Supporting Information for

Monodentate Phosphorus Ligand-Enabled General Palladium-Catalyzed Allylic C–H Alkylation of Terminal Alkenes

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Table of Contents

1. General Data

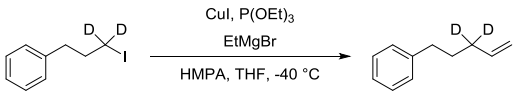
NMR spectra were recorded on a Bruker-400 MHz spectrometer. The high resolution mass spectra (HRMS) were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Brucker DaltonicsInc (EI+). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Enantiomeric excesses were performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm). Chiralpak OD-H, AD-H, IC, IF columns were purchased from Daicel Chemical Industries, LTD and Kromasil CHI-TBB columns were purchased from Akzo Nobel. Optical rotations were measured on Perkin Elmer Model 343 Polarimeter and Jasco P-1010 Polarimeter.

Materials: Starting materials were purchased from commercial suppliers (Aldrich, Acros, TCI, J&K, etc.) and used as supplied unless otherwise stated. $Pd_2(dba)_3$ and Pd(dba)2 were purchased from Aldrich. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

2. Synthesis of Starting Materials

Nucleophiles substrates **1d**, **1f-1k**, **2a-2c**, **2j-2n**, **2q-2s** were commercially available reagents and used without further purification.

Alkenes substrates **1a, 1c**[1], **1e**[2], **1l**[3], **1m**[4], **1n**[5], **1o**[6], **2d**[7], **2e**[8], **2f**[9], **2g**[10], **2h**[11], **2i**[12], **2o-2p**[13], **2t**[14], **2u**[15], **2v**[16], **2w**[13], **2x**[17] were synthesized according to the reported literature procedure.



CuI (3.6 g, 19 mmol) was added into a flame-dried flask and flashed with N_2. Anhydrous THF (80 mL) was added and the suspension was cooled to -40 °C. Vinylmagnesium bromide (57 mL, 57 mmol, 1 M in THF) was added and the reaction was stirred for 15 min at -40 °C. Then HMPA (6.6 mL, 38 mmol), triethyl phosphite (6.3 g, 38 mmol), and (3-iodopropyl-3,3-d_2)benzene (4.8 g, 19 mmol, dissolved in 5 mL THF) were added consecutively and the mixture was stirred at -40 °C for 1 h and room temperature for 2 h. Then saturated aq. NH_4Cl was added to quench the reaction and the crude product was washed with brine, extracted with EtOAc (50 mL x 3). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane afforded **2d**-d_2 (2.1 g, 74% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 5.84 (dd, J = 17.1, 10.2 Hz, 1H), 5.03 (dd, J = 17.1, 2.1 Hz, 1H), 4.99 (dd, J = 10.2, 2.1 Hz, 1H), 2.69 – 2.54 (m, 2H), 1.71 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.62, 138.69, 128.59, 128.41, 125.81, 114.91, 35.40, 30.61. **IR** (KBr) γ 3229, 2923, 959, 857 cm^{-1}.

3. General procedure for Allylic C−H alkylation and Optimization of the Reaction Conditions

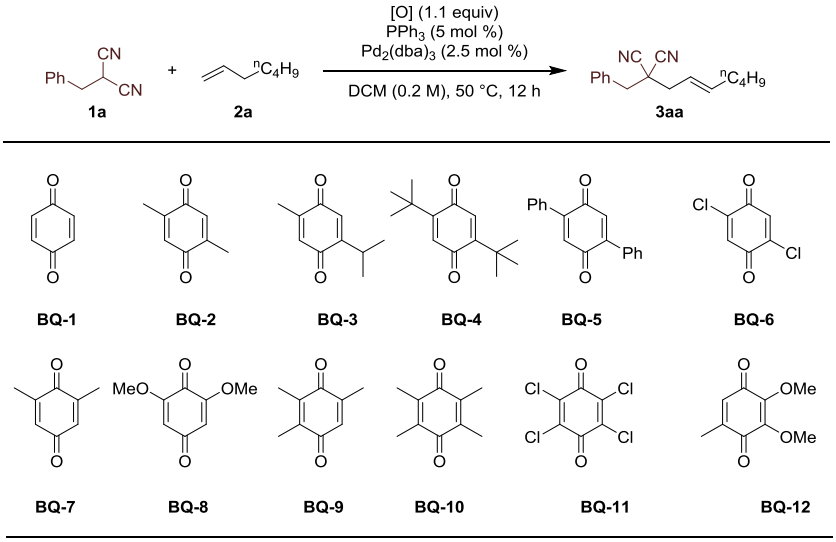
3.1 General Procedure for Allylic C−H Alkylation

*Using **L11** as the ligand*: To a flame-dried and N_2-purged Schlenk tube (10 mL) were added **1** (0.2

mmol), $Pd_2(dba)_3$ (2.5 mol %), phosphoramidite **L11** (5 mol%), 2,5-DTBQ (1.1 equiv) and a stirring bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by addition of 1,4-dioxane (1 mL) and alkene **2** (0.4 mmol). The mixture was stirred at 50 °C for 24 h. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to provide product.

Using PPh_3 as the ligand: To a flame-dried and N_2-purged Schlenk tube (10 mL) were added **1** (0.1 mmol), $Pd_2(dba)_3$ (2.5 mol %), PPh_3 (5 mol%), 2,5-DTBQ (1.1 equiv) and a stirring bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by addition of 1,4-dioxane (0.5 mL) and alkene **2** (0.2 mmol). The mixture was stirred at 50 °C for 24 h. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to provide product.

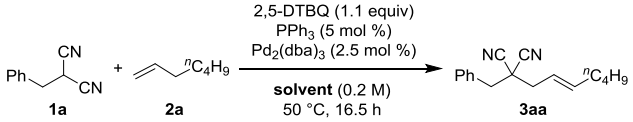
Table S1. Screening of Oxidants[a]



entry	[O]	Yield (%)[b]
1	**BQ-1**	3
2	**BQ-2**	35
3	**BQ-3**	21
4	**BQ-4**	48
5	**BQ-5**	41
6	**BQ-6**	n.r.
7	**BQ-7**	13
8	**BQ-8**	n.r.
9	**BQ-9**	n.r.
10	**BQ-10**	n.r.
11	**BQ-11**	n.r.
12	**BQ-12**	n.r.

[a] Reaction conditions: Unless indicated otherwise, reactions of **1a** (0.10 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (0.0025 mmol), PPh_3 (0.005 mmol), and [**BQ**] (0.11 mmol) were carried out in DCM (0.5 mL) at 50 °C for 12 h. [b] The yields were determined by ^{1}H-NMR analysis of the crude products based on 1,3,5-triacetylbenzene as the internal standard.

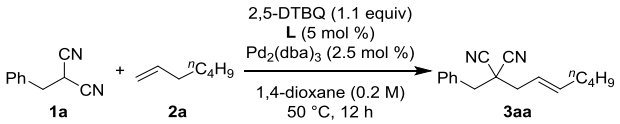
Table S2. Screening of Solvents[a]

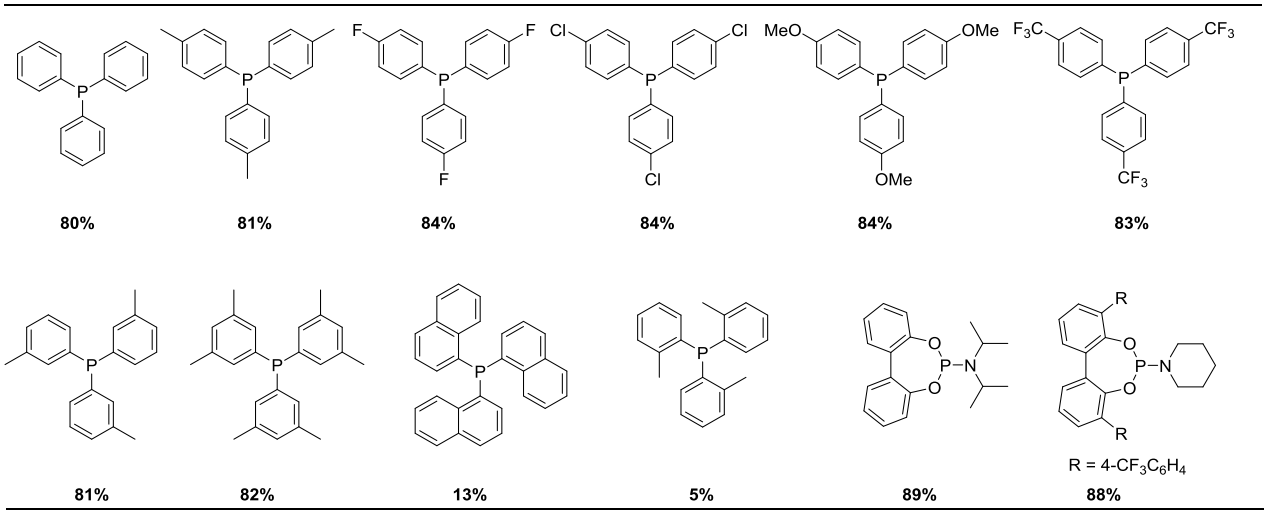


entry	solvent	Yield (%)[b]
1	DCM	48
2	$CHCl_3$	12
3	DCE	37
4	toluene	81
5	EtOH	58
6	THF	63
7	MTBE	73
8	1,4-dioxane	82
9	acetone	81
10	EtOAc	68
11	CH_3CN	25

[a] Reaction conditions: Unless indicated otherwise, reactions of **1a** (0.10 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (0.0025 mmol), PPh_3 (0.005 mmol), and 2,5-DTBQ (0.11 mmol) were carried out in solvent (0.5 mL) at 50 °C for 16.5 h. [b] The yields were determined by ^{1}H-NMR analysis of the crude products based on 1,3,5-triacetylbenzene as the internal standard.

Table S3. Monodentate Phosphine Ligands Screening[a]



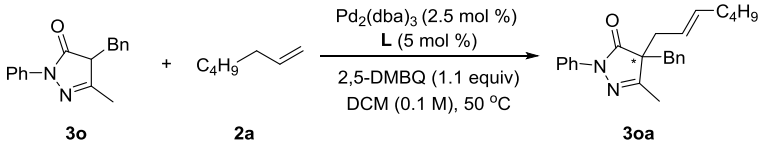


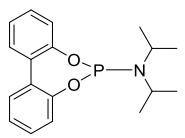
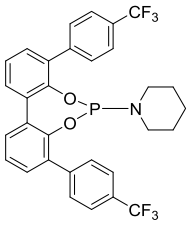
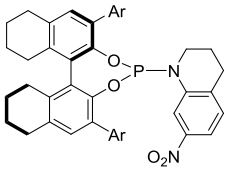
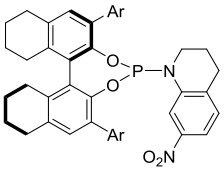
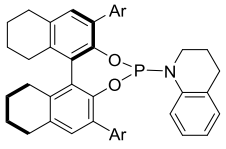
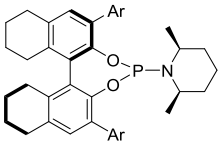
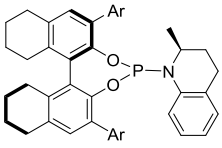
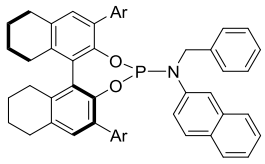
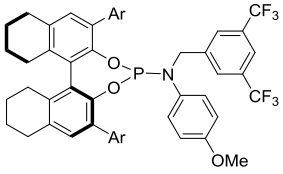
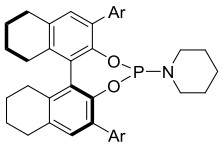
[a] Reaction conditions: Unless indicated otherwise, reactions of **1a** (0.10 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (0.0025 mmol), **L** (0.005 mmol), and 2,5-DTBQ (0.11 mmol) were carried out in 1,4-dioxane (0.5 mL) at 50 °C for 12 h. The yields were determined by ^{1}H-NMR analysis of the crude products based on 1,3,5-triacetylbenzene as the internal standard.

3.2 General Procedure for Asymmetric Allylic C−H Alkylation with pyrazol-5-ones

To a flame-dried and N_2-purged Schlenk tube (10 mL) were added **5** (0.1 mmol), $Pd(dba)_2$ (10 mol %), phosphoramidite **L13** (10 mol %), 2,5-DTBQ (1.1 equiv), **A5** (10 mol %), 5 Å (60 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by addition of toluene (1 mL) and alkene **2** (0.12 mmol). The mixture was stirred at 50 °C for 48 h. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to provide product **6**.

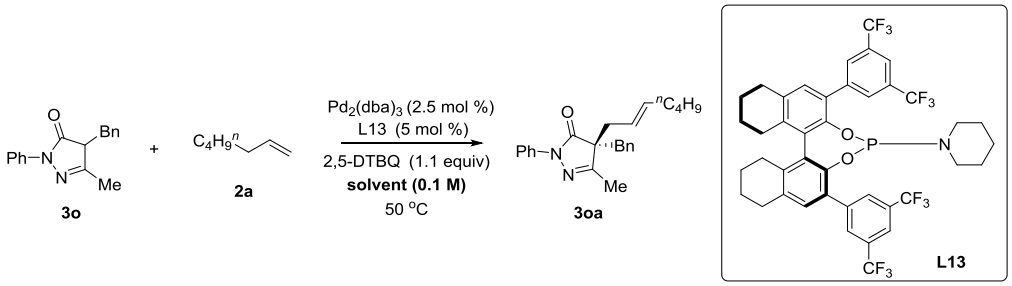
Table S4. Screening of Ligands[a]



 trace[b]	 73% yield[b]	 Ar = 4-NO_2-C_6H_3 ee: 4%	 Ar = 3,5-$(CF_3)_2$-C_6H_3 ee: 12%	 Ar = 3,5-$(CF_3)_2$-C_6H_3 45% yield 14% ee
 Ar = 3,5-$(CF_3)_2$-C_6H_3 10% yield 0% ee	 Ar = 3,5-$(CF_3)_2$-C_6H_3 45% yield 13% ee	 Ar = 3,5-$(CF_3)_2$-C_6H_3 28% yield 10% ee	 Ar = 3,5-$(CF_3)_2$-C_6H_3 11% yield 18% ee	 Ar = 3,5-$(CF_3)_2$-C_6H_3 18% yield 4% ee

[a] Reaction conditions: unless indicated otherwise, reactions of **3o** (0.1 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (2.5 mol %), **L** (5 mol %), and 2,5-DMBQ (0.11 mmol) were carried out in DCM (1.0 mL) at 50 °C for 20 h. The yields were determined by ^{1}H-NMR analysis of the crude products based on 1,3,5-triacetylbenzene as the internal standard. The ee value was determined by chiral HPLC analysis. [b] The reaction was carried out in 1,4-dioxane at 70 °C.

Table S5. Screening of Solvents[a]



entry	solvent	Yield (%)	L/B	ee (%)
1	toluene	63	4.5:1	64
2	EtOAc	35	4.4:1	44

3	1,4-dioxane	53	4.2:1	50
4	THF	47	3.3:1	27
5	acetone	35	14:1	20

[a] Reaction conditions: unless indicated otherwise, reactions of **3o** (0.1 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (2.5 mol %), **L13** (5 mol %), and 2,5-DMBQ (0.11 mmol) were carried out in solvent (1.0 mL) at 50 °C for 20 h. The yields were determined by ^{1}H-NMR analysis of the crude products based on 1,3,5-triacetylbenzene as the internal standard. The ee value was determined by chiral HPLC analysis.

4. Characterization Data for the Products

(*E*)-2-benzyl-2-(hept-2-en-1-yl)malononitrile (3aa). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow solid. Yield: 93% (46.9 mg) for **L11**, 76% (17.8 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.32 (m, 5H), 5.83 (dt, J = 15.0, 6.8 Hz, 1H), 5.62 – 5.48 (m, 1H), 3.18 (s, 2H), 2.65 (dd, J = 7.3, 0.7 Hz, 2H), 2.19 – 2.06 (m, 2H), 1.45 – 1.28 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.39, 132.21, 130.34, 129.09, 128.87, 119.95, 115.25, 42.71, 40.68, 39.89, 32.36, 31.17, 22.25, 14.00. **IR** (KBr) γ 3033, 2929, 2858, 2247, 1497, 1456, 1059, 971, 764, 702, 593 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{17}H_{21}N_2$: 253.1705, observed: 253.1701.

(*E*)-2-(hept-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3ba). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow solid. Yield: 95% (57.4 mg) for **L11**, 92% (27.8 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 4H), 7.57 – 7.42 (m, 3H), 5.91 – 5.78 (m, 1H), 5.65 – 5.52 (m, 1H), 3.36 (s, 2H), 2.69 (d, J = 7.2 Hz, 2H), 2.13 (q, J = 6.9 Hz, 2H), 1.47 – 1.23 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.45, 133.36, 133.28, 129.81, 129.65, 128.92, 128.15, 127.87, 127.61, 126.78, 126.73, 119.96, 115.32, 42.87, 40.74, 39.86, 32.37, 31.19, 22.27, 14.00. **IR** (KBr) γ 2957, 2928, 2856, 1652, 1508, 971, 859, 820, 752, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{21}H_{23}N_2$: 303.1861, observed: 303.1860.

methyl (*E*)-2-benzyl-2-cyanonon-4-enoate (3ca). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 95% (54.1 mg) for **L11**, 31% (8.8 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 5H), 5.66 (dt, J = 15.0, 6.8 Hz, 1H), 5.50 – 5.39 (m, 1H), 3.66 (s, 3H), 3.19 (d, J = 13.5 Hz, 1H), 3.04 (d, J = 13.5 Hz, 1H), 2.68 (ddd, J = 13.7, 7.5, 0.6 Hz, 1H), 2.52 (ddd, J = 13.7, 7.0, 0.8 Hz, 1H), 2.04 (q, J = 6.8 Hz, 2H), 1.41 – 1.26 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.89, 137.83, 134.33, 129.96, 128.69, 127.95, 121.80, 118.75, 53.19, 51.99, 42.56, 40.63, 32.28, 31.36, 22.17, 13.97. **IR** (KBr) γ 3033, 2956, 2929, 2857, 1746, 1455, 1233, 1053, 971, 701, 497 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{18}H_{24}NO_2$: 286.1807, observed: 286.1806.

ethyl (*E*)-2-cyano-2-methylnon-4-enoate (3da). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 92% (41.0 mg) for **L11**, 64% (14.3 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.68 – 5.58 (m, 1H), 5.46 – 5.35 (m, 1H), 4.31 – 4.17 (m, 2H), 2.59 (ddd, J = 13.7, 7.3, 0.9 Hz, 1H), 2.43 (ddd, J = 13.7, 7.3, 0.9 Hz, 1H), 2.03 (q, J = 6.6 Hz, 2H), 1.55 (s, 3H), 1.39 – 1.22 (m, 7H), 0.91 – 0.84 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.21, 137.68, 121.92, 120.00, 62.76, 44.21, 41.33, 32.28, 31.38, 22.69, 22.22, 14.16, 13.99. **IR** (KBr) γ 2959, 2930, 2873, 2244, 1744,

1457, 1380, 1226, 972, 858, 502 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{22}NO_2$: 224.1651, observed: 224.1652.

(*E*)-2-methyl-2-nitro-1-phenylnon-4-en-1-one (3ea). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 55% (30.3 mg) for **L11**, 7% (1.9 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H), 7.60 – 7.52 (m, 1H), 7.46 – 7.38 (m, 2H), 5.54 (dt, J = 15.0, 6.8 Hz, 1H), 5.25 (dtt, J = 15.1, 7.4, 1.4 Hz, 1H), 3.03 (dd, J = 14.2, 7.2 Hz, 1H), 2.93 (dd, J = 14.2, 7.6 Hz, 1H), 1.99 (q, J = 6.6 Hz, 2H), 1.88 (s, 3H), 1.35 – 1.21 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.95, 138.34, 133.74, 133.71, 128.95, 128.56, 120.72, 95.59, 41.55, 32.37, 31.37, 22.45, 22.21, 14.01. **IR** (KBr) γ 2957, 2929, 2858, 1693, 1548, 1448, 1383, 1345, 973, 791, 699 cm^{-1}. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{16}H_{21}NO_3Na$: 298.1419, observed: 298.1432.

ethyl (*E*)-2-cyanonon-4-enoate (3fa). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 92% (38.5 mg) for **L11**, 64% (13.4 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.72 – 5.61 (m, 1H), 5.41 (dt, J = 14.4, 7.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.54 – 3.47 (m, 1H), 2.66 – 2.59 (m, 2H), 2.03 (q, J = 6.7 Hz, 2H), 1.32 (dd, J = 9.0, 5.3 Hz, 7H), 0.89 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.89, 136.85, 122.75, 116.45, 62.90, 38.34, 33.19, 32.24, 31.36, 22.25, 14.18, 14.03. **IR** (KBr) γ 2958, 2928, 2856, 1748, 1540, 1196, 1034, 971 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{12}H_{20}NO_2$: bserved: 210.1494, observed: 210.1490.

ethyl (*E*)-2-acetylnon-4-enoate (3ga). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 55% (24.9 mg) for **L11**, 28% (6.3 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.55 – 5.44 (m, 1H), 5.36 – 5.26 (m, 1H), 4.23 – 4.14 (m, 2H), 3.46 (t, J = 7.5 Hz, 1H), 2.55 – 2.49 (m, 2H), 2.21 (s, 3H), 2.00 – 1.91 (m, 2H), 1.35 – 1.18 (m, 7H), 0.92 – 0.81 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.05, 169.58, 134.07, 125.41, 61.45, 60.09, 32.27, 31.59, 31.44, 29.22, 22.24, 14.26, 14.04. **IR** (KBr) γ 2959, 2930, 2873, 2244, 1744, 1457, 1380, 1226, 972, 858, 502 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{23}O_3$: 227.1647, observed: 227.1645.

ethyl (*E*)-2-nitronon-4-enoate (3ha). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 73% (33.4 mg) for **L11**, 58% (13.3 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.70 – 5.55 (m, 1H), 5.38 – 5.26 (m, 1H), 5.09 (dd, J = 9.3, 5.5 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.00 – 2.74 (m, 2H), 1.99 (q, J = 6.6 Hz, 2H), 1.36 – 1.20 (m, 7H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.32, 137.20, 121.43, 88.13, 63.11, 33.62, 32.24, 31.27, 22.20, 14.04, 14.00. **IR** (KBr) γ 2959, 2930, 2873, 1751, 1560, 1466, 1203, 1052, 972, 859 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{11}H_{20}NO_4$: 230.1392, observed: 230.1403.

ethyl (*E*)-2-(phenylsulfonyl)non-4-enoate (3ia). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 58% (37.6 mg) for **L11**, 11% (3.6 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.72 – 7.65 (m, 1H), 7.61 – 7.53 (m, 2H), 5.52 (dt, J = 15.0, 6.8 Hz, 1H), 5.22 (ddd, J = 15.1, 7.6, 6.3 Hz, 1H), 4.09 (qd, J = 7.1, 1.3 Hz, 2H), 3.95 (dd, J = 11.5, 3.8 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.66 – 2.53 (m, 1H), 1.93 (q, J = 6.5 Hz, 2H), 1.31 – 1.19 (m, 4H), 1.14 (t,

J = 7.1 Hz, 3H), 0.84 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.60, 137.31, 135.89, 134.37, 129.52, 129.15, 122.80, 70.82, 62.22, 32.21, 31.34, 30.12, 22.13, 14.04, 13.98. **IR** (KBr) γ 2929, 1739, 1541, 1447, 1326, 1149, 1083, 970, 857 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{17}H_{25}O_4S$: 325.1474, observed: 325.1476.

(*E*)-2-acetyl-2-(hept-2-en-1-yl)cyclopentan-1-one (3ja). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 70% (31.1 mg) for **L11**, 63% (14.0 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.57 – 5.43 (m, 1H), 5.21 – 5.09 (m, 1H), 2.67 – 2.56 (m, 2H), 2.39 – 2.21 (m, 3H), 2.20 (s, 3H), 1.96 (q, J = 6.7 Hz, 2H), 1.90 – 1.80 (m, 2H), 1.79 – 1.70 (m, 1H), 1.36 – 1.20 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 215.87, 204.34, 135.64, 123.62, 68.99, 38.86, 38.35, 32.33, 31.58, 30.26, 26.30, 22.26, 19.43, 14.03. **IR** (KBr) γ 2959, 2928, 1739, 1703, 1457, 1045, 971, 739 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{14}H_{23}O_2$: 223.1698, observed: 223.1689.

methyl (*E*)-1-(hept-2-en-1-yl)-2-oxocyclopentane-1-carboxylate (3ka). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 62% (29.5 mg) for **L11**, 46% (10.9 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.49 (dt, J = 15.0, 6.8 Hz, 1H), 5.32 – 5.16 (m, 1H), 3.69 (s, 3H), 2.59 (ddd, J = 13.8, 7.1, 0.8 Hz, 1H), 2.49 – 2.34 (m, 2H), 2.33 – 2.15 (m, 2H), 2.05 – 1.81 (m, 5H), 1.37 – 1.19 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.91, 171.61, 135.77, 124.04, 60.52, 52.64, 38.32, 36.96, 32.36, 32.06, 31.65, 22.26, 19.62, 14.02. **IR** (KBr) γ 2956, 2928, 1753, 1729, 1434, 1162, 972 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{14}H_{23}O_3$: 239.1647, observed: 239.1647.

methyl (*E*)-3-(hept-2-en-1-yl)-2-oxotetrahydrofuran-3-carboxylate (3la). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 48% (23.0 mg) for **L11**, 38% (9.1 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.65 – 5.53 (m, 1H), 5.34 – 5.23 (m, 1H), 4.38 – 4.25 (m, 2H), 3.77 (s, 3H), 2.76 – 2.60 (m, 2H), 2.54 (ddd, J = 14.0, 6.9, 1.1 Hz, 1H), 2.30 (dt, J = 13.2, 8.6 Hz, 1H), 2.00 (q, J = 6.6 Hz, 2H), 1.42 – 1.18 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.80, 170.18, 137.12, 122.89, 66.37, 54.26, 53.28, 37.23, 32.37, 31.53, 30.94, 22.27, 14.03. **IR** (KBr) γ 2956, 2926, 1777, 1739, 1213, 1167, 974 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{21}O_4$: 241.1440, observed: 241.1440.

(*E*)-4-(hept-2-en-1-yl)-2-(4-methoxyphenyl)-4-methyloxazol-5(4H)-one (3ma). Silica gel column chromatography (PE/EtOAc = 20/1), Yellow oil. Yield: 65% (39.1 mg) for **L11**, <5% for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 5.60 – 5.48 (m, 1H), 5.24 (dt, J = 15.0, 7.3 Hz, 1H), 3.87 (s, 3H), 2.59 – 2.45 (m, 2H), 1.91 (q, J = 6.7 Hz, 2H), 1.50 (s, 3H), 1.29 – 1.07 (m, 4H), 0.75 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.86, 163.21, 159.49, 137.02, 129.87, 122.28, 118.45, 114.29, 70.14, 55.63, 41.62, 32.24, 31.43, 23.42, 22.03, 13.94. **IR** (KBr) γ 2957, 2930, 2871, 1819, 1653, 1609, 1513, 1257, 1172, 1016, 999, 840, 688 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{18}H_{24}NO_3$: 302.1756, observed: 302.1755.

tert-butyl (*E*)-3-(hept-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (3na). Silica gel column

chromatography (PE/EtOAc = 20/1), Yellow solid. Yield: 80% (64.8 mg) for **L11**, 75% (30.4 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.91 (d, J = 8.2 Hz, 1H), 7.39 – 7.17 (m, 8H), 5.42 (dt, J = 15.1, 6.9 Hz, 1H), 5.05 – 4.95 (m, 1H), 3.07 (dd, J = 13.4, 8.1 Hz, 1H), 2.92 (ddd, J = 13.3, 6.4, 1.1 Hz, 1H), 1.81 (q, J = 6.7 Hz, 2H), 1.61 (s, 9H), 1.18 – 1.02 (m, 4H), 0.78 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.60, 149.43, 140.08, 139.60, 136.43, 130.79, 128.67, 128.42, 127.64, 127.43, 125.32, 124.37, 123.03, 115.18, 84.28, 57.30, 41.77, 32.10, 31.36, 28.20, 21.89, 13.91. **IR** (KBr) γ 2929, 1765, 1731, 1347, 1347, 1150, 968 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{32}NO_3$: 406.2382, observed: 406.2408.

(*E*)-4-benzyl-4-(hept-2-en-1-yl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3oa). Silica gel column chromatography (PE/EtOAc = 20/1), Yellow solid. Yield: 73% (52.6 mg) for **L11**, <5% for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.36 – 7.27 (m, 2H), 7.19 – 7.03 (m, 6H), 5.58 (dt, J = 15.0, 6.9 Hz, 1H), 5.11 (dt, J = 14.9, 7.3 Hz, 1H), 3.24 (d, J = 13.7 Hz, 1H), 2.88 (d, J = 13.7 Hz, 1H), 2.69 (dd, J = 13.7, 6.9 Hz, 1H), 2.44 (dd, J = 13.7, 7.6 Hz, 1H), 2.12 (s, 3H), 1.89 (q, J = 6.6 Hz, 2H), 1.27 – 1.13 (m, 4H), 0.76 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.91, 161.61, 137.80, 136.28, 135.18, 129.06, 128.77, 128.50, 127.31, 125.12, 122.13, 119.45, 61.44, 40.98, 38.55, 32.16, 31.44, 22.07, 14.81, 13.91. **IR** (KBr) γ 2956, 2922, 2852, 1707, 1596, 1500, 1366, 755, 722 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{24}H_{29}N_2O$: 361.2280, observed: 361.2269.

2-allyl-2-(naphthalen-2-ylmethyl)malononitrile (3bb). Silica gel column chromatography (PE/EtOAc = 15/1), White solid. Yield: 54% (26.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 4H), 7.56 – 7.51 (m, 2H), 7.49 (dd, J = 8.4, 1.9 Hz, 1H), 6.06 – 5.88 (m, 1H), 5.51 – 5.40 (m, 2H), 3.38 (s, 2H), 2.75 (dt, J = 7.3, 1.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.34, 133.30, 129.83, 129.43, 128.96, 128.70, 128.14, 127.87, 127.55, 126.83, 126.76, 123.59, 115.07, 42.90, 41.51, 39.29. **IR** (KBr) γ 3061, 2248, 1508, 1444, 1062, 943, 820, 755, 475 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{17}H_{15}N_2$: 247.1235, observed: 247.1236.

(*E*)-2-(3-cyclohexylallyl)-2-(naphthalen-2-ylmethyl)malononitrile (3bc). Silica gel column chromatography (PE/EtOAc = 15/1), White solid. Yield: 78% (51.2 mg) for **L11**, 20% (6.6 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 4H), 7.56 – 7.51 (m, 2H), 7.49 (dd, J = 8.4, 1.8 Hz, 1H), 5.79 (dd, J = 15.3, 6.8 Hz, 1H), 5.54 (dtd, J = 15.5, 7.3, 1.3 Hz, 1H), 3.35 (s, 2H), 2.67 (d, J = 7.3 Hz, 2H), 2.14 – 1.98 (m, 1H), 1.85 – 1.73 (m, 4H), 1.72 – 1.62 (m, 1H), 1.39 – 1.07 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.07, 133.30, 133.22, 129.77, 129.63, 128.85, 128.09, 127.83, 127.59, 126.73, 126.67, 117.51, 115.27, 42.73, 40.82, 40.62, 39.84, 32.70, 26.10, 25.92. **IR** (KBr) γ 2956, 2925, 2851, 2247, 1509, 1448, 971, 859, 820, 753, 477 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{25}N_2$: 329.2018, observed: 329.2018.

(*E*)-2-(naphthalen-2-ylmethyl)-2-(5-phenylpent-2-en-1-yl)malononitrile (3bd). Silica gel column chromatography (PE/EtOAc = 15/1), Yellow solid. Yield: 90% (63.0 mg) for **L11**, 83% (29.1 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, 3H), 7.81 (d, J = 1.3 Hz, 1H), 7.58 – 7.50 (m,

2H), 7.45 (dd, J = 8.5, 1.8 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 5.85 (dt, J = 14.9, 6.8 Hz, 1H), 5.64 – 5.52 (m, 1H), 3.24 (s, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.67 (d, J = 7.3 Hz, 2H), 2.48 (q, J = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.20, 139.02, 133.28, 133.20, 129.75, 129.60, 128.82, 128.58, 128.51, 128.09, 127.83, 127.57, 126.73, 126.67, 126.12, 120.88, 115.21, 42.57, 40.56, 39.62, 35.28, 34.20. **IR** (KBr) γ 3059, 3026, 2927, 2854, 1601, 1454, 970, 821, 752, 700, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}N_2$: 351.1861, observed: 351.1862.

(*E*)-2-(naphthalen-2-ylmethyl)-2-(7-phenylhept-2-en-6-yn-1-yl)malononitrile (3be). Silica gel column chromatography (PE/EtOAc = 15/1), Yellow solid. Yield: 73% (54.6 mg) for **L11**, 29% (10.8 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.72 (m, 4H), 7.59 – 7.48 (m, 2H), 7.47 – 7.35 (m, 3H), 7.32 – 7.17 (m, 3H), 6.00 – 5.88 (m, 1H), 5.79 – 5.67 (m, 1H), 3.35 (s, 2H), 2.74 (d, J = 7.2 Hz, 2H), 2.57 (t, J = 6.8 Hz, 2H), 2.49 – 2.41 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.10, 133.31, 133.24, 131.71, 129.80, 129.55, 128.89, 128.37, 128.16, 127.86, 127.85, 127.59, 126.76, 126.68, 123.73, 121.69, 115.23, 88.99, 81.61, 42.67, 40.60, 39.51, 31.84, 19.44. **IR** (KBr) γ 3055, 2926, 2849, 1508, 1489, 1178, 968, 821, 692, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{27}H_{23}N_2$: 375.1861, observed: 375.1862.

(*E*)-2-(6-(benzyloxy)hex-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3bf). Silica gel column chromatography (PE/EtOAc = 15/1), Colorless oil. Yield: 83% (65.4 mg) for **L11**, 74% (29.2 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 5H), 7.54 (dd, J = 6.3, 3.3 Hz, 2H), 7.49 (dd, J = 8.4, 1.9 Hz, 1H), 7.39 – 7.26 (m, 4H), 5.90 – 5.79 (m, 1H), 5.66 – 5.56 (m, 1H), 4.52 (s, 2H), 3.52 (t, J = 6.3 Hz, 2H), 3.34 (s, 2H), 2.68 (dd, J = 7.3, 1.1 Hz, 2H), 2.32 – 2.24 (m, 2H), 1.82 – 1.70 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.56, 138.61, 133.32, 133.25, 129.78, 129.58, 128.89, 128.48, 128.12, 127.84, 127.78, 127.66, 127.57, 126.76, 126.70, 120.58, 115.26, 73.06, 69.45, 42.81, 40.62, 39.80, 29.33, 29.12. **IR** (KBr) γ 3029, 2931, 2855, 2247, 1508, 1454, 1101, 970, 859, 821, 752, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{27}H_{27}N_2O$: 395.2123, observed: 395.2126.

(*E*)-2-(naphthalen-2-ylmethyl)-2-(5-phenoxypent-2-en-1-yl)malononitrile (3bg). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 96% (70.3 mg) for **L11**, 74% (27.1 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.81 (m, 4H), 7.63 – 7.52 (m, 2H), 7.50 (dd, J = 8.4, 1.8 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.04 – 6.88 (m, 3H), 6.04 – 5.88 (m, 1H), 5.82 – 5.67 (m, 1H), 4.06 (t, J = 6.3 Hz, 2H), 3.36 (s, 2H), 2.73 (d, J = 7.1 Hz, 2H), 2.64 (q, J = 6.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.77, 135.85, 133.30, 133.23, 129.78, 129.58, 129.52, 128.87, 128.10, 127.82, 127.54, 126.75, 126.68, 122.74, 120.94, 115.18, 114.63, 66.72, 42.69, 40.55, 39.56, 32.59. **IR** (KBr) γ 3058, 2928, 2247, 1600, 1496, 1244, 1172, 1037, 969, 754, 692, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{26}H_{22}N_2ONa$: 389.1630, observed: 389.1635.

(*E*)-2-(6-(tert-butyldiphenylsilyl)hex-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3bh). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 79% (85.6 mg) for **L11**, 68% (36.8 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 4H), 7.72 – 7.66 (m, 4H), 7.58 – 7.52 (m, 2H), 7.49 (dd, J = 8.4, 1.9 Hz, 1H), 7.45 – 7.36 (m, 6H), 5.87 – 5.73 (m, 1H), 5.64 –

5.54 (m, 1H), 3.72 (t, J = 6.2 Hz, 2H), 3.34 (s, 2H), 2.71 – 2.62 (m, 2H), 2.34 – 2.19 (m, 2H), 1.80 – 1.62 (m, 2H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.83, 135.68, 134.03, 133.34, 133.27, 129.79, 129.69, 129.62, 128.90, 128.13, 127.86, 127.75, 127.60, 126.77, 126.72, 120.30, 115.27, 63.13, 42.81, 40.67, 39.73, 31.94, 29.06, 27.00, 19.35. **IR** (KBr) γ 3051, 2931, 2857, 1651, 1472, 1428, 1110, 971, 859, 752, 703, 505 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{36}H_{39}N_2OSi$: 543.2832, observed: 543.2838.

(*E*)-7,7-dicyano-8-(naphthalen-2-yl)oct-4-en-1-yl acetate (3bi). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 81% (56.1 mg) for **L11**, 52% (18.0 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 4H), 7.56 – 7.50 (m, 2H), 7.48 (dd, J = 8.4, 1.9 Hz, 1H), 5.89 – 5.78 (m, 1H), 5.69 – 5.57 (m, 1H), 4.10 (t, J = 6.6 Hz, 2H), 3.35 (s, 2H), 2.68 (d, J = 7.2 Hz, 2H), 2.28 – 2.15 (m, 2H), 2.06 (s, 3H), 1.82 – 1.65 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.18, 138.62, 133.25, 133.17, 129.72, 129.48, 128.84, 128.06, 127.79, 127.50, 126.72, 126.65, 121.11, 115.14, 63.58, 42.76, 40.50, 39.78, 28.93, 27.91, 21.04. **IR** (KBr) γ 3056, 2955, 2852, 1735, 1440, 1366, 1245, 1042, 971, 822, 754, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{22}H_{23}N_2O_2$: 347.1760, observed: 347.1750.

(*E*)-2-(naphthalen-2-ylmethyl)-2-(4-(oxiran-2-yl)but-2-en-1-yl)malononitrile (3bj). Silica gel column chromatography (PE/EtOAc = 10/1), White solid. Yield: 91% (55.0 mg) for **L11**, 75% (22.7 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 4H), 7.57 – 7.50 (m, 2H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 5.90 – 5.80 (m, 1H), 5.78 – 5.68 (m, 1H), 3.37 (s, 2H), 3.07 – 2.98 (m, 1H), 2.79 (dd, J = 4.7, 4.0 Hz, 1H), 2.74 – 2.69 (m, 2H), 2.55 (dd, J = 4.9, 2.7 Hz, 1H), 2.51 – 2.42 (m, 1H), 2.42 – 2.32 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.10, 133.33, 133.27, 129.81, 129.44, 128.94, 128.12, 127.85, 127.53, 126.81, 126.75, 123.42, 115.14, 51.01, 46.51, 42.90, 40.62, 39.65, 35.24. **IR** (KBr) γ 3054, 2991, 2924, 1508, 973, 823, 754, 477 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{20}H_{19}N_2O$: 303.1497, observed: 303.1499.

(*E*)-2-(naphthalen-2-ylmethyl)-2-(11-oxoundec-2-en-1-yl)malononitrile (3bk). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 59% (43.9 mg) for **L11**, 55% (20.5 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.75 (d, J = 2.3 Hz, 1H), 7.87 (ddt, J = 9.5, 6.2, 2.6 Hz, 4H), 7.56 – 7.43 (m, 3H), 5.88 – 5.76 (m, 1H), 5.63 – 5.51 (m, 1H), 3.35 (d, J = 2.3 Hz, 2H), 2.68 (dd, J = 7.1, 2.2 Hz, 2H), 2.49 – 2.37 (m, 2H), 2.12 (q, J = 7.3 Hz, 2H), 1.68 – 1.53 (m, 2H), 1.46 – 1.31 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.94, 140.17, 133.25, 133.18, 129.70, 129.52, 128.82, 128.04, 127.77, 127.50, 126.69, 126.63, 120.04, 115.21, 43.90, 42.82, 40.63, 39.80, 32.50, 29.14, 29.09, 28.81, 22.04. **IR** (KBr) γ 3056, 2928, 2854, 1721, 1508, 1457, 969, 754, 504 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{29}N_2O$: 373.2280, observed: 373.2276.

(*E*)-2-(8-chlorooct-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3bl). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 93% (65.1 mg) for **L11**, 81% (28.4 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.78 (m, 4H), 7.58 – 7.50 (m, 2H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 5.83 (dt, J = 14.9, 6.8 Hz, 1H), 5.67 – 5.52 (m, 1H), 3.54 (t, J = 6.7 Hz, 2H), 3.36 (s, 2H),

2.69 (d, J = 7.2 Hz, 2H), 2.23 – 2.08 (m, 2H), 1.86 – 1.68 (m, 2H), 1.51 – 1.40 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.83, 133.34, 133.27, 129.80, 129.58, 128.92, 128.13, 127.86, 127.58, 126.79, 126.73, 120.47, 115.27, 45.13, 42.92, 40.70, 39.90, 32.49, 32.45, 28.27, 26.39. **IR** (KBr) γ 3056, 2932, 1508, 1442, 971, 821, 753 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{22}H_{24}N_2Cl$: 351.1628, observed: 351.1627.

(*E*)-2-(4-hydroxybut-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3bm). Silica gel column chromatography (PE/EtOAc = 5/1), White solid. Yield: 68% (37.5 mg) for **L11**, 45% (12.4 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 4H), 7.58 – 7.51 (m, 2H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 6.02 (dt, J = 15.3, 4.9 Hz, 1H), 5.94 – 5.82 (m, 1H), 4.24 (s, 2H), 3.38 (s, 2H), 2.76 (dd, J = 7.2, 0.7 Hz, 2H), 1.60 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.26, 133.35, 133.31, 129.84, 129.39, 129.00, 128.15, 127.88, 127.54, 126.86, 126.79, 121.14, 115.10, 62.73, 42.99, 40.25, 39.64. **IR** (KBr) γ 3335, 3055, 2927, 2855, 2248, 1508, 972, 822, 754, 477 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{18}H_{17}N_2O$: 277.1341, observed: 277.1339.

tert-butyl (*E*)-(5,5-dicyano-6-(naphthalen-2-yl)hex-2-en-1-yl)carbamate (3bn). Silica gel column chromatography (PE/EtOAc = 5/1), Yellow solid. Yield: 85% (63.8 mg) for **L11**, 42% (15.8 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 11.1, 7.0 Hz, 4H), 7.58 – 7.49 (m, 2H), 7.47 (dd, J = 8.4, 1.6 Hz, 1H), 5.85 (dt, J = 15.2, 5.2 Hz, 1H), 5.78 – 5.67 (m, 1H), 4.76 (s, 1H), 3.80 (s, 2H), 3.35 (s, 2H), 2.71 (d, J = 7.1 Hz, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.78, 136.12, 133.29, 133.23, 129.78, 129.41, 128.90, 128.09, 127.82, 127.50, 126.78, 126.71, 121.53, 115.06, 79.74, 42.76, 41.99, 40.09, 39.47, 28.45. **IR** (KBr) γ 3429, 3056, 2978, 2931, 2248, 1704, 1508, 1366, 1249, 1170, 970, 754, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{26}N_3O_2$: 376.2025, observed: 376.2027.

(*E*)-7,7-dicyano-8-(naphthalen-2-yl)oct-4-en-1-yl furan-2-carboxylate (3bo). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 75% (59.7 mg) for **L11**, 63% (25.1 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.77 (m, 4H), 7.57 (dd, J = 1.7, 0.8 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 7.19 (dd, J = 3.5, 0.8 Hz, 1H), 6.50 (dd, J = 3.5, 1.7 Hz, 1H), 5.86 (dt, J = 13.7, 6.8 Hz, 1H), 5.65 (dt, J = 15.1, 7.3 Hz, 1H), 4.34 (t, J = 6.5 Hz, 2H), 3.36 (s, 2H), 2.69 (d, J = 7.2 Hz, 2H), 2.28 (q, J = 7.1 Hz, 2H), 1.89 (p, J = 6.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.83, 146.43, 144.78, 138.61, 133.34, 133.27, 129.81, 129.53, 128.94, 128.14, 127.86, 127.57, 126.80, 126.73, 121.32, 118.06, 115.21, 111.97, 64.11, 42.89, 40.62, 39.83, 29.05, 28.12. **IR** (KBr) γ 3056, 2956, 1723, 1475, 1399, 1297, 1230, 1180, 1120, 971, 762 cm^{-1}. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{25}H_{22}N_2O_3Na$: 421.1528, observed: 421.1522.

(*E*)-7,7-dicyano-8-(naphthalen-2-yl)oct-4-en-1-yl thiophene-2-carboxylate (3bp). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 96% (79.5 mg) for **L11**, 46% (19.0 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 4H), 7.81 (dd, J = 3.7, 1.3 Hz, 1H), 7.54 (ddd, J = 9.5, 5.6, 2.3 Hz, 3H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 7.10 (dd, J = 5.0, 3.8 Hz, 1H), 5.87 (dt, J = 15.0, 6.8 Hz, 1H), 5.70 – 5.60 (m, 1H), 4.34 (t, J = 6.5 Hz, 2H), 3.36 (s, 2H), 2.69

(d, J = 7.3 Hz, 2H), 2.29 (q, J = 7.2 Hz, 2H), 1.99 – 1.80 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.33, 138.70, 133.92, 133.56, 133.36, 133.29, 132.48, 129.82, 129.54, 128.95, 128.16, 127.90, 127.87, 127.58, 126.81, 126.74, 121.30, 115.23, 64.30, 42.90, 40.64, 39.83, 29.15, 28.14. **IR** (KBr) γ 3056, 2958, 1705, 1525, 1419, 1279, 1261, 1099, 1076, 970, 821, 751 cm^{-1}. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{25}H_{22}N_2O_2NaS$: 437.1300, observed: 437.1302.

(*E*)-5-(naphthalen-2-yl)pent-1-ene-1,4,4-tricarbonitrile (3bq). Silica gel column chromatography (PE/EtOAc = 5/1), White solid. Yield: 51% (27.6 mg) for **L11**, 45% (12.2 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.75 (m, 2H), 7.60 – 7.50 (m, 1H), 7.45 (dd, J = 8.4, 1.9 Hz, 1H), 6.76 (dt, J = 16.1, 7.5 Hz, 1H), 5.67 (dt, J = 16.2, 1.3 Hz, 4H), 3.42 (s, 2H), 2.86 (dd, J = 7.6, 1.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.96, 133.42, 133.31, 129.94, 129.32, 128.40, 128.13, 127.93, 127.23, 127.16, 127.04, 115.65, 114.11, 107.77, 43.18, 40.16, 38.25. **IR** (KBr) γ 3057, 2924, 2851, 2229, 1508, 1270, 965, 861, 755, 476 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{18}H_{14}N_3$: 272.1188, observed: 272.1170.

tert-butyl (*E*)-5,5-dicyano-6-(naphthalen-2-yl)hex-2-enoate (3br). Silica gel column chromatography (PE/EtOAc = 5/1), Yellow solid. Yield: 76% (52.6 mg) for **L11**, 77% (26.6 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.80 (m, 4H), 7.57 – 7.51 (m, 2H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 6.88 (dt, J = 15.3, 7.5 Hz, 1H), 6.06 (dt, J = 15.4, 1.2 Hz, 1H), 3.39 (s, 2H), 2.85 (dd, J = 7.5, 1.2 Hz, 2H), 1.51 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.25, 135.50, 133.33, 133.31, 130.64, 129.88, 129.07, 129.00, 128.14, 127.87, 127.41, 126.93, 126.83, 114.58, 81.50, 43.00, 39.47, 38.50, 28.16. **IR** (KBr) γ 2979, 2923, 1715, 1368, 1156, 979, 859, 754 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{22}H_{23}N_2O_2$: 347.1760, observed: 347.1771.

2-cinnamyl-2-(naphthalen-2-ylmethyl)malononitrile (3bs). Silica gel column chromatography (PE/EtOAc = 10/1), White solid. Yield: 75% (48.3 mg) for **L11**, 41% (13.2 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.82 (m, 4H), 7.57 – 7.49 (m, 3H), 7.47 – 7.41 (m, 2H), 7.40 – 7.28 (m, 3H), 6.72 (d, J = 15.7 Hz, 1H), 6.40 – 6.24 (m, 1H), 3.43 (s, 2H), 2.92 (d, J = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.18, 135.79, 133.36, 133.32, 129.88, 129.45, 129.02, 128.88, 128.69, 128.17, 127.90, 127.58, 126.87, 126.79, 119.23, 115.18, 43.00, 41.08, 39.65. **IR** (KBr) γ 3056, 2925, 2248, 1448, 1265, 1041, 967, 827, 754, 696, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{23}H_{18}N_2Na$: 345.1368, observed: 345.1374.

(*E*)-2-(naphthalen-2-ylmethyl)-2-(3-(3-oxocyclohex-1-en-1-yl)allyl)malononitrile (3bt). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 65% (44.2 mg) for **L11**, 70% (23.8 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 7.75 (m, 4H), 7.57 – 7.50 (m, 2H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 6.46 (d, J = 15.7 Hz, 1H), 6.26 – 6.11 (m, 1H), 5.97 (s, 1H), 3.41 (s, 2H), 2.93 – 2.81 (m, 2H), 2.48 (t, J = 5.7 Hz, 2H), 2.45 – 2.38 (m, 2H), 2.11 – 1.99 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.11, 154.91, 138.83, 133.32, 133.30, 129.87, 129.44, 129.07, 129.04, 128.10, 127.87, 127.43, 126.95, 126.86, 126.29, 114.83, 43.22, 40.79, 39.21, 37.72, 24.98, 22.19. **IR** (KBr) γ 2938, 1664, 1191, 1059, 968, 860, 755, 507 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for

$C_{23}H_{21}N_2O$: 341.1654, observed: 341.1648.

