

AlCl₃ Catalyzed Coupling of N-benzylic Sulfonamides with 2-Substituted Cyanoacetates through Carbon-Nitrogen Bond Cleavage

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SUPPORTING INFORMATION

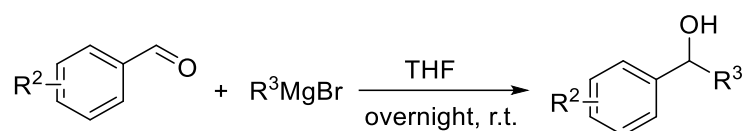
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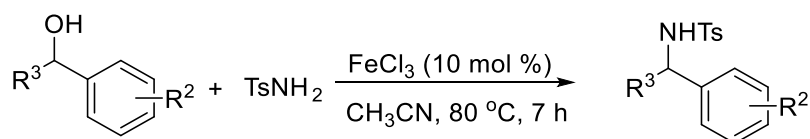
EXPERIMENTAL SECTION

General Information. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Chemicals were commercially available and used without purification. Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

1.1 Synthesis of N-benzylic sulfonamides¹



To an over-dried, argon purged round flask containing the aldehyde (5 mmol) in the THF (10 mL) at room temperature, was added phenylmagnesium bromide (15 mmol) dropwise over 5 minutes. The reaction was then allowed to stir overnight. The reaction mixture was quenched by addition of the saturated aqueous ammonium chloride (40 mL) and extracted with ethyl ether (2×40 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 . Purification was performed by flash column chromatography on silica gel when needed.



To a stirred solution of diphenylmethanol (1 mmol) in 10 mL anhydrous CH_3CN was added 4-methylbenzenesulfonamide (1.1 mmol) and FeCl_3 (0.1 mmol) successively at $80\text{ }^\circ\text{C}$. After 7 hours, the crude product was purified by column chromatography on silica gel to afford the corresponding product.

1.2 Synthesis of substituted cyanoacetates²

A solution of cyanoethyl acetate (20 mmol) in 20 mL THF was added to a suspension of sodium hydride (7 mmol) and THF (10 mL) under argon atmosphere at 0 °C. After 30 min, a solution of hydrocarbon bromide (7 mmol) in THF was slowly added and after stirring the suspension for 15 min at 0 °C, the reaction mixture was removed to warm temperature and stirring for 8 h. The reaction was then quenched with 1M HCl and extracted using EtOAc (3×50 mL). The organic layer was dried by Na₂SO₄. Purification was performed by flash column chromatography on silica gel when needed.

1.3 Synthesis of 2-nitroesters³

The alkyl 2-bromoalkanoate (60 mmol) was added to a suspension of sodium hydride (104 mmol) and phloroglucinol dehydrate (52 mol) in dry DMF (40 mL) at room temperature. After 2.5 h, the reaction was then quenched with ice water (200 mL) and extracted using EtOAc (3×50 mL). The organic layer was dried by Na₂SO₄. Purification was performed by flash column chromatography on silica gel when needed.

1.4 Synthesis of substituted malononitrile⁴

A solution of malononitrile (20 mmol) in 20 mL THF was added to a suspension of sodium hydride (7 mmol) and THF (10 mL) under argon atmosphere at 0 °C. After 30 min, a solution of hydrocarbon bromide (7 mmol) in THF was slowly added and after stirring the suspension for 15 min at 0 °C, the reaction mixture was removed to warm temperature and stirring for 8 h. The reaction was then quenched with 1M HCl and extracted using EtOAc (3×50 mL). The organic layer was dried by Na₂SO₄. Purification was performed by flash column chromatography on silica gel when needed.

1.5 Synthesis of substituted diethyl malonate⁵

To a solution of diethyl malonate (20 mmol) in 20 mL THF was added to a suspension of sodium

hydride (7 mmol) and THF (10 mL) under argon atmosphere at 0 °C. After 30 min, a solution of hydrocarbon bromide (7 mmol) in THF was slowly added and after stirring the suspension for 15 min at 0 °C, the reaction mixture was removed to warm temperature and stirring for 8 h. The reaction was then quenched with 1M HCl and extracted using EtOAc (3 × 50 mL). The organic layer was dried by Na₂SO₄. Purification was performed by flash column chromatography on silica gel when needed.

1.6 General Experimental Procedures and Characterizations.

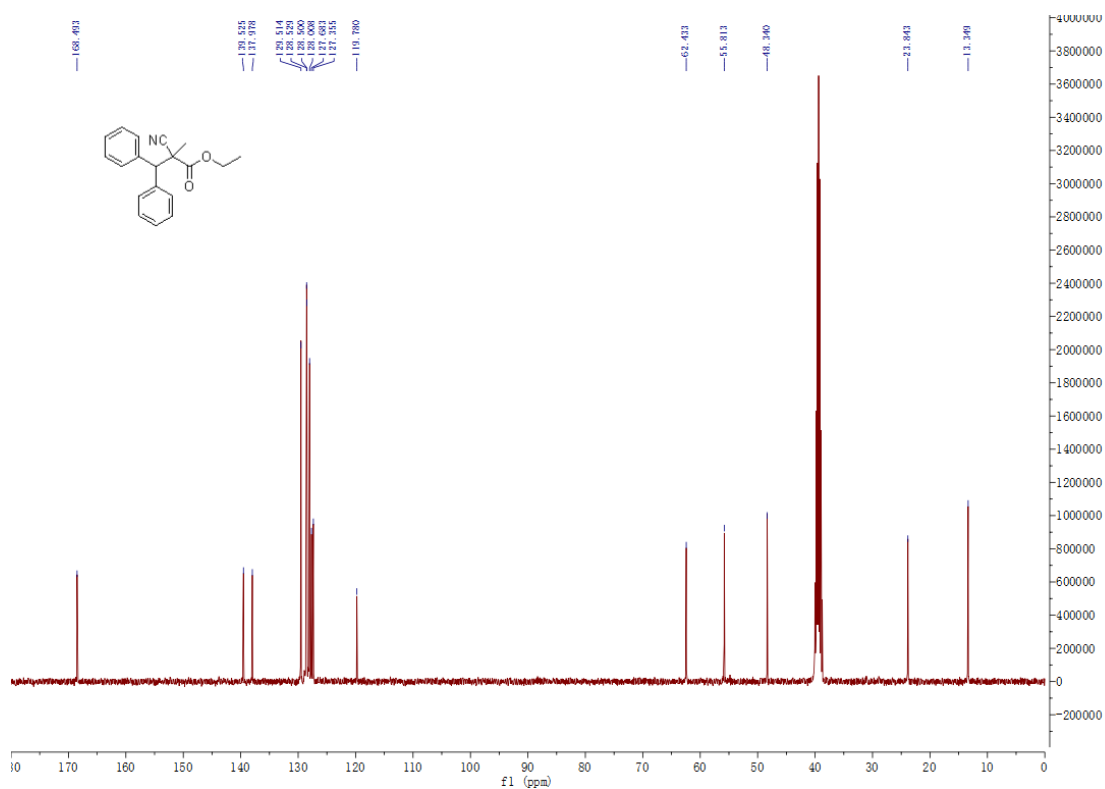
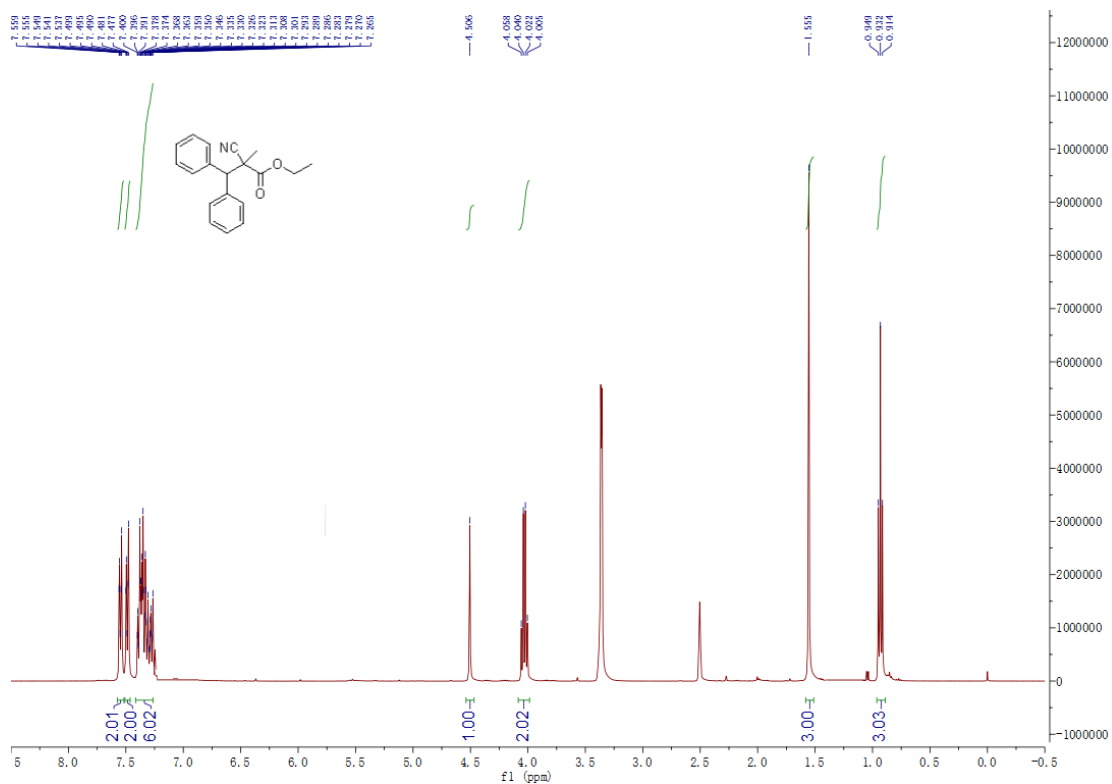
2-substituted cyanoacetates (0.25 mmol, 1 equiv), *N*-benzylic sulfonamides (0.3 mmol, 1.2 equiv), AlCl₃ (100 mol %), dry CHCl₃ (1 mL) and a stir bar were added to a sealed tube. After being stirred at 80 °C for indicated time, the mixture was evaporated under vacuum. The corresponding product was isolated by silica gel column chromatography with a dichloromethane/petroleum ether mixture as eluent.

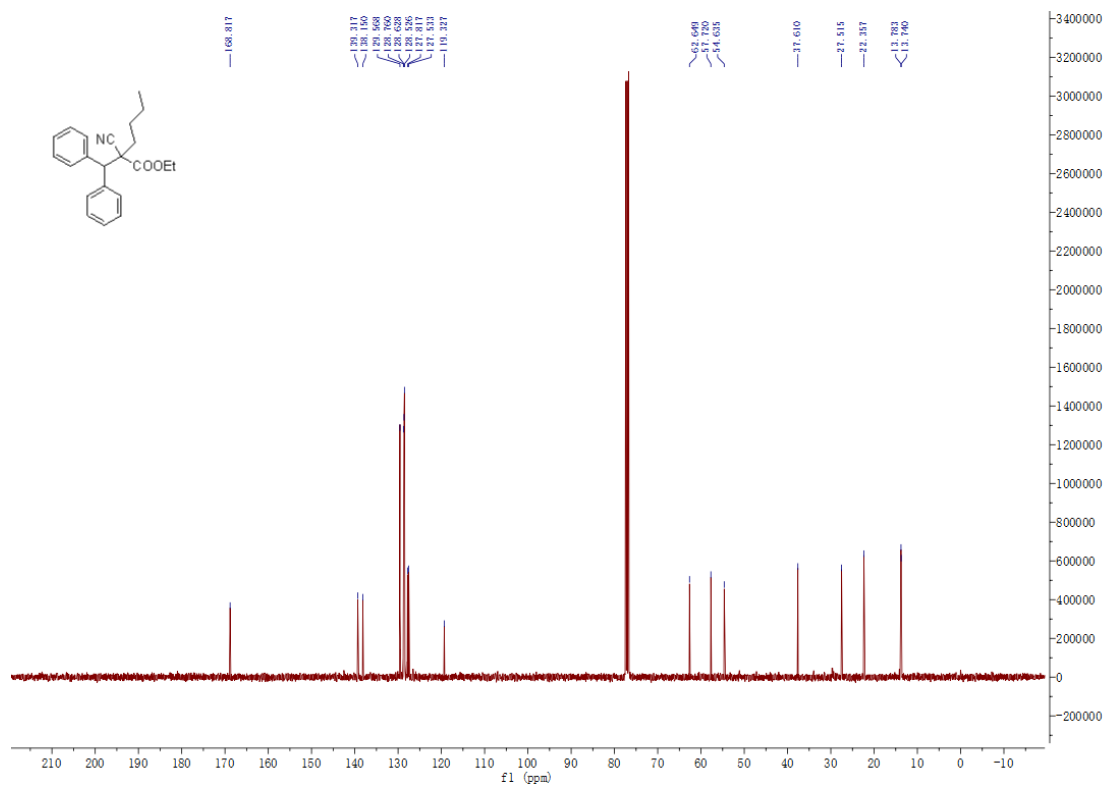
1.7 Reference

- [1] (a) H. Li, R.Y. Zhu, W. J. Shi, K. H. He and Z. J. Shi, *Org. Lett.*, 2012, **14**, 4850. (b) U. Jana, S. Maiti, S. Biswas, *Tetrahedron Lett.*, 2008, **48**, 858.
- [2] (a) C. J. Mallia, L. Englert, G. C. Walter and I. R. Baxendale, *Beilstein J. Org. Chem.*, 2015, **11**, 875. (b) X. Y. Zhang, X. F. Jia, L. L. Fang, N. Liu, J. J. Wang and X. S. Fan, *Org. Lett.*, 2011, **13**, 5024.
- [3] J. Ramírez, D. P. Huber and A. Togni, *Synlett.*, 2007, **7**, 1143.
- [4] A. Schnyder, A. F. Indolese, T. Maetzke, J. Wenger, H. U. Blaser, *Synlett*, 2006, **18**, 3167.
- [5] K. Yoshihisa, C. Werngard and K. Yoshito, *Org. Lett.*, 2003, **5**, 93.

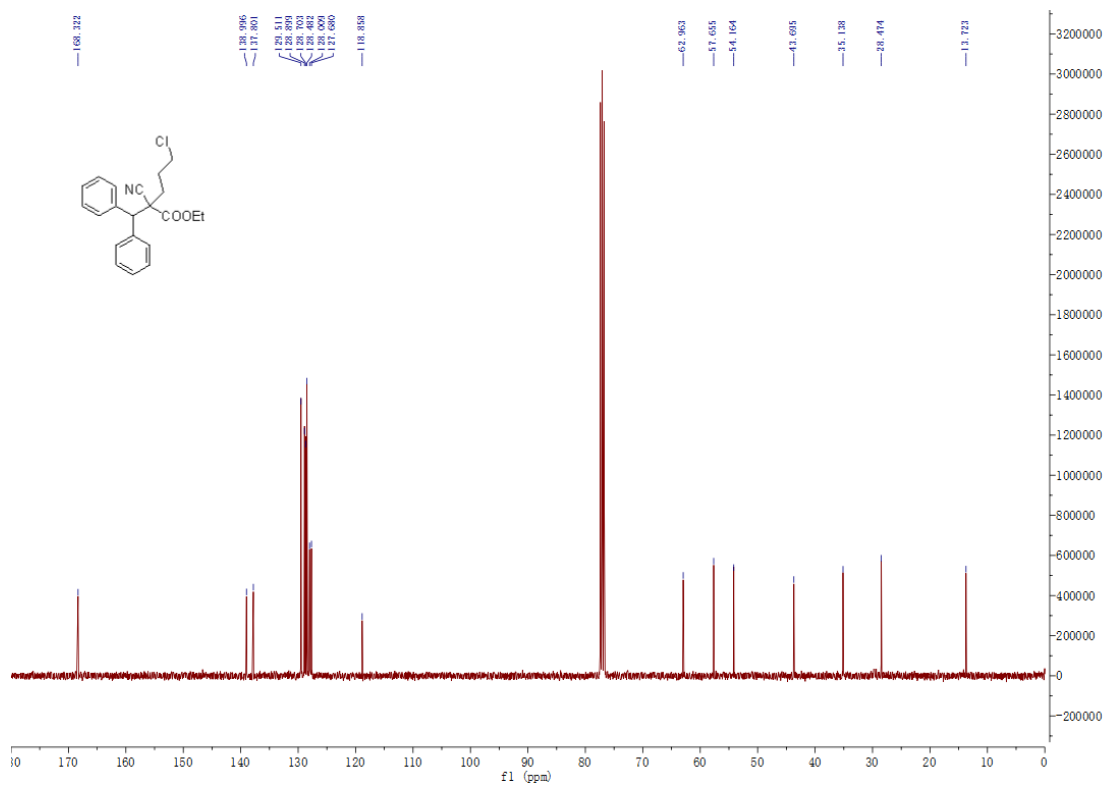
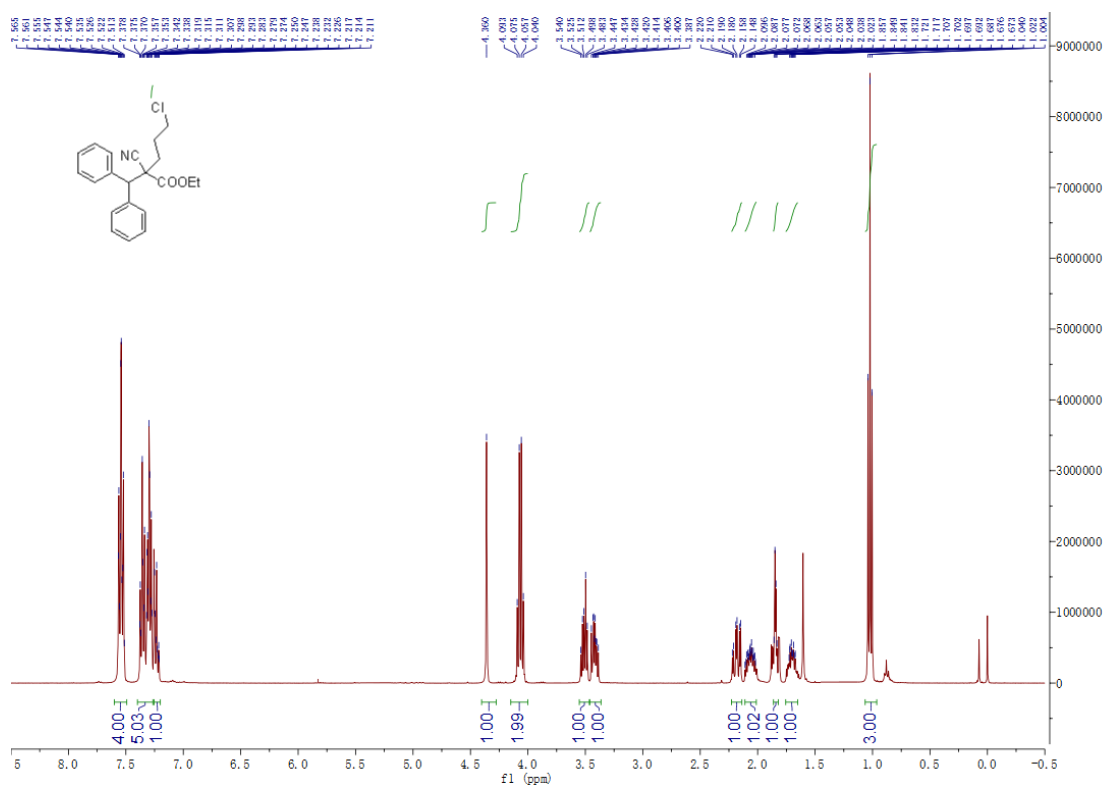
Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR

3a

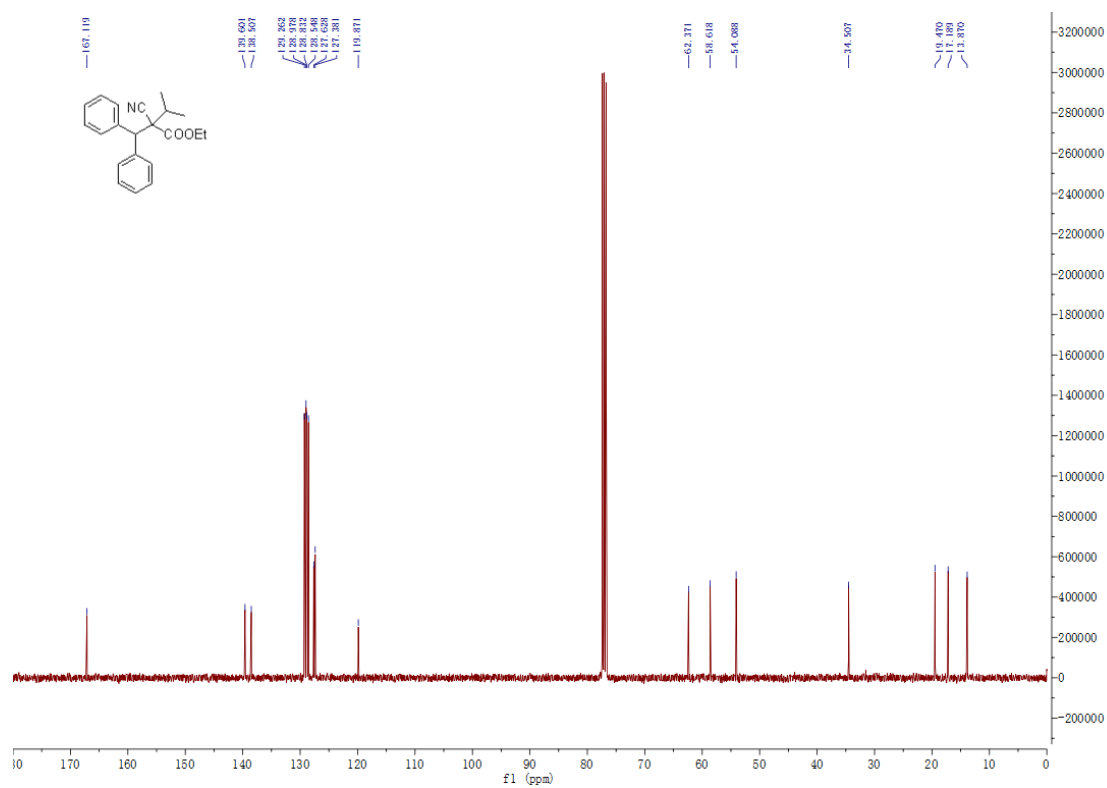
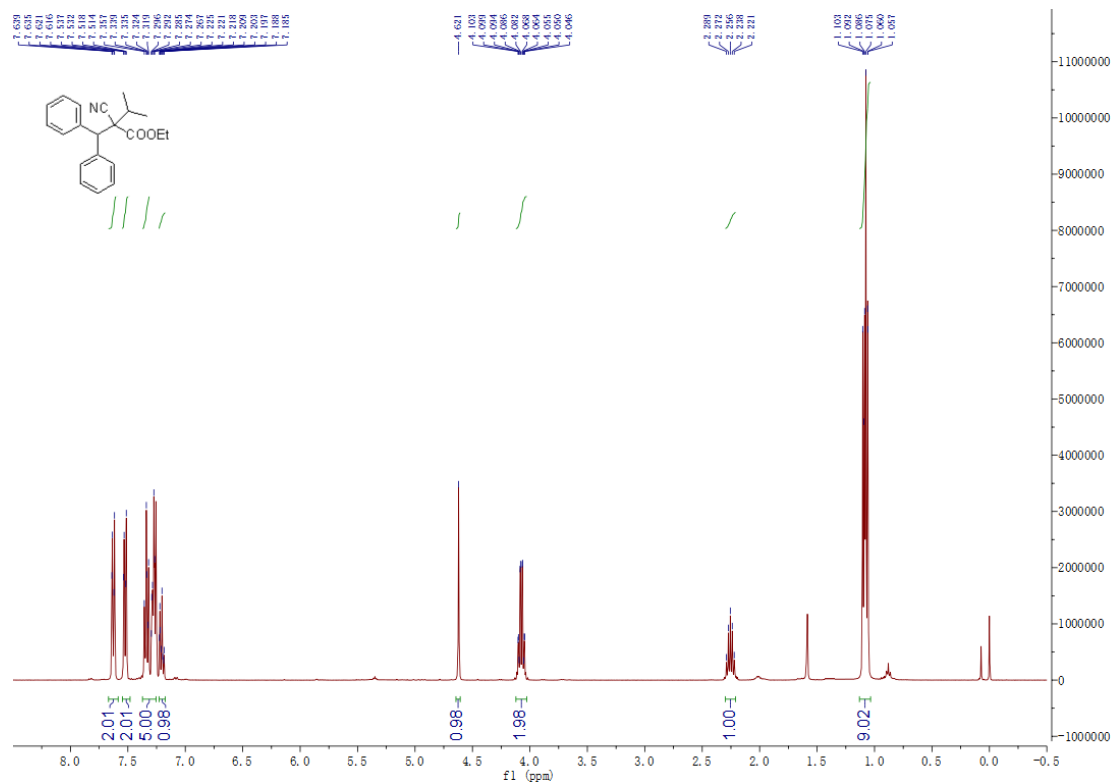


