

An Efficient Method for the Preparation of Tertiary Esters by Palladium-Catalyzed Alkoxy carbonylation of Aryl Bromides

*Zhuo Xin, Thomas M. Gøgsig, Anders T. Lindhardt, and Troels Skrydstrup**

Department of Chemistry, Center for Insoluble Protein Structures (InSpin), and the Interdisciplinary Nanoscience Center, Aarhus University, Langelandsgade 140, 8000 Aarhus, Denmark.

ts@chem.au.dk

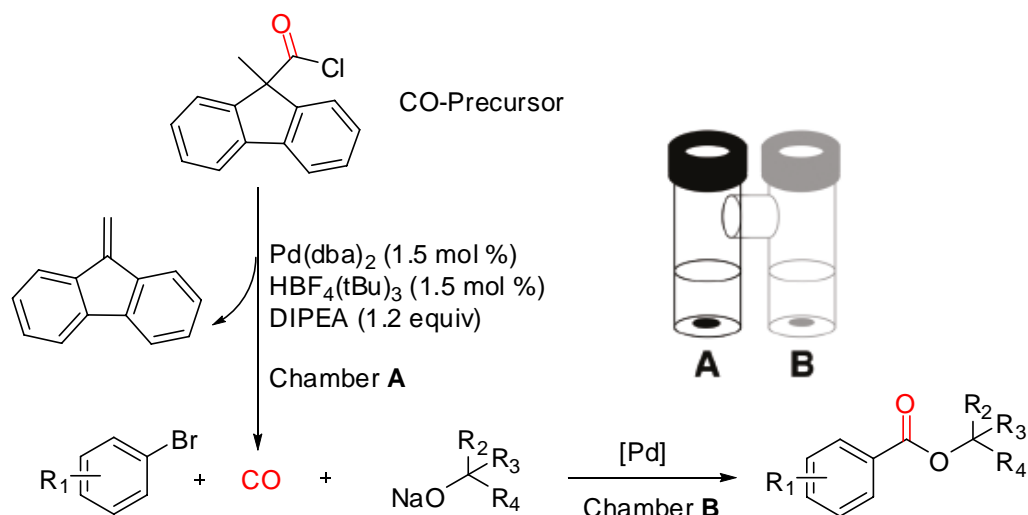
Supporting Information

Table of contents

General methods	2
General procedure	2
Compounds 2-30	3
NMR spectra	10

General Methods. Solvents were dried according to standard procedures. All purchased chemicals were used as received without further purification. Flash chromatography was performed on silica gel 60 (230-400 mesh). The ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz and 367 MHz, respectively, on a Varian Mercury 400 spectrometer. The chemical shifts of the NMR spectra are reported in parts per million (ppm) relative to the solvent residual peak.¹ NMR spectra are reported as follows (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, m = multiplet, b = broad, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets). MS and HRMS spectra were recorded on a LC TOF (ES) apparatus. GC-MS was performed on a Hewlett Packard 5890A gas chromatograph equipped with a 5971A MSD using a HP5 25 m, 0.25 mm internal diameter GCcolumn. GC-MS data are reported as m/z (relative intensity) for the major peaks. The reactions were performed in a previously reported Two-Chamber system.² The Two-Chamber glassware and 9-methyl-fluorene-9-carbonyl chloride is commercially available from SyTracks.

General procedure.



Chamber A

In a glovebox under argon, to chamber A of the two-chamber system was added 9-methyl-fluorene-9-carbonyl chloride (181mg, 750 μmol), HBF₄P(tBu)₃ (2.2 mg, 7.5 μmol), Pd(dba)₂ (4.3 mg, 7.5 μmol), N,N-diisopropylethylamine (154.4 μL , 900 μmol) and THF (2 mL). The chamber was sealed with a screwcap fitted with a Teflon® seal.

Chamber B

In a glovebox under argon, to chamber B of the two-chamber system was added aryl bromide (0.500 mmol), DⁱPrPF (12.5 mg, 0.030 mmol), Pd(dba)₂ (14.4 mg, 0.025 mmol), NaO^tBu

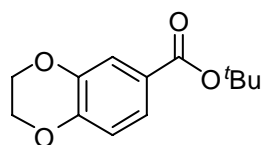
¹ Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

² Hermange, P.; Lindhardt, A. T.; Taaning, R. H.; Bjerglund, K.; Lupp, D.; Skrydstrup, T. *J. Am. Chem. Soc.* **2011**, *133*, 6061.

(57.7 mg 0.600 mmol) and THF (2 ml). The chamber was sealed with a screwcap fitted with a Teflon® seal. The loaded two-chamber system was heated to 70 °C for 16-20 hours. The desired compound was obtained after flash chromatography.

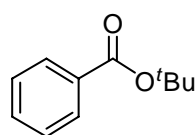
Alkoxyacylation reactions

2,3-Dihydro-benzo[1,4]dioxine-6-carboxylic acid *t*-butyl ester (2)



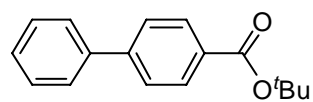
The product was obtained according to general procedure, as a colorless oil. (eluent CH₂Cl₂). **Yield:** 88% (104 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.51 (s, 1H), 7.50 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.8 Hz, 1H), 4.31-4.23 (m, 4H), 1.56 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.2, 147.3, 142.9, 125.4, 123.2, 118.8, 116.9, 80.6, 64.6, 64.1, 28.2 (3C). **HRMS:** C₁₃H₁₆O₄ [M+Na⁺]; calculated: 259.0946, found: 259.0948.

Benzoic acid *t*-butyl ester (3)³



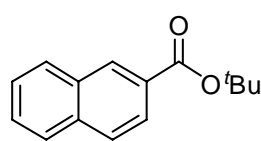
The product was obtained according to general procedure, as a colorless oil. (eluent 20% CH₂Cl₂ in pentane). **Yield:** 60% (53 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.00 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 1.60 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.8, 132.4, 132.0, 129.4 (2C), 128.2 (2C), 80.9, 28.2 (3C). **HRMS:** C₁₁H₁₄O₂ [M+Na⁺]; calculated: 201.0891, found: 201.0889.

Biphenyl-4-carboxylic acid *t*-butyl ester (4)⁴



The product was obtained according to general procedure, as a colorless oil. (eluent 3% Et₂O in pentane). **Yield:** 90% (114 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.06 (d, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.41-7.36 (m, 1H), 1.62 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.7, 145.2, 140.2, 130.8, 130.0 (2C), 128.9 (2C), 128.0, 127.3 (2C), 126.9 (2C), 81.0, 28.3 (3C). **HRMS:** C₁₇H₁₈O₂ [M+Na⁺]; calculated: 277.1204, found: 277.1201.

2-Naphthoic acid *t*-butyl ester (5)⁵



The product was obtained according to general procedure, as a colorless oil. (eluent 3% Et₂O in pentane). **Yield:** 88% (100 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.56 (s, 1H), 8.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.59-7.50 (m, 2H), 1.62 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.9, 135.3, 132.5, 130.6, 129.3 (2C), 127.92, 127.89, 127.7, 126.5, 125.3, 81.1, 28.3 (3C). **HRMS:** C₁₅H₁₆O₂ [M+Na⁺]; calculated: 251.1048, found: 251.1053.

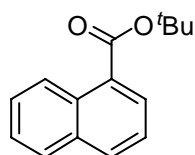
1-Naphthoic acid *t*-butyl ester (6)⁶

³ Kissling, R. M.; Gagné, M. R. *Org. Lett.* **2000**, *2*, 4209.

⁴ Hu, Y.; Liu, J.; Lu⁺, Z.; Luo, X.; Zhang, H.; Lei, A. *J. Am. Chem. Soc.* **2010**, *132*, 3153.

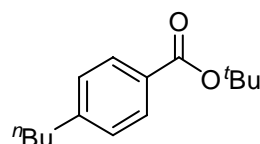
⁵ Nishimoto, Y.; BaBu, S. A.; Yasuda, M.; Baba, A. *J. Org. Chem.* **2008**, *73*, 9465.

⁶ Shimano, M.; Meyers, A. I. *J. Org. Chem.* **1995**, *60*, 7445.



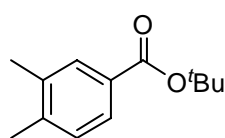
The product was obtained according to general procedure, as a colorless oil. (eluent 3% Et₂O in pentane). **Yield:** 73% (83 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.85 (d, *J* = 8.8 Hz, 1H), 8.08 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.61-7.46 (m, 3H), 1.68 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 167.1, 133.8, 132.6, 131.2, 129.6, 129.3, 128.5, 127.4, 126.0, 125.8, 124.5, 81.5, 28.4 (3C). **HRMS:** C₁₅H₁₆O₂ [M+Na⁺]; calculated: 251.1048, found: 251.1048.

4-Butylbenzoic acid *t*-butyl ester (7)⁷



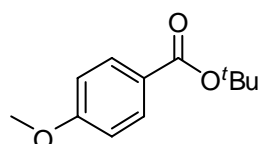
The product was obtained according to general procedure, as a colorless oil. (eluent 1.5% Et₂O in pentane). **Yield:** 86% (101 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.89 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.64-1.54 (m, 11H), 1.35 (sext, *J* = 7.6 Hz, 2H), 0.92 (t, *J* = 7.6 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.9, 147.8, 129.48, 129.42 (2C), 128.2 (2C), 80.6, 35.6, 33.3, 28.2, 22.3 (3C), 13.9. **HRMS:** C₁₅H₂₂O₂ [M+Na⁺]; calculated: 257.1517, found: 257.1519.

3,4-Dimethylbenzoic acid *t*-butyl ester (8)



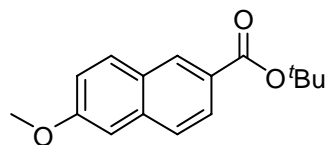
The product was obtained according to general procedure, as a colorless oil. (eluent 3% EtOAc in pentane). **Yield:** 78% (80 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.75 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.29 (s, 6H), 1.58 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 166.1, 141.6, 136.4, 130.4, 129.6, 129.4, 126.9, 80.5, 28.2 (3C), 19.9, 19.7. **HRMS:** C₁₃H₁₈O₂ [M+Na⁺]; calculated: 229.1204, found: 229.1201.

4-Methoxybenzoic acid *t*-butyl ester (9)⁴



The product was obtained according to general procedure, as a colorless oil. (eluent 15% Et₂O in pentane). **Yield:** 77% (80 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.94 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 1.58 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.6, 162.9, 131.3 (2C), 124.5, 113.3 (2C), 80.4, 55.3, 28.2 (3C). **HRMS:** C₁₂H₁₆O₃ [M+Na⁺]; calculated: 231.0997, found: 231.1001.

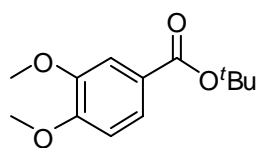
6-Methoxy-2-naphthoic acid *t*-butyl ester (10)



The product was obtained according to general procedure, as a colorless oil. (eluent 7% Et₂O in pentane). **Yield:** 86% (111 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.46 (s, 1H), 7.99 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H), 7.17 (td, *J* = 8.6, 2.4 Hz, 1H), 3.94 (s, 3H), 1.64 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 166.1, 159.3, 136.9, 130.8, 130.4, 127.9, 127.1, 126.6, 126.0, 119.4, 105.6, 80.9, 55.3, 28.3 (3C). **HRMS:** C₁₆H₁₈O₃ [M+Na⁺]; calculated: 281.1154, found: 281.1179.

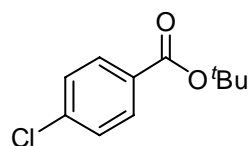
⁷ Nakao, Y.; Takeda, M.; Matsumoto, T.; Hiyama, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 4447.

3,4-Dimethoxybenzoic acid *t*-butyl ester (11)



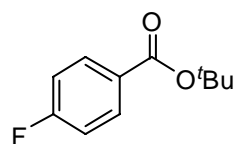
The product was obtained according to general procedure, as a colorless oil. (eluent 25% Et₂O in pentane). **Yield:** 76% (90 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.59 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 6H), 1.57 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.6, 152.5, 148.5, 124.5, 123.2, 111.9, 110.1, 80.7, 55.94, 55.87, 28.2 (3C). **HRMS:** C₁₃H₁₈O₄ [M+Na⁺]; calculated: 261.1103, found: 261.1104.

4-Chlorobenzoic acid *t*-butyl ester (12)⁸



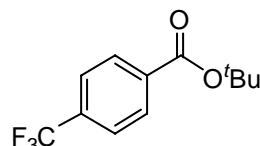
The product was obtained according to general procedure, as a colorless oil. (eluent 20% CH₂Cl₂ in pentane). **Yield:** 64% (68 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.91 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 1.58 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 164.8, 138.7, 130.8 (2C), 130.4, 128.4 (2C), 81.4, 28.1 (3C). **HRMS:** C₁₁H₁₃ClO₂ [M+Na⁺]; calculated: 235.0502, found: 235.0504.

4-Fluorobenzoic acid *t*-butyl ester (13)



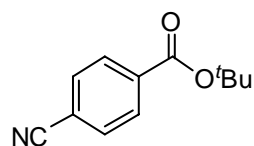
The product was obtained according to general procedure, as a colorless oil. (eluent 6% Et₂O in pentane). **Yield:** 44% (43 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.03-7.94 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 1.59 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.4 (d, *J*_{C-F} = 251.2 Hz), 164.8, 131.8 (d, *J*_{C-F} = 9.1 Hz, 2C), 128.2 (d, *J*_{C-F} = 3.0 Hz), 115.2 (d, *J*_{C-F} = 21.6 Hz, 2C), 81.2, 28.2 (3C). **¹⁹F NMR (400 MHz, CDCl₃):** δ (ppm) -107.0. **GCMS:** C₁₁H₁₃FO₂ [M]; calculated: 196.0900, found: 141 (76.9%), 123 (100%), 95 (35.9%), 57 (36.5%).

4-(Trifluoromethyl)benzoic acid *t*-butyl ester (14)⁹



The product was obtained according to general procedure, as a colorless oil. (eluent 3% EtOAc in pentane). **Yield:** 67% (82 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.09 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 1.60 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 164.4, 135.2, 133.9 (q, *J*_{C-F} = 32.3 Hz), 129.8 (2C), 125.2 (q, *J*_{C-F} = 3.7 Hz, 2C), 123.7 (q, *J*_{C-F} = 270.8 Hz), 81.9, 28.1 (3C). **¹⁹F NMR (400 MHz, CDCl₃):** δ (ppm) -63.1. **GCMS:** C₁₂H₁₃F₃O₂ [M]; calculated: 246.0868, found: 191 (11.6%), 173 (100%), 145 (30.5%), 57 (23.1%).

4-Cyanobenzoic acid *t*-butyl ester (15)¹⁰



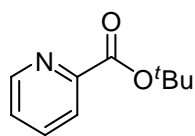
The product was obtained according to general procedure, as a colorless solid. (eluent 5% EtOAc in pentane). **Yield:** 76% (77 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.08 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 1.60 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 163.9, 135.8, 132.0 (2C), 129.9 (2C), 118.1, 115.8, 82.3, 28.1 (3C). **HRMS:** C₁₂H₁₃NO₂ [M+Na⁺]; calculated: 226.0844, found: 226.0852.

⁸ Yamamoto, Y. *Adv. Synth. Catal.* **2010**, *352*, 478.

⁹ Stanton, M. G.; Gagné, M. R. *J. Org. Chem.* **1997**, *62*, 8240.

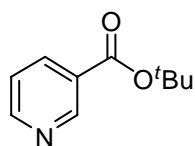
¹⁰ Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 12595.

Pyridine-2-carboxylic acid *t*-butyl ester (16)¹¹



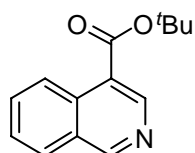
The product was obtained according to general procedure, as a yellow oil. (eluent 50% Et₂O in pentane). **Yield:** 62% (56 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.70 (dq, *J* = 4.8, 0.8 Hz, 1H), 8.01 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.76 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 (m, 1H), 1.60 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 164.2, 149.8, 149.5, 136.8, 126.3, 124.7, 82.2, 28.1 (3C). **HRMS:** C₁₀H₁₃NO₂ [M+Na⁺]; calculated: 202.0844, found: 202.0839.

Pyridine-3-carboxylic acid *t*-butyl ester (17)



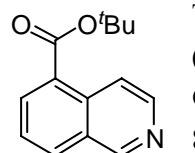
The product was obtained according to general procedure, as a yellow oil. (eluent 30% Et₂O in pentane). **Yield:** 68% (61 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 9.15 (s, 1H), 8.72 (d, *J* = 3.6 Hz, 1H), 8.22 (dt, *J* = 8.0 Hz, *J* = 1.8 Hz, 1H), 7.36-7.31 (m, 1H), 1.58 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 164.3, 152.9, 150.8, 136.9, 127.7, 123.1, 82.0, 28.1 (3C). **HRMS:** C₁₀H₁₃NO₂ [M+Na⁺]; calculated: 202.0844, found: 202.0841.

Isoquinoline-4-carboxylic acid *t*-butyl ester (18)



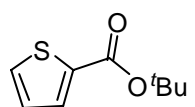
The product was obtained according to general procedure, as a yellow oil. (eluent 50% Et₂O in pentane). **Yield:** 56% (64 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 9.30 (s, 1H), 9.08 (s, 1H), 8.89 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 1.66 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.7, 156.4, 146.5, 133.8, 131.9, 128.4, 128.1, 127.4, 125.0, 122.2, 82.1, 28.3 (3C). **HRMS:** C₁₄H₁₅NO₂ [M+H⁺]; calculated: 230.1181, found: 230.1198.

Isoquinoline-5-carboxylic acid *t*-butyl ester (19)



The product was obtained according to general procedure, as a yellow oil. (eluent 50% Et₂O in pentane). **Yield:** 78% (89 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 9.23 (s, 1H), 8.71 (d, *J* = 6.4 Hz, 1H), 8.59 (d, *J* = 6.4 Hz, 1H), 8.32 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 1.64 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.7, 153.0, 144.6, 134.12, 134.08, 132.5, 128.9, 127.7, 126.0, 118.5, 82.0, 28.3 (3C). **HRMS:** C₁₄H₁₅NO₂ [M+H⁺]; calculated: 230.1181, found: 230.1198.

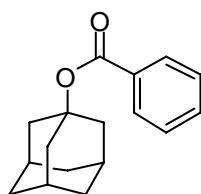
Thiophene-2-carboxylic acid *t*-butyl ester (20)



The product was obtained according to general procedure, as a colorless oil. (eluent 20% CH₂Cl₂ in pentane). **Yield:** 50% (46 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.71 (d, *J* = 4.0 Hz, 1H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.06 (t, *J* = 4.4 Hz, 1H), 1.57 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 161.5, 135.9, 132.7, 131.6, 127.5, 81.7, 28.2 (3C). **HRMS:** C₉H₁₂O₂S [M+Na⁺]; calculated: 207.0456, found: 207.0458.

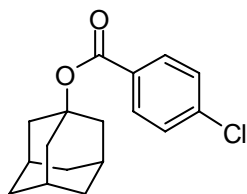
¹¹ Yamamoto, Y.; Ouchi, H.; Tanaka, T. *Chem. Pharm. Bull.* **1995**, *43*, 916.

1-Adamantanol benzoate (21)¹²



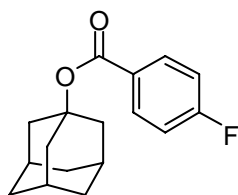
The product was obtained according to general procedure, as a colorless solid. (eluent 3% Et₂O in pentane). **Yield:** 89% (114 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.00 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 2.31-2.18 (m, 9H), 1.77-1.66 (m, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 165.4, 132.3, 132.1, 129.4 (2C), 128.1 (2C), 81.0, 41.4 (3C), 36.3 (3C), 30.9 (3C). **HRMS:** C₁₇H₂₀O₂ [M+Na⁺]; calculated: 279.1361, found: 279.1374.

1-Adamantanol 4-chlorobenzoate (22)



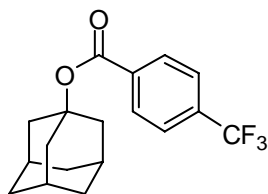
The product was obtained according to general procedure, as a colorless solid. (eluent 3% Et₂O in pentane). **Yield:** 76% (110 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.91 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.33-2.15 (m, 9H), 1.79-1.64 (m, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 164.5, 138.7, 130.8 (2C), 130.5, 128.4 (2C), 81.5, 41.4 (3C), 36.2 (3C), 30.9 (3C). **HRMS:** C₁₇H₁₉ClO₂ [M+Na⁺]; calculated: 313.0971, found: 313.0973.

1-Adamantanol 4-fluorobenzoate (23)



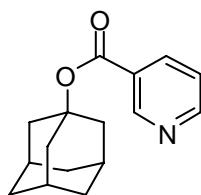
The product was obtained according to general procedure, as a colorless solid. (eluent 3% Et₂O in pentane). **Yield:** 86% (118 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.02-7.96 (m, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 2.28-2.19 (m, 9H), 1.77-1.66 (m, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 166.7 (d, *J*_{C-F} = 251.0 Hz), 164.4, 131.8 (d, *J*_{C-F} = 9.1 Hz, 2C), 128.3 (d, *J*_{C-F} = 3.0 Hz), 115.1 (d, *J*_{C-F} = 21.7 Hz, 2C), 81.2, 41.4 (3C), 36.2 (3C), 30.9 (3C). **¹⁹F NMR (400 MHz, CDCl₃):** δ (ppm) -107.0. **GCMS:** C₁₇H₁₉FO₂ [M]; calculated: 274.1369, found: 274 (27.2%), 134 (100%), 123 (77%), 92 (66.1%), 79 (23.1%).

1-Adamantanol 4-(trifluoromethyl)benzoate (24)



The product was obtained according to general procedure, as a colorless solid. (eluent 3% Et₂O in pentane). **Yield:** 63% (102 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 8.09 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 2.30-2.20 (m, 9H), 1.78-1.66 (m, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 164.1, 135.3, 133.9 (q, *J*_{C-F} = 32.3 Hz), 129.8 (2C), 125.1 (q, *J*_{C-F} = 3.7 Hz, 2C), 123.7 (q, *J*_{C-F} = 271.1 Hz), 82.0, 41.3 (3C), 36.2 (3C), 30.9 (3C). **¹⁹F NMR (400 MHz, CDCl₃):** δ (ppm) -63.1. **GCMS:** C₁₈H₁₉F₃O₂ [M]; calculated: 324.1337, found: 324 (8.6%), 305 (12%), 173 (59.2%), 145 (45.8%), 134 (100%), 92 (65.4%), 79 (18.8%).

1-Adamantanol nicotinate (25)

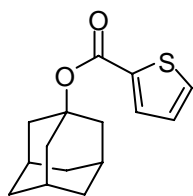


The product was obtained according to general procedure, as a yellow oil. (eluent 30% Et₂O in pentane). **Yield:** 78% (95 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 9.17 (d, *J* = 1.8 Hz, 1H), 8.74 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.26 (dt, *J* = 7.6, 1.8 Hz, 1H), 7.40-7.36 (m, 1H), 2.29-2.20 (m, 9H),

¹² Mukaiyama, T.; Shintou, T.; Fukumoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 10538.

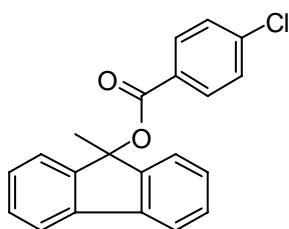
1.77-1.66 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 164.0, 152.8, 150.8, 136.9, 127.8, 123.1, 82.1, 41.1 (3C), 36.1 (3C), 30.9 (3C). HRMS: $\text{C}_{16}\text{H}_{19}\text{NO}_2$ [$\text{M}+\text{H}^+$]; calculated: 258.1494, found: 258.1503.

1-Adamantanol thiophene-2-carboxylate (26)



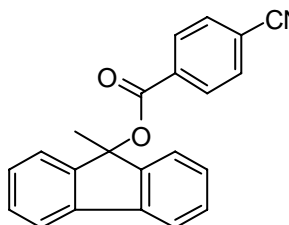
The product was obtained according to general procedure, as a colorless solid. (eluent 3% Et_2O in pentane). Yield: 67% (88 mg). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.71 (s, 1H), 7.47 (d, $J = 4.8$ Hz, 1H), 7.06 (d, $J = 4.8$ Hz, 1H), 2.33-2.16 (m, 9H), 1.77-1.64 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 161.2, 136.0, 132.6, 131.6, 127.5, 81.8, 41.5 (3C), 36.2 (3C), 30.9 (3C). HRMS: $\text{C}_{15}\text{H}_{18}\text{O}_2\text{S}$ [$\text{M}+\text{H}^+$]; calculated: 263.1106, found: 263.1112.

