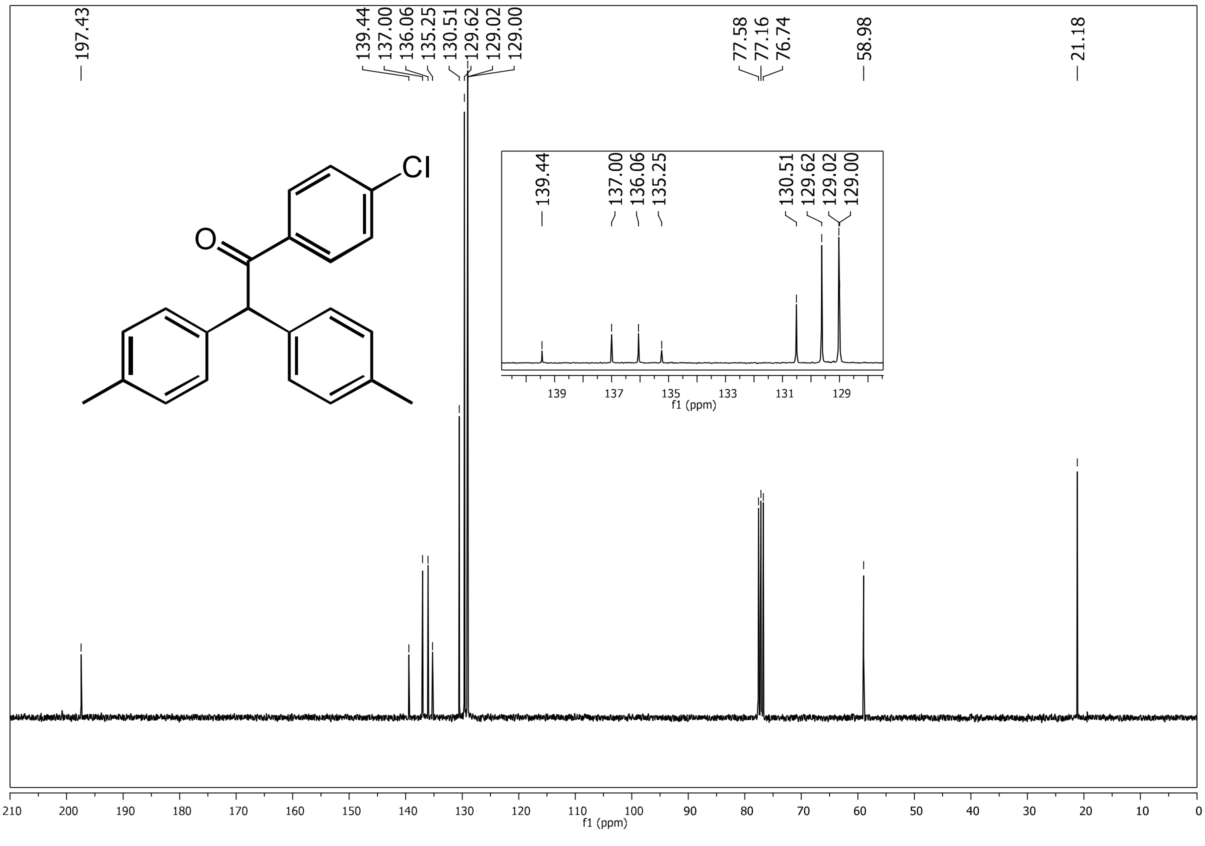
2,2-Diphenyl-1-(thiophen-3-yl)ethanone (3n)