[illegible]

3c



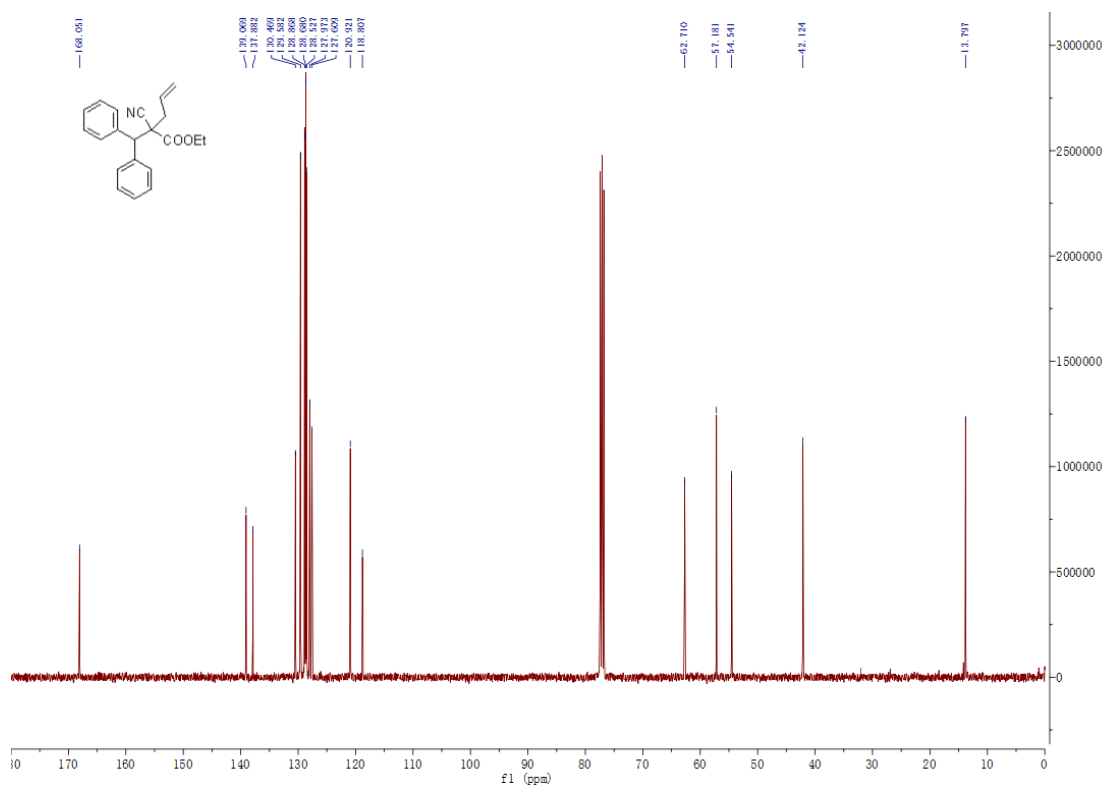
3d



Chemical structure: CCOC(=O)C(C=C)C(=O)c1ccccc1

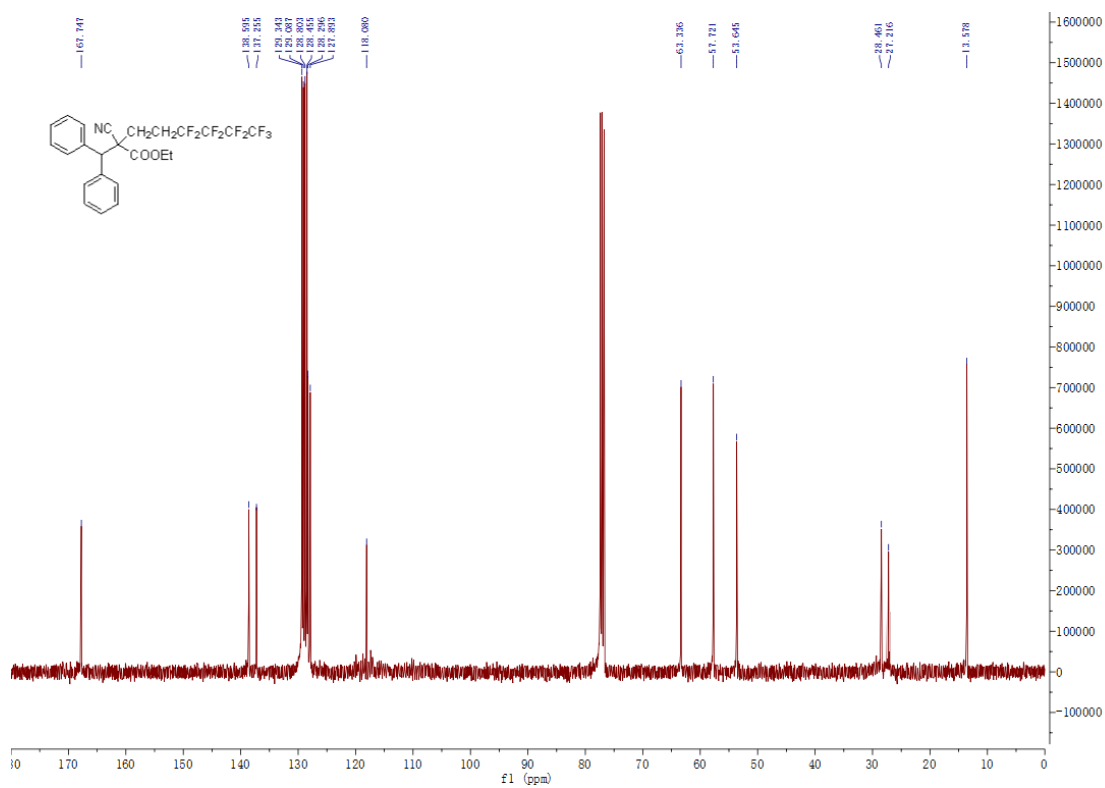
¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. The x-axis is labeled 'f1 (ppm)' and ranges from -0.5 to 10.0. The y-axis represents intensity from 0 to 10,000,000. The spectrum includes the following peaks and integrations:

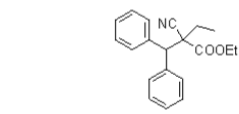
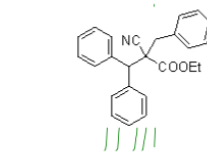
- 7.511 ppm (d, 4.02H)
- 7.502 ppm (d, 5.00H)
- 7.500 ppm (d, 1.02H)
- 7.496 ppm (d, 1.02H)
- 7.532 ppm (d, 1.02H)
- 7.528 ppm (d, 1.02H)
- 7.376 ppm (d, 1.02H)
- 7.355 ppm (d, 1.02H)
- 7.350 ppm (d, 1.02H)
- 7.346 ppm (d, 1.02H)
- 7.336 ppm (d, 1.02H)
- 7.325 ppm (d, 1.02H)
- 7.314 ppm (d, 1.02H)
- 7.305 ppm (d, 1.02H)
- 7.296 ppm (d, 1.02H)
- 7.285 ppm (d, 1.02H)
- 7.277 ppm (d, 1.02H)
- 7.269 ppm (d, 1.02H)
- 7.260 ppm (d, 1.02H)
- 7.243 ppm (d, 1.02H)
- 7.232 ppm (d, 1.02H)
- 7.213 ppm (d, 1.02H)
- 7.200 ppm (d, 1.02H)
- 5.825 ppm (d, 1.02H)
- 5.799 ppm (d, 1.02H)
- 5.804 ppm (d, 1.02H)
- 5.788 ppm (d, 1.02H)
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- 5.747 ppm (d, 1.02H)
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- 5.716 ppm (d, 1.02H)
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- 5.656 ppm (d, 1.02H)
- 5.646 ppm (d, 1.02H)
- 5.636 ppm (d, 1.02H)
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- 4.906 ppm (d, 1.02H)
- 4.896 ppm (d, 1.02H)
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- 4.866 ppm (d, 1.02H)
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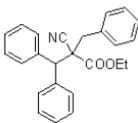


Chemical structure: CCOC(=O)C(c1ccccc1)C(=O)c2ccccc2CCF(C)(F)F

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 9 ppm. The spectrum includes aromatic protons (7.2-7.6 ppm), nitrile proton (2.1 ppm), ethyl ester protons (2.3 ppm quartet, 1.2 ppm triplet), and 2,2,2-trifluoroethyl protons (2.7-2.9 ppm multiplet). Integration values are provided below the baseline.



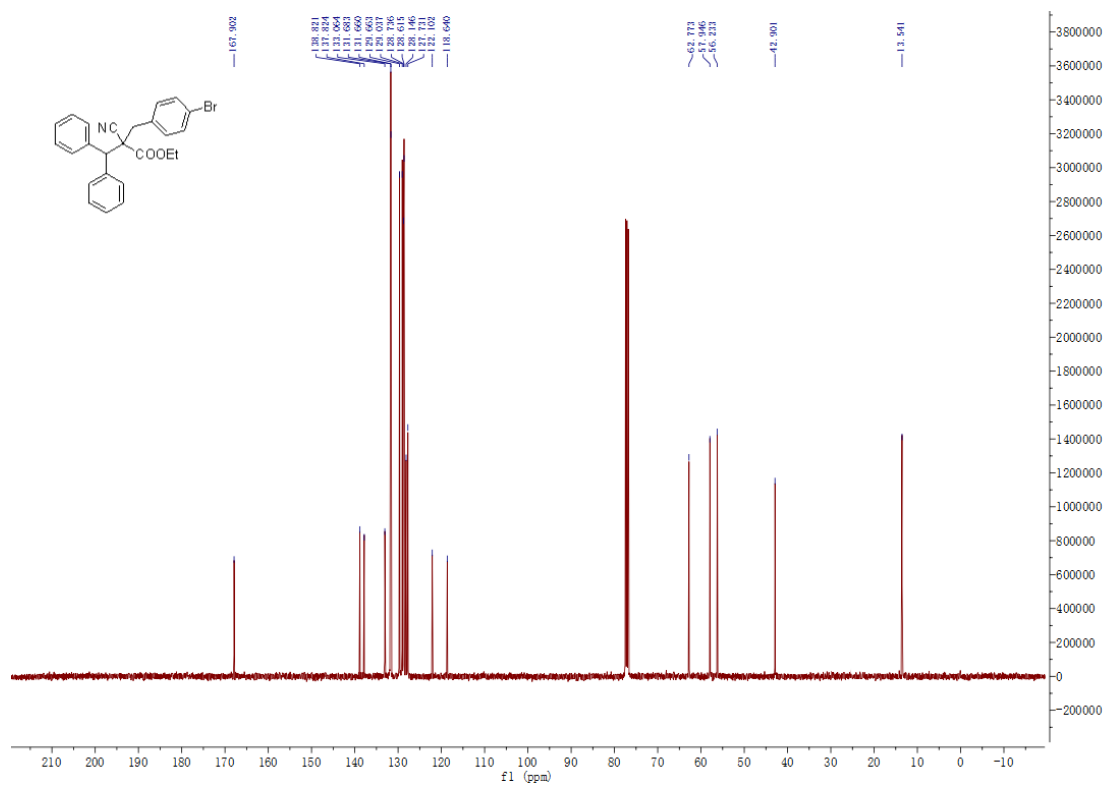
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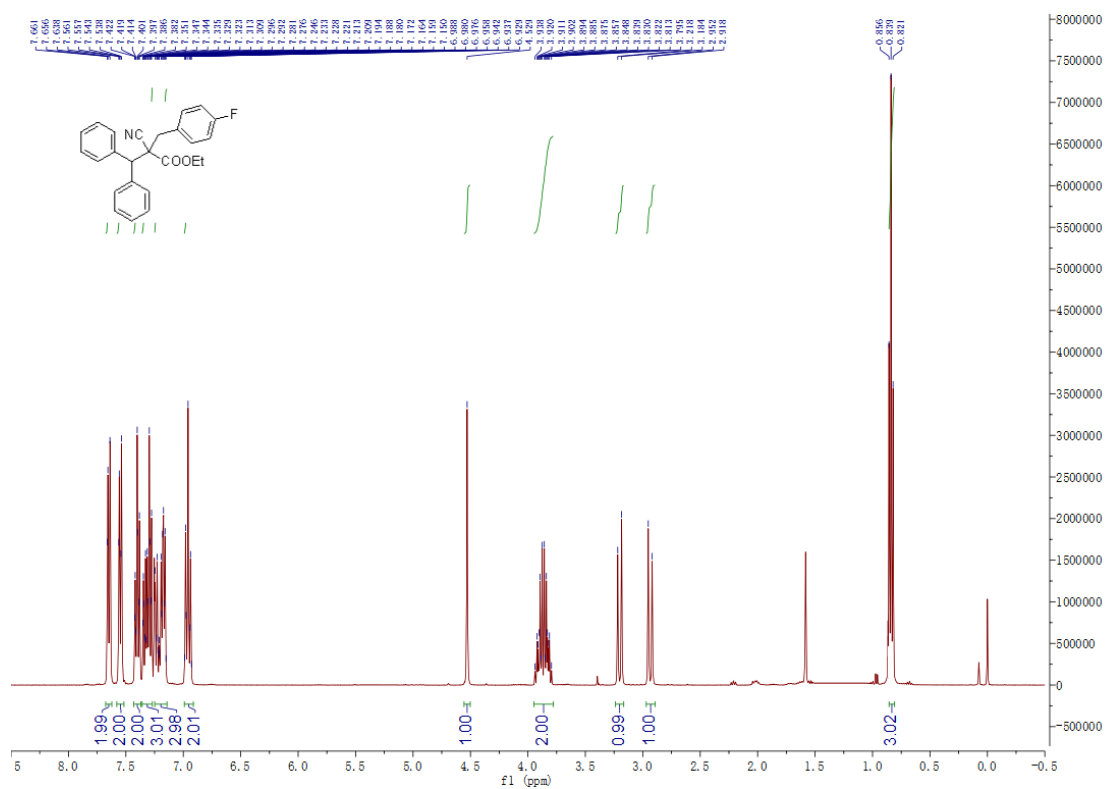
CCOC(=O)C(c1ccccc1)(c2ccccc2)c3cc(Br)ccc3

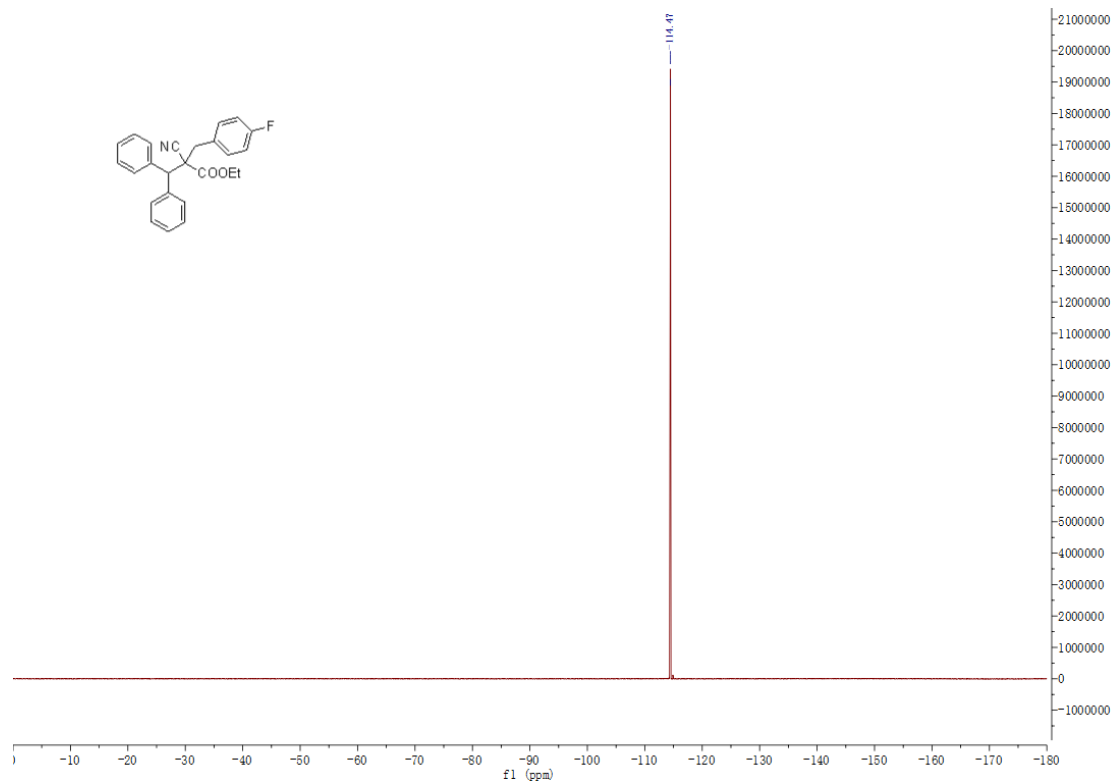
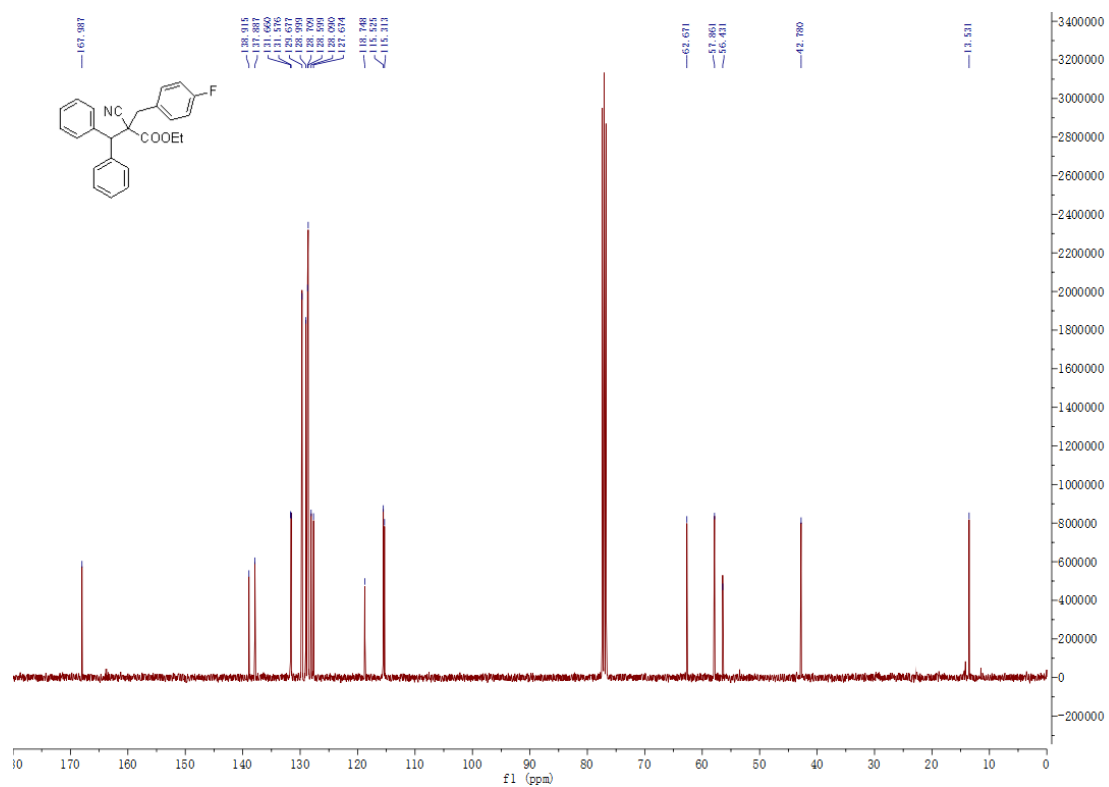
¹H NMR spectrum (CDCl₃) of ethyl 2-(2-bromophenyl)-2,2-diphenylacetate. The spectrum shows peaks in the aromatic region (7.0-7.6 ppm) and aliphatic region (1.4-1.6 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.53	2.00
7.51	1.99
7.48	3.96
7.46	3.01
7.44	1.00
7.42	2.01
4.48	1.00
3.88	2.01
3.12	0.99
3.08	0.99
1.52	3.02