9-Methyl-9-fluorenyl 4-chlorobenzoate (27)



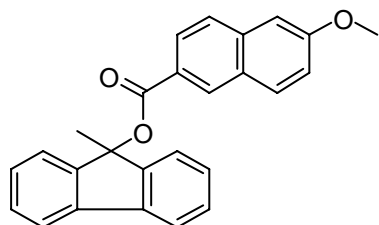
The product was obtained according to general procedure, as a colorless solid. (eluent 3% Et_2O in pentane). Yield: 73% (122 mg). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.95 (d, $J = 8.8$ Hz, 2H), 7.75 (d, $J = 7.6$ Hz, 2H), 7.56 (d, $J = 7.6$ Hz, 2H), 7.46-7.30 (m, 6H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.5, 146.5 (2C), 139.6 (2C), 139.2, 131.1 (2C), 129.2, 129.1 (2C), 128.6 (2C), 128.0 (2C), 122.8 (2C), 120.3 (2C), 85.9, 26.0. HRMS: $\text{C}_{21}\text{H}_{15}\text{ClO}_2$ [$\text{M}+\text{Na}^+$]; calculated: 357.0658, found: 357.0658.

9-Methyl-9-fluorenyl 4-cyanobenzoate (28)



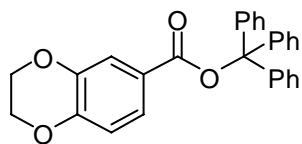
The product was obtained according to general procedure, as a colorless solid. (eluent 7% EtOAc in pentane). Yield: 77% (126 mg). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.07 (d, $J = 8.4$ Hz, 2H), 7.74 (dt, $J = 7.6, 1.0$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.54 (dt, $J = 7.6, 0.8$ Hz, 2H), 7.42 (td, $J = 7.6, 1.2$ Hz, 2H), 7.31 (td, $J = 7.6, 1.2$ Hz, 2H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 162.7, 146.0 (2C), 139.7 (2C), 134.5, 132.1 (2C), 130.2 (2C), 129.3 (2C), 128.0 (2C), 122.8 (2C), 120.3 (2C), 118.0, 116.2, 86.6, 25.8. HRMS: $\text{C}_{22}\text{H}_{15}\text{NO}_2$ [$\text{M}+\text{Na}^+$]; calculated: 348.1000, found: 348.0995.

9-Methyl-9-fluorenyl 6-methoxy-2-naphthoate (29)



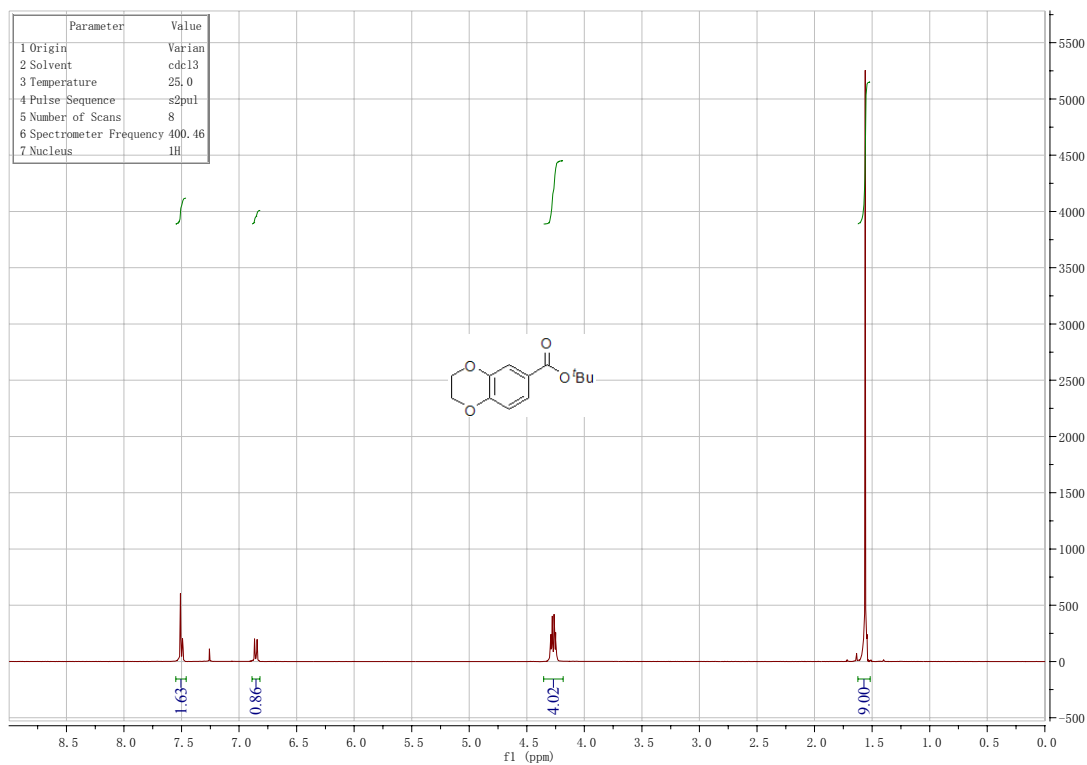
The product was obtained according to general procedure, as a colorless solid. (eluent 50% CH_2Cl_2 in pentane). Yield: 89% (169 mg). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.49 (s, 1H), 7.96 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.81 (d, $J = 9.2$ Hz, 1H), 7.76-7.69 (m, 3H), 7.58 (d, $J = 7.2$ Hz, 2H), 7.41 (t, $J = 7.2$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.18 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.13 (d, $J = 2.4$ Hz, 1H), 3.94 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 164.6, 159.5, 146.9, 139.6, 137.1, 130.86, 130.85 (2C), 128.9 (2C), 127.87 (2C), 127.82, 126.7 (2C), 126.1, 125.8, 122.8 (2C), 120.2 (2C), 119.5, 105.6, 85.6, 55.4, 26.2. HRMS: $\text{C}_{26}\text{H}_{20}\text{O}_3$ [$\text{M}+\text{Na}^+$]; calculated: 403.1310, found: 403.1313.

2,3-Dihydro-benzo[1,4]dioxine-6-carboxylic acid trityl ester (30)

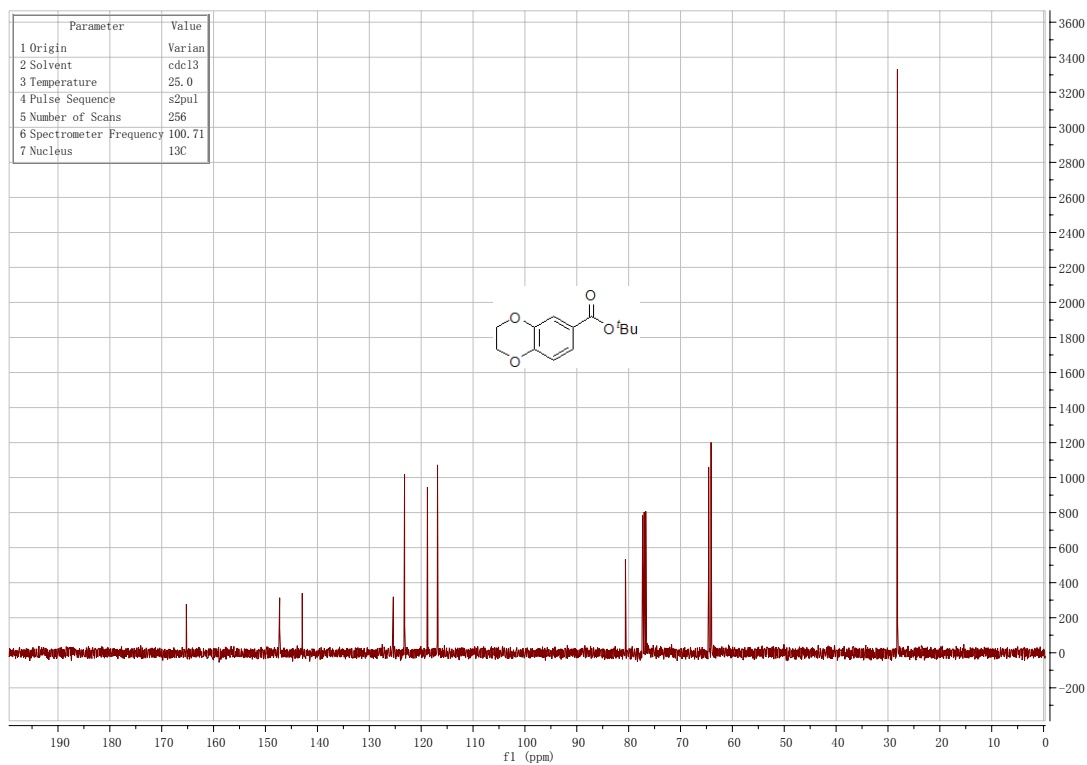


The product was obtained according to general procedure, as a yellow solid. (eluent 30% Et₂O in pentane). **Yield:** 57% (120 mg). **¹H NMR (400 MHz, CDCl₃):** δ (ppm) 7.70-7.64 (m, 2H), 7.46 (d, *J* = 7.2 Hz, 6H), 7.37-7.23 (m, 9H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.33-4.25 (m, 4H). **¹³C NMR (100 MHz, CDCl₃):** δ (ppm) 164.0, 147.9, 143.6 (3C), 143.2, 128.4 (6C), 127.8 (6C), 127.3 (3C), 124.6, 123.8, 119.2, 117.2, 90.3, 64.7, 64.1. **HRMS:** C₂₈H₂₂O₄ [M+Na⁺]; calculated: 445.1416, found: 445.1429.

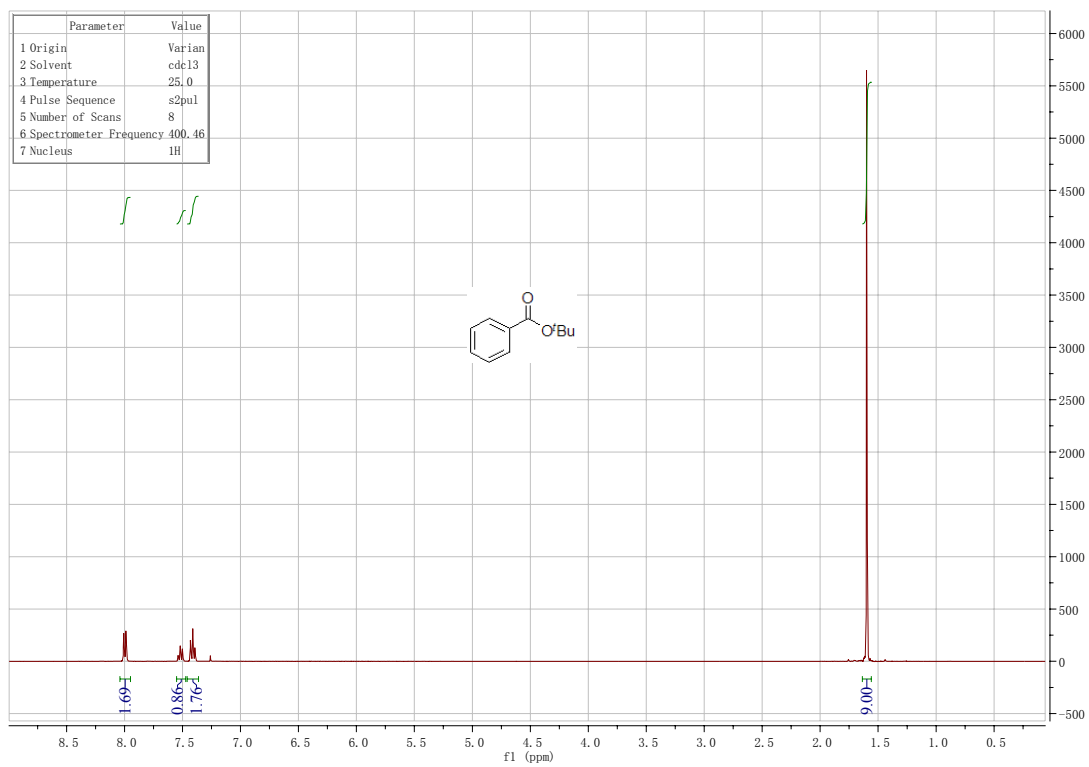
¹H NMR for 2,3-Dihydro-benzo[1,4]dioxine-6-carboxylic acid *t*-butyl ester (2)



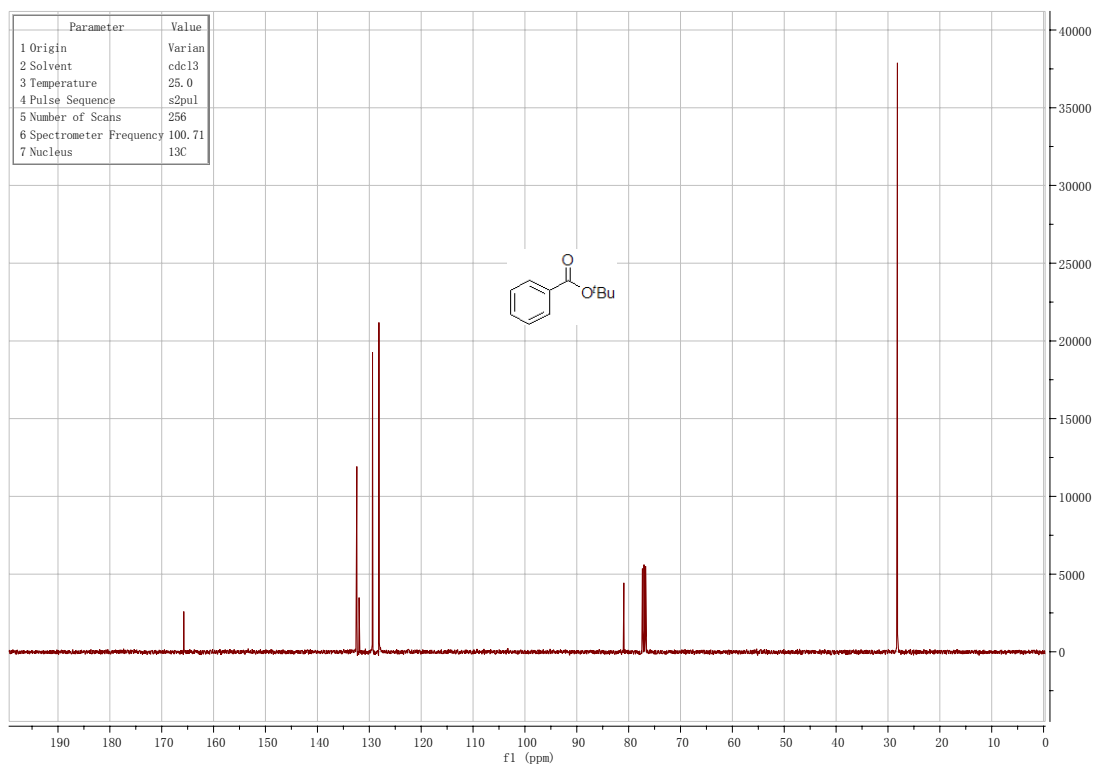
¹³C NMR for 2,3-Dihydro-benzo[1,4]dioxine-6-carboxylic acid *t*-butyl ester (2)



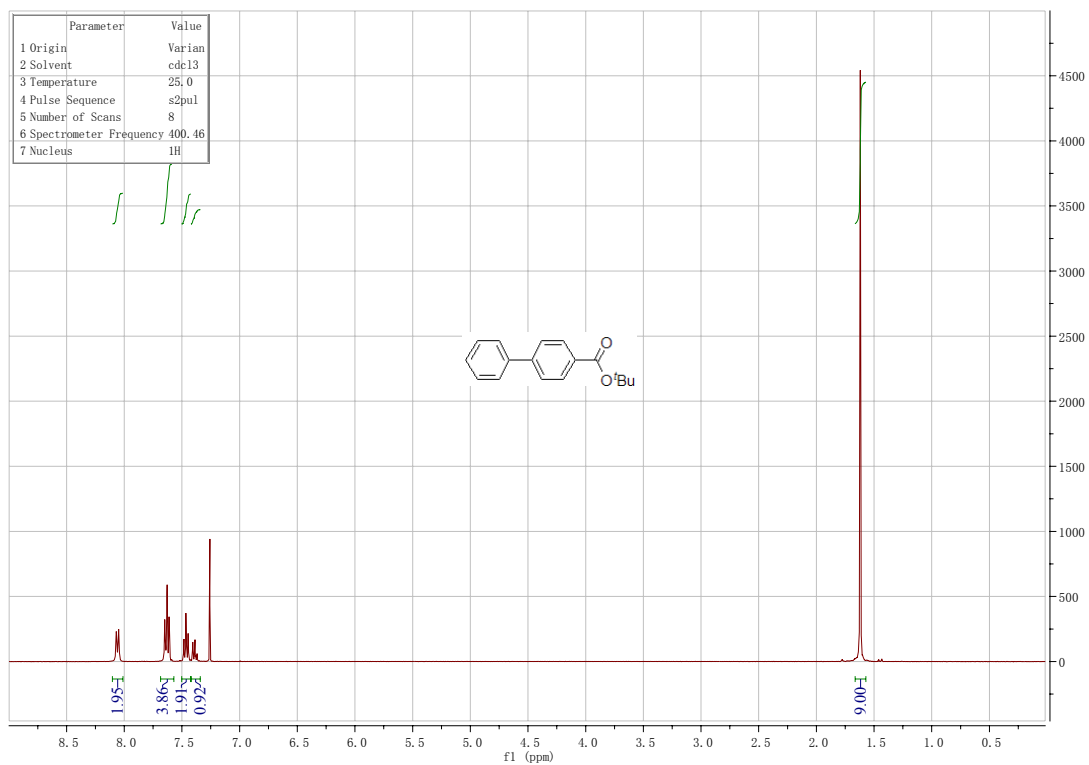
¹H NMR for Benzoic acid *t*-butyl ester (3)



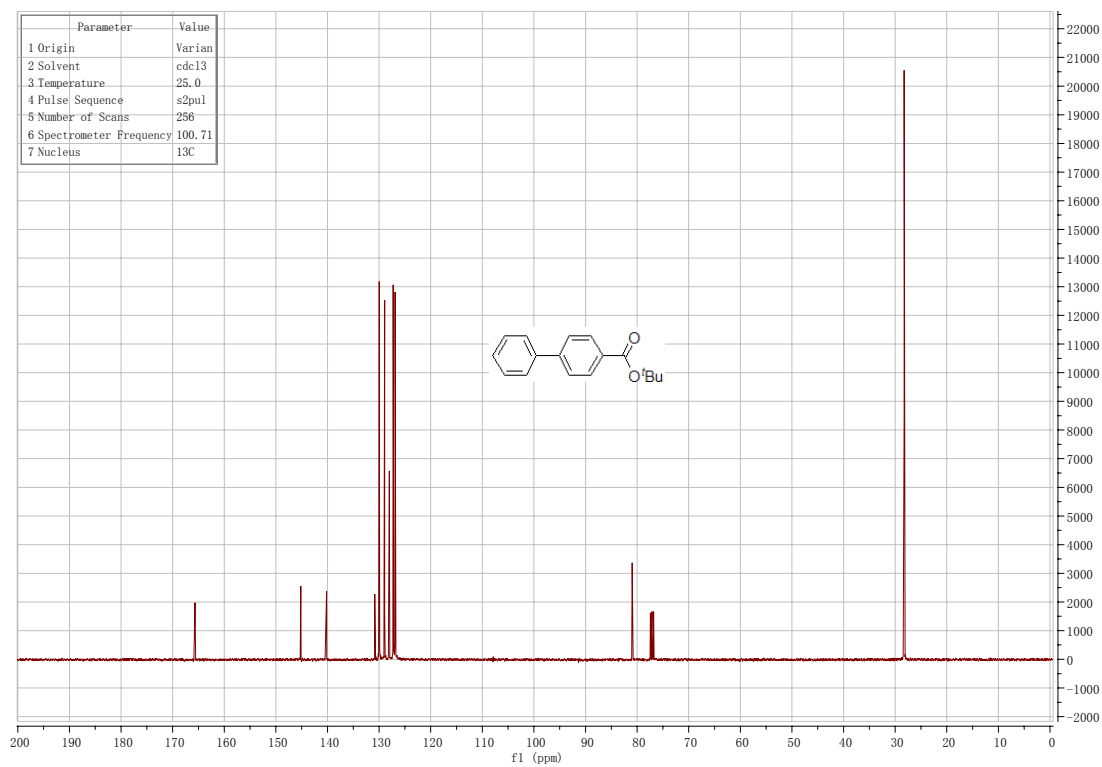
¹³C NMR for Benzoic acid *t*-butyl ester (3)



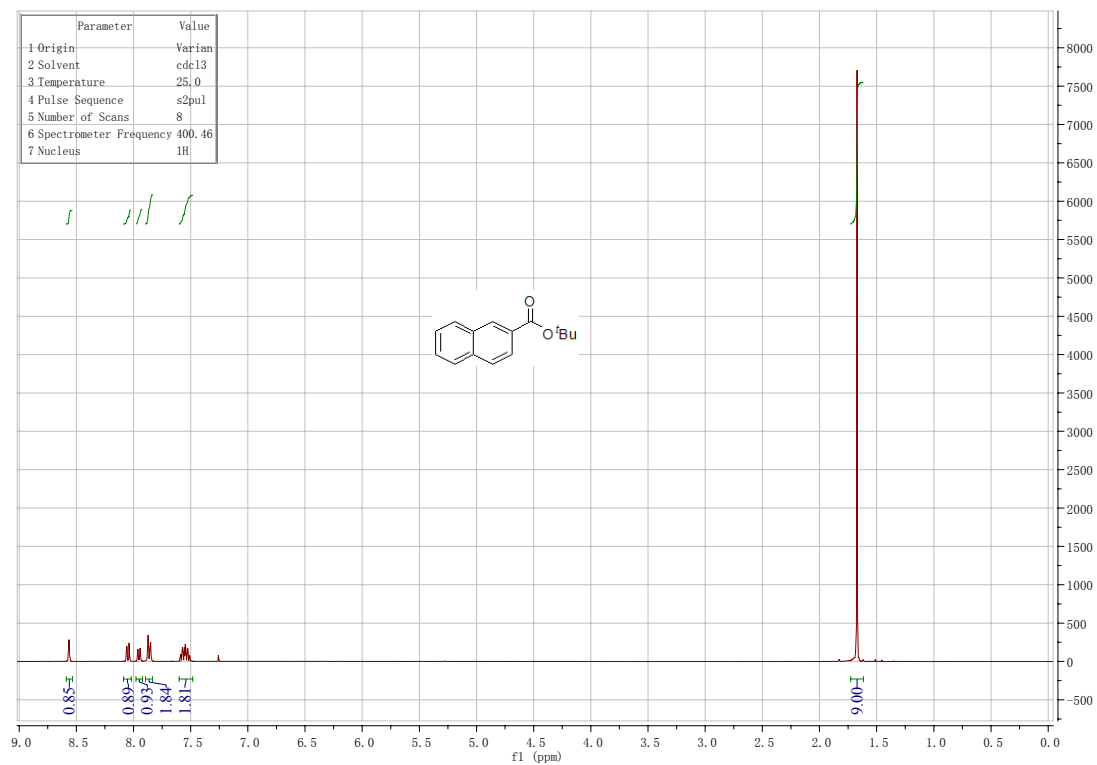
¹H NMR for Biphenyl-4-carboxylic acid *t*-butyl ester (4)



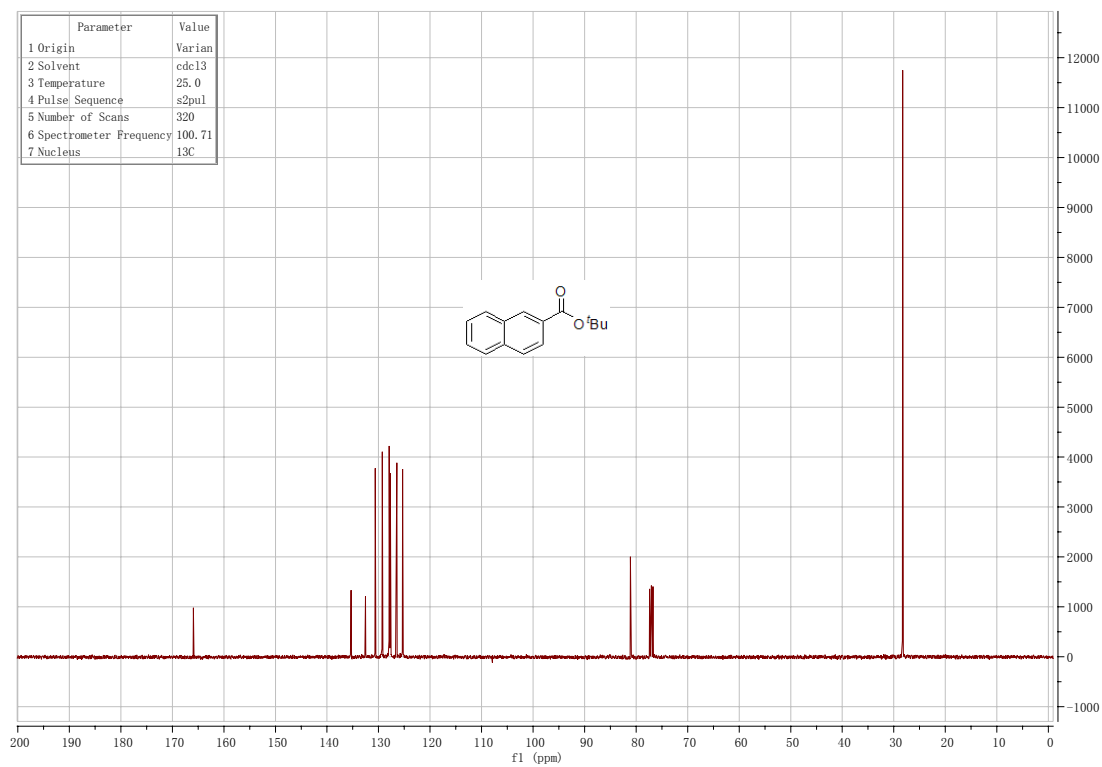
¹³C NMR for Biphenyl-4-carboxylic acid *t*-butyl ester (4)