2-((*E*)-8-(((*Z*)-3,7-dimethylocta-2,6-dien-1-yl)oxy)oct-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3bu). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 73% (68.3 mg) for **L11**, 57% (26.7 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 4H), 7.56 – 7.44 (m, 3H), 5.89 – 5.78 (m, 1H), 5.64 – 5.51 (m, 1H), 5.35 (t, J = 6.7 Hz, 1H), 5.15 – 5.05 (m, 1H), 3.93 (d, J = 6.8 Hz, 2H), 3.40 (t, J = 6.6 Hz, 2H), 3.35 (s, 2H), 2.68 (d, J = 7.2 Hz, 2H), 2.13 (dd, J = 13.7, 6.8 Hz, 2H), 2.08 – 2.02 (m, 4H), 1.74 (s, 3H), 1.68 (s, 3H), 1.63 – 1.58 (m, 5H), 1.49 – 1.32 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.16, 140.10, 133.25, 133.18, 131.90, 129.70, 129.52, 128.81, 128.04, 127.76, 127.49, 126.67, 126.61, 123.94, 122.09, 120.00, 115.19, 42.77, 40.63, 39.73, 32.54, 32.27, 29.67, 28.84, 26.74, 25.78, 25.73, 23.52, 17.67. **IR** (KBr) γ 2931, 2856, 1508, 1447, 1375, 1180, 1100, 972, 820, 752, 477 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{32}H_{41}N_2O$: 469.3219, observed: 469.3217.

(*R*,*E*)-2-(6-((tert-butyldimethylsilyl)oxy)-5-hydroxyhex-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3bv). Silica gel column chromatography (PE/EtOAc = 5/1), Colorless oil. Yield: 80% (69.4 mg) for **L11**, 68% (29.5 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 4H), 7.57 – 7.50 (m, 2H), 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 5.90 (dt, J = 15.1, 7.1 Hz, 1H), 5.74 – 5.60 (m, 1H), 3.79 – 3.69 (m, 1H), 3.65 (dd, J = 9.9, 3.7 Hz, 1H), 3.47 (dd, J = 10.0, 7.0 Hz, 1H), 3.37 (s, 2H), 2.72 (d, J = 7.2 Hz, 2H), 2.47 (d, J = 4.0 Hz, 1H), 2.31 (t, J = 6.6 Hz, 2H), 0.91 (s, 9H), 0.08 (d, J = 0.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.92, 133.35, 133.29, 129.83, 129.51, 128.95, 128.15, 127.87, 127.58, 126.81, 126.74, 122.85, 115.25, 71.15, 66.62, 42.91, 40.77, 39.76, 36.41, 26.01, 18.41, -5.23, -5.26. **IR** (KBr) γ 3055, 2928, 2305, 1652, 1540, 1061, 969, 837, 502 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{35}N_2O_2Si$: 435.2468, observed: 435.2466.

2-((*E*)-6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)hex-2-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (3bw). Silica gel column chromatography (PE/EtOAc = 5/1), White solid. Yield: 99% (110.1 mg) for **L11**, 28% (15.6 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.79 (m, 4H), 7.58 – 7.51 (m, 2H), 7.47 (dd, J = 8.4, 1.8 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 6.74 (dd, J = 8.6, 2.7 Hz, 1H), 6.67 (d, J = 2.6 Hz, 1H), 5.95 – 5.83 (m, 1H), 5.73 – 5.59 (m, 1H), 3.98 (t, J = 6.3 Hz, 2H), 3.32 (s, 2H), 2.98 – 2.83 (m, 2H), 2.70 (d, J = 7.3 Hz, 2H), 2.51 (dd, J = 19.0, 8.5 Hz, 1H), 2.41 – 2.29 (m, 3H), 2.25 – 2.18 (m, 1H), 2.13 (dd, J = 18.9, 9.0 Hz, 1H), 2.08 – 1.88 (m, 5H), 1.69 – 1.34 (m, 6H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.96, 139.07, 137.77, 133.22, 133.14, 132.03, 129.68, 129.54, 128.78, 128.04, 127.77, 127.50, 126.69, 126.62, 126.37, 120.90, 115.18, 114.54, 112.11, 66.76, 50.35, 48.00, 43.92, 42.63, 40.54, 39.74, 38.31, 35.89, 31.57, 29.64, 29.11, 28.57, 26.53, 25.90, 21.58, 13.86. **IR** (KBr) γ 3055, 2930, 2866, 2247, 1736, 1608, 1499, 1472, 1453, 1427, 1280, 1254, 1157, 1056, 1006, 971, 820, 753, 736, 478 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{38}H_{41}N_2O_2$: 557.3168, observed: 557.3157.

(2*R*,3*S*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((*E*)-7,7-dicyano-8-(naphthalen-2-yl)oct-4-en-1-

yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3bx). Silica gel column chromatography (PE/EtOAc = 5/1), Colorless oil. Yield: 84% (106.5 mg) for **L11**, 21% (13.3 mg) for PPh_3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 4H), 7.56 – 7.49 (m, 2H), 7.47 (dd, J = 8.5, 1.8 Hz, 1H), 5.87 – 5.74 (m, 1H), 5.65 – 5.51 (m, 1H), 5.38 (dd, J = 3.5, 1.1 Hz, 1H), 5.20 (dd, J = 10.5, 7.9 Hz, 1H), 5.01 (dd, J = 10.5, 3.4 Hz, 1H), 4.46 (d, J = 7.9 Hz, 1H), 4.14 (qd, J = 11.2, 6.7 Hz, 2H), 3.96 – 3.85 (m, 2H), 3.51 (ddd, J = 9.7, 7.4, 5.9 Hz, 1H), 3.36 (s, 2H), 2.73 – 2.52 (m, 2H), 2.21 – 2.14 (m, 2H), 2.13 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.81 – 1.60 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.48, 170.38, 170.24, 169.52, 139.08, 133.31, 133.25, 129.77, 129.50, 128.91, 128.10, 127.83, 127.54, 126.78, 126.72, 121.03, 115.25, 101.42, 71.04, 70.67, 69.13, 69.02, 67.16, 61.33, 42.95, 40.60, 39.94, 28.81, 28.79, 20.90, 20.77, 20.69. **IR** (KBr) γ 2937, 2884, 1750, 1435, 1369, 1224, 1174, 1078, 1056, 972, 755, 736 cm^{-1}. **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{34}H_{38}N_2O_{10}Na$: 657.2424, observed: 657.2423.

(*R*,*E*)-4-(hept-2-en-1-yl)-5-methyl-4-(4-methylbenzyl)-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6a). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 68% (25.4 mg). Enantiomeric ratio: 93.5:6.5, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 13.635 min (major), t_R = 16.432 min (minor). **$[\alpha]_D^{20}$** = -110 (c 0.4, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 7.02 – 6.93 (m, 4H), 5.61 – 5.48 (m, 1H), 5.14 – 5.04 (m, 1H), 3.20 (d, J = 13.7 Hz, 1H), 2.83 (d, J = 13.7 Hz, 1H), 2.66 (dd, J = 13.6, 7.1 Hz, 1H), 2.41 (dd, J = 13.7, 7.7 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.09 (s, 3H), 1.88 (q, J = 6.6 Hz, 2H), 1.24 – 1.10 (m, 4H), 0.77 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.86, 161.62, 136.80, 136.11, 135.44, 134.79, 132.15, 129.29, 129.18, 128.93, 122.25, 119.58, 61.38, 40.59, 38.58, 32.18, 31.47, 22.10, 21.13, 21.08, 14.82, 13.94. **IR** (KBr) γ 3025, 2957, 2922, 2857, 1705, 1615, 1513, 1440, 1365, 1302, 1125, 970, 817, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{33}N_2O$: 389.2587, observed: 389.2582.

(*R*,*E*)-4-(hept-2-en-1-yl)-4-(4-methoxybenzyl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6b). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 74% (29.9 mg). Enantiomeric ratio: 93.5:6.5, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 92.5/7.5, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 14.316 min (minor), t_R = 19.842 min (major). **$[\alpha]_D^{20}$** = -108 (c 0.64, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 6.74 – 6.66 (m, 2H), 5.64 – 5.47 (m, 1H), 5.09 (dt, J = 14.9, 7.3 Hz, 1H), 3.70 (s, 3H), 3.17 (d, J = 13.8 Hz, 1H), 2.82 (d, J = 13.8 Hz, 1H), 2.65 (dd, J = 13.6, 7.0 Hz, 1H), 2.40 (dd, J = 13.7, 7.6 Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H), 1.88 (q, J = 6.6 Hz, 2H), 1.23 – 1.10 (m, 4H), 0.77 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.85, 161.61, 158.69, 136.07, 135.41, 134.80, 130.11, 129.29, 127.27, 122.27, 119.57, 113.83, 61.48, 55.24, 40.16, 38.44, 32.17, 31.46, 22.09, 21.07, 14.79, 13.93. **IR** (KBr) γ 3034, 2957, 2924, 2855, 1705, 1613, 1513, 1440, 1366, 1303, 1251, 1179, 1035, 970, 818, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{33}N_2O_2$: 405.2537, observed: 405.2534.

(*R*,*E*)-4-(4-fluorobenzyl)-4-(hept-2-en-1-yl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one

(6c). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 58% (22.7 mg). Enantiomeric ratio: 93:7, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 30°C, 254 nm): t_R = 15.712 min (major), t_R = 17.884 min (minor). **$[\alpha]_D^{20}$** = -74 (c 0.32, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.89 – 6.80 (m, 2H), 5.63 – 5.47 (m, 1H), 5.17 – 4.99 (m, 1H), 3.18 (d, J = 13.8 Hz, 1H), 2.85 (d, J = 13.7 Hz, 1H), 2.66 (dd, J = 13.7, 7.1 Hz, 1H), 2.41 (dd, J = 13.8, 7.6 Hz, 1H), 2.31 (s, 3H), 2.11 (s, 3H), 1.89 (q, J = 6.9 Hz, 2H), 1.26 – 1.05 (m, 4H), 0.77 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.57, 162.06 (d, J = 245.6 Hz), 161.27, 136.31, 135.26, 135.00, 130.98 (d, J = 3.3 Hz), 130.64 (d, J = 8.0 Hz), 129.36, 122.07, 119.52, 115.36 (d, J = 21.3 Hz), 61.39, 40.05, 38.43, 32.18, 31.46, 22.10, 21.08, 14.79, 13.93. **IR** (KBr) γ 3037, 2961, 2923, 2856, 1074, 1615, 1509, 1437, 1399, 1261, 1224, 1097, 1018, 970, 817, 508 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{30}ON_2F$: 393.2337, observed: 393.2340.

(*R*,*E*)-4-(hept-2-en-1-yl)-4-(3-methoxybenzyl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6d). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 52% (21.0 mg). Enantiomeric ratio: 90.5:9.5, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 30°C, 254 nm): t_R = 9.762 min (major), t_R = 10.934 min (minor). **$[\alpha]_D^{20}$** = -88 (c 0.36, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 7.07 (t, J = 7.9 Hz, 1H), 6.72 – 6.62 (m, 3H), 5.61 – 5.49 (m, 1H), 5.16 – 5.01 (m, 1H), 3.61 (s, 3H), 3.22 (d, J = 13.7 Hz, 1H), 2.83 (d, J = 13.7 Hz, 1H), 2.67 (dd, J = 13.6, 7.0 Hz, 1H), 2.42 (dd, J = 13.7, 7.6 Hz, 1H), 2.31 (s, 3H), 2.09 (s, 3H), 1.88 (q, J = 6.5 Hz, 2H), 1.24 – 1.08 (m, 4H), 0.77 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.86, 161.56, 159.56, 136.82, 136.24, 135.45, 134.80, 129.45, 129.31, 122.14, 121.37, 119.43, 114.16, 113.22, 61.28, 55.16, 41.01, 38.65, 32.18, 31.46, 22.10, 21.08, 14.82, 13.94. **IR** (KBr) γ 2957, 2922, 1705, 1512, 1365, 1262, 1042, 970, 818, 695, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{33}N_2O_2$: 405.2537, observed: 405.2533.

(*R*,*E*)-4-(2-fluorobenzyl)-4-(hept-2-en-1-yl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6e). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 67% (26.3 mg). Enantiomeric ratio: 92:8, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 9.662 min (major), t_R = 10.374 min (minor). **$[\alpha]_D^{20}$** = -54 (c 0.43, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 2H), 7.20 – 7.06 (m, 4H), 6.99 – 6.87 (m, 2H), 5.64 – 5.49 (m, 1H), 5.16 – 4.98 (m, 1H), 3.19 (d, J = 13.8 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.69 (dd, J = 13.6, 7.0 Hz, 1H), 2.46 (dd, J = 13.6, 7.7 Hz, 1H), 2.31 (s, 3H), 2.12 – 2.08 (m, 3H), 1.89 (q, J = 6.6 Hz, 2H), 1.25 – 1.10 (m, 4H), 0.77 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.60, 160.76 (d, J = 244.8 Hz), 161.90, 136.35, 135.35, 134.88, 131.63 (d, J = 3.9 Hz), 129.33, 129.07 (d, J = 8.4 Hz), 124.24 (d, J = 3.5 Hz), 122.26 (d, J = 15.4 Hz), 122.09, 119.51, 115.36 (d, J = 22.9 Hz), 60.80, 38.40, 32.79 (d, J = 3.0 Hz), 32.18, 31.45, 22.09, 21.08, 14.22 (d, J = 5.7 Hz), 13.93. **IR** (KBr) γ 3036, 2957, 2925, 2857, 1705, 1651, 1513, 1367, 1279, 1230, 969, 818, 757, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{30}ON_2F$: 393.2337, observed: 393.2333.

(*S*,*E*)-4-(hept-2-en-1-yl)-4,5-dimethyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6f). Silica gel

column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 40% (11.9 mg). Enantiomeric ratio: 91:9, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 94/6, flow rate 0.8 mL/min, T = 30°C, 254 nm): t_R = 9.560 min (minor), t_R = 11.899 min (major). **$[\alpha]_D^{20}$** = +123 (c 0.21, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 5.59 – 5.44 (m, 1H), 5.14 – 4.98 (m, 1H), 2.52 (dd, J = 13.5, 7.4 Hz, 1H), 2.34 (s, 3H), 2.29 (dd, J = 13.7, 7.5 Hz, 1H), 2.08 (s, 3H), 1.87 (q, J = 8.0, 6.7 Hz, 2H), 1.29 (s, 3H), 1.22 – 1.10 (m, 4H), 0.76 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.85, 163.55, 135.95, 135.83, 134.57, 129.40, 122.56, 118.97, 54.99, 39.09, 32.15, 31.48, 22.08, 21.08, 19.96, 13.96, 13.93. **IR** (KBr) γ 2959, 2926, 2856, 1708, 1616, 1512, 1455, 1363, 1311, 1080, 970, 818, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{19}H_{27}N_2O$: 299.2118, observed: 299.2116.

(*R*,*E*)-4-(4-methoxybenzyl)-5-methyl-4-(5-phenoxypent-2-en-1-yl)-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6g). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 69% (32.3 mg). Enantiomeric ratio: 93:7, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 13.845 min (major), t_R = 18.468 min (minor). **$[\alpha]_D^{20}$** = -81 (c 0.92, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 2H), 7.25 – 7.19 (m, 2H), 7.11 (d, J = 8.2 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.91 (t, J = 7.3 Hz, 1H), 6.80 – 6.74 (m, 2H), 6.72 – 6.65 (m, 2H), 5.68 (dt, J = 14.5, 6.9 Hz, 1H), 5.27 (dt, 1H), 3.84 – 3.76 (m, 2H), 3.70 (s, 3H), 3.18 (d, J = 13.8 Hz, 1H), 2.83 (d, J = 13.8 Hz, 1H), 2.69 (dd, J = 13.8, 7.1 Hz, 1H), 2.44 (dd, J = 13.7, 7.6 Hz, 1H), 2.37 (q, J = 7.0 Hz, 2H), 2.31 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.75, 161.50, 158.85, 158.74, 135.36, 134.86, 131.44, 130.12, 129.48, 129.39, 127.17, 125.25, 120.72, 119.48, 114.60, 113.88, 67.29, 61.45, 55.26, 40.09, 38.33, 32.51, 21.11, 14.82. **IR** (KBr) γ 3036, 2918, 2836, 1704, 1613, 1585, 1513, 1497, 1366, 1302, 1248, 1178, 1034, 819, 755, 692, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{30}H_{33}O_3N_2$: 469.2485, observed: 469.2478.

(*R*,*E*)-6-(4-(4-methoxybenzyl)-3-methyl-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)hex-4-en-1-yl acetate (6h). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 73% (32.7 mg). Enantiomeric ratio: 94.5:5.5, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 17.926 min (major), t_R = 27.699 min (minor). **$[\alpha]_D^{20}$** = -97 (c 0.74, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.43 (m, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.75 – 6.62 (m, 2H), 5.66 – 5.44 (m, 1H), 5.15 (dt, J = 15.1, 7.4 Hz, 1H), 3.94 (tt, J = 7.2, 3.6 Hz, 2H), 3.70 (s, 3H), 3.17 (d, J = 13.8 Hz, 1H), 2.82 (d, J = 13.8 Hz, 1H), 2.66 (dd, J = 13.8, 7.0 Hz, 1H), 2.41 (dd, J = 13.8, 7.6 Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.98 – 1.90 (m, 2H), 1.60 – 1.48 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.76, 171.20, 161.53, 158.73, 135.35, 134.88, 134.43, 130.11, 129.34, 127.15, 123.48, 119.53, 113.87, 63.77, 61.39, 55.26, 40.17, 38.29, 28.83, 28.32, 21.08, 14.80. **IR** (KBr) γ 2918, 2837, 1736, 1704, 1613, 1513, 1440, 1366, 1303, 1249, 1179, 1035, 970, 819, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{27}H_{33}O_4N_2$: 449.2434, observed: 449.2433.

(*R*,*E*)-4-(6-((tert-butyldiphenylsilyl)oxy)hex-2-en-1-yl)-4-(4-methoxybenzyl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6i). Silica gel column chromatography (PE/EtOAc = 10/1),

Yellow oil. Yield: 64% (41.2 mg). Enantiomeric ratio: 95:5, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 6.284 min (major), t_R = 7.722 min (minor). **$[\alpha]_D^{20}$** = -62 (c 0.48, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 4H), 7.50 (d, J = 8.5 Hz, 2H), 7.45 – 7.32 (m, 6H), 7.13 – 7.08 (m, 2H), 7.04 – 6.97 (m, 2H), 6.76 – 6.67 (m, 2H), 5.63 – 5.48 (m, 1H), 5.18 – 5.04 (m, 1H), 3.71 (s, 3H), 3.57 (t, J = 6.4 Hz, 2H), 3.17 (d, J = 13.8 Hz, 1H), 2.81 (d, J = 13.8 Hz, 1H), 2.68 – 2.57 (m, 1H), 2.39 (dd, J = 13.8, 7.7 Hz, 1H), 2.30 (s, 3H), 2.08 (s, 3H), 1.99 (q, J = 7.1 Hz, 2H), 1.55 – 1.44 (m, 2H), 1.02 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.83, 161.58, 158.70, 135.66, 135.52, 135.36, 134.84, 134.12, 130.12, 129.63, 129.33, 127.71, 127.25, 122.58, 119.63, 113.85, 63.32, 61.39, 55.25, 40.12, 38.38, 32.40, 28.86, 26.97, 21.08, 19.33, 14.81. **IR** (KBr) γ 3034, 2930, 2857, 1705, 1613, 1513, 1427, 1364, 1250, 1110, 1035, 819, 703, 507 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{41}H_{49}O_3N_2Si$: 645.3507, observed: 645.3508.

(*R*,*E*)-6-(4-(4-methoxybenzyl)-3-methyl-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)hex-4-en-1-yl furan-2-carboxylate (6j). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 62% (31.0 mg). Enantiomeric ratio: 96:4, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 92.5/7.5, flow rate 0.7 mL/min, T = 30°C, 254 nm): t_R = 37.540 min (major), t_R = 43.540 min (minor). **$[\alpha]_D^{20}$** = -45 (c 0.66, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 3H), 7.13 – 7.07 (m, 3H), 7.01 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 6.48 (dd, J = 3.5, 1.7 Hz, 1H), 5.63 – 5.53 (m, 1H), 5.23 – 5.11 (m, 1H), 4.23 – 4.11 (m, 2H), 3.70 (s, 3H), 3.17 (d, J = 13.8 Hz, 1H), 2.82 (d, J = 13.8 Hz, 1H), 2.66 (dd, J = 13.7, 7.1 Hz, 1H), 2.41 (dd, J = 13.8, 7.6 Hz, 1H), 2.29 (s, 3H), 2.10 (s, 3H), 2.02 (q, J = 7.1 Hz, 2H), 1.72 – 1.64 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.76, 161.53, 158.79, 158.72, 146.32, 144.86, 135.34, 134.85, 134.32, 130.11, 129.33, 127.15, 123.63, 119.49, 117.88, 113.86, 111.90, 64.20, 61.39, 55.25, 40.15, 38.28, 28.80, 28.38, 21.06, 14.80. **IR** (KBr) γ 3035, 2961, 2924, 2854, 1704, 1613, 1513, 1294, 1260, 1178, 1113, 1031, 884, 801, 764, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{30}H_{33}N_2O_5$: 501.2389, observed: 501.2386.

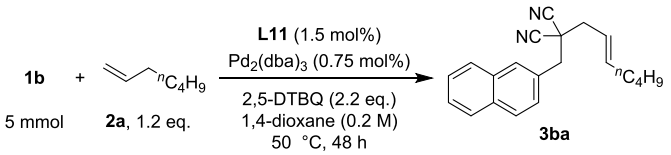
tert-butyl (*R*,*E*)-(4-(4-(4-methoxybenzyl)-3-methyl-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)but-2-en-1-yl)carbamate (6k). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 82% (39.1 mg). Enantiomeric ratio: 92.5:7.5, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 21.014 min (major), t_R = 41.247 min (minor). **$[\alpha]_D^{20}$** = -64 (c 0.22, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 5.61 (dt, J = 13.0, 6.0 Hz, 1H), 5.33 – 5.22 (m, 1H), 4.38 (s, 1H), 3.70 (s, 3H), 3.62 – 3.47 (m, 2H), 3.17 (d, J = 13.8 Hz, 1H), 2.82 (d, J = 13.8 Hz, 1H), 2.68 (dd, J = 13.9, 7.1 Hz, 1H), 2.44 (dd, J = 13.9, 7.6 Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.61, 161.42, 158.78, 155.71, 135.26, 135.03, 131.98, 130.12, 129.42, 127.00, 124.73, 119.58, 113.89, 61.12, 55.26, 42.20, 40.12, 37.74, 28.48, 21.09, 14.80. **IR** (KBr) γ 3034, 2991, 2933, 1705, 1508, 1179, 1128, 1035, 970, 814, 507 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{28}H_{36}N_3O_4$: 478.2706, observed: 478.2701.

(*R*,*E*)-4-(8-chlorooct-2-en-1-yl)-4-(4-methoxybenzyl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-

pyrazol-3-one (6l). Silica gel column chromatography (PE/EtOAc = 10/1), Colorless oil. Yield: 78% (35.2 mg). Enantiomeric ratio: 93:7, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 10.041 min (major), t_R = 14.025 min (minor). **$[\alpha]_D^{20}$** = -113 (c 0.63, acetone). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.03 – 6.97 (m, 2H), 6.69 (d, J = 8.7 Hz, 2H), 5.54 (dt, J = 14.4, 6.9 Hz, 1H), 5.17 – 4.99 (m, 1H), 3.70 (s, 3H), 3.37 (t, J = 6.8 Hz, 2H), 3.17 (d, J = 13.7 Hz, 1H), 2.81 (d, J = 13.9 Hz, 1H), 2.65 (dd, J = 13.7, 7.2 Hz, 1H), 2.40 (dd, J = 13.7, 7.5 Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H), 1.89 (q, J = 7.0 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.33 – 1.12 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.81, 161.56, 158.72, 135.59, 135.42, 134.87, 130.11, 129.35, 127.23, 122.74, 119.42, 113.87, 61.55, 55.26, 45.04, 40.18, 38.38, 32.57, 32.28, 28.59, 26.25, 21.09, 14.81. **IR** (KBr) γ 3034, 2995, 2932, 2856, 1704, 1613, 1513, 1440, 1366, 1250, 1179, 1126, 1034, 970, 819, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{27}H_{34}ClN_2O_2$: 453.2308, observed: 453.2306.

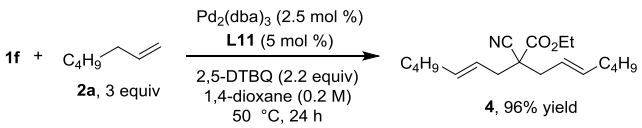
(*R*)-4-cinnamyl-4-(4-methoxybenzyl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6m). Silica gel column chromatography (PE/EtOAc = 10/1), Yellow oil. Yield: 86% (36.5 mg). Enantiomeric ratio: 95:5, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R = 15.785 min (major), t_R = 19.515 min (minor). **$[\alpha]_D^{20}$** = -24 (c 1.1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 2H), 7.25 – 7.16 (m, 5H), 7.12 (d, J = 8.2 Hz, 2H), 7.07 – 6.96 (m, 2H), 6.71 (d, J = 8.7 Hz, 2H), 6.51 (d, J = 15.7 Hz, 1H), 5.96 – 5.80 (m, 1H), 3.71 (s, 3H), 3.24 (d, J = 13.7 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.70 – 2.55 (m, 1H), 2.31 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.69, 161.49, 158.79, 136.76, 135.26, 135.06, 134.44, 130.16, 129.36, 128.62, 127.72, 127.01, 126.44, 122.48, 119.84, 113.89, 61.18, 55.27, 40.30, 38.68, 21.10, 14.90. **IR** (KBr) γ 3029, 2960, 2836, 1704, 1612, 1513, 1440, 1366, 1303, 1250, 1179, 1034, 818, 745, 693, 509 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{28}H_{29}N_2O_2$: 425.2229, observed: 425.2221.

5. Scale-up Reaction



To a N_2-purged 100 ml Schlenk tube were added $Pd_2(dba)_3$ (35 mg, 0.75 mol %), **L11** (24 mg, 1.5 mol %), 2,5-DTBQ (1.21 g, 1.1 equiv), **1b** (1.03 g, 5 mmol), **2a** (0.84 ml, 6 mmol), and 1,4-dioxane (25.0 mL) and a stirring bar. The mixture was stirred at 50 °C for 48 h. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (EtOAc/Hexane = 1:15) to provide product **3ba** (1.43 g, 95% yield).

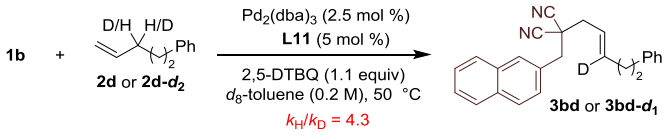
6. Pd-catalyzed Twice Allylic C-H Alkylations



To a N_2-purged 10 ml Schlenk tube were added $Pd_2(dba)_3$ (2.5 mol %), **L11** (5 mol %), 2,5-DTBQ (2.2 equiv), **1f** (0.2 mmol), **2a** (0.6 mmol), and 1,4-dioxane (1 mL) and a stirring bar. The mixture was stirred at 50 °C for 24 h. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (EtOAc/Hexane = 1:20) to provide product **4** (58 mg, 96% yield) as colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 5.66 – 5.54 (m, 2H), 5.45 – 5.34 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 2.59 – 2.51 (m, 2H), 2.45 (dd, J = 13.7, 7.0 Hz, 2H), 2.01 (q, J = 6.9 Hz, 4H), 1.39 – 1.20 (m, 11H), 0.88 (t, J = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.49, 137.41, 121.99, 119.08, 62.53, 50.43, 39.86, 32.30, 31.39, 22.23, 14.28, 14.02. **IR** (KBr) γ 2958, 2928, 2872, 2858, 1743, 1456, 1437, 1223, 971 cm^{-1}. **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{19}H_{32}NO_2$: 306.2433, observed: 306.2426.

7. Mechanistic Investigations

a) Kinetic experiments



To an oven-dried NMR tube were added **1b** (0.1 mmol), $Pd_2(dba)_3$ (0.0025 mmol), phosphoramidite **L11** (0.005 mmol), 2,5-DTBQ (0.11 mmol), trimethyl benzene-1,3,5-tricarboxylate (0.02 mmol), the NMR tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by addition of alkene **2d** or **2d-*d*$_2$** (0.2 mmol) in acetone-d_6 (0.5 mL). The NMR tube was vibrated for a few seconds to make the reaction homogeneous. Then ^{1}H-NMR scan was conducted every 5 minutes at 50 ℃ to determined the yields.

time(min)	yield of **3bd** (%)	yield of **3bd-*d*$_1$** (%)
0	0	0
5	8.1	1.3
10	14.5	2.9
15	20.8	4.6
20	25.9	6.2
25	31.2	7.2
30	36.5	8.4

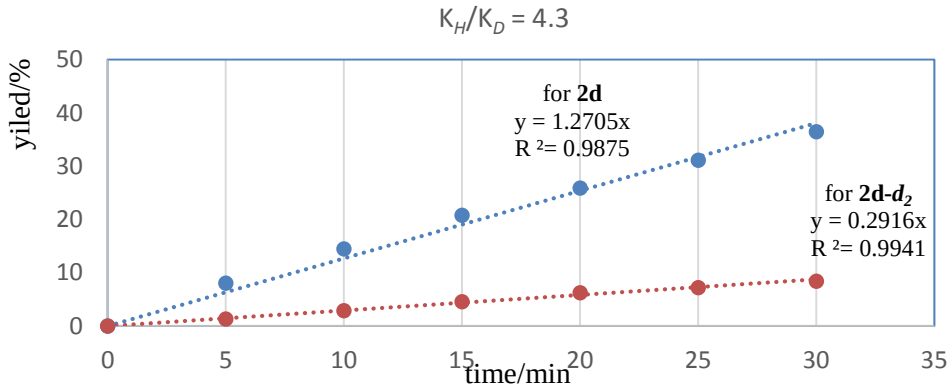
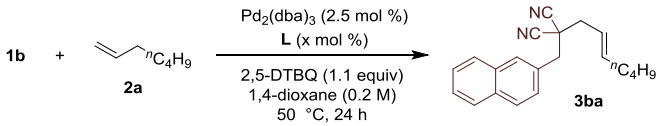


Figure S1. Yields determined from 2d and 2d-d_2.

b). Effect of mole ratio of L/Pd



To a flame-dried and N_2-purged Schlenk tube (10 mL) were added **1b** (0.1 mmol), $Pd_2(dba)_3$ (2.5 mol %), PPh_3 or phosphoramidite **L11** (x mol %), 2,5-DTBQ (0.11 mmol) and a stirring bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by addition of 1,4-dioxane (0.5 mL) and alkene **2a** (0.2 mmol). The mixture was stirred at 50 °C for 24 h. The solvent was removed under vacuum and the crude residue was analyzed by ^{1}H-NMR analysis to determine yield using 1,3,5-triacetylbenzene as internal standard.

entry	x	mole ratio of L/Pd	yield(%)	
			L11	PPh_3
1	5	1	95	91
2	6	1.2	98	87
3	7.5	1.5	97	82
4	10	2	97	24
5	12.5	2.5	97	0

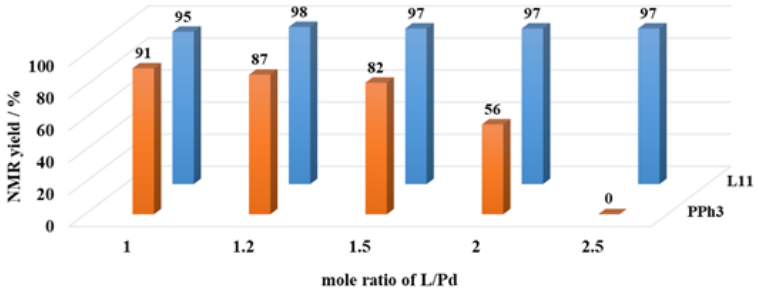
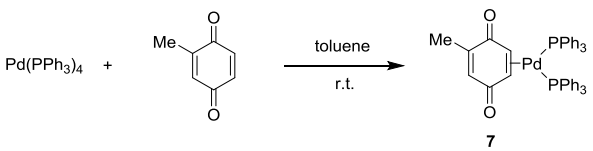


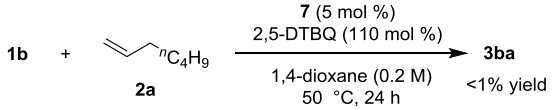
Figure S2. Yields affected by the mole ratio of L/Pd.

c) Control reactions



Synthesis of complex 7[18] :To a suspension of $Pd(Ph_3P)_4$ (360 mg, 0.3 mmol) in 3 mL toluene, 2-

Methyl-1,4-benzoquinone (44 mg, 3.6 mmol) in 1 mL toluene was added, the mixture was stirred until it became homogeneous. After the solution was concentrated to about 0.5 ml, a mixture of 8 ml ether and 4 ml hexane was added to afford red crystal **7**.



To a flame-dried and N_2-purged Schlenk tube (10 mL) were added **1b** (0.1 mmol), **7** (0.025 mmol), 2,5-DTBQ (110 mol %) and a stir bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by addition of 1,4-dioxane (0.5 mL) and alkene **2a** (0.2 mmol). The mixture was stirred at 50 °C for 24 h. The yield was determined by ^{1}H-NMR spectroscopic analysis using trimethyl benzene-1,3,5-tricarboxylate as the internal standard.

8. References

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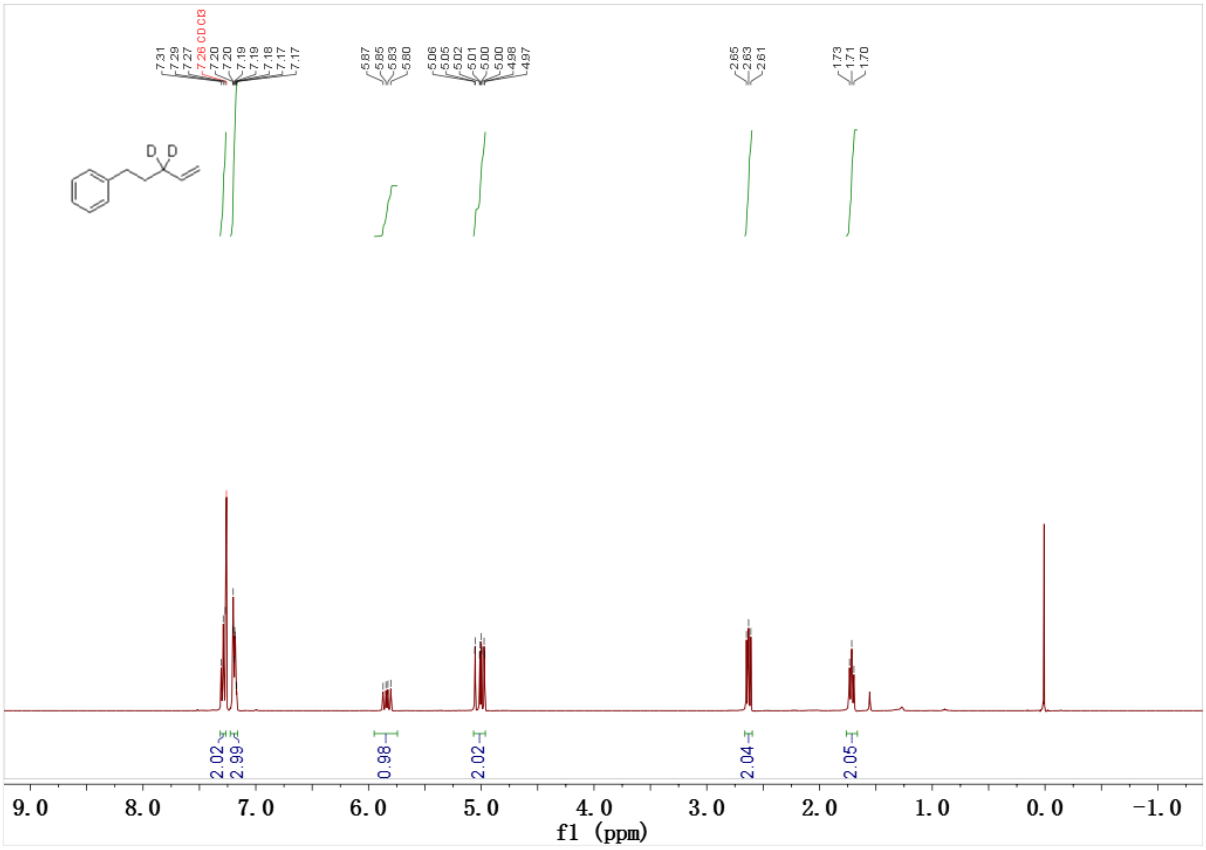
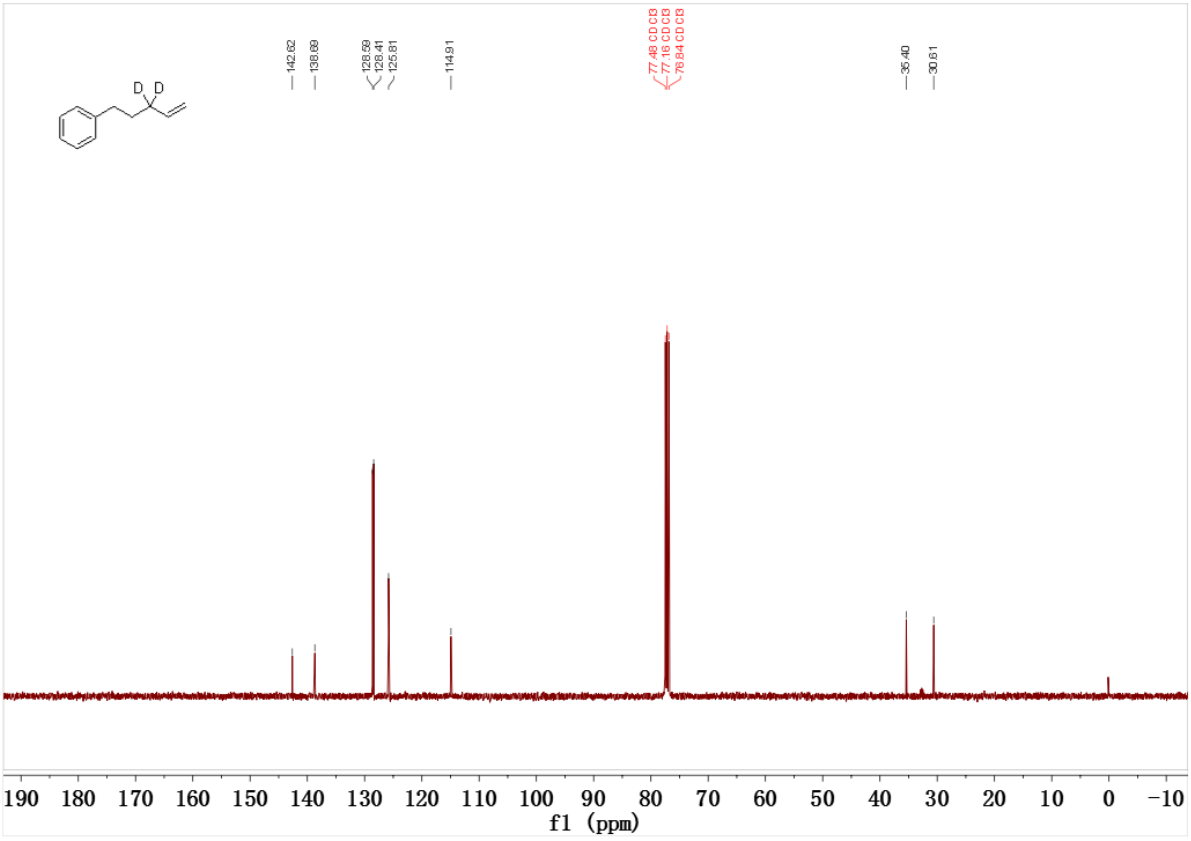
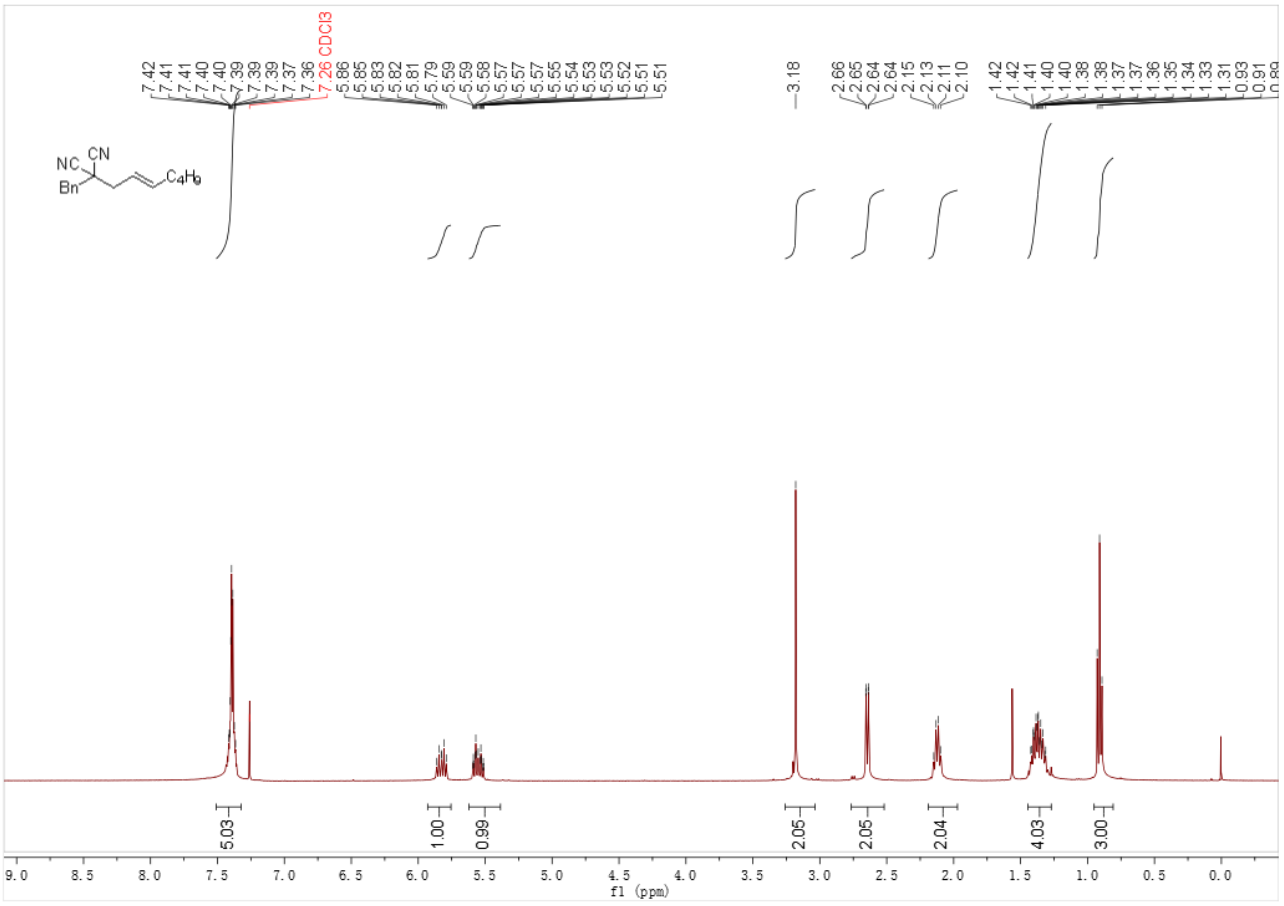
9. NMR and HLPC Spectra

2d-d_2





3aa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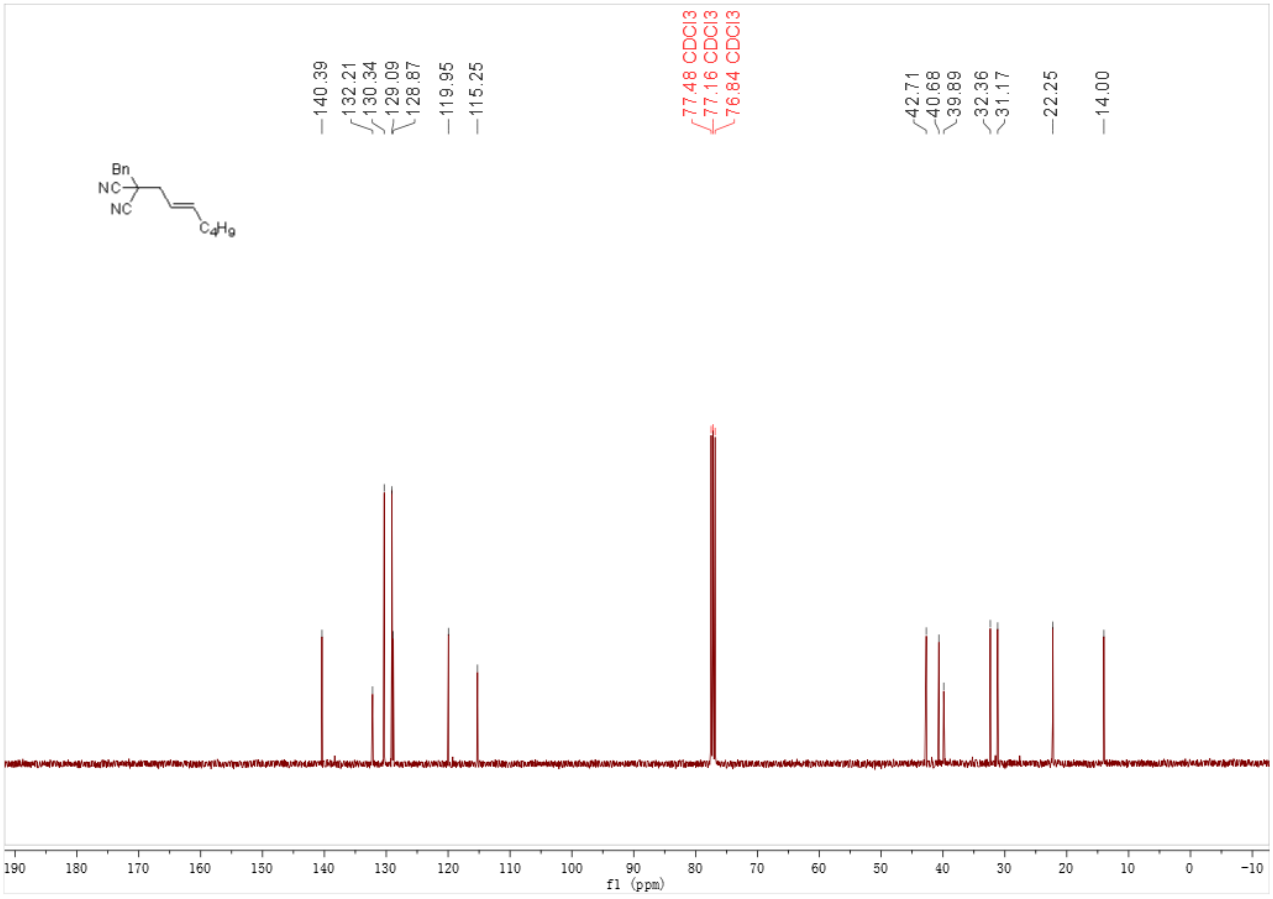
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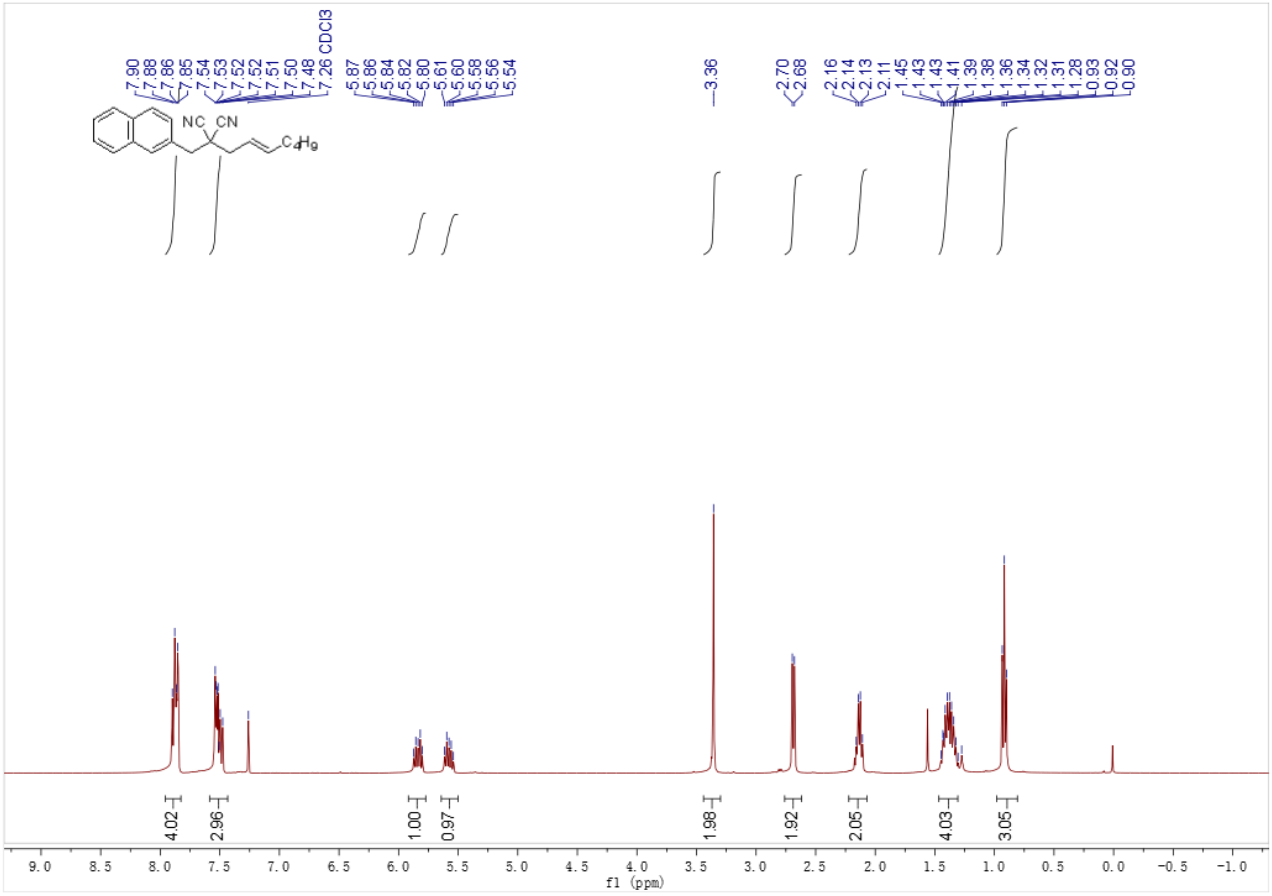
3ba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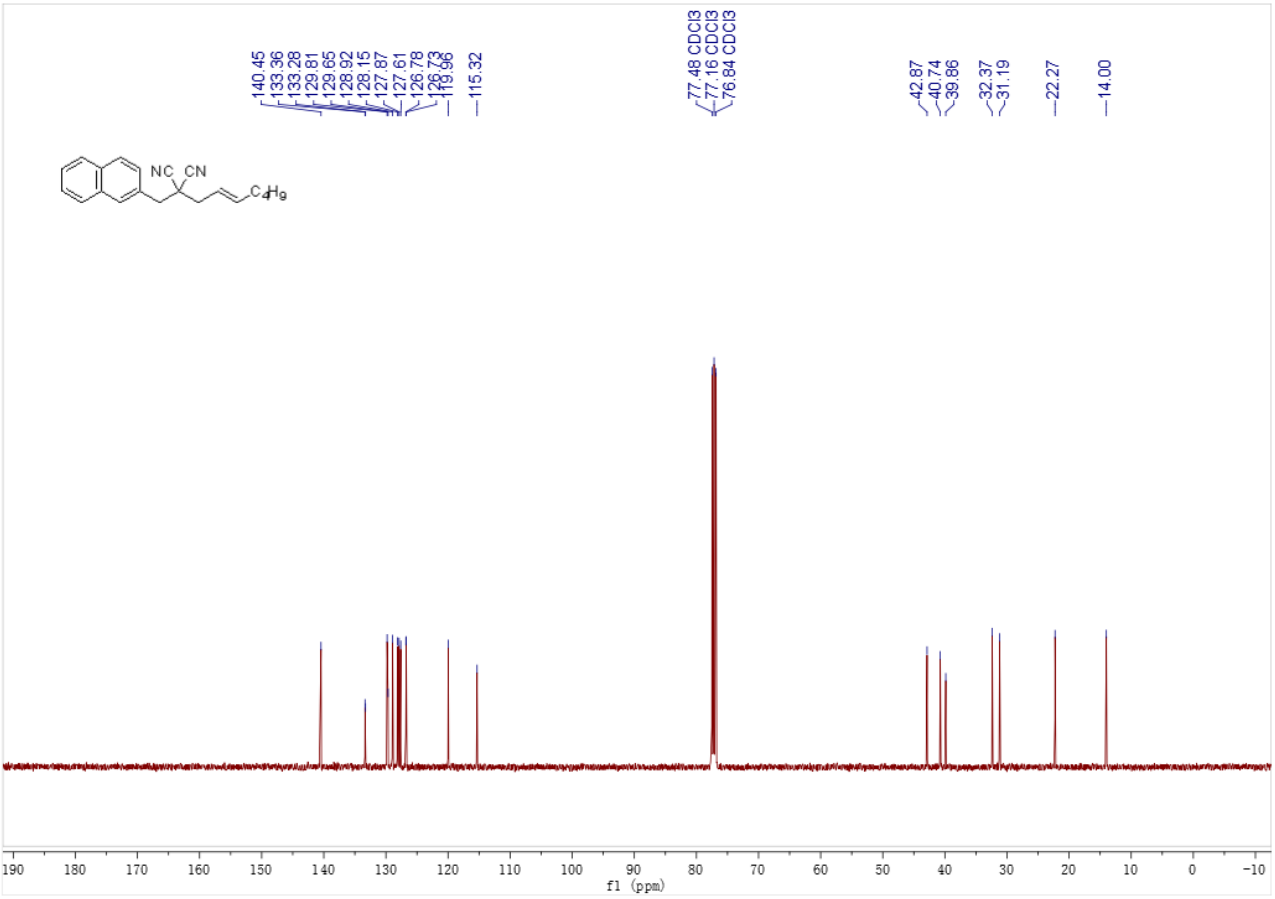
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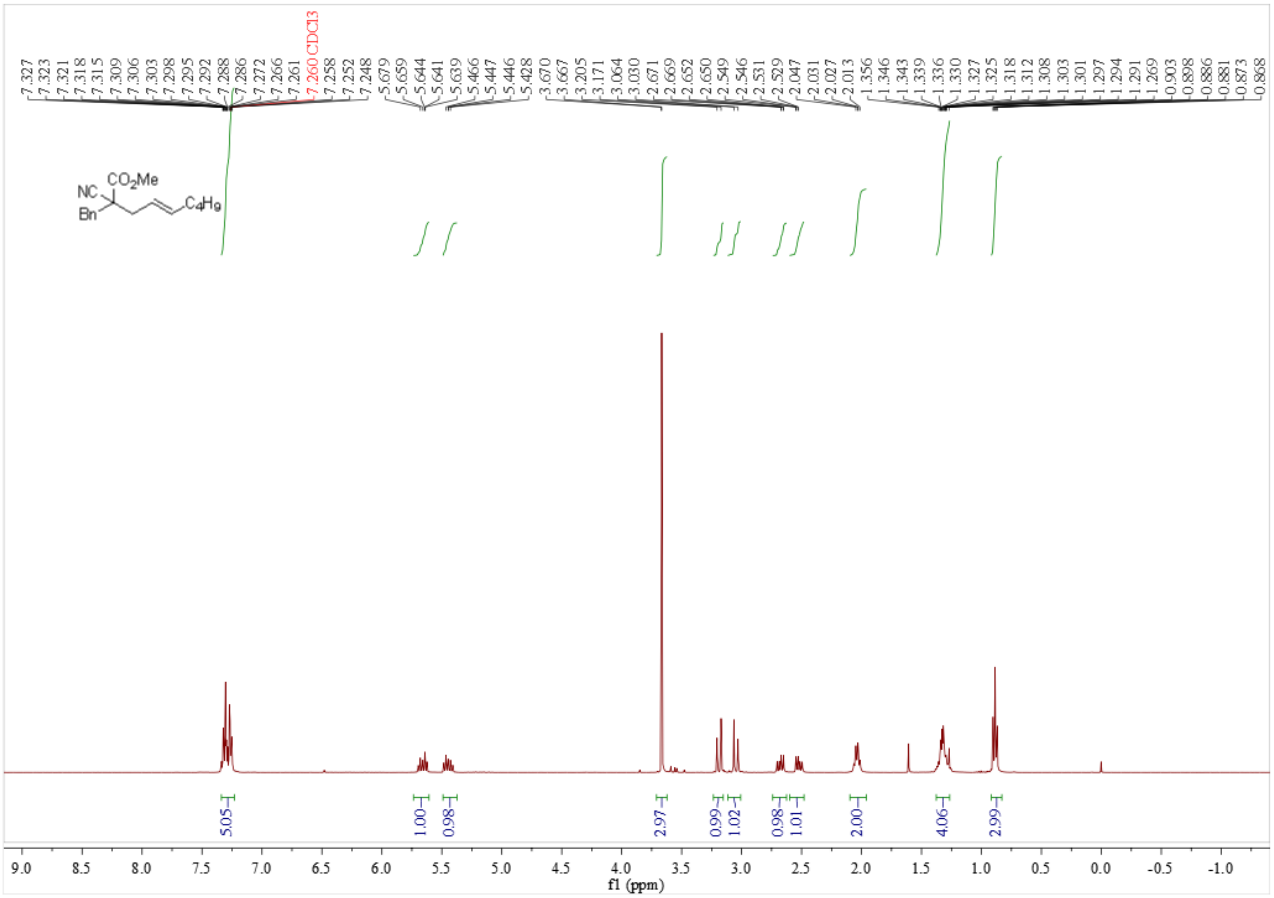
f1 (ppm)