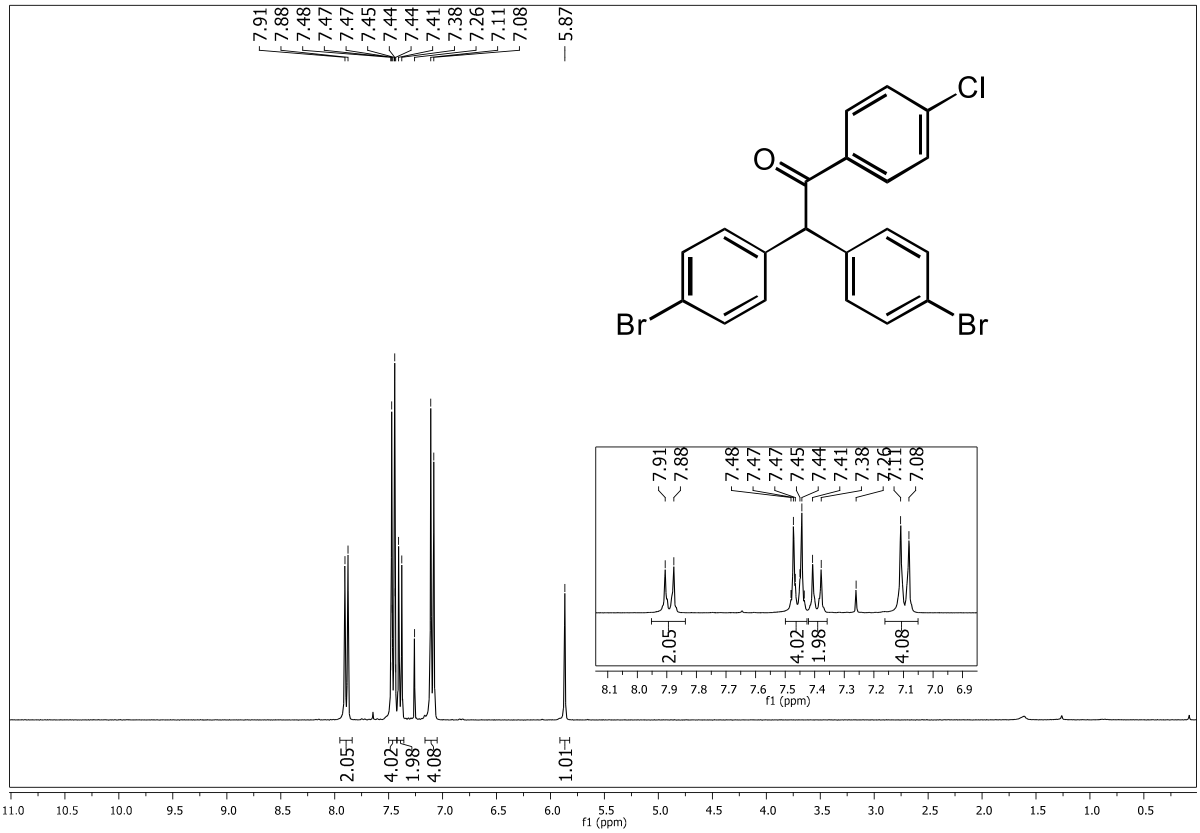


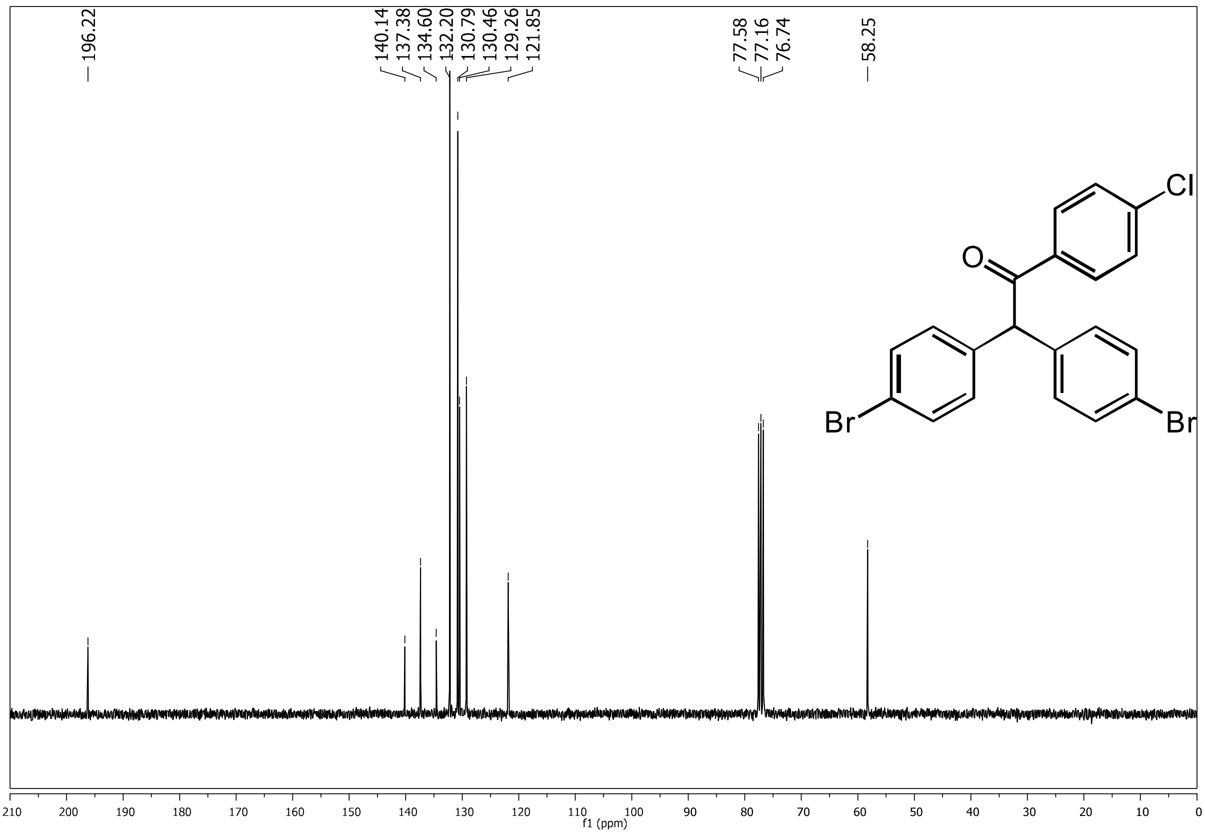
1-(4-Chlorophenyl)-2,2-di-p-tolylethanone (3o)