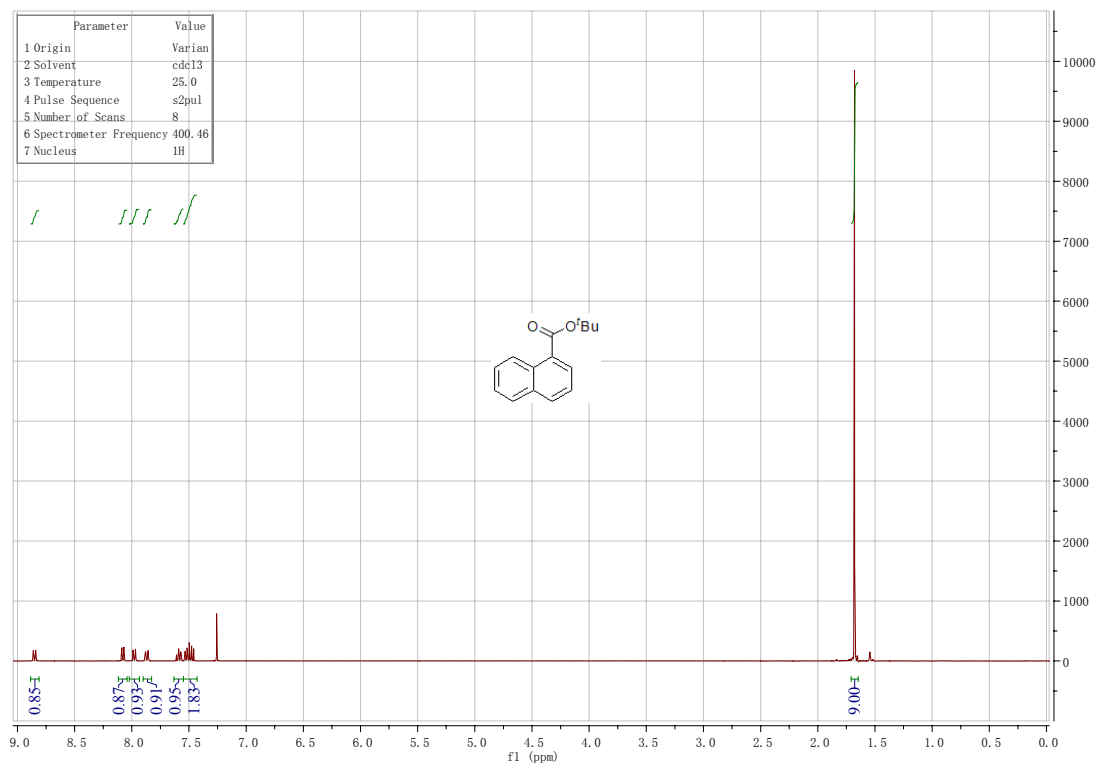
¹H NMR for 2-Naphthoic acid *t*-butyl ester (5)



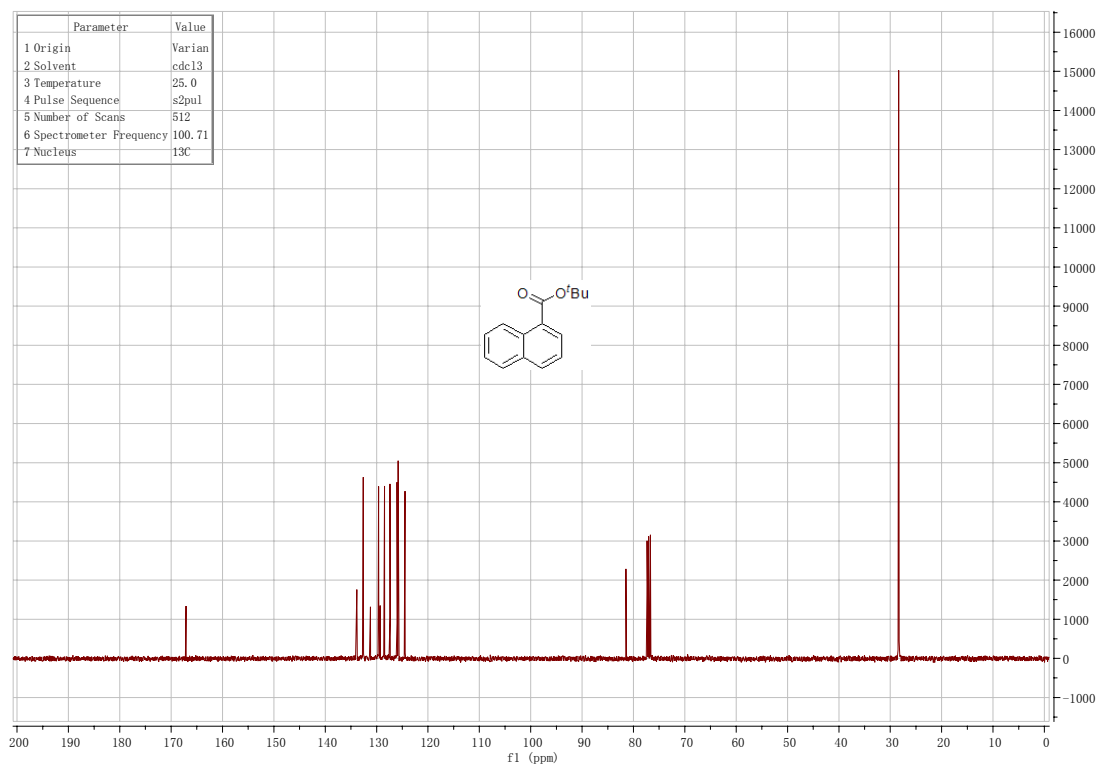
¹³C NMR for 2-Naphthoic acid *t*-butyl ester (5)



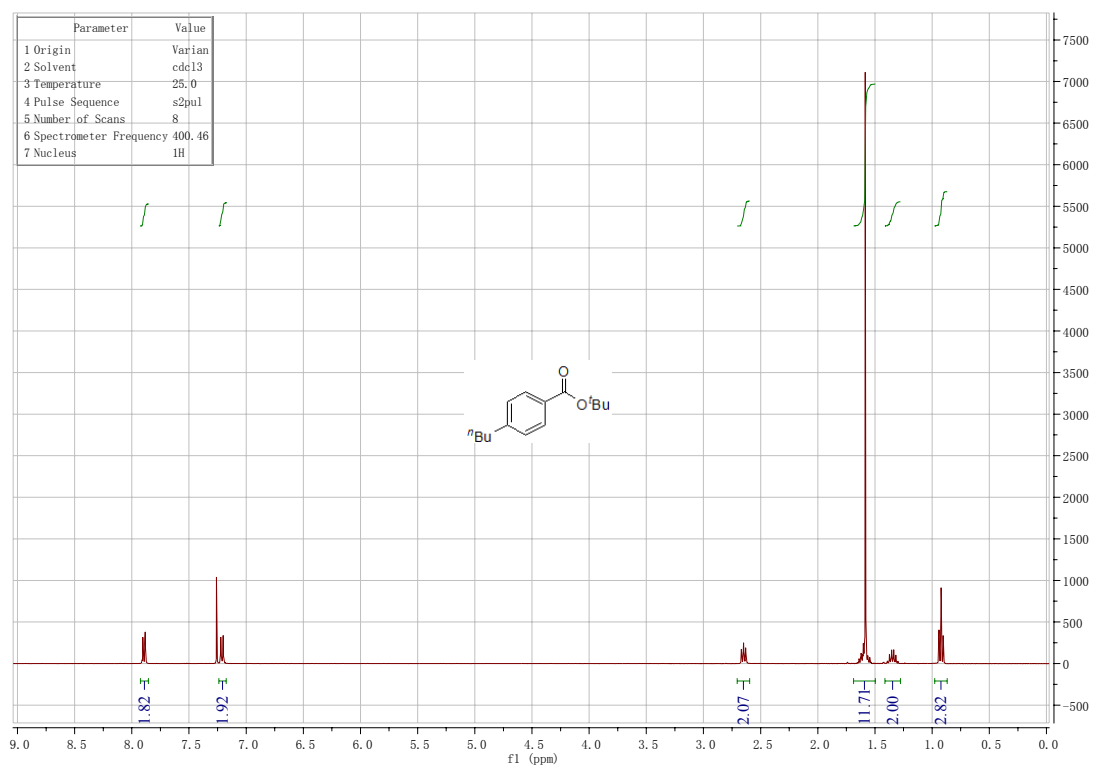
¹H NMR for 1-Naphthoic acid *t*-butyl ester (6)



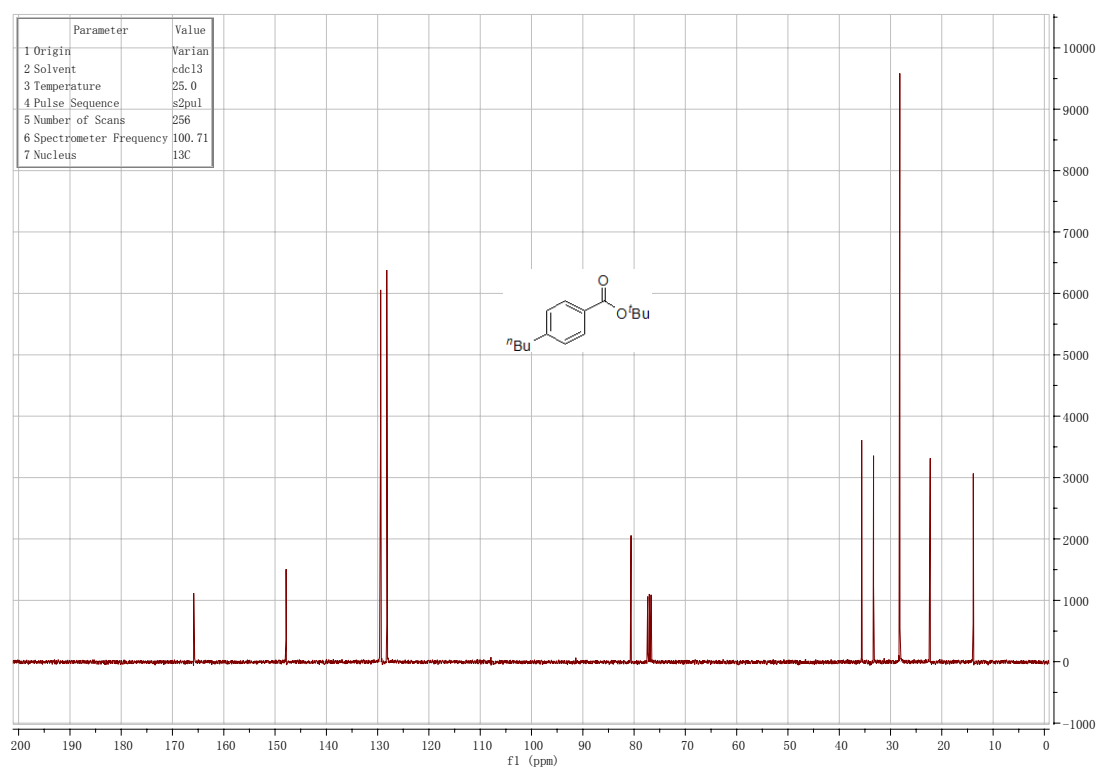
¹³C NMR for 1-Naphthoic acid *t*-butyl ester (6)



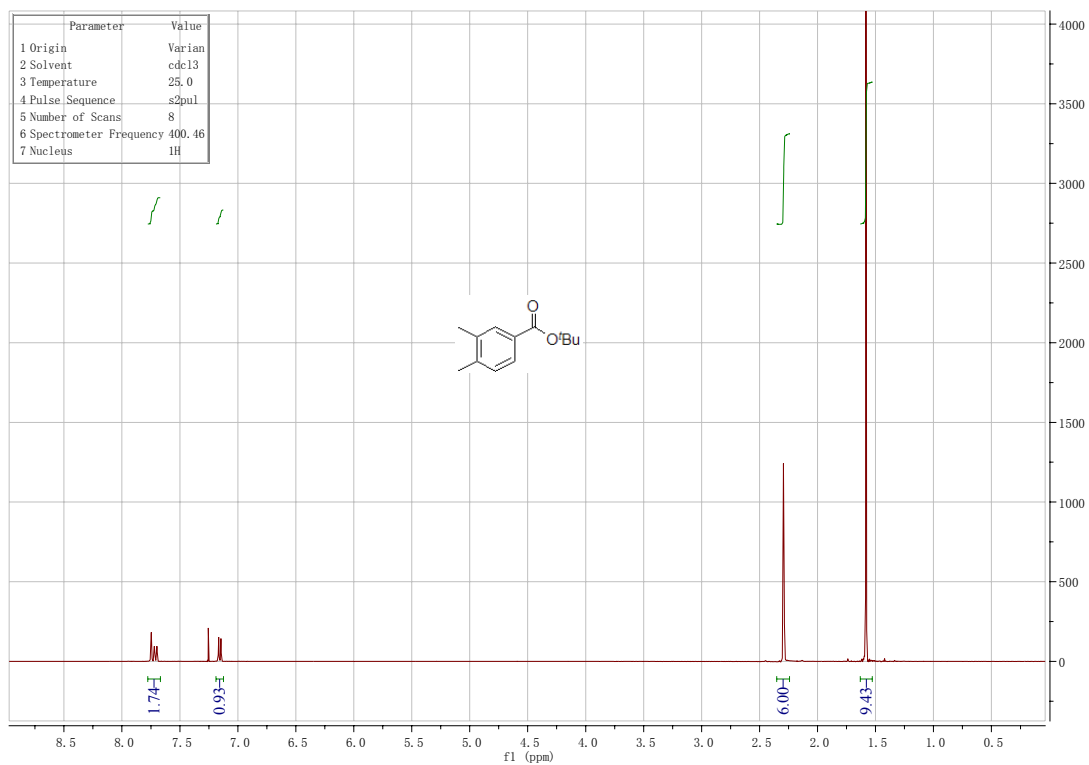
¹H NMR for 4-Butylbenzoic acid *t*-butyl ester (7)



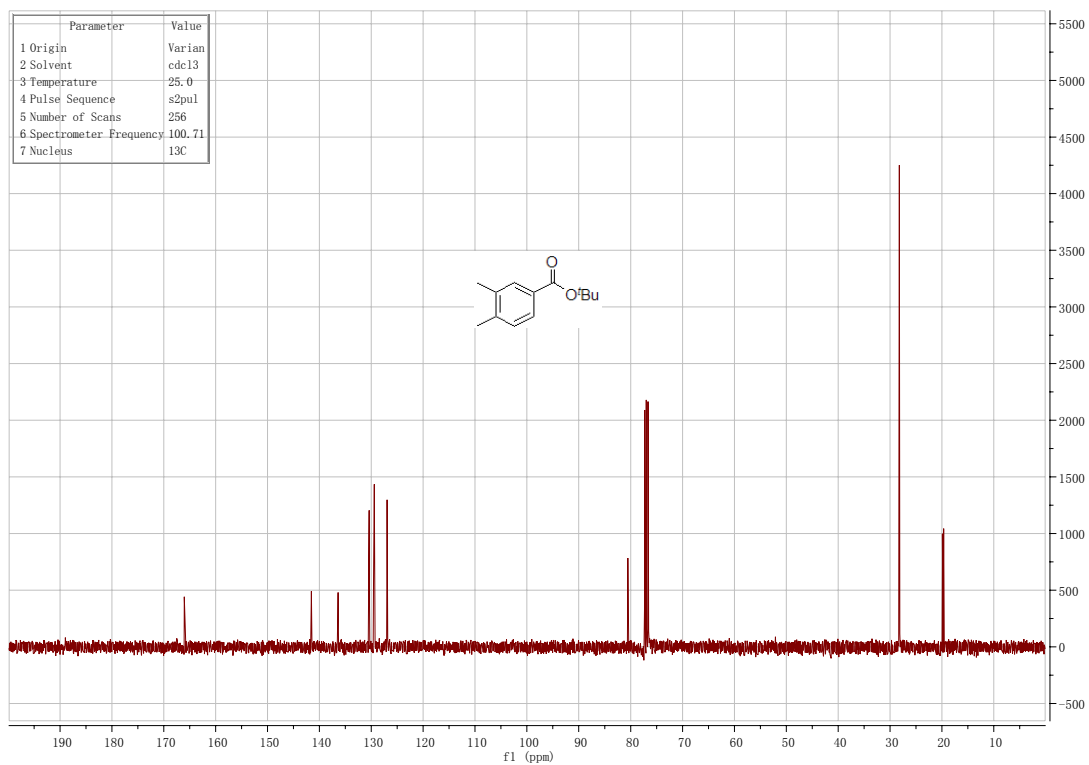
¹³C NMR for 4-Butylbenzoic acid *t*-butyl ester (7)



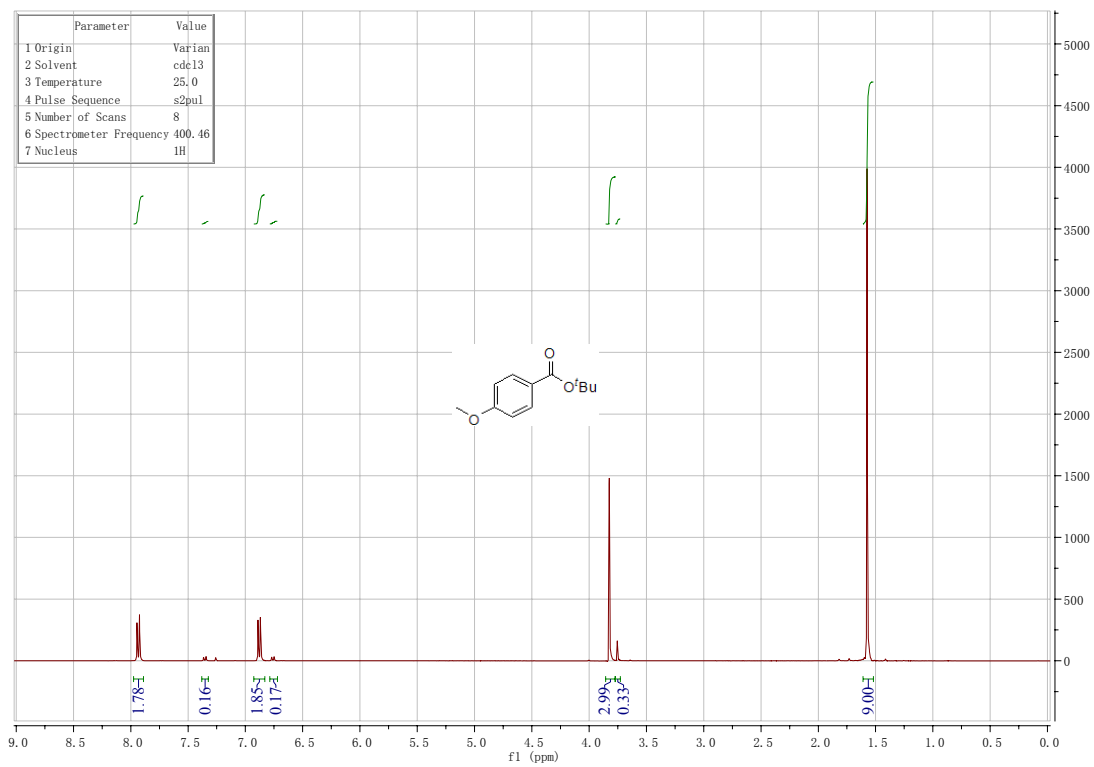
¹H NMR for 3,4-Dimethylbenzoic acid *t*-butyl ester (8)



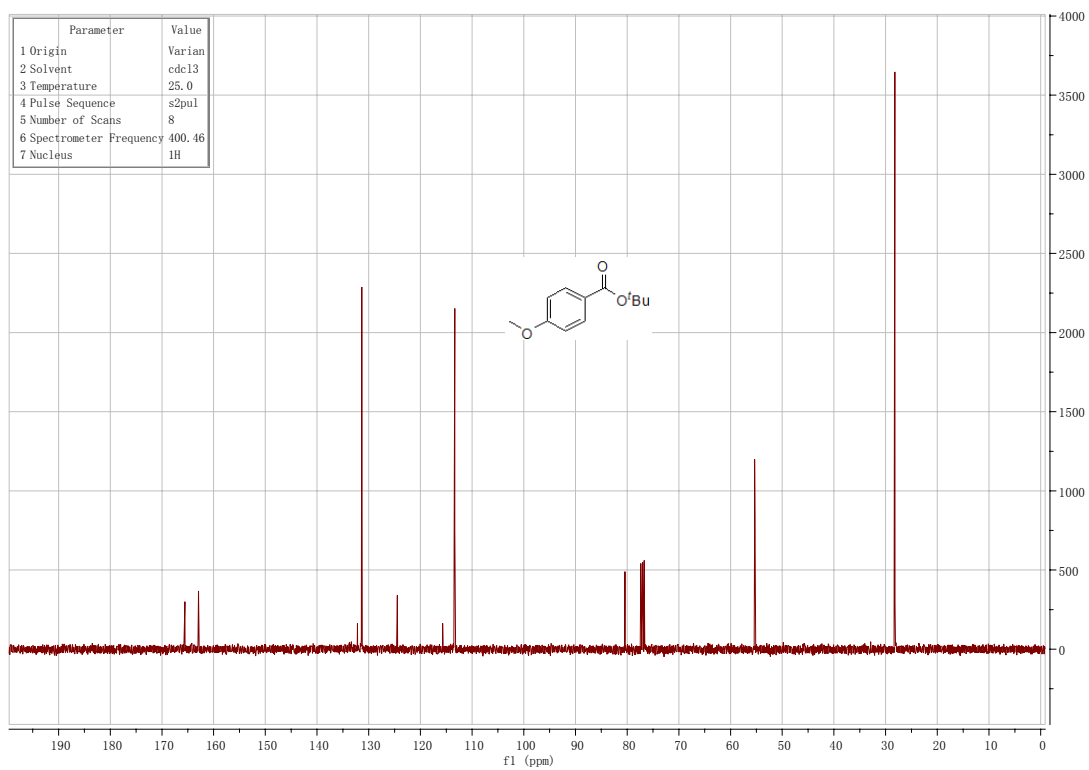
¹³C NMR for 3,4-Dimethylbenzoic acid *t*-butyl ester (8)