3ca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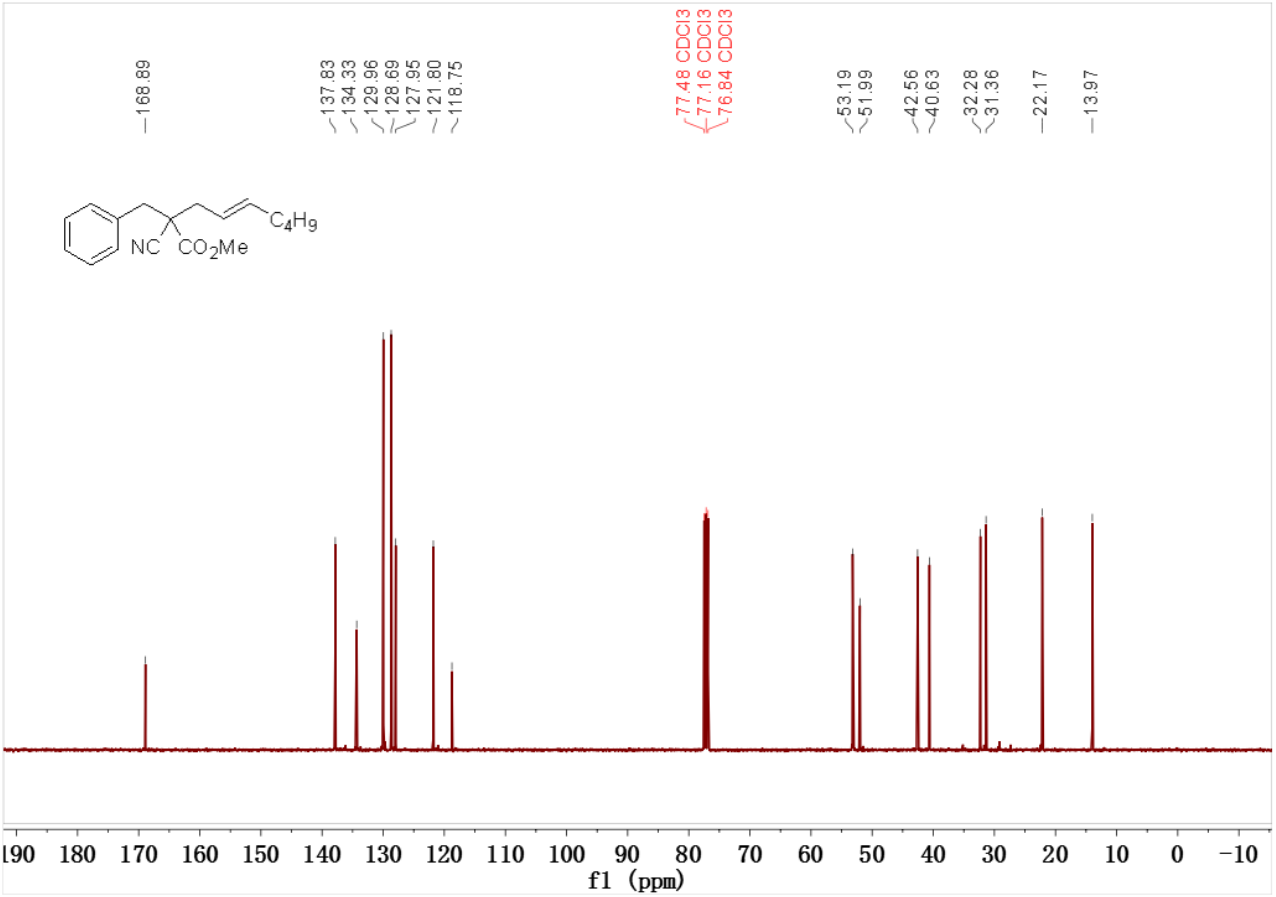
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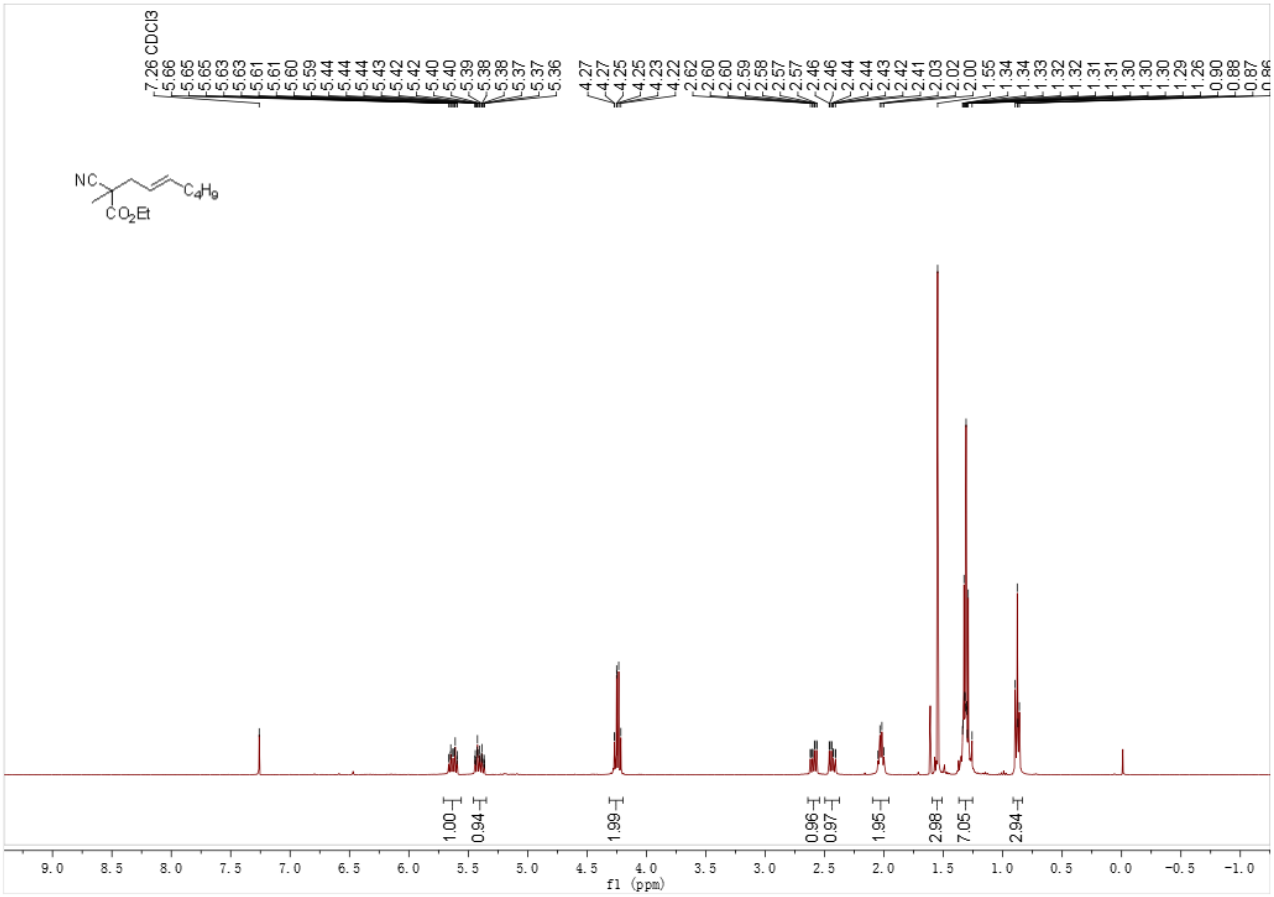
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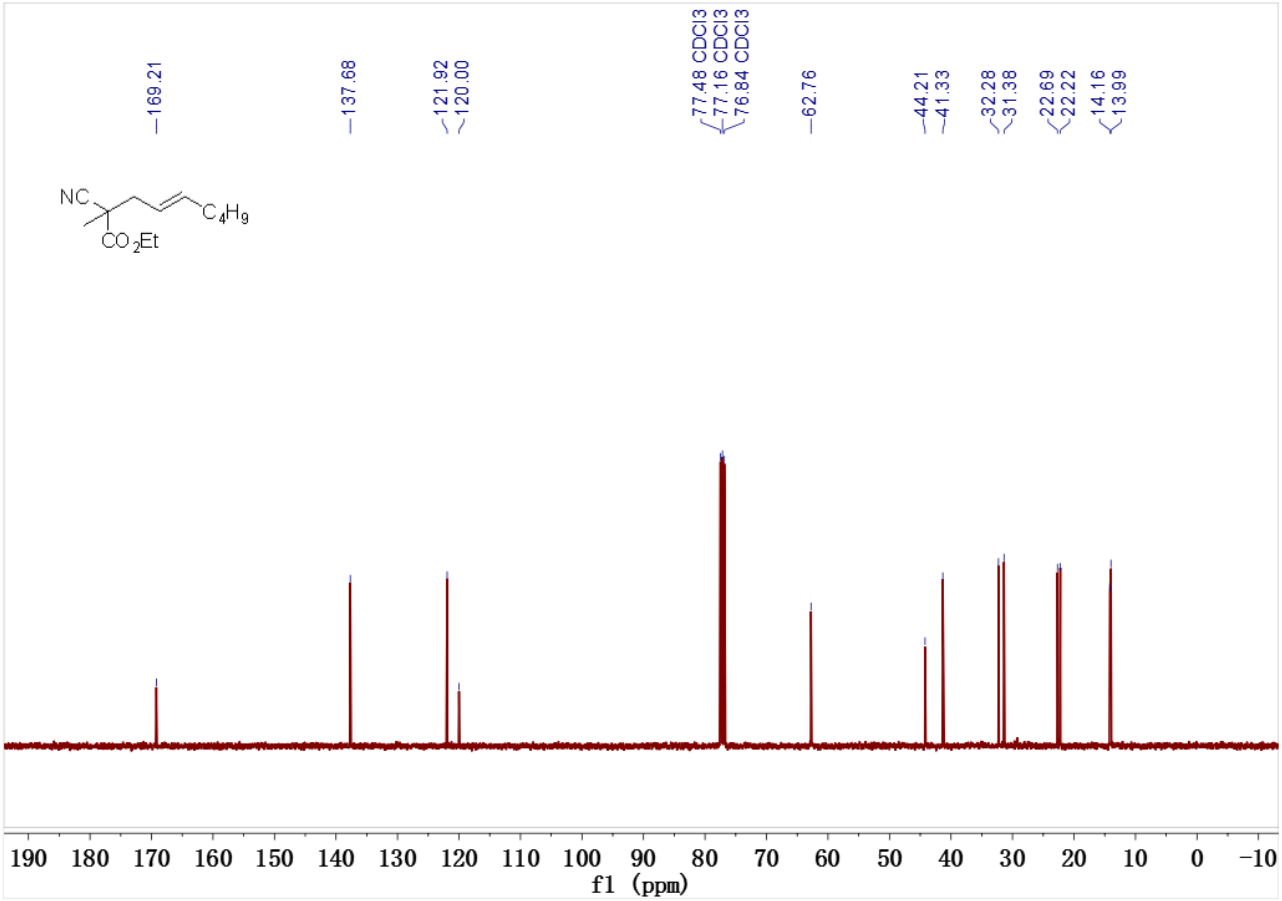
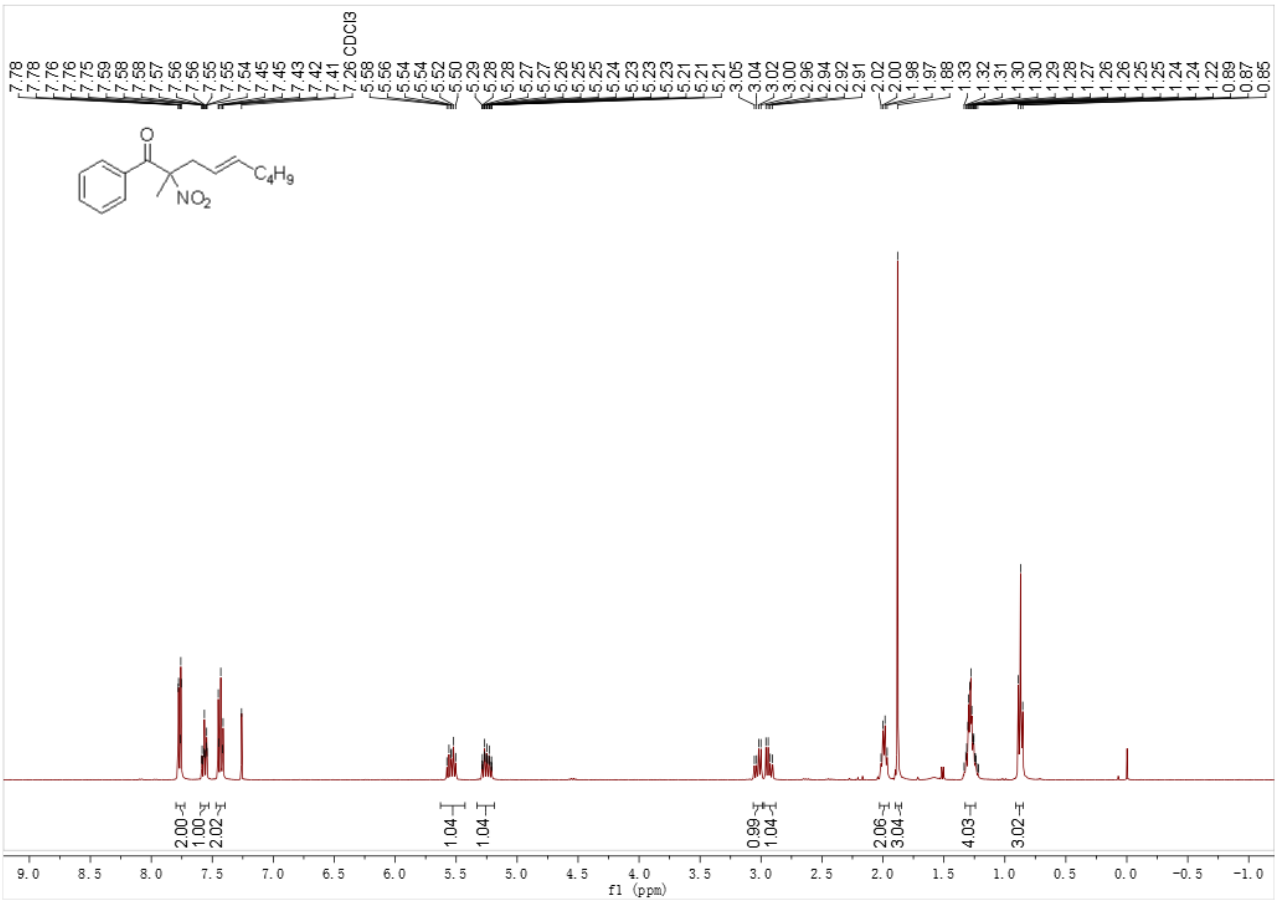
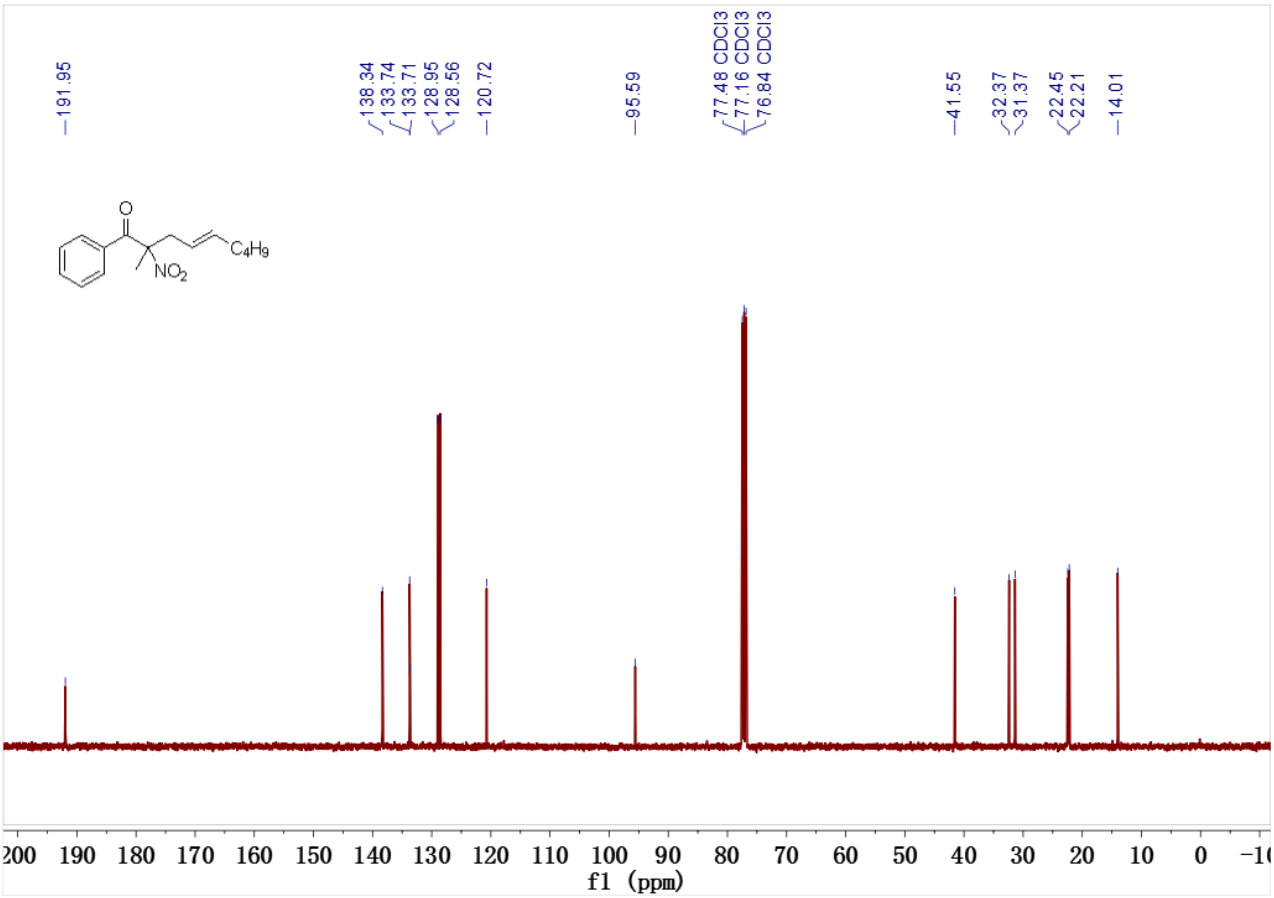
7.05
2.94
f1 (ppm)

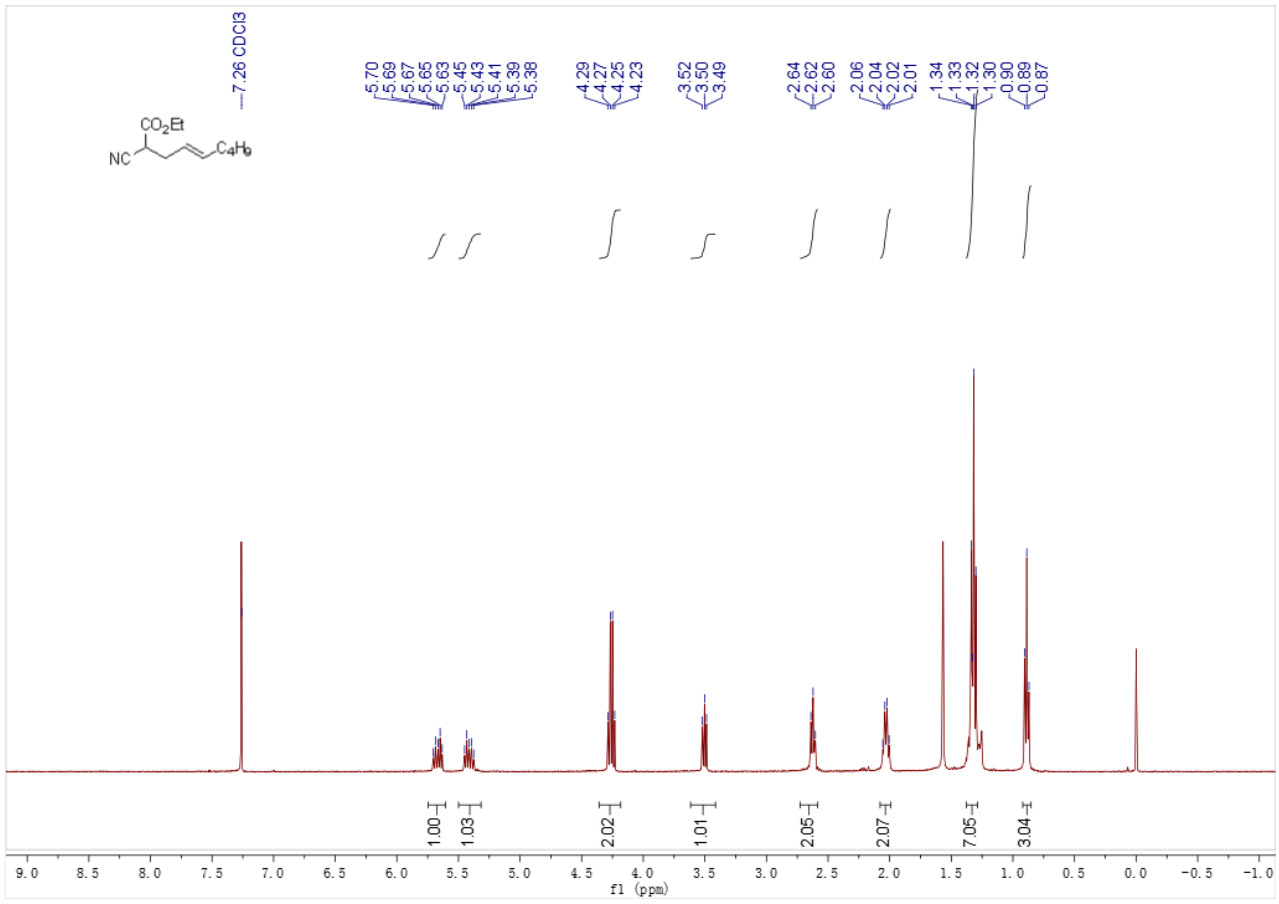

169.21
137.68
121.92
120.00
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.76
44.21
41.33
32.28
31.38
22.69
22.22
14.16
13.99
NC
CO2Et
C4H9
f1 (ppm)

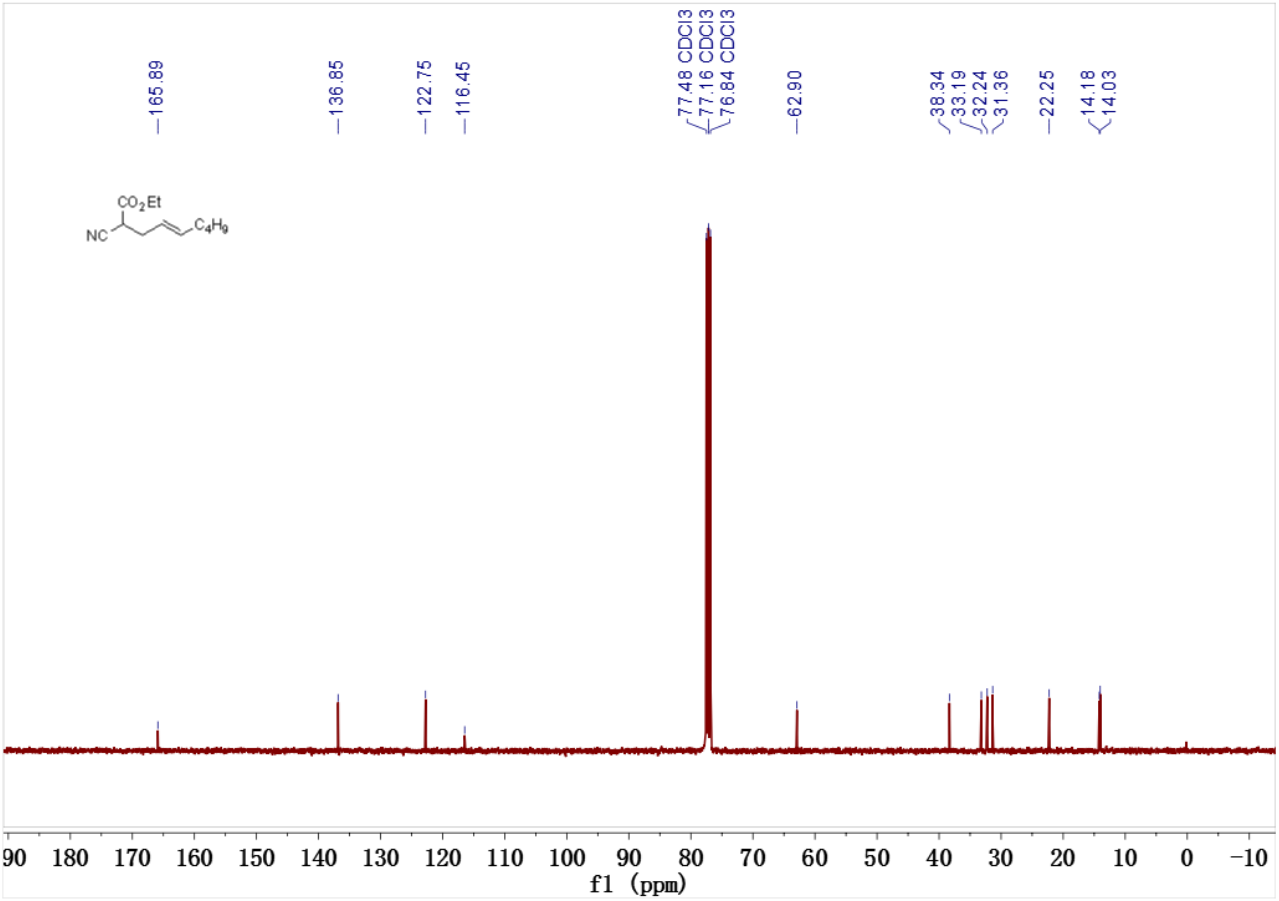
3ea


7.78 7.78 7.76 7.76 7.75 7.59 7.58 7.58 7.57 7.56 7.56 7.55 7.55 7.54 7.45 7.45 7.43 7.42 7.41 7.26 CDCl3
5.58 5.56 5.54 5.54 5.52 5.50 5.29 5.28 5.28 5.27 5.27 5.26 5.25 5.25 5.24 5.23 5.23 5.23 5.21 5.21 5.21
3.05 3.04 3.02 3.00 2.96 2.94 2.92 2.91
2.02 2.00 1.98 1.97 1.88 1.33 1.32 1.31 1.30 1.30 1.29 1.28 1.27 1.26 1.26 1.25 1.25 1.24 1.24 1.22 0.89 0.87 0.85
C4H9
NO2
2.00 1.00 2.02 1.04 1.04 0.99 1.04 2.06 3.04 4.03 3.02
f1 (ppm)

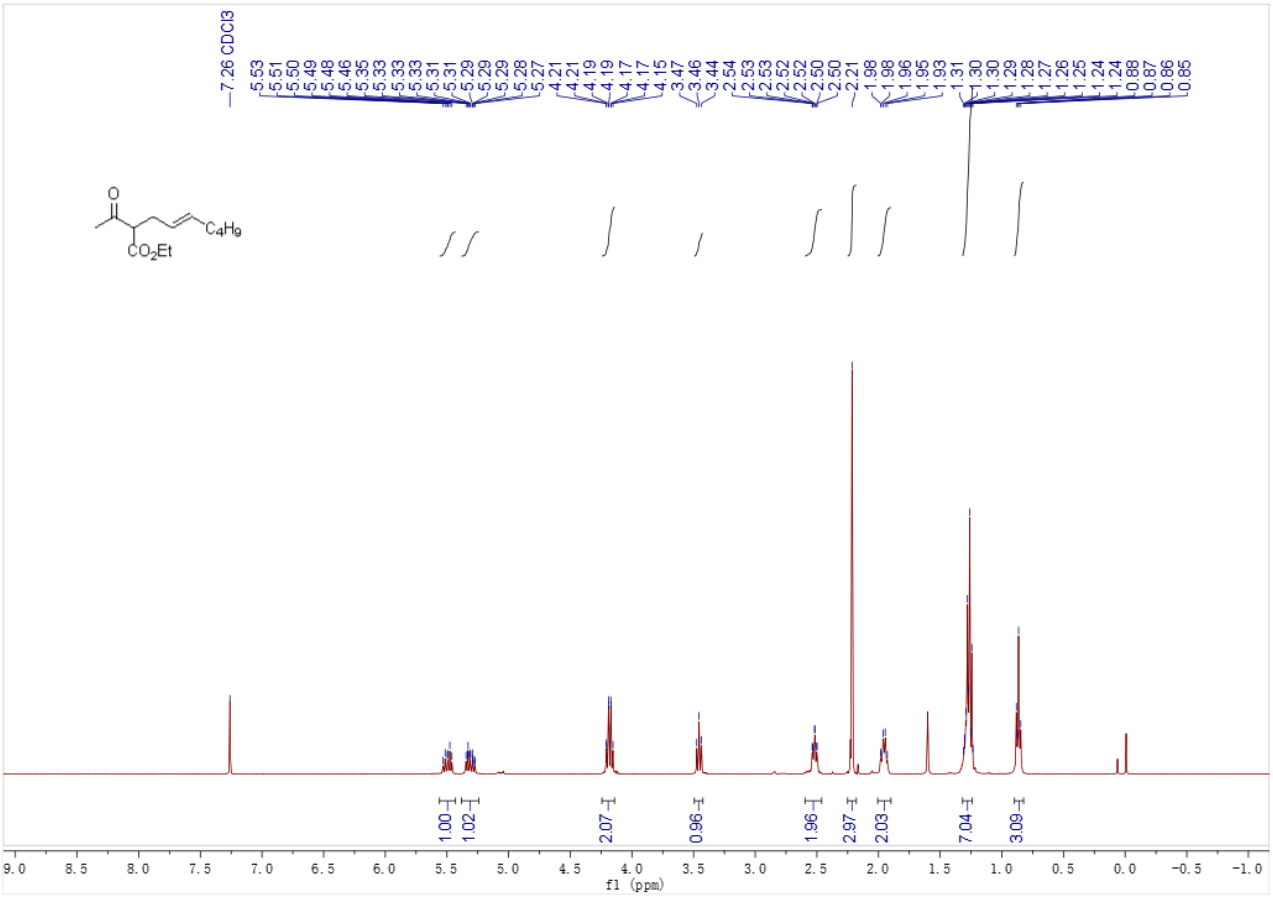

191.95
138.34 133.74 133.71 128.95 128.56 120.72 95.59
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
41.55 32.37 31.37 22.45 22.21 14.01
C4H9
NO2
f1 (ppm)

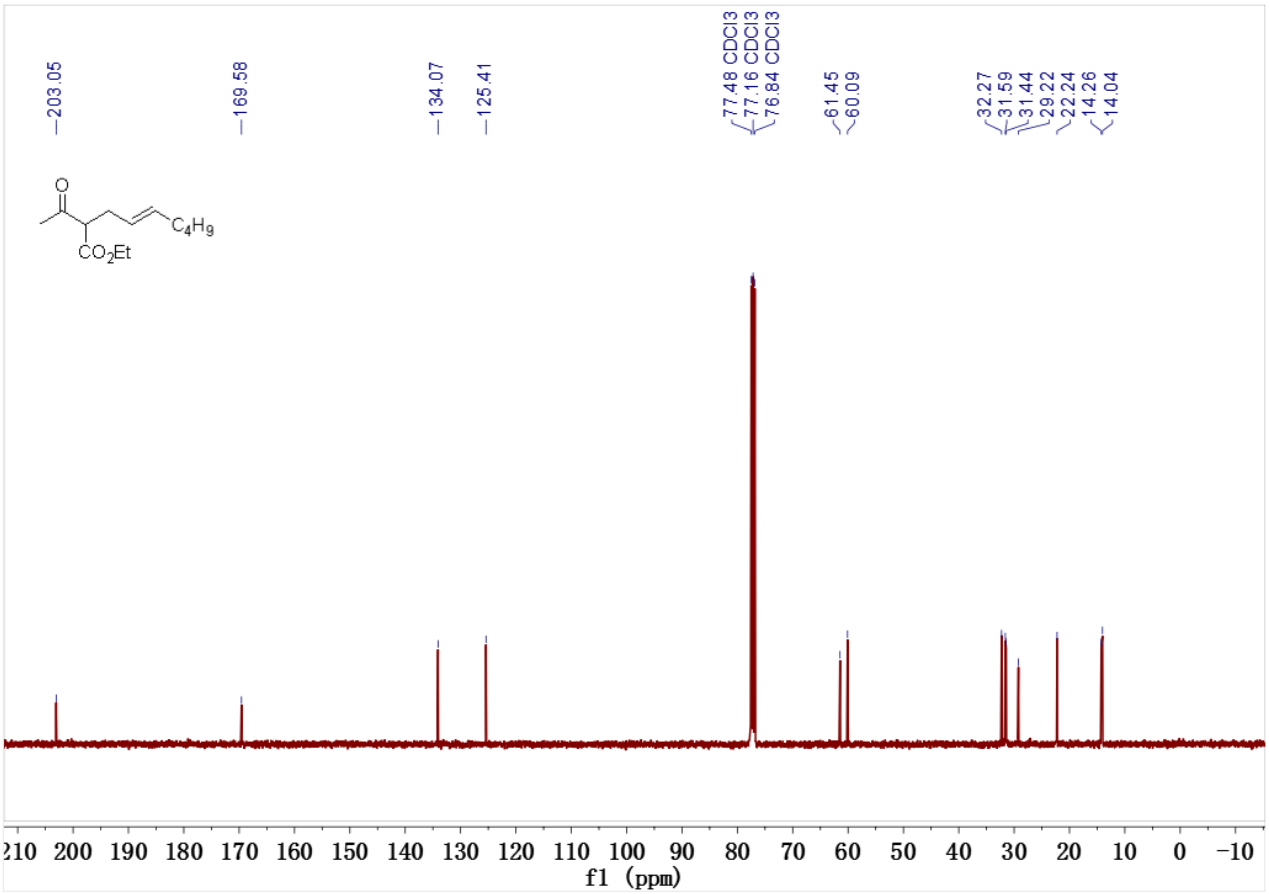
3fa


7.26 CDCl3
5.70
5.69
5.67
5.65
5.63
5.45
5.43
5.41
5.39
5.38
4.29
4.27
4.25
4.23
3.52
3.50
3.49
2.64
2.62
2.60
2.06
2.04
2.02
2.01
1.34
1.33
1.32
1.30
0.90
0.89
0.87
CO2Et
NC
C4H9
1.00
1.03
2.02
1.01
2.05
2.07
7.05
3.04
f1 (ppm)

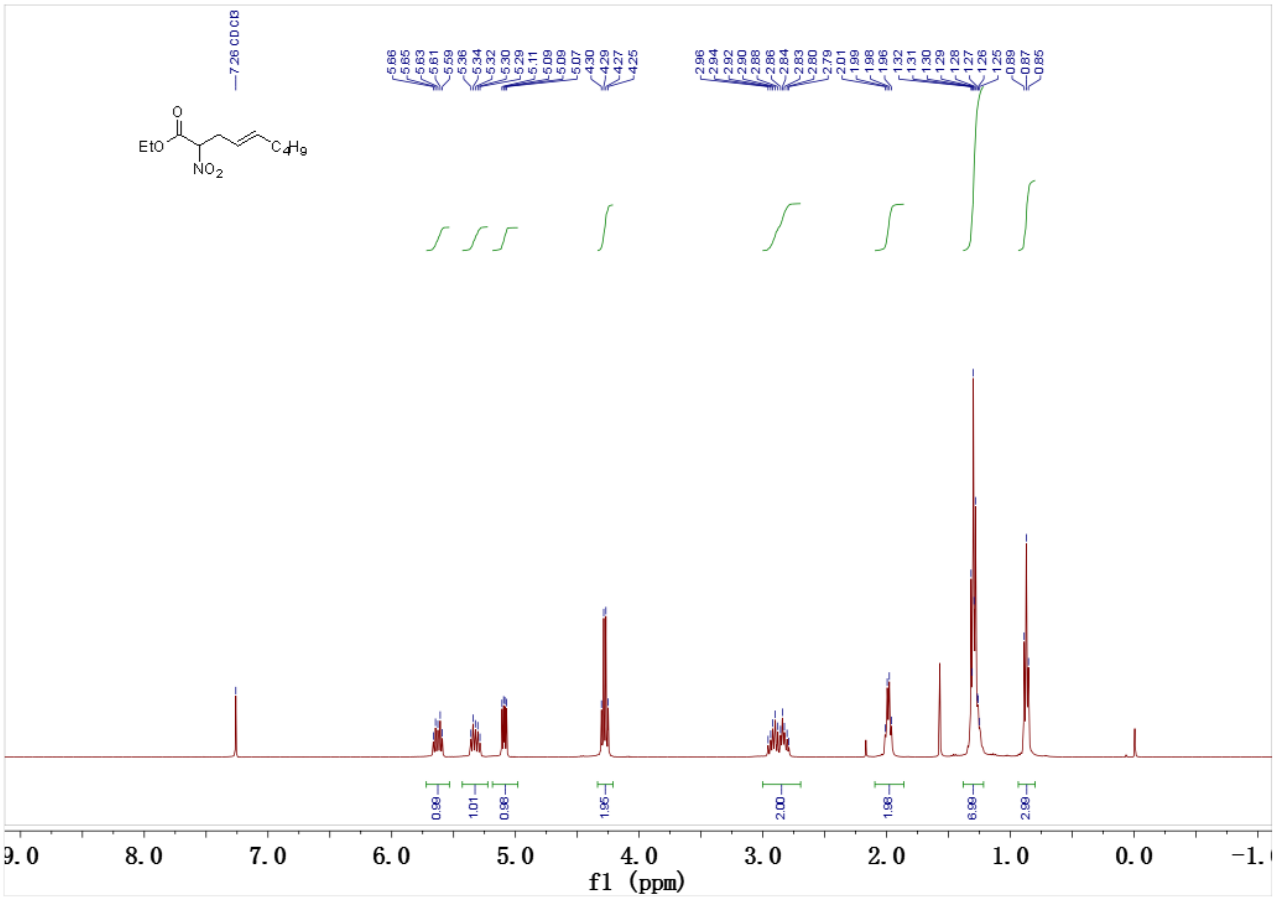

165.89
136.85
122.75
116.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.90
38.34
33.19
32.24
31.36
22.25
14.18
14.03
CO2Et
NC
C4H9
f1 (ppm)

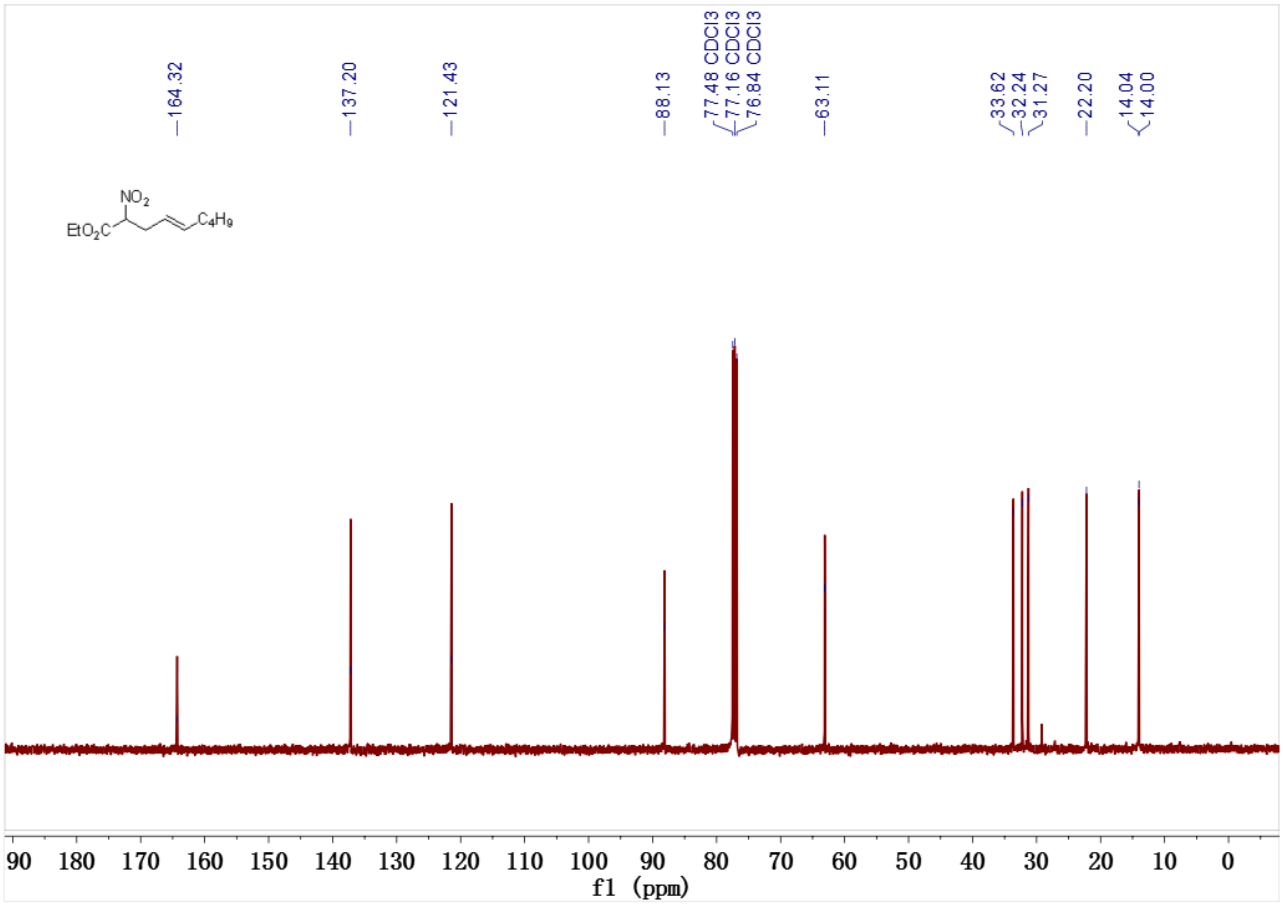
3ga


7.26 CDCl3
5.53
5.51
5.50
5.49
5.48
5.46
5.35
5.33
5.33
5.33
5.31
5.31
5.29
5.29
5.29
5.28
5.27
4.21
4.21
4.19
4.19
4.17
4.17
4.15
3.47
3.46
3.44
2.54
2.53
2.53
2.52
2.52
2.50
2.50
2.21
1.98
1.98
1.96
1.95
1.93
1.31
1.30
1.30
1.29
1.28
1.27
1.26
1.25
1.24
1.24
0.88
0.87
0.86
0.85
C4H9
CO2Et
1.00
1.02
2.07
0.96
1.96
2.97
2.03
7.04
3.09
f1 (ppm)