31

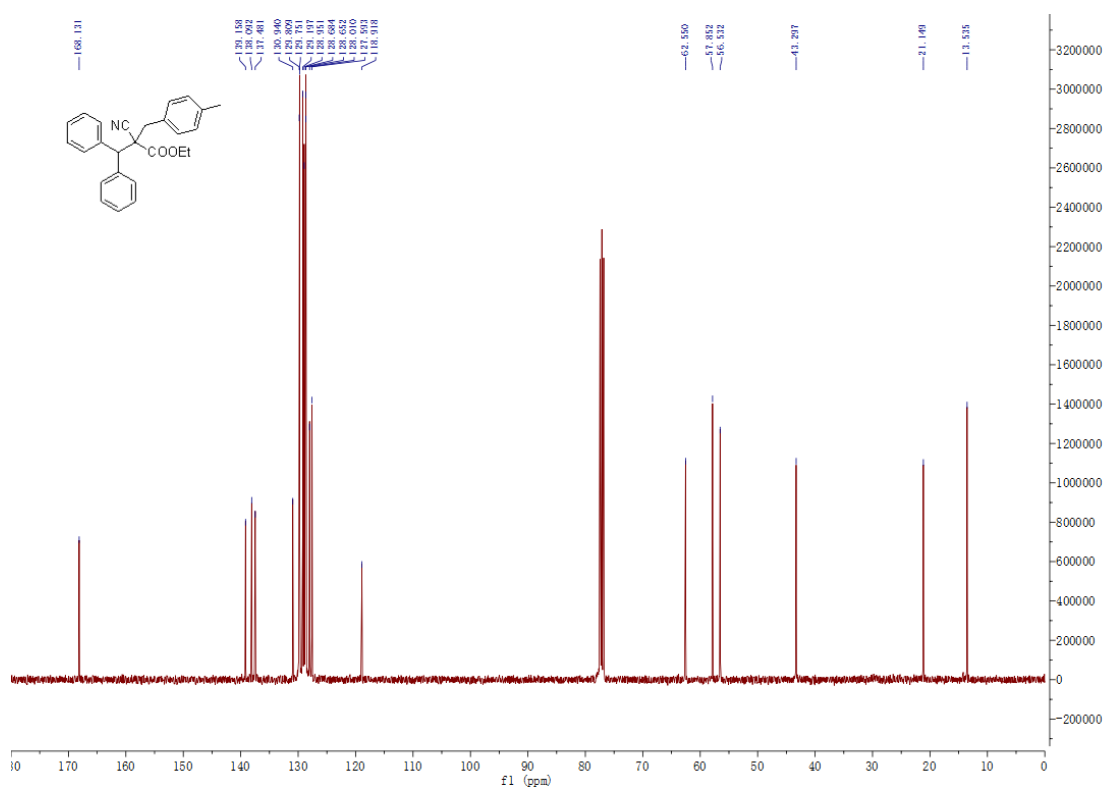




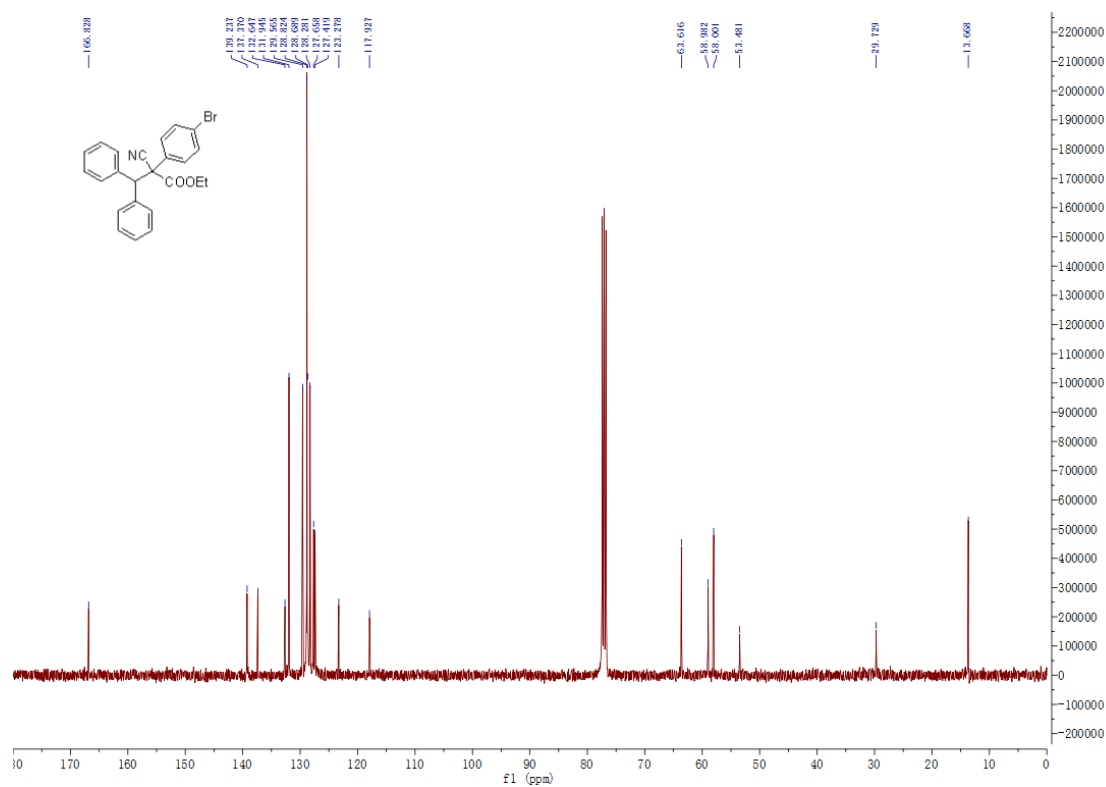
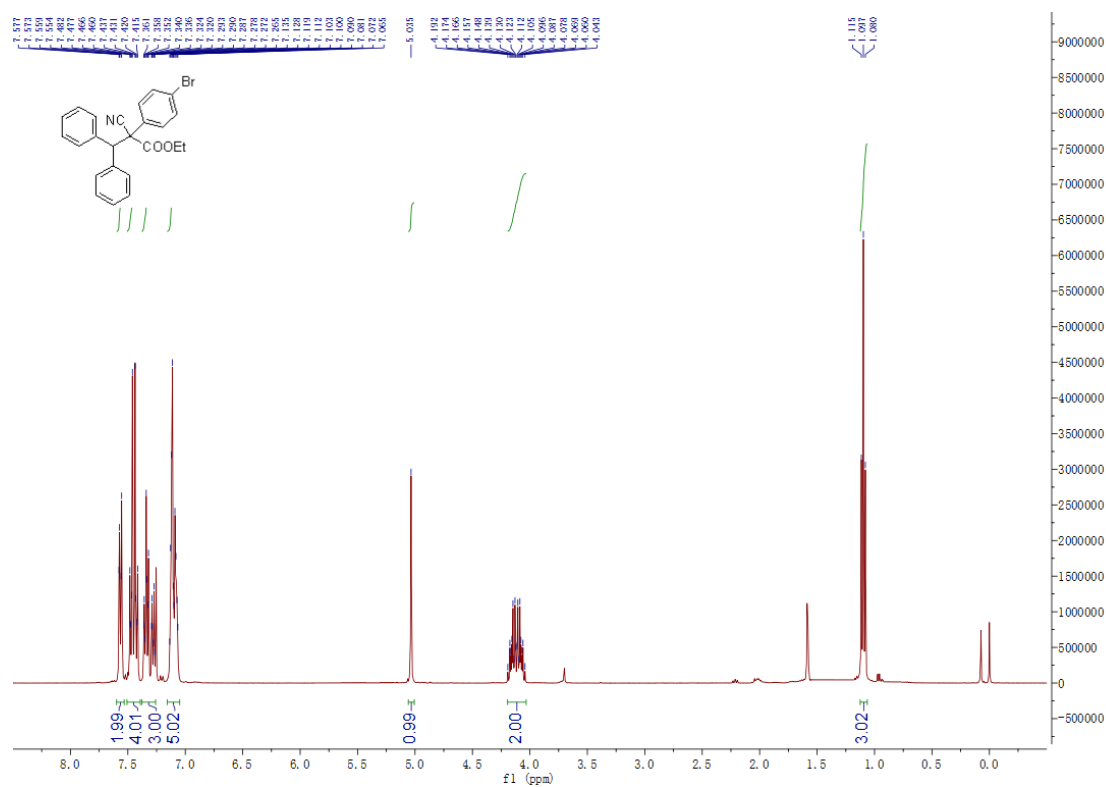
Chemical structure: CCOC(=O)C(CNc1ccccc1)C(c2ccccc2)c3ccccc3

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 9 ppm. The x-axis is labeled f1 (ppm) and the y-axis is labeled intensity. The spectrum includes integration values for each peak group.

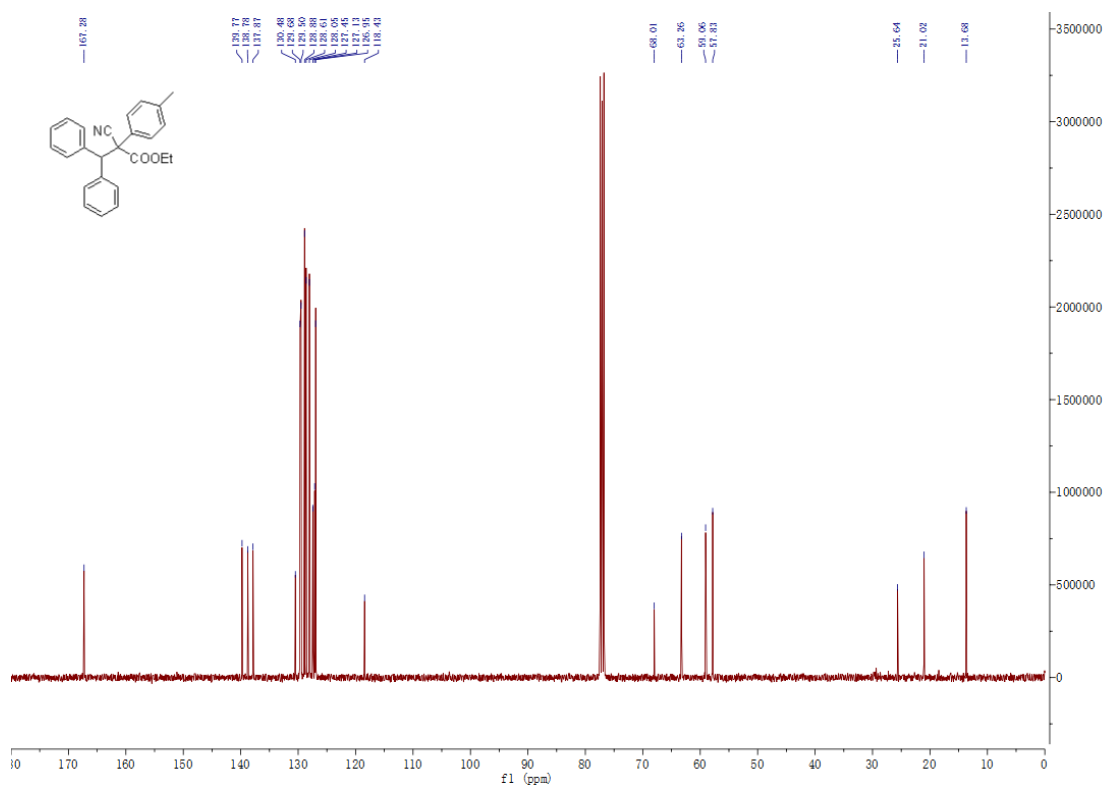
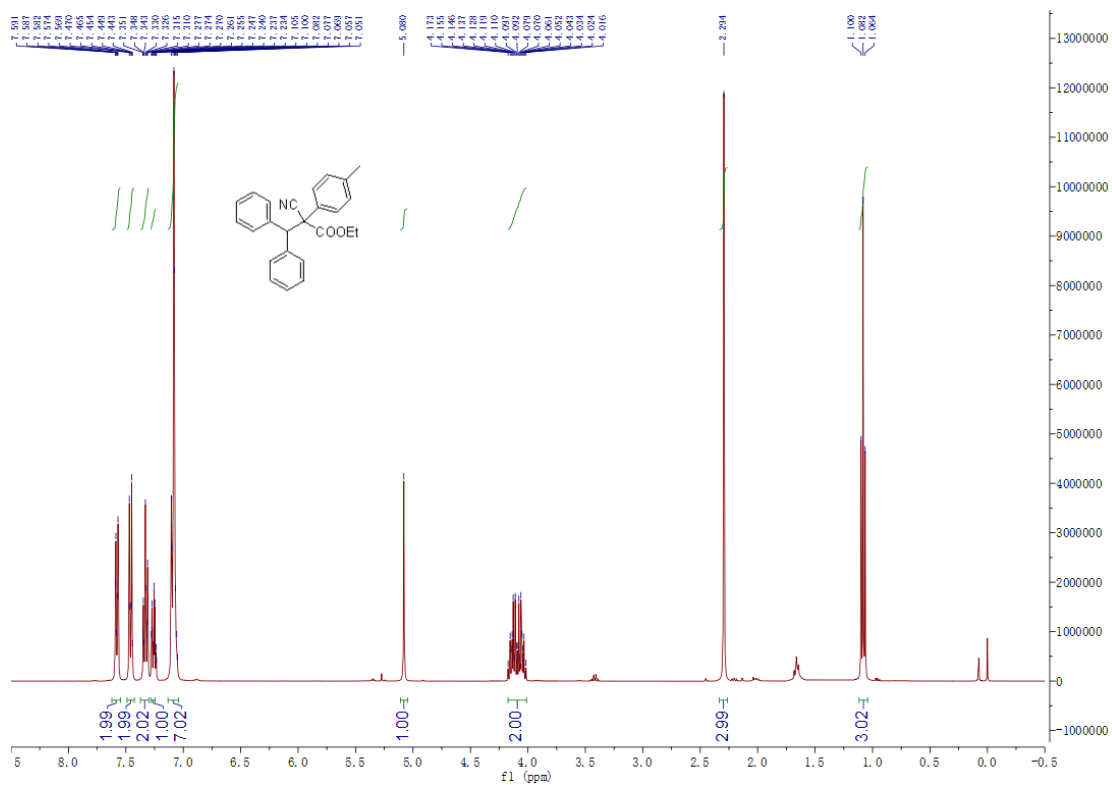
Chemical Shift (ppm)	Integration
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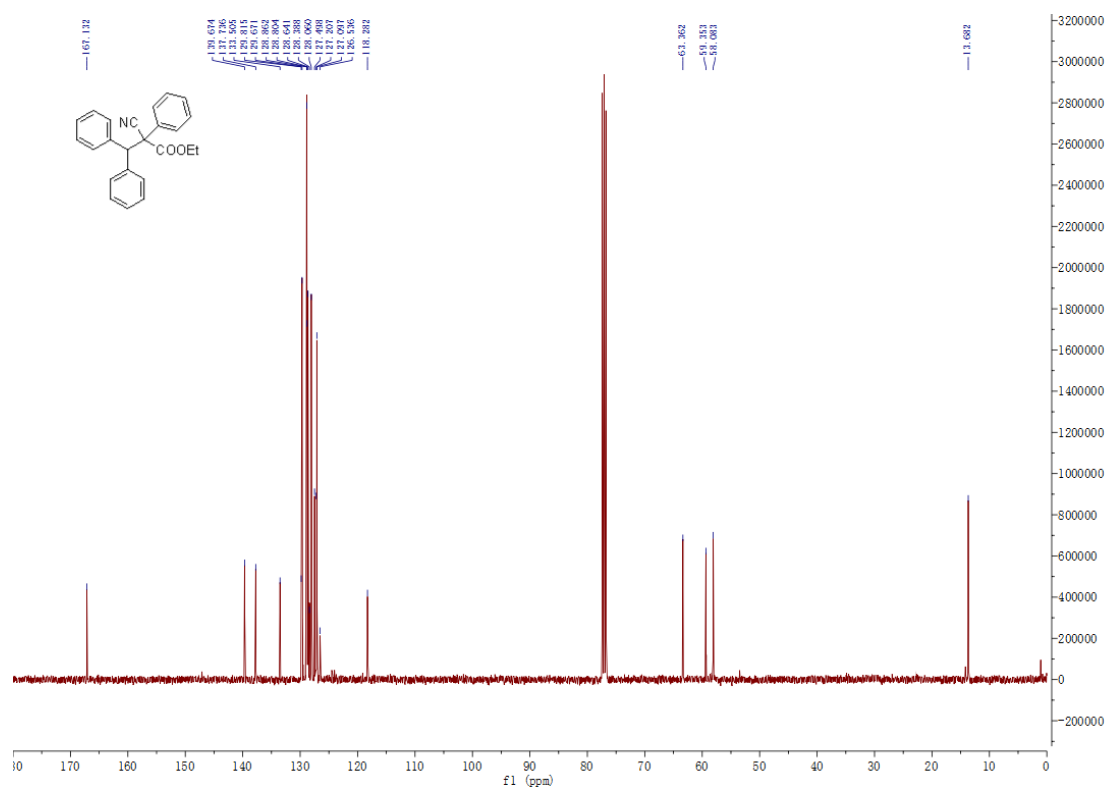
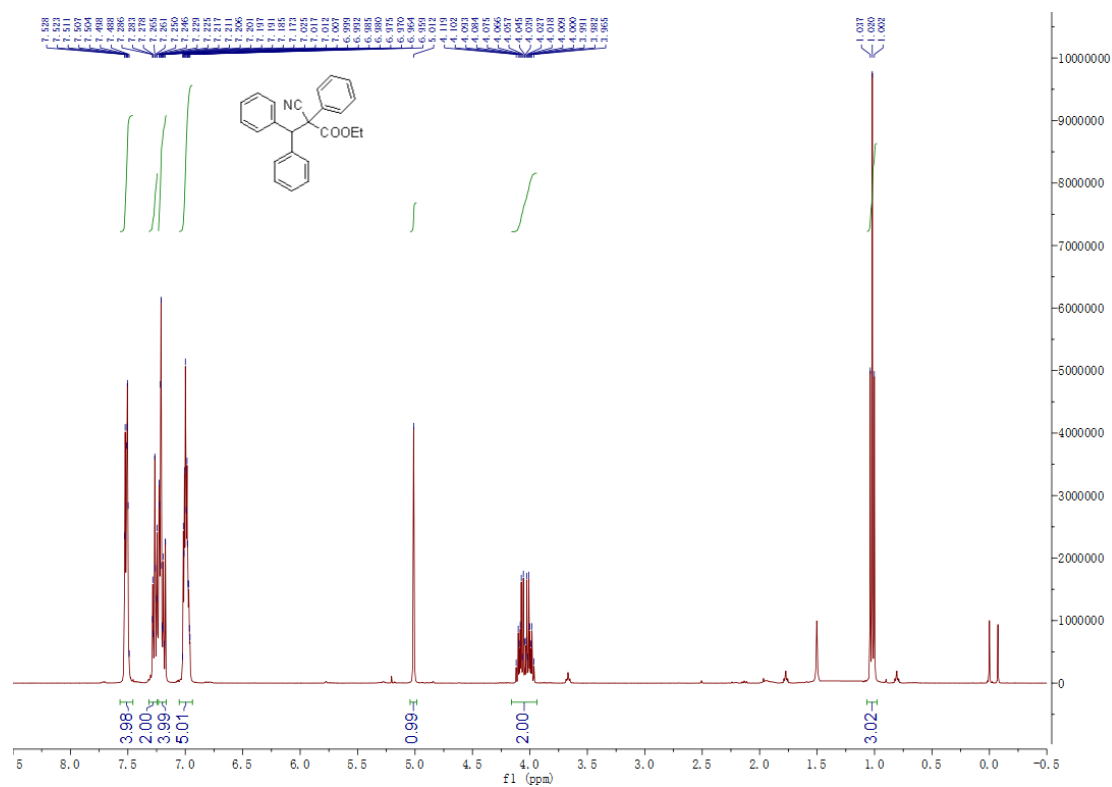
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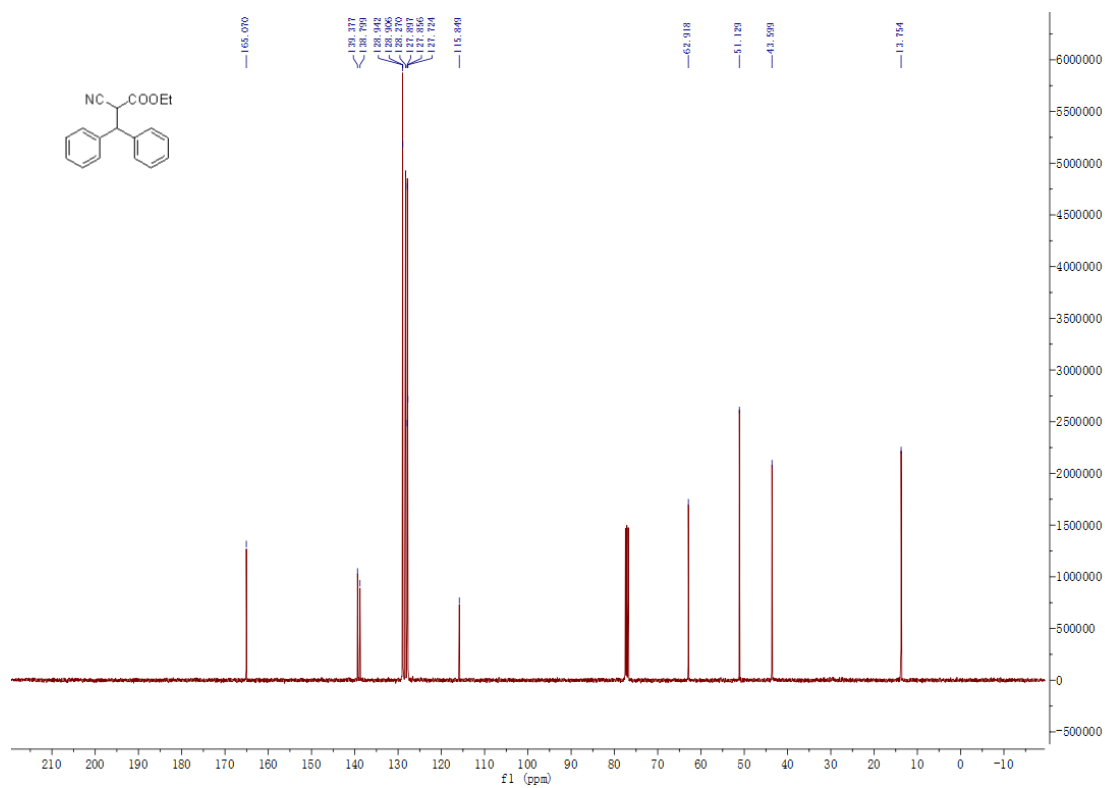
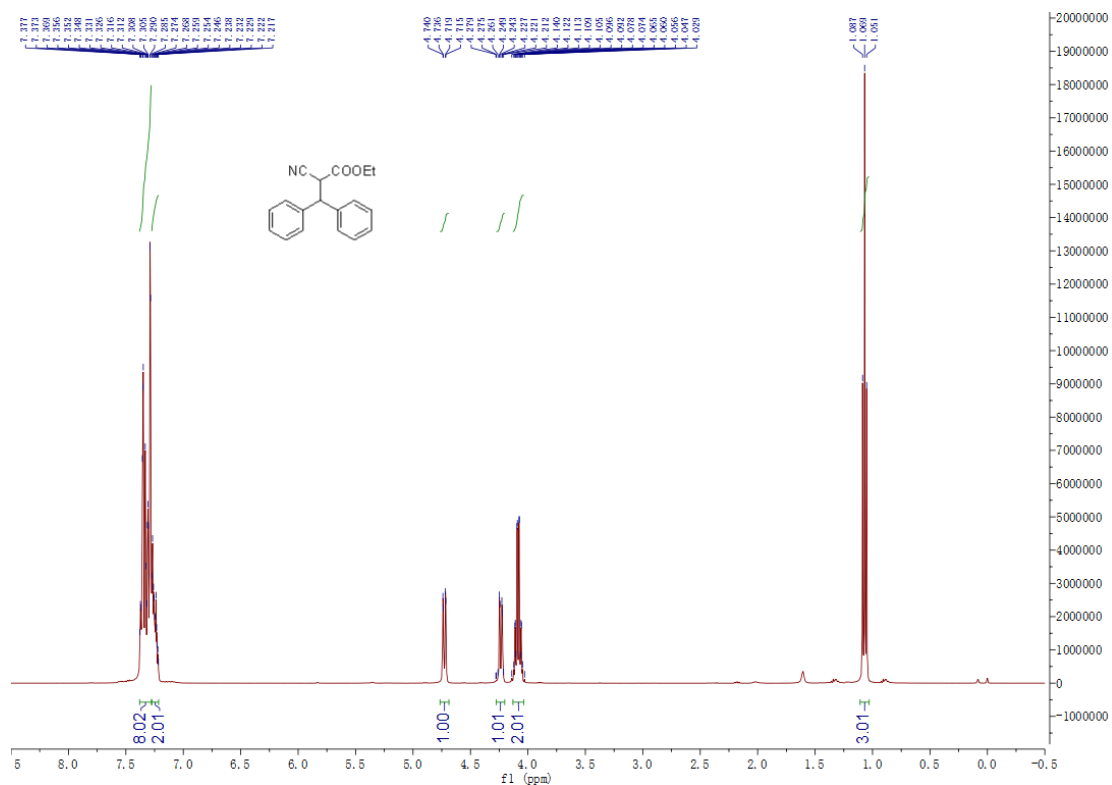
3o