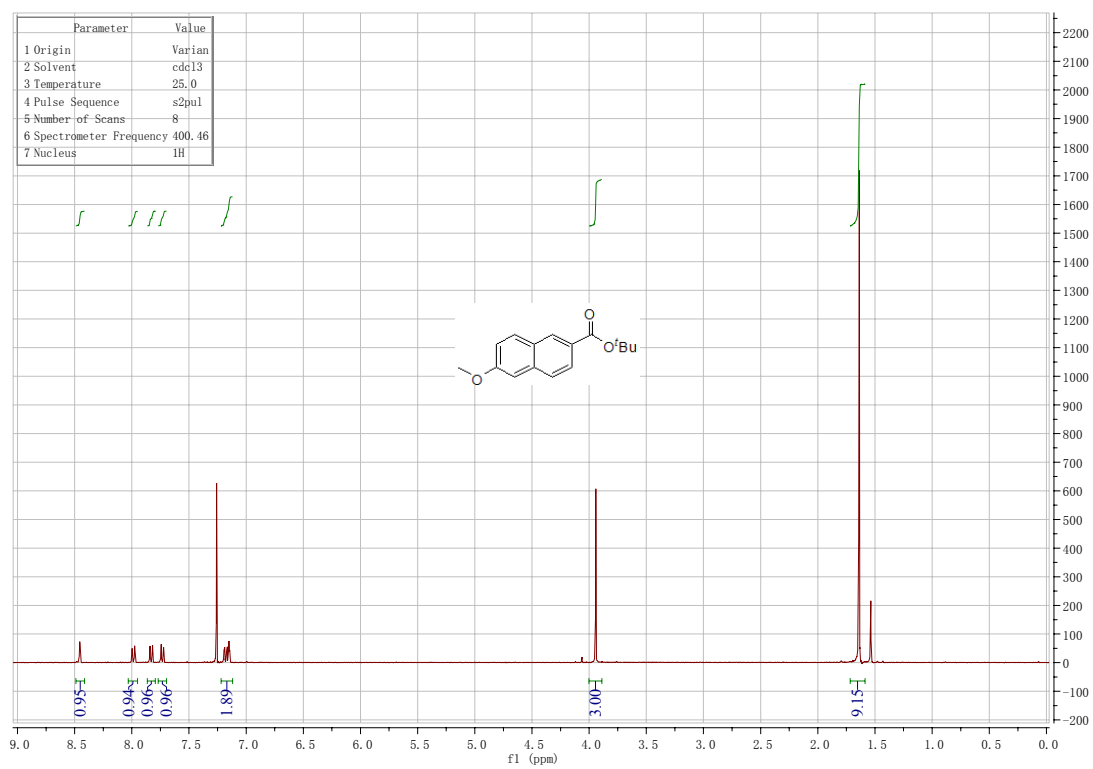
¹H NMR for 4-Methoxybenzoic acid *t*-butyl ester (9)



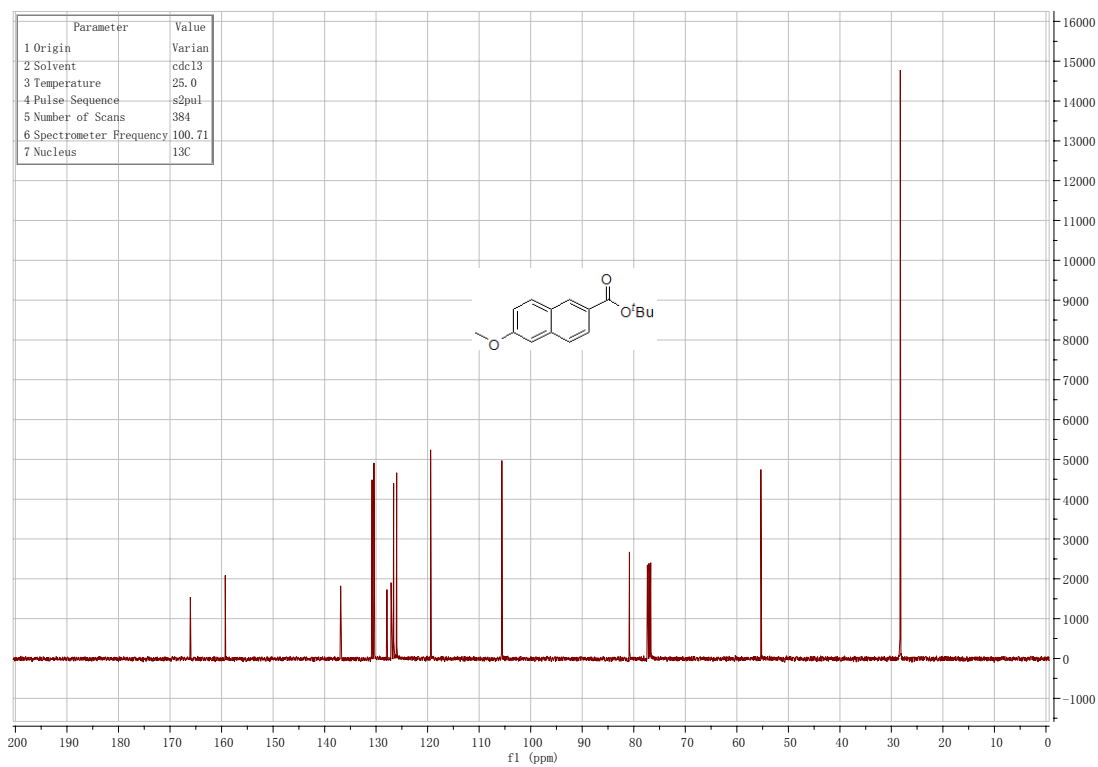
¹³C NMR for 4-Methoxybenzoic acid *t*-butyl ester (9)



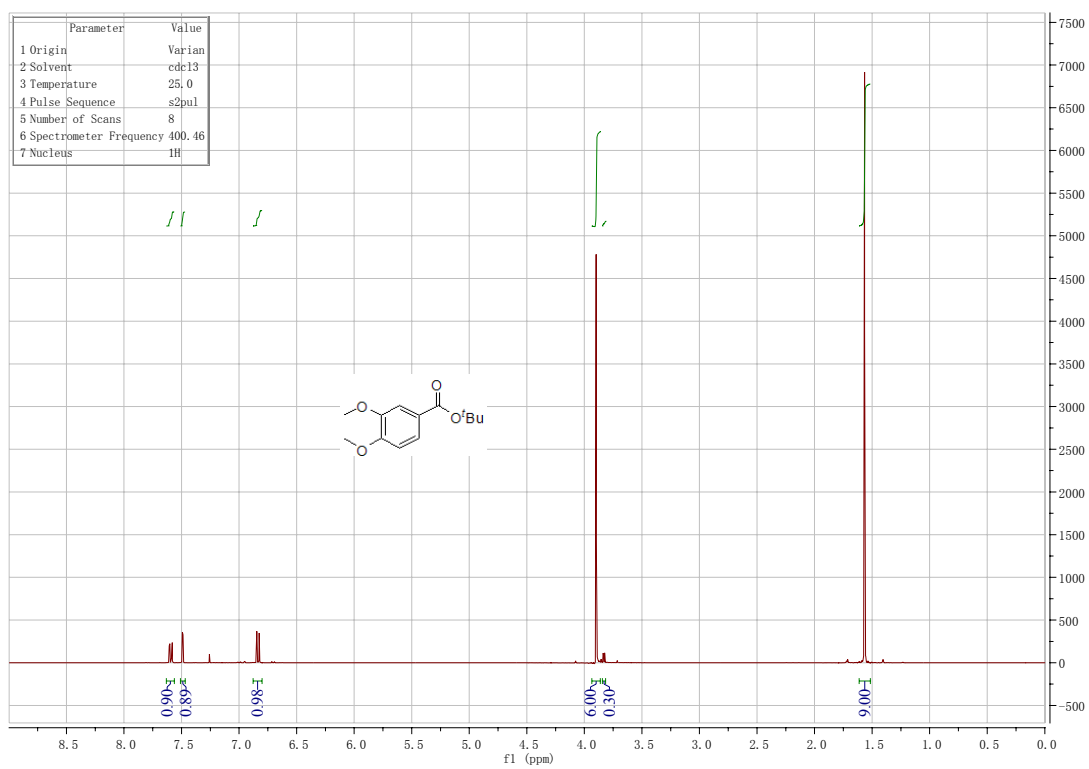
¹H NMR for 6-Methoxy-2-naphthoic acid *t*-butyl ester (10)



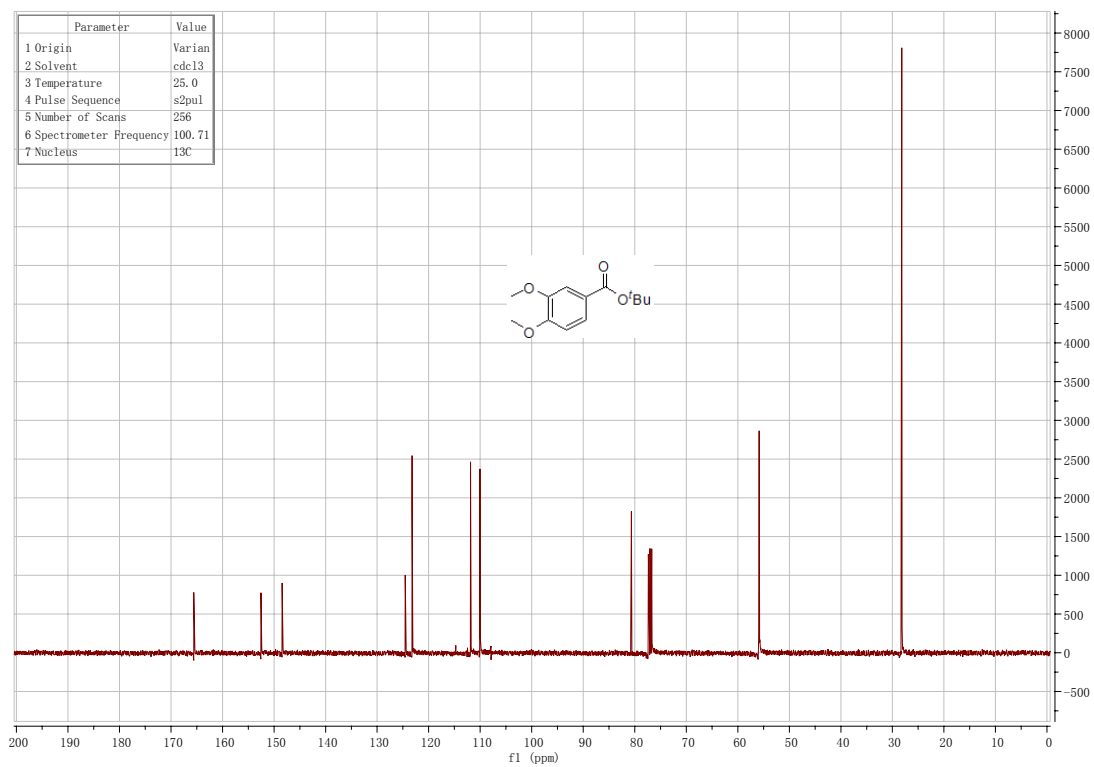
¹³C NMR for 6-Methoxy-2-naphthoic acid *t*-butyl ester (10)



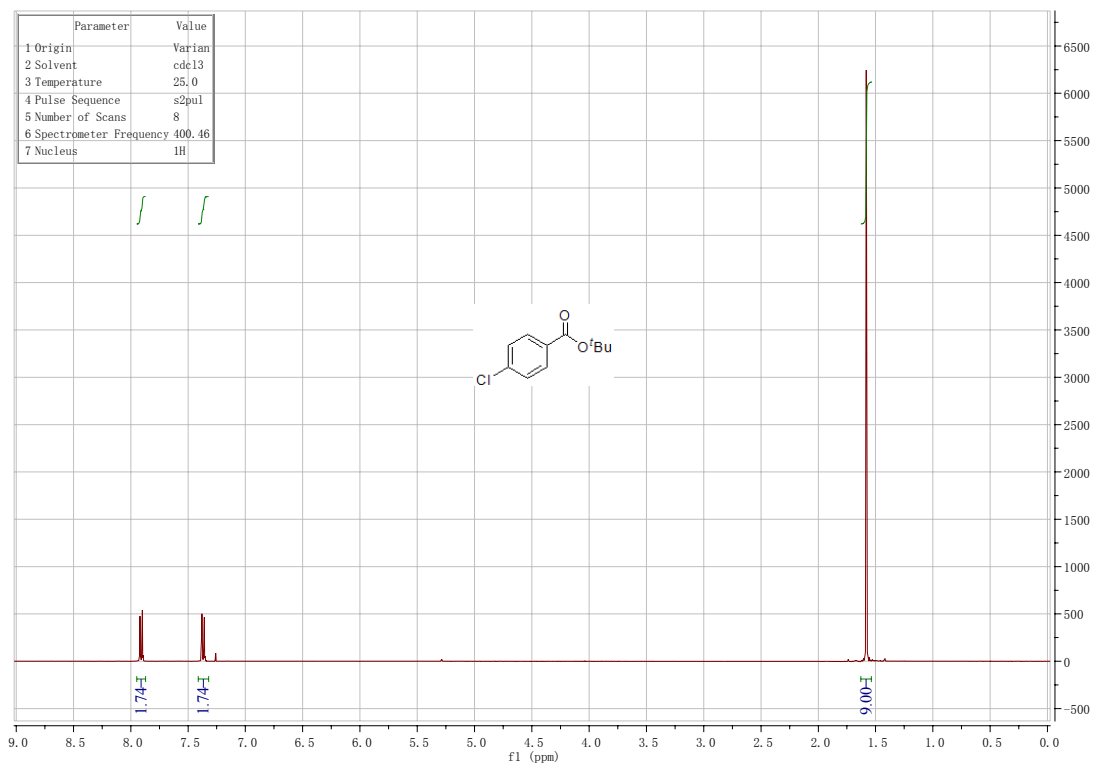
¹H NMR for 3,4-Dimethoxybenzoic acid *t*-butyl ester (11)



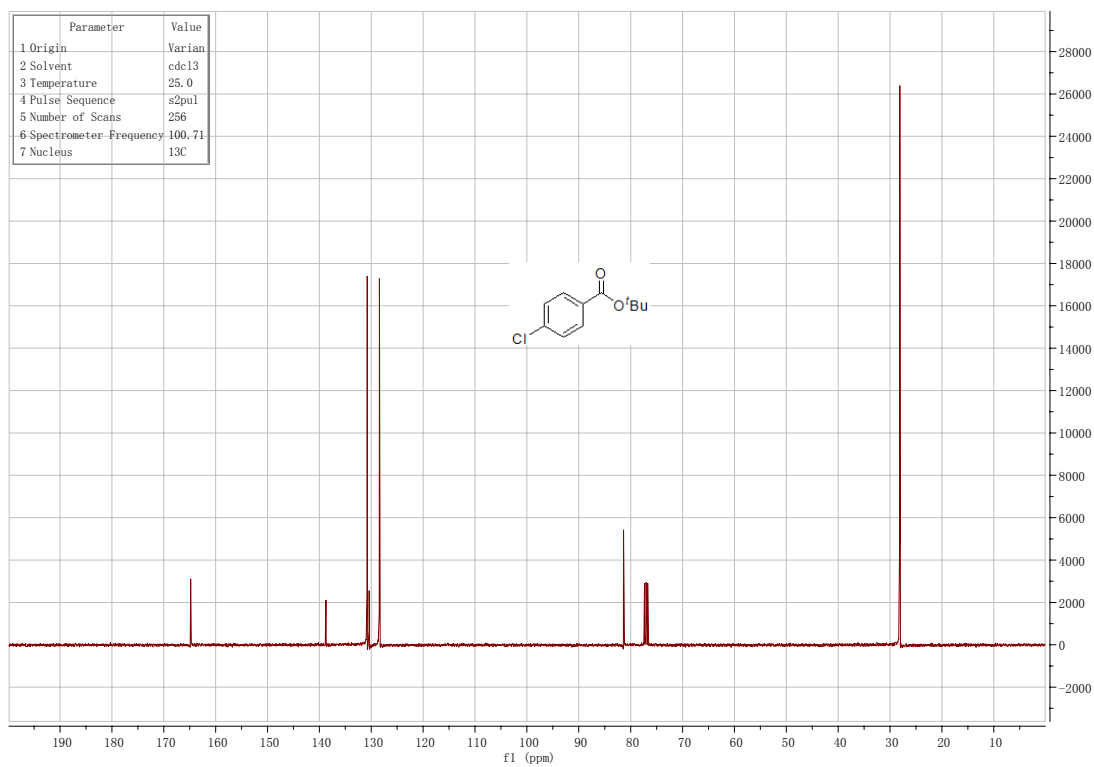
¹³C NMR for 3,4-Dimethoxybenzoic acid *t*-butyl ester (11)



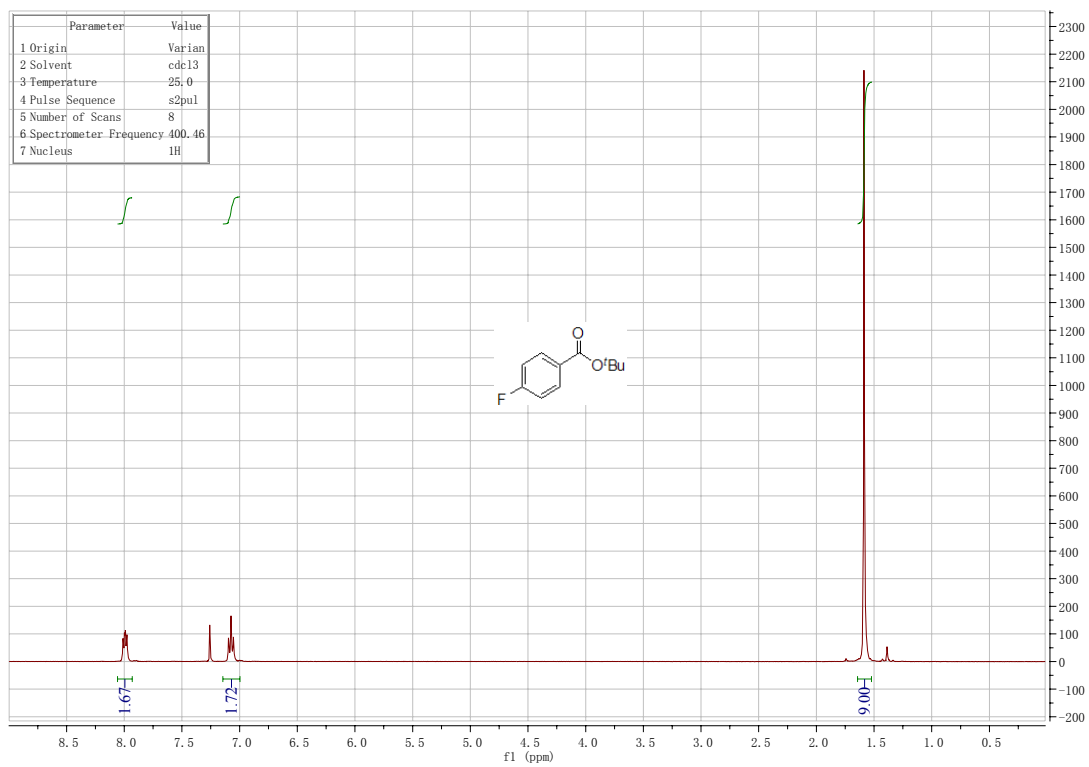
¹H NMR for 4-Chlorobenzoic acid *t*-butyl ester (12)



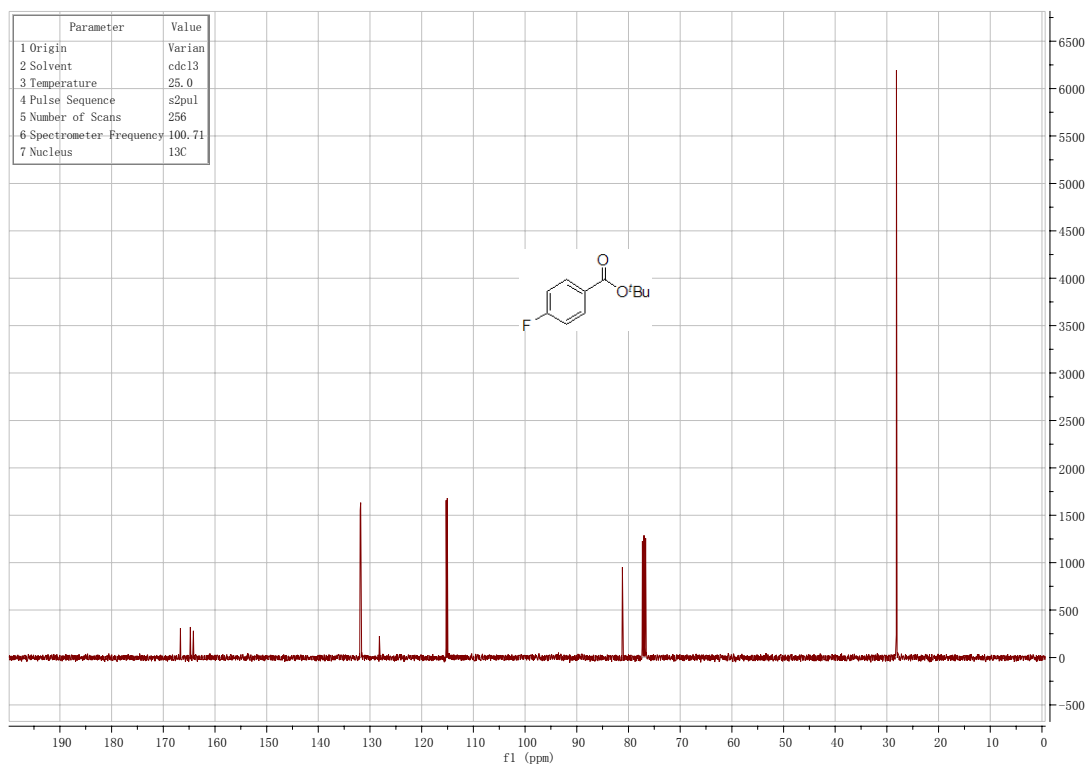
¹³C NMR for 4-Chlorobenzoic acid *t*-butyl ester (12)



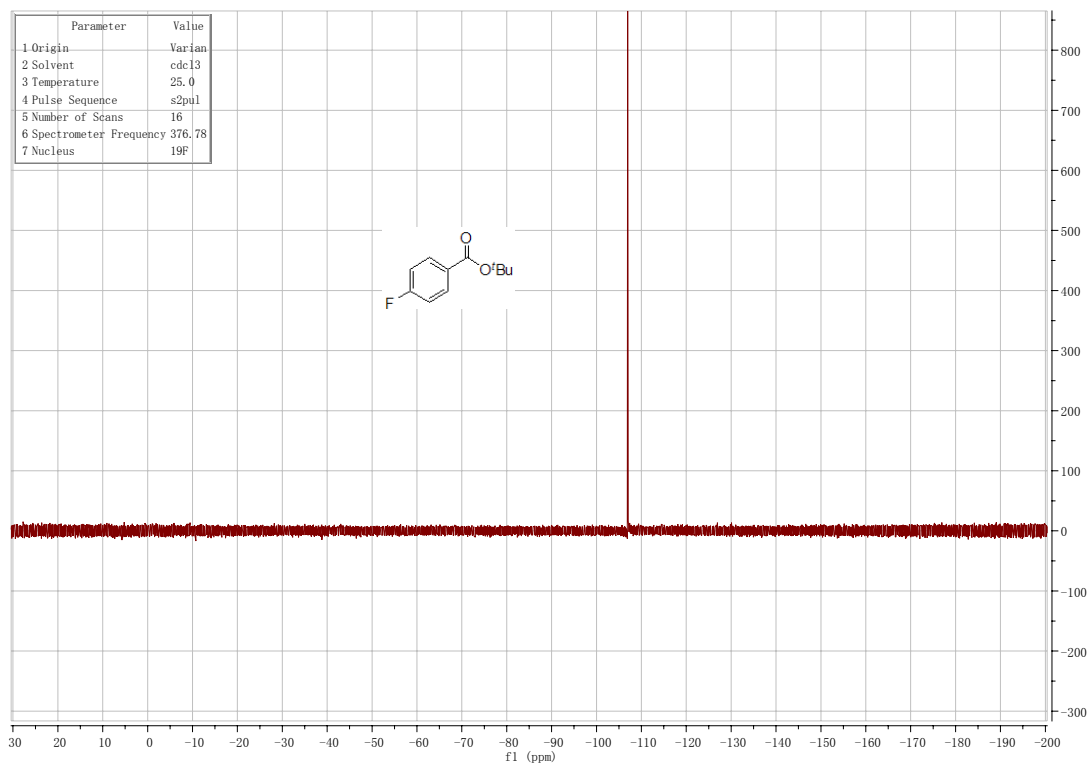
¹H NMR for 4-Fluorobenzoic acid *t*-butyl ester (13)