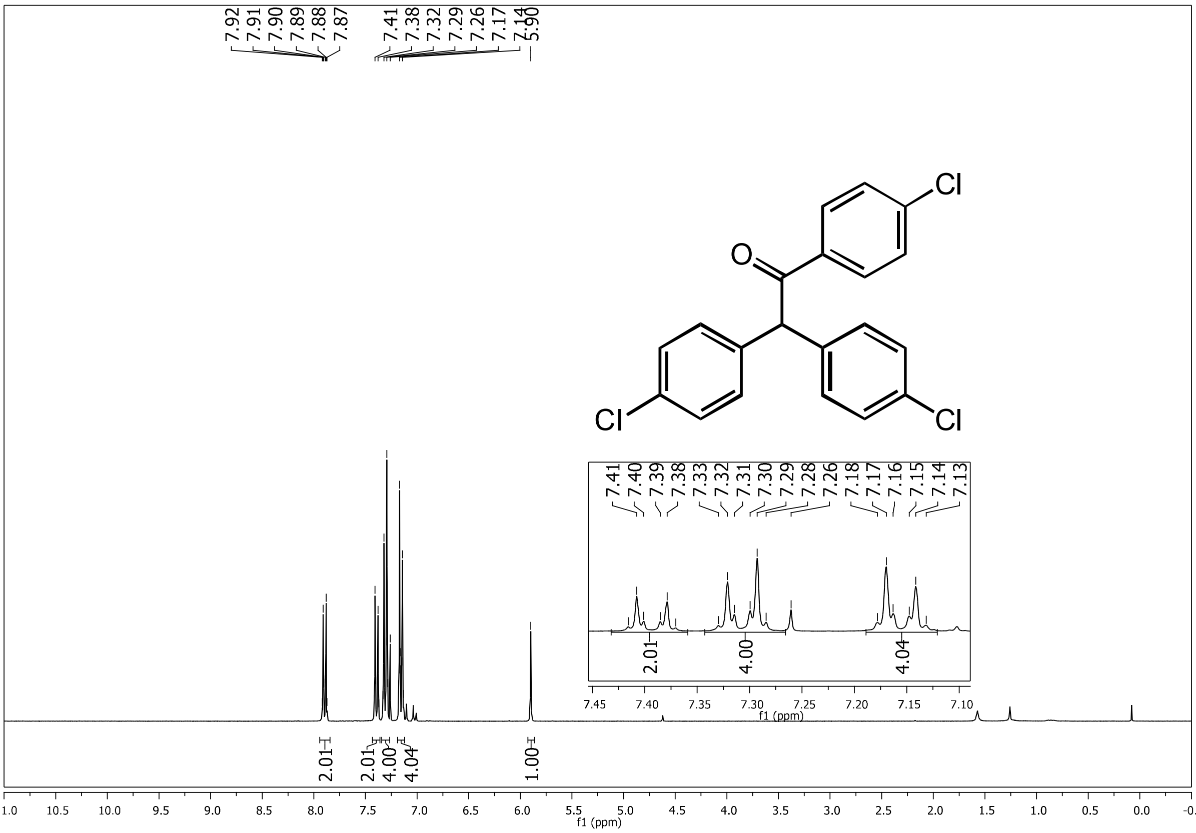


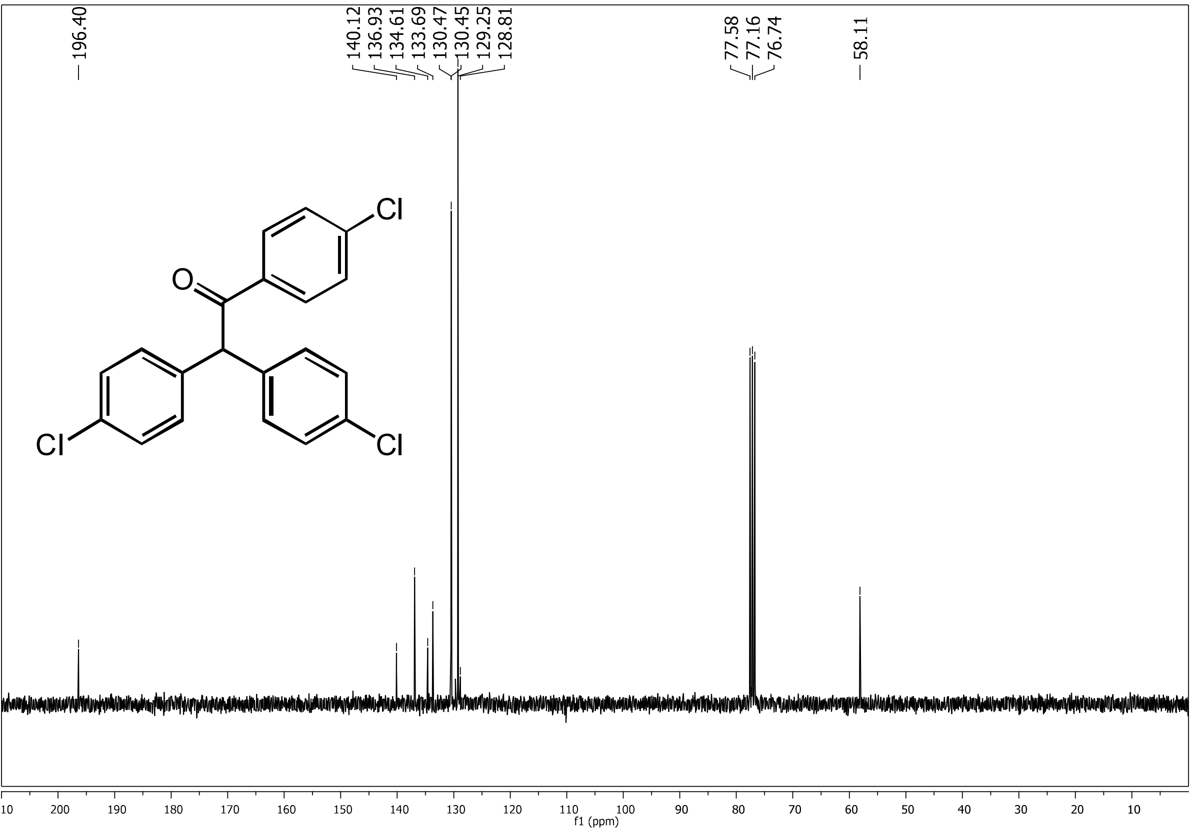
2,2-Bis(4-bromophenyl)-1-(4-chlorophenyl)ethanone (3p)