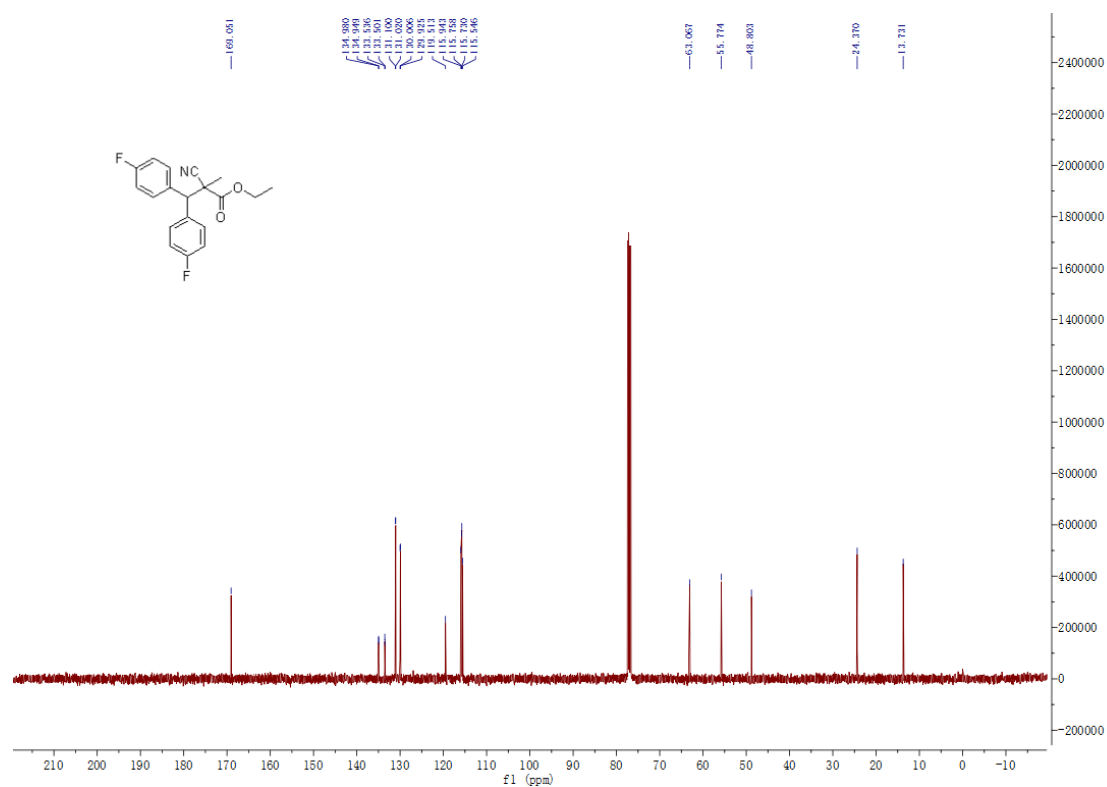
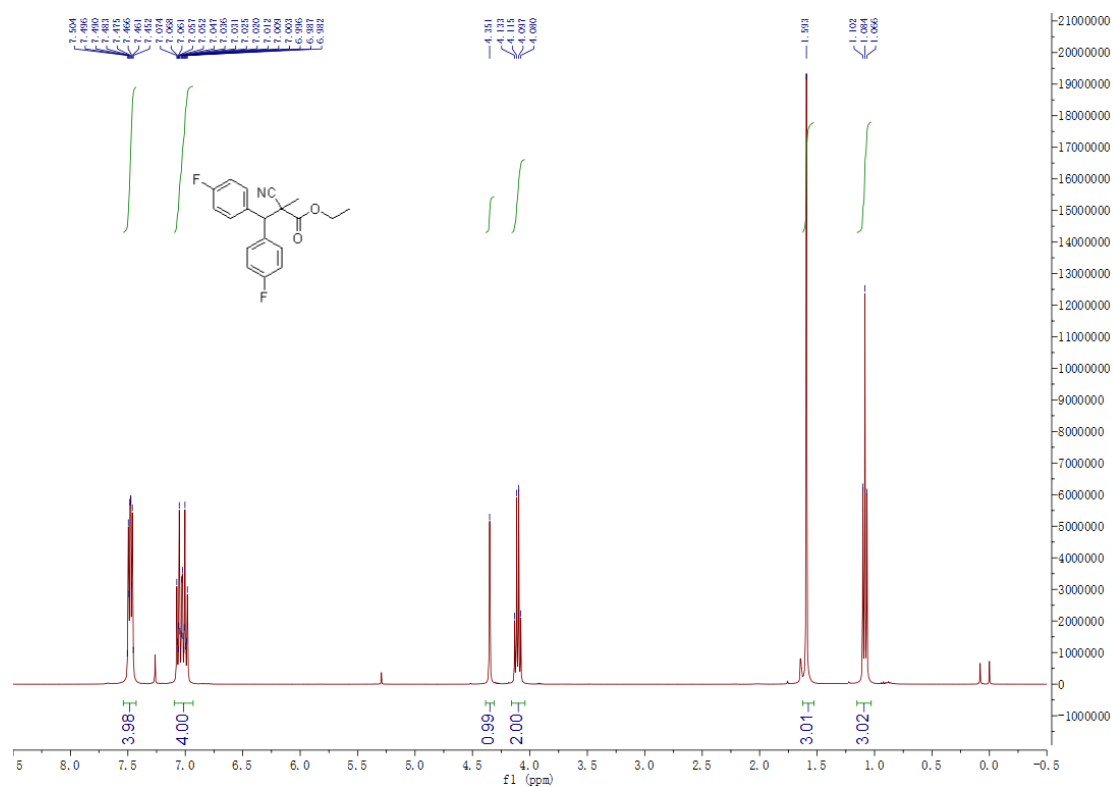
3p