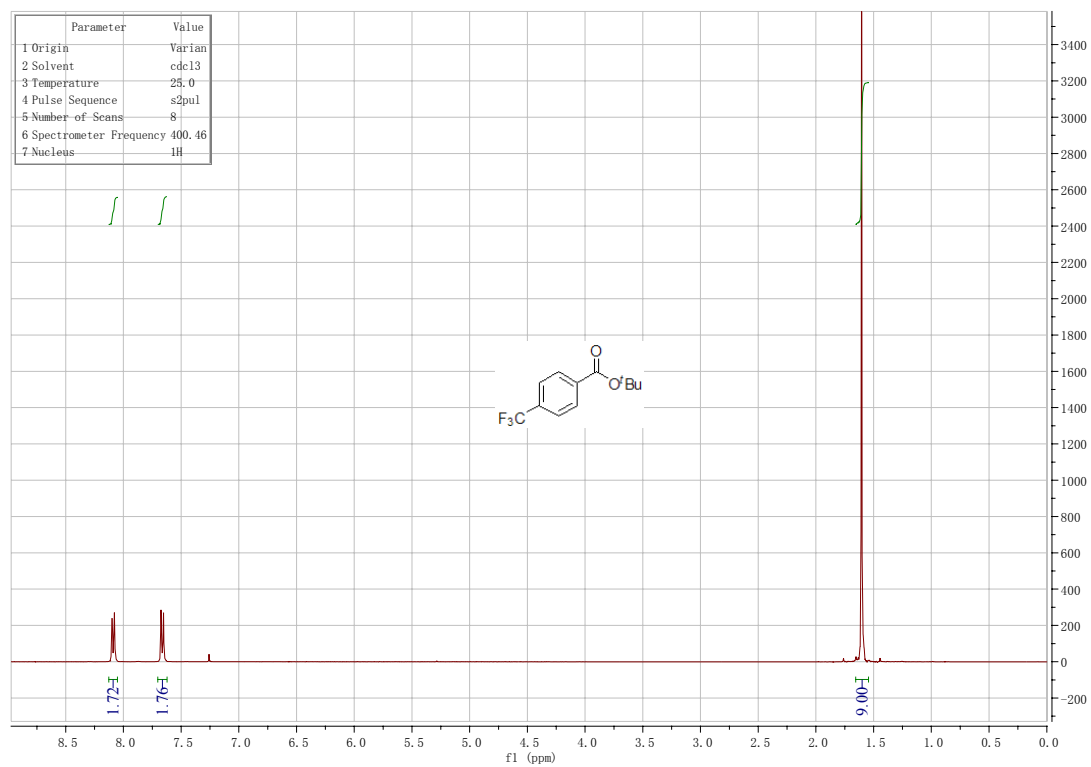
¹³C NMR for 4-Fluorobenzoic acid *t*-butyl ester (13)



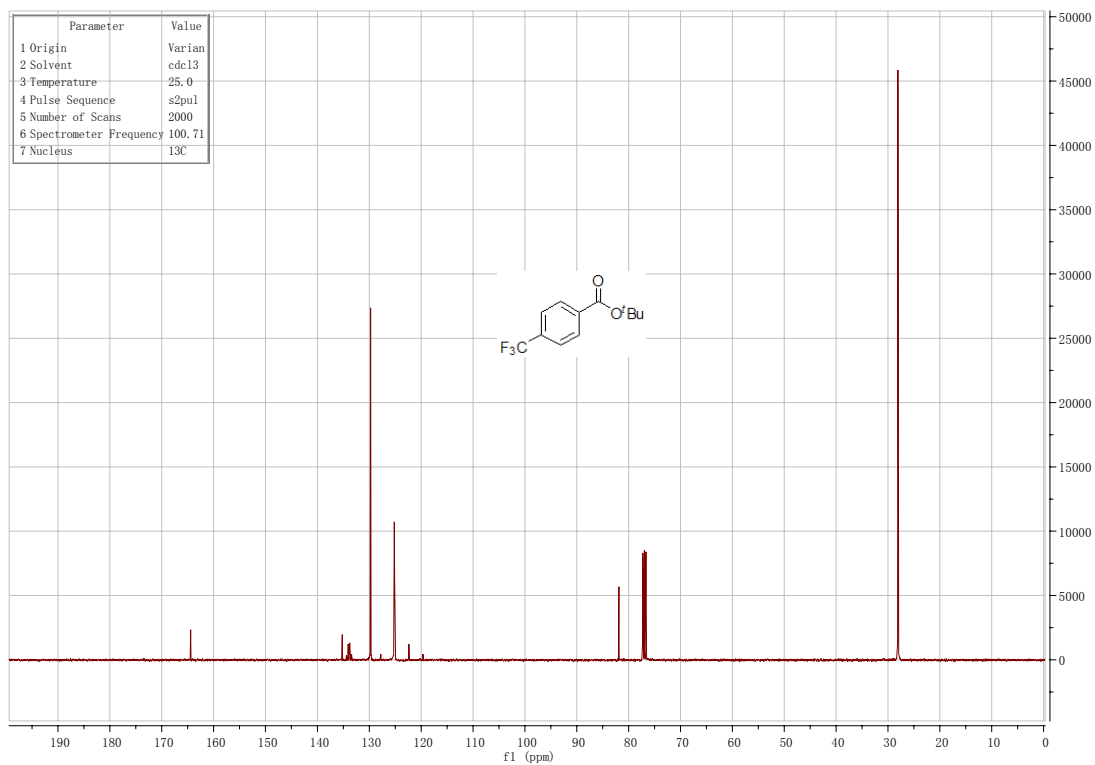
¹⁹F NMR for 4-Fluorobenzoic acid *t*-butyl ester (13)



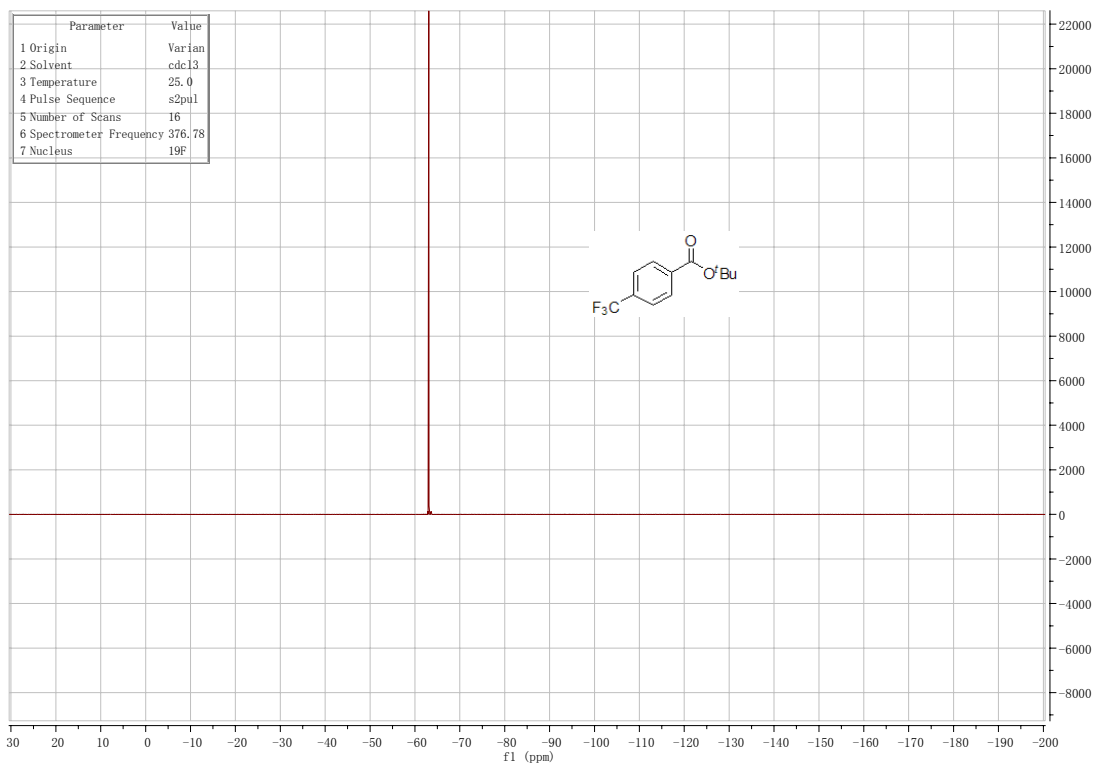
¹H NMR for 4-(Trifluoromethyl)benzoic acid *t*-butyl ester (14)



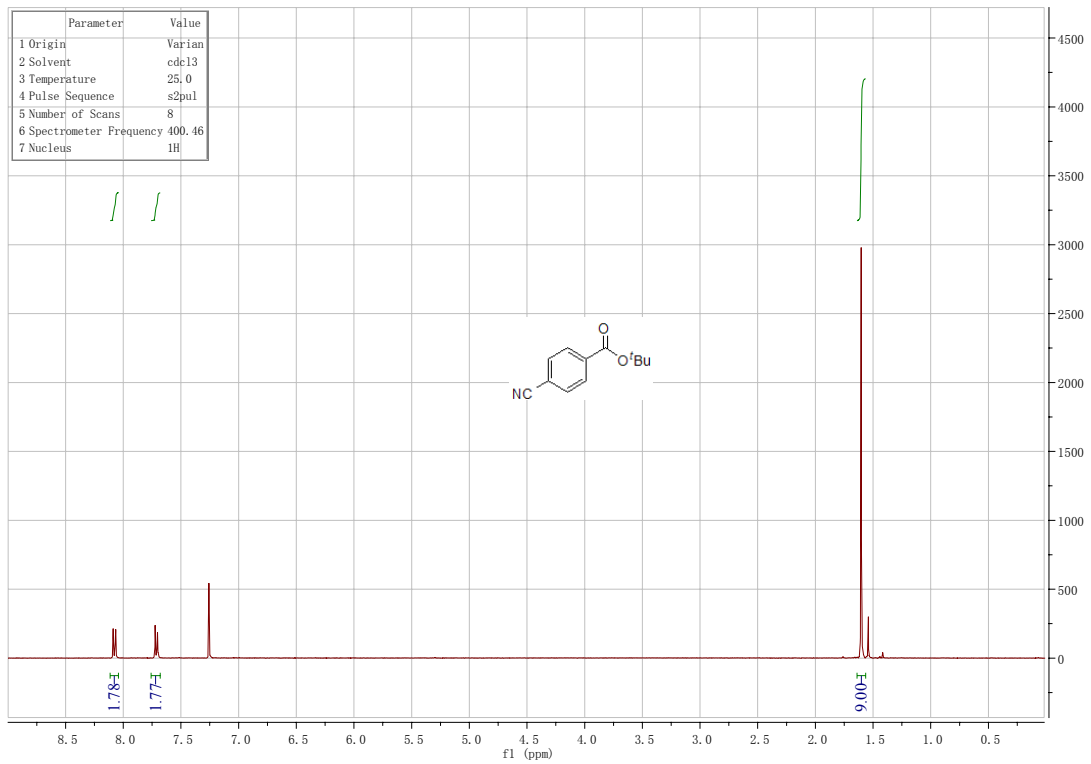
¹³C NMR for 4-(Trifluoromethyl)benzoic acid *t*-butyl ester (14)



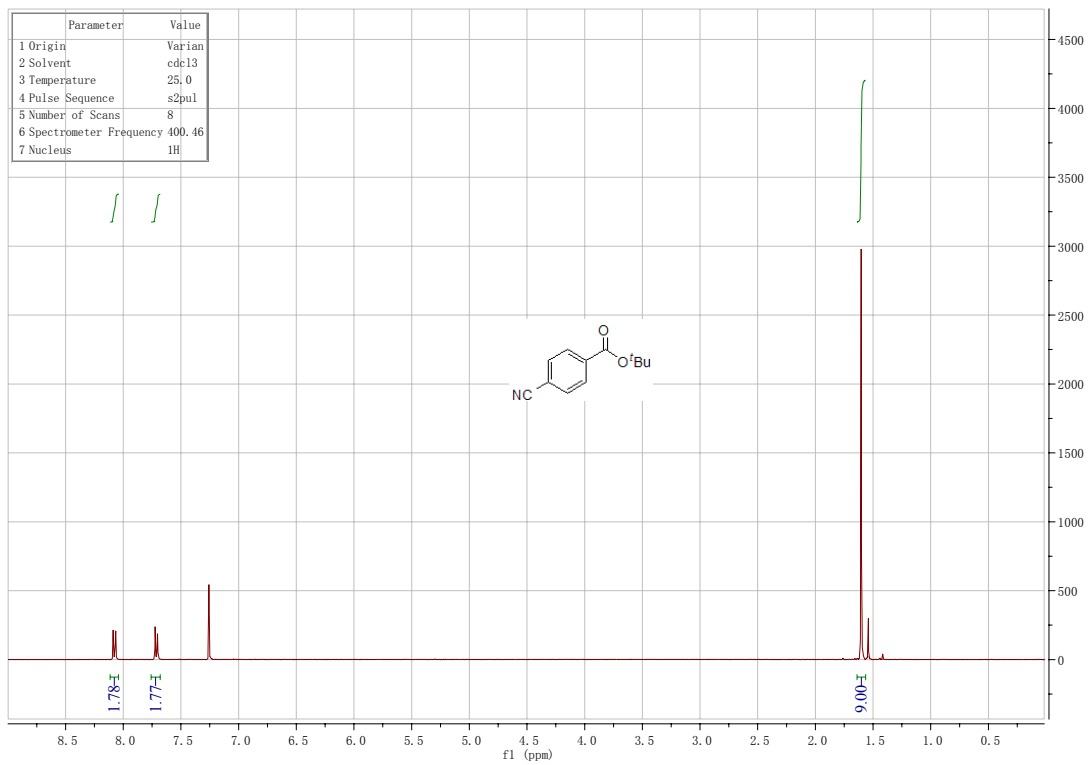
¹⁹F NMR for 4-(Trifluoromethyl)benzoic acid *t*-butyl ester (14)



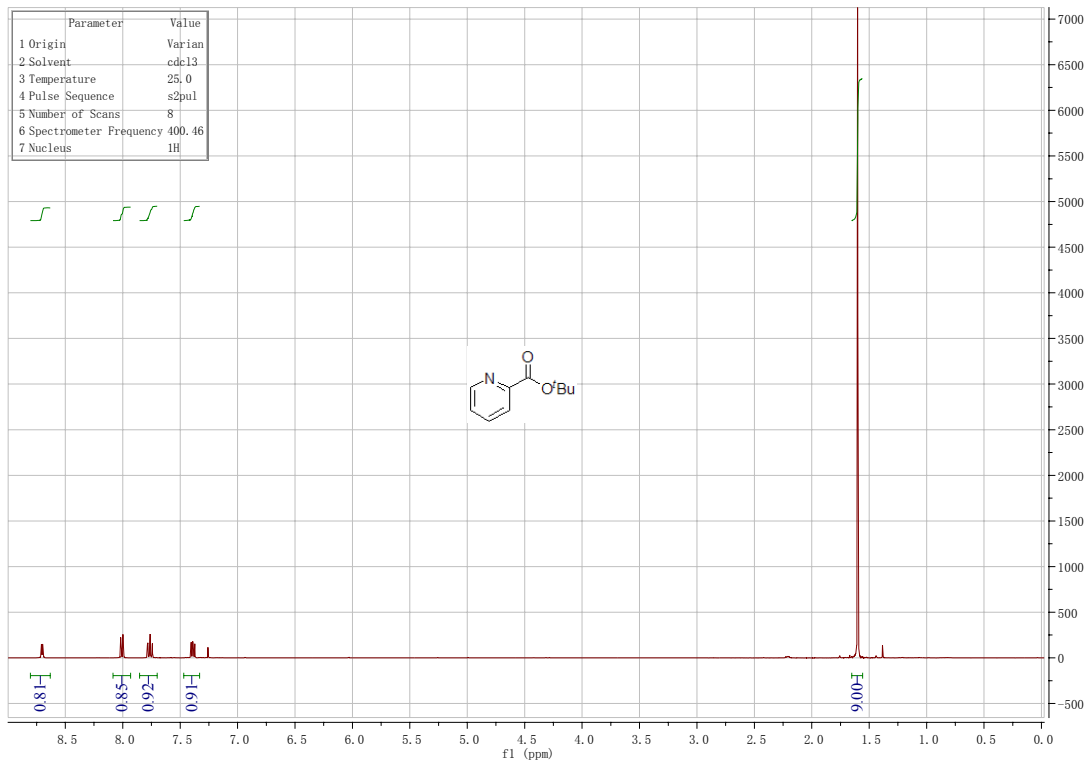
¹H NMR for 4-Cyanobenzoic acid *t*-butyl ester (15)



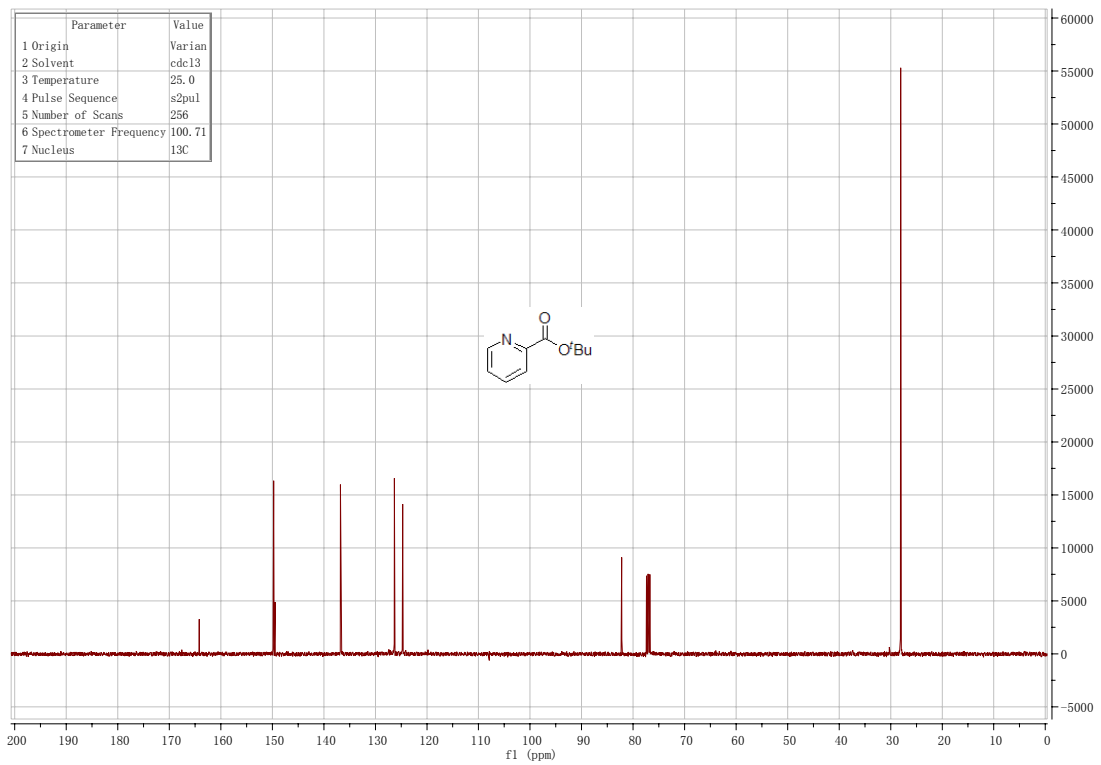
¹³C NMR for 4-Cyanobenzoic acid *t*-butyl ester (15)



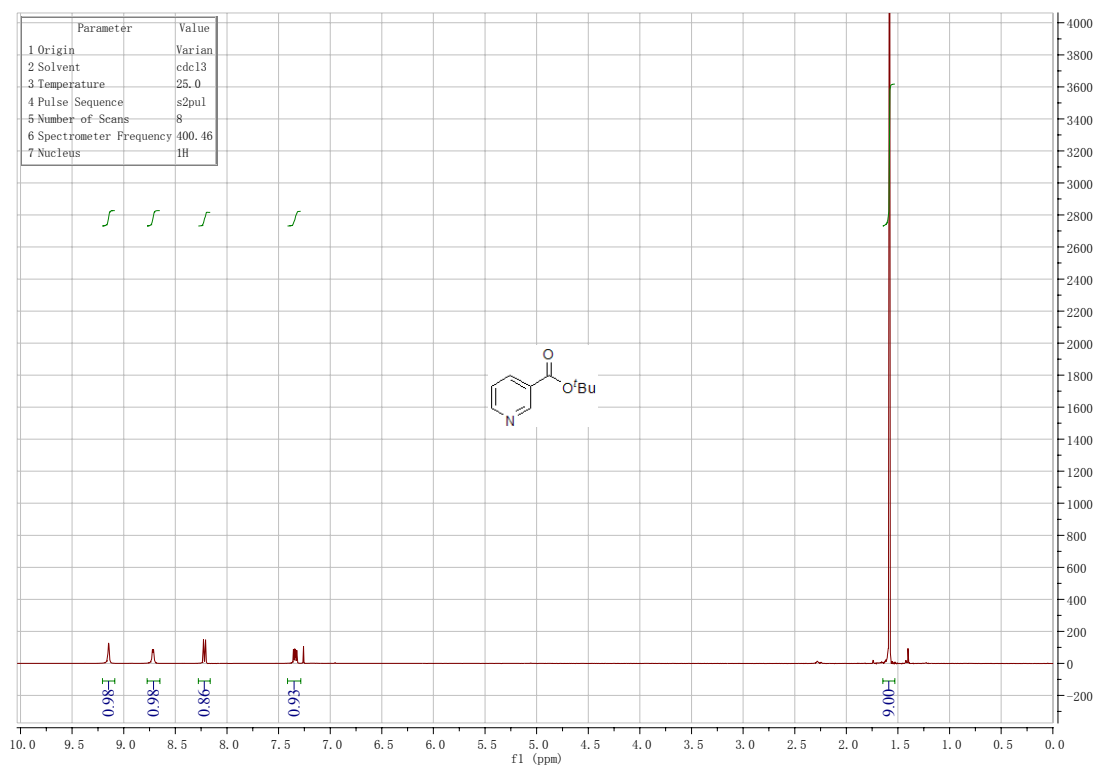
¹H NMR for Pyridine-2-carboxylic acid t-butyl ester (16)



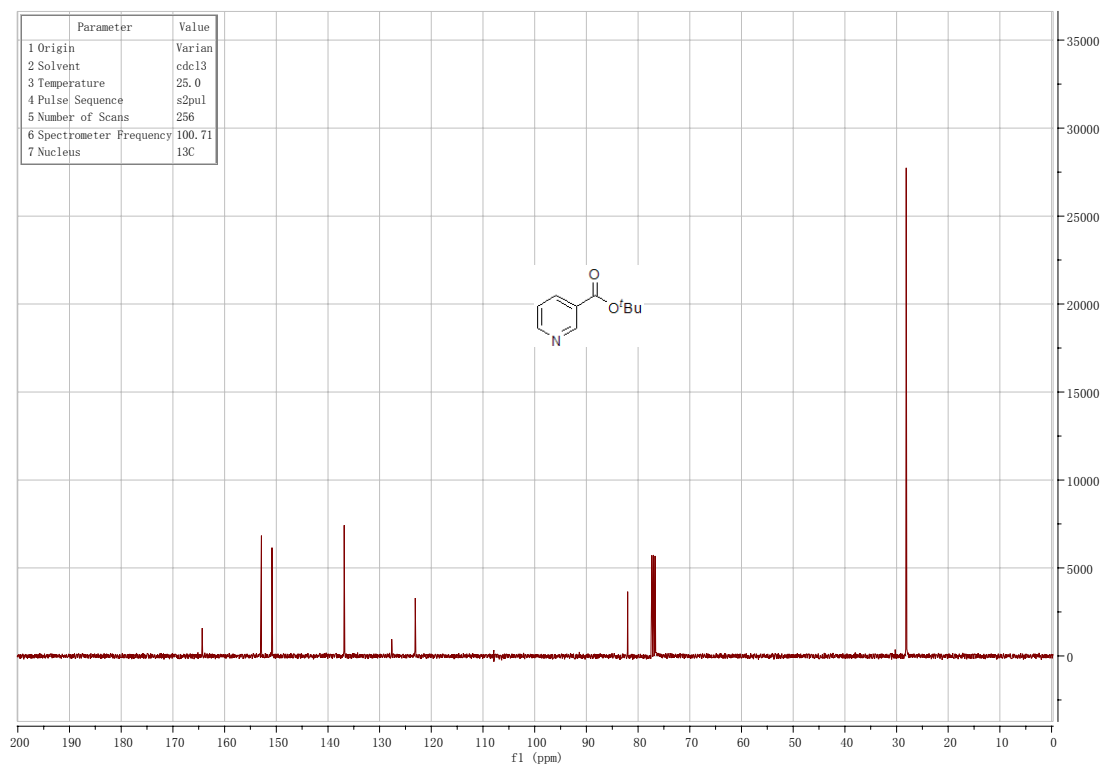
¹³C NMR for Pyridine-2-carboxylic acid t-butyl ester (16)