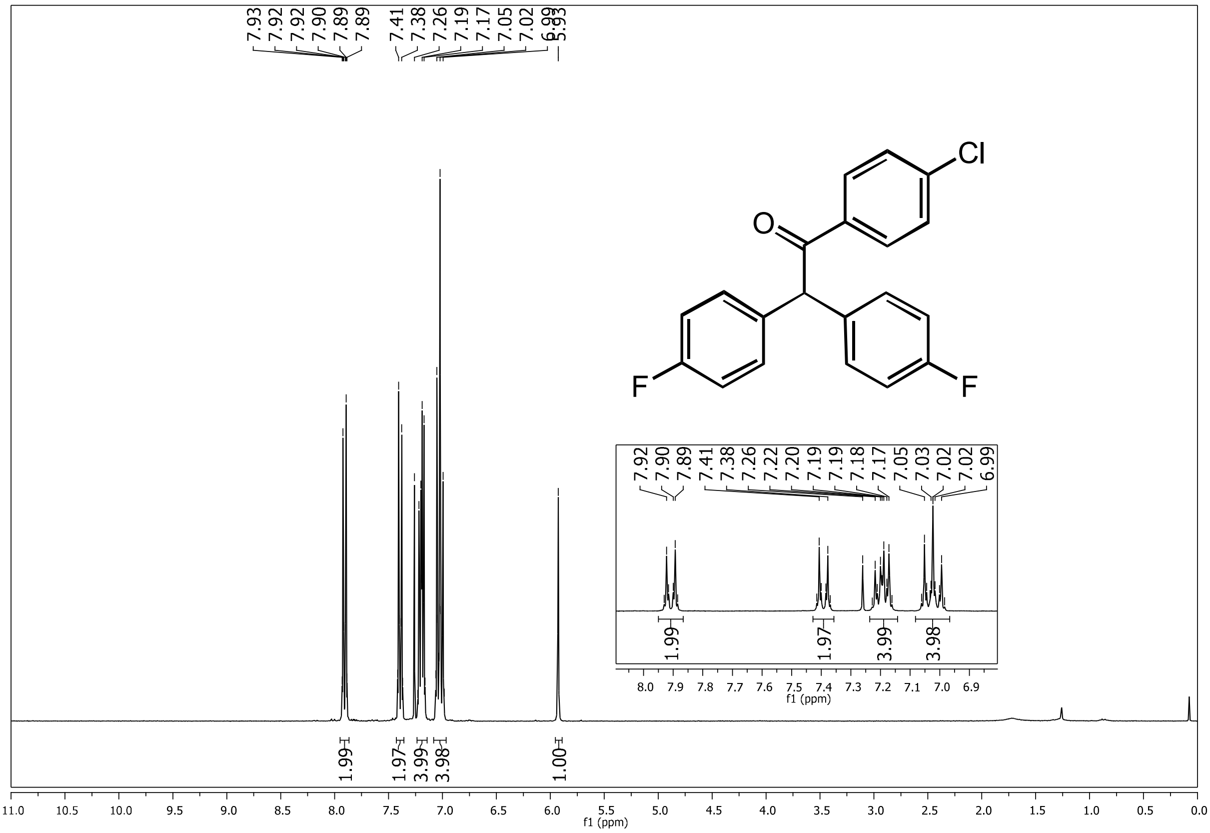


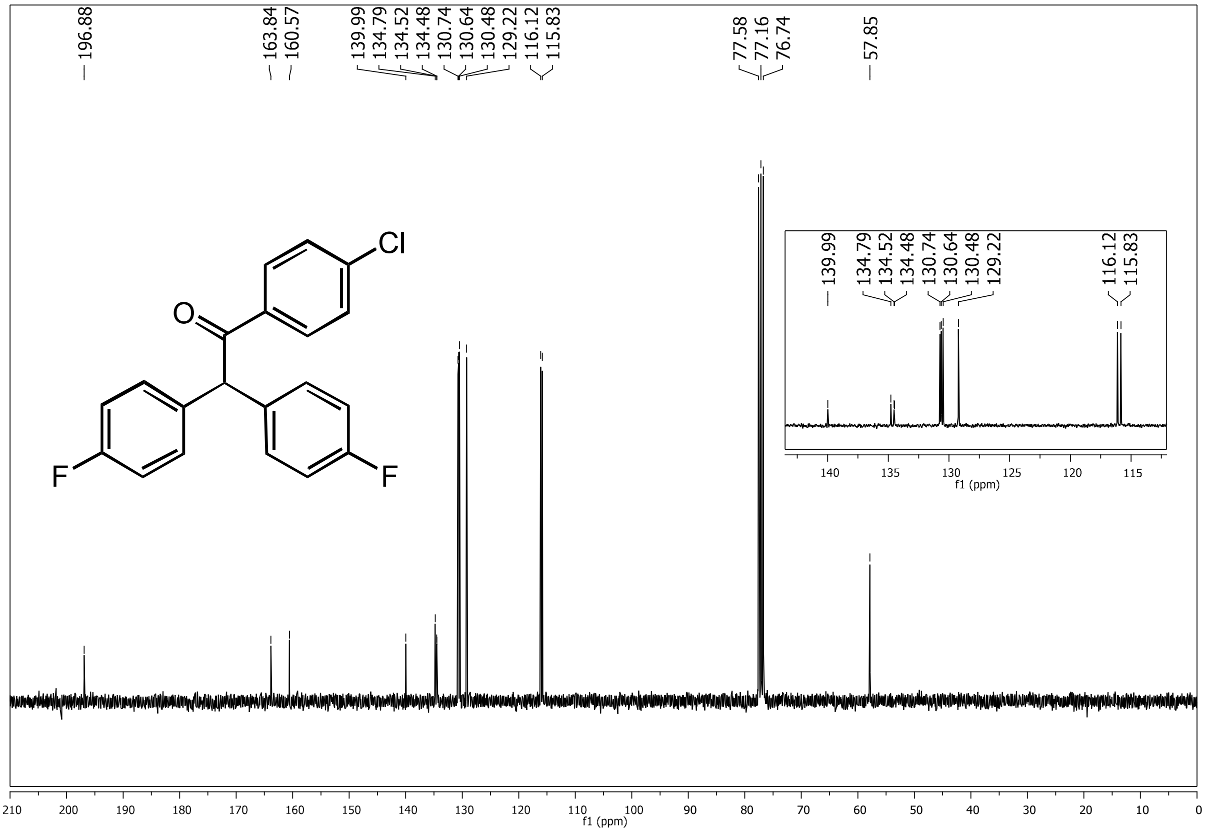
1,2,2-Tris(4-chlorophenyl)ethanone (3q)