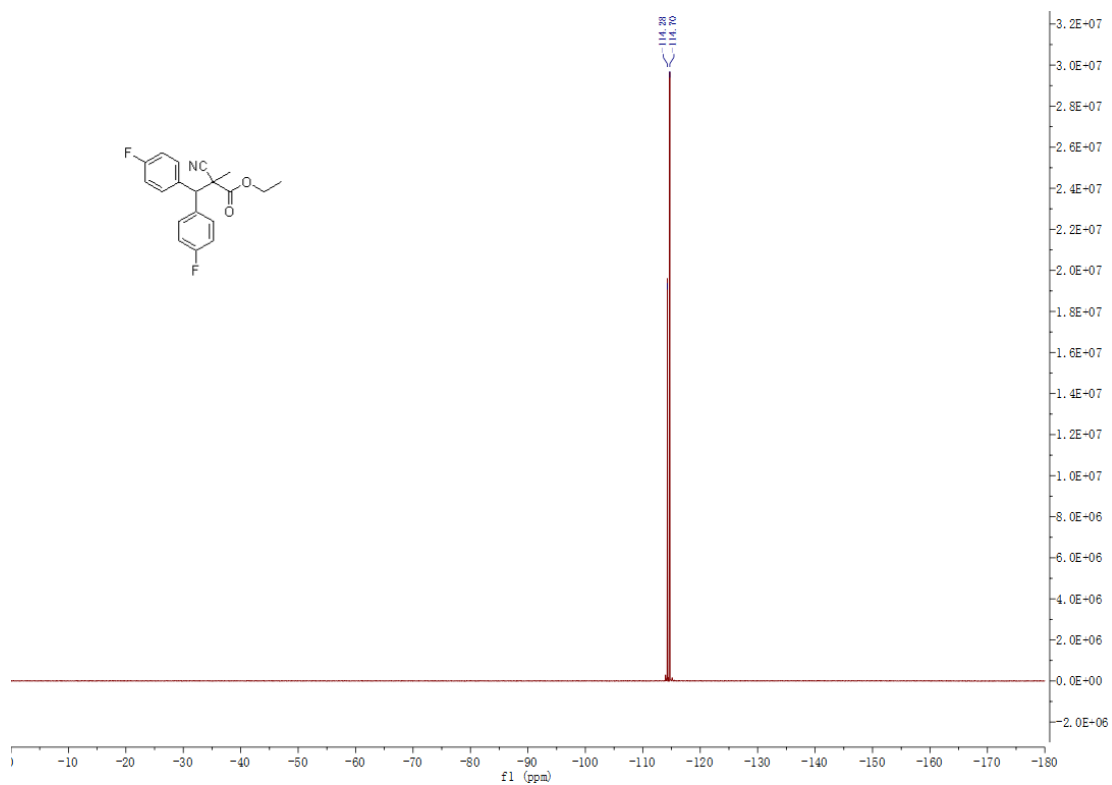


3q

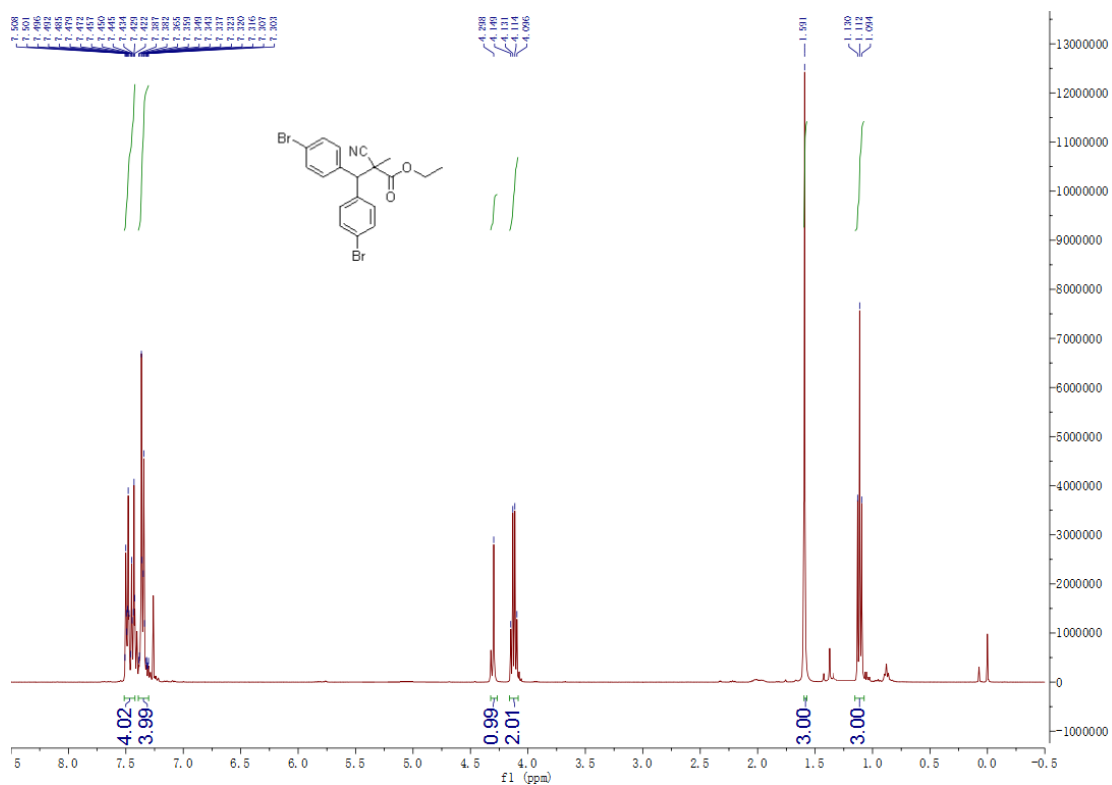


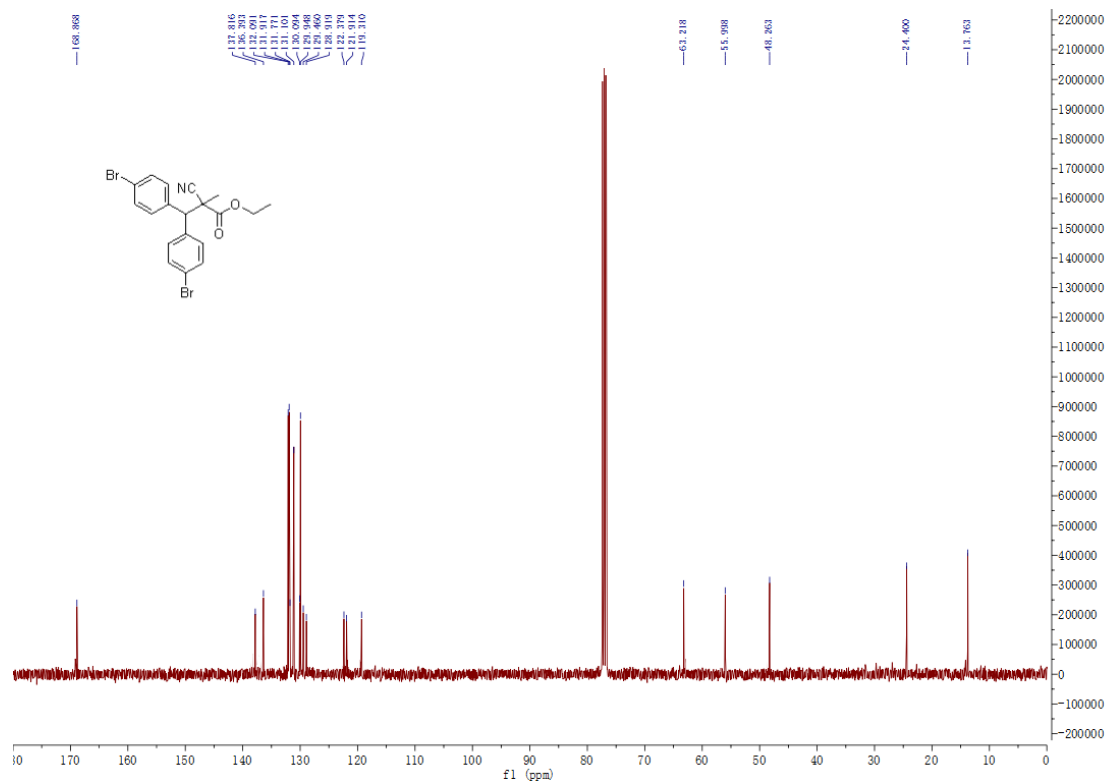
3r



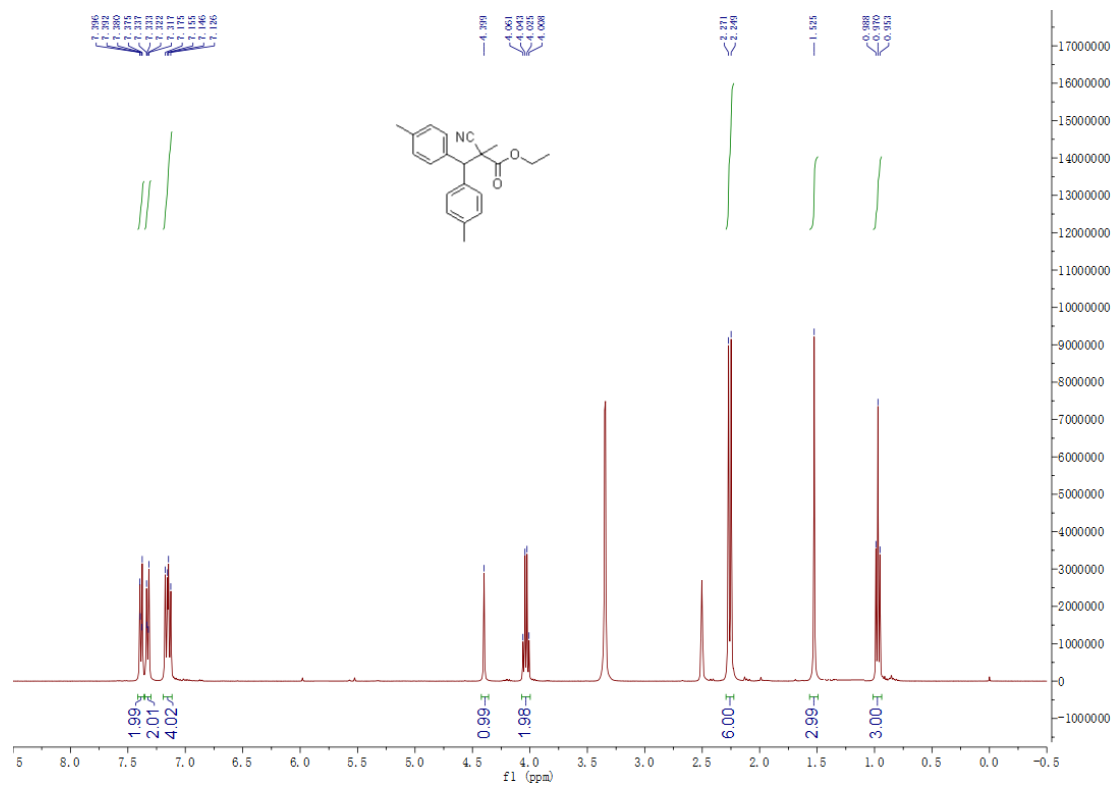


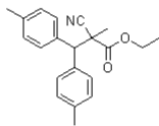
3s





3t

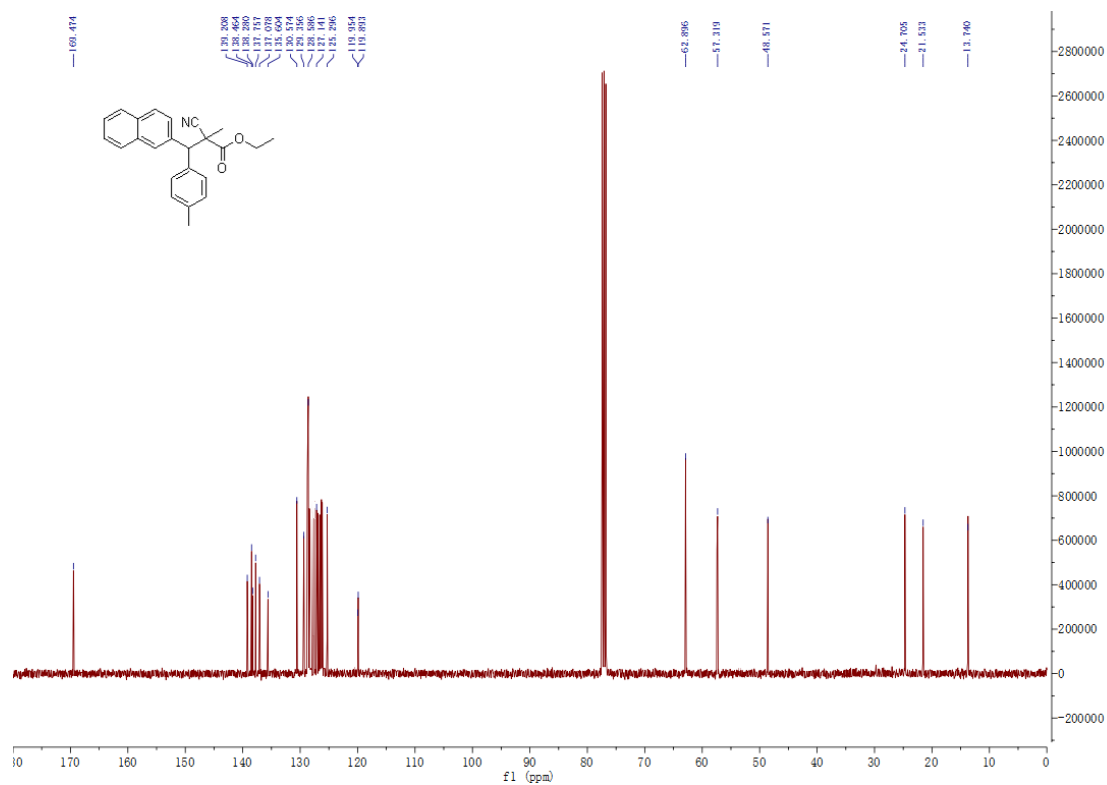




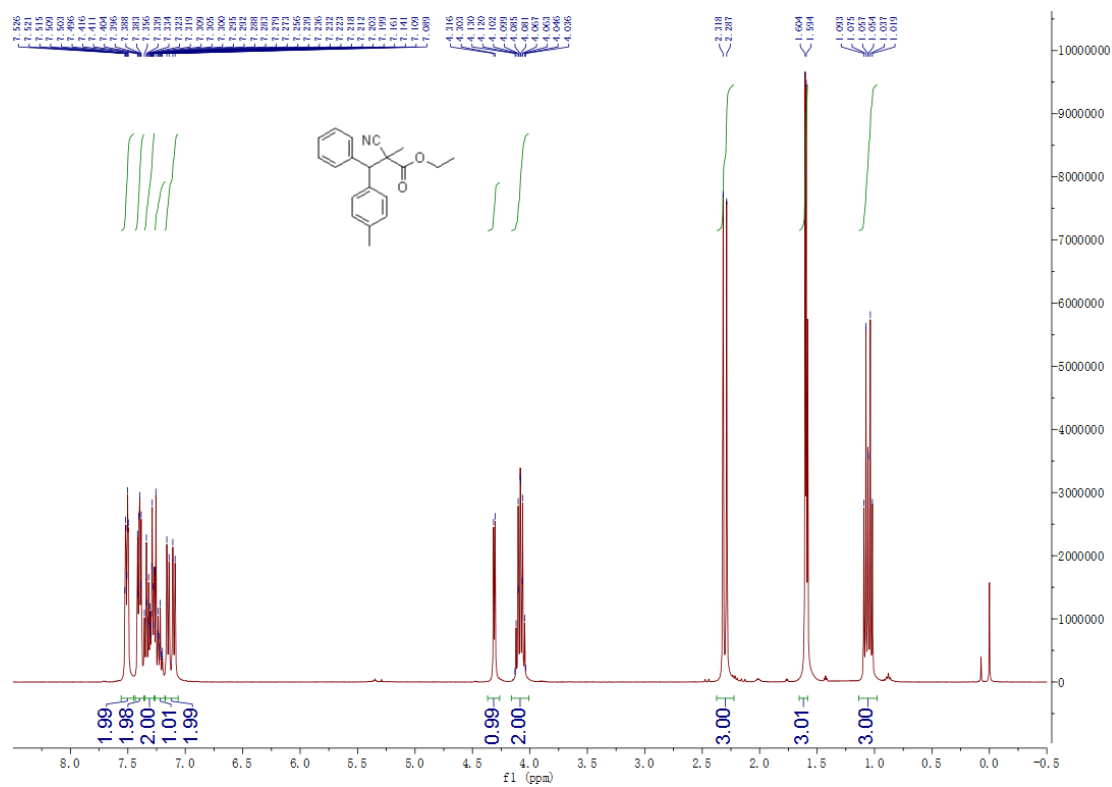
Chemical structure: CCOC(=O)C(C#N)(c1ccccc1)c2ccccc2

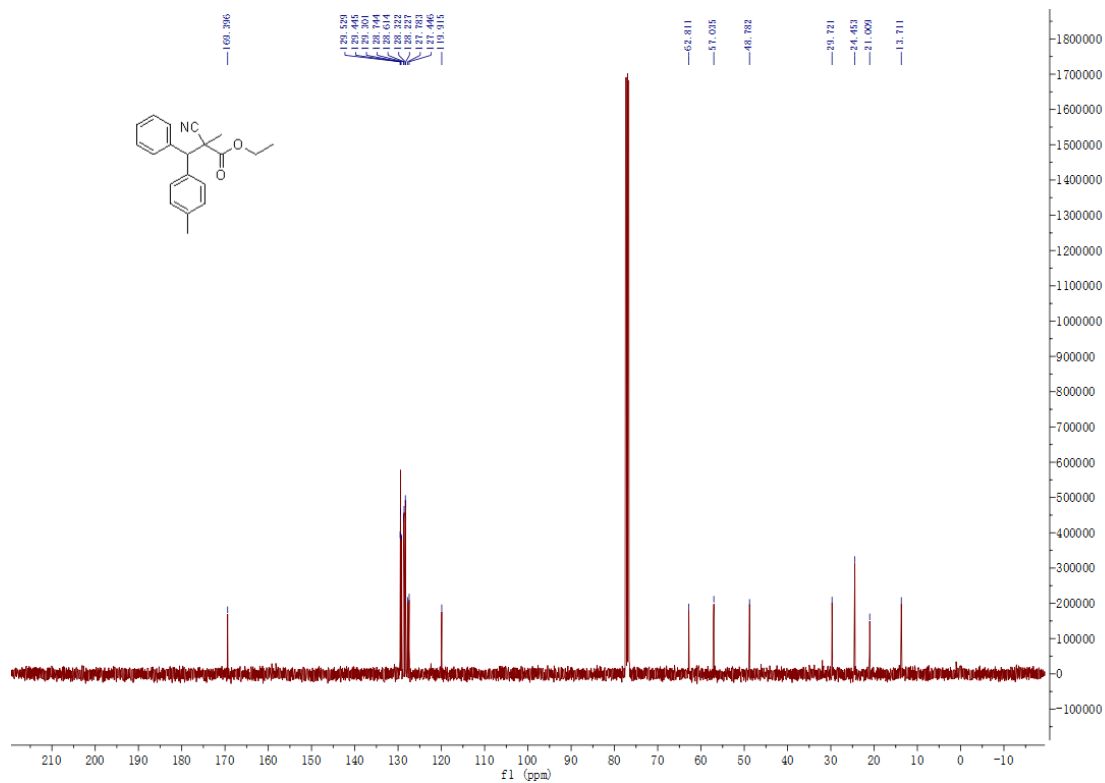
¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. The x-axis is labeled f1 (ppm) and the y-axis is labeled intensity. Integration values are shown below the peaks.

Chemical Shift (ppm)	Integration
7.8-7.9	1.00
7.5-7.6	3.02
7.3-7.4	3.99
7.1-7.2	0.99
6.9-7.0	1.00
6.7-6.8	0.99
4.4	0.98
4.1-4.2	2.00
2.3	2.99
1.6	3.00
1.1	3.01

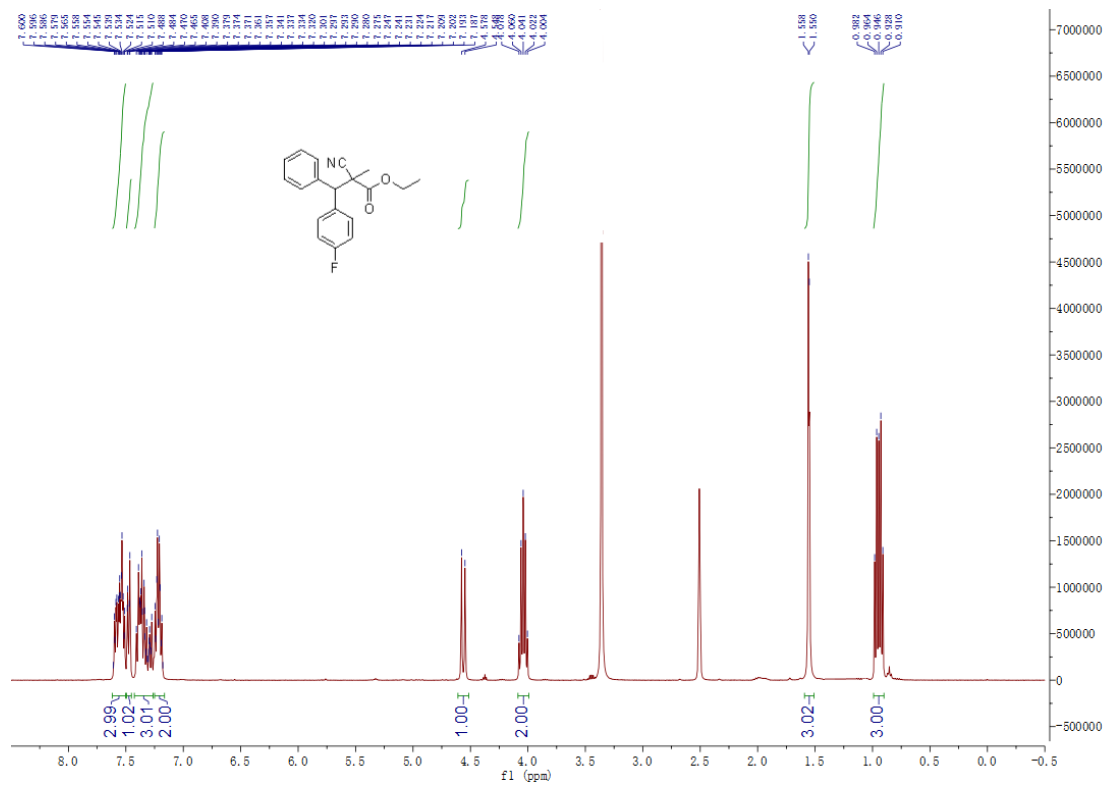


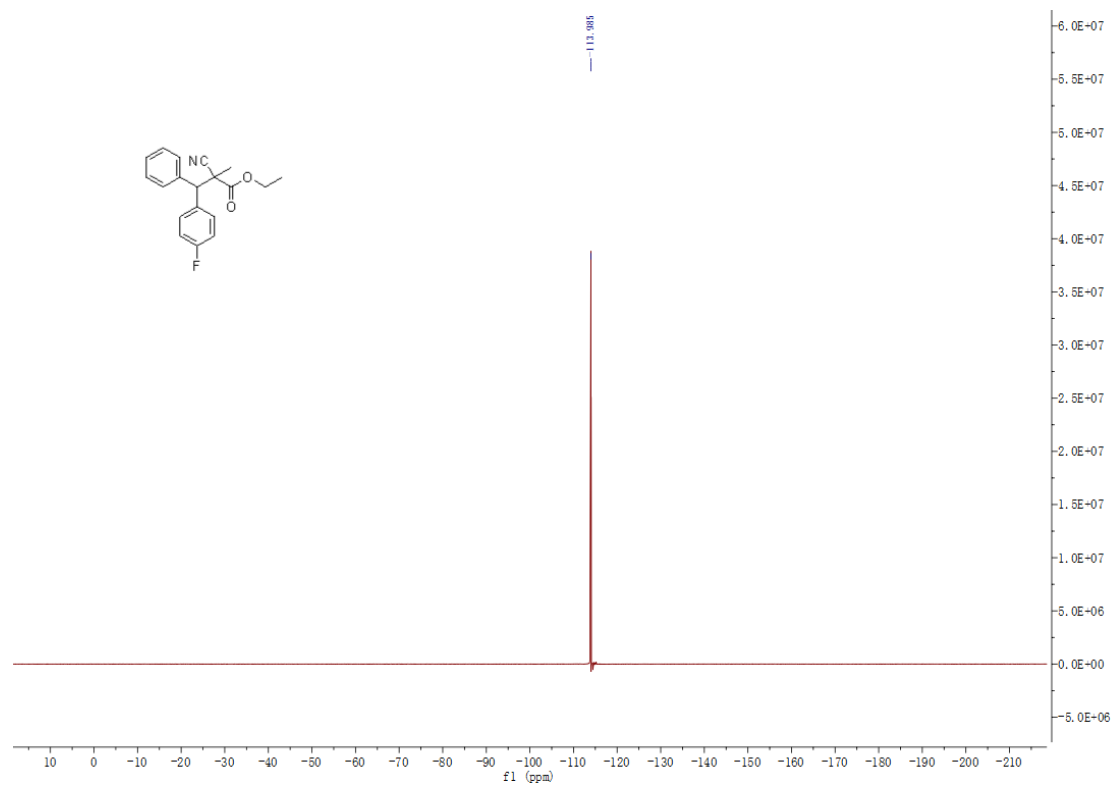
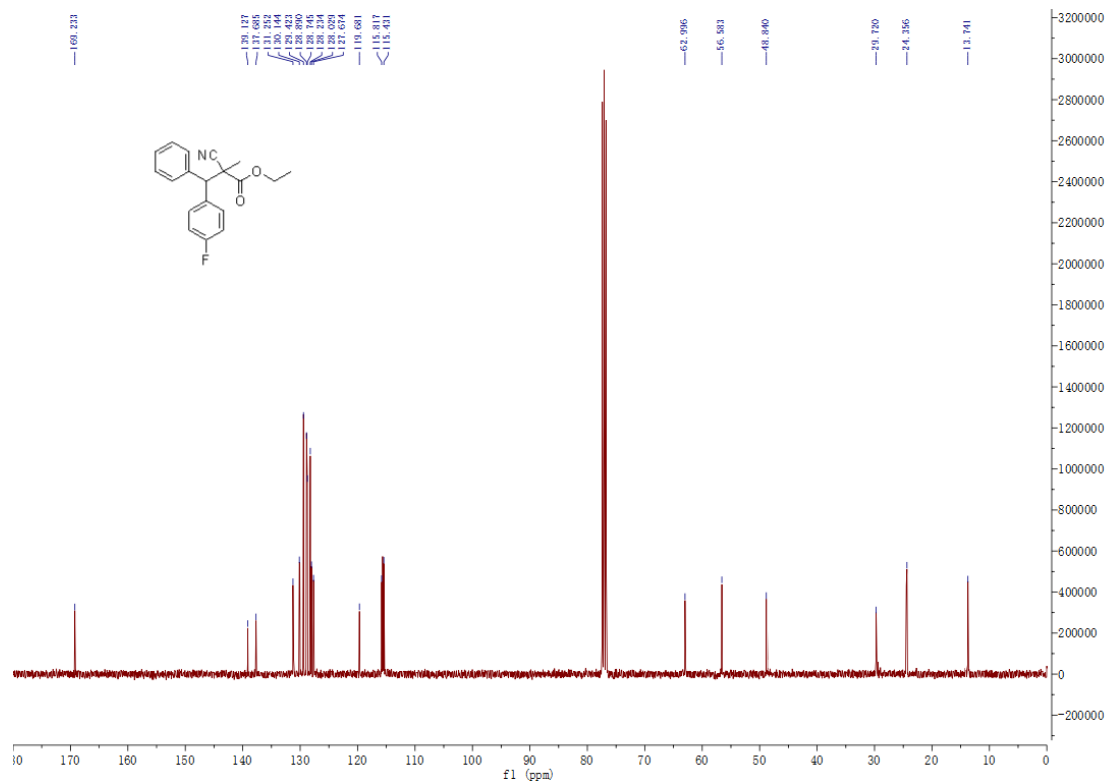
3v



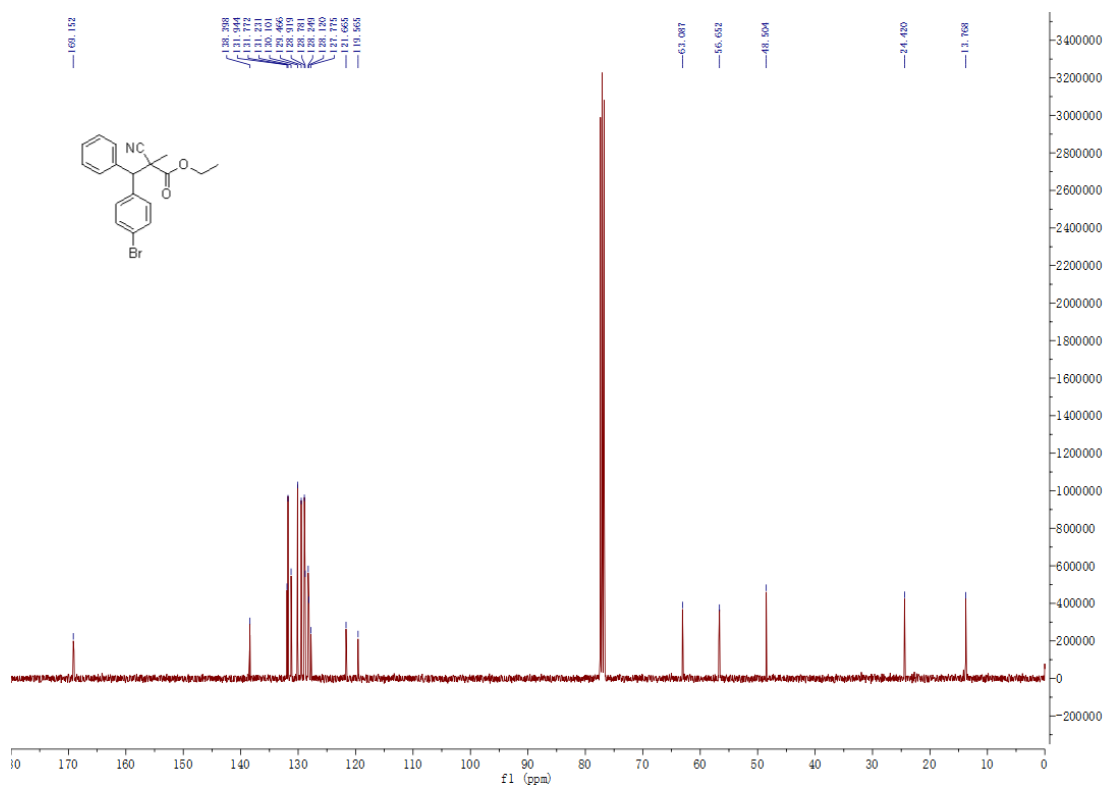
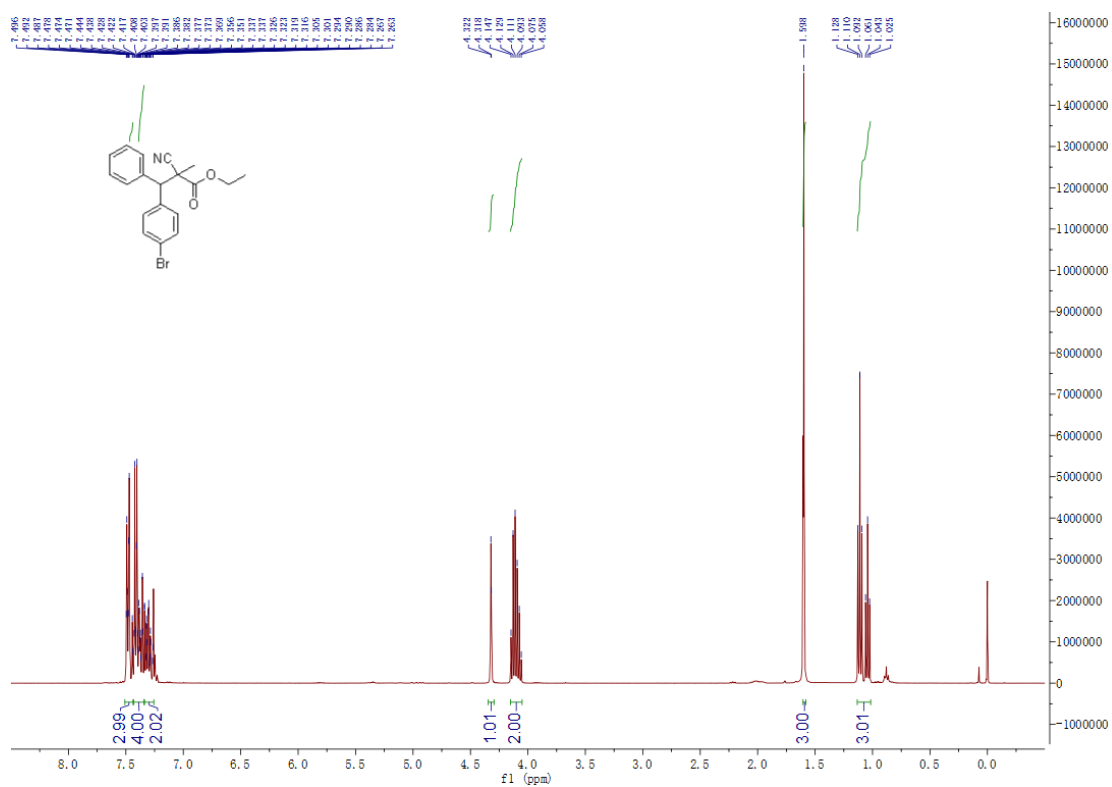