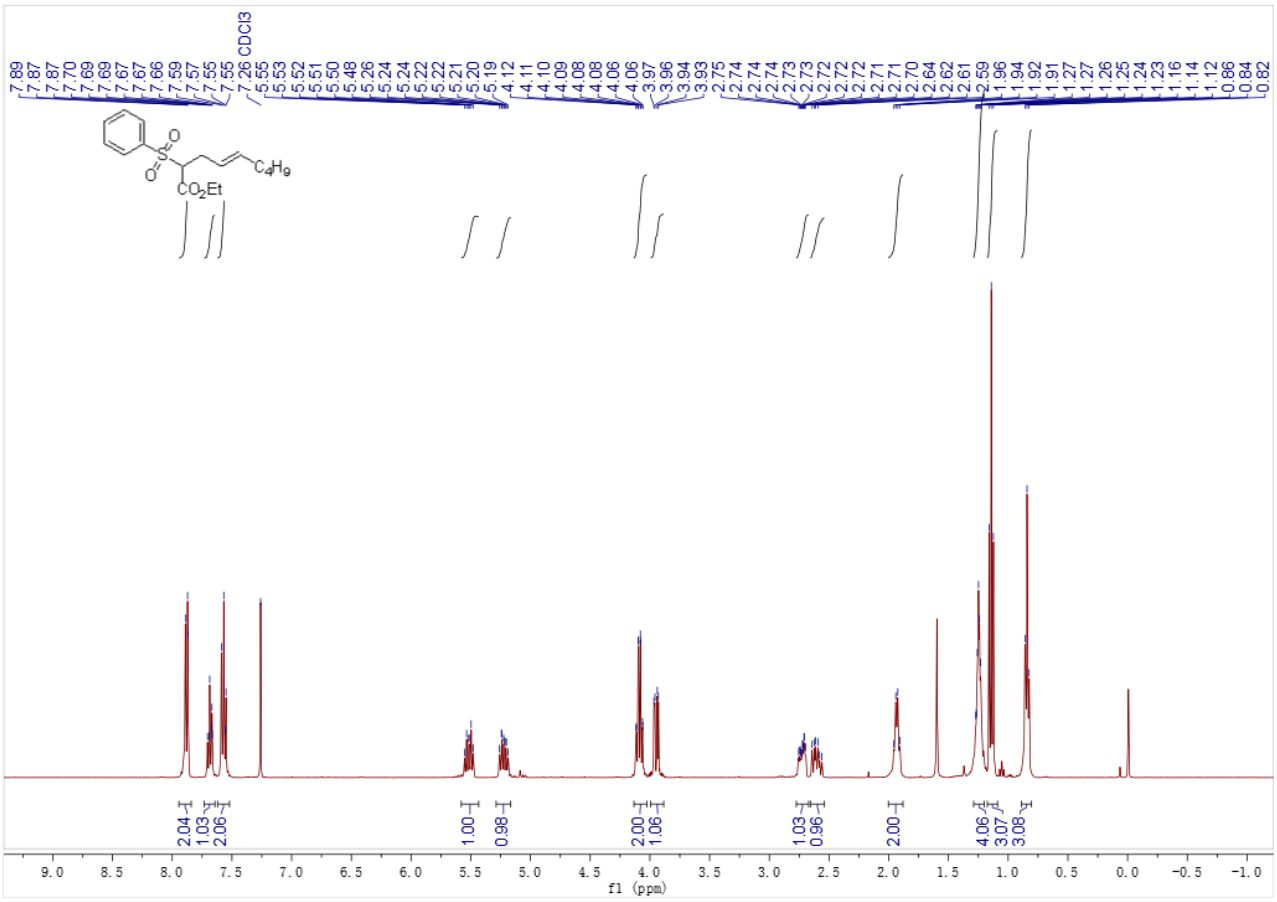

203.05
169.58
134.07
125.41
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.45
60.09
32.27
31.59
31.44
29.22
22.24
14.26
14.04
C4H9
CO2Et
f1 (ppm)

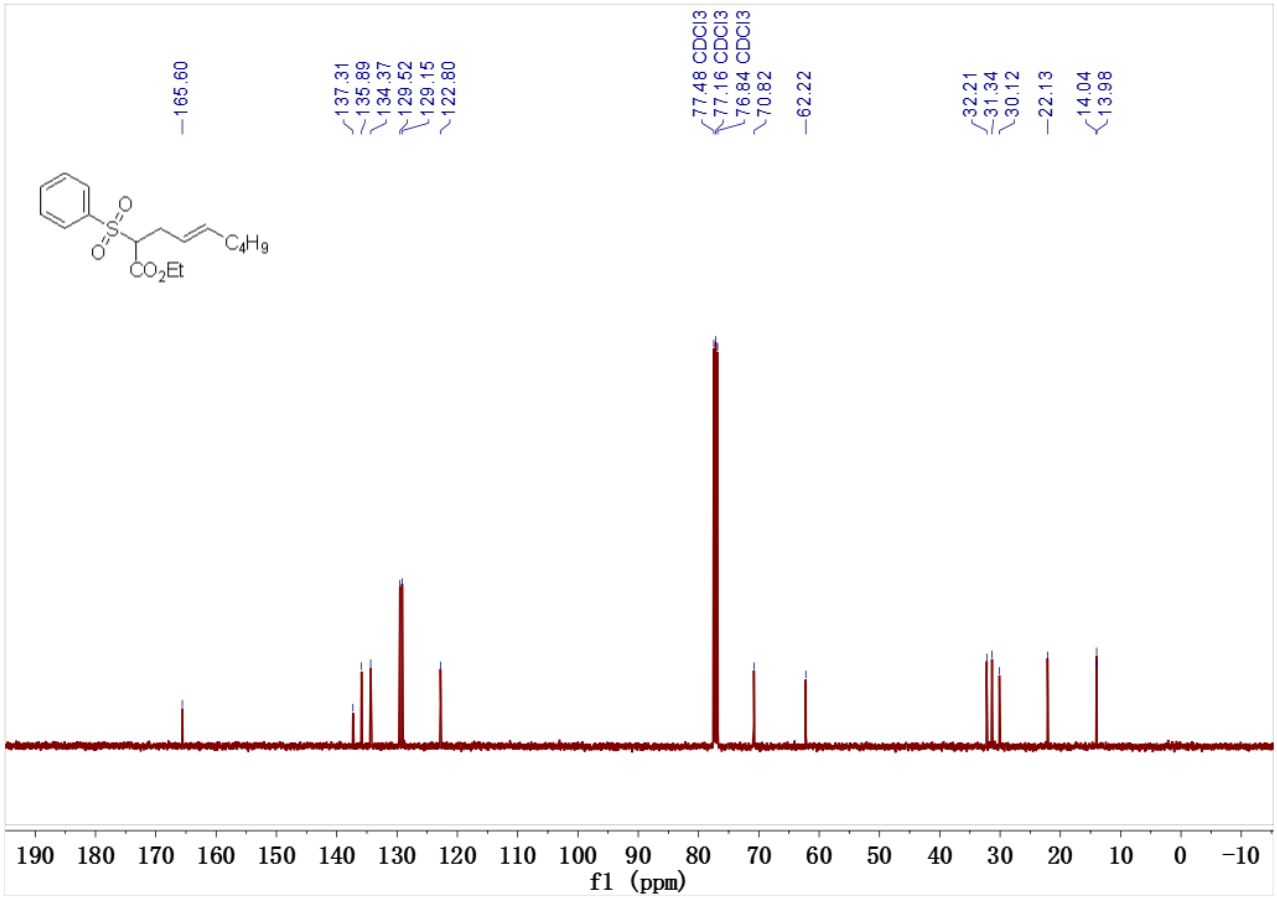
3ha


7.26 CDCl3
5.66
5.65
5.63
5.61
5.59
5.36
5.34
5.32
5.30
5.29
5.11
5.09
5.09
5.07
4.30
4.29
4.27
4.25
2.96
2.94
2.92
2.90
2.88
2.86
2.84
2.83
2.80
2.79
2.01
1.99
1.98
1.96
1.32
1.31
1.30
1.29
1.28
1.27
1.26
1.25
0.89
0.87
0.85
EtO
O
NO2
C4H9
0.99
1.01
0.98
1.95
2.00
1.98
6.99
2.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

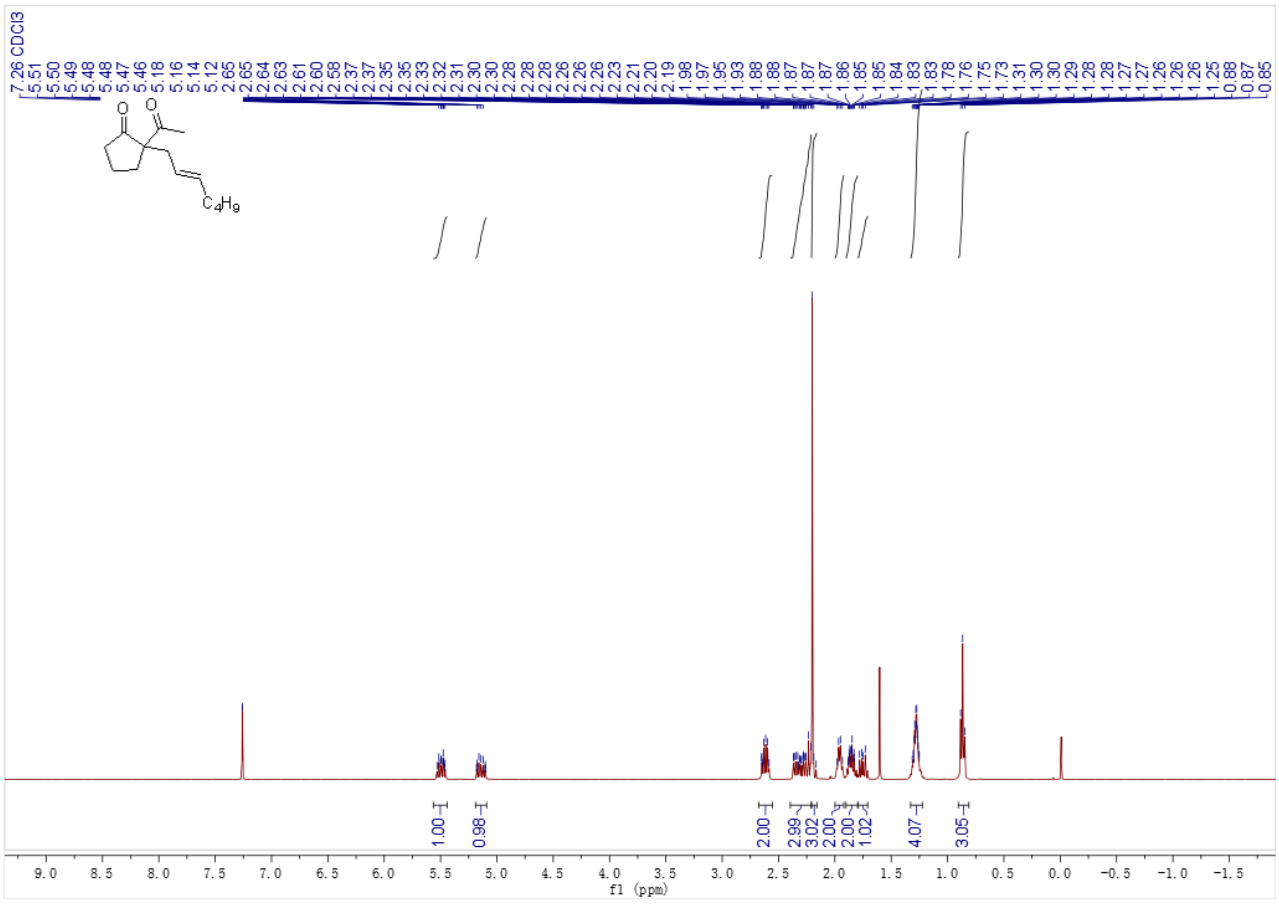

164.32
137.20
121.43
88.13
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.11
33.62
32.24
31.27
22.20
14.04
14.00
NO2
EtO2C
C4H9
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

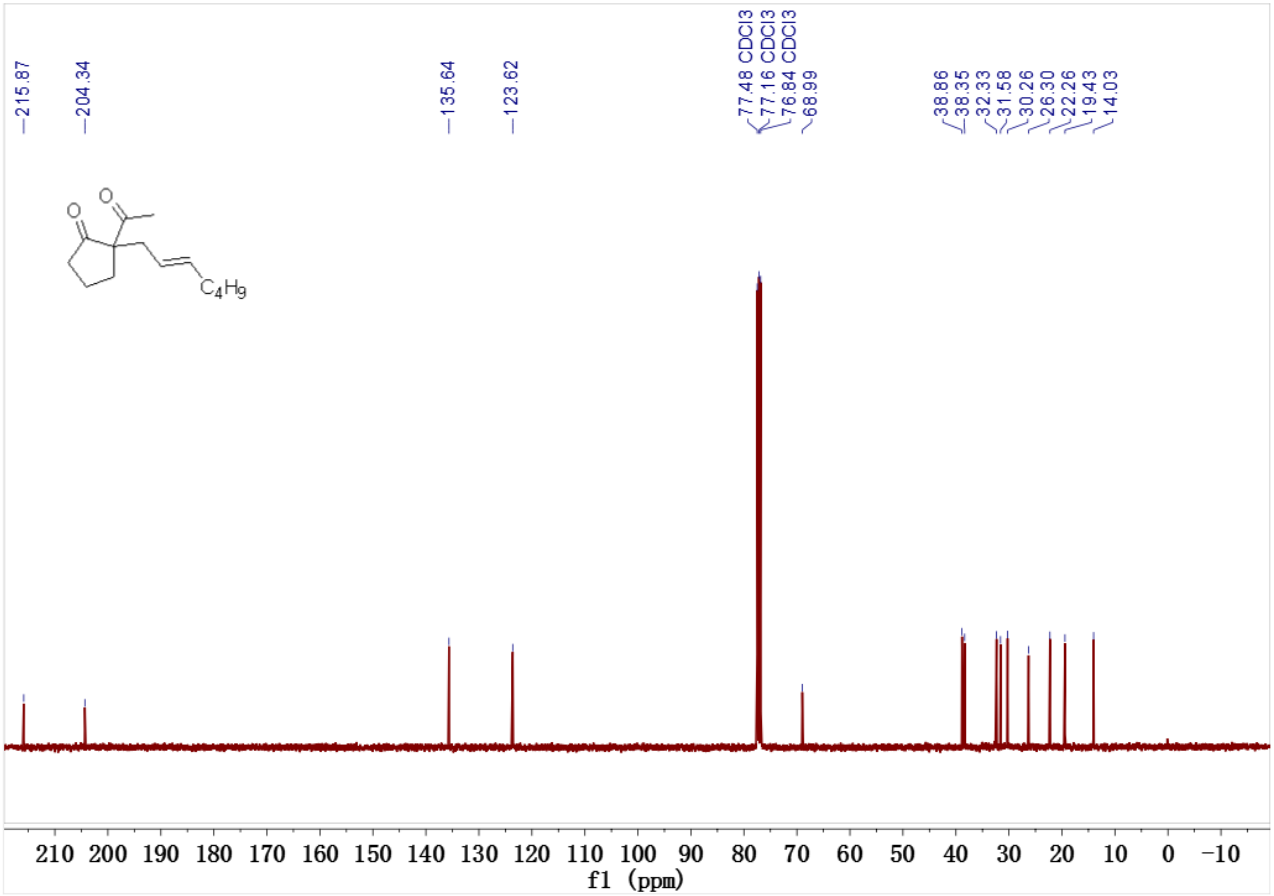
3ia


7.89 7.87 7.87 7.70 7.69 7.69 7.67 7.67 7.66 7.59 7.57 7.55 7.55 7.26 CDCl3 5.55 5.53 5.52 5.51 5.50 5.48 5.26 5.24 5.24 5.22 5.22 5.21 5.20 5.19 4.12 4.11 4.10 4.09 4.08 4.08 4.06 4.06 3.97 3.96 3.94 3.93 2.75 2.74 2.74 2.74 2.73 2.73 2.72 2.72 2.72 2.71 2.71 2.70 2.64 2.62 2.61 2.59 1.96 1.94 1.92 1.91 1.27 1.27 1.26 1.25 1.24 1.23 1.16 1.14 1.12 0.86 0.84 0.82
C4H9
CO2Et
2.04 1.03 2.06 1.00 0.98 2.00 1.06 1.03 0.96 2.00 4.06 3.07 3.08
f1 (ppm)

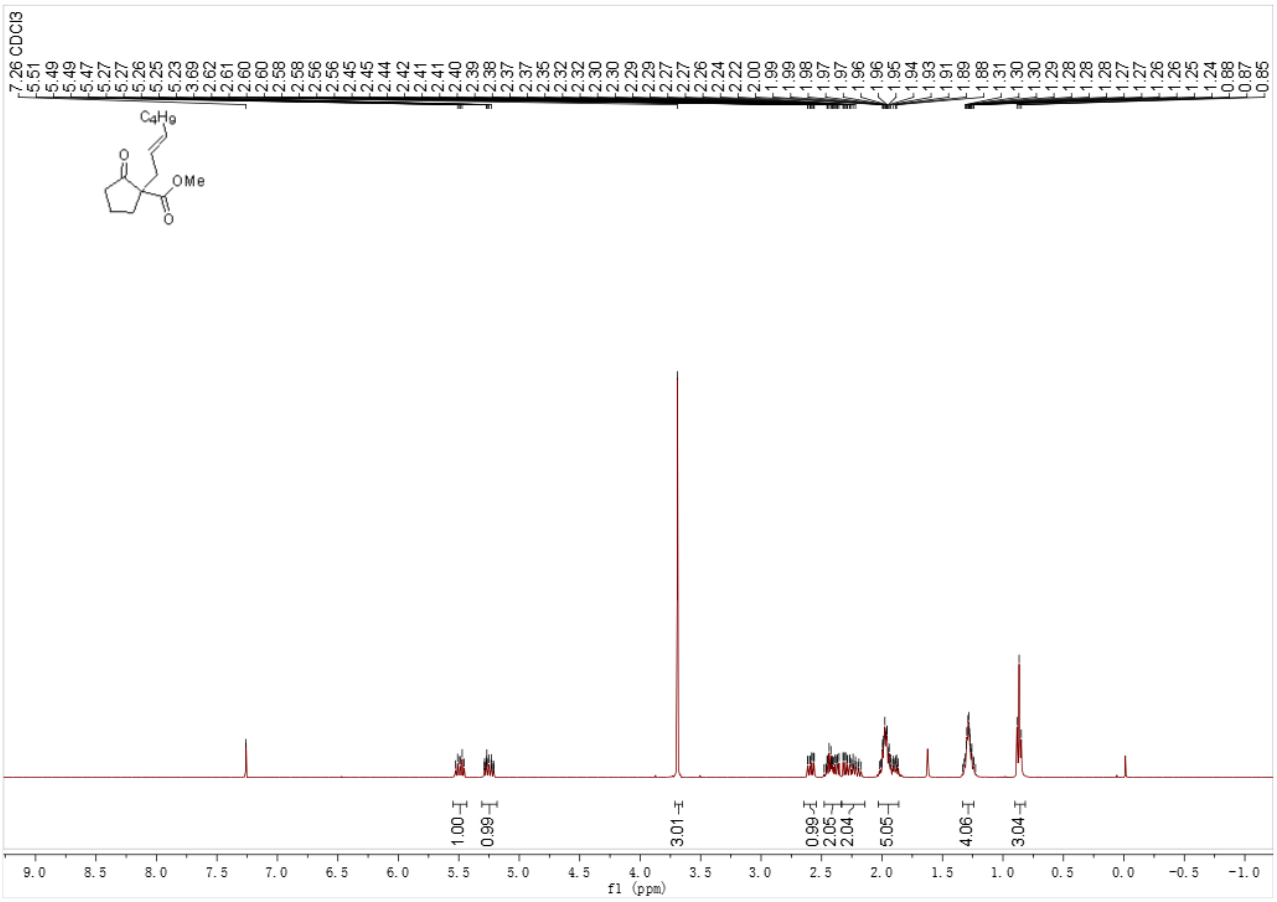

165.60
137.31 135.89 134.37 129.52 129.15 122.80
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 70.82 62.22
32.21 31.34 30.12 22.13 14.04 13.98
C4H9
CO2Et
f1 (ppm)

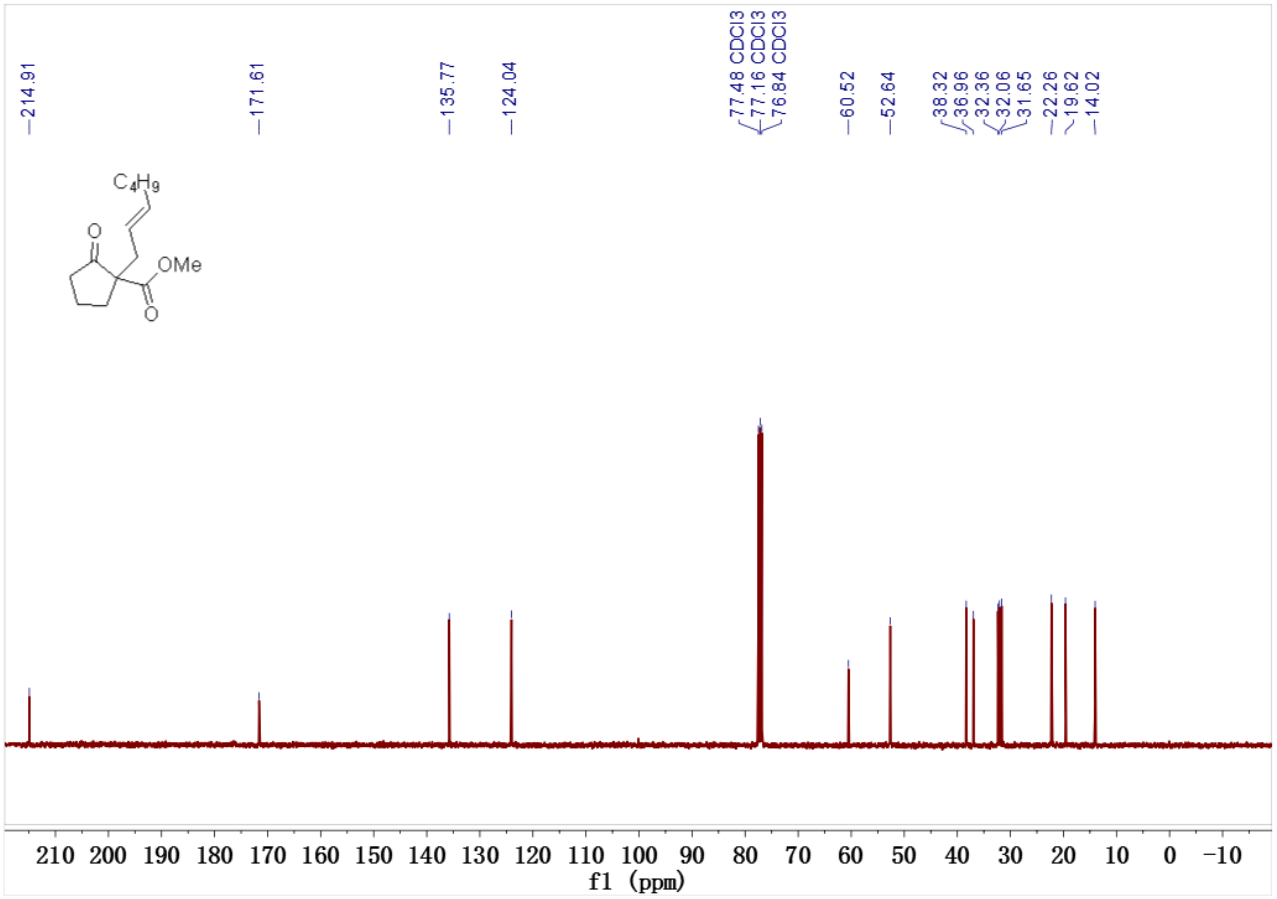
3ja


7.26 CDCl3
1.00
0.98
2.00
2.99
3.02
2.00
2.00
1.02
4.07
3.05
f1 (ppm)

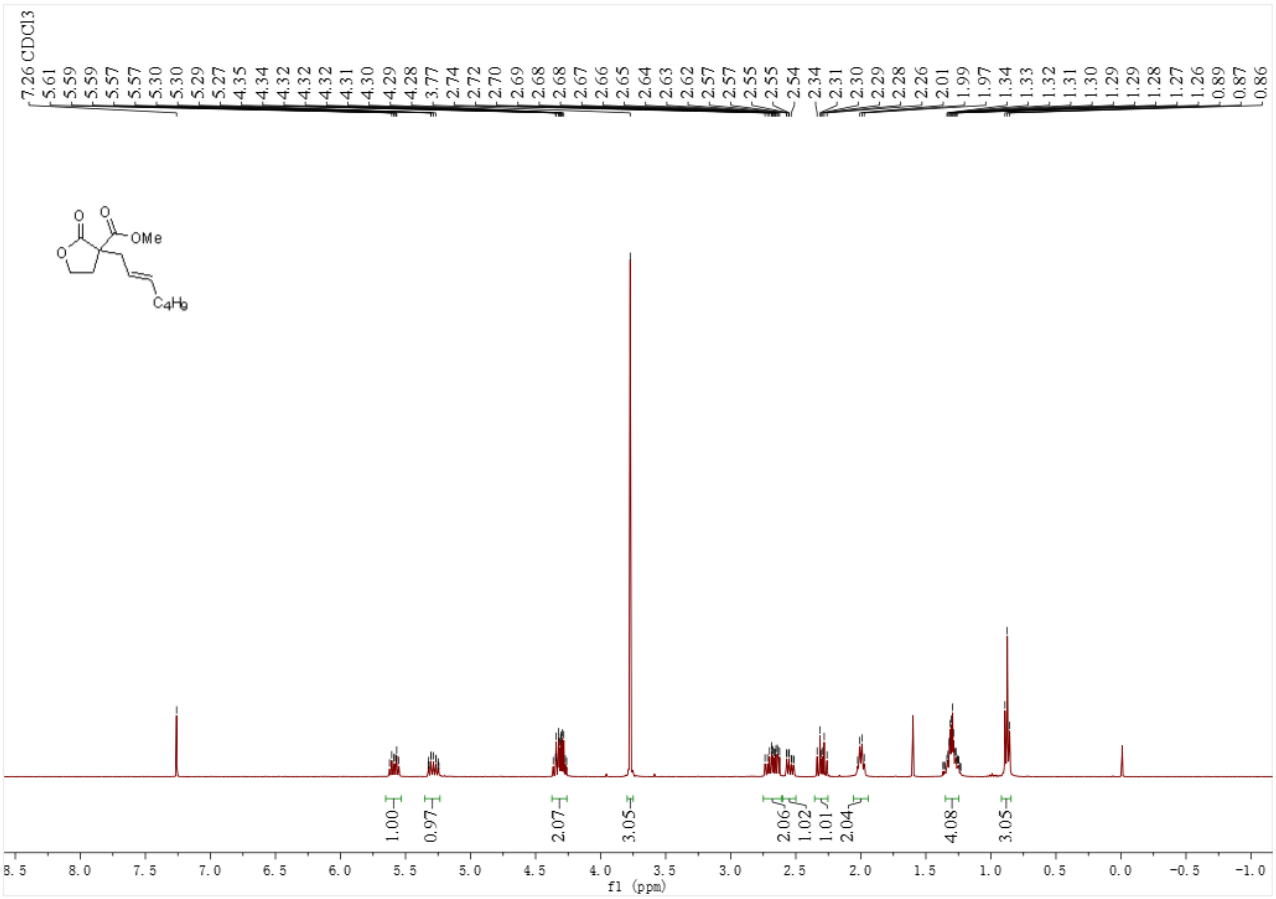

215.87
204.34
135.64
123.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.99
38.86
38.35
32.33
31.58
30.26
26.30
22.26
19.43
14.03
f1 (ppm)

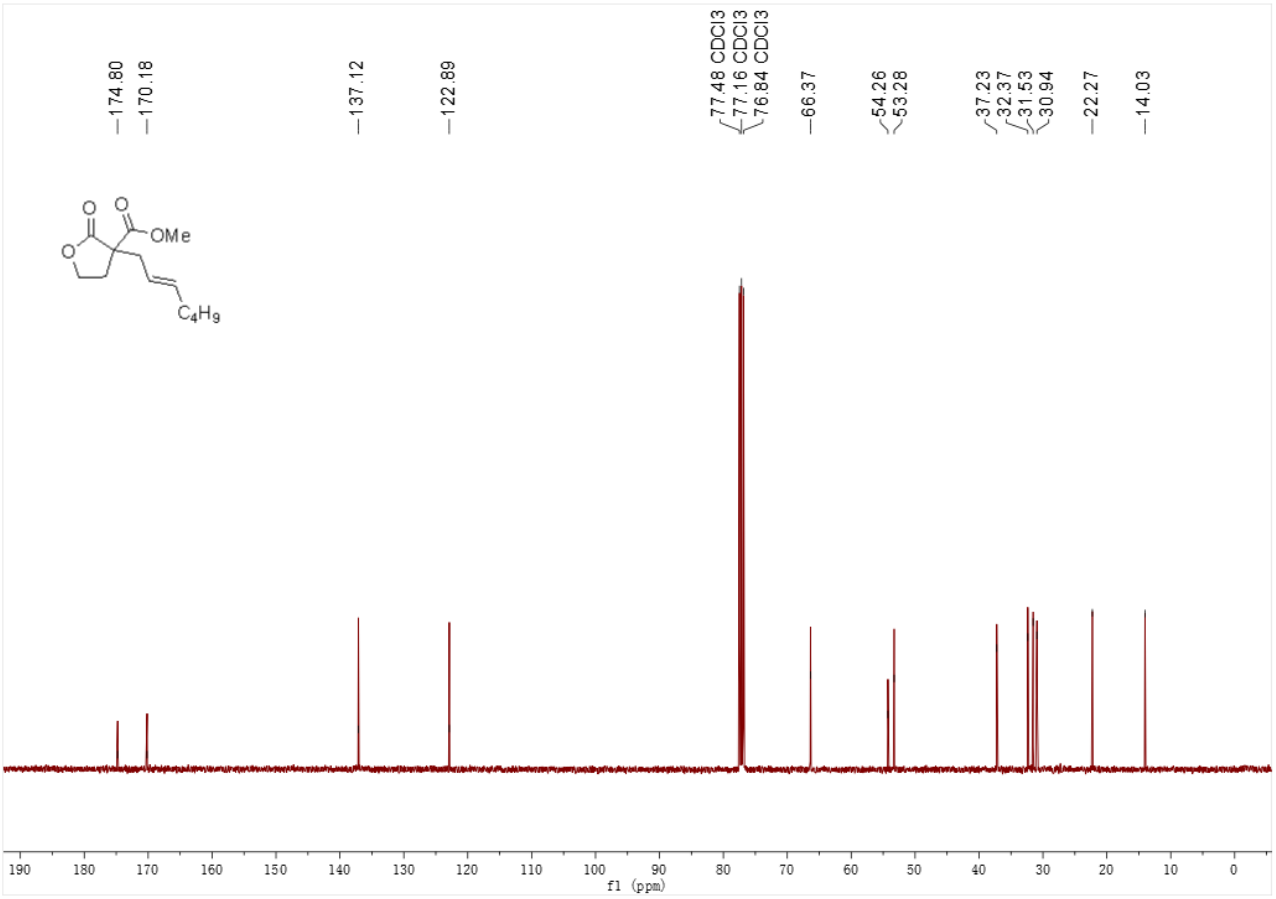
3ka


7.26 CDCl3
C4H9
OMe
1.00
0.99
3.01
0.99
2.05
2.04
5.05
4.06
3.04
f1 (ppm)

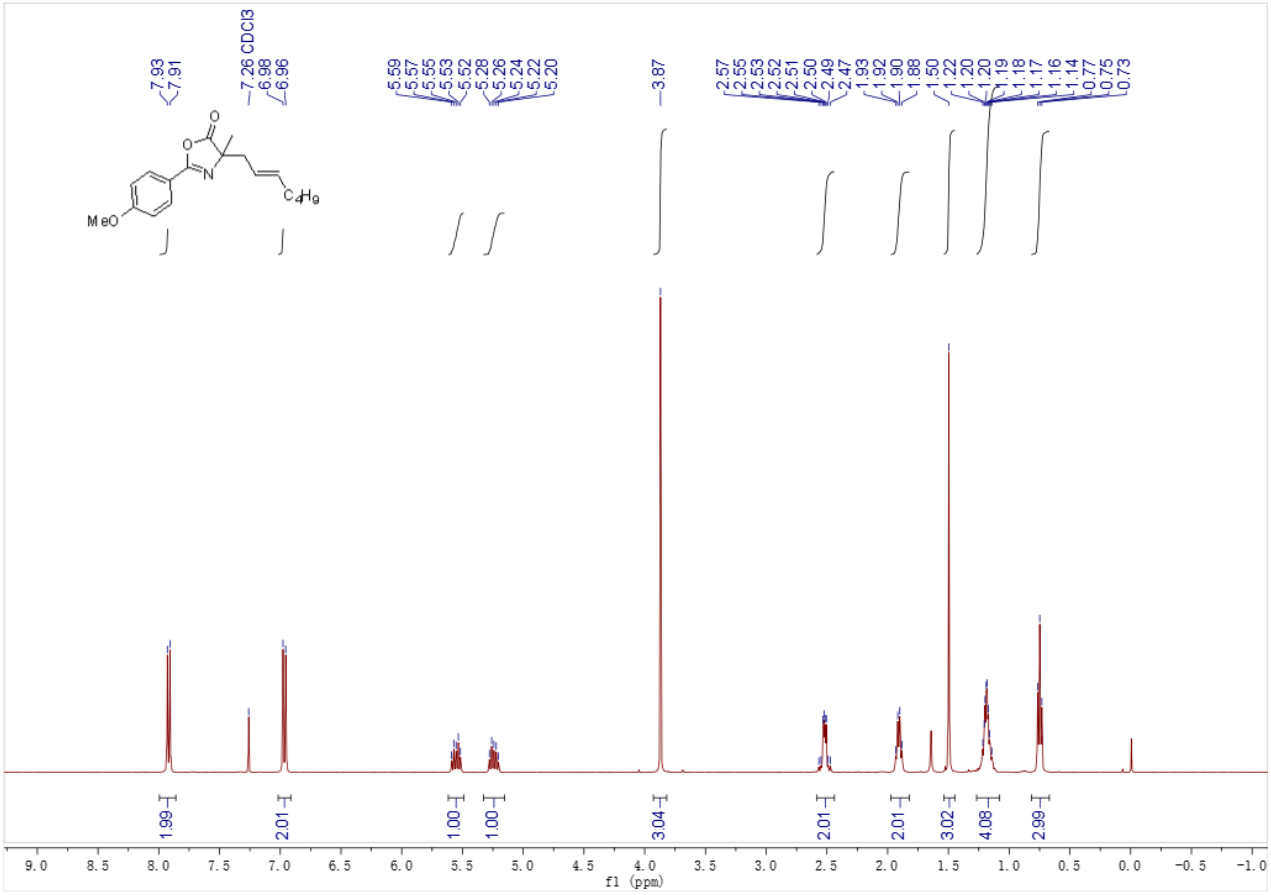

214.91
171.61
135.77
124.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
60.52
52.64
38.32
36.96
32.36
32.06
31.65
22.26
19.62
14.02
C4H9
OMe
f1 (ppm)

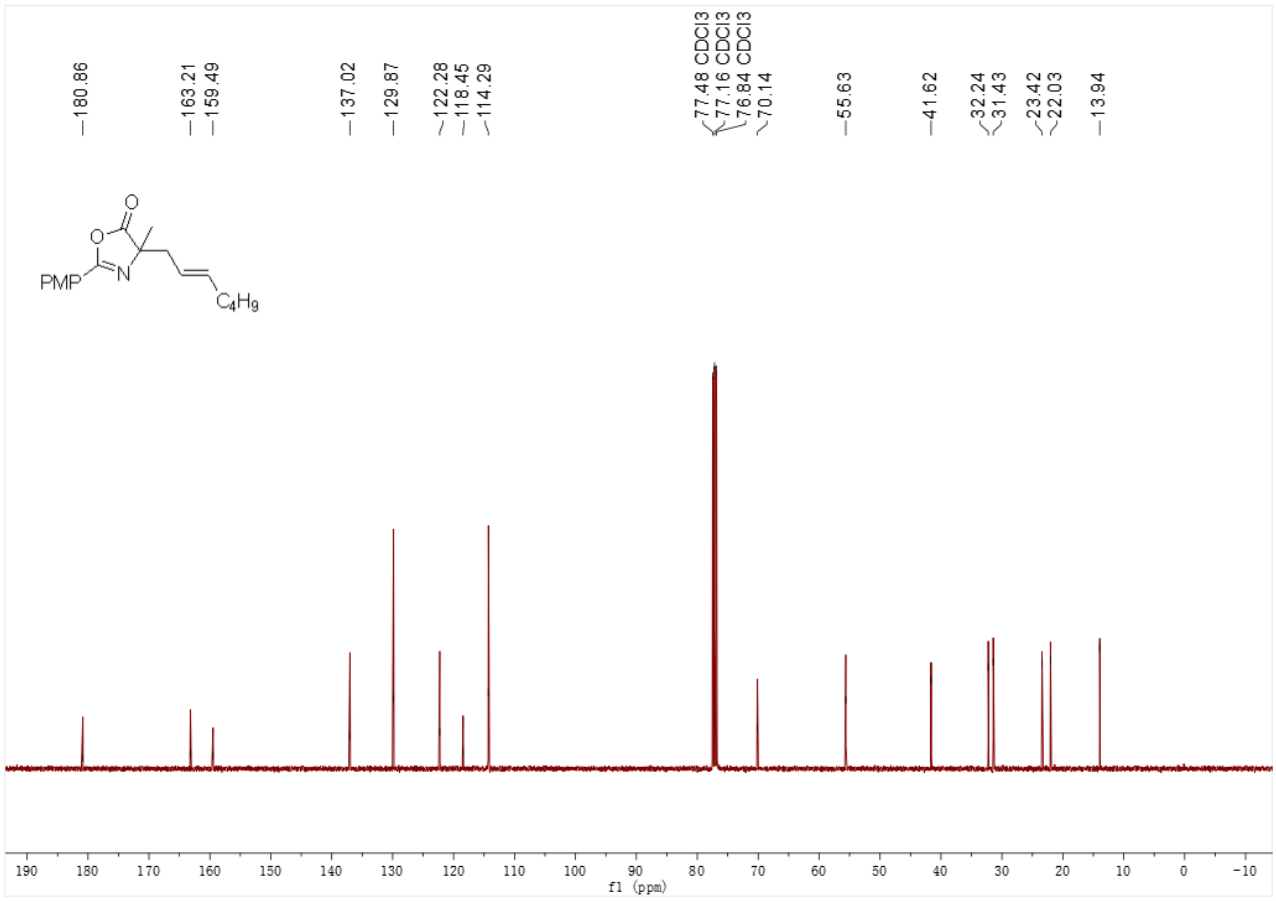
3la


7.26 CDCl3
5.61
5.59
5.59
5.57
5.57
5.30
5.30
5.29
5.27
4.35
4.34
4.32
4.32
4.32
4.31
4.30
4.29
4.28
3.77
2.74
2.72
2.70
2.69
2.68
2.68
2.67
2.66
2.65
2.64
2.63
2.62
2.57
2.57
2.55
2.55
2.54
2.34
2.31
2.30
2.29
2.28
2.26
2.01
1.99
1.97
1.34
1.33
1.32
1.31
1.30
1.29
1.29
1.28
1.27
1.26
0.89
0.87
0.86
OMe
C4H9
1.00
0.97
2.07
3.05
2.06
1.02
1.01
2.04
4.08
3.05
f1 (ppm)

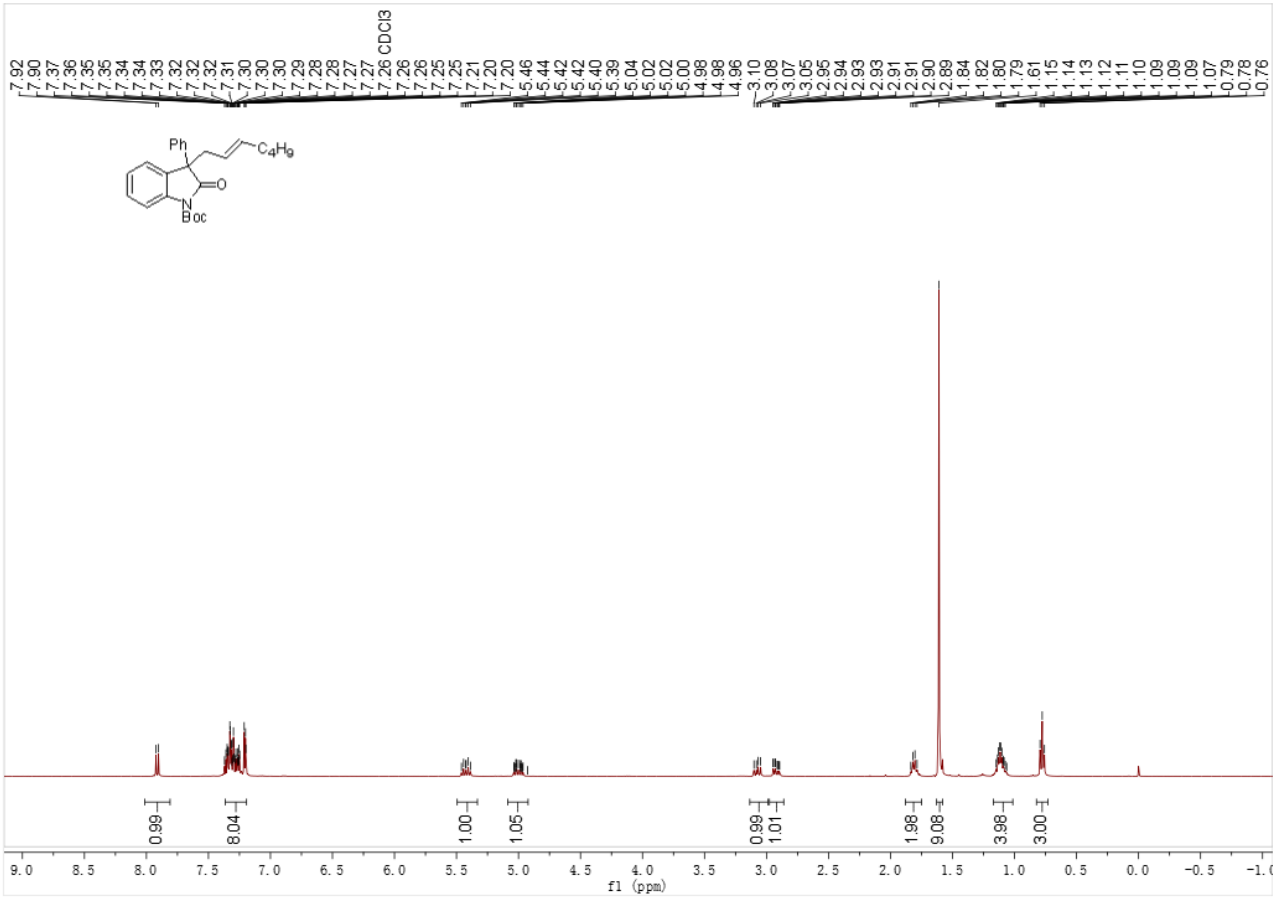

174.80
170.18
137.12
122.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.37
54.26
53.28
37.23
32.37
31.53
30.94
22.27
14.03
OMe
C4H9
f1 (ppm)

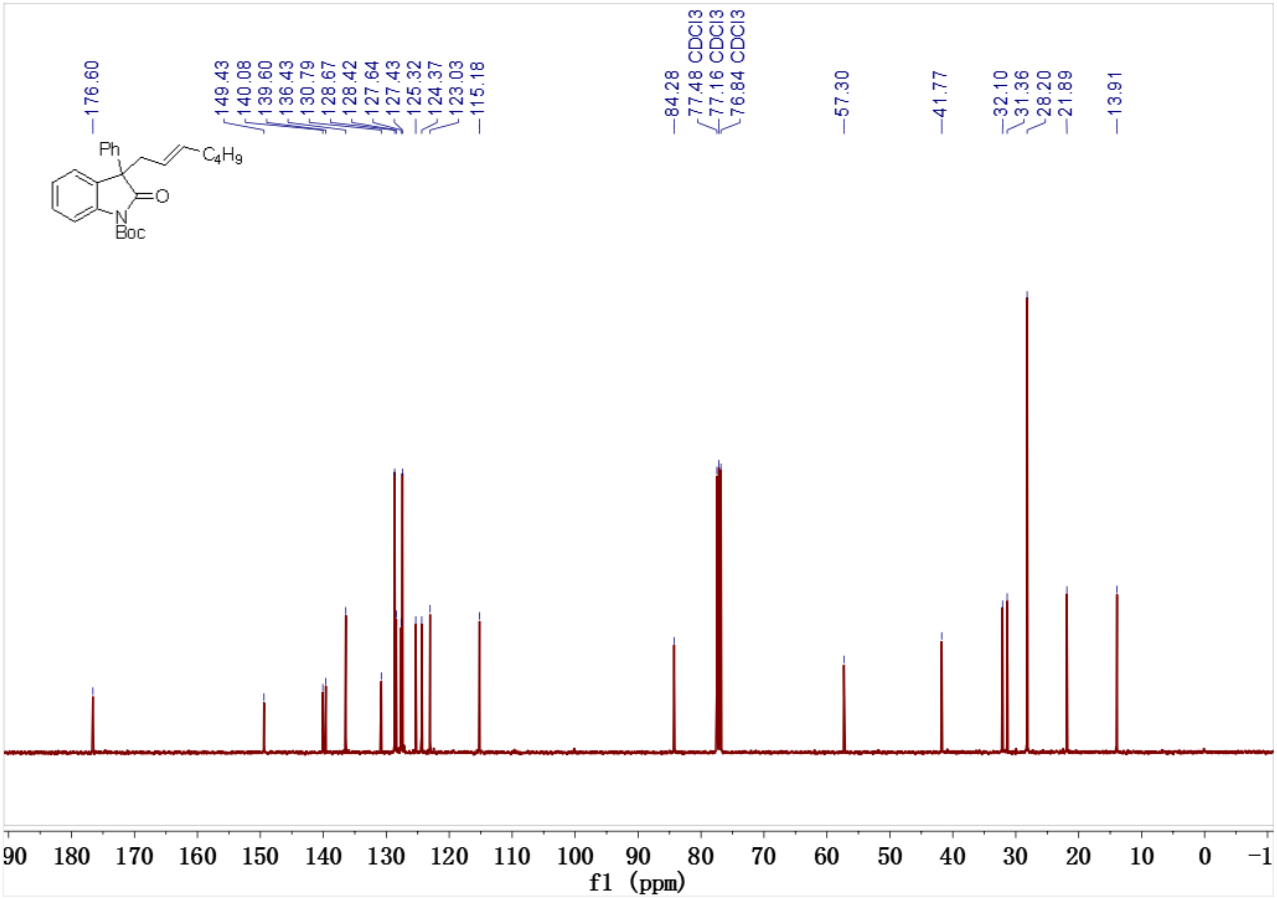
3ma


7.93
7.91
7.26 CDCl3
6.98
6.96
5.59
5.57
5.55
5.53
5.52
5.28
5.26
5.24
5.22
5.20
3.87
2.57
2.55
2.53
2.52
2.51
2.50
2.49
2.47
1.93
1.92
1.90
1.88
1.50
1.22
1.20
1.19
1.18
1.17
1.16
1.14
0.77
0.75
0.73
MeO
C4H9
1.99
2.01
1.00
1.00
3.04
2.01
2.01
3.02
4.08
2.99
f1 (ppm)

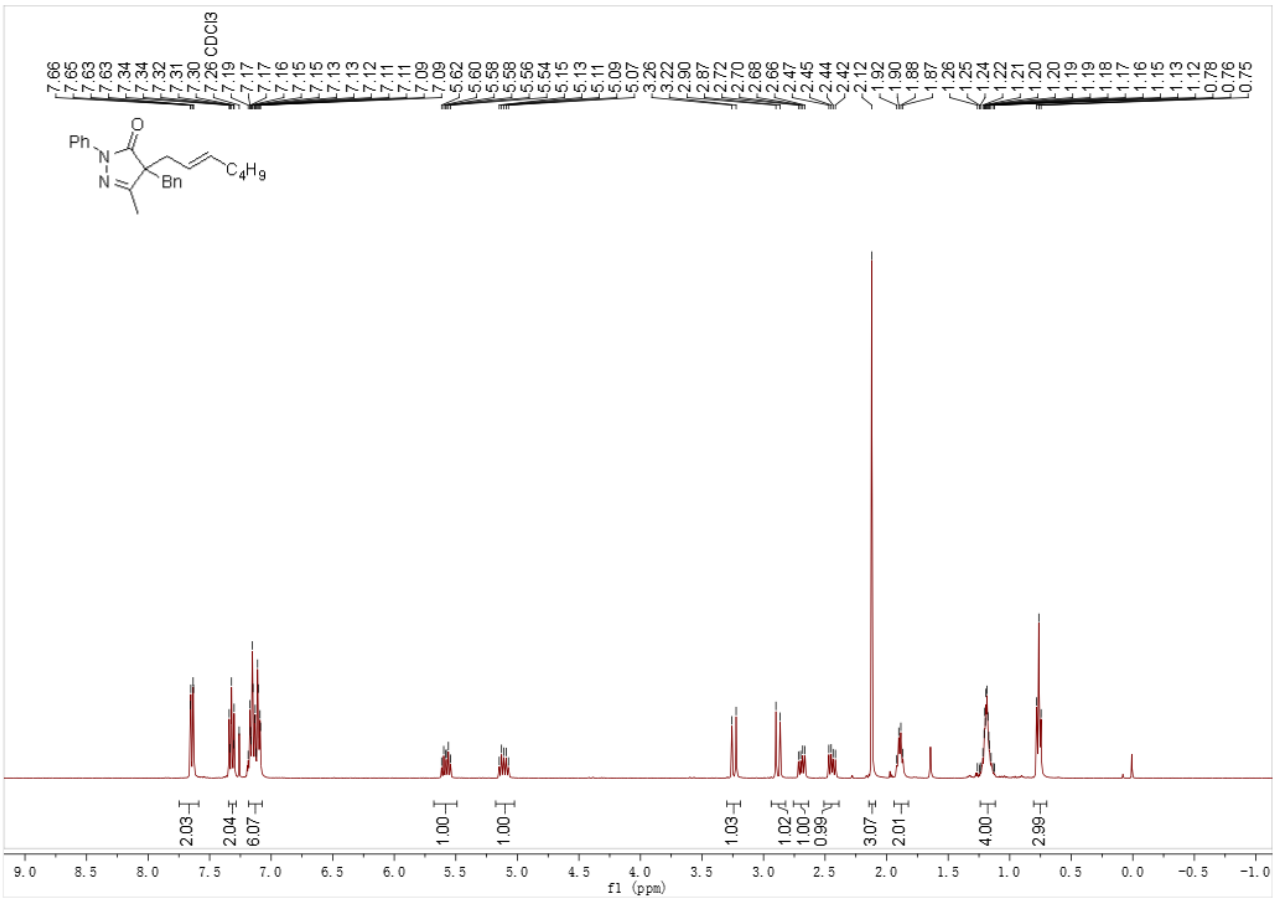

180.86
163.21
159.49
137.02
129.87
122.28
118.45
114.29
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.14
55.63
41.62
32.24
31.43
23.42
22.03
13.94
PMP
C4H9
f1 (ppm)