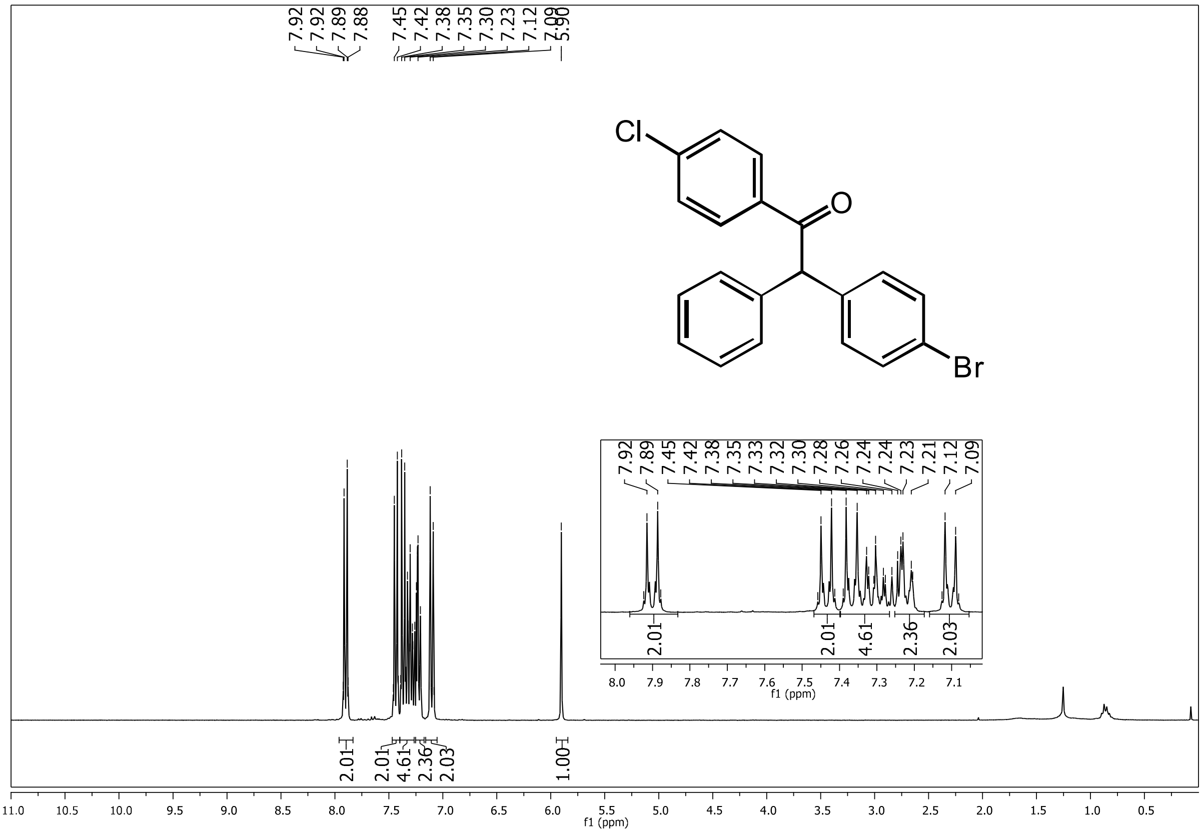


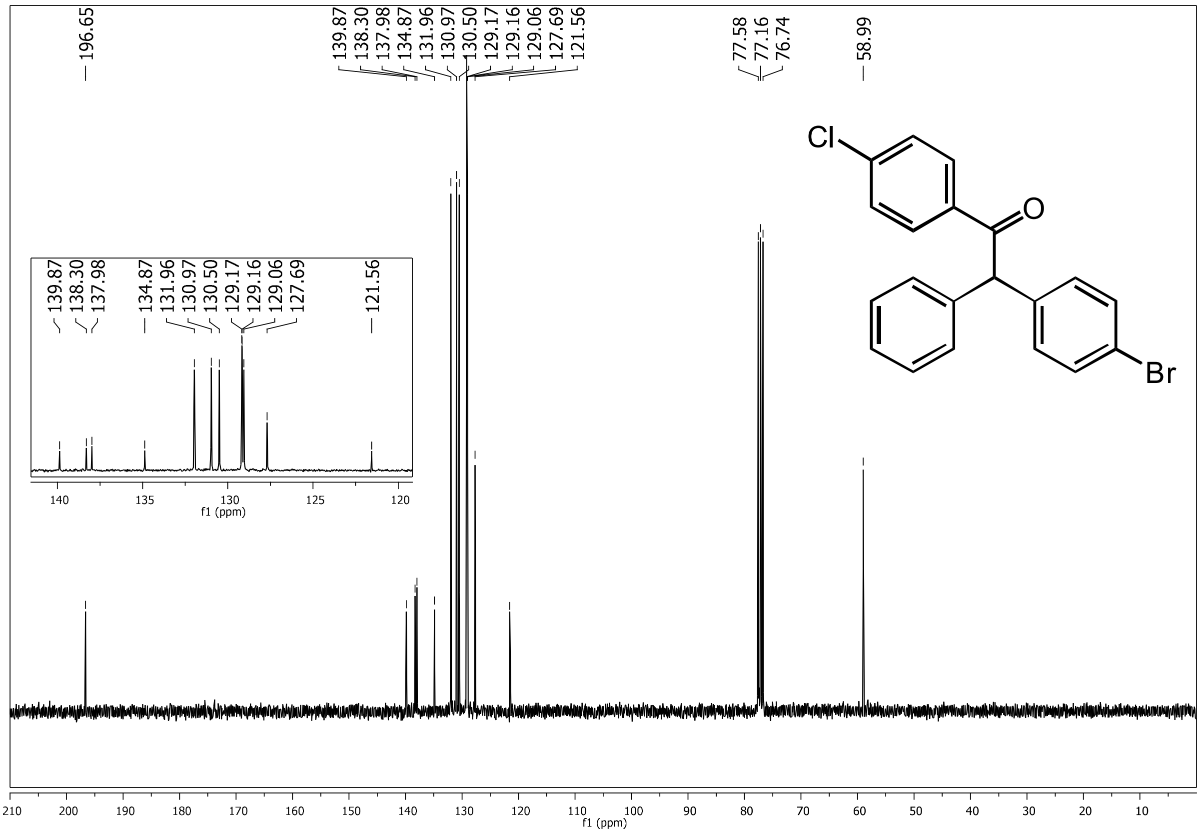
1-(4-Chlorophenyl)-2,2-bis(4-fluorophenyl)ethanone (3r)