3w

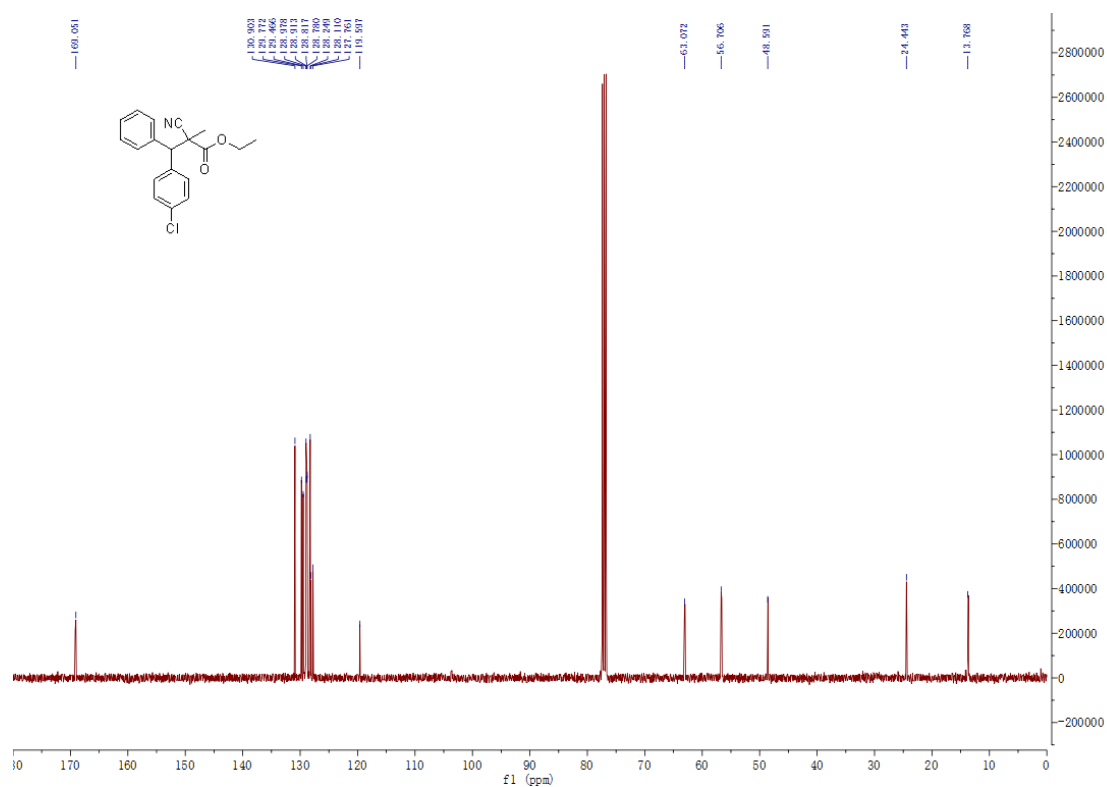
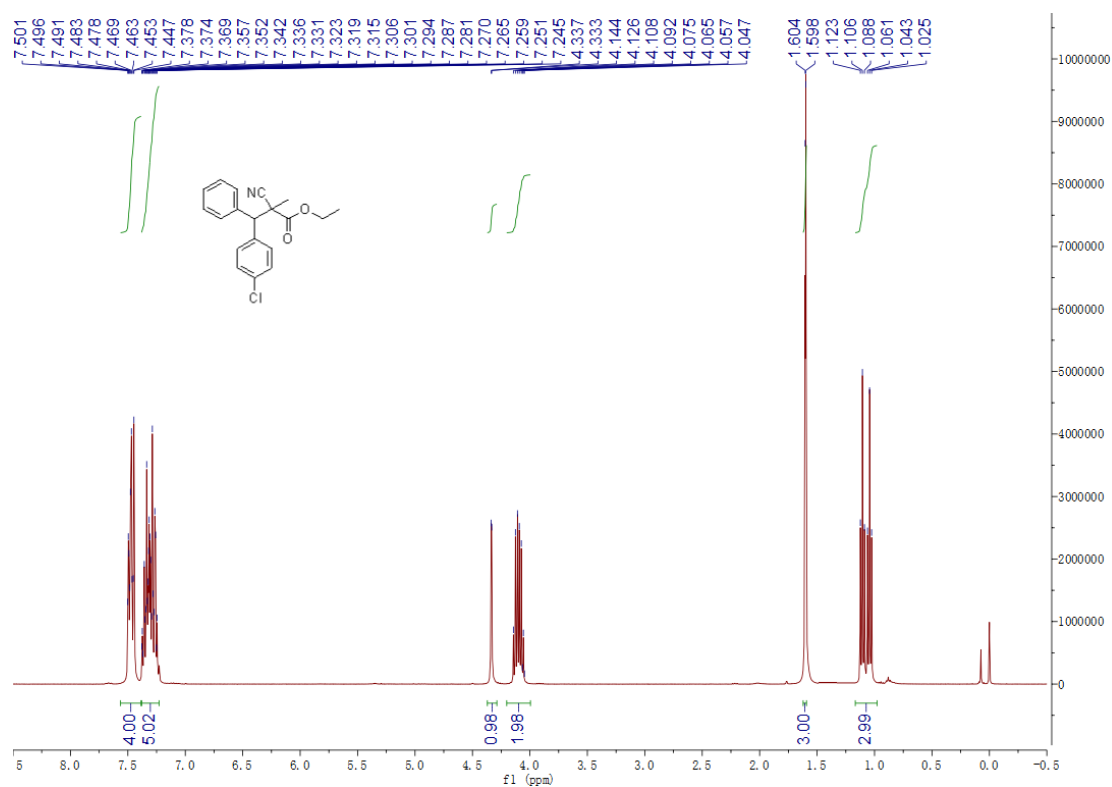




3x

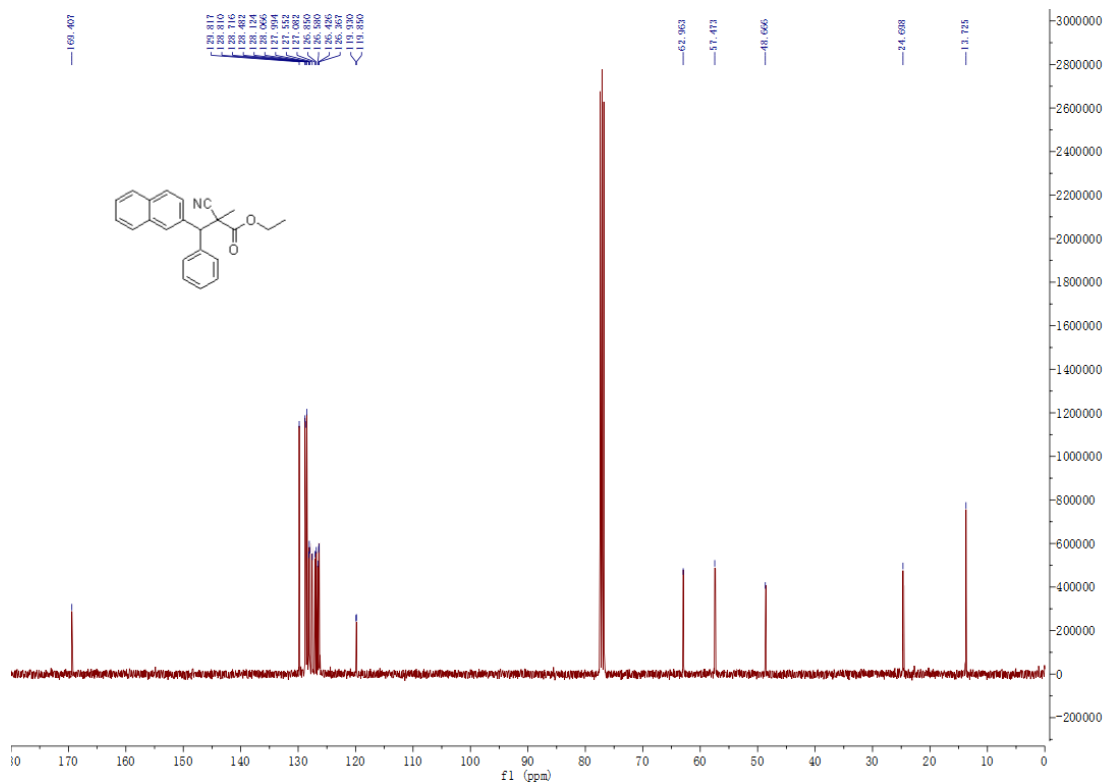


3y

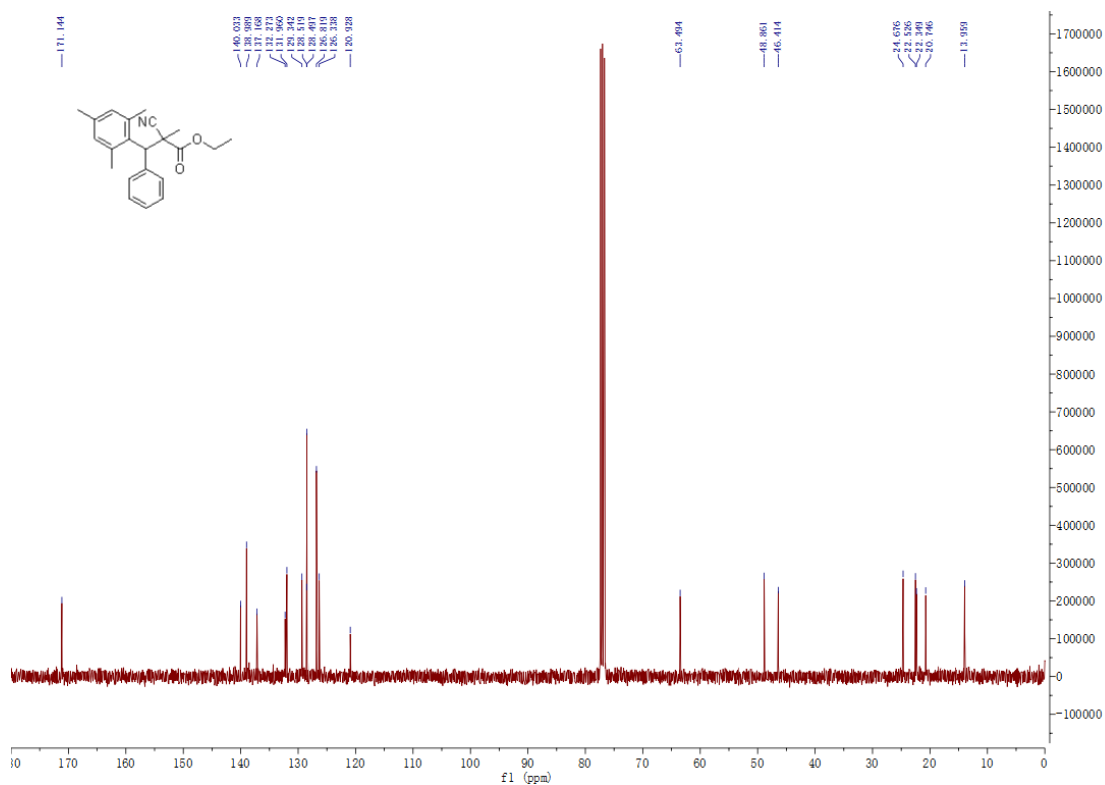
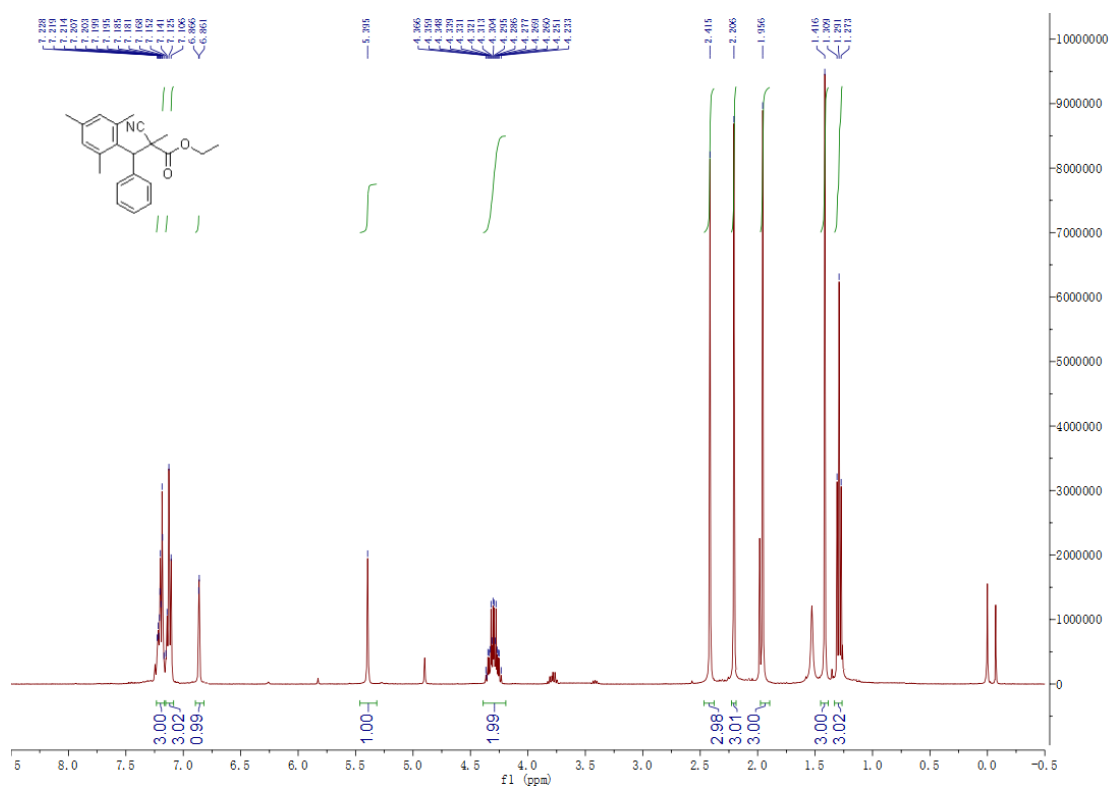


Chemical structure: CCOC(=O)c1ccc(cc1)C(=O)Nc2ccccc2C3=CC=CC=C3

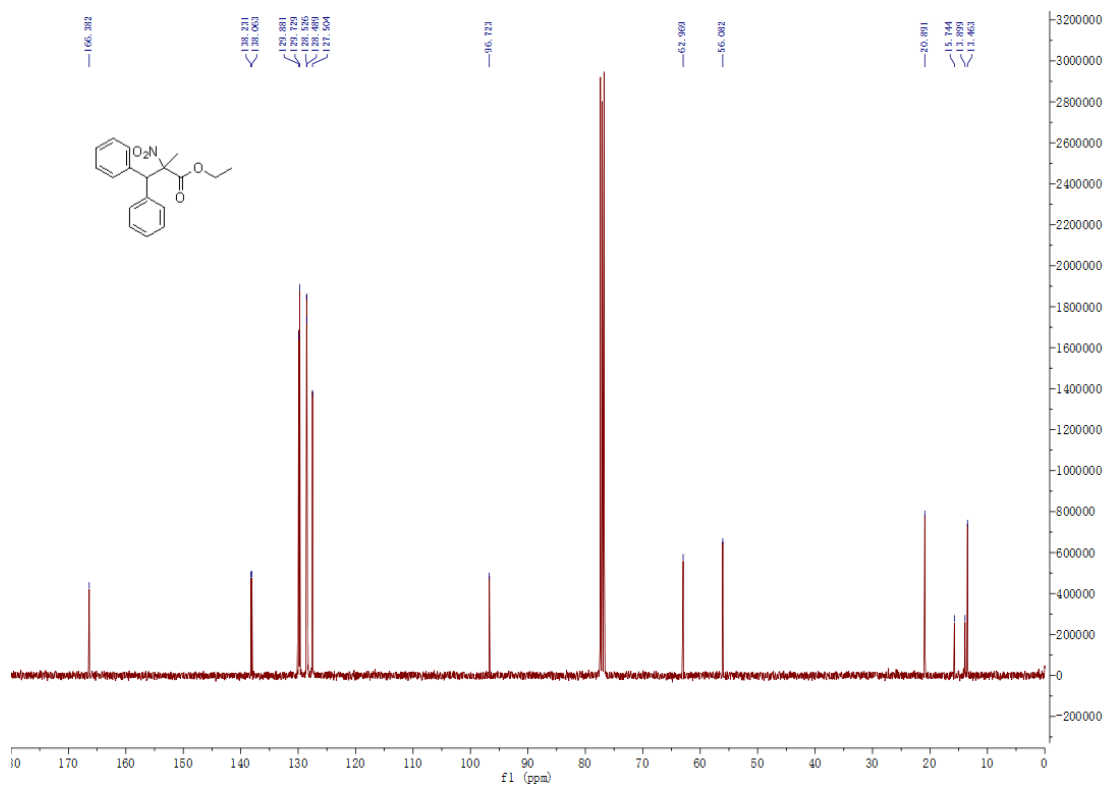
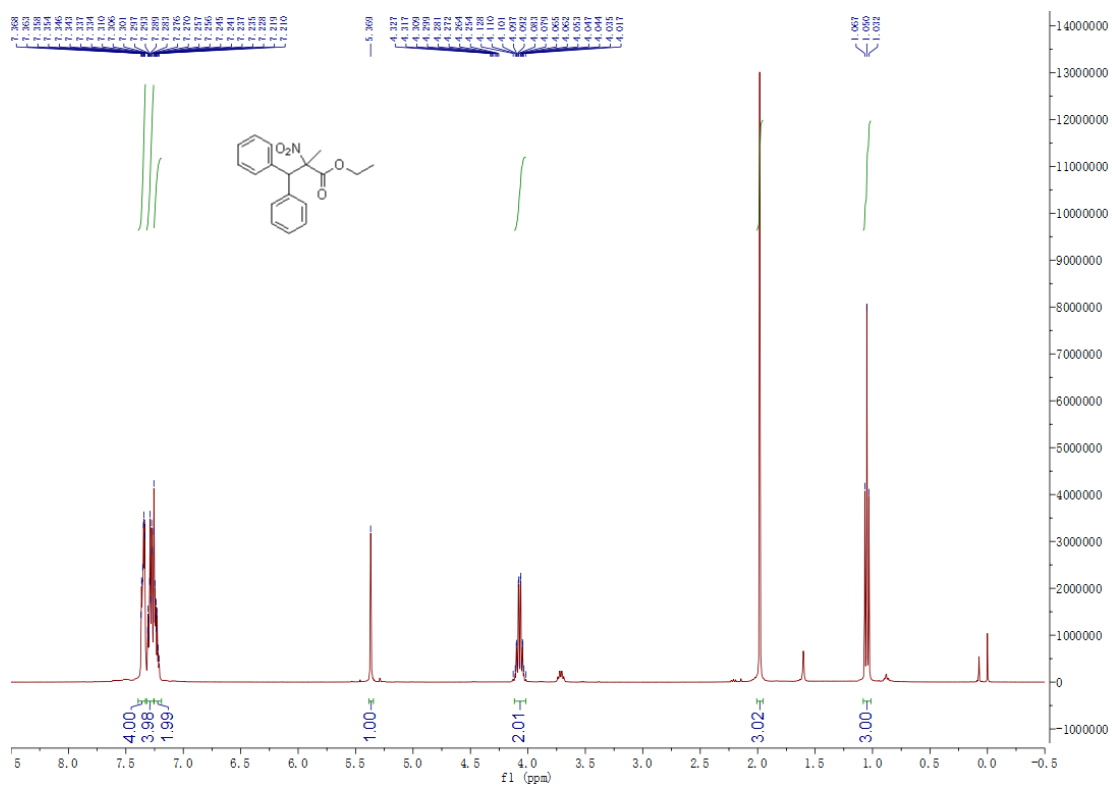
¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. Integration values are shown below the peaks: 1.02, 3.00, 5.01, 3.02, 1.00, 2.01, 3.01, 3.02.



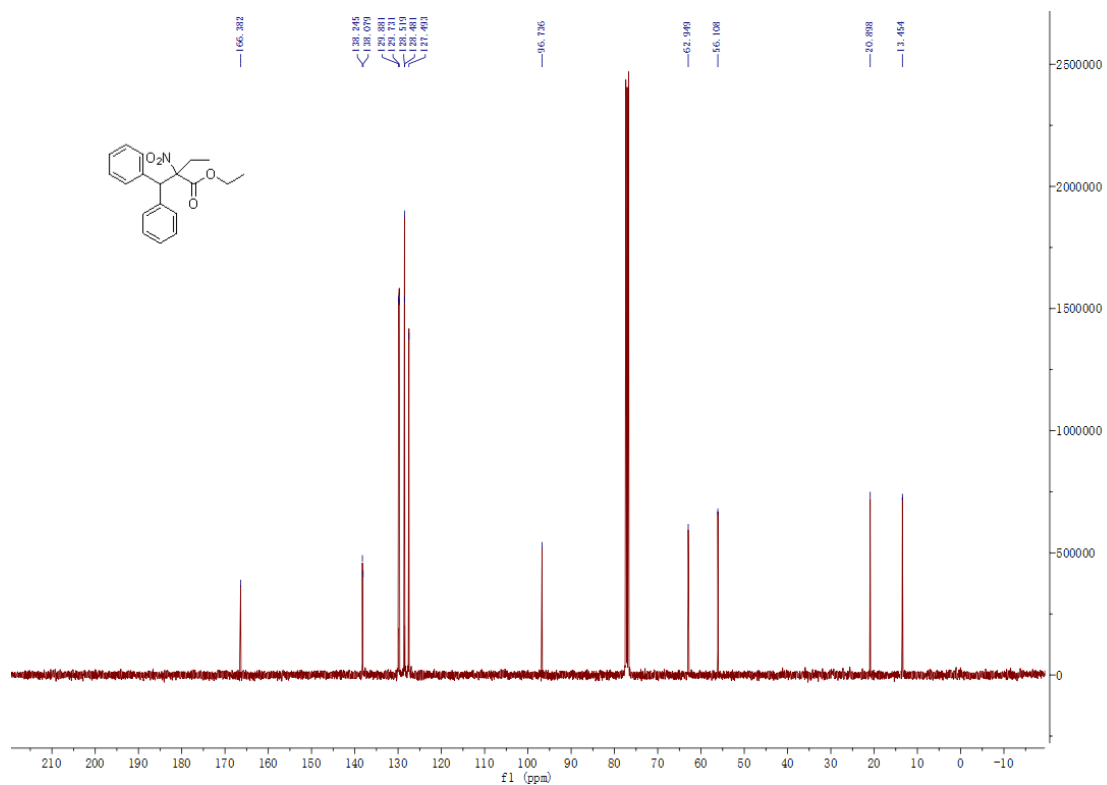
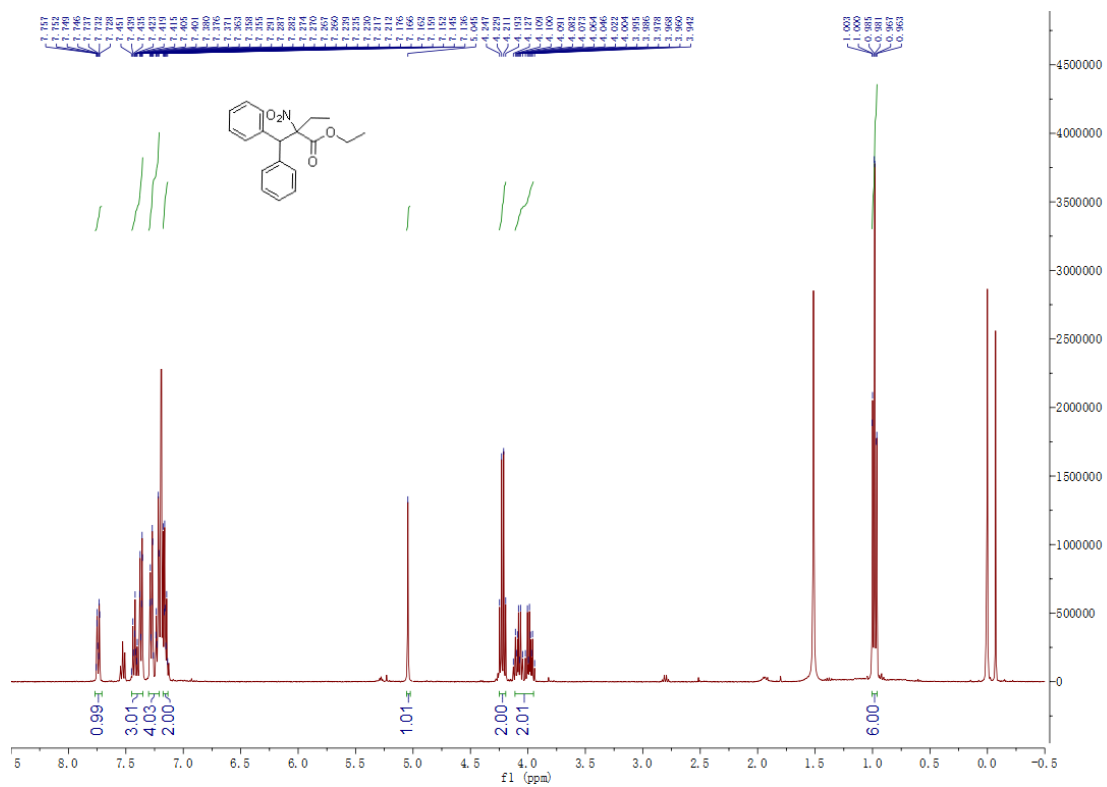
3aa