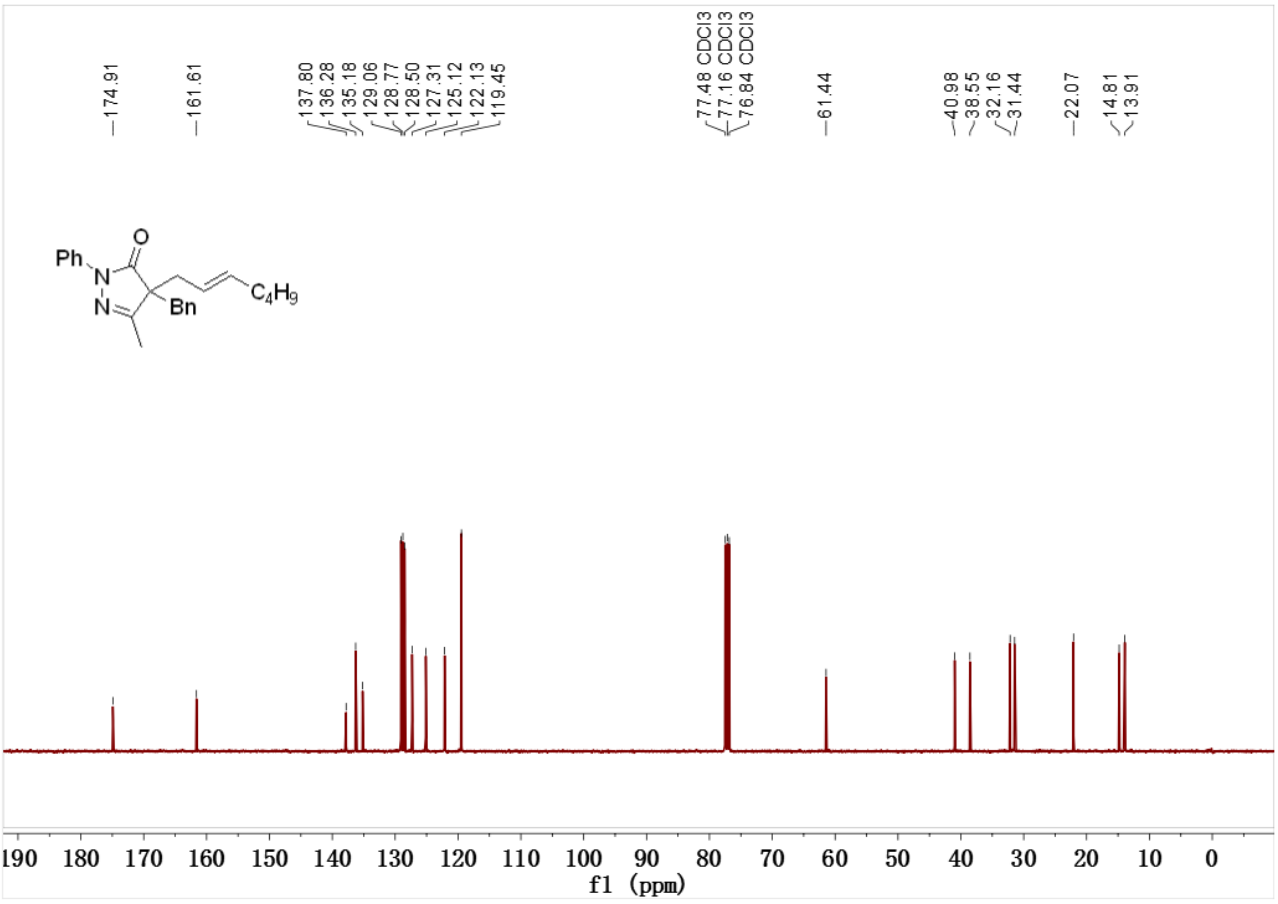
3na


7.92 7.90 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.26 7.26 7.25 7.25 7.21 7.20 7.20 5.46 5.44 5.42 5.42 5.40 5.39 5.04 5.02 5.02 5.00 4.98 4.98 4.96 3.10 3.08 3.07 3.05 2.95 2.94 2.93 2.93 2.91 2.91 2.90 2.89 1.84 1.82 1.80 1.79 1.61 1.15 1.14 1.13 1.12 1.11 1.10 1.09 1.09 1.09 1.07 0.79 0.78 0.76
Ph
C4H9
O
N
Boc
0.99
8.04
1.00
1.05
0.99
1.01
1.98
9.08
3.98
3.00
f1 (ppm)

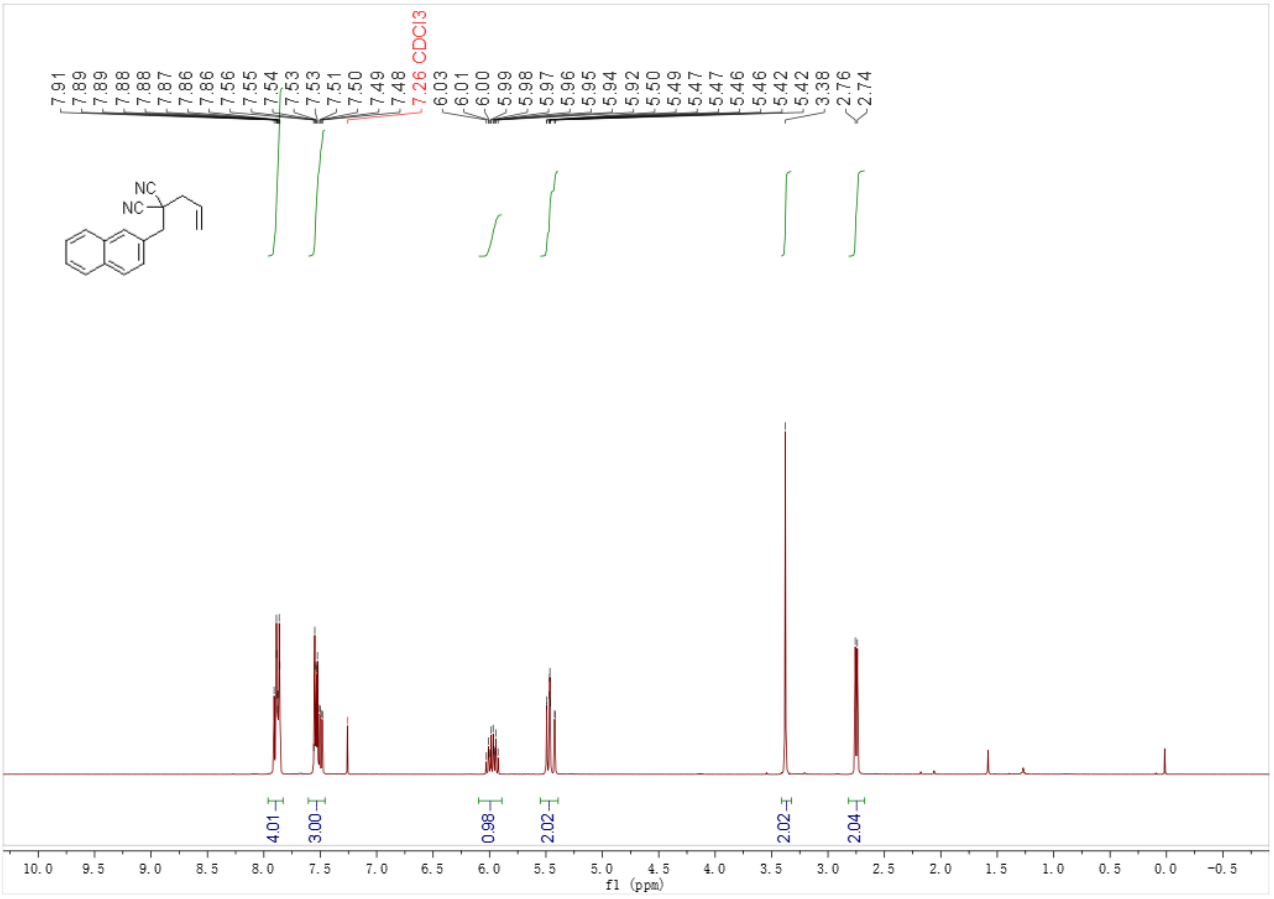

176.60
149.43 140.08 139.60 136.43 130.79 128.67 128.42 127.64 127.43 125.32 124.37 123.03 115.18
84.28
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
57.30
41.77
32.10 31.36 28.20 21.89
13.91
Ph
C4H9
O
N
Boc
f1 (ppm)

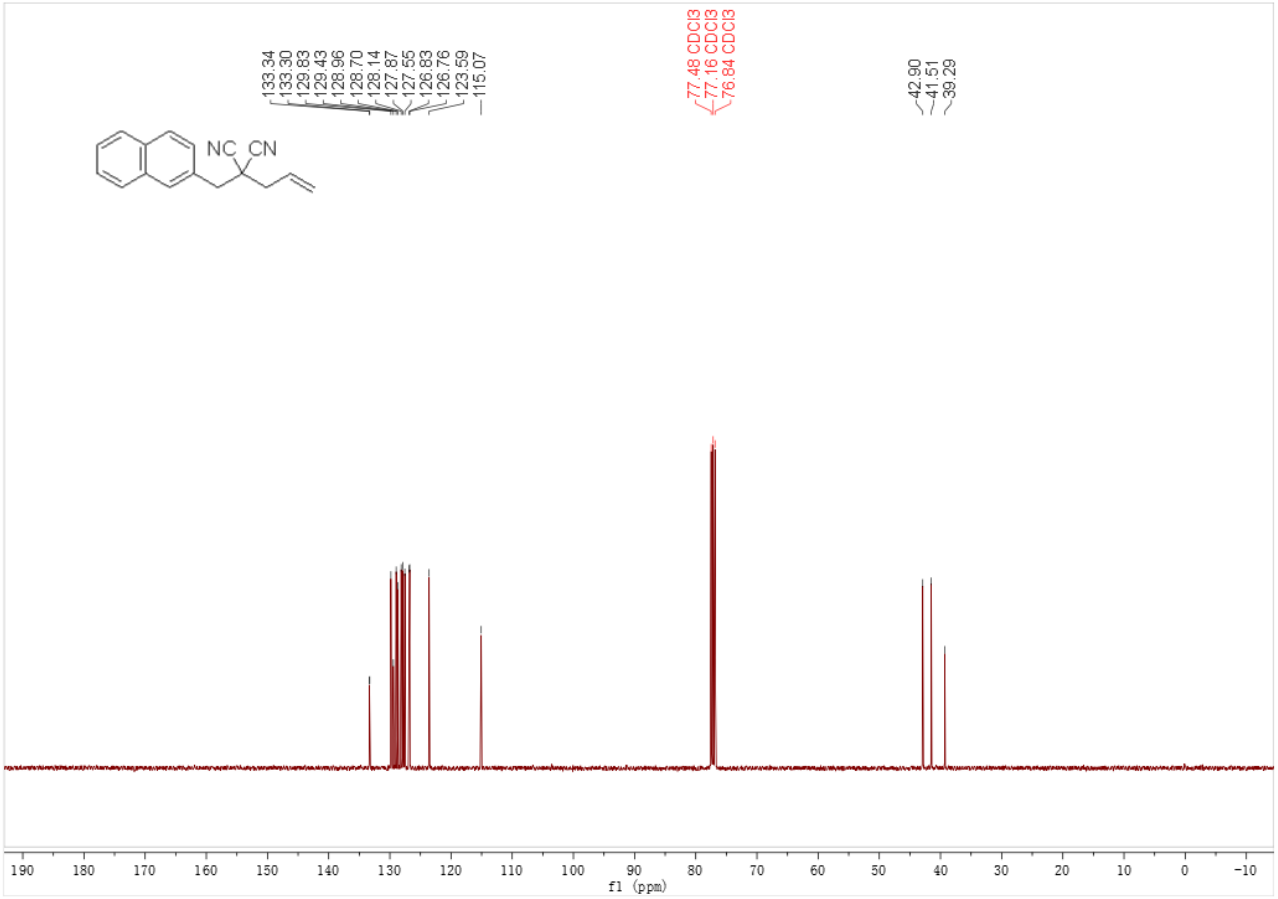
3oa


CDCl3
Ph
N
N
O
Bn
C4H9
2.03
2.04
6.07
1.00
1.00
1.03
1.02
1.00
0.99
3.07
2.01
4.00
2.99
f1 (ppm)

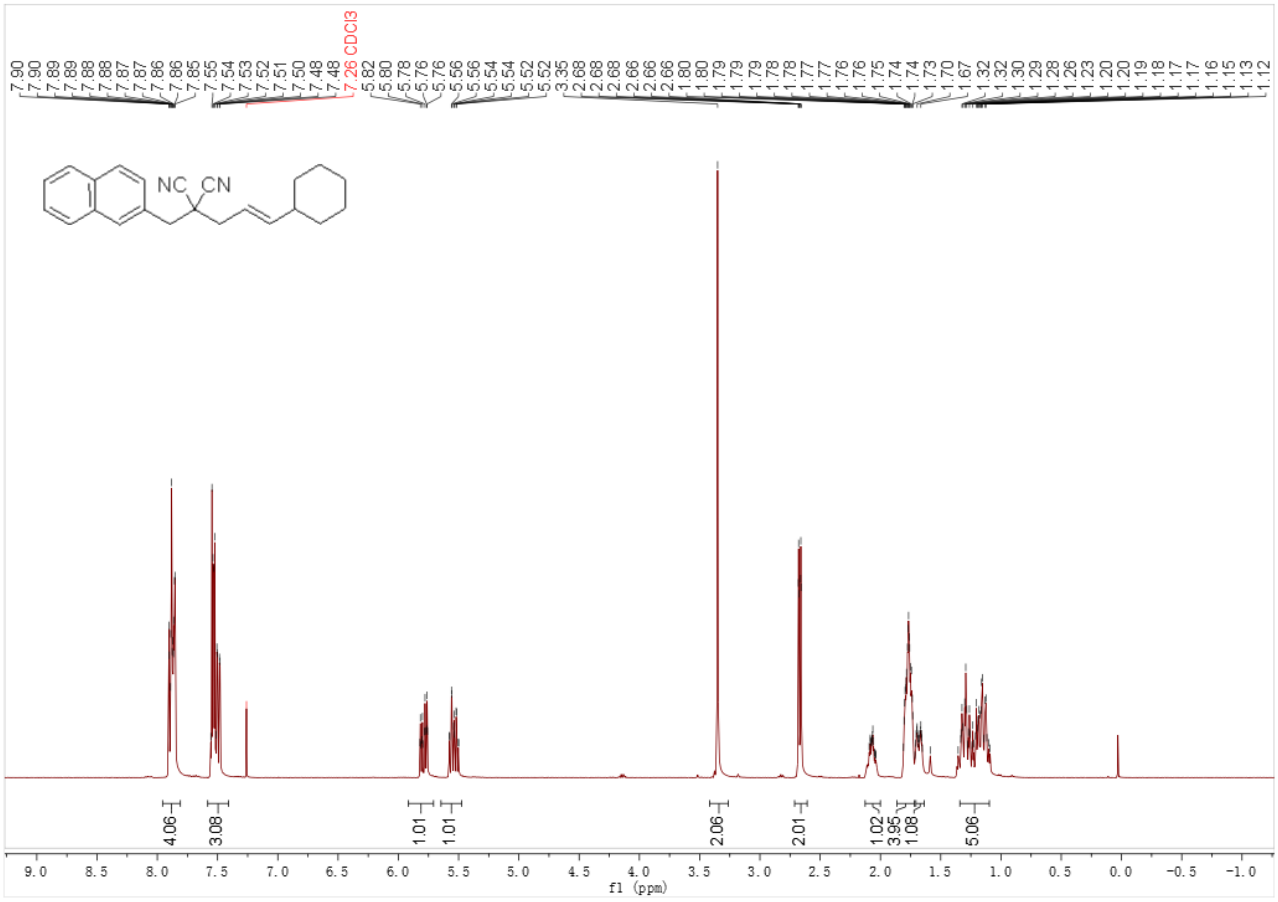

174.91
161.61
137.80
136.28
135.18
129.06
128.77
128.50
127.31
125.12
122.13
119.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.44
40.98
38.55
32.16
31.44
22.07
14.81
13.91
Ph
N
N
O
Bn
C4H9
f1 (ppm)

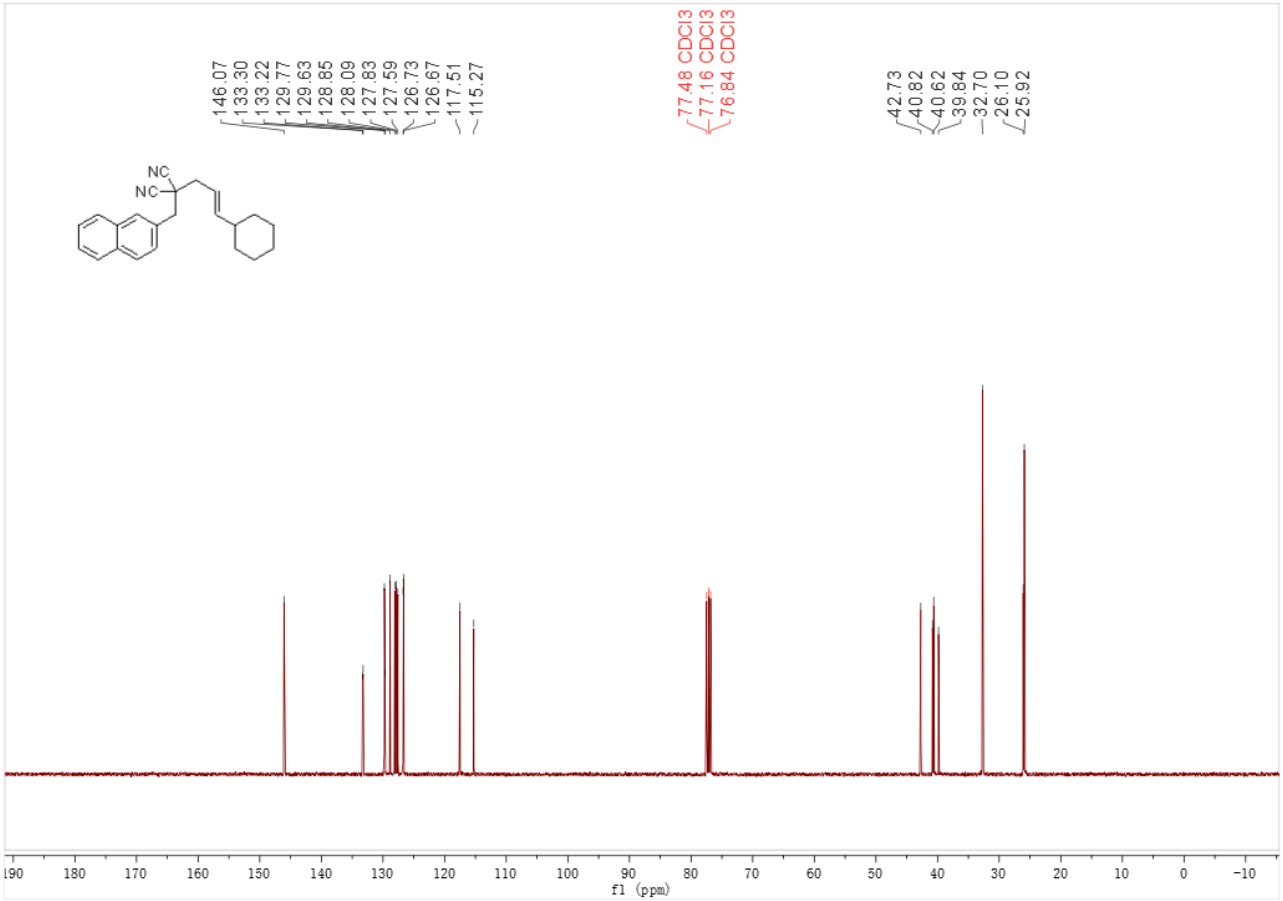
3bb


7.91
7.89
7.89
7.88
7.88
7.87
7.86
7.86
7.56
7.55
7.54
7.53
7.53
7.51
7.50
7.49
7.48
7.26 CDCl3
6.03
6.01
6.00
5.99
5.98
5.97
5.96
5.95
5.94
5.92
5.50
5.49
5.47
5.47
5.46
5.46
5.42
5.42
3.38
2.76
2.74
NC
NC
4.01
3.00
0.98
2.02
2.02
2.04
f1 (ppm)

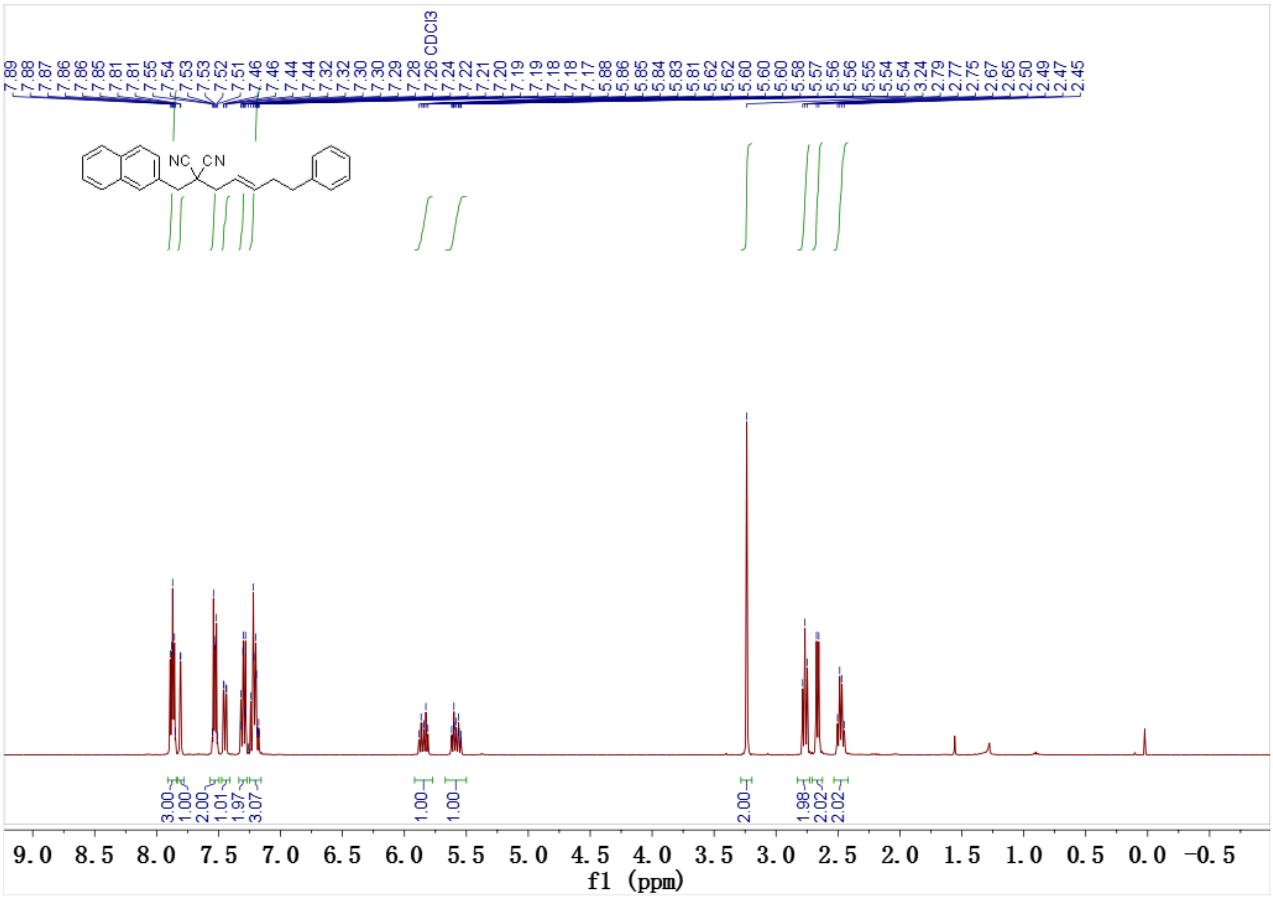

133.34
133.30
129.83
129.43
128.96
128.70
128.14
127.87
127.55
126.83
126.76
123.59
115.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.90
41.51
39.29
NC
CN
f1 (ppm)

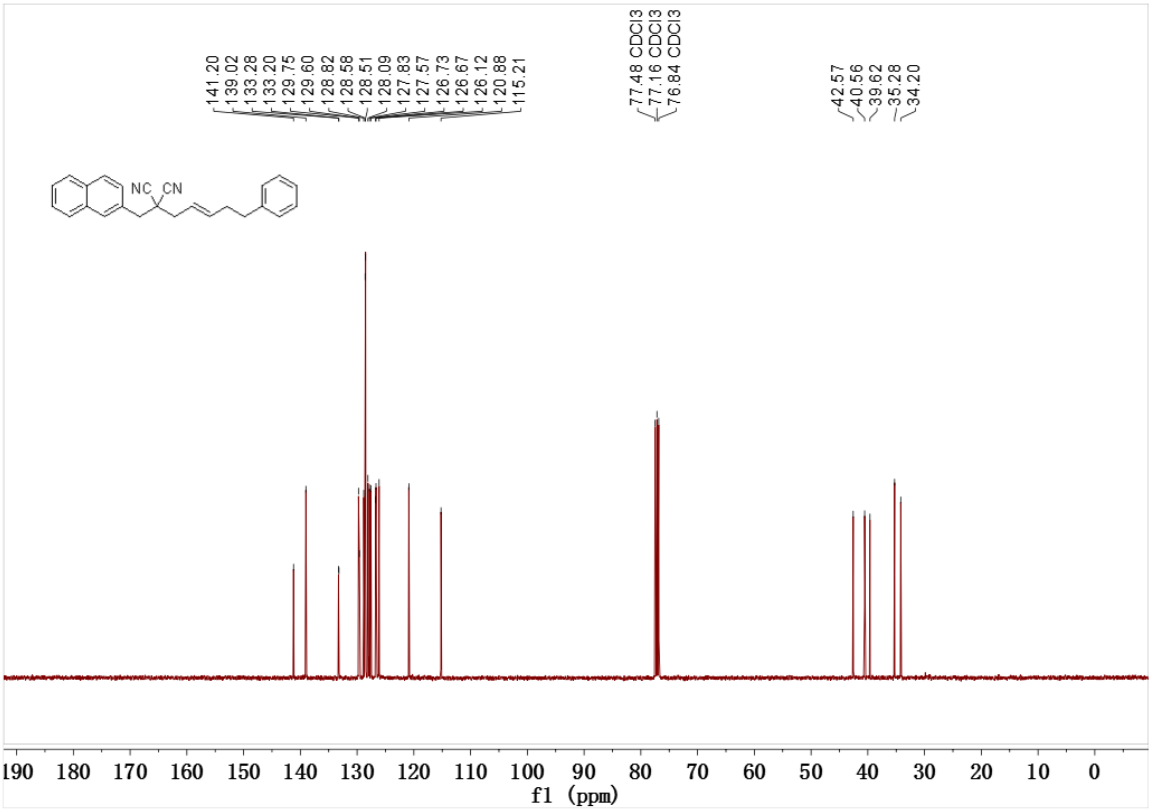
3bc


7.90 7.90 7.89 7.89 7.88 7.88 7.87 7.87 7.86 7.86 7.85 7.55 7.54 7.53 7.52 7.51 7.50 7.48 7.48 7.26 CDCl3 5.82 5.80 5.78 5.76 5.76 5.56 5.56 5.54 5.54 5.52 5.52 3.35 2.68 2.68 2.68 2.66 2.66 2.66 1.80 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.74 1.73 1.70 1.67 1.32 1.32 1.30 1.29 1.28 1.26 1.23 1.20 1.20 1.19 1.18 1.17 1.17 1.16 1.15 1.13 1.12
NC CN
4.06 3.08 1.01 1.01 2.06 2.01 1.02 3.95 1.08 5.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

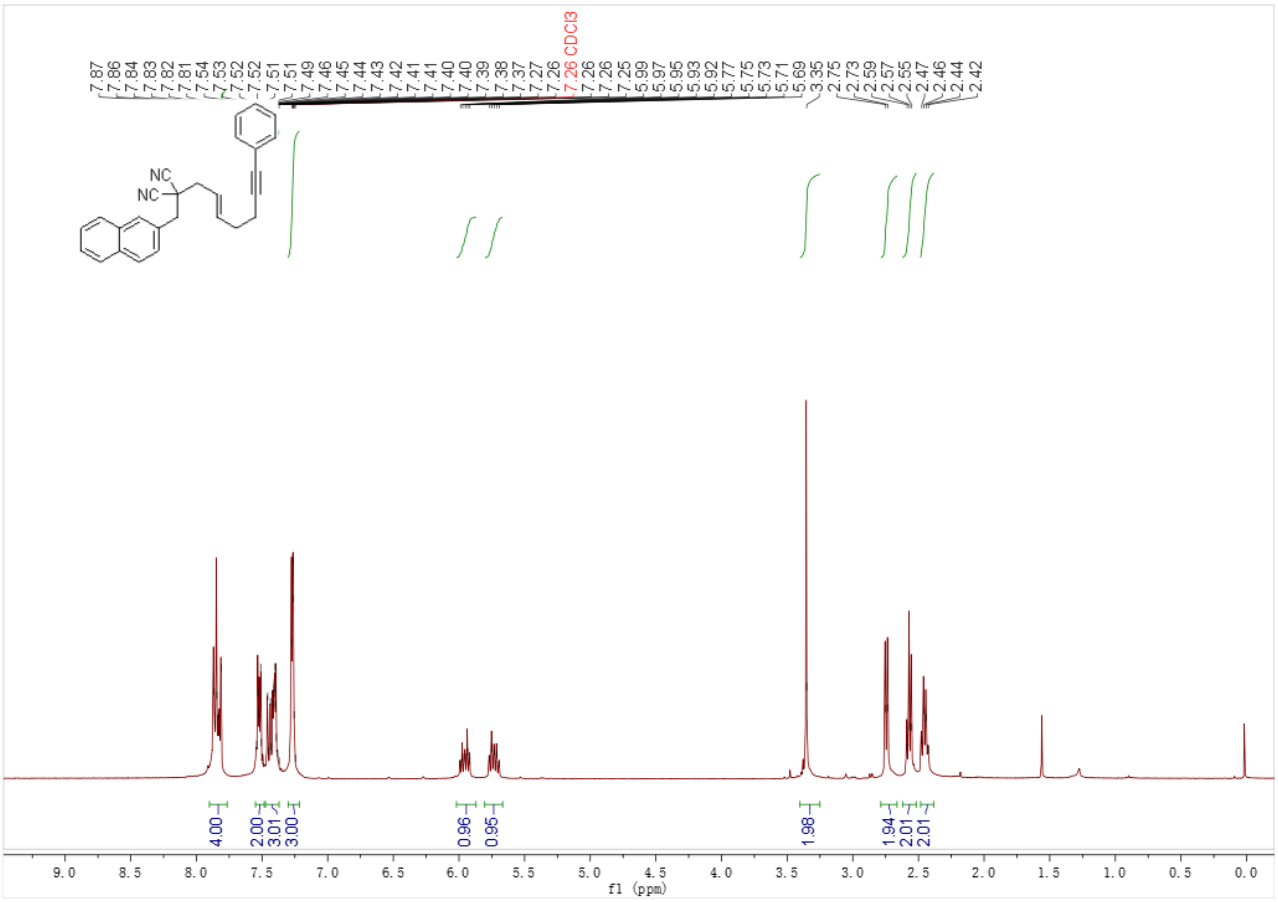

146.07 133.30 133.22 129.77 129.63 128.85 128.09 127.83 127.59 126.73 126.67 117.51 115.27
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
42.73 40.82 40.62 39.84 32.70 26.10 25.92
NC NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

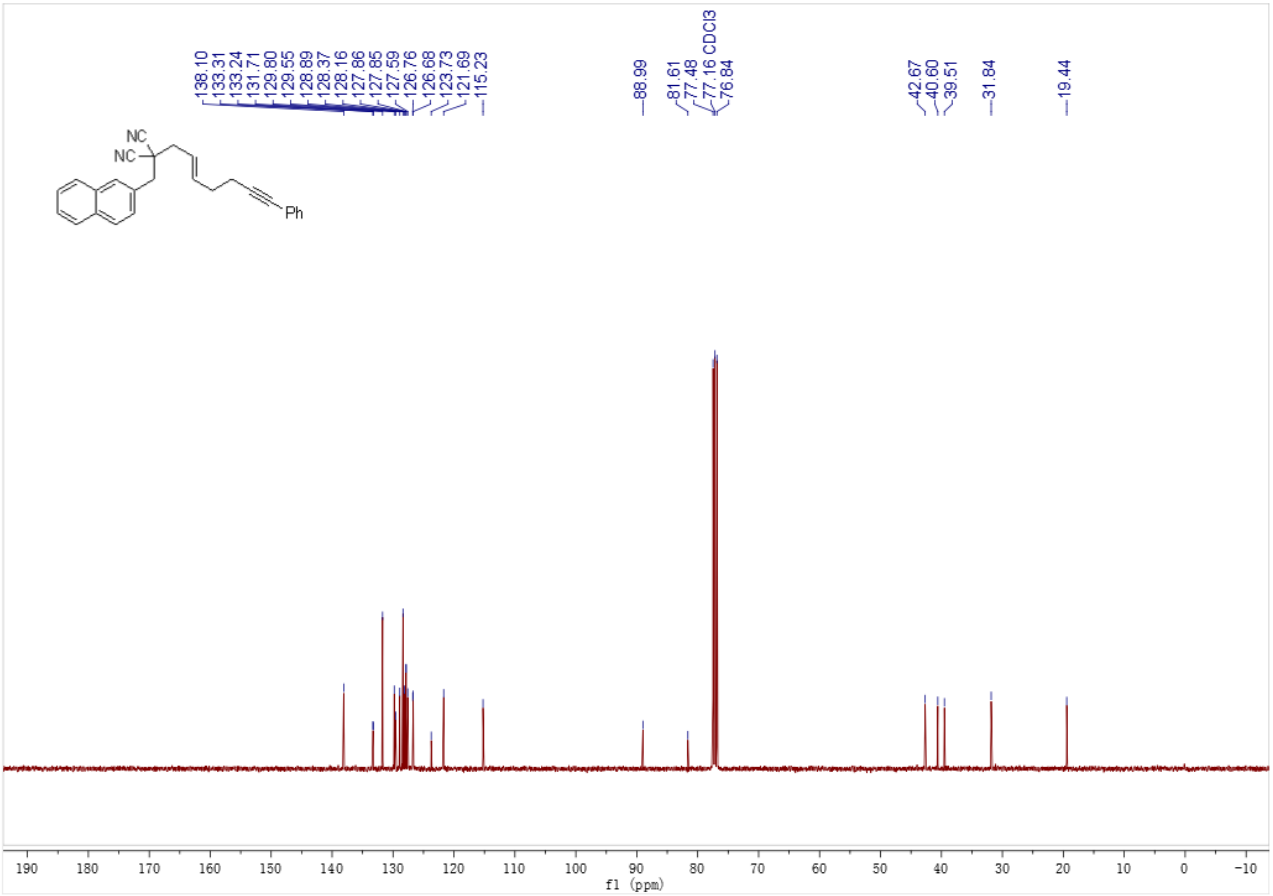
3bd


7.89 7.88 7.87 7.86 7.86 7.85 7.81 7.81 7.55 7.54 7.53 7.53 7.52 7.51 7.46 7.44 7.44 7.32 7.30 7.30 7.29 7.28 7.26 CDCl3 7.24 7.22 7.21 7.20 7.19 7.19 7.18 7.18 7.17 5.88 5.86 5.85 5.84 5.83 5.81 5.62 5.62 5.60 5.60 5.60 5.58 5.57 5.56 5.56 5.55 5.54 5.54 3.24 2.79 2.77 2.75 2.67 2.65 2.50 2.49 2.47 2.45
NC CN
3.00 1.00 2.00 1.01 1.97 3.07 1.00 1.00 2.00 1.98 2.02 2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

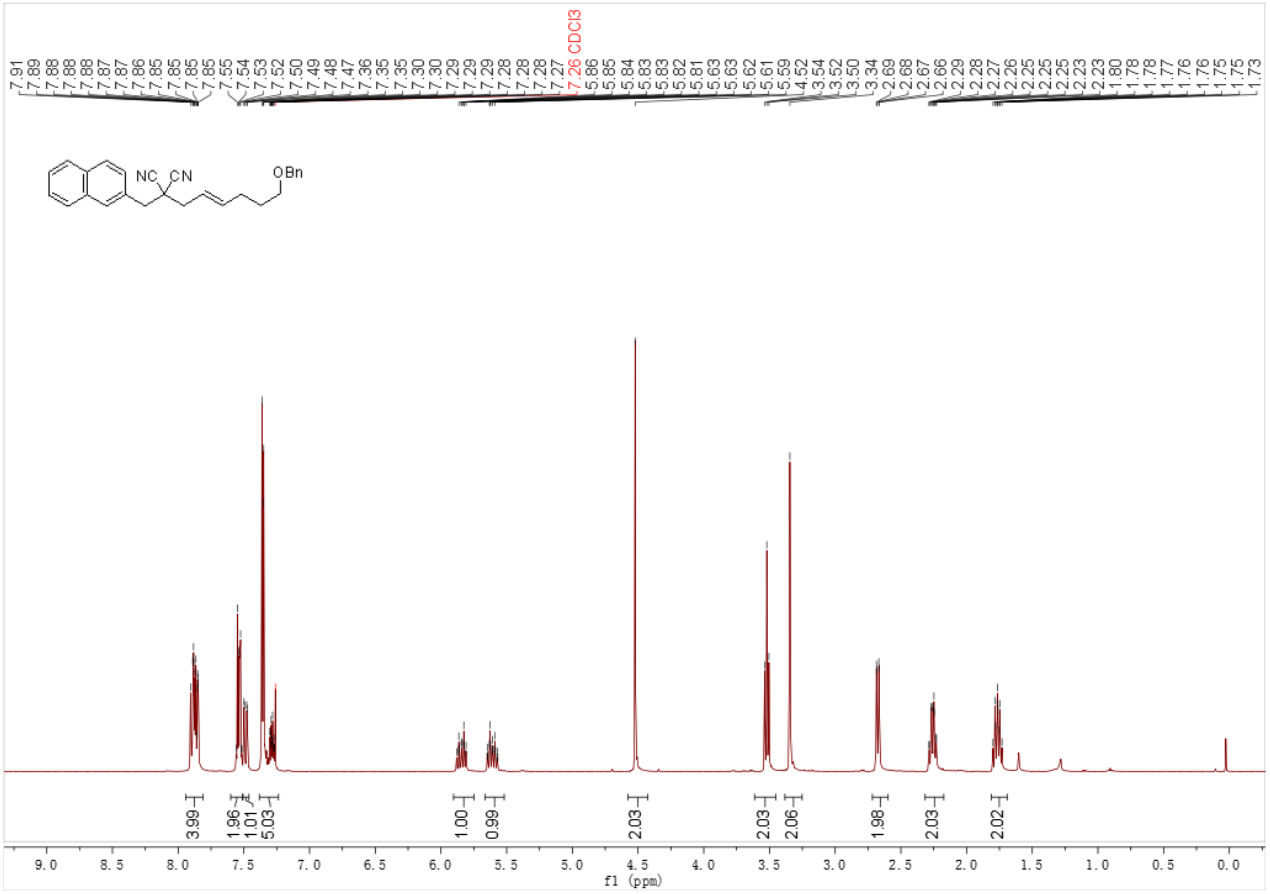

141.20 139.02 133.28 133.20 129.75 129.60 128.82 128.58 128.51 128.09 127.83 127.57 126.73 126.67 126.12 120.88 115.21
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
42.57 40.56 39.62 35.28 34.20
NC CN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

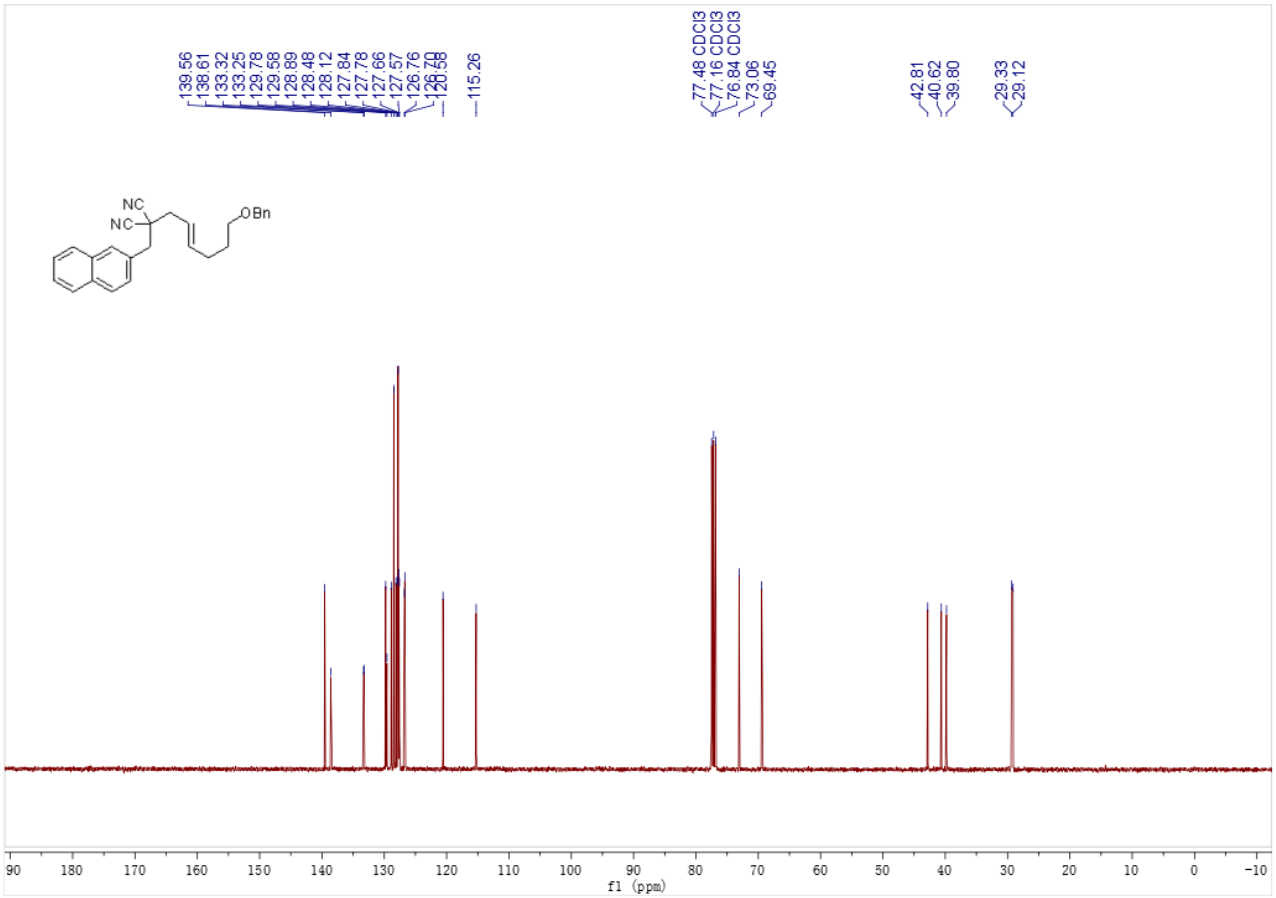
3be


7.87
7.86
7.84
7.83
7.82
7.81
7.54
7.53
7.52
7.52
7.51
7.51
7.49
7.46
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.27
7.26
7.26 CDCl3
7.26
7.25
5.99
5.97
5.95
5.93
5.92
5.77
5.75
5.73
5.71
5.69
3.35
2.75
2.73
2.59
2.57
2.55
2.47
2.46
2.44
2.42
NC
NC
4.00
2.00
3.01
3.00
0.96
0.95
1.98
1.94
2.01
2.01
f1 (ppm)

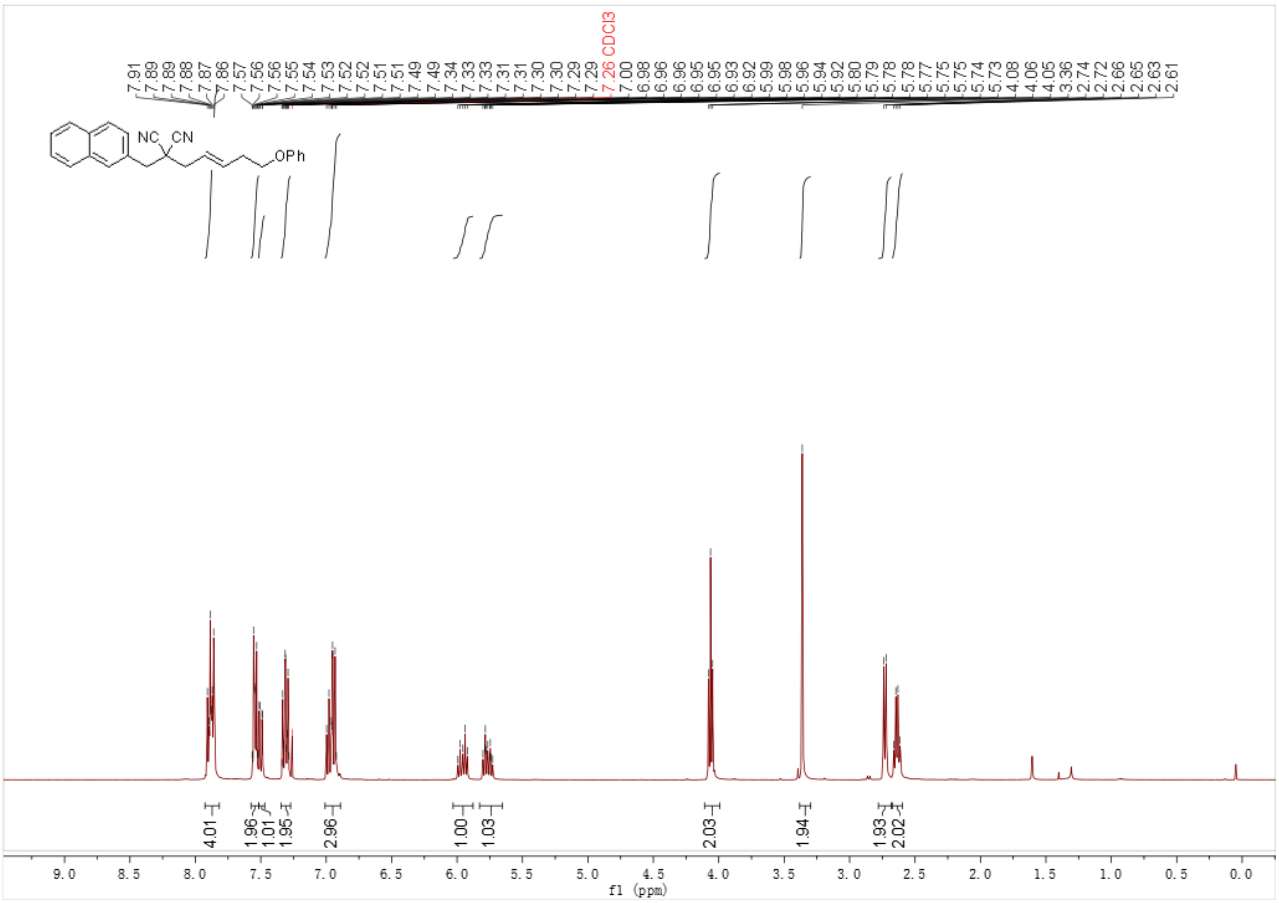

138.10
133.31
133.24
131.71
129.80
129.55
128.89
128.37
128.16
127.86
127.85
127.59
126.76
126.68
123.73
121.69
115.23
88.99
81.61
77.48
77.16 CDCl3
76.84
42.67
40.60
39.51
31.84
19.44
NC
NC
Ph
f1 (ppm)

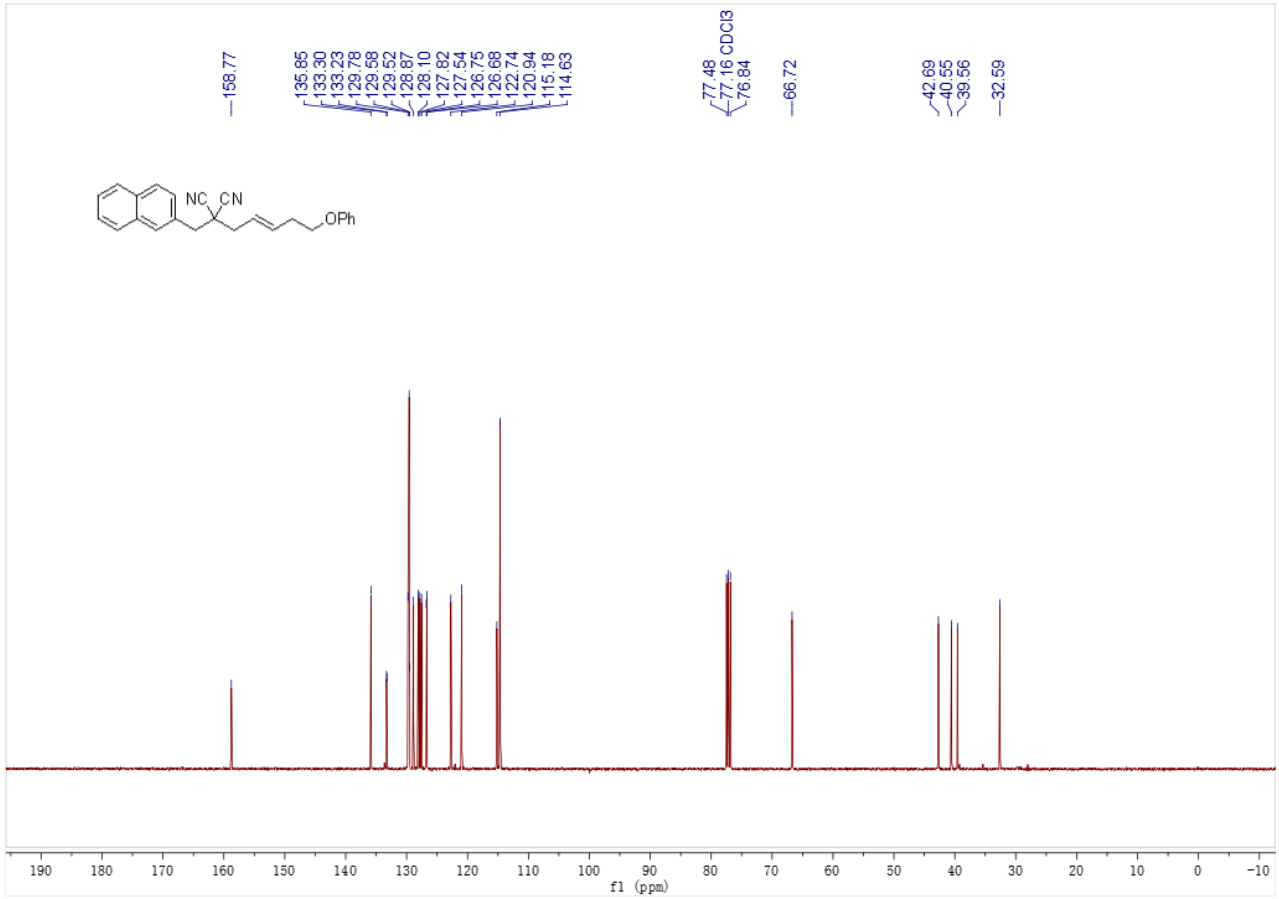
3bf


7.91 7.89 7.88 7.88 7.88 7.87 7.87 7.86 7.85 7.85 7.85 7.55 7.54 7.53 7.52 7.50 7.49 7.48 7.47 7.36 7.35 7.35 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.26 CDCl3 5.86 5.85 5.84 5.83 5.82 5.81 5.63 5.63 5.62 5.61 5.59 4.52 3.54 3.52 3.50 3.34 2.69 2.68 2.67 2.66 2.29 2.28 2.27 2.26 2.25 2.25 2.25 2.23 2.23 1.80 1.78 1.78 1.77 1.76 1.76 1.75 1.75 1.73
NC CN OBn
3.99 1.96 1.01 5.03 1.00 0.99 2.03 2.03 2.06 1.98 2.03 2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