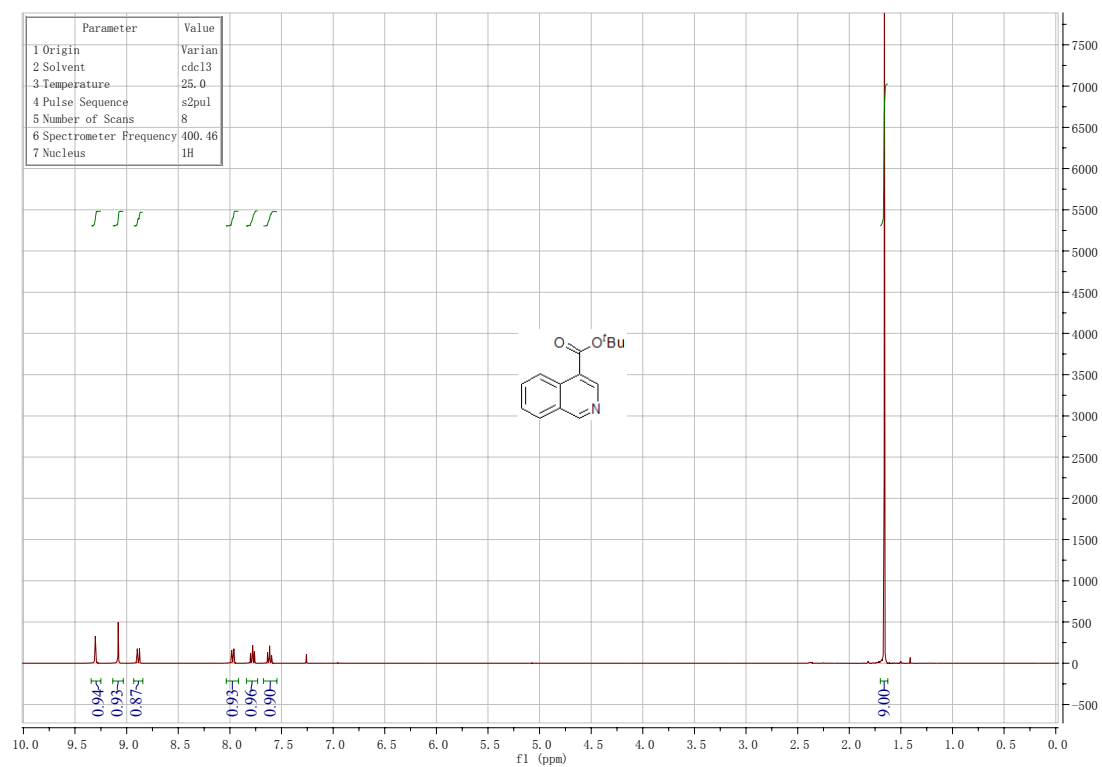
¹H NMR for Pyridine-3-carboxylic acid *t*-butyl ester (17)



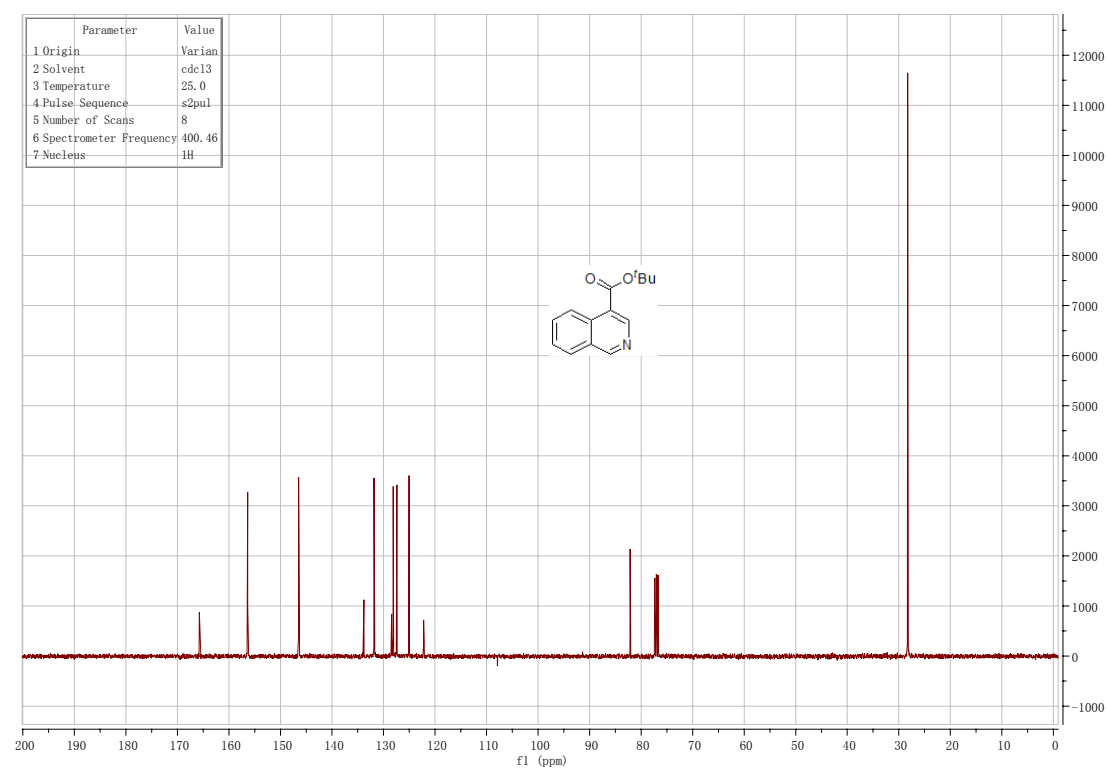
¹³C NMR for Pyridine-3-carboxylic acid *t*-butyl ester (17)



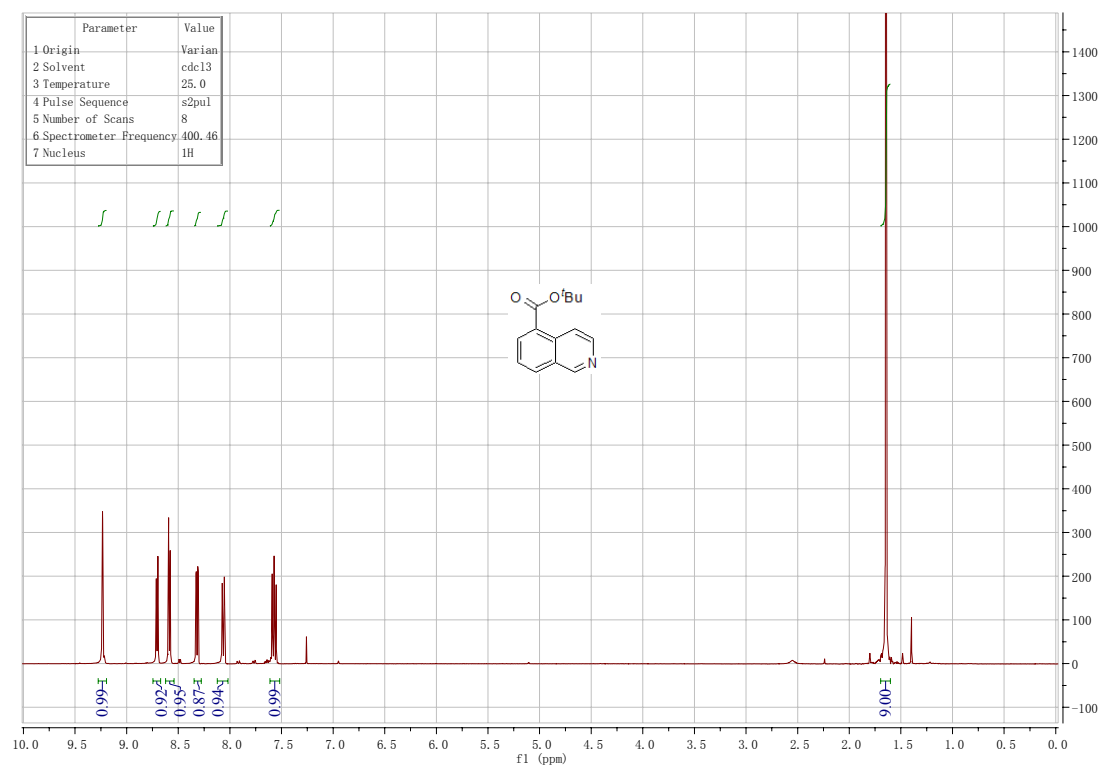
¹H NMR for Isoquinoline-4-carboxylic acid *t*-butyl ester (18)



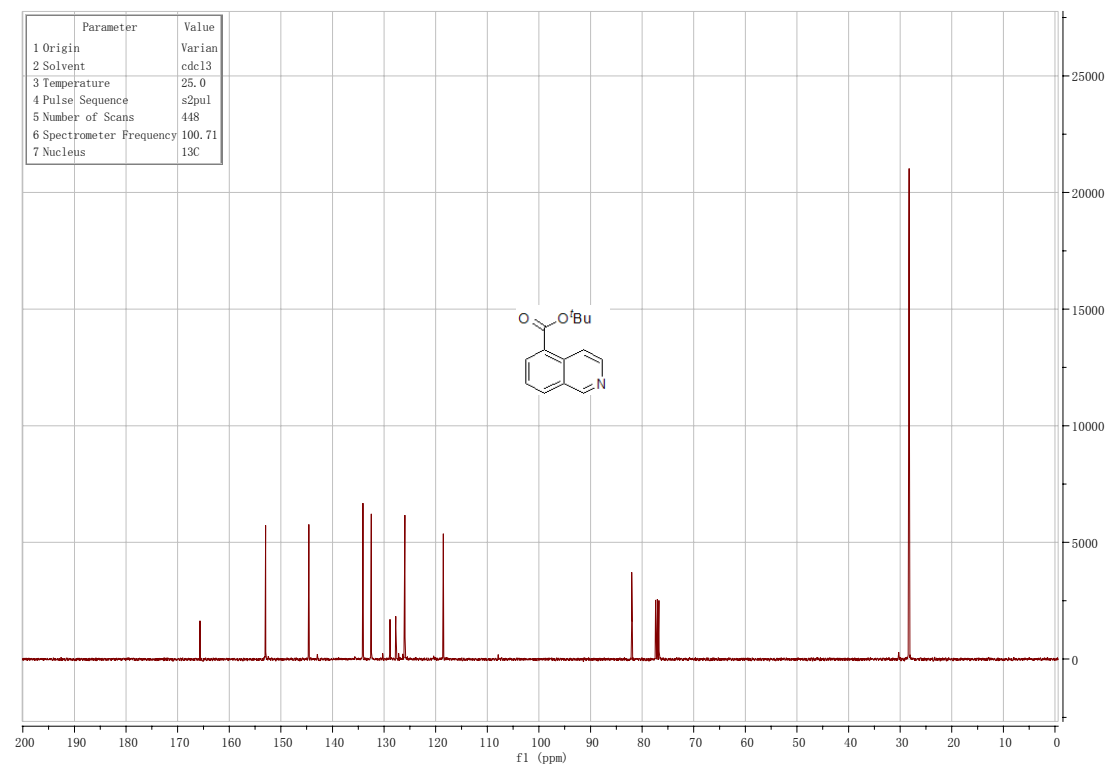
¹³C NMR for Isoquinoline-4-carboxylic acid *t*-butyl ester (18)



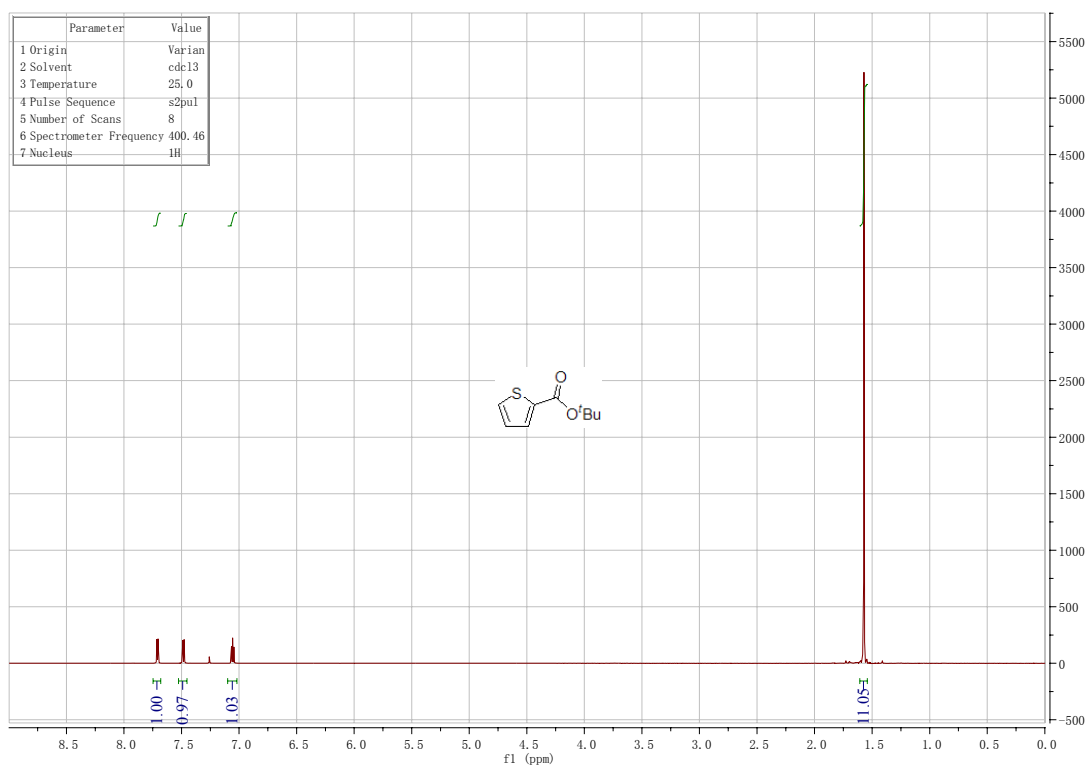
¹H NMR for Isoquinoline-5-carboxylic acid *t*-butyl ester (19)



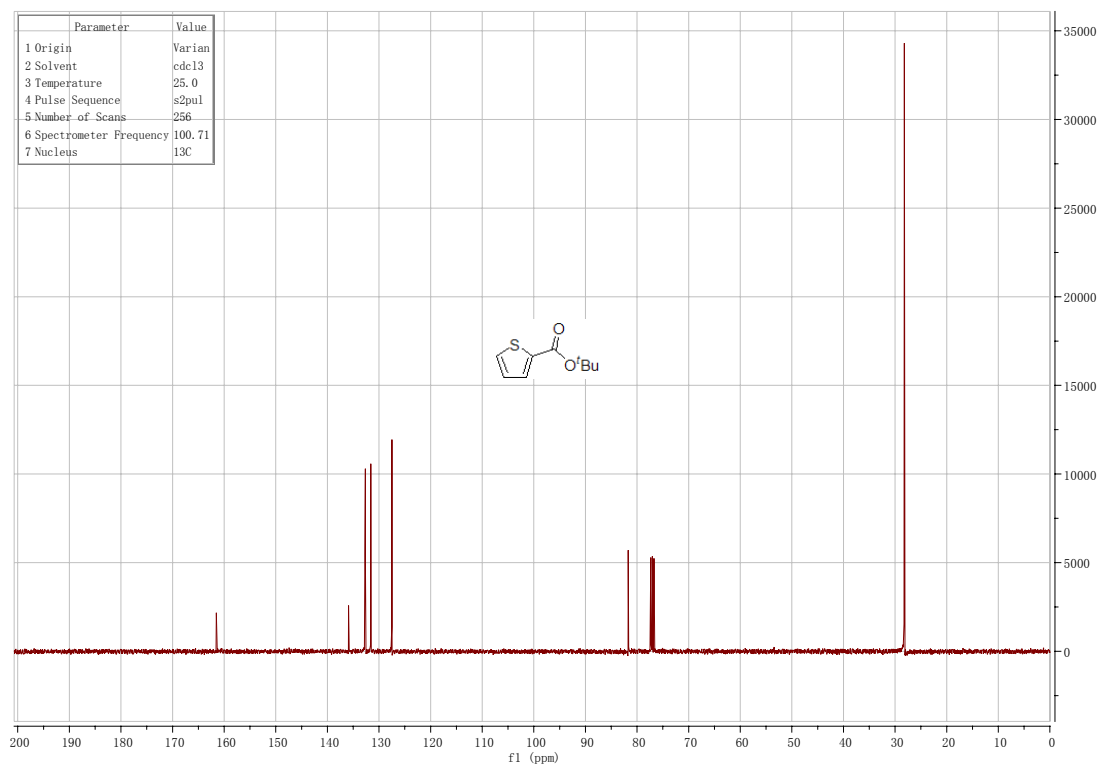
¹³C NMR for Isoquinoline-5-carboxylic acid *t*-butyl ester (19)



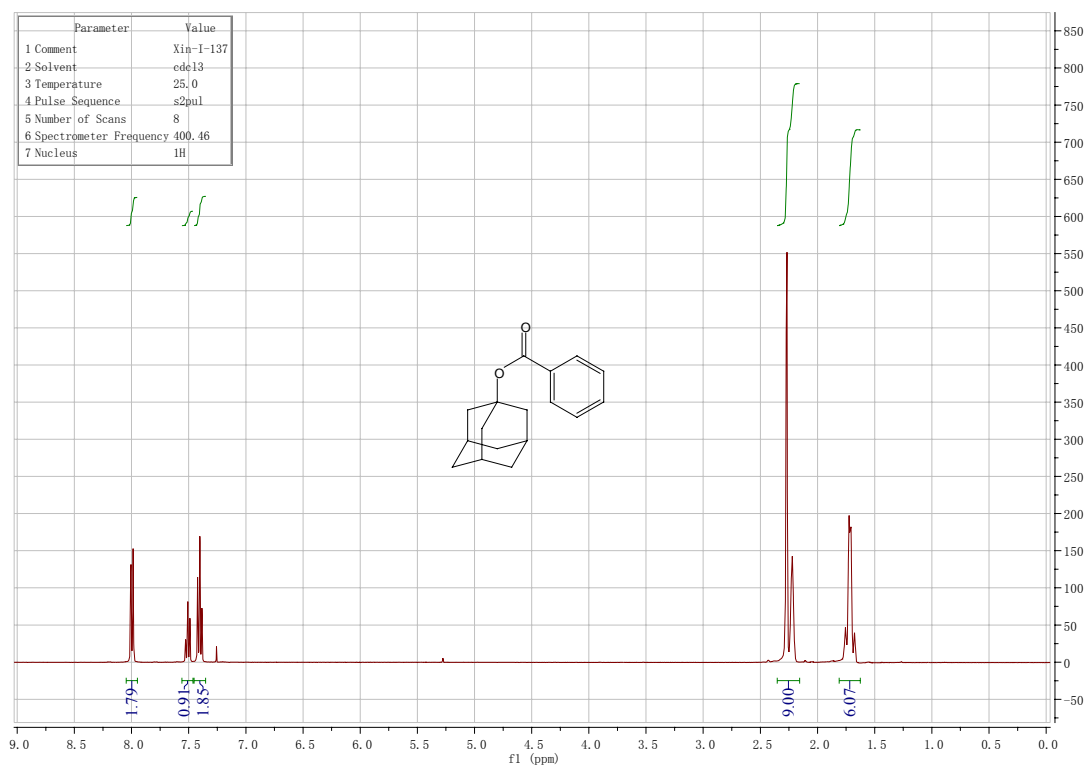
¹H NMR for Thiophene-2-carboxylic acid *t*-butyl ester (20)



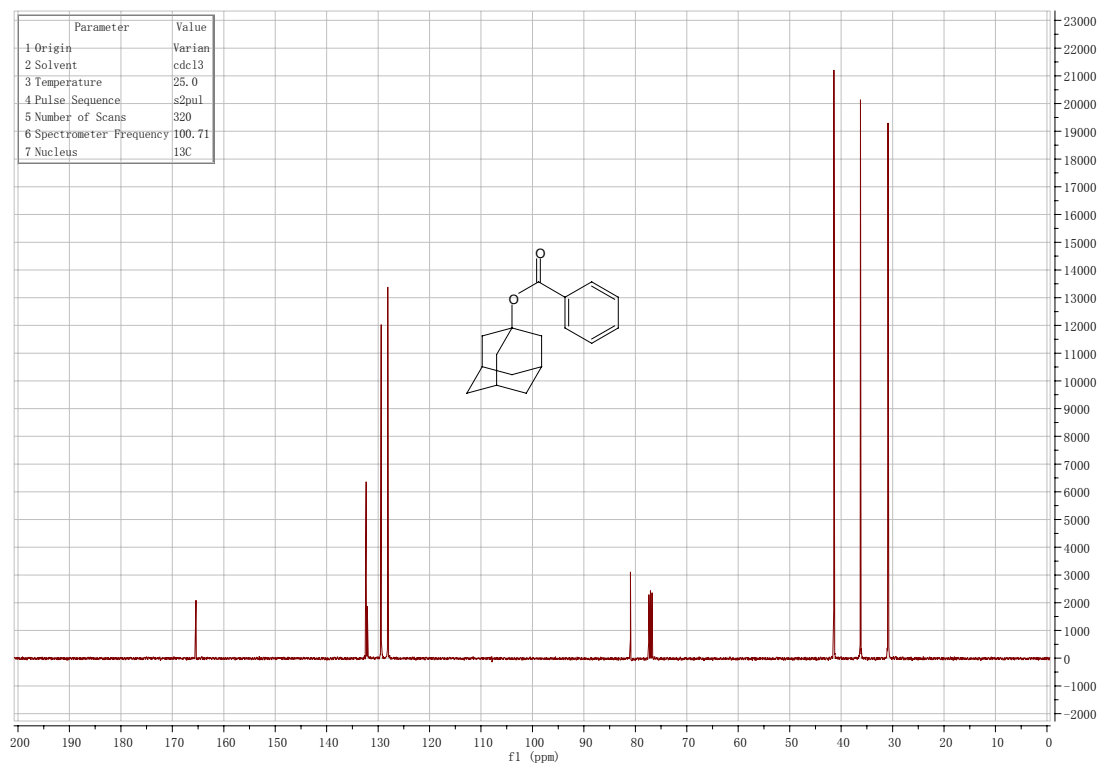
¹³C NMR for Thiophene-2-carboxylic acid *t*-butyl ester (20)



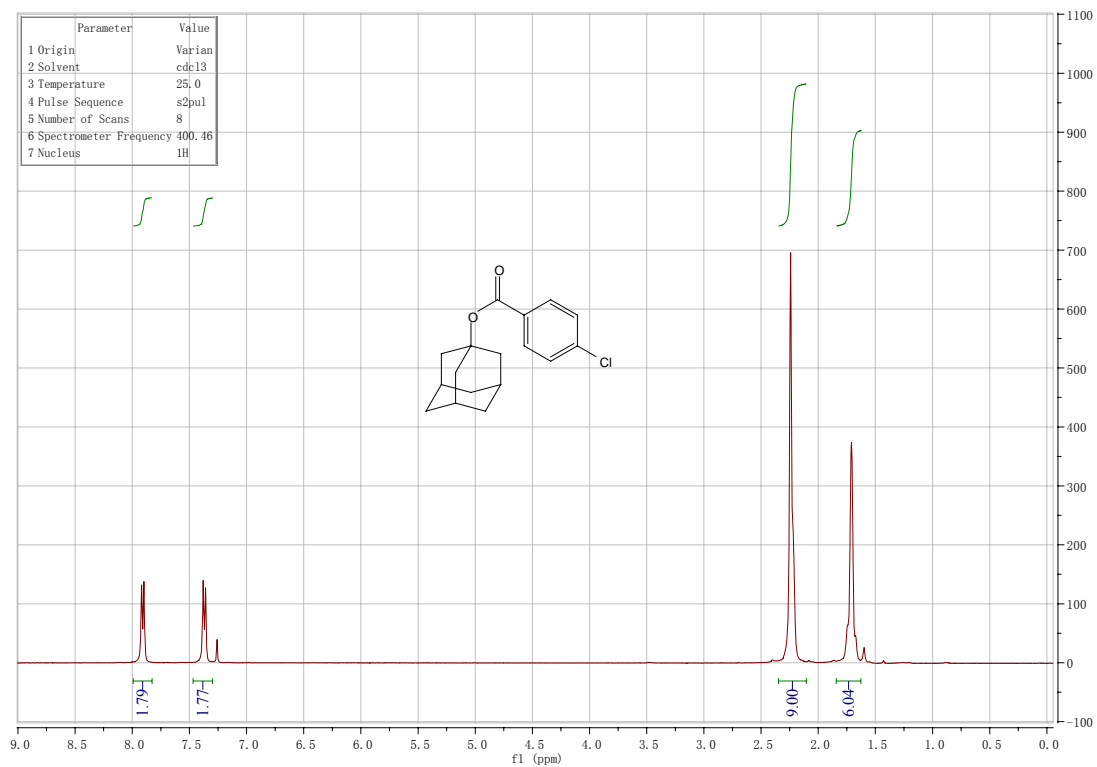
¹H NMR for 1-Adamantanol benzoate (21)