5a



5b

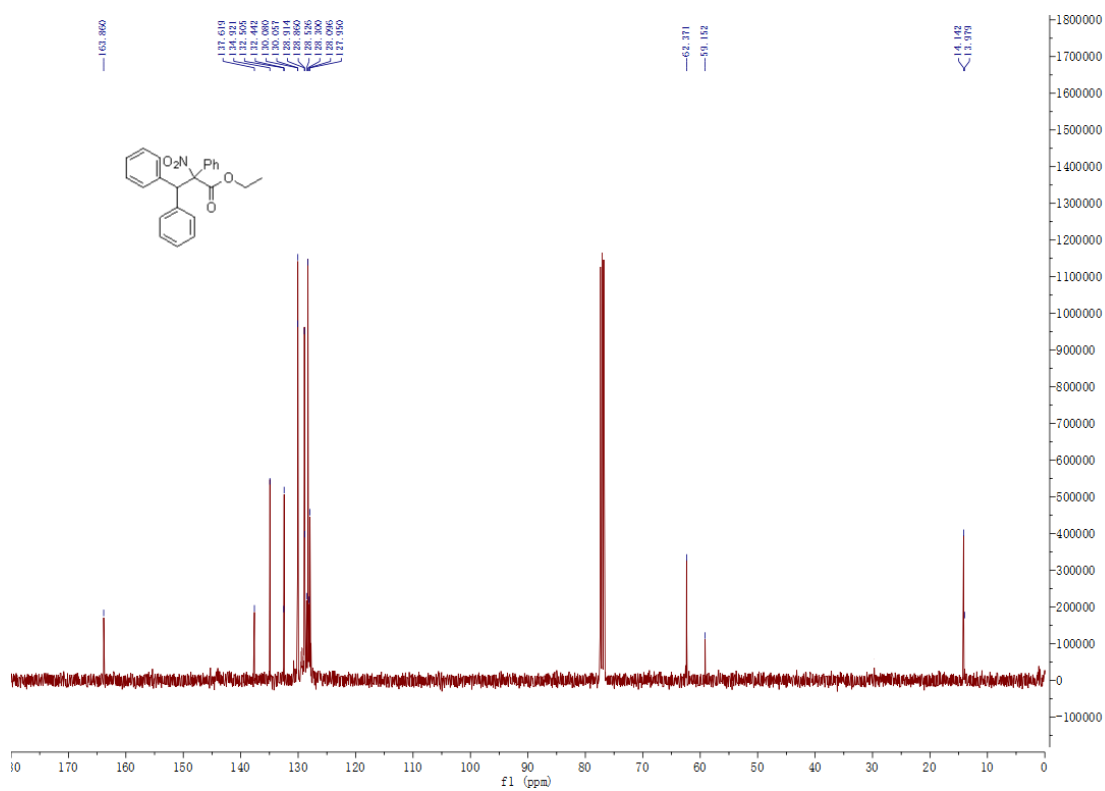


Chemical structure: CCOC(=O)C(c1ccccc1)C(=O)OCC

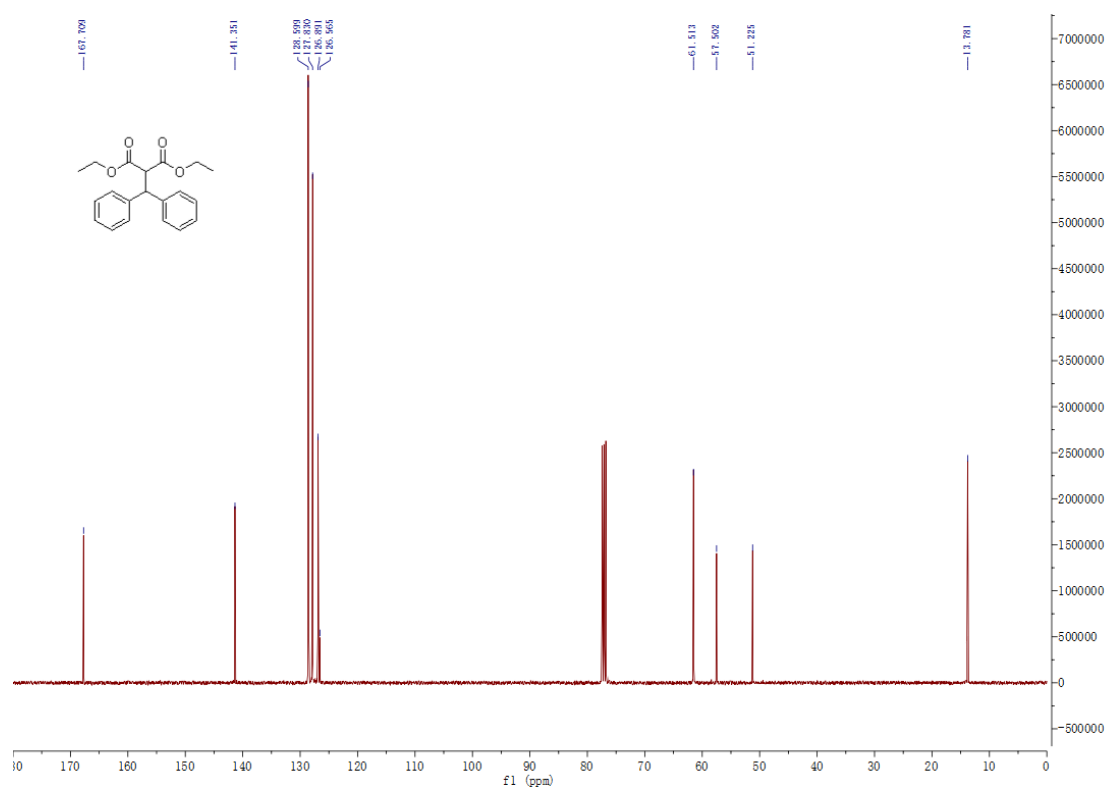
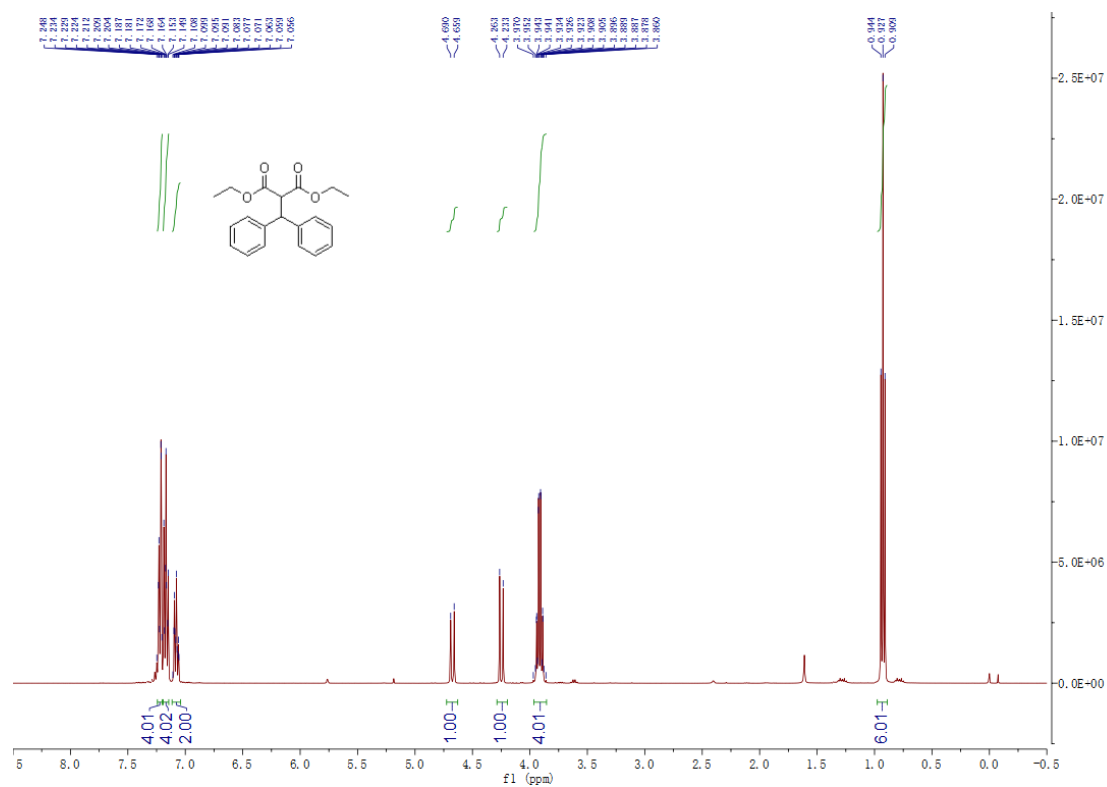
¹H NMR spectrum (ppm):

- 7.96, 7.94, 7.92, 7.90, 7.88, 7.86, 7.84, 7.82, 7.80, 7.78, 7.76, 7.74, 7.72, 7.70, 7.68, 7.66, 7.64, 7.62, 7.60, 7.58, 7.56, 7.54, 7.52, 7.50, 7.48, 7.46, 7.44, 7.42, 7.40, 7.38, 7.36, 7.34, 7.32, 7.30, 7.28, 7.26, 7.24, 7.22, 7.20, 7.18, 7.16, 7.14, 7.12, 7.10, 7.08, 7.06, 7.04, 7.02, 7.00, 6.98, 6.96, 6.94, 6.92, 6.90, 6.88, 6.86, 6.84, 6.82, 6.80, 6.78, 6.76, 6.74, 6.72, 6.70, 6.68, 6.66, 6.64, 6.62, 6.60, 6.58, 6.56, 6.54, 6.52, 6.50, 6.48, 6.46, 6.44, 6.42, 6.40, 6.38, 6.36, 6.34, 6.32, 6.30, 6.28, 6.26, 6.24, 6.22, 6.20, 6.18, 6.16, 6.14, 6.12, 6.10, 6.08, 6.06, 6.04, 6.02, 6.00, 5.98, 5.96, 5.94, 5.92, 5.90, 5.88, 5.86, 5.84, 5.82, 5.80, 5.78, 5.76, 5.74, 5.72, 5.70, 5.68, 5.66, 5.64, 5.62, 5.60, 5.58, 5.56, 5.54, 5.52, 5.50, 5.48, 5.46, 5.44, 5.42, 5.40, 5.38, 5.36, 5.34, 5.32, 5.30, 5.28, 5.26, 5.24, 5.22, 5.20, 5.18, 5.16, 5.14, 5.12, 5.10, 5.08, 5.06, 5.04, 5.02, 5.00, 4.98, 4.96, 4.94, 4.92, 4.90, 4.88, 4.86, 4.84, 4.82, 4.80, 4.78, 4.76, 4.74, 4.72, 4.70, 4.68, 4.66, 4.64, 4.62, 4.60, 4.58, 4.56, 4.54, 4.52, 4.50, 4.48, 4.46, 4.44, 4.42, 4.40, 4.38, 4.36, 4.34, 4.32, 4.30, 4.28, 4.26, 4.24, 4.22, 4.20, 4.18, 4.16, 4.14, 4.12, 4.10, 4.08, 4.06, 4.04, 4.02, 4.00, 3.98, 3.96, 3.94, 3.92, 3.90, 3.88, 3.86, 3.84, 3.82, 3.80, 3.78, 3.76, 3.74, 3.72, 3.70, 3.68, 3.66, 3.64, 3.62, 3.60, 3.58, 3.56, 3.54, 3.52, 3.50, 3.48, 3.46, 3.44, 3.42, 3.40, 3.38, 3.36, 3.34, 3.32, 3.30, 3.28, 3.26, 3.24, 3.22, 3.20, 3.18, 3.16, 3.14, 3.12, 3.10, 3.08, 3.06, 3.04, 3.02, 3.00, 2.98, 2.96, 2.94, 2.92, 2.90, 2.88, 2.86, 2.84, 2.82, 2.80, 2.78, 2.76, 2.74, 2.72, 2.70, 2.68, 2.66, 2.64, 2.62, 2.60, 2.58, 2.56, 2.54, 2.52, 2.50, 2.48, 2.46, 2.44, 2.42, 2.40, 2.38, 2.36, 2.34, 2.32, 2.30, 2.28, 2.26, 2.24, 2.22, 2.20, 2.18, 2.16, 2.14, 2.12, 2.10, 2.08, 2.06, 2.04, 2.02, 2.00, 1.98, 1.96, 1.94, 1.92, 1.90, 1.88, 1.86, 1.84, 1.82, 1.80, 1.78, 1.76, 1.74, 1.72, 1.70, 1.68, 1.66, 1.64, 1.62, 1.60, 1.58, 1.56, 1.54, 1.52, 1.50, 1.48, 1.46, 1.44, 1.42, 1.40, 1.38, 1.36, 1.34, 1.32, 1.30, 1.28, 1.26, 1.24, 1.22, 1.20, 1.18, 1.16, 1.14, 1.12, 1.10, 1.08, 1.06, 1.04, 1.02, 1.00, 0.98, 0.96, 0.94, 0.92, 0.90, 0.88, 0.86, 0.84, 0.82, 0.80, 0.78, 0.76, 0.74, 0.72, 0.70, 0.68, 0.66, 0.64, 0.62, 0.60, 0.58, 0.56, 0.54, 0.52, 0.50, 0.48, 0.46, 0.44, 0.42, 0.40, 0.38, 0.36, 0.34, 0.32, 0.30, 0.28, 0.26, 0.24, 0.22, 0.20, 0.18, 0.16, 0.14, 0.12, 0.10, 0.08, 0.06, 0.04, 0.02, 0.00.

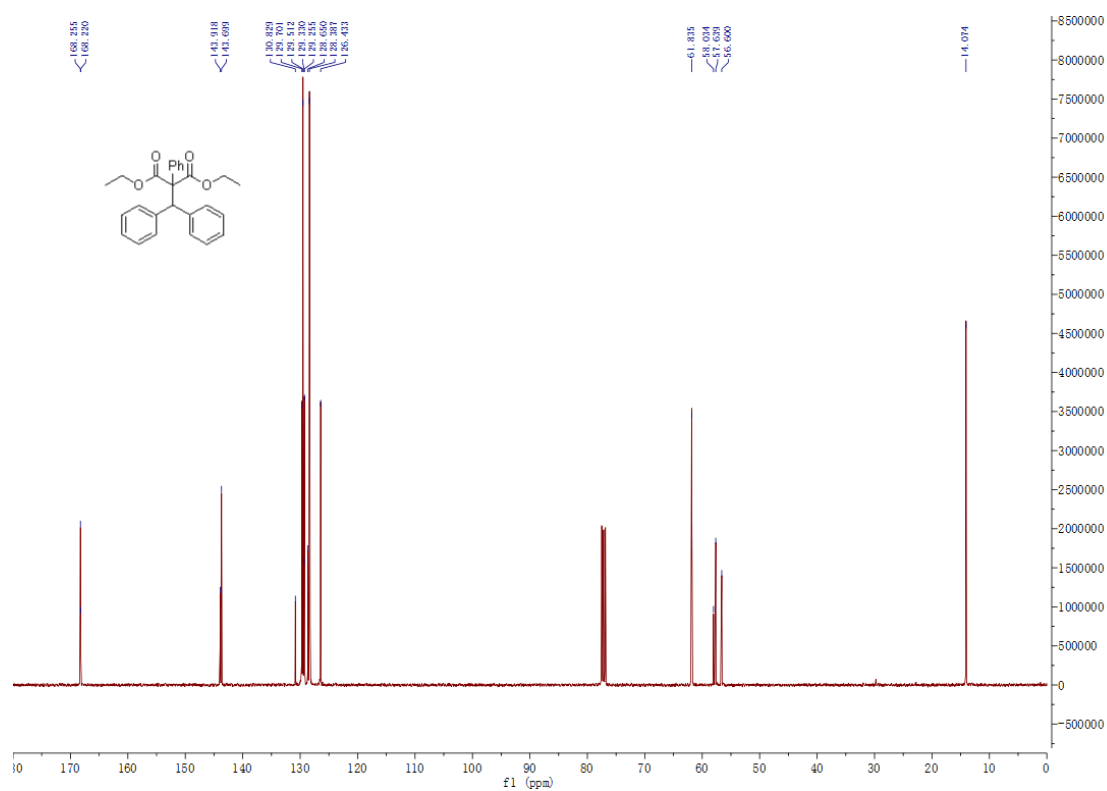
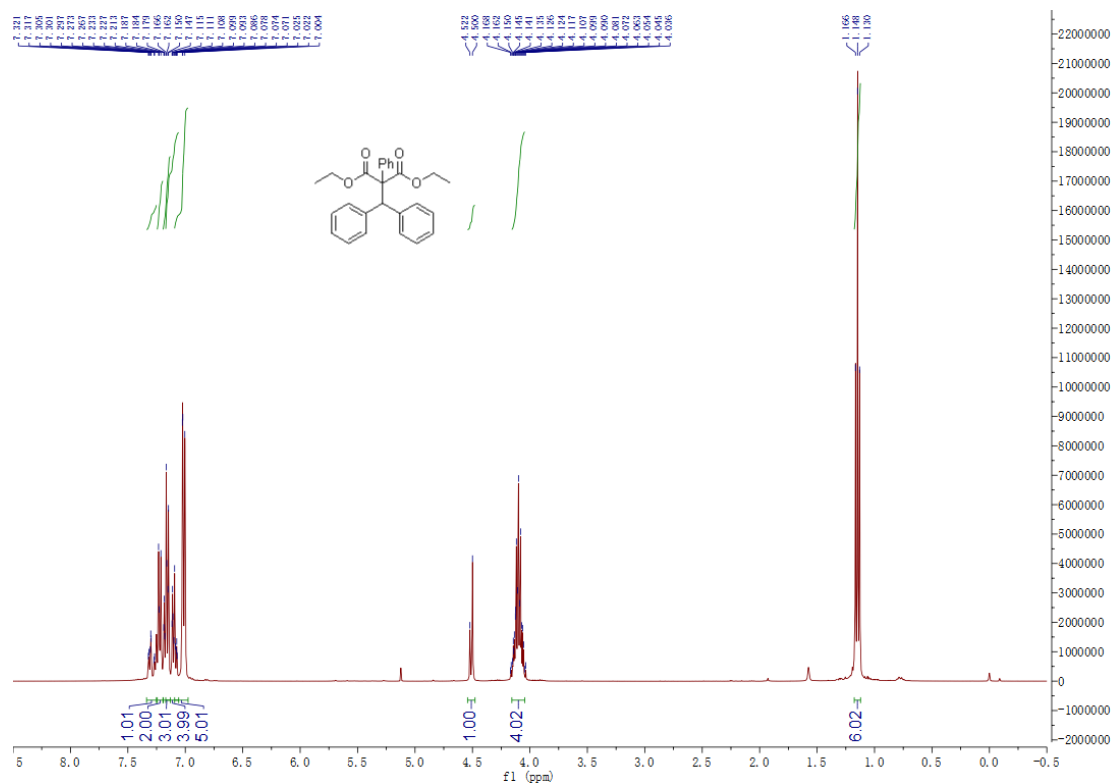
Integration values: 2.00, 1.99, 3.99, 2.01, 3.98, 1.00, 1.00, 1.98, 3.01.