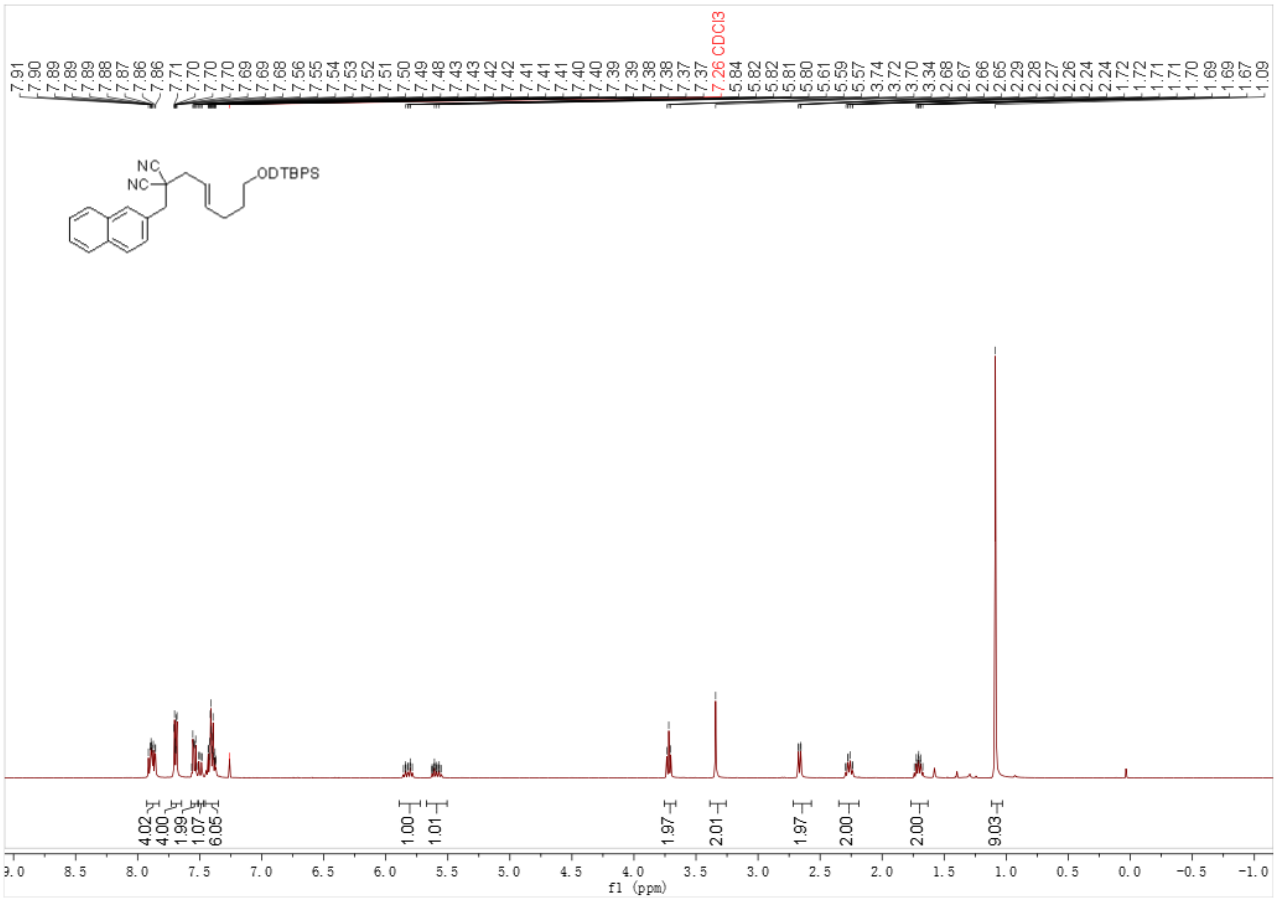

139.56 138.61 133.32 133.25 129.78 129.58 128.89 128.48 128.12 127.84 127.78 127.66 127.57 126.76 126.70 120.58 115.26
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 73.06 69.45
42.81 40.62 39.80
29.33 29.12
NC NC OBn
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

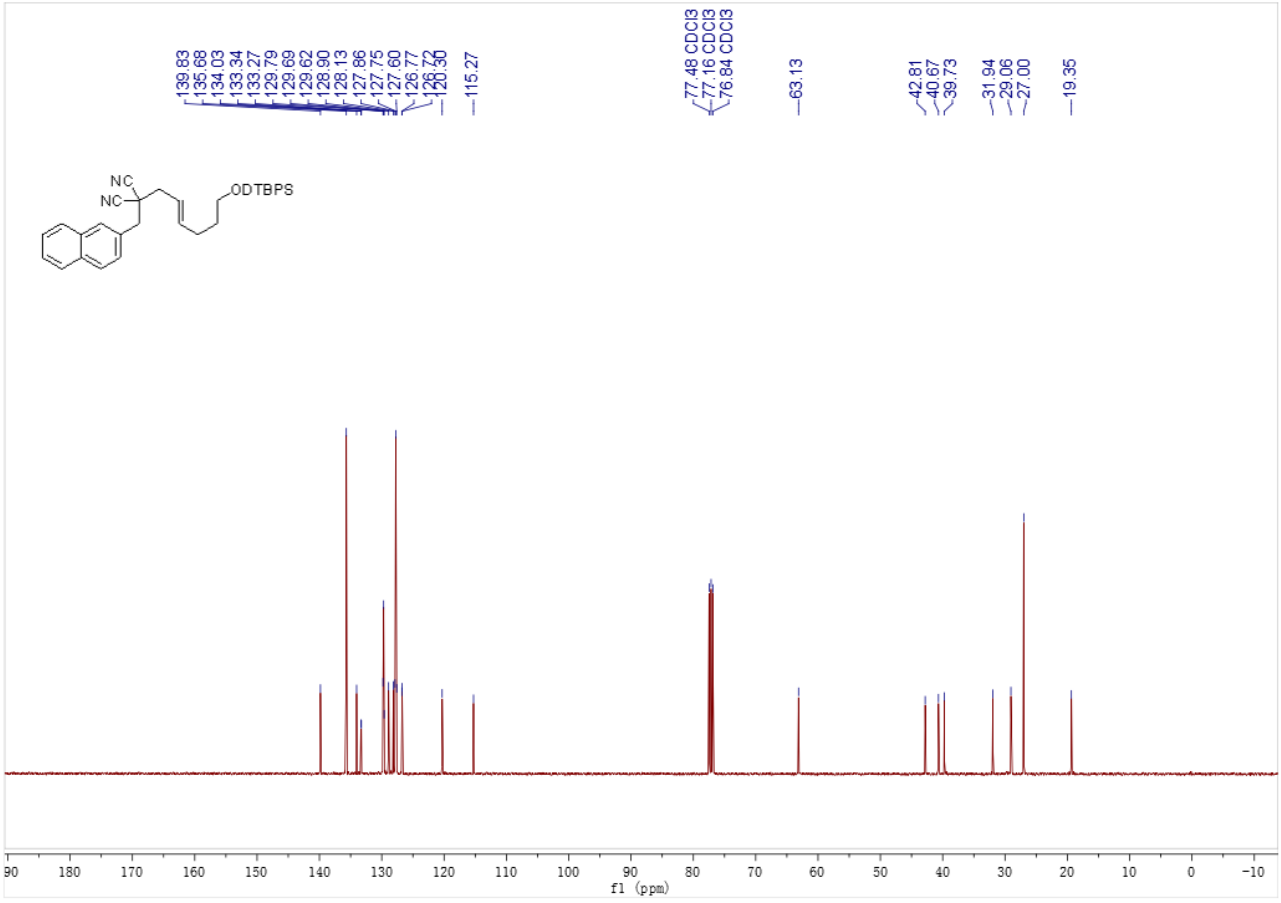
3bg


7.91 7.89 7.89 7.88 7.87 7.86 7.57 7.56 7.56 7.55 7.54 7.53 7.52 7.52 7.51 7.51 7.49 7.49 7.34 7.33 7.33 7.31 7.31 7.30 7.30 7.29 7.29 7.26 CDCl3 7.00 6.98 6.96 6.96 6.95 6.93 6.92 5.99 5.98 5.96 5.94 5.92 5.80 5.79 5.78 5.78 5.77 5.75 5.75 5.74 5.73 4.08 4.06 4.05 3.36 2.74 2.72 2.66 2.65 2.63 2.61
NC CN
OPh
4.01 1.96 1.01 1.95 2.96 1.00 1.03 2.03 1.94 1.93 2.02
f1 (ppm)

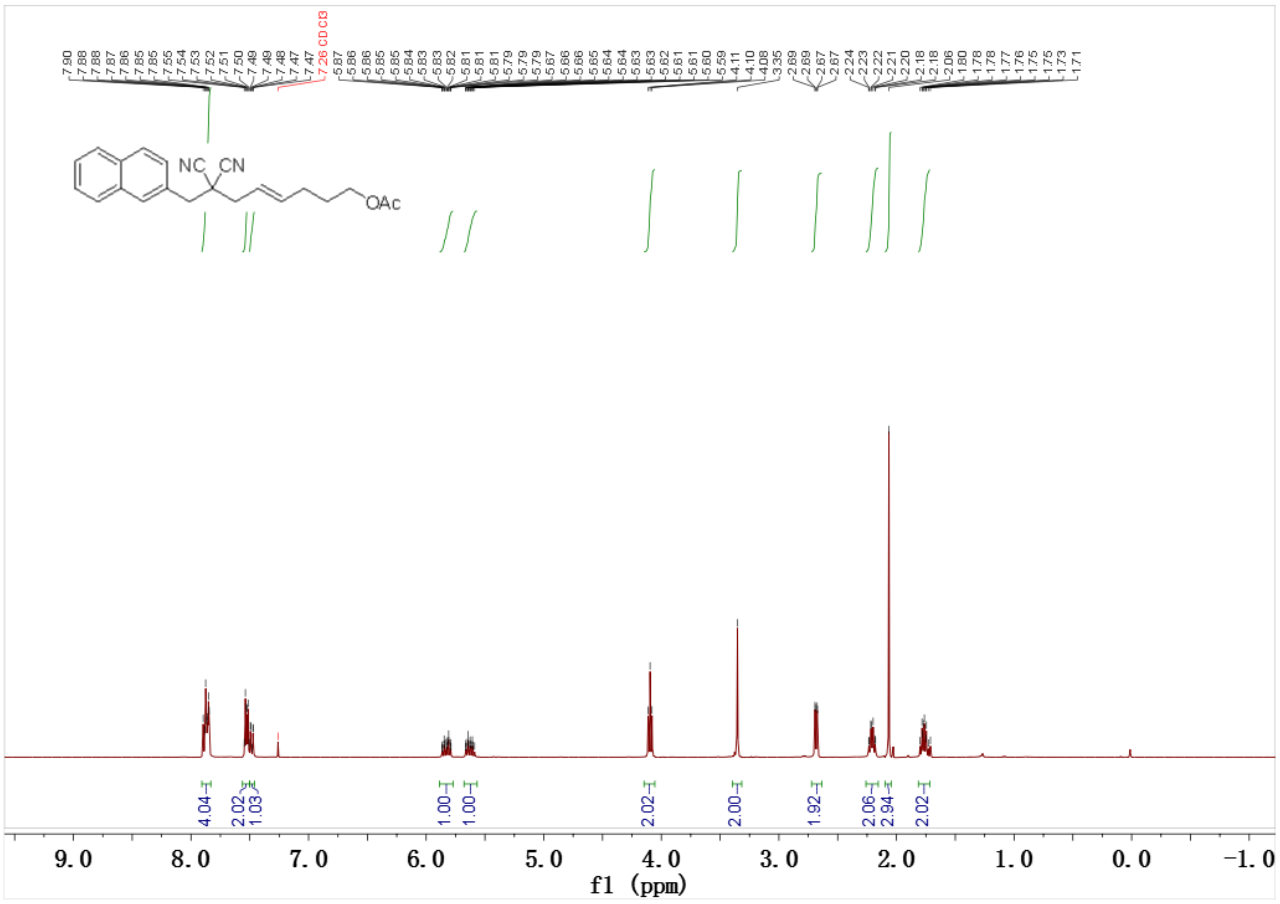

158.77
135.85 133.30 133.23 129.78 129.58 129.52 128.87 128.10 127.82 127.54 126.75 126.68 122.74 120.94 115.18 114.63
77.48 77.16 CDCl3 76.84
66.72
42.69 40.55 39.56
32.59
NC CN
OPh
f1 (ppm)

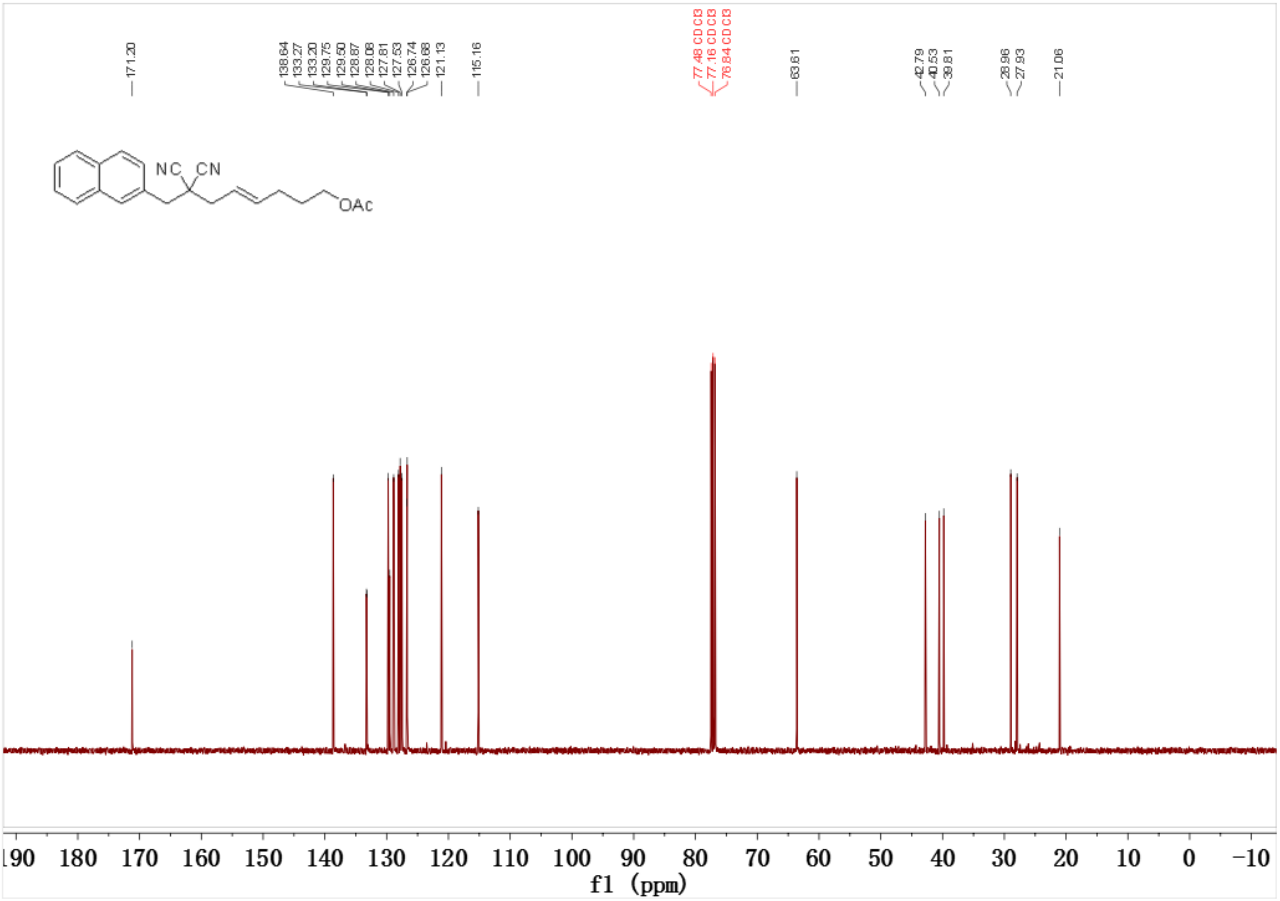
3bh



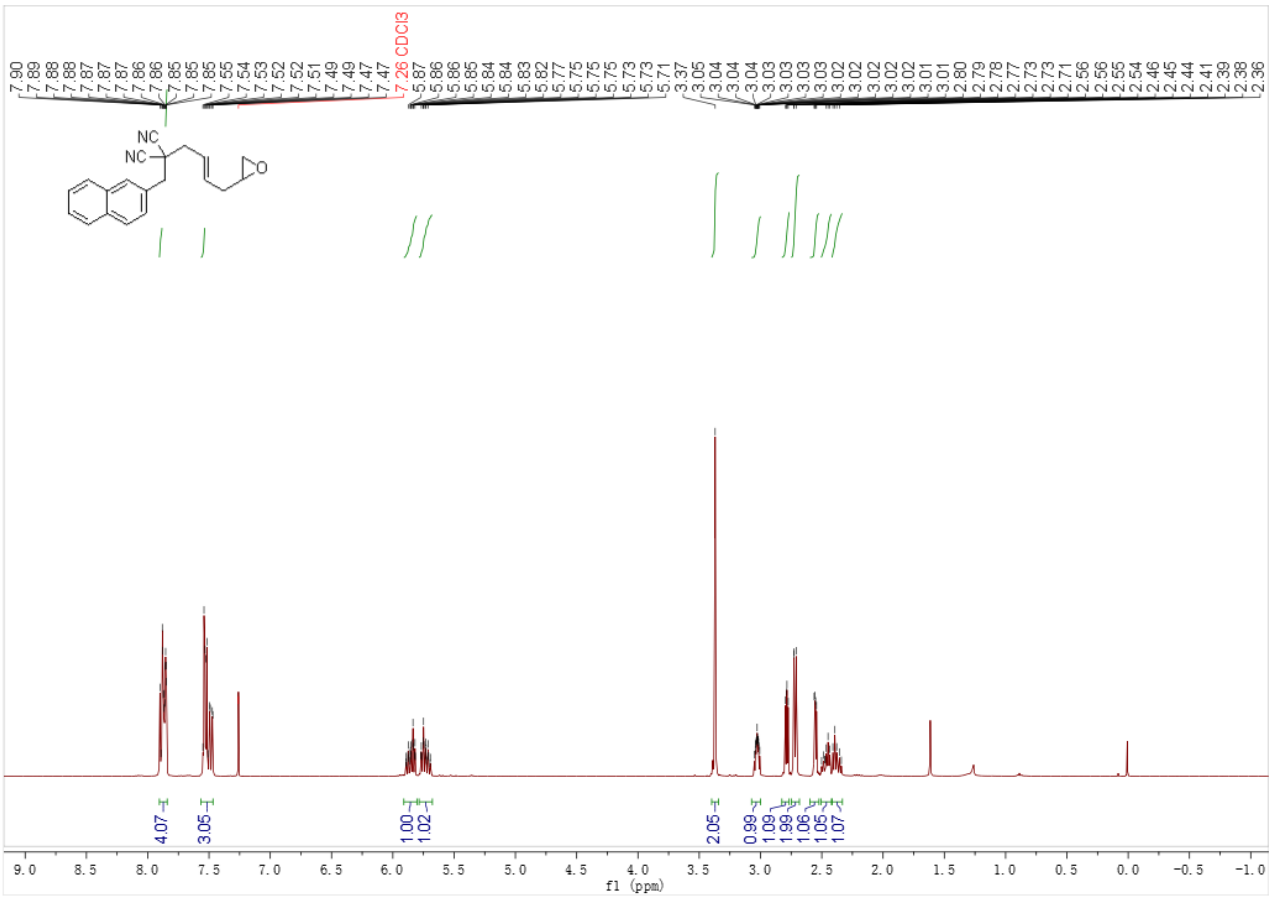


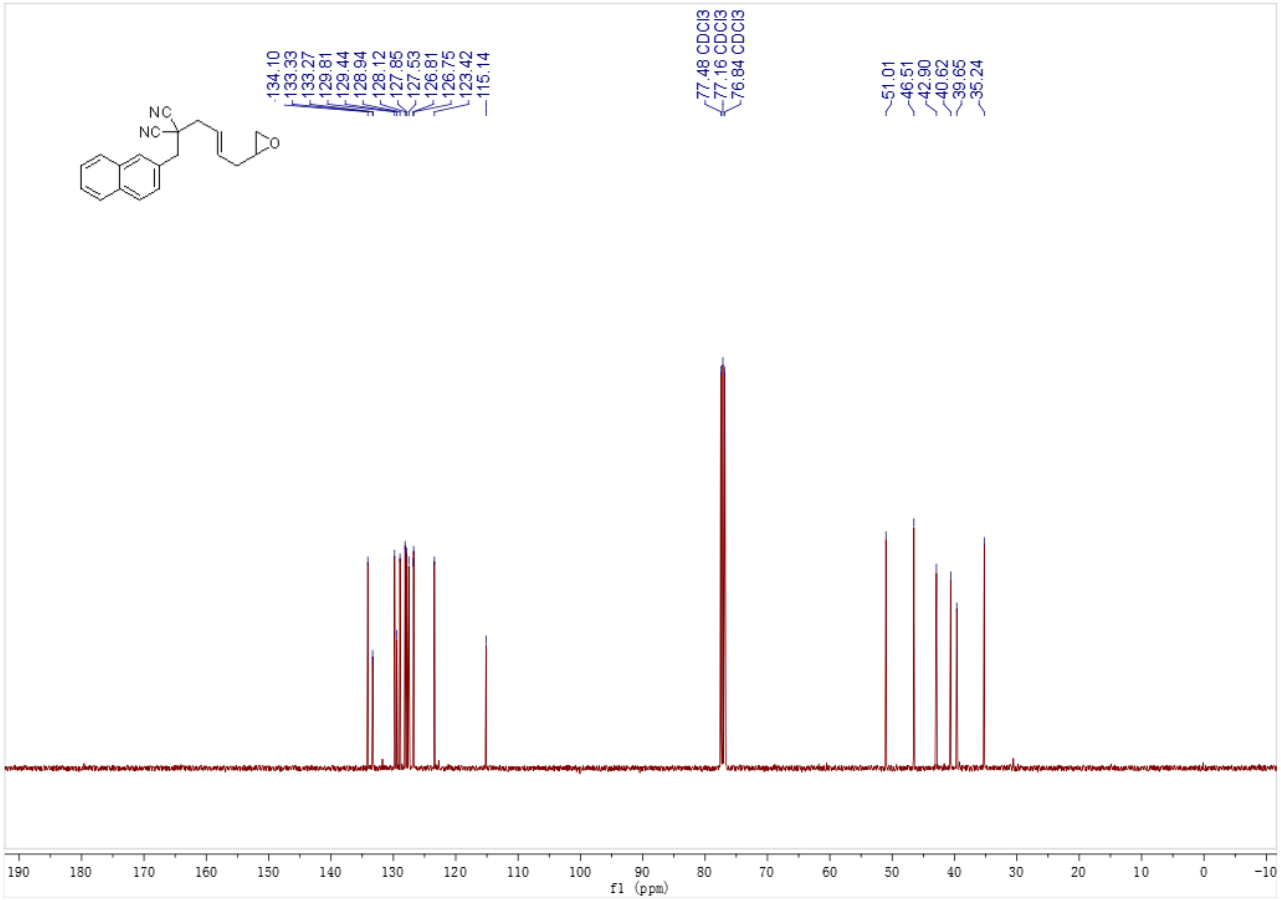
3bi


NC CN
OAc
4.04
2.02
1.03
1.00
1.00
2.02
2.00
1.92
2.06
2.94
2.02
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)

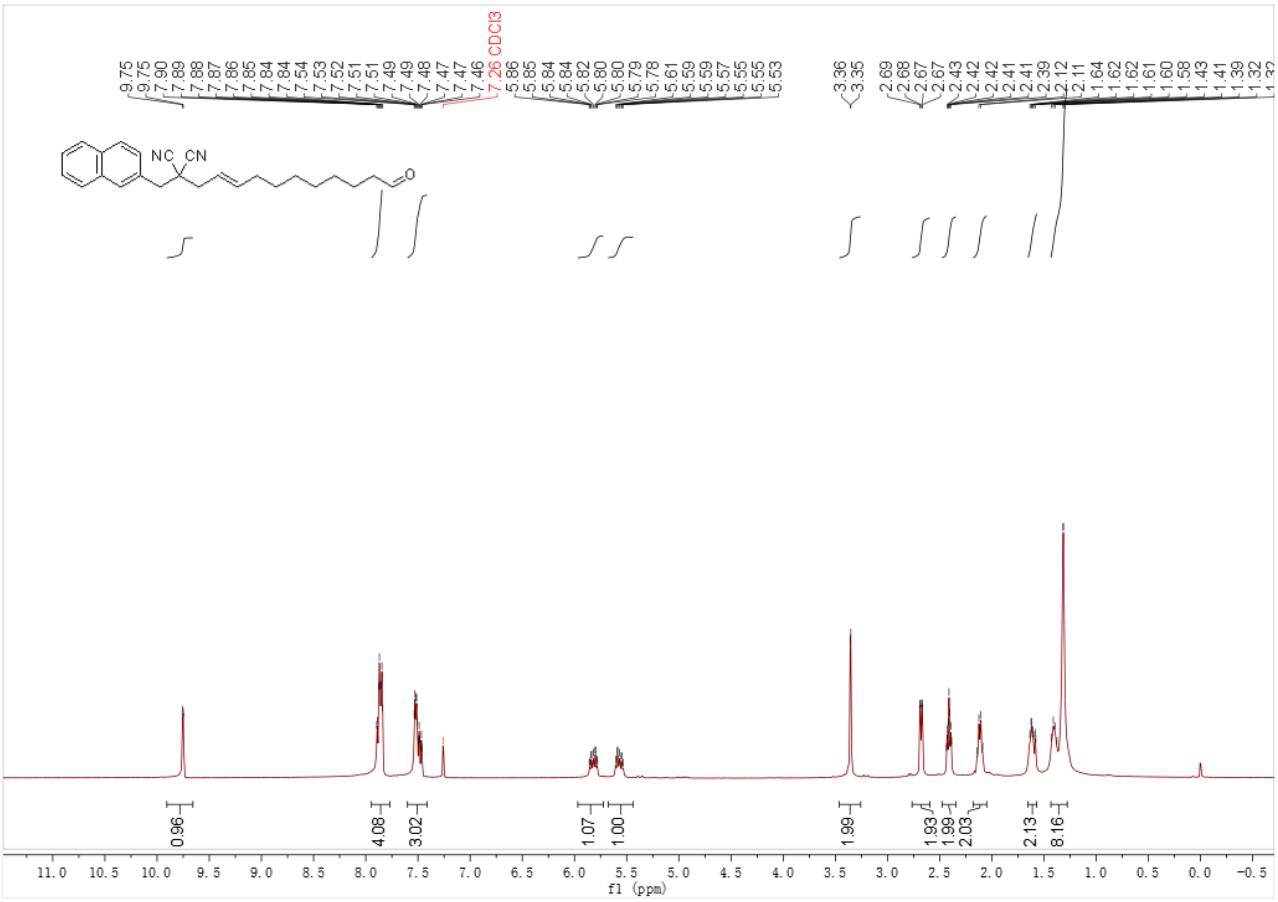

NC CN
OAc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

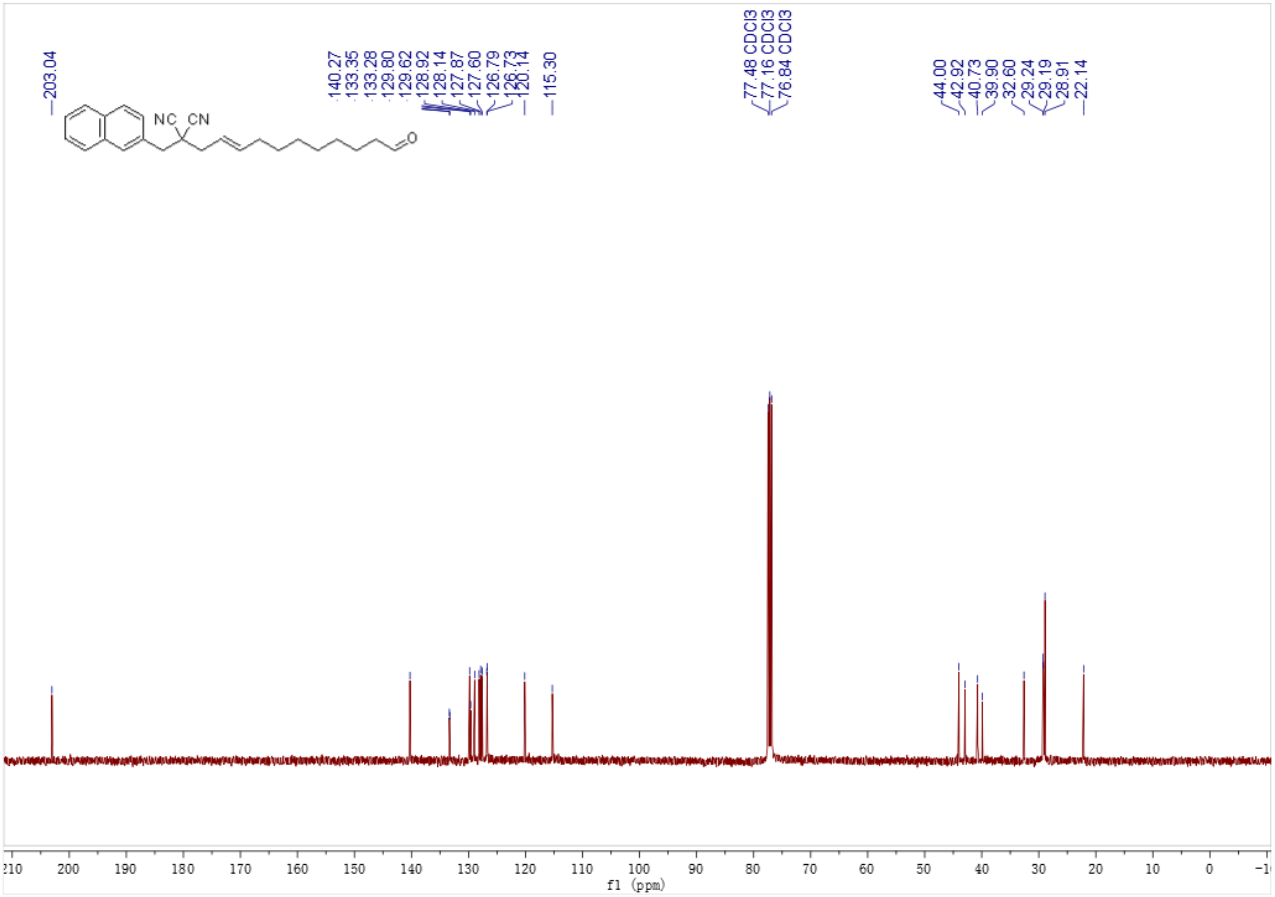
3bj


7.26 CDCl3
NC
NC
O
4.07
3.05
1.00
1.02
2.05
0.99
1.09
1.99
1.06
1.05
1.07
f1 (ppm)

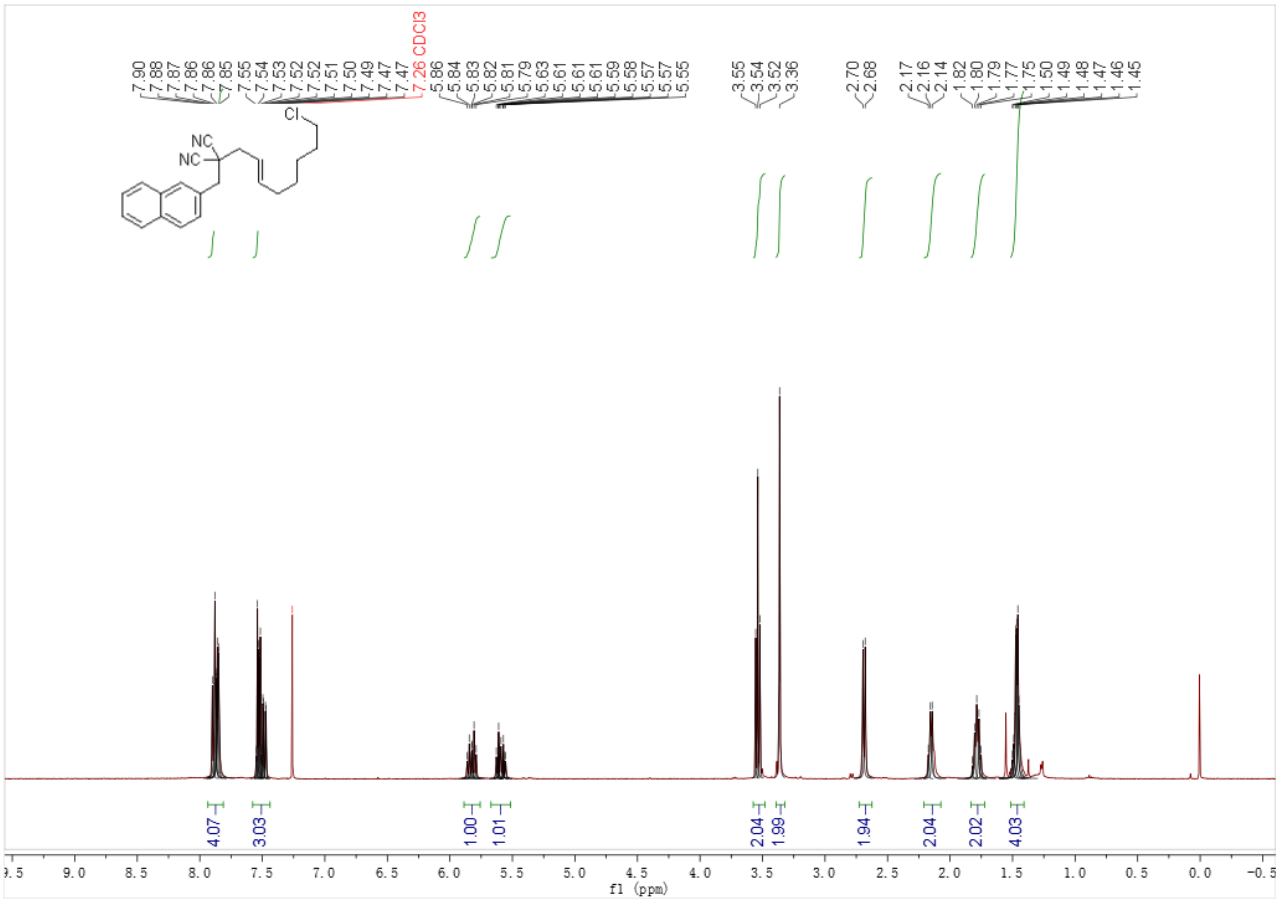

134.10
133.33
133.27
129.81
129.44
128.94
128.12
127.85
127.53
126.81
126.75
123.42
115.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
51.01
46.51
42.90
40.62
39.65
35.24
NC
NC
O
f1 (ppm)

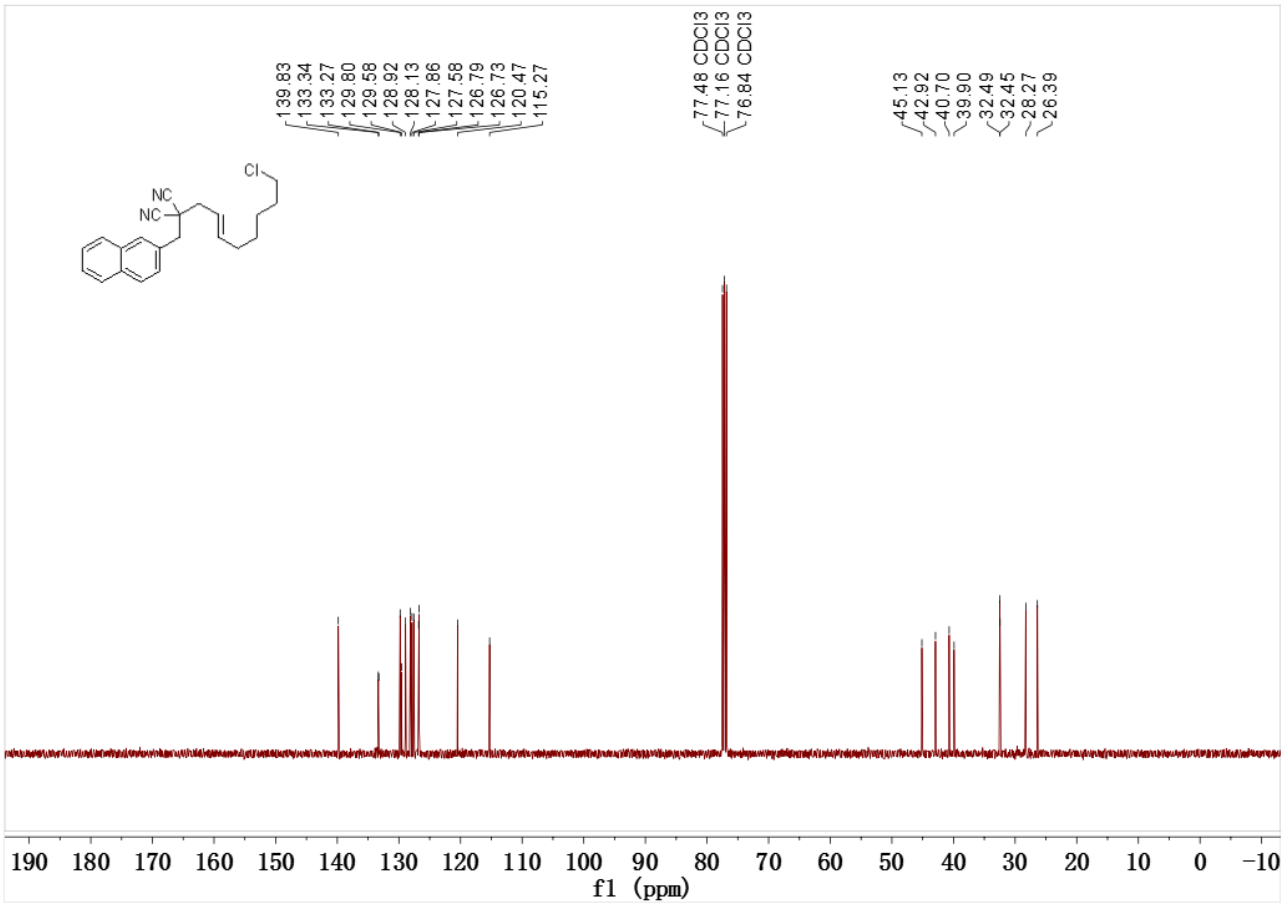
3bk


NC CN
O
7.26 CDCl3
0.96
4.08
3.02
1.07
1.00
1.99
1.93
1.99
2.03
2.13
8.16
f1 (ppm)

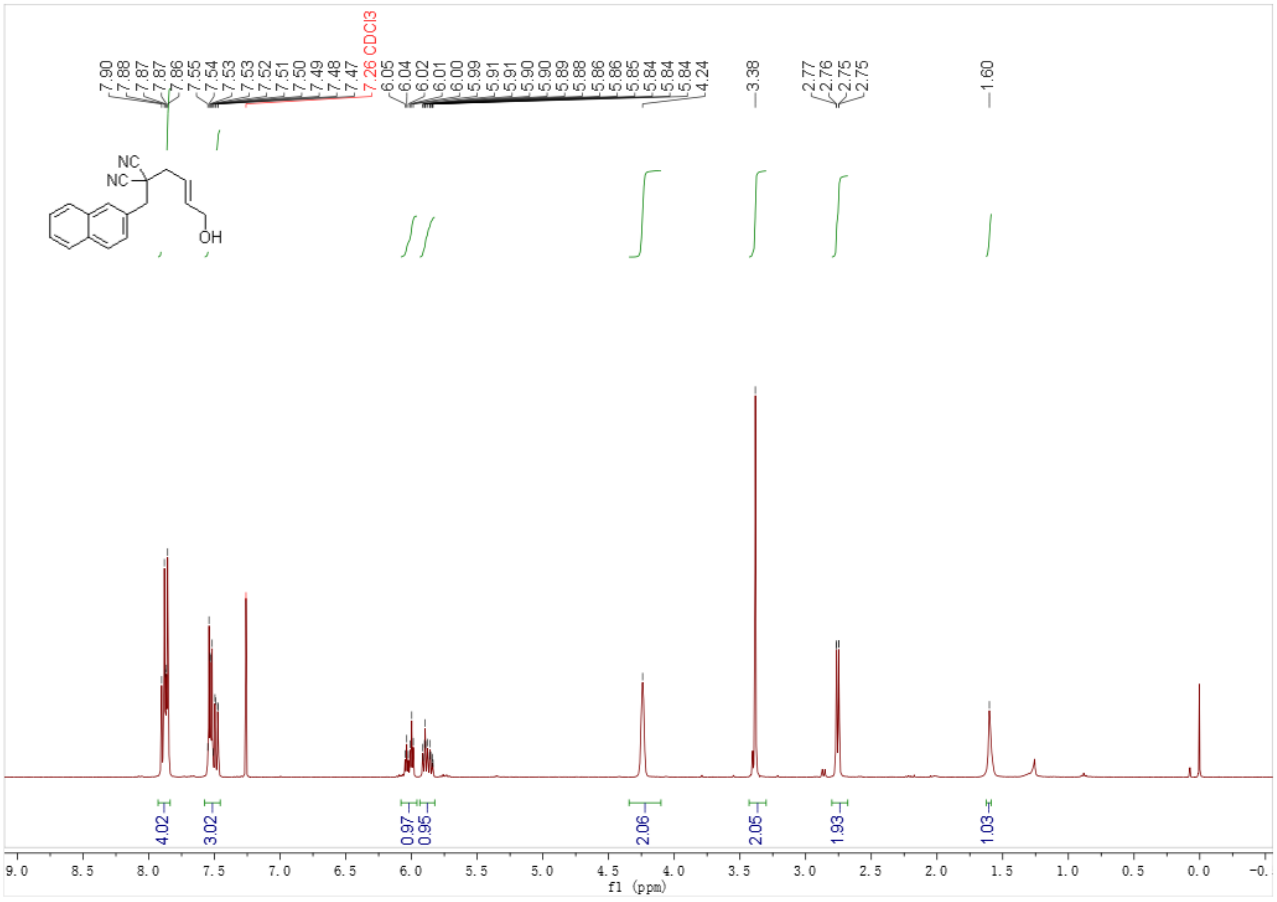

203.04
NC CN
O
140.27
133.35
133.28
129.80
129.62
128.92
128.14
127.87
127.60
126.79
126.73
120.14
115.30
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.00
42.92
40.73
39.90
32.60
29.24
29.19
28.91
22.14
f1 (ppm)

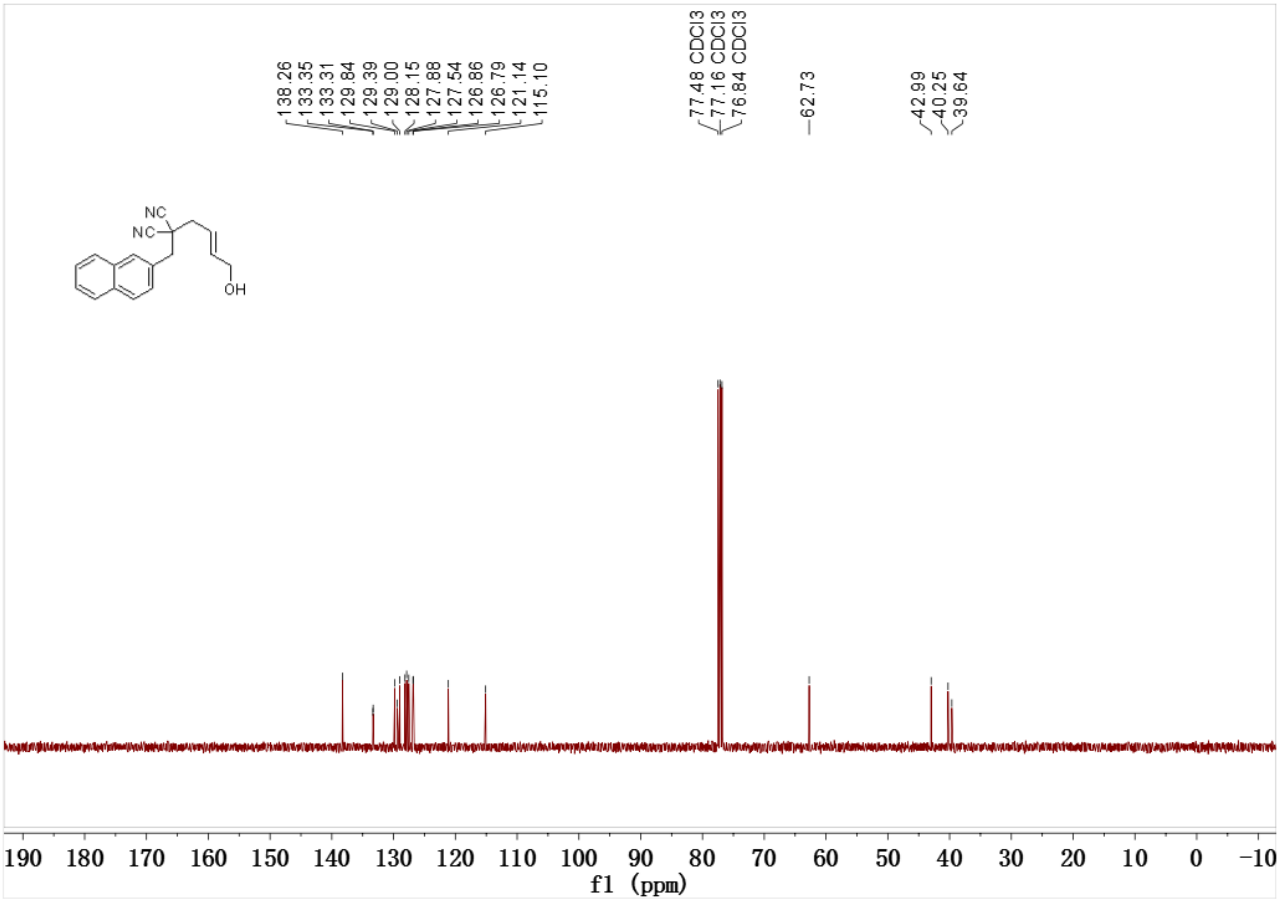
3bl


7.90
7.88
7.87
7.86
7.86
7.85
7.55
7.54
7.53
7.52
7.52
7.51
7.50
7.49
7.47
7.47
7.26 CDCl3
5.86
5.84
5.83
5.82
5.81
5.79
5.63
5.61
5.61
5.61
5.59
5.58
5.57
5.57
5.55
3.55
3.54
3.52
3.36
2.70
2.68
2.17
2.16
2.14
1.82
1.80
1.79
1.77
1.75
1.50
1.49
1.48
1.47
1.46
1.45
Cl
NC
NC
4.07
3.03
1.00
1.01
2.04
1.99
1.94
2.04
2.02
4.03
f1 (ppm)

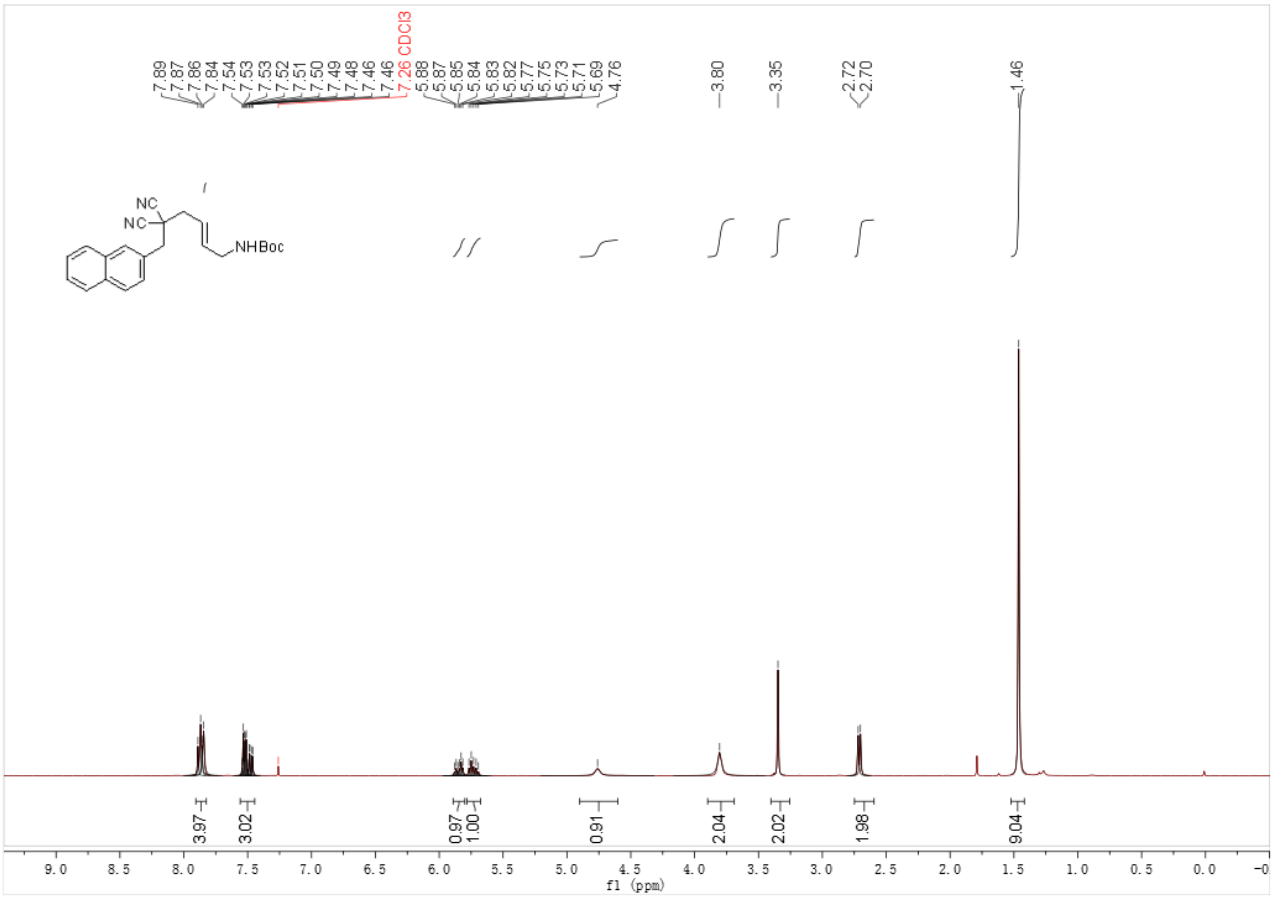

139.83
133.34
133.27
129.80
129.58
128.92
128.13
127.86
127.58
126.79
126.73
120.47
115.27
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.13
42.92
40.70
39.90
32.49
32.45
28.27
26.39
Cl
NC
NC
f1 (ppm)