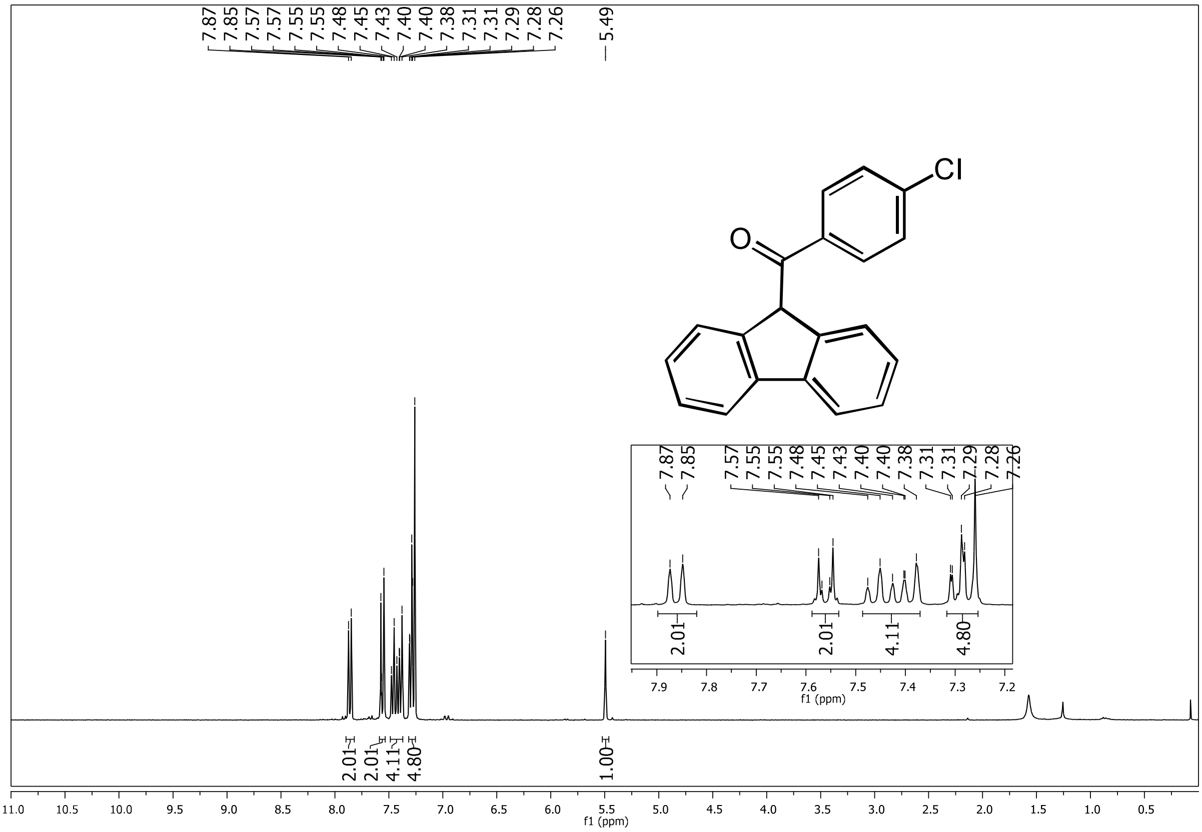


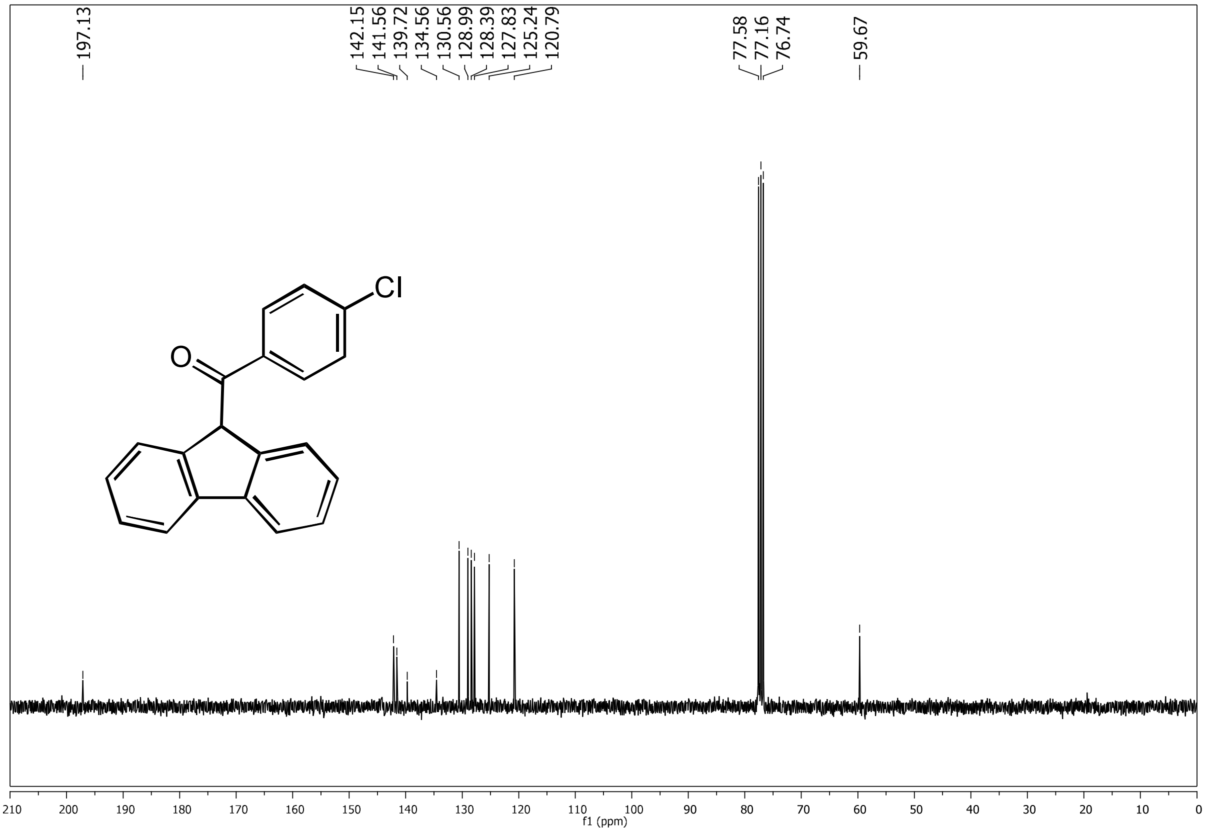
2-(4-Bromophenyl)-1-(4-chlorophenyl)-2-phenylethanone (3s)