7a

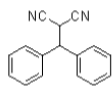


7c

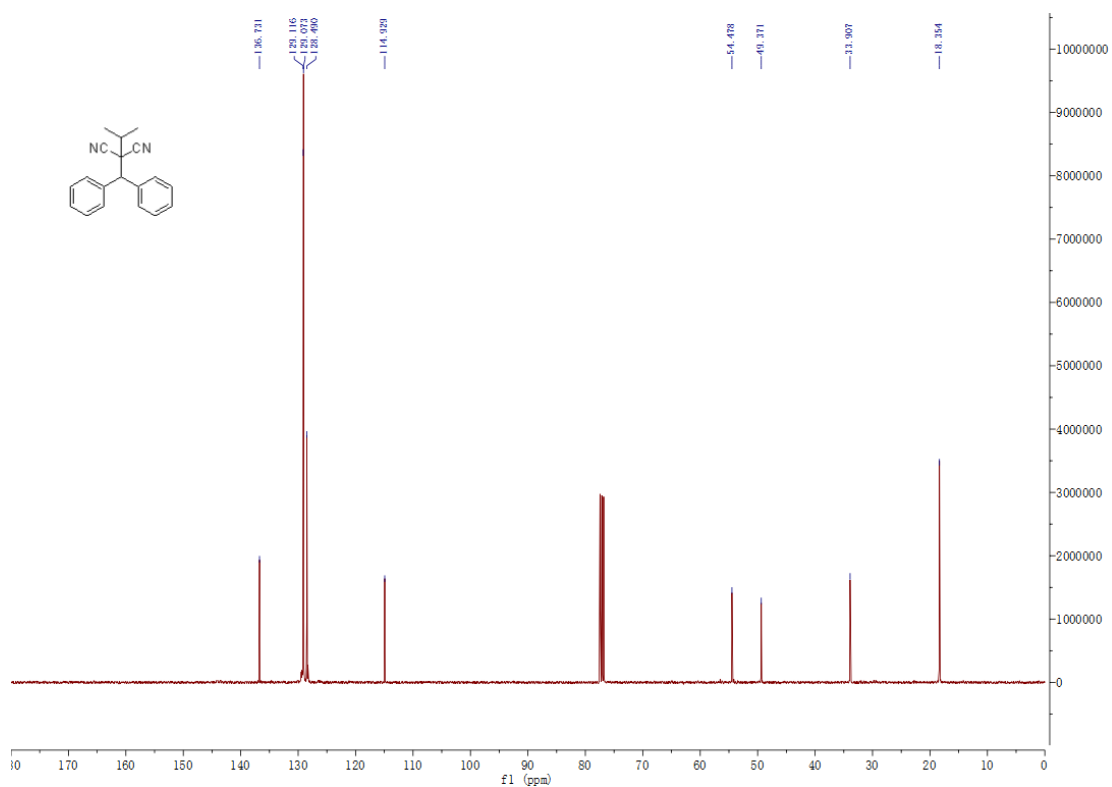
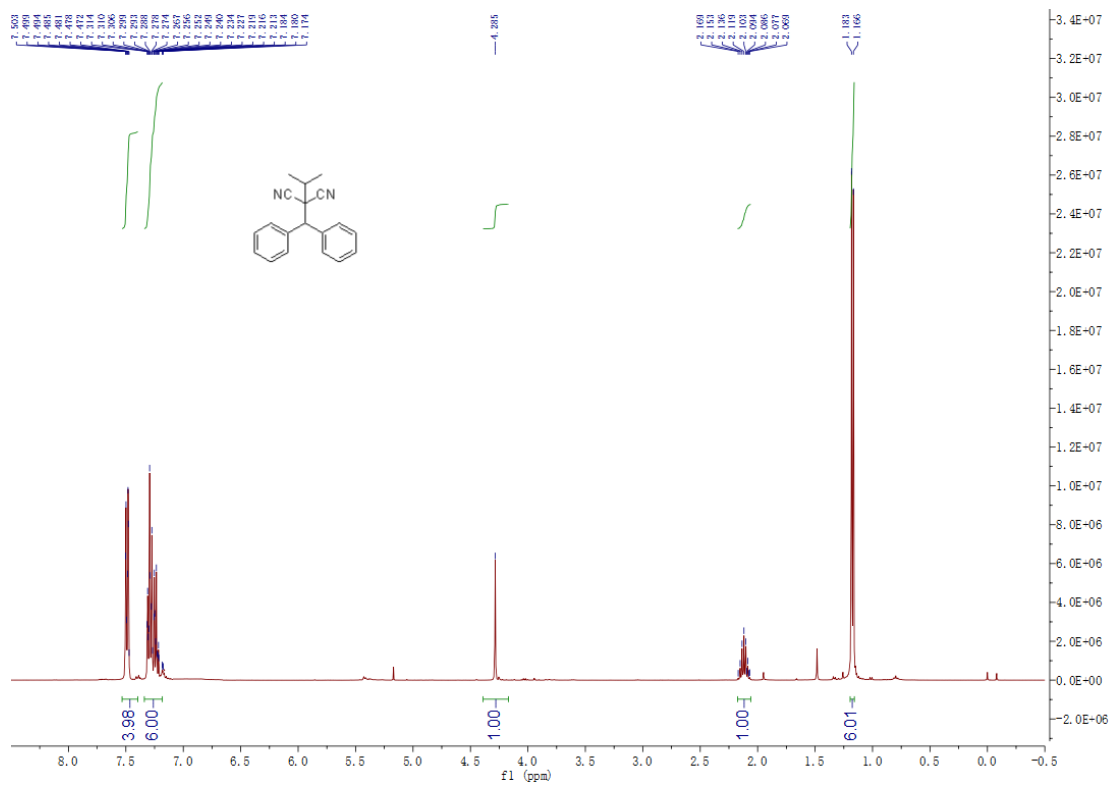


Chemical structure: N#CC(c1ccccc1)C(c2ccccc2)C#N

¹H NMR spectrum (DMSO-d₆) showing peaks at approximately 7.3 ppm (aromatic protons, integral 4.98), 4.5 ppm (methine protons, integral 1.00), and 4.2 ppm (methylene protons, integral 0.99). The x-axis is labeled f1 (ppm) and ranges from 0.0 to 8.0. The y-axis represents intensity, ranging from -1,000,000 to 14,000,000.

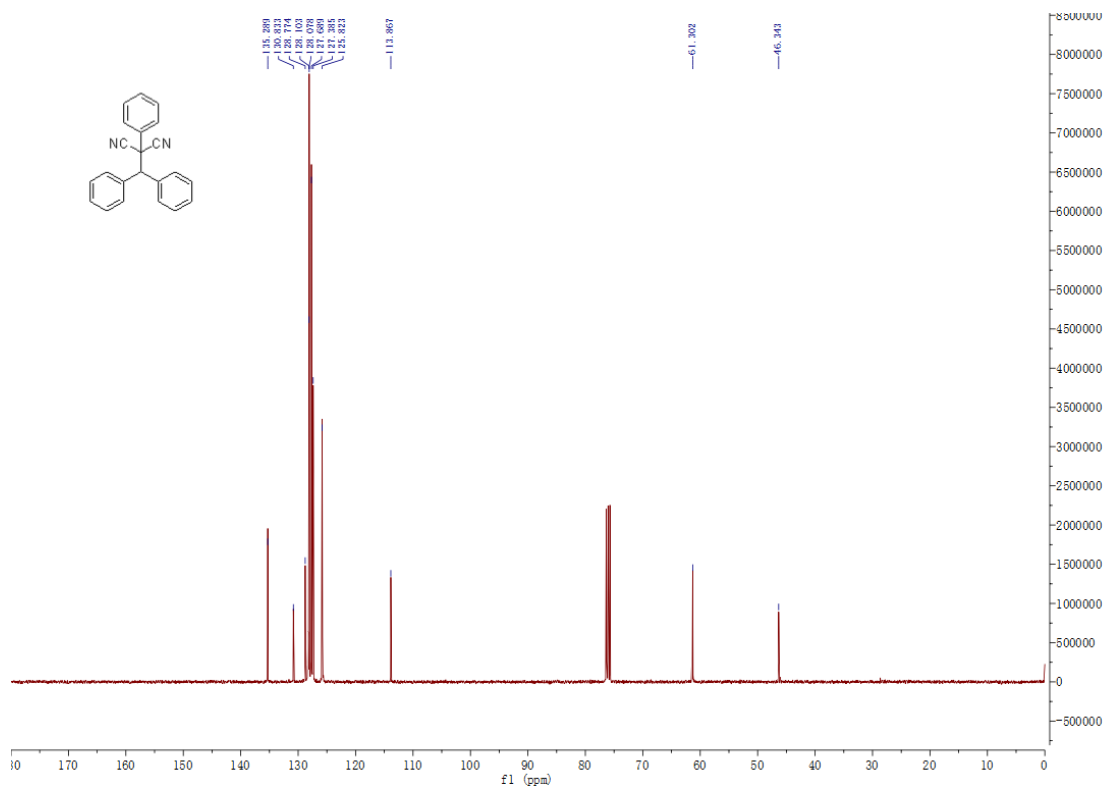


9b

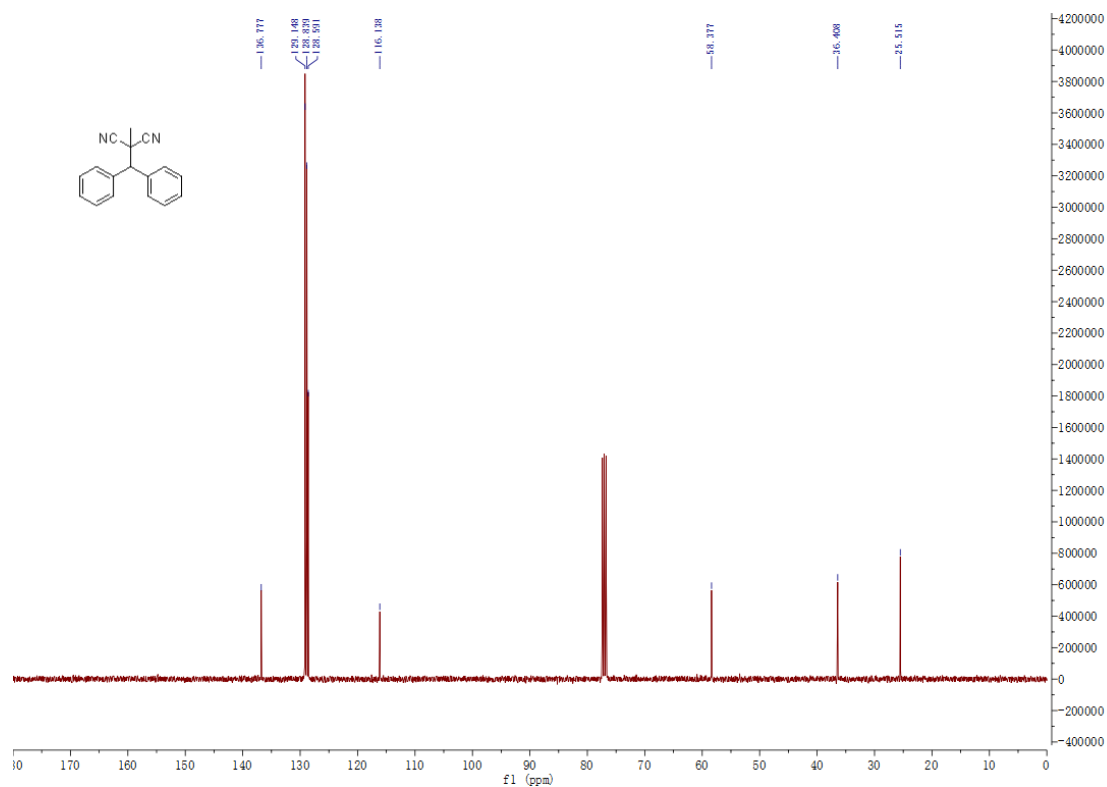
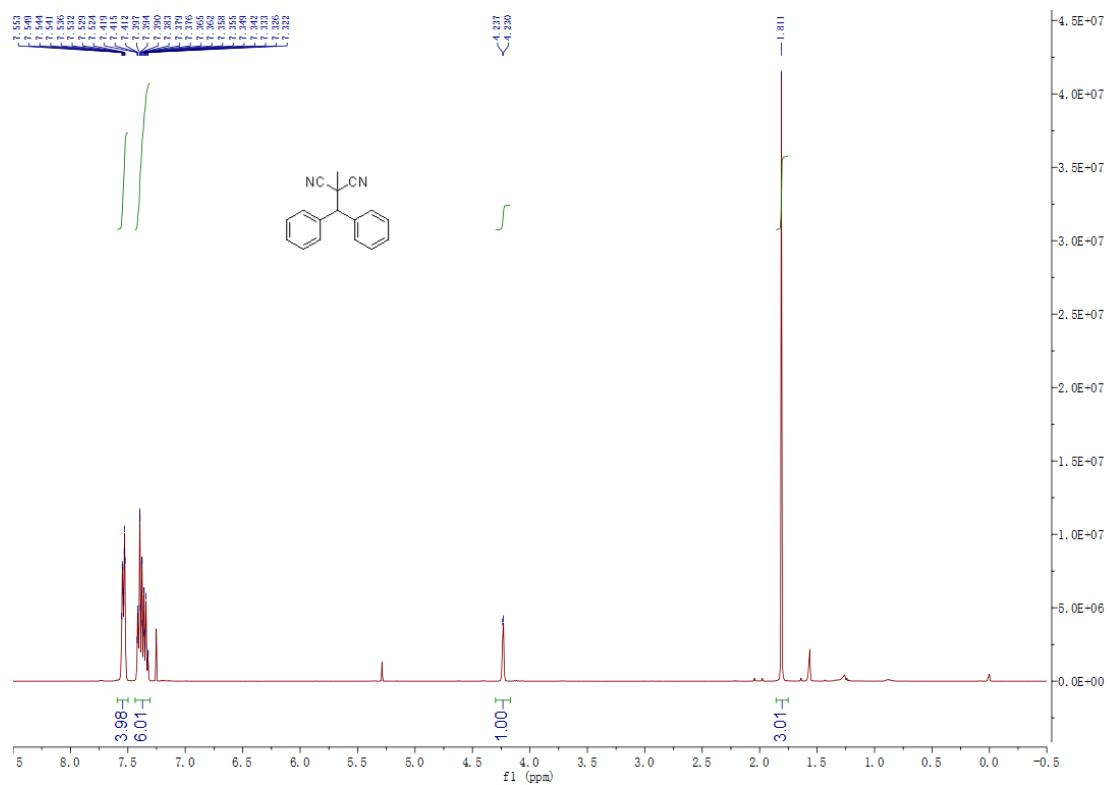


Chemical structure: N#CC(=C1C=CC=CC=C1)C(=C2C=CC=CC=C2)C#N

¹H NMR spectrum (CDCl₃) showing aromatic signals (7.0-7.6 ppm) and a singlet at 4.44 ppm. Integration values are 10.02 and 1.00.



9d



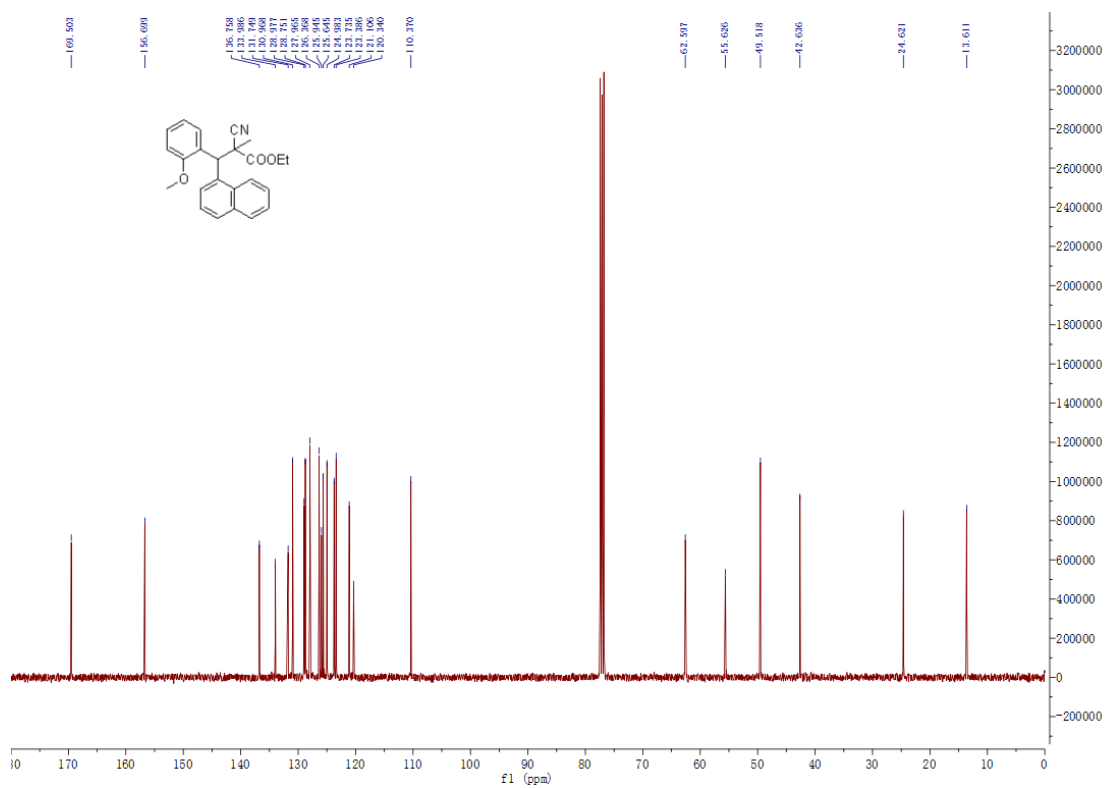
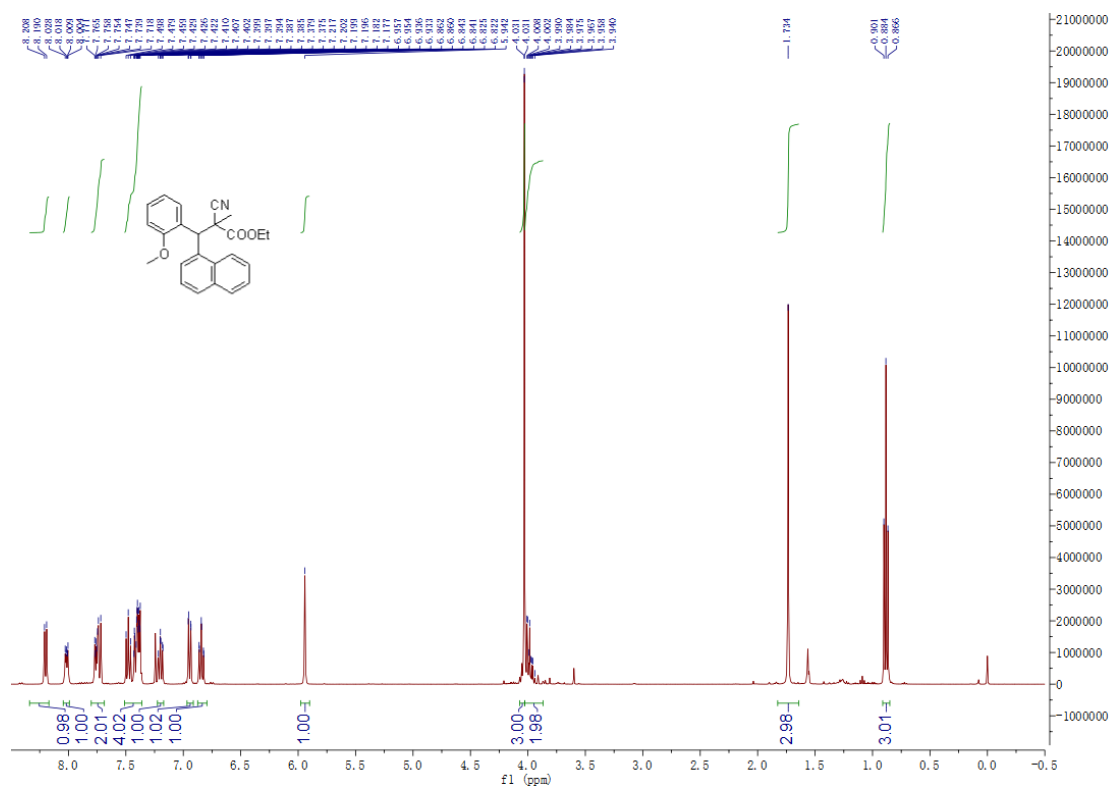
Chemical structure: CC1=CC=C(C=C1)C(NC(=O)OC2=CC=CC=C2)C3=CC=CC=C3

¹H NMR spectrum (CDCl₃) showing peaks and integrations:

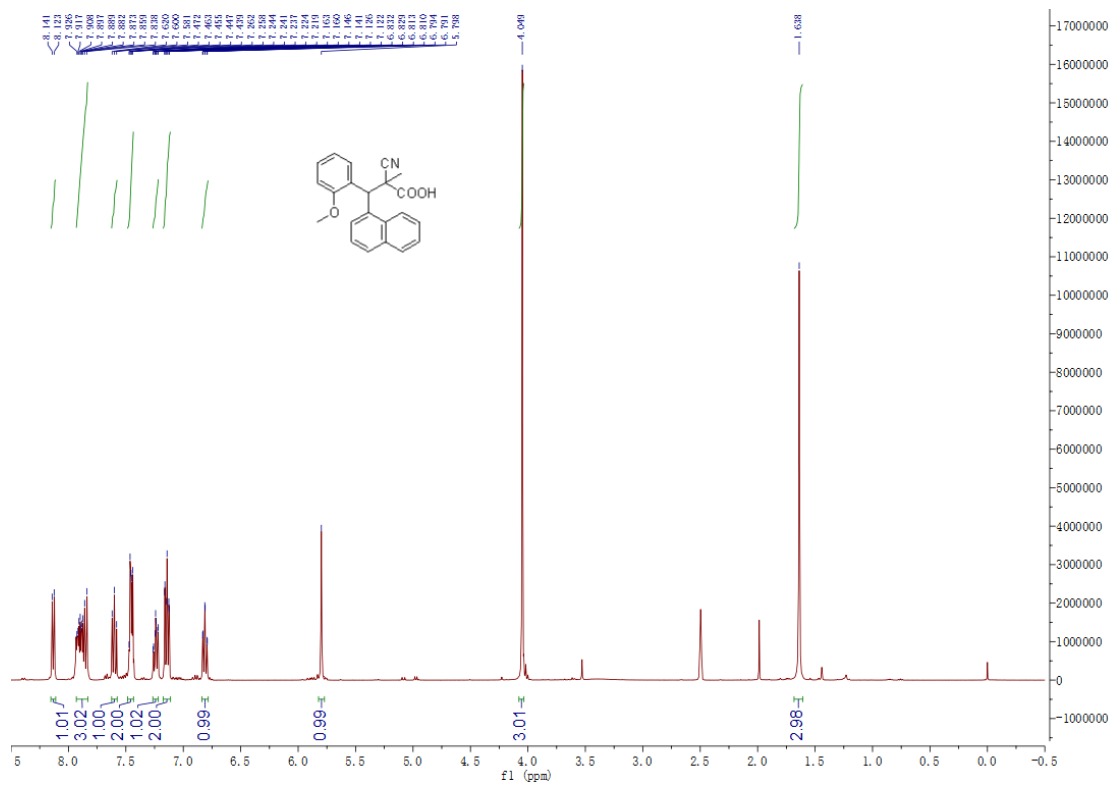
Chemical Shift (ppm)	Integration
7.80 - 7.60	1.02
7.50 - 7.40	2.00
7.30 - 7.20	3.02
7.10 - 7.00	2.00
6.90 - 6.80	0.98
6.70 - 6.60	1.00
6.50 - 6.40	3.01
6.30 - 6.20	1.00
6.10 - 6.00	1.00
5.60	1.00
3.80	2.99
2.30	2.98



11



12



13