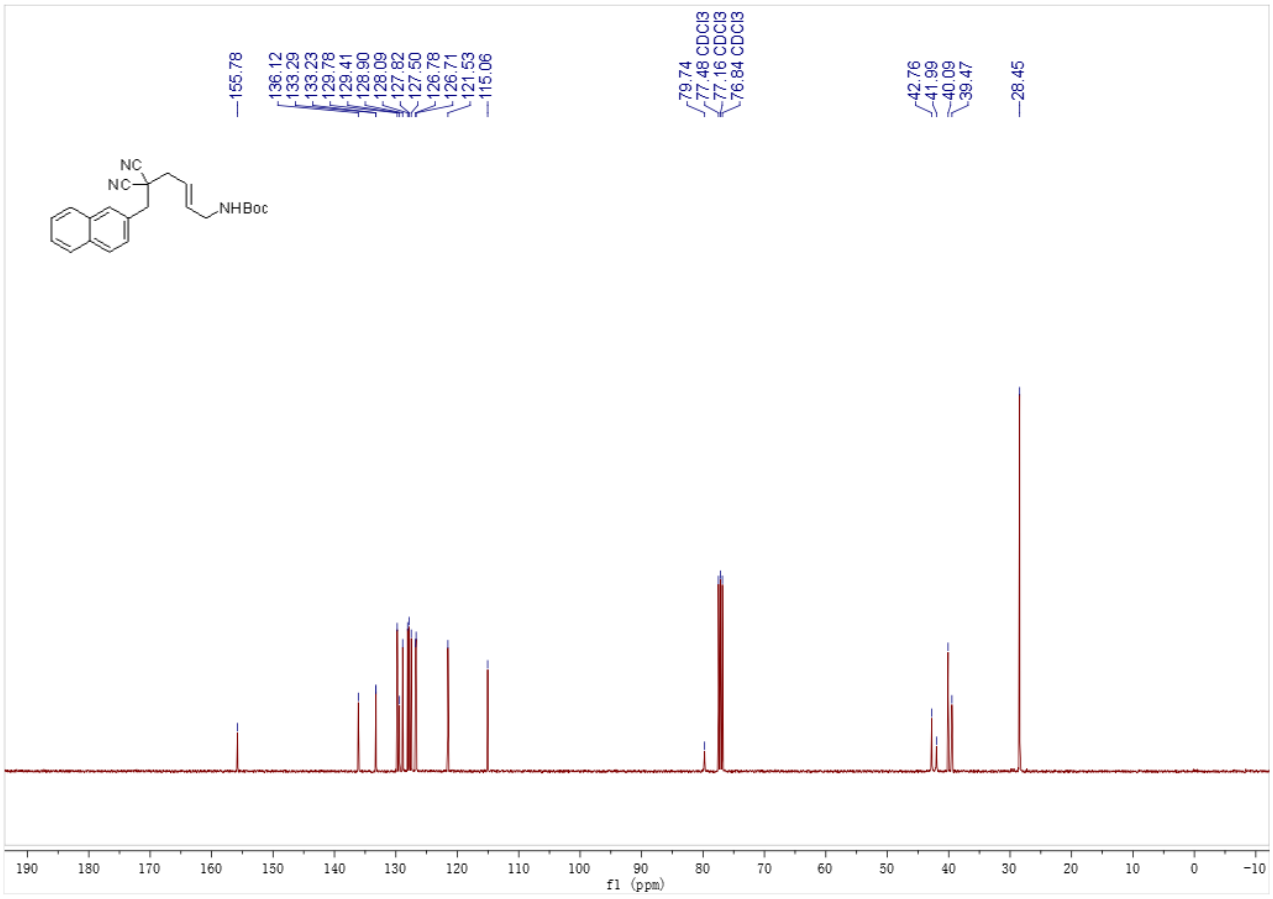
3bm


7.90
7.88
7.87
7.87
7.86
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.26 CDCl3
6.05
6.04
6.02
6.01
6.00
5.99
5.91
5.91
5.90
5.90
5.89
5.88
5.86
5.86
5.85
5.84
5.84
5.84
4.24
3.38
2.77
2.76
2.75
2.75
1.60
NC
NC
OH
4.02
3.02
0.97
0.95
2.06
2.05
1.93
1.03
f1 (ppm)

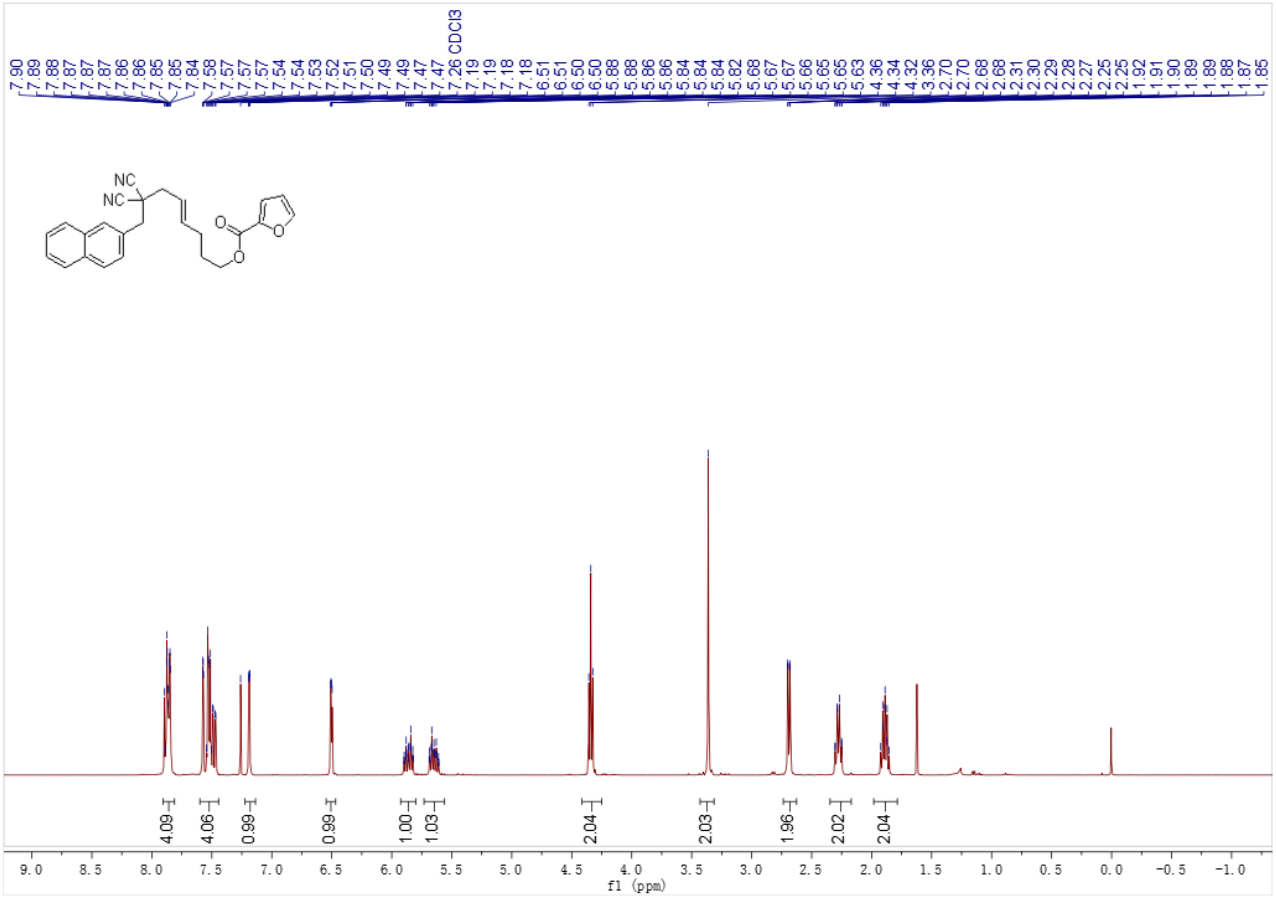

138.26
133.35
133.31
129.84
129.39
129.00
128.15
127.88
127.54
126.86
126.79
121.14
115.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.73
42.99
40.25
39.64
NC
NC
OH
f1 (ppm)

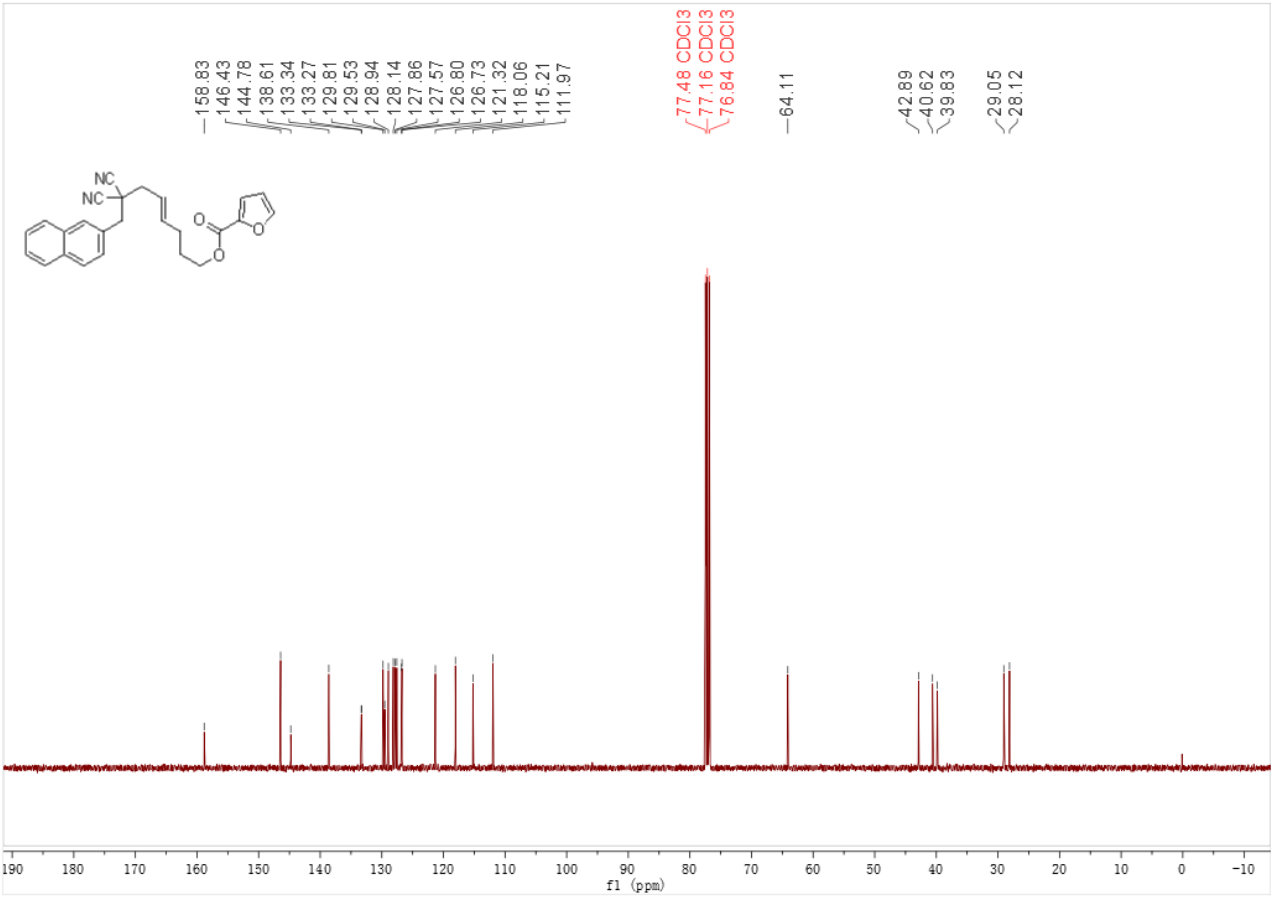
3bn


7.89
7.87
7.86
7.84
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.46
7.46
7.26 CDCl3
5.88
5.87
5.85
5.84
5.83
5.82
5.77
5.75
5.73
5.71
5.69
4.76
3.80
3.35
2.72
2.70
1.46
NC
NC
NHBoc
3.97
3.02
0.97
1.00
0.91
2.04
2.02
1.98
9.04
f1 (ppm)

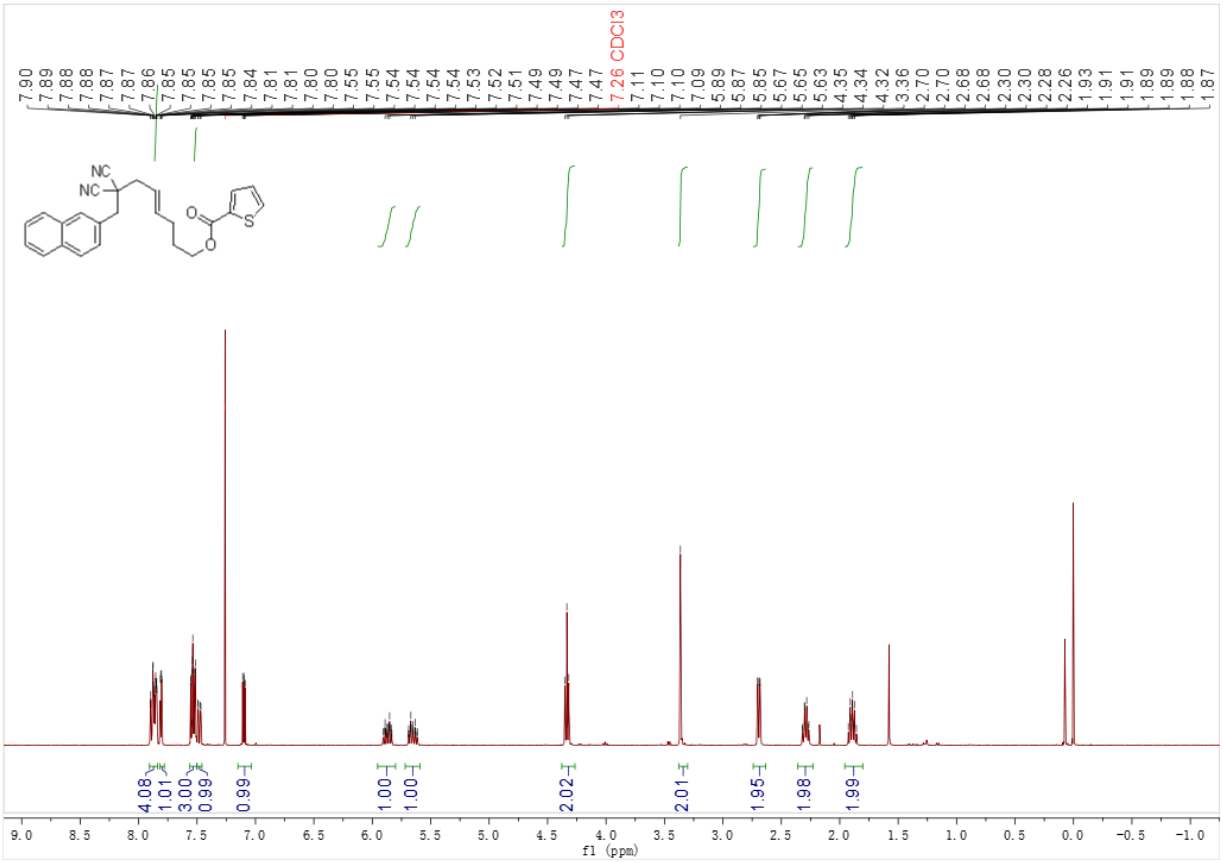

155.78
136.12
133.29
133.23
129.78
129.41
128.90
128.09
127.82
127.50
126.78
126.71
121.53
115.06
79.74
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.76
41.99
40.09
39.47
28.45
NC
NC
NHBoc
f1 (ppm)

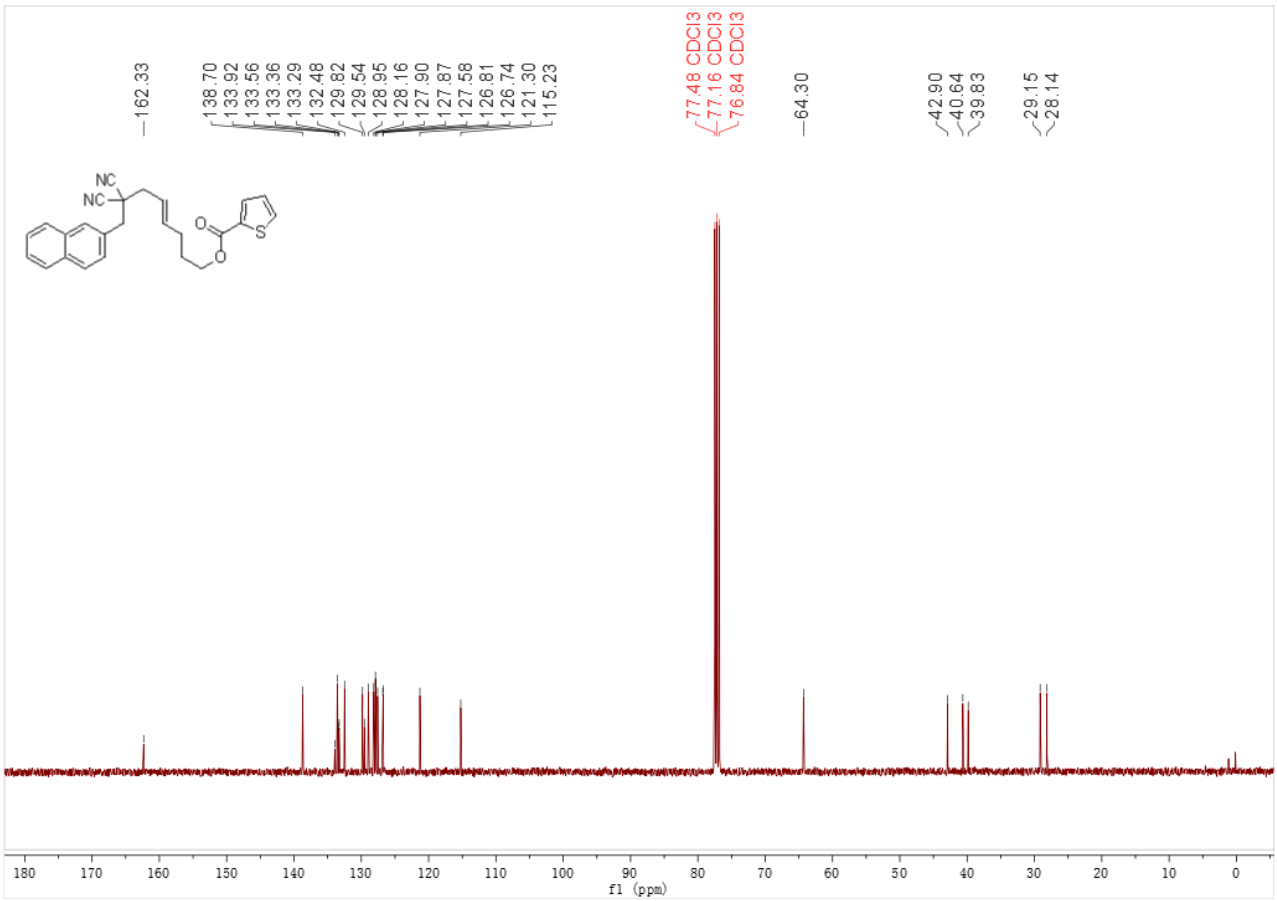
3bo


7.90 7.89 7.88 7.87 7.87 7.87 7.86 7.86 7.85 7.85 7.84 7.58 7.57 7.57 7.57 7.54 7.54 7.53 7.52 7.51 7.50 7.49 7.49 7.47 7.47 7.26 CDCl3 7.19 7.19 7.18 7.18 6.51 6.51 6.50 6.50 5.88 5.86 5.86 5.84 5.84 5.84 5.82 5.68 5.67 5.67 5.66 5.65 5.65 5.63 4.36 4.34 4.32 3.36 2.70 2.70 2.68 2.68 2.31 2.30 2.29 2.28 2.27 2.25 2.25 1.92 1.91 1.90 1.89 1.89 1.88 1.87 1.85
NC
NC
O
O
4.09
4.06
0.99
0.99
1.00
1.03
2.04
2.03
1.96
2.02
2.04
f1 (ppm)


158.83
146.43
144.78
138.61
133.34
133.27
129.81
129.53
128.94
128.14
127.86
127.57
126.80
126.73
121.32
118.06
115.21
111.97
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
64.11
42.89
40.62
39.83
29.05
28.12
NC
NC
O
O
f1 (ppm)

3bp


7.90 7.89 7.88 7.88 7.87 7.87 7.86 7.85 7.85 7.85 7.84 7.81 7.81 7.80 7.80 7.55 7.55 7.54 7.54 7.54 7.53 7.52 7.51 7.49 7.49 7.47 7.47 7.26 CDCl3 7.11 7.10 7.10 7.09 5.89 5.87 5.85 5.67 5.65 5.63 4.35 4.34 4.32 3.36 2.70 2.70 2.68 2.68 2.30 2.30 2.28 2.26 1.93 1.91 1.91 1.89 1.89 1.88 1.87
NC
NC
O
O
S
4.08 1.01 3.00 0.99 0.99 1.00 1.00 2.02 2.01 1.95 1.98 1.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


162.33
138.70 133.92 133.56 133.36 133.29 132.48 129.82 129.54 128.95 128.16 127.90 127.87 127.58 126.81 126.74 121.30 115.23
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
64.30
42.90 40.64 39.83
29.15 28.14
NC
NC
O
O
S
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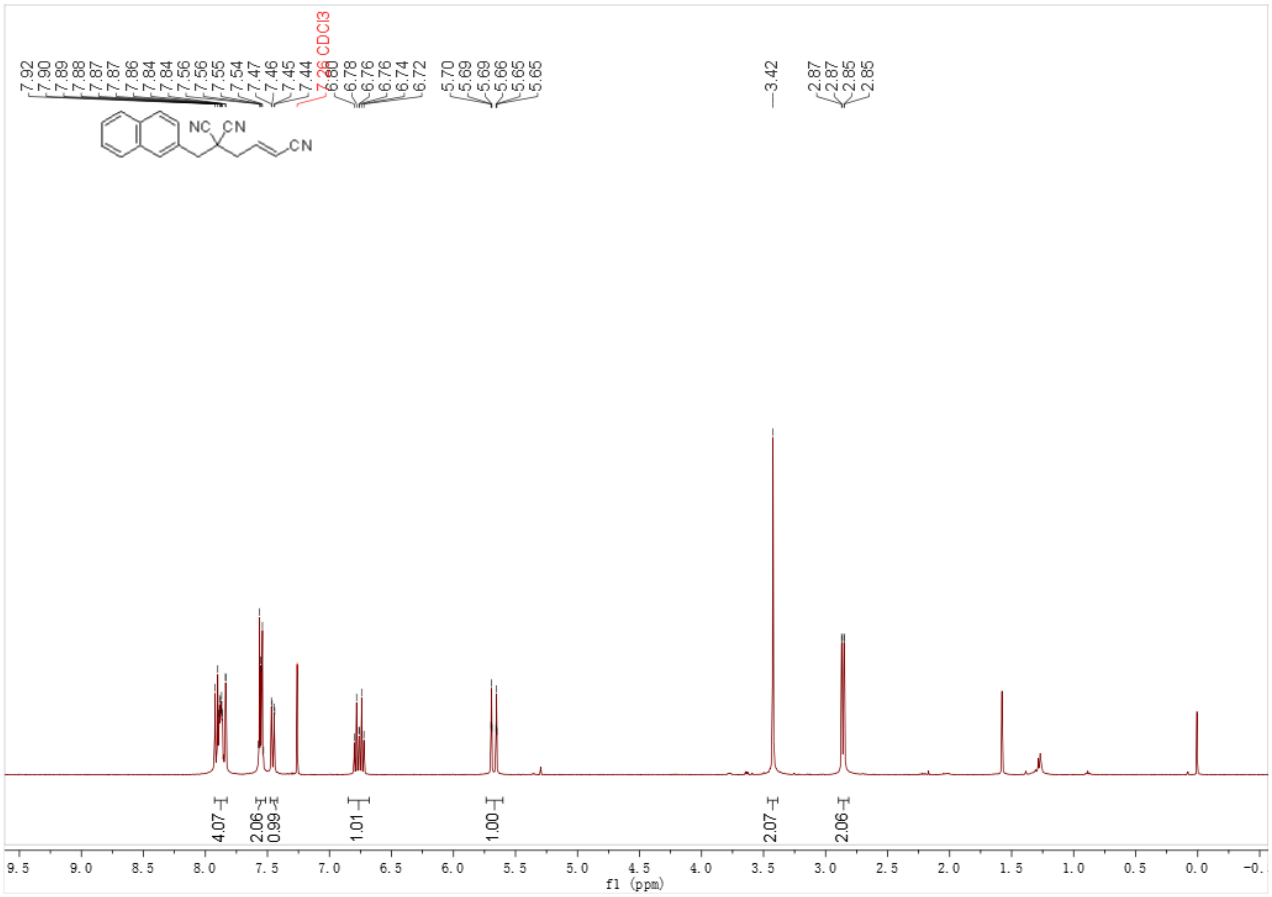
f1 (ppm)

3bq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7.90
7.89
7.88
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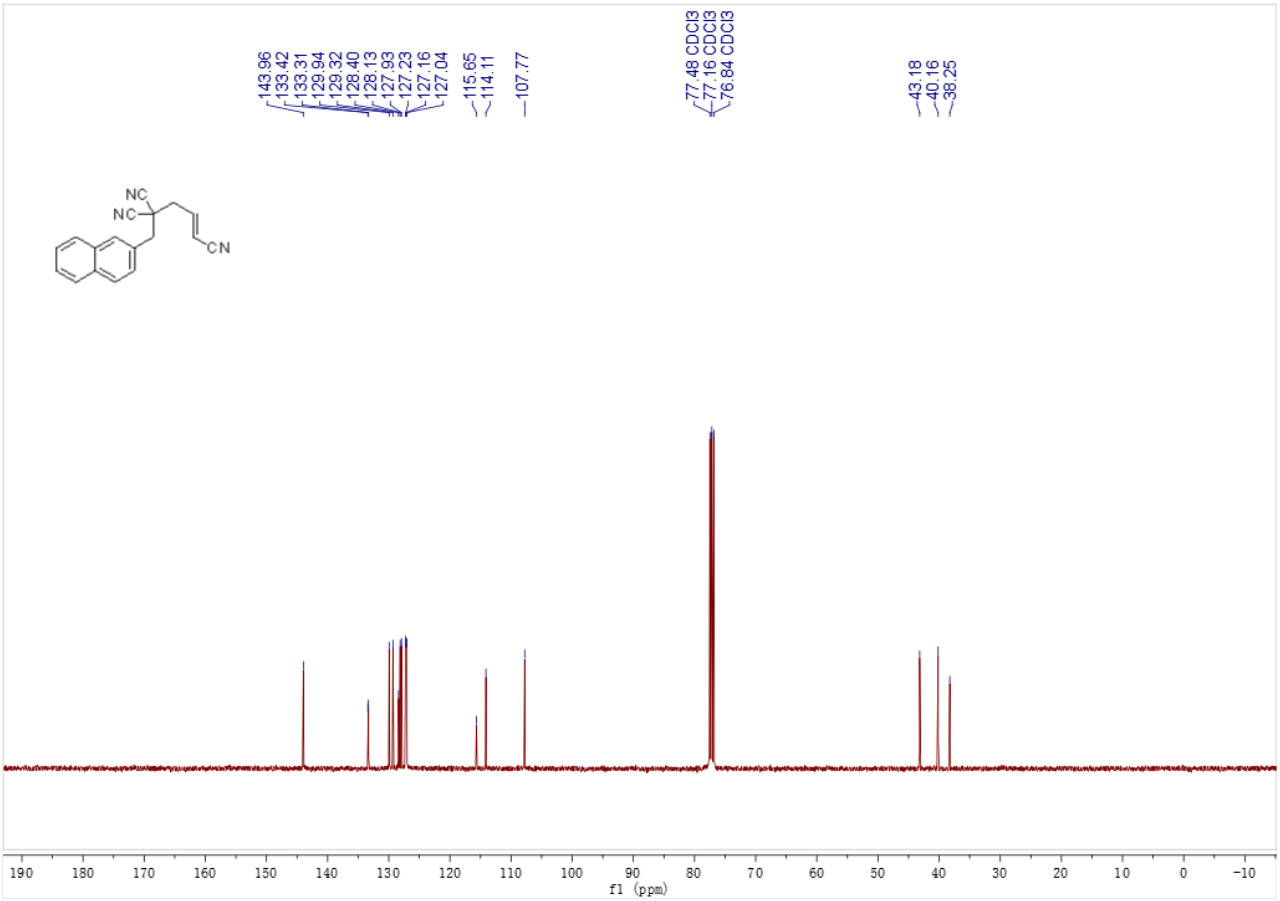
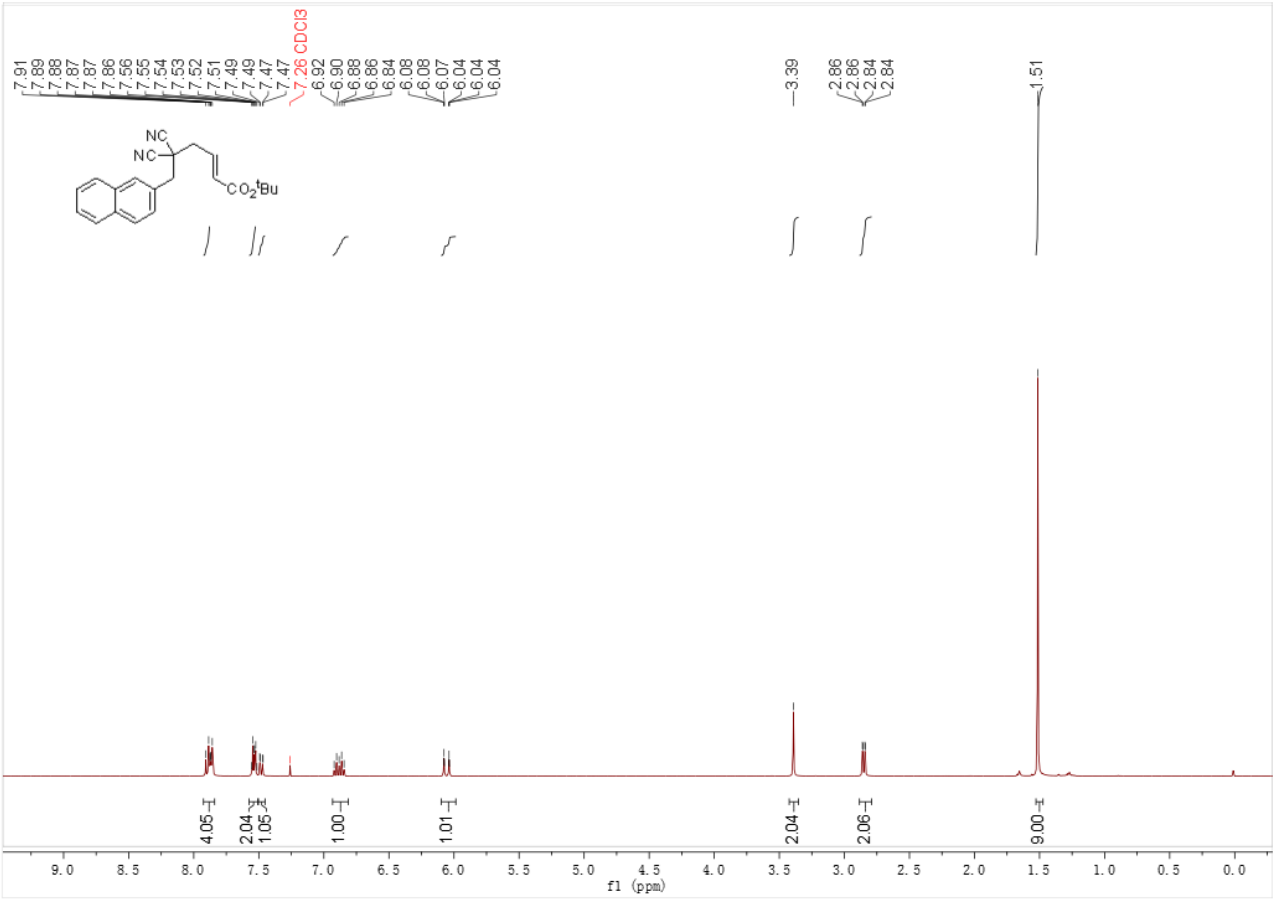
7.87
7.86
7.84
7.84
7.56
7.56
7.55
7.54
7.47
7.46
7.45
7.44
7.26 CDCl3
6.80
6.78
6.76
6.76
6.74
6.72
5.70
5.69
5.69
5.66
5.65
5.65
3.42
2.87
2.87
2.85
2.85
NC
CN
CN
4.07
2.06
0.99
1.01
1.00
2.07
2.06
f1 (ppm)


143.96
133.42
133.31
129.94
129.32
128.40
128.13
127.93
127.23
127.16
127.04
115.65
114.11
107.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
43.18
40.16
38.25
NC
NC
CN
f1 (ppm)

3br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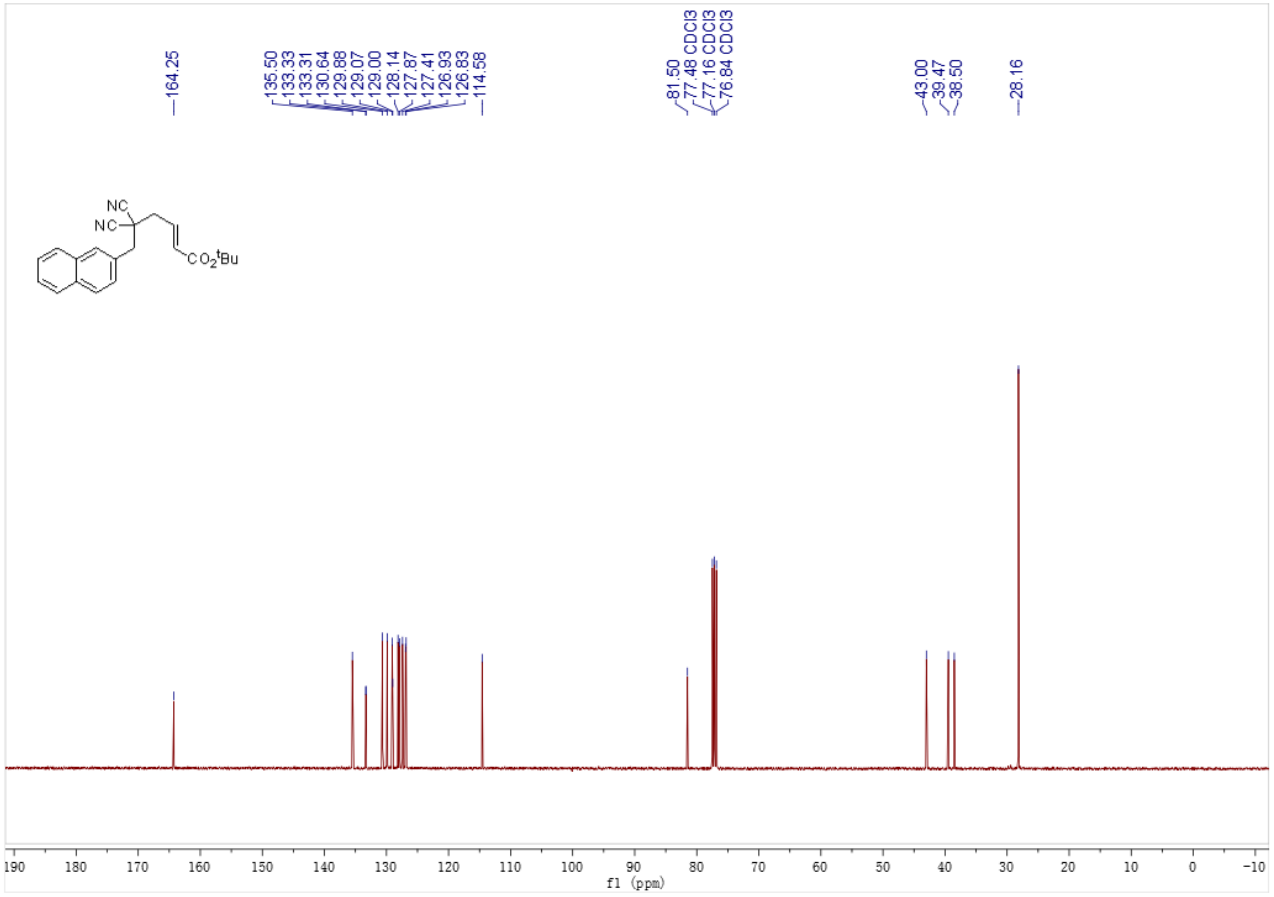
7.87
7.86
7.56
7.55
7.54
7.53
7.52
7.51
7.49
7.49
7.47
7.47
7.26 CDCl3
6.92
6.90
6.88
6.86
6.84
6.08
6.08
6.07
6.04
6.04
6.04
3.39
2.86
2.86
2.84
2.84
1.51
NC
NC
CO2tBu
4.05
2.04
1.05
1.00
1.01
2.04
2.06
9.00
f1 (ppm)


164.25
135.50
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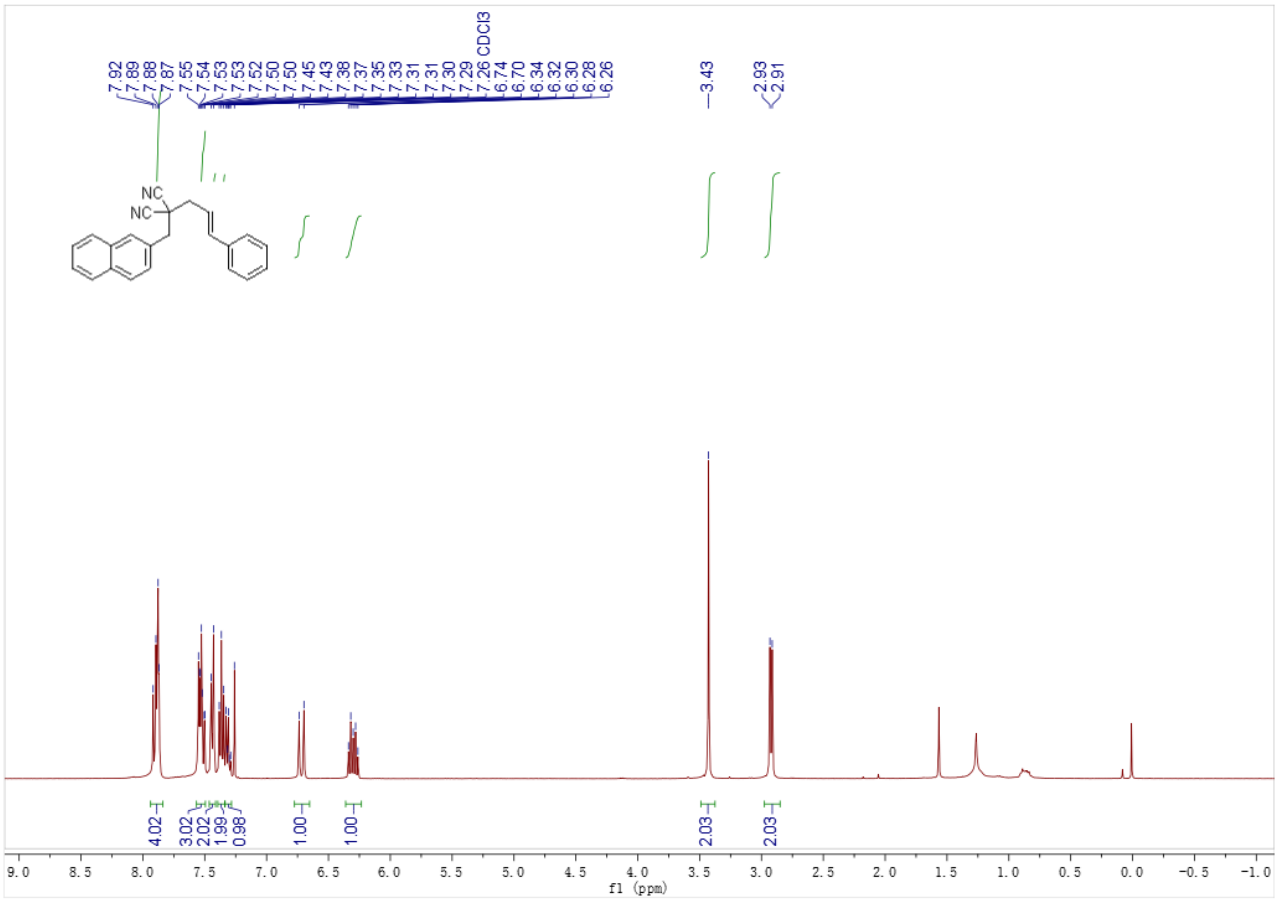
133.31
130.64
129.88
129.07
129.00
128.14
127.87
127.41
126.93
126.83
114.58
81.50
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
43.00
39.47
38.50
28.16
NC
NC
CO2tBu
f1 (ppm)

3bs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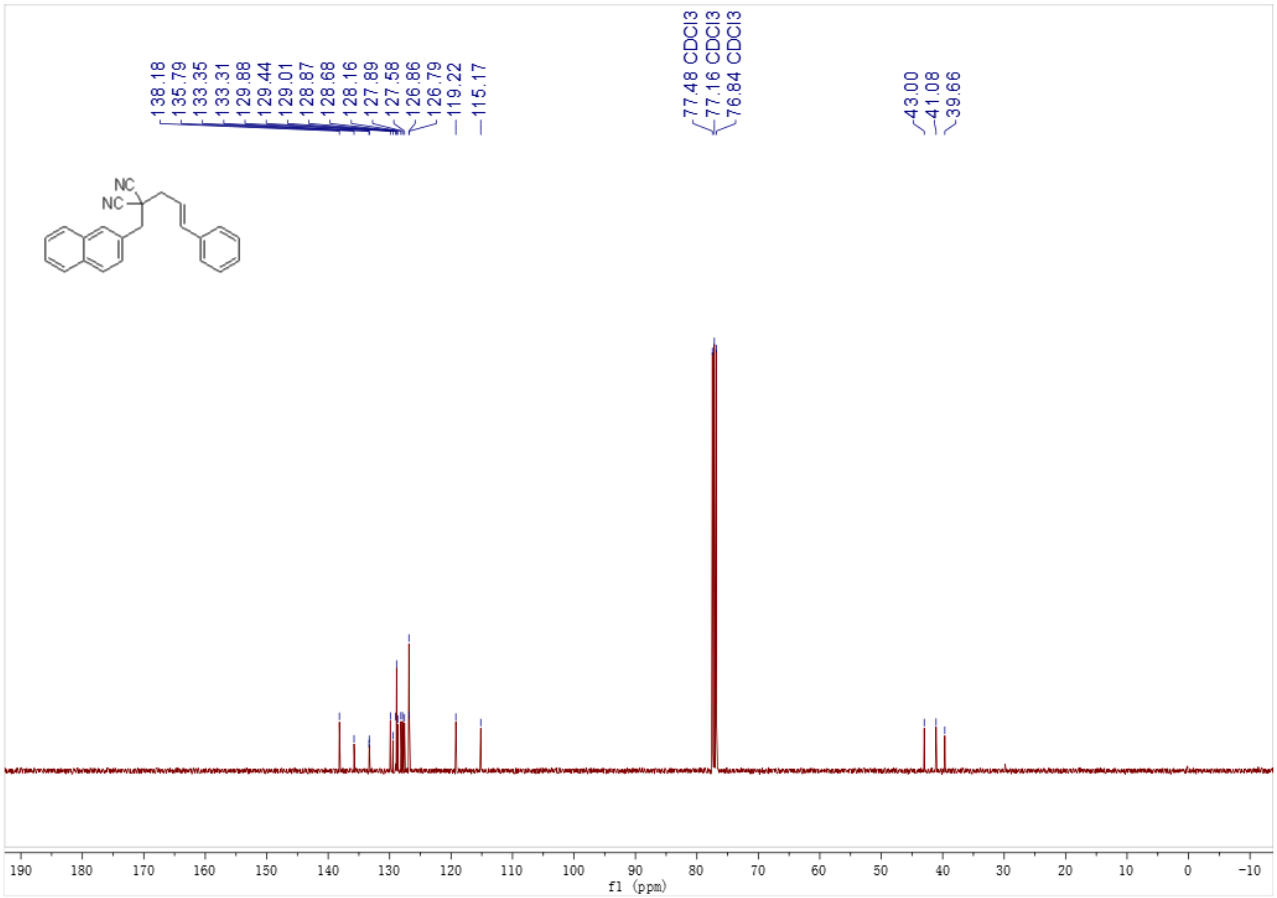
7.89
7.88
7.87
7.55
7.54
7.53
7.53
7.52
7.50
7.50
7.45
7.43
7.38
7.37
7.35
7.33
7.31
7.31
7.30
7.29
7.26 CDCl3
6.74
6.70
6.34
6.32
6.30
6.28
6.26
3.43
2.93
2.91
NC
NC
4.02
3.02
2.02
1.99
0.98
1.00
1.00
2.03
2.03
f1 (ppm)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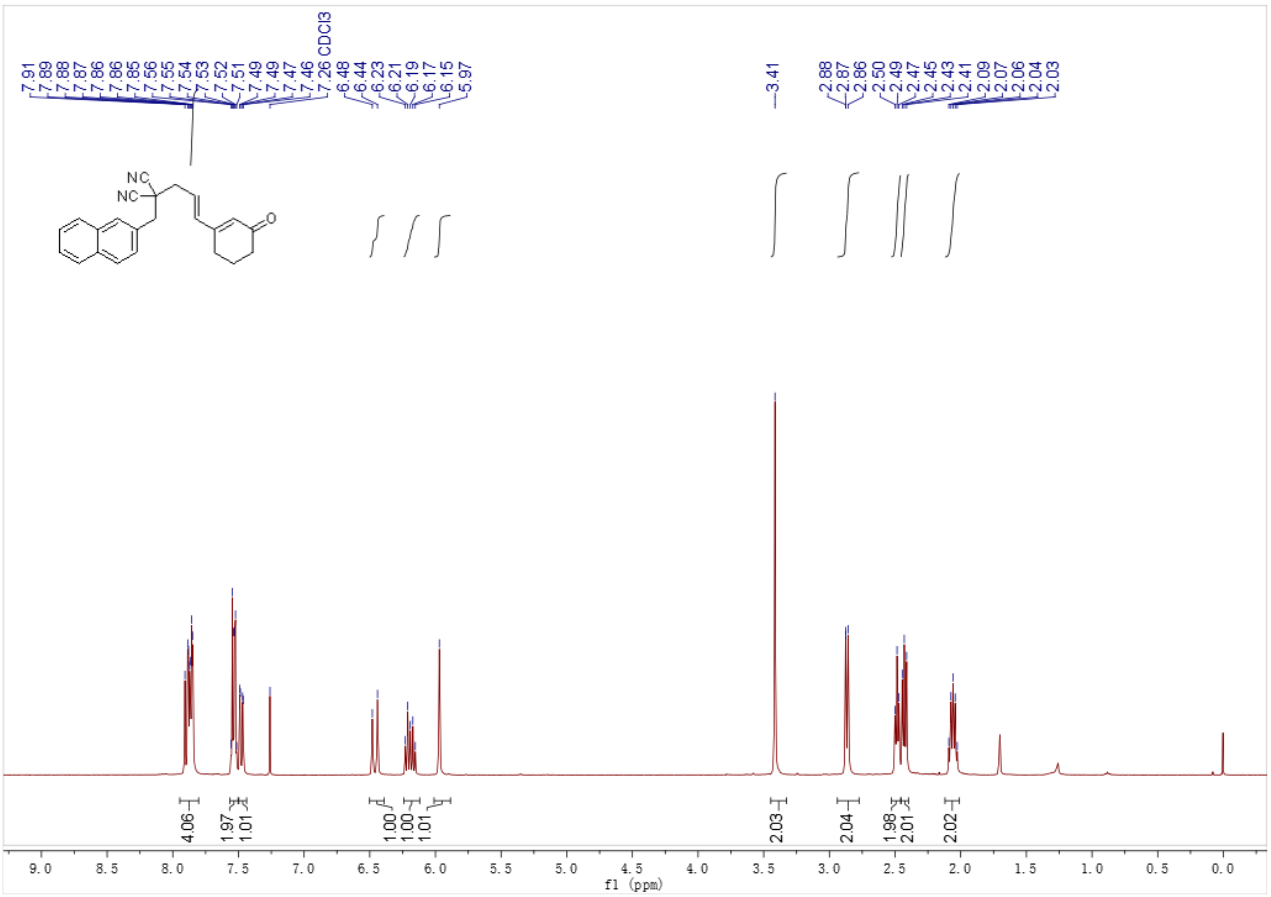
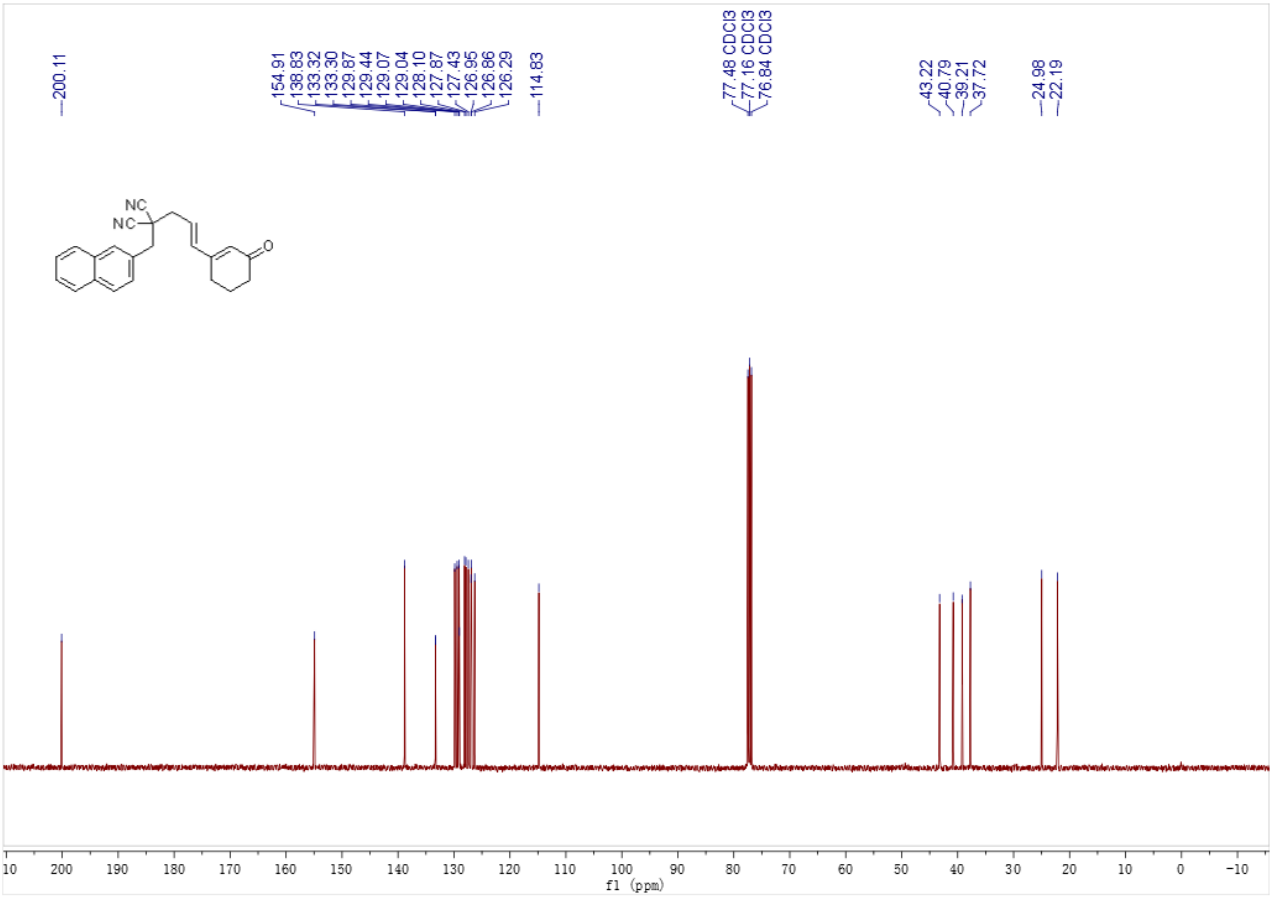
129.44
129.01
128.87
128.68
128.16
127.89
127.58
126.86
126.79
119.22
115.17
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
43.00
41.08
39.66
NC
NC
f1 (ppm)