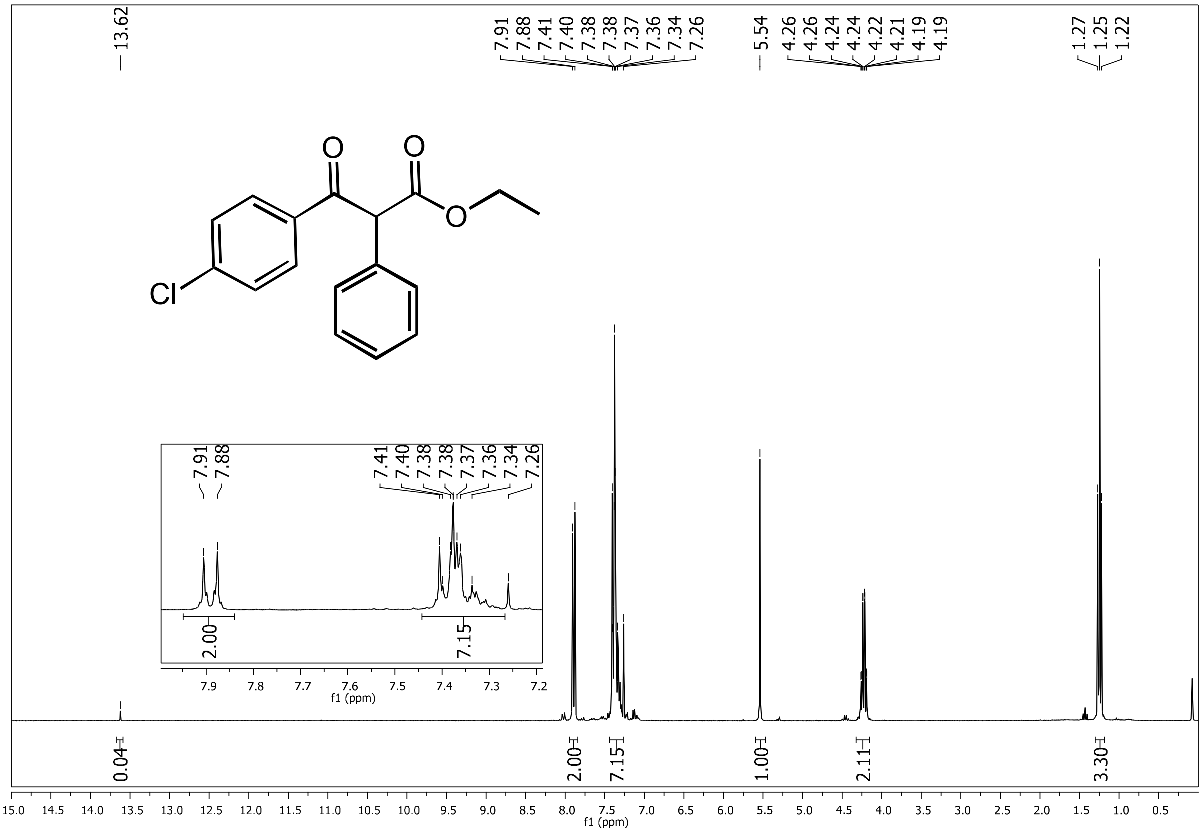


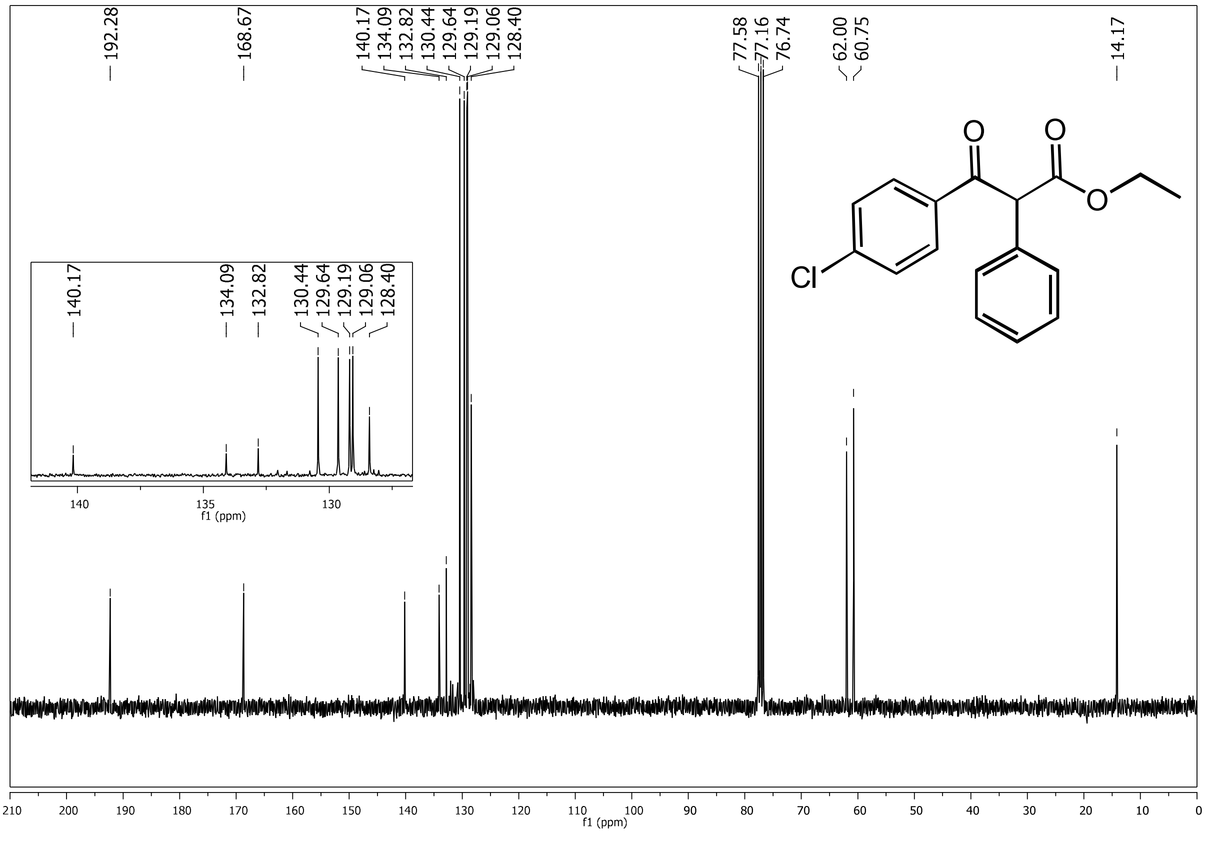
(4-Chlorophenyl)(9H-fluoren-9-yl)methanone (3t)