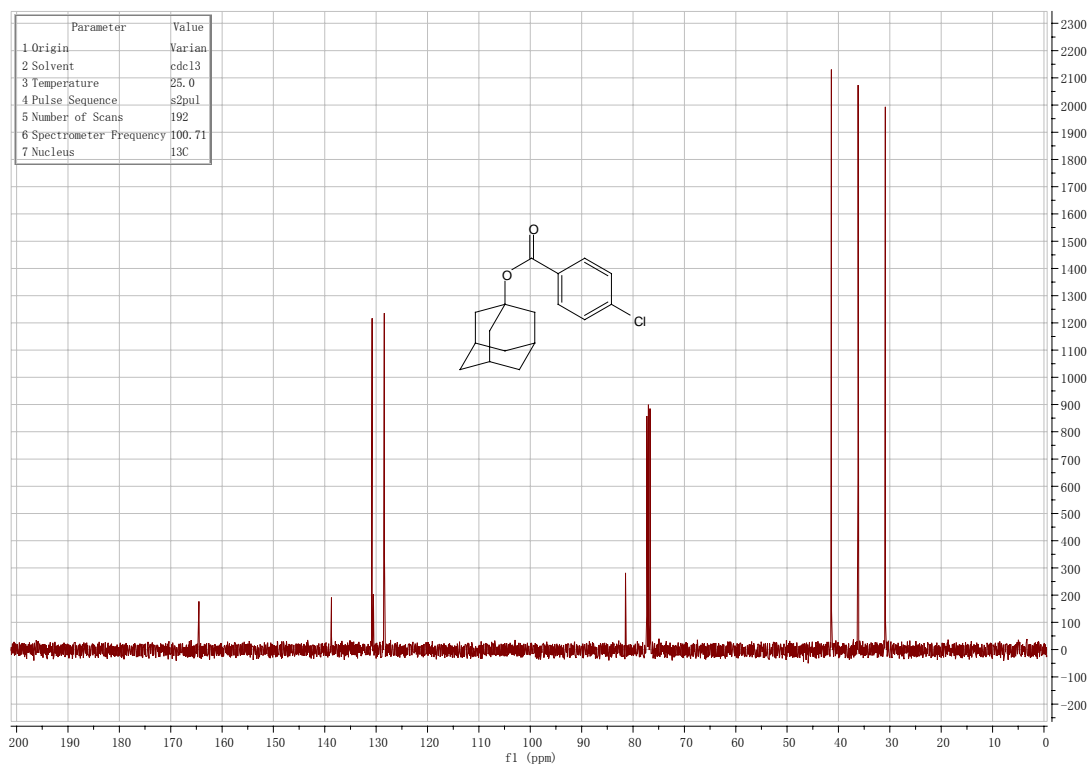
¹³C NMR for 1-Adamantanol benzoate (21)



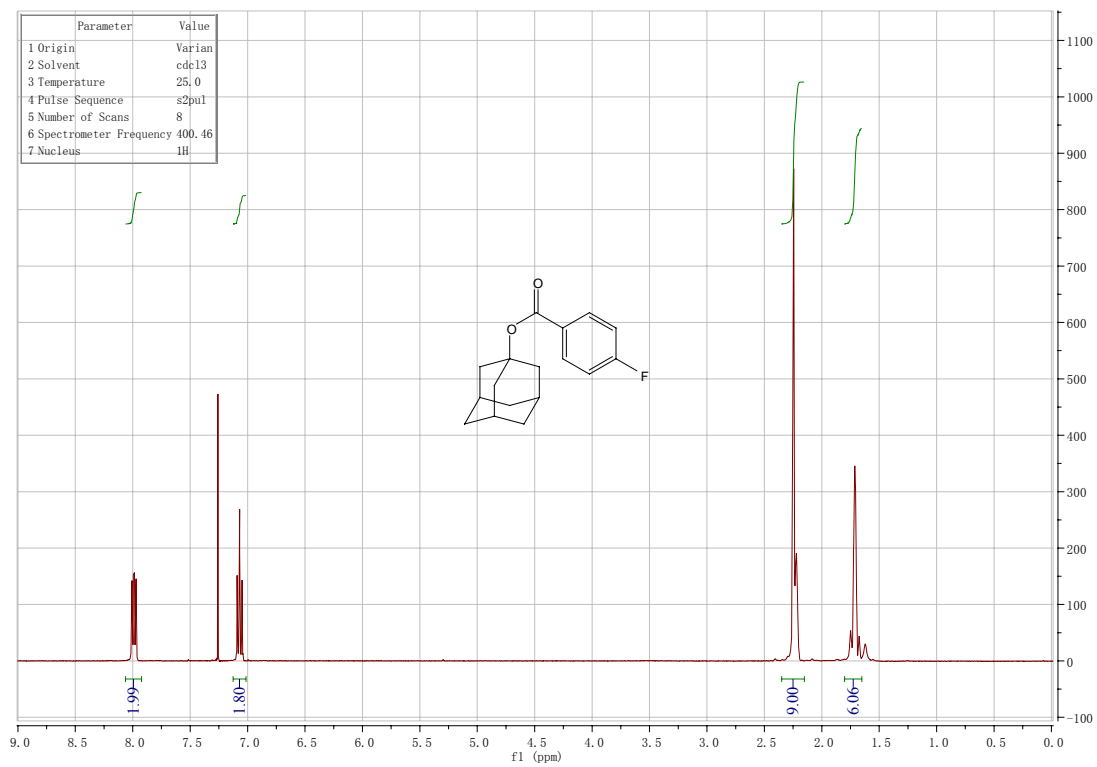
¹H NMR for 1-Adamantanol 4-chlorobenzoate (22)



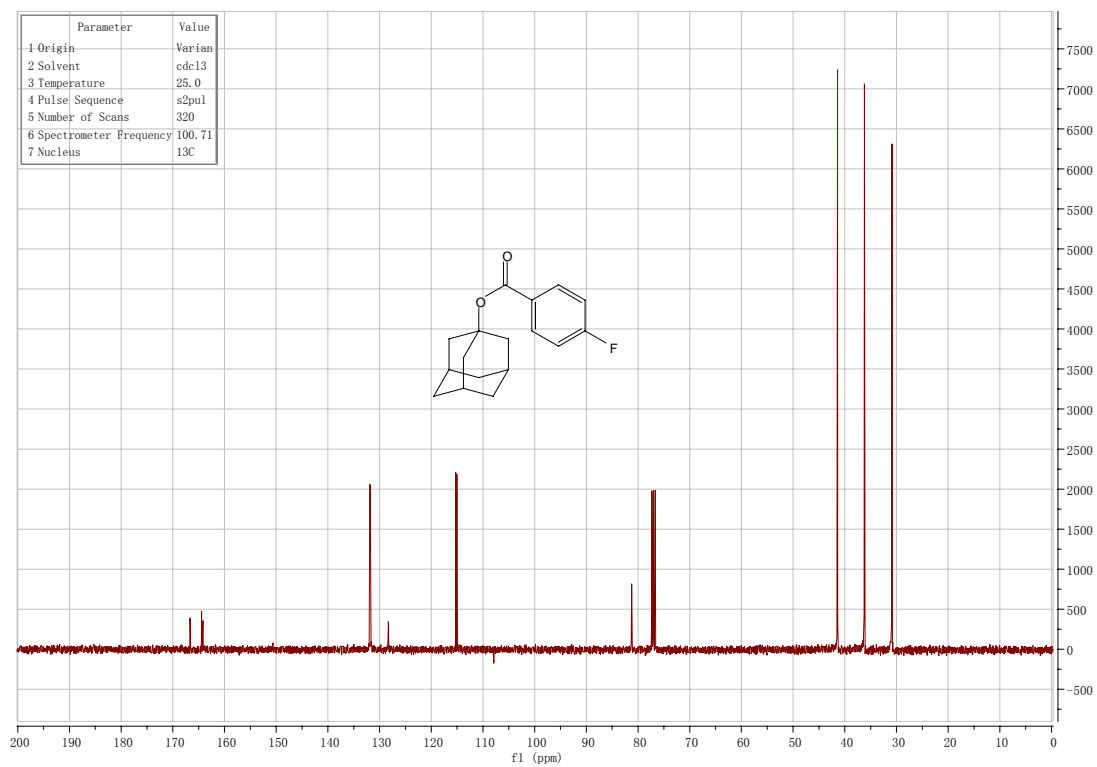
¹³C NMR for 1-Adamantanol 4-chlorobenzoate (22)



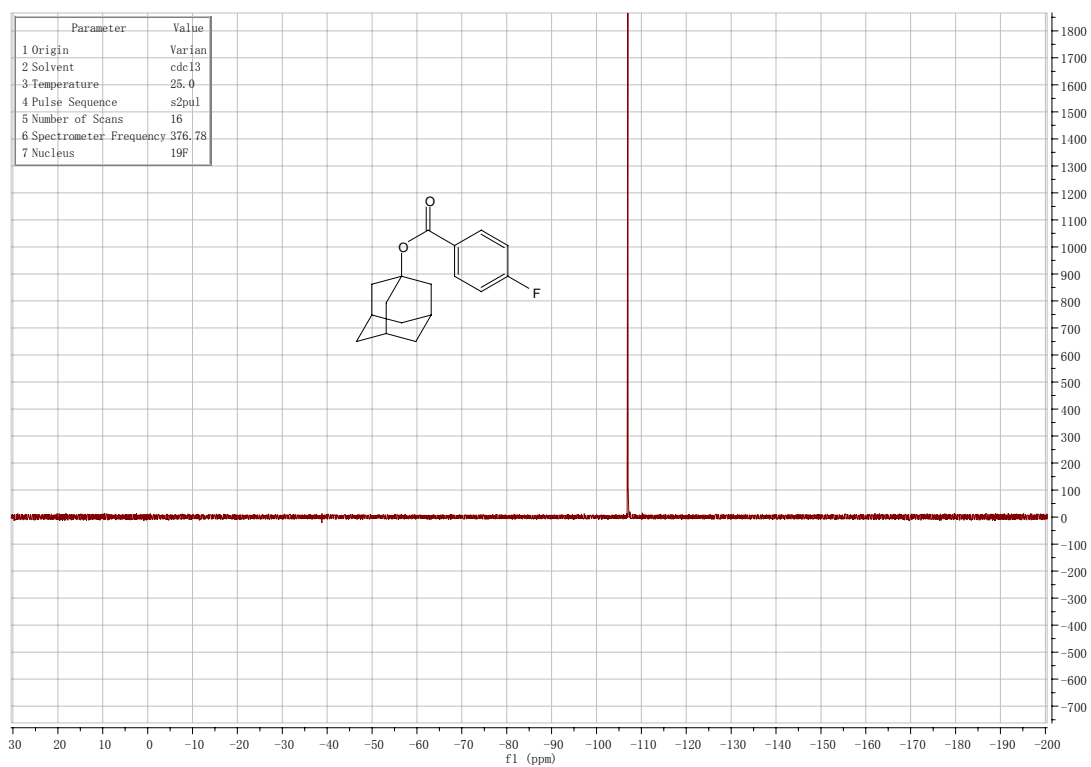
¹H NMR for 1-Adamantanol 4-fluorobenzoate (23)



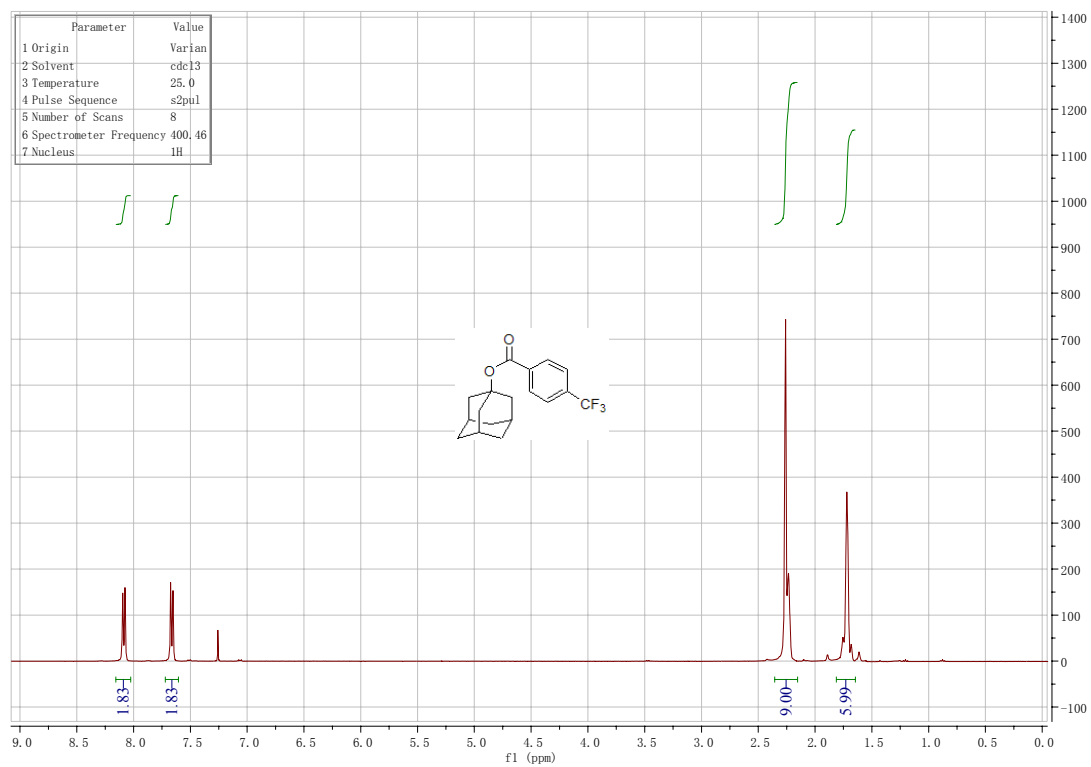
¹³C NMR for 1-Adamantanol 4-fluorobenzoate (23)



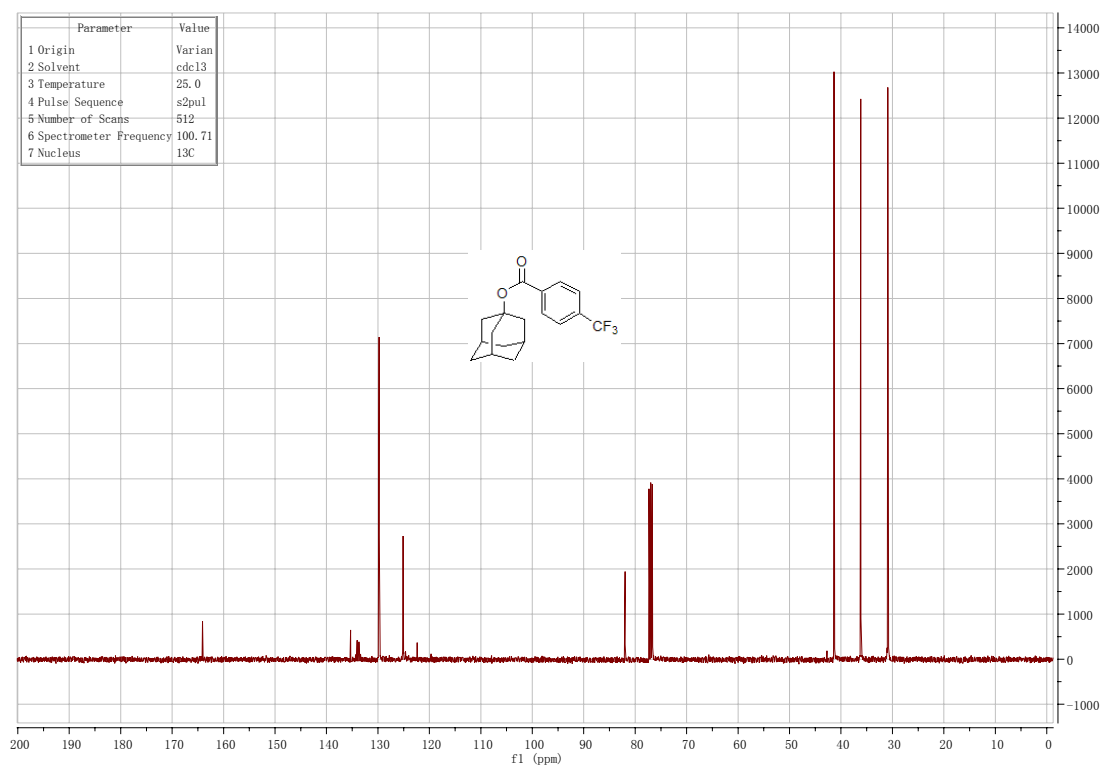
¹⁹F NMR for 1-Adamantanol 4-fluorobenzoate (23)



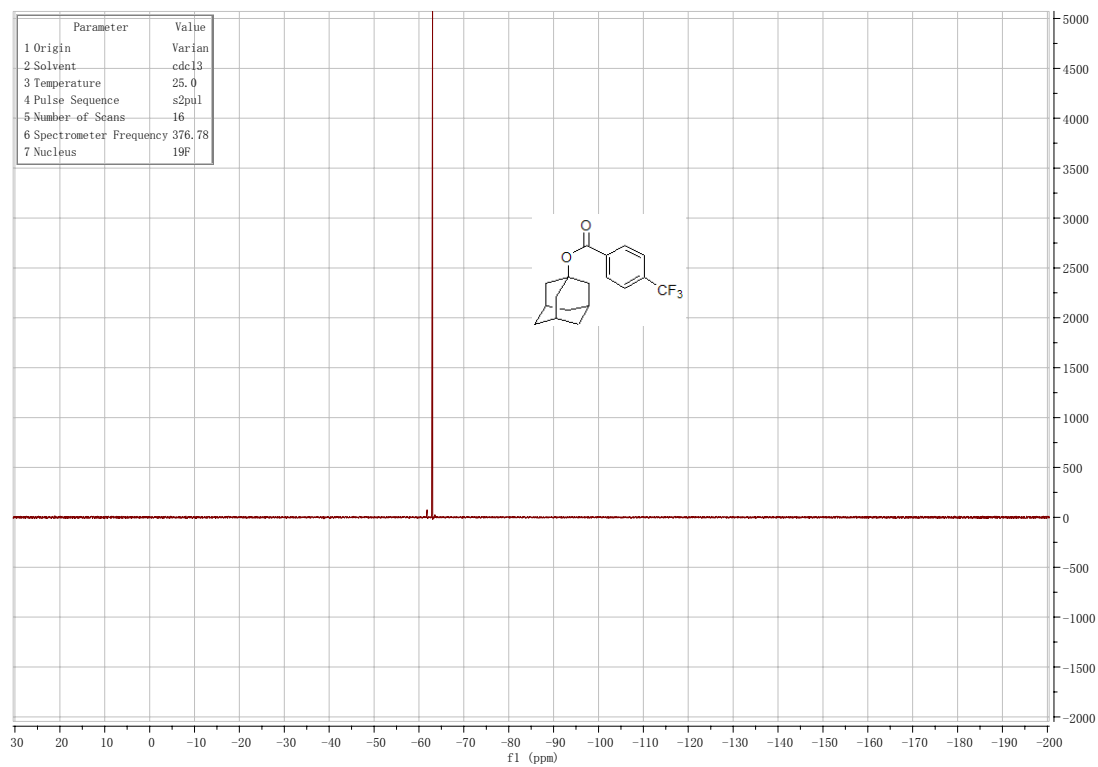
¹H NMR for 1-Adamantanol 4-(trifluoromethyl)benzoate (24)



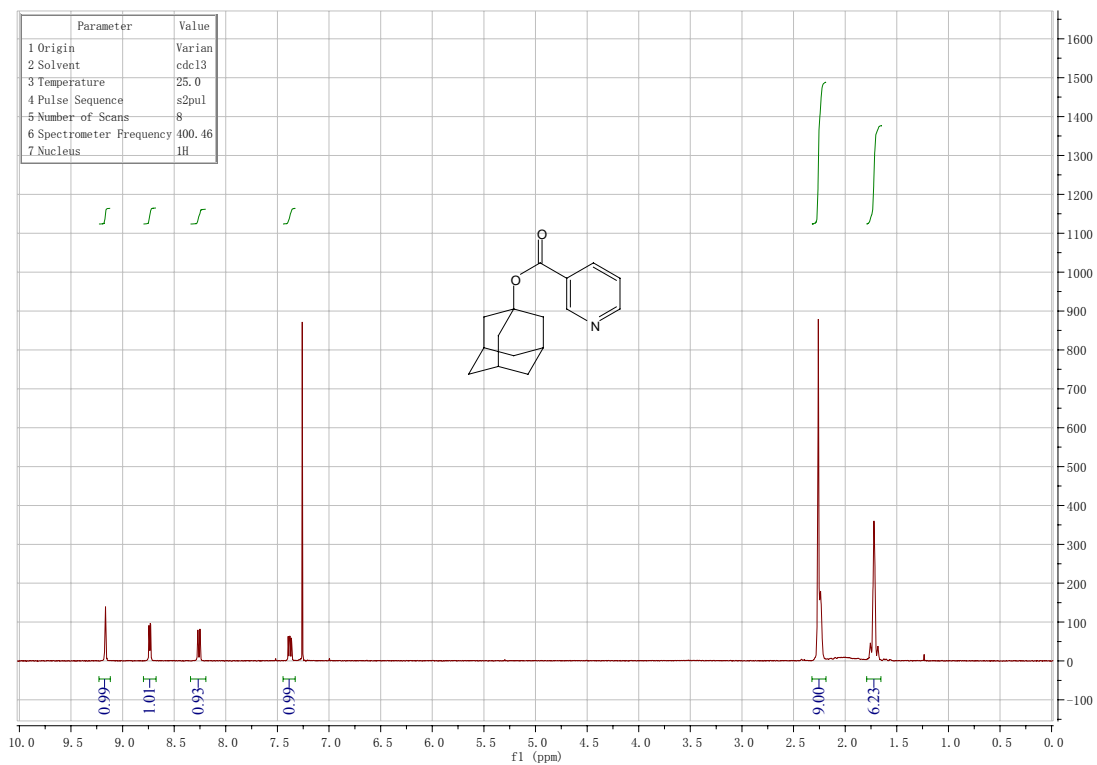
¹³C NMR for 1-Adamantanol 4-(trifluoromethyl)benzoate (24)



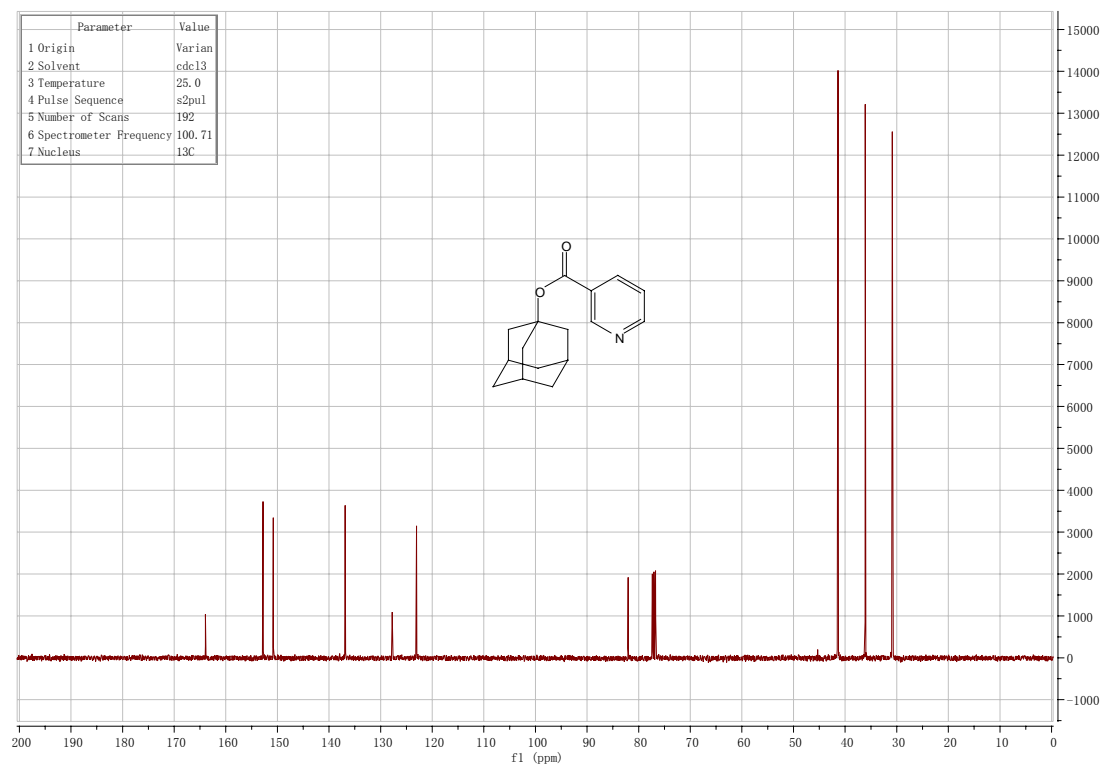
¹⁹F NMR for 1-Adamantanol 4-(trifluoromethyl)benzoate (24)



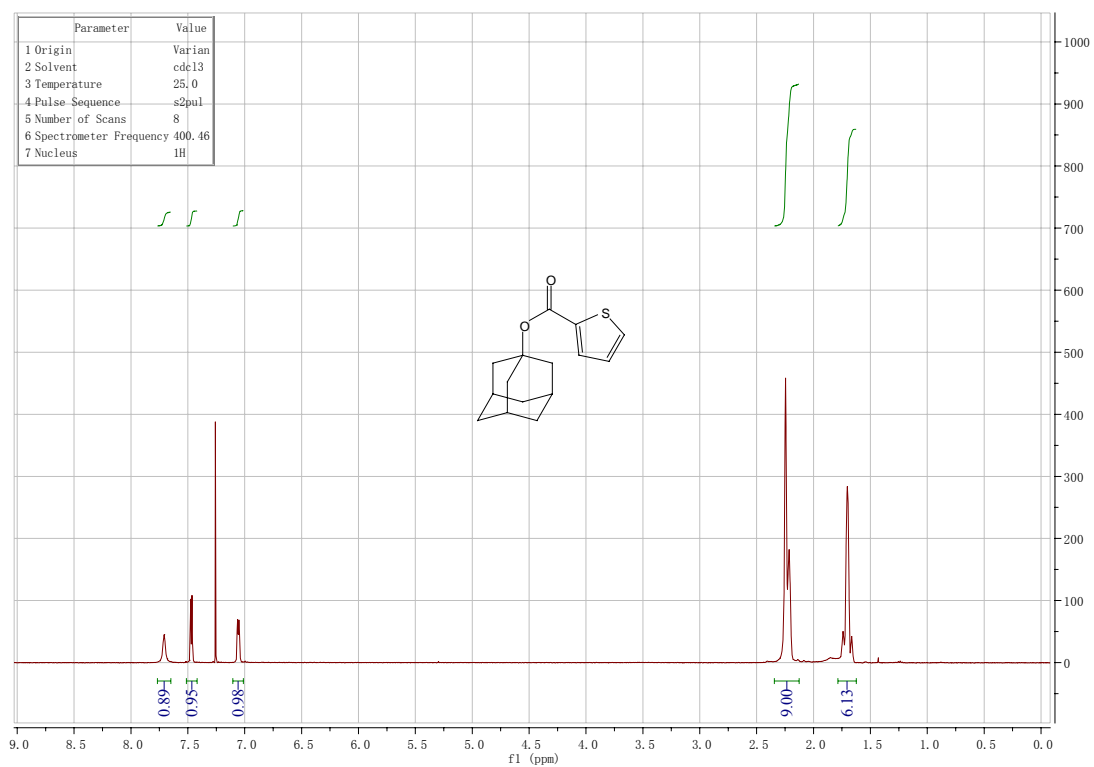
¹H NMR for 1-Adamantanol nicotinate (25)



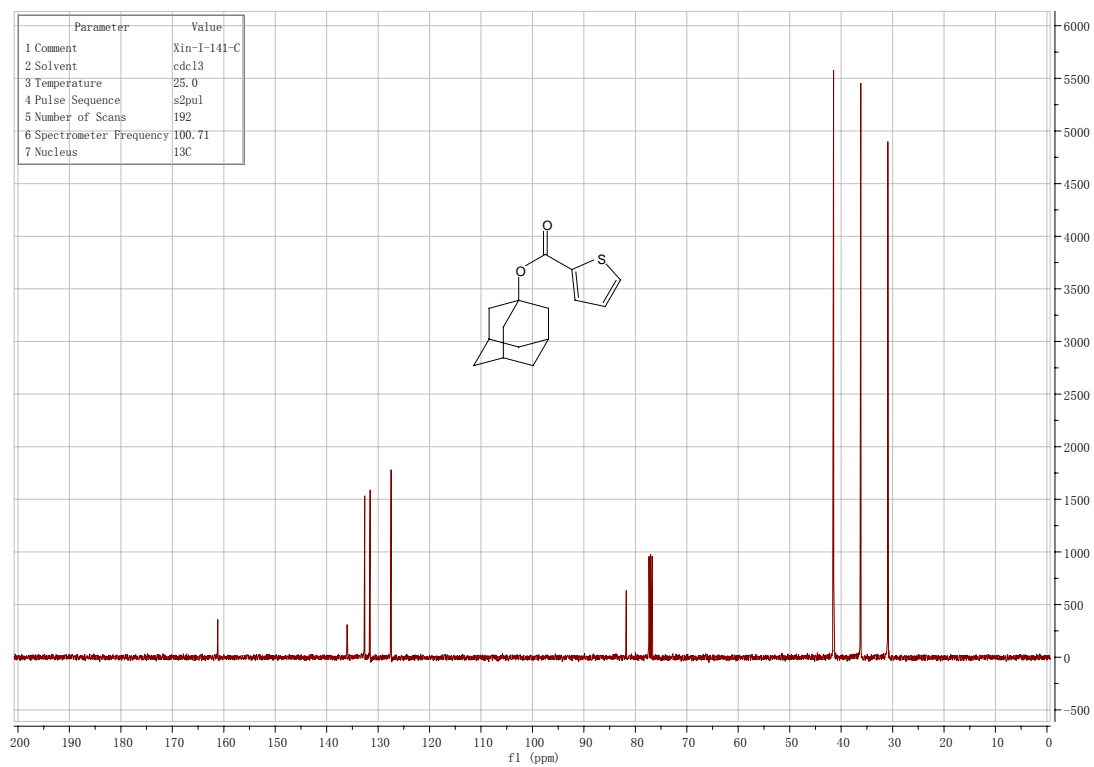
¹³C NMR for 1-Adamantanol nicotinate (25)



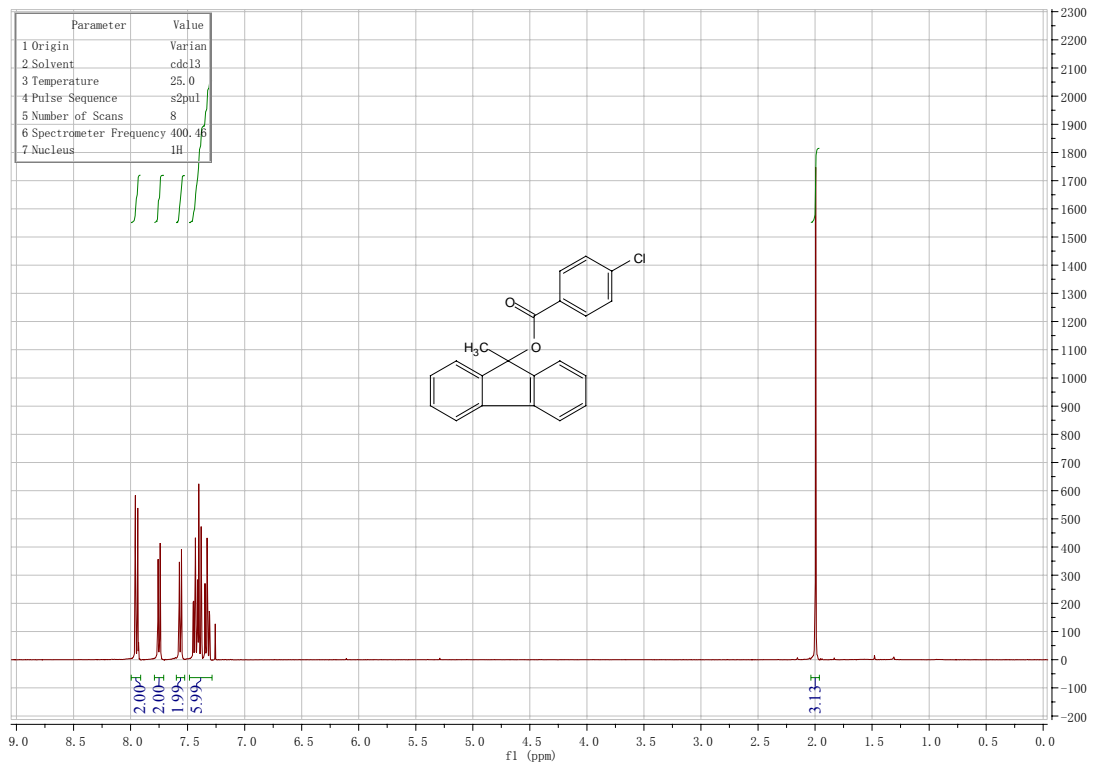
¹H NMR for 1-Adamantanol thiophene-2-carboxylate (26)



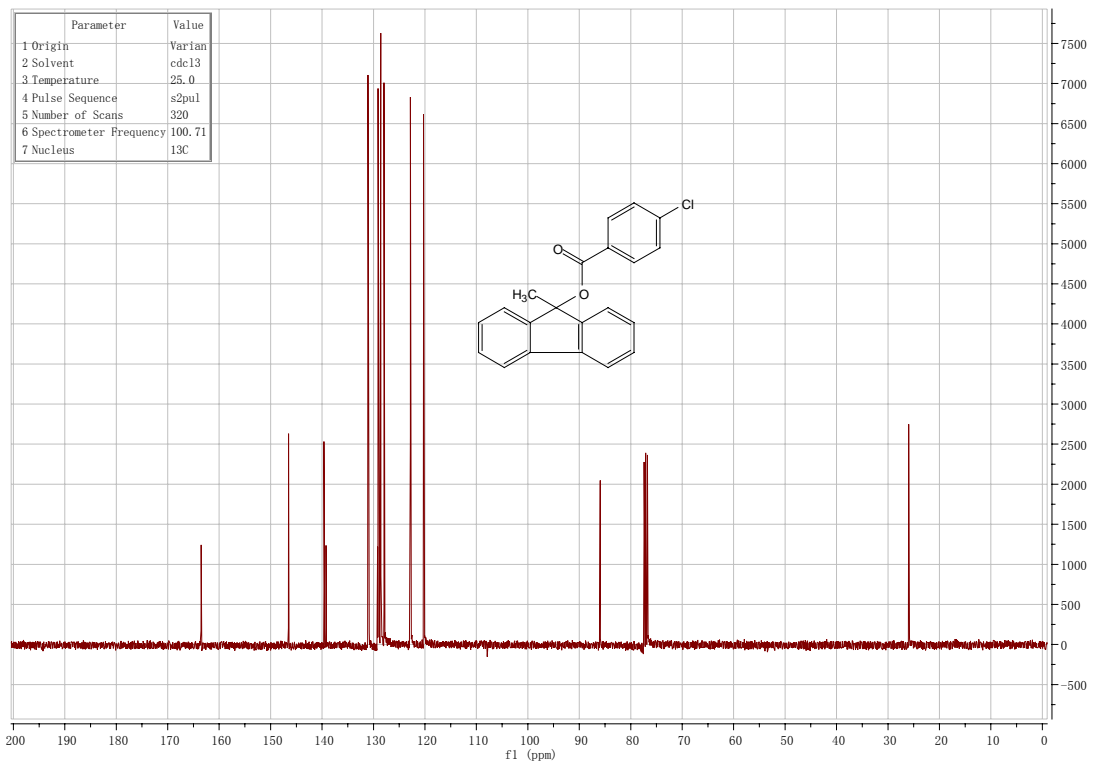
¹³C NMR for 1-Adamantanol thiophene-2-carboxylate (26)



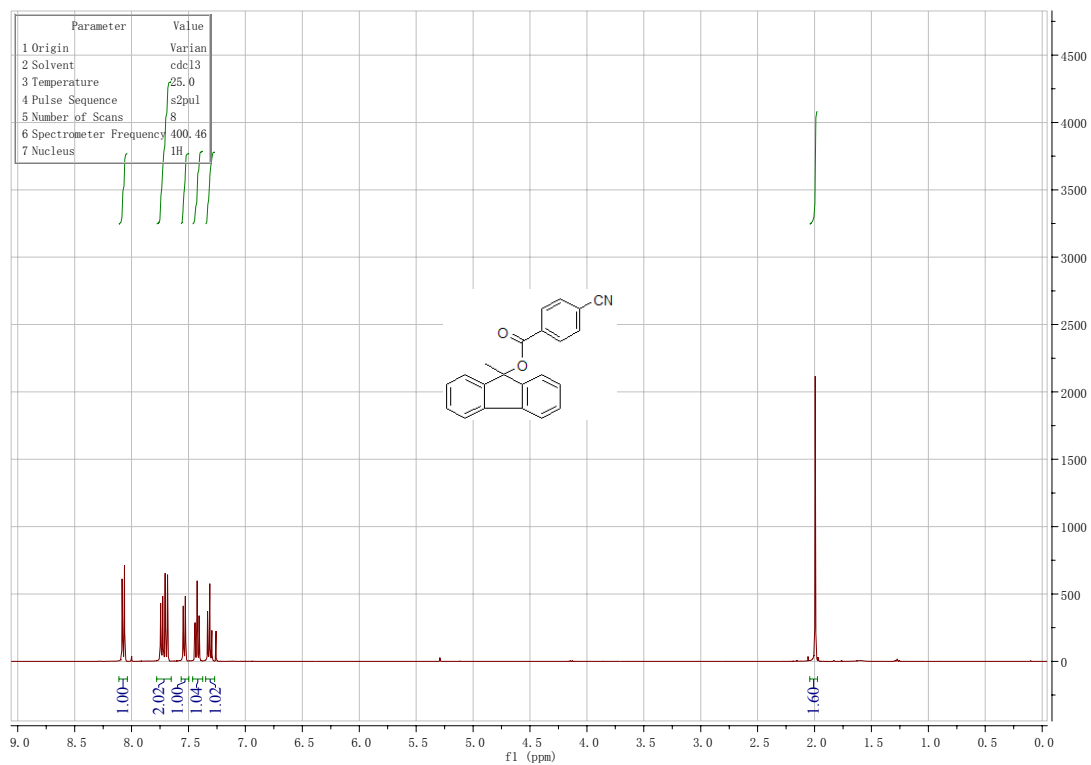
¹H NMR for 9-Methyl-9-fluorenol 4-chlorobenzoate (27)



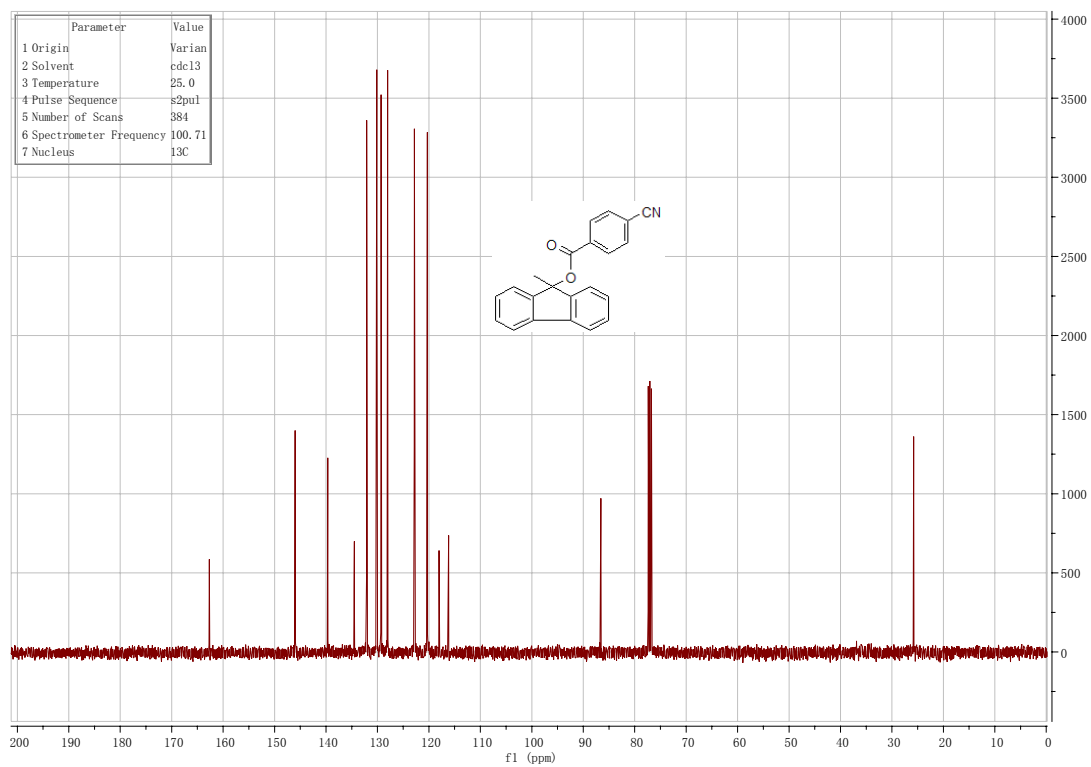
¹³C NMR for 9-Methyl-9-fluorenol 4-chlorobenzoate (27)



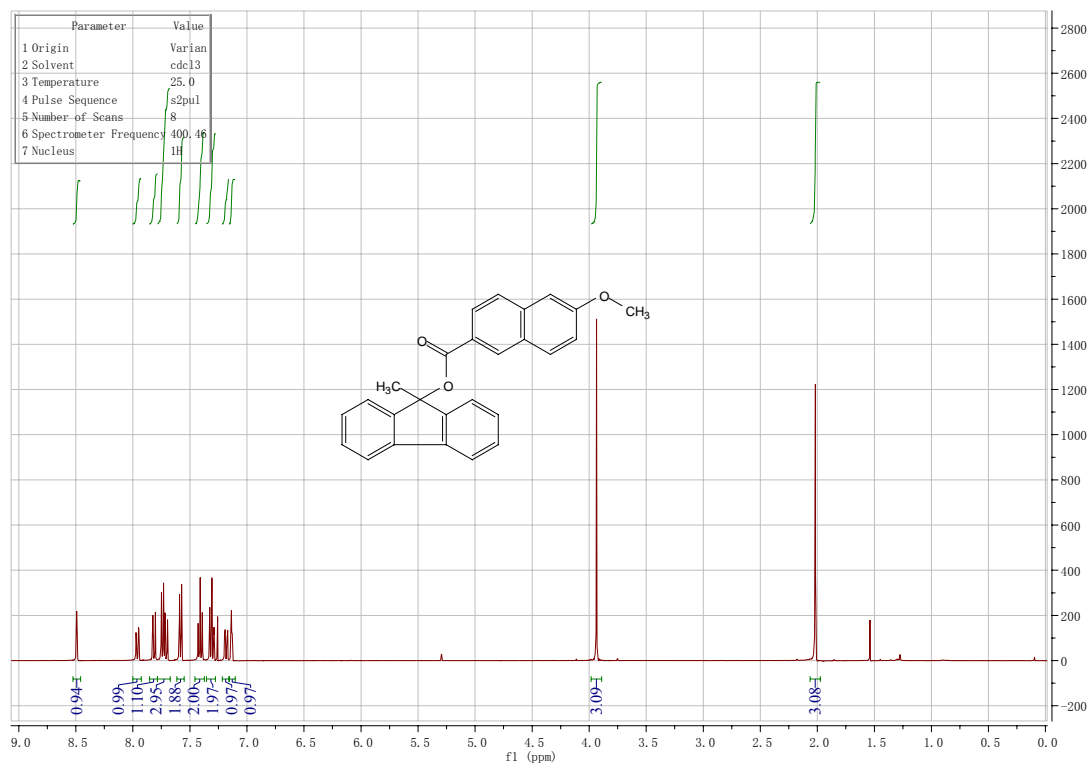
¹H NMR for 9-Methyl-9-fluorenol 4-cyanobenzoate (28)



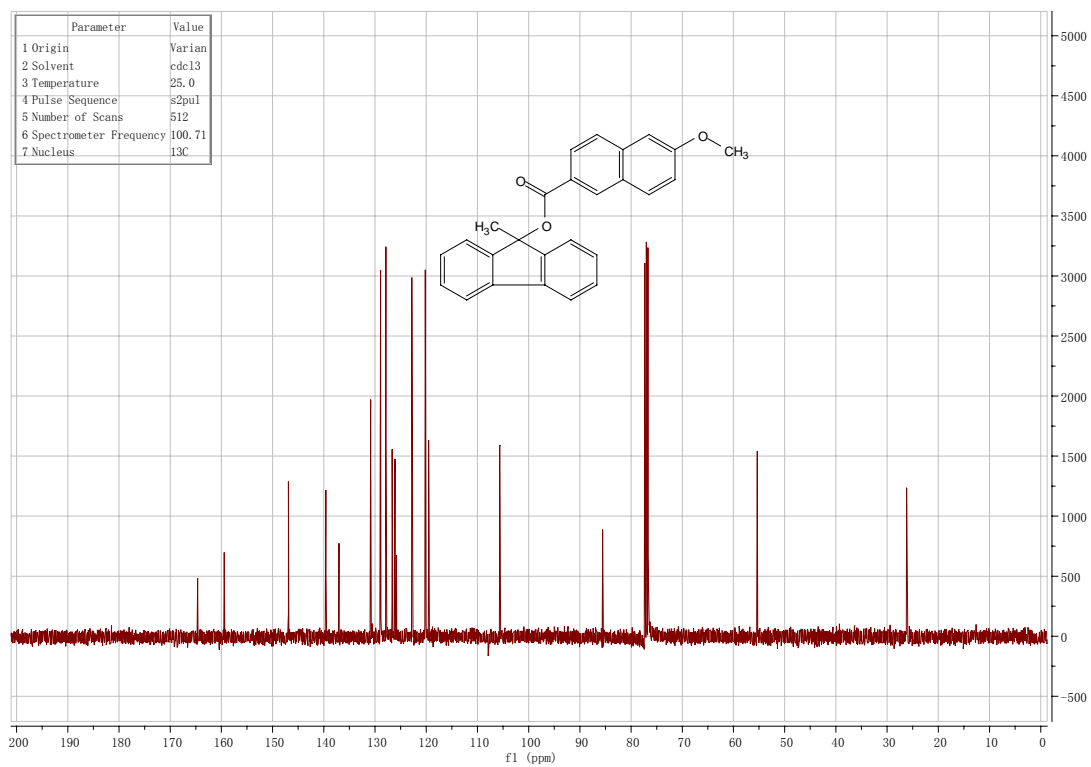
¹³C NMR for 9-Methyl-9-fluorenol 4-cyanobenzoate (28)



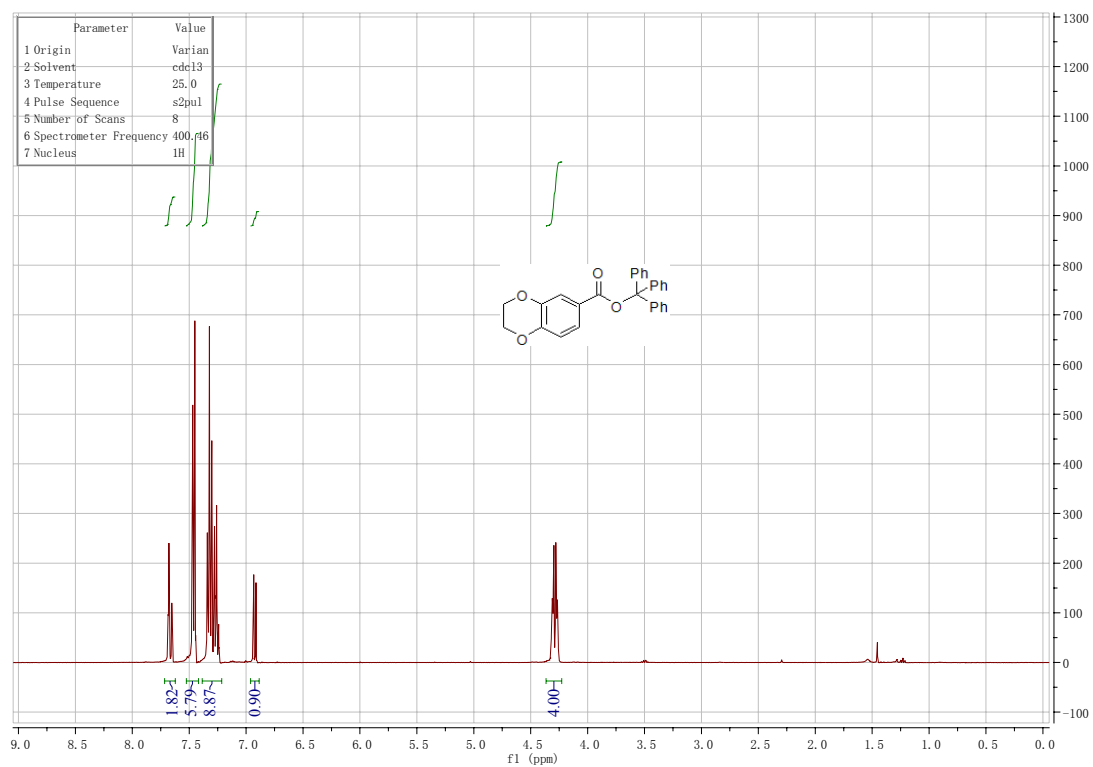
¹H NMR for 9-Methyl-9-fluorenyl 6-methoxy-2-naphthoate (29)



¹³C NMR for 9-Methyl-9-fluorenyl 6-methoxy-2-naphthoate (29)



¹H NMR for 2,3-Dihydro-benzo[1,4]dioxine-6-carboxylic acid trityl ester (30)



¹³C NMR for 2,3-Dihydro-benzo[1,4]dioxine-6-carboxylic acid trityl ester (30)