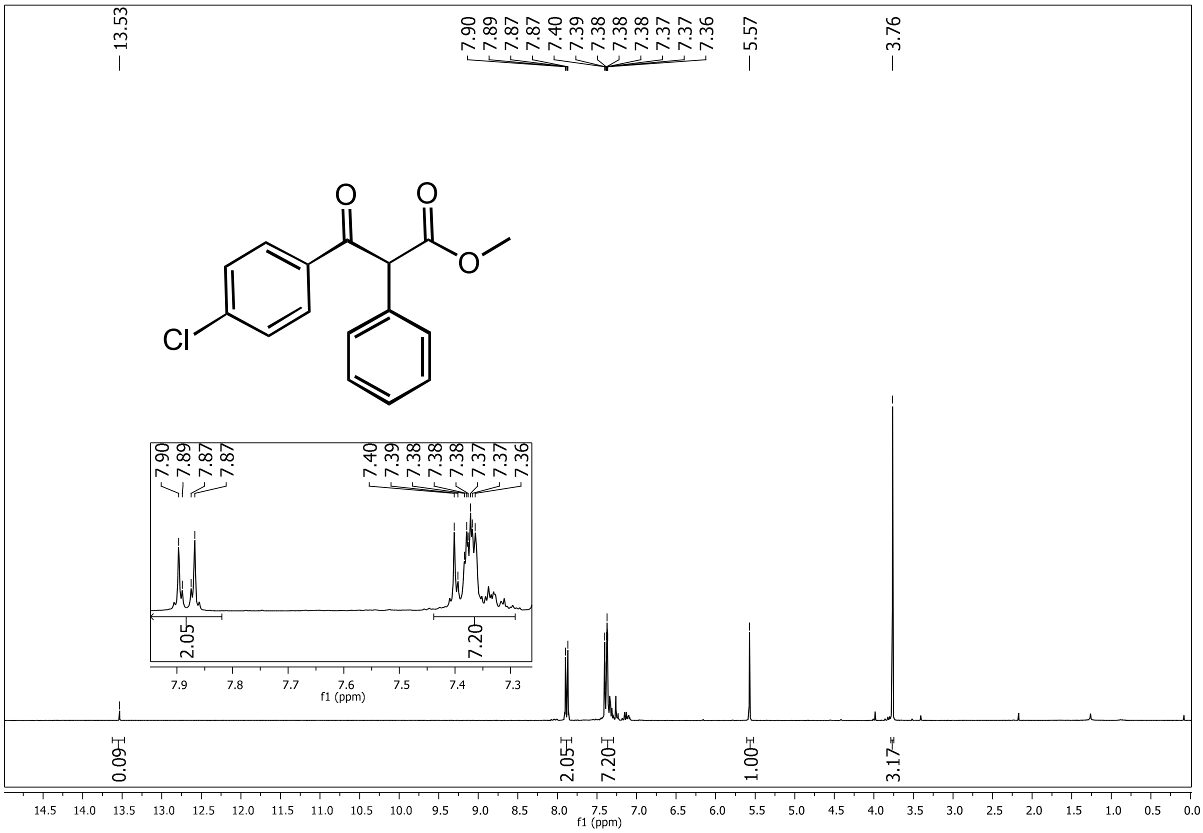


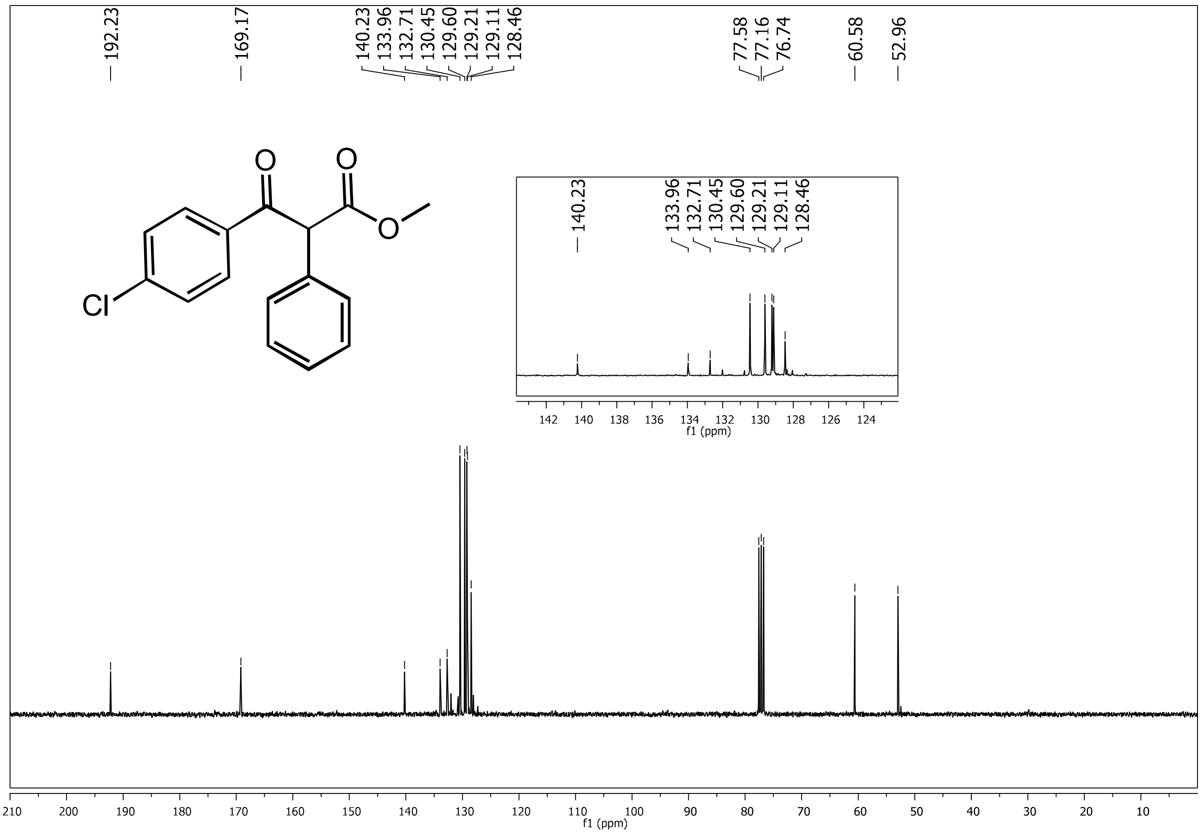
Ethyl 3-(4-chlorophenyl)-3-oxo-2-phenylpropanoate (12a)





Methyl 3-(4-chlorophenyl)-3-oxo-2-phenylpropanoate (12b)





1-(4-Chlorophenyl)-2-methyl-3-phenylpropane-1,3-dione (12c)