3bt


7.91
7.89
7.88
7.87
7.86
7.86
7.85
7.56
7.55
7.54
7.53
7.52
7.51
7.49
7.49
7.47
7.46
CDCl3
6.48
6.44
6.23
6.21
6.19
6.17
6.15
5.97
3.41
2.88
2.87
2.86
2.50
2.49
2.47
2.45
2.43
2.41
2.09
2.07
2.06
2.04
2.03
NC
NC
O
4.06
1.97
1.01
1.00
1.00
1.01
2.03
2.04
1.98
2.01
2.02
f1 (ppm)


200.11
154.91
138.83
133.32
133.30
129.87
129.44
129.07
129.04
128.10
127.87
127.43
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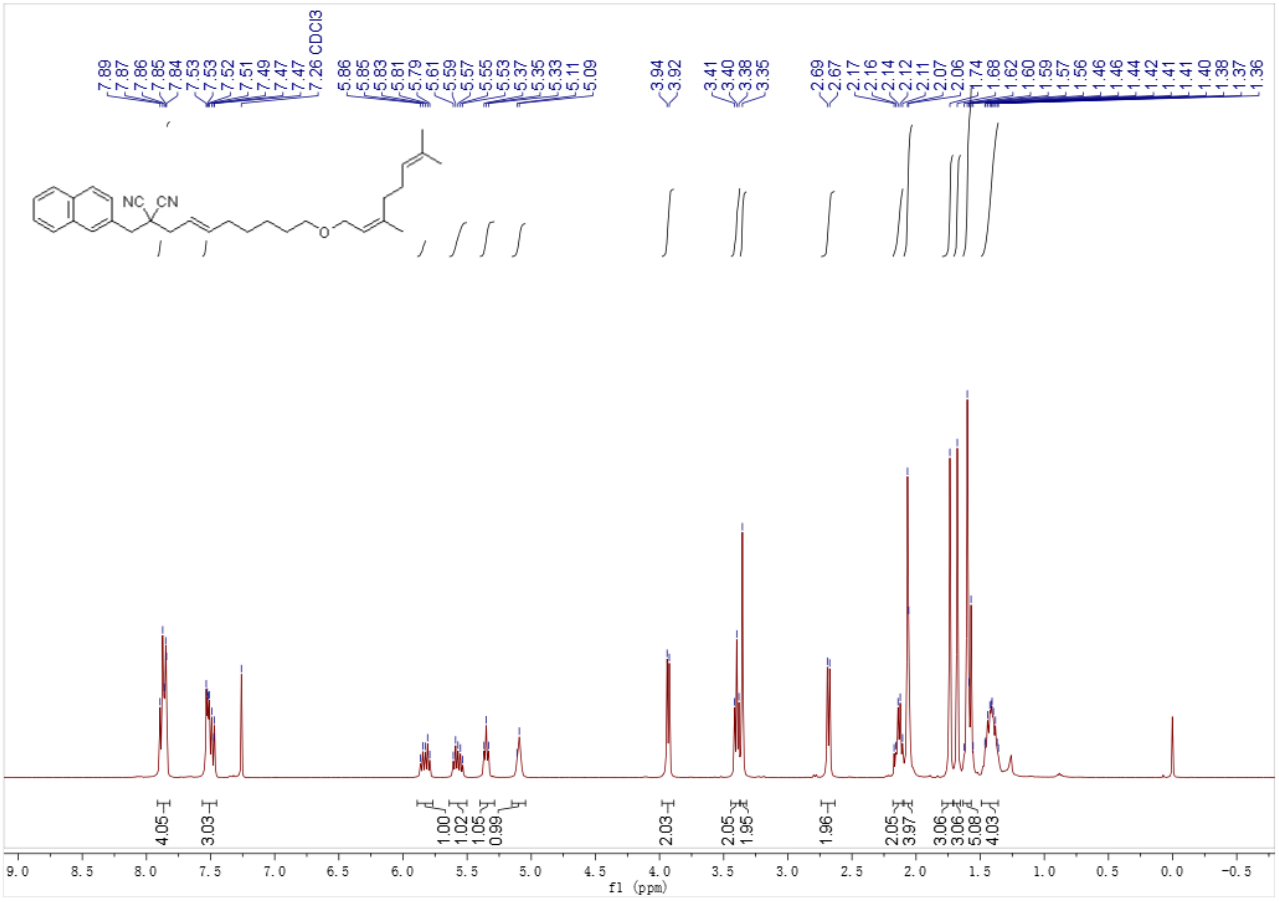
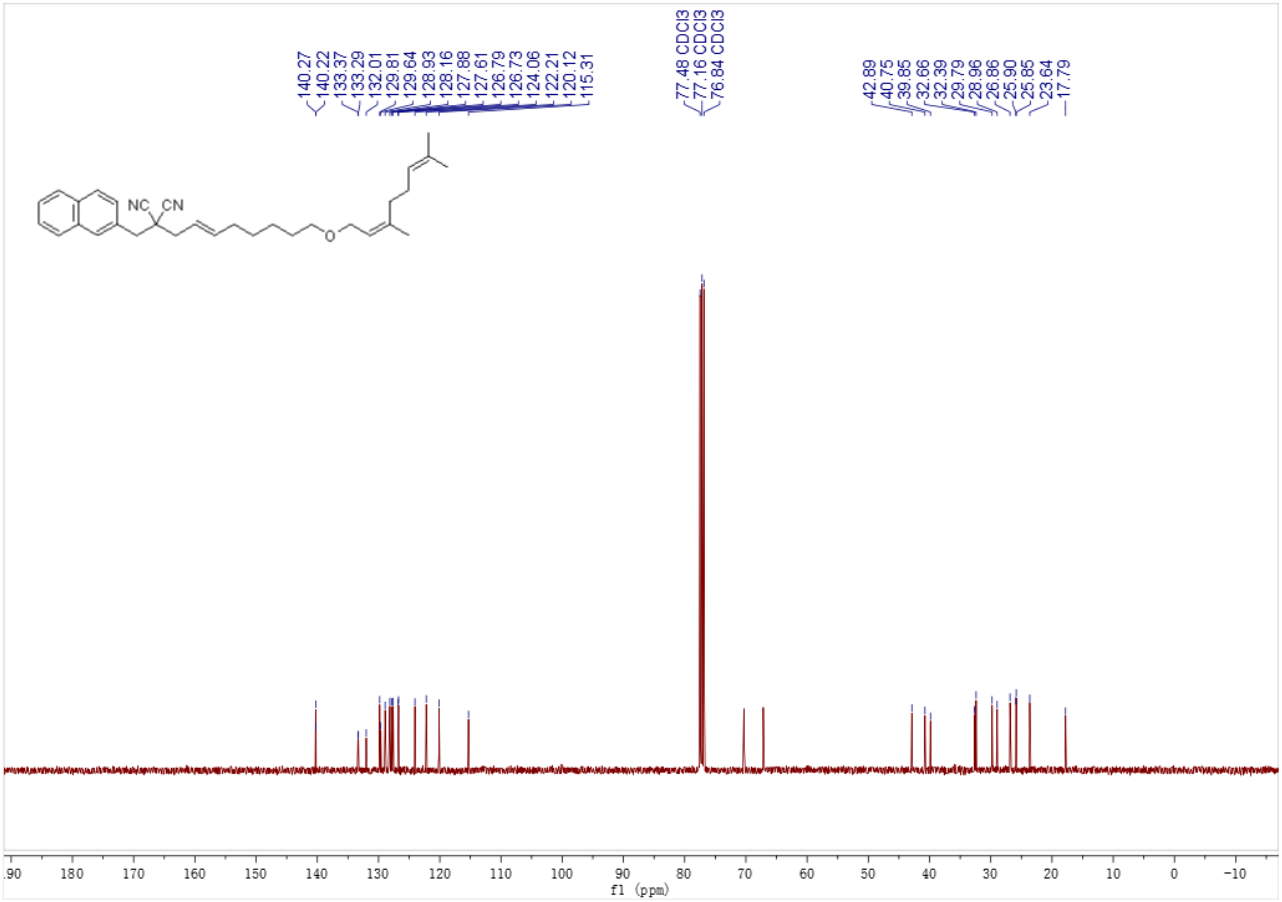
126.86
126.29
114.83
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
43.22
40.79
39.21
37.72
24.98
22.19
NC
NC
O
f1 (ppm)

3bu


7.89
7.87
7.86
7.85
7.84
7.53
7.53
7.52
7.51
7.49
7.47
7.47
7.26 CDCl3
5.86
5.85
5.83
5.81
5.79
5.61
5.59
5.57
5.55
5.53
5.37
5.35
5.33
5.11
5.09
3.94
3.92
3.41
3.40
3.38
3.35
2.69
2.67
2.17
2.16
2.14
2.12
2.11
2.07
2.06
1.74
1.68
1.62
1.60
1.59
1.57
1.56
1.46
1.46
1.44
1.42
1.41
1.41
1.40
1.38
1.37
1.36
NC
CN
O
4.05
3.03
1.00
1.02
1.05
0.99
2.03
2.05
1.95
1.96
2.05
3.97
3.06
3.06
5.08
4.03
f1 (ppm)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140.22
133.37
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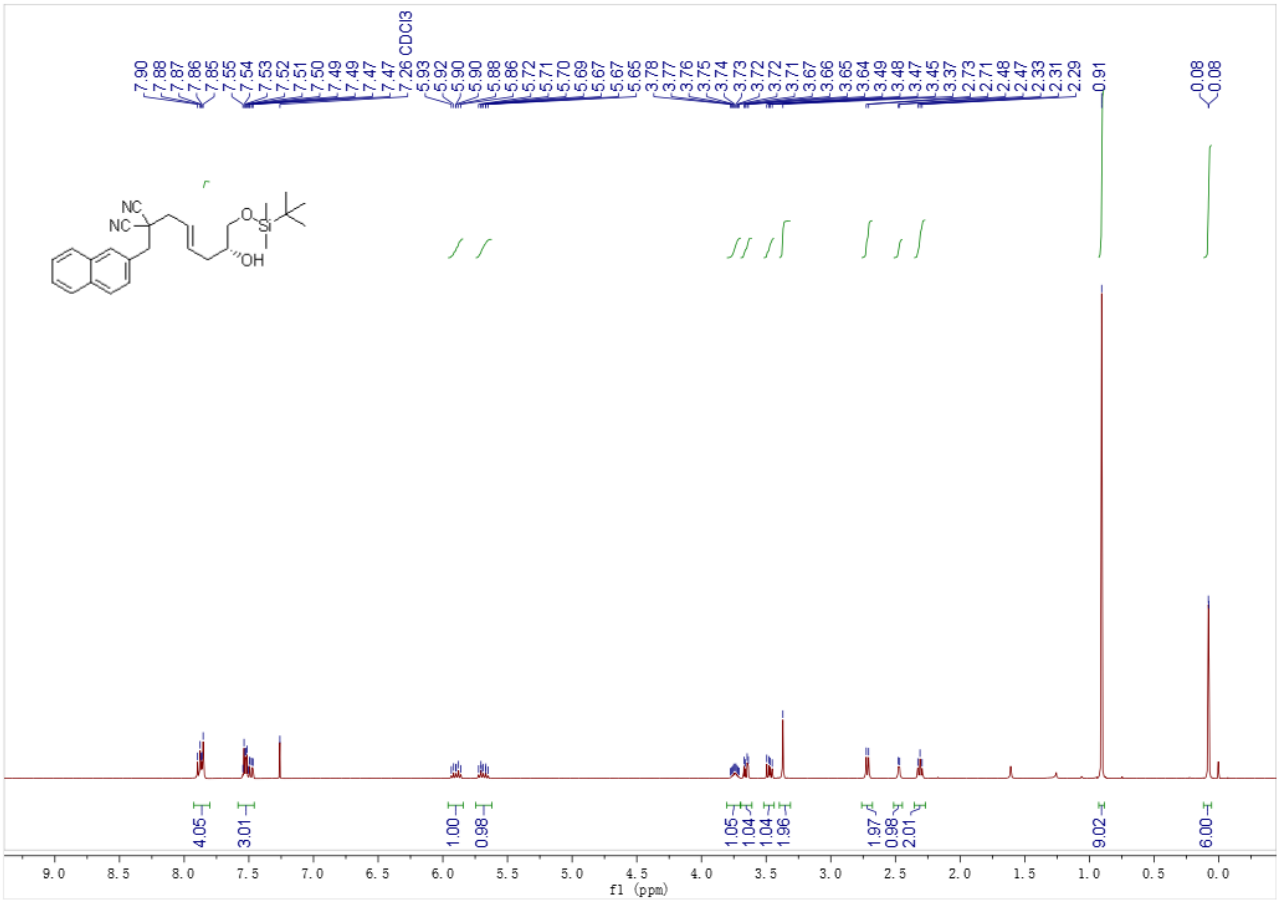
132.01
129.81
129.64
128.93
128.16
127.88
127.61
126.79
126.73
124.06
122.21
120.12
115.31
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.89
40.75
39.85
32.66
32.39
29.79
28.96
26.86
25.90
25.85
23.64
17.79
NC
CN
O
f1 (ppm)

3bv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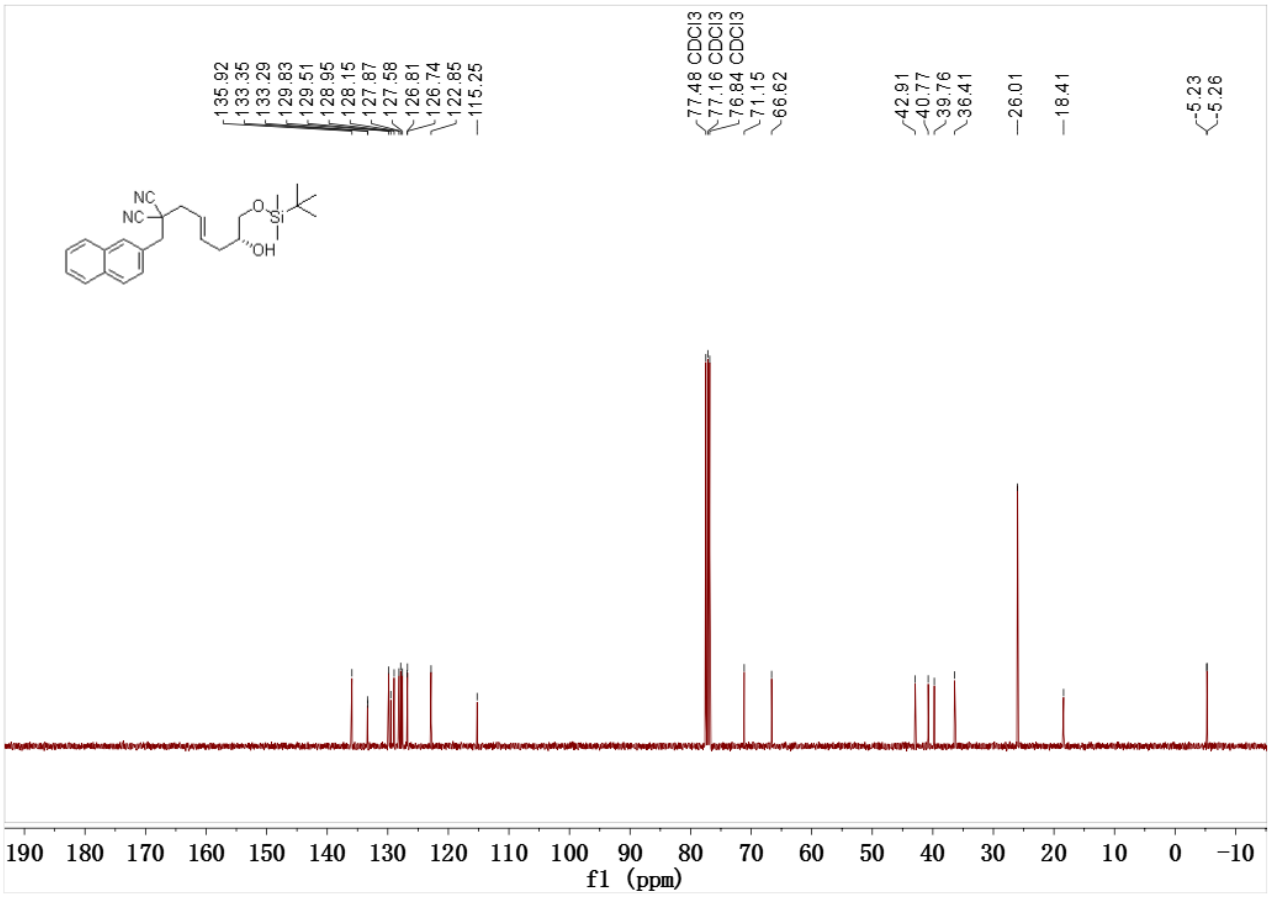
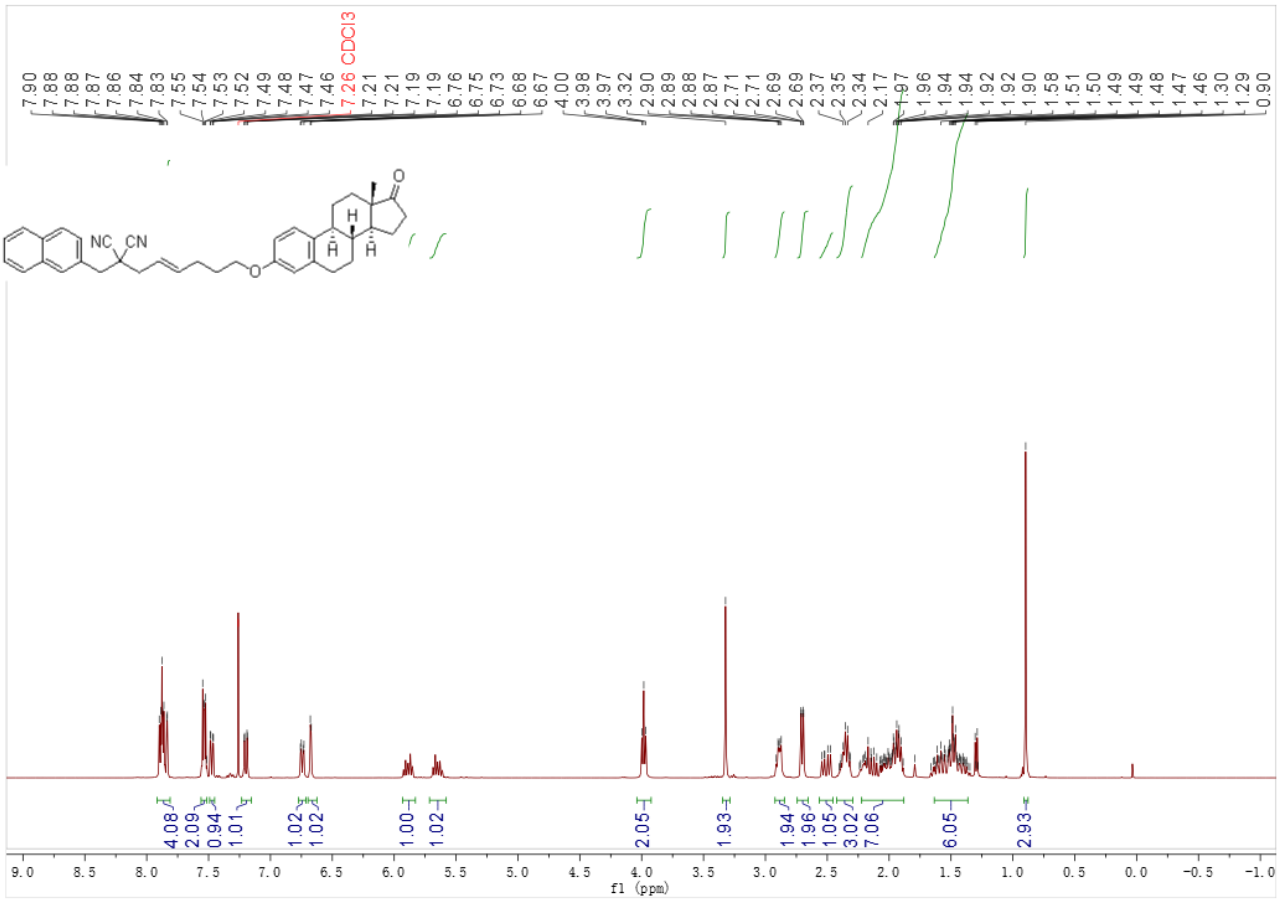
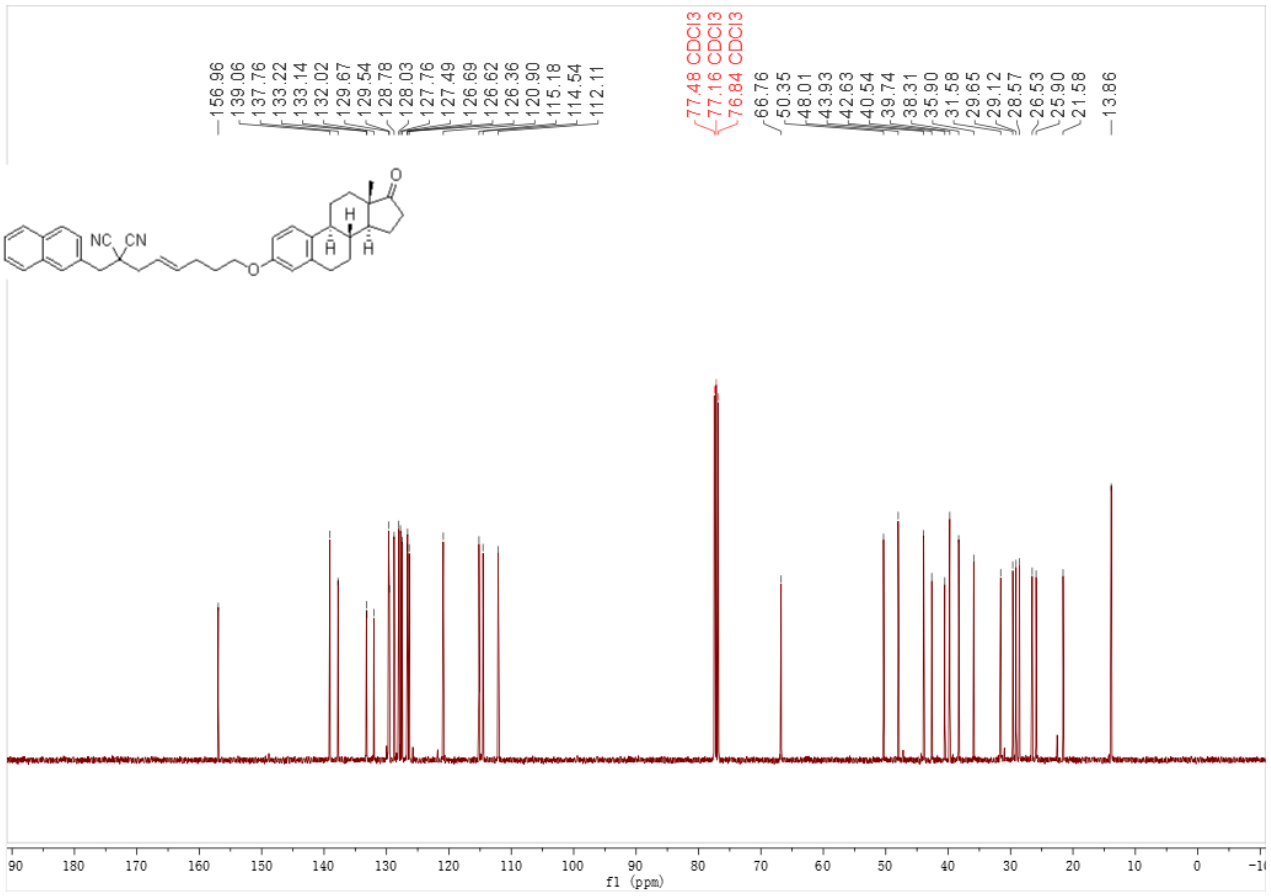
7.88
7.87
7.86
7.85
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.49
7.47
7.47
7.26 CDCl3
5.93
5.92
5.90
5.90
5.88
5.86
5.72
5.71
5.70
5.69
5.67
5.67
5.65
3.78
3.77
3.76
3.75
3.74
3.73
3.72
3.72
3.71
3.67
3.66
3.65
3.64
3.49
3.48
3.47
3.45
3.37
2.73
2.71
2.48
2.47
2.33
2.31
2.29
0.91
0.08
0.08
NC
NC
O
Si
OH
4.05
3.01
1.00
0.98
1.05
1.04
1.04
1.96
1.97
0.98
2.01
9.02
6.00
f1 (ppm)

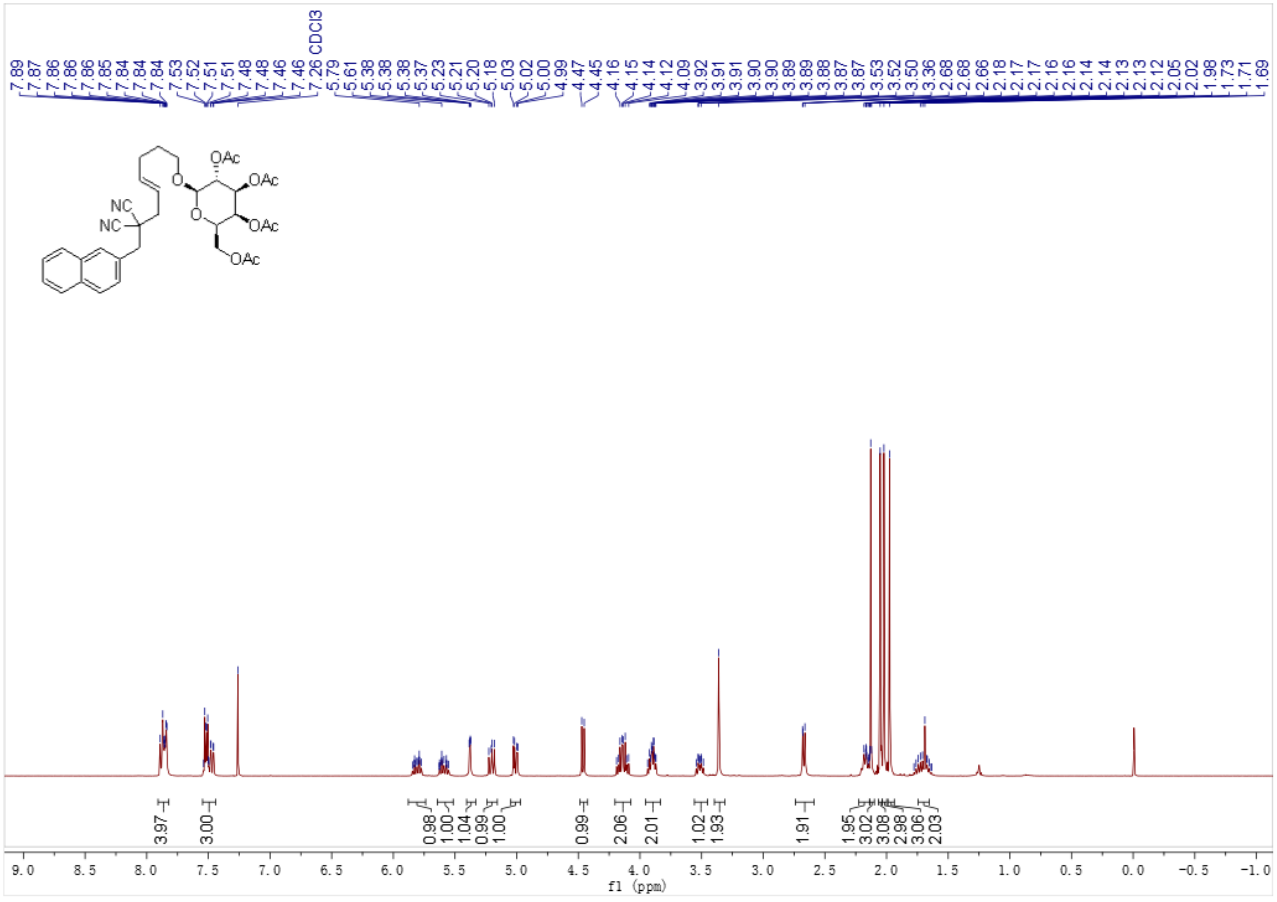

135.92
133.35
133.29
129.83
129.51
128.95
128.15
127.87
127.58
126.81
126.74
122.85
115.25
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.15
66.62
42.91
40.77
39.76
36.41
26.01
18.41
-5.23
-5.26
NC
NC
O
Si
OH
f1 (ppm)

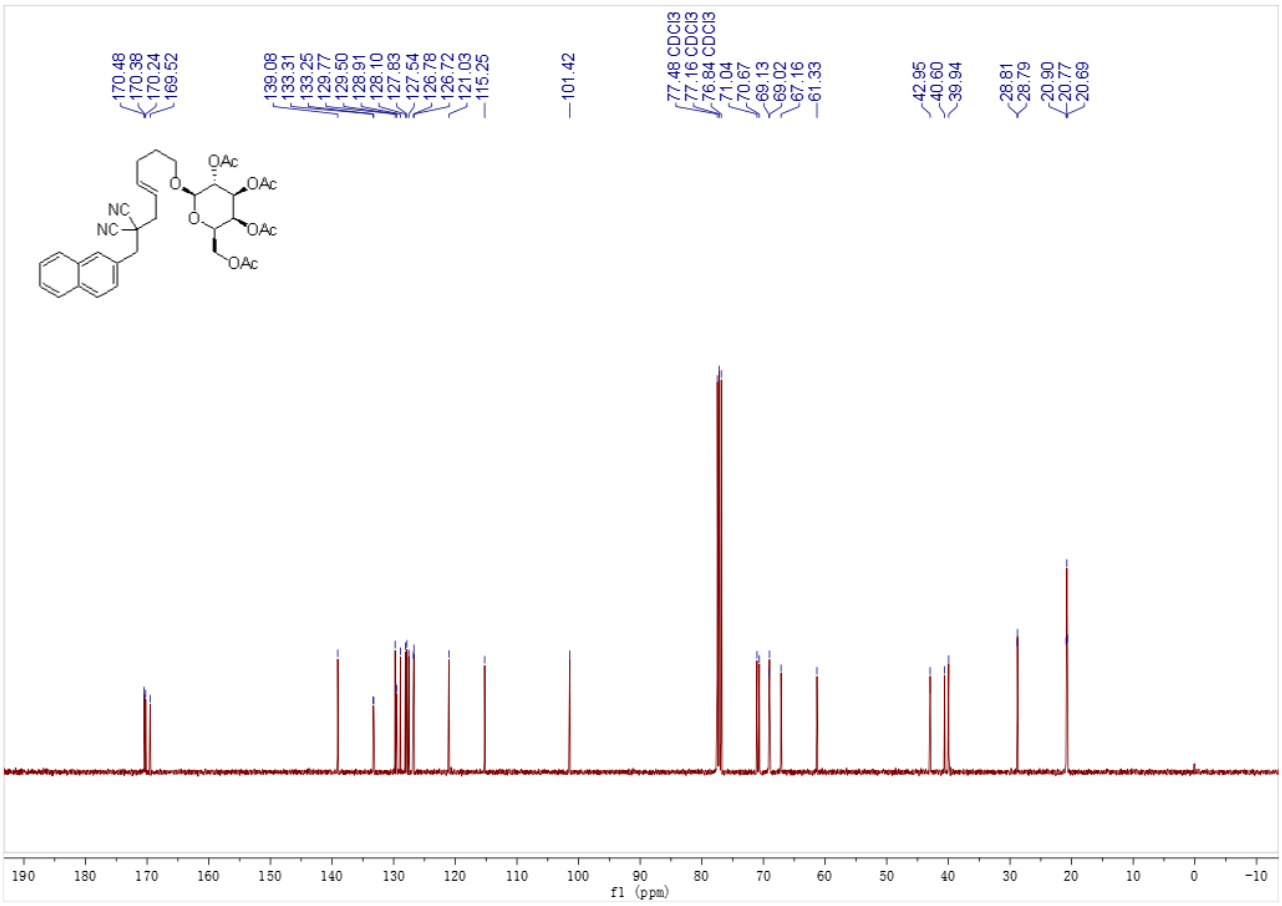
3bw


7.90 7.88 7.88 7.87 7.86 7.84 7.83 7.55 7.54 7.53 7.52 7.49 7.48 7.47 7.46 7.26 CDCl3 7.21 7.21 7.19 7.19 6.76 6.75 6.73 6.68 6.67 4.00 3.98 3.97 3.32 2.90 2.89 2.88 2.87 2.71 2.71 2.69 2.69 2.37 2.35 2.34 2.17 1.97 1.96 1.94 1.94 1.92 1.92 1.90 1.58 1.51 1.50 1.49 1.49 1.48 1.47 1.46 1.30 1.29 0.90
NC CN
O
H
H
H
4.08 2.09 0.94 1.01 1.02 1.02 1.00 1.02 2.05 1.93 1.94 1.96 1.05 3.02 7.06 6.05 2.93
f1 (ppm)

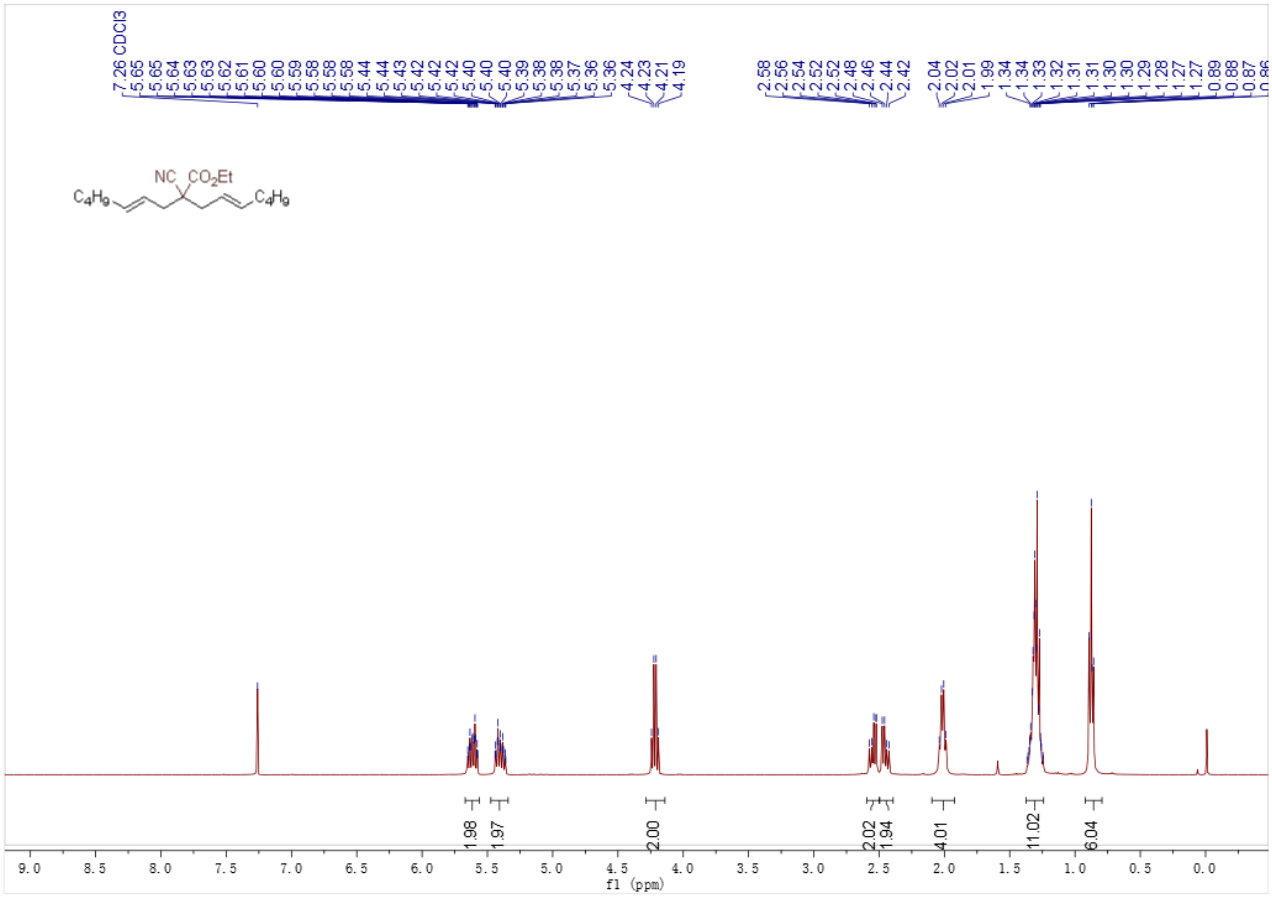

156.96 139.06 137.76 133.22 133.14 132.02 129.67 129.54 128.78 128.03 127.76 127.49 126.69 126.62 126.36 120.90 115.18 114.54 112.11
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
66.76 50.35 48.01 43.93 42.63 40.54 39.74 38.31 35.90 31.58 29.65 29.12 28.57 26.53 25.90 21.58 13.86
NC CN
O
H
H
H
f1 (ppm)

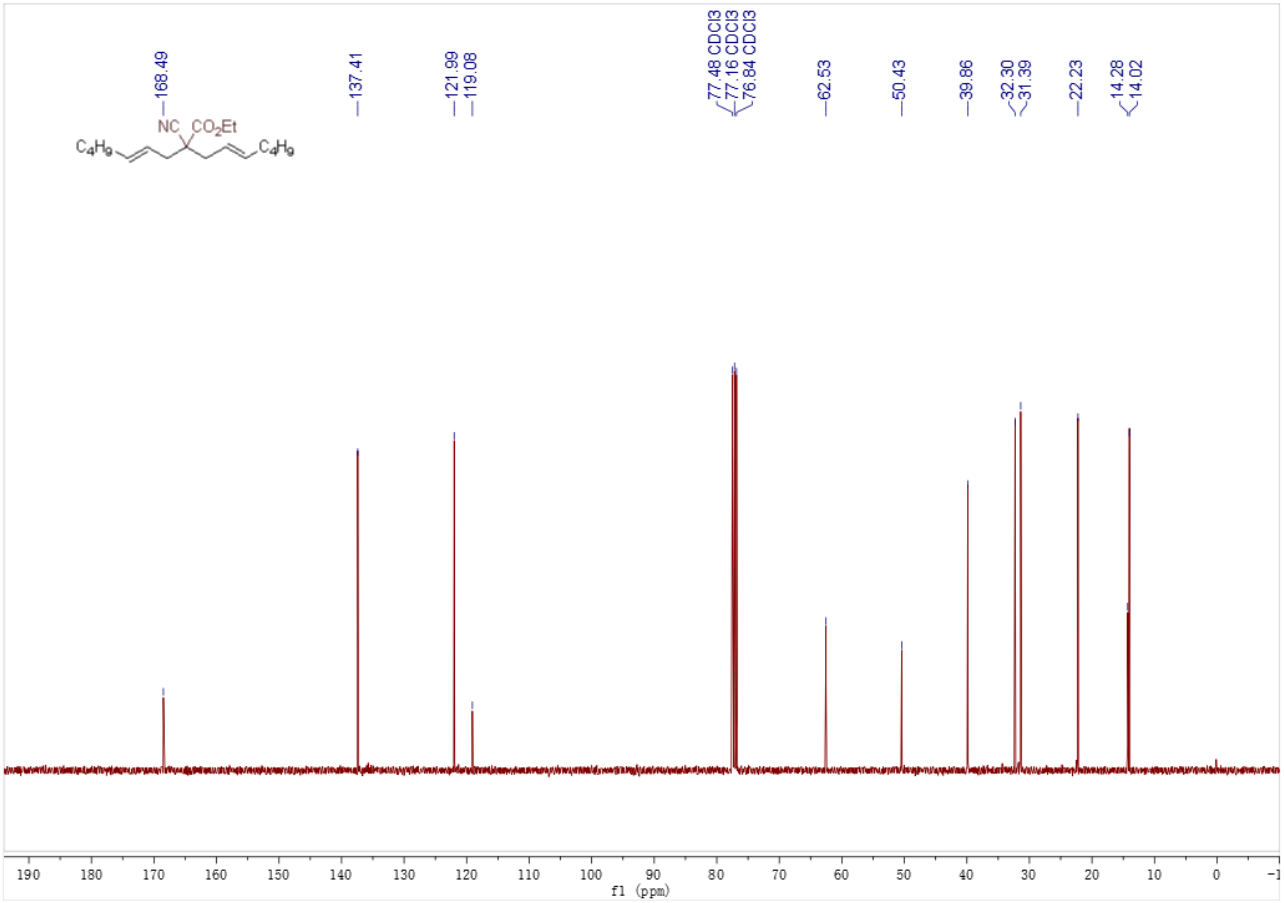
3bx


7.89 7.87 7.86 7.86 7.86 7.85 7.84 7.84 7.84 7.53 7.52 7.51 7.51 7.48 7.48 7.46 7.46 7.26 CDCl3 5.79 5.61 5.38 5.38 5.38 5.37 5.23 5.21 5.20 5.18 5.03 5.02 5.00 4.99 4.47 4.45 4.16 4.15 4.14 4.12 4.09 3.92 3.91 3.91 3.90 3.90 3.89 3.89 3.88 3.87 3.87 3.53 3.52 3.50 3.36 2.68 2.68 2.66 2.18 2.17 2.16 2.16 2.14 2.14 2.13 2.13 2.12 2.05 2.02 1.98 1.73 1.71 1.69
OAc
OAc
OAc
OAc
NC
NC
3.97 3.00 0.98 1.00 1.04 0.99 1.00 0.99 2.06 2.01 1.02 1.93 1.91 1.95 3.02 3.08 2.98 3.06 2.03
f1 (ppm)

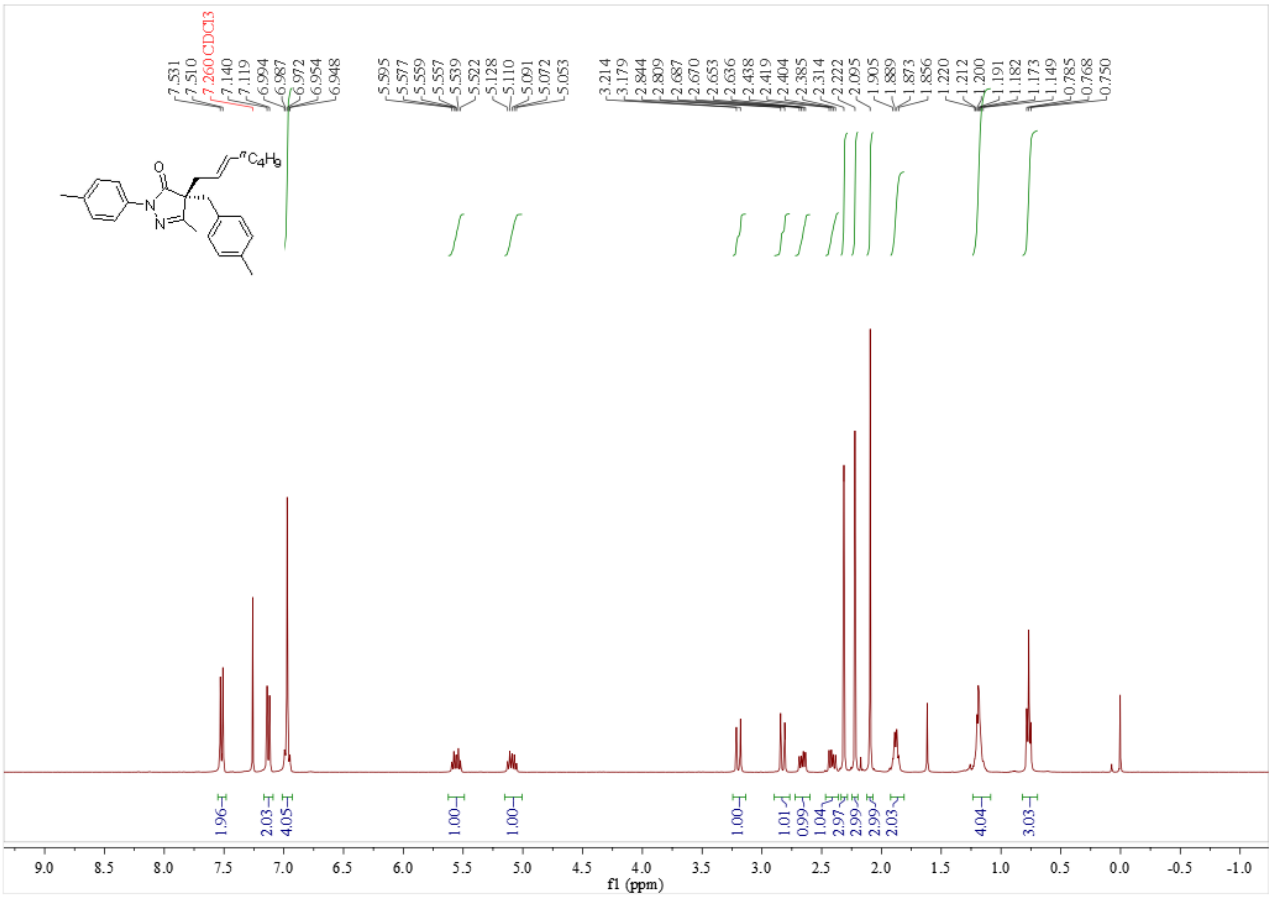

170.48 170.38 170.24 169.52 139.08 133.31 133.25 129.77 129.50 128.91 128.10 127.83 127.54 126.78 126.72 121.03 115.25 101.42 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 71.04 70.67 69.13 69.02 67.16 61.33 42.95 40.60 39.94 28.81 28.79 20.90 20.77 20.69
OAc
OAc
OAc
OAc
NC
NC
f1 (ppm)

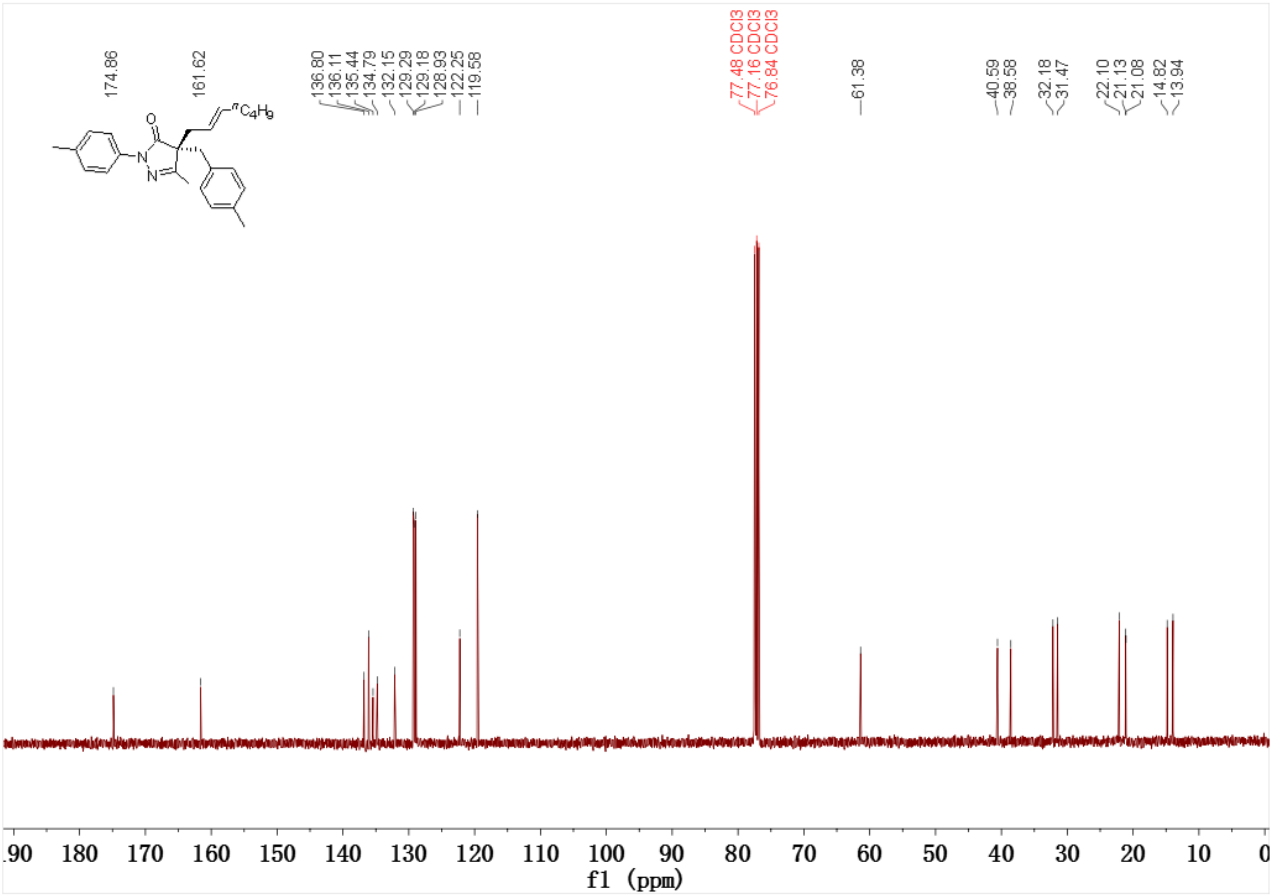
4


7.26 CDCl3
NC CO2Et
C4H9
C4H9
1.98
1.97
2.00
2.02
1.94
4.01
11.02
6.04
f1 (ppm)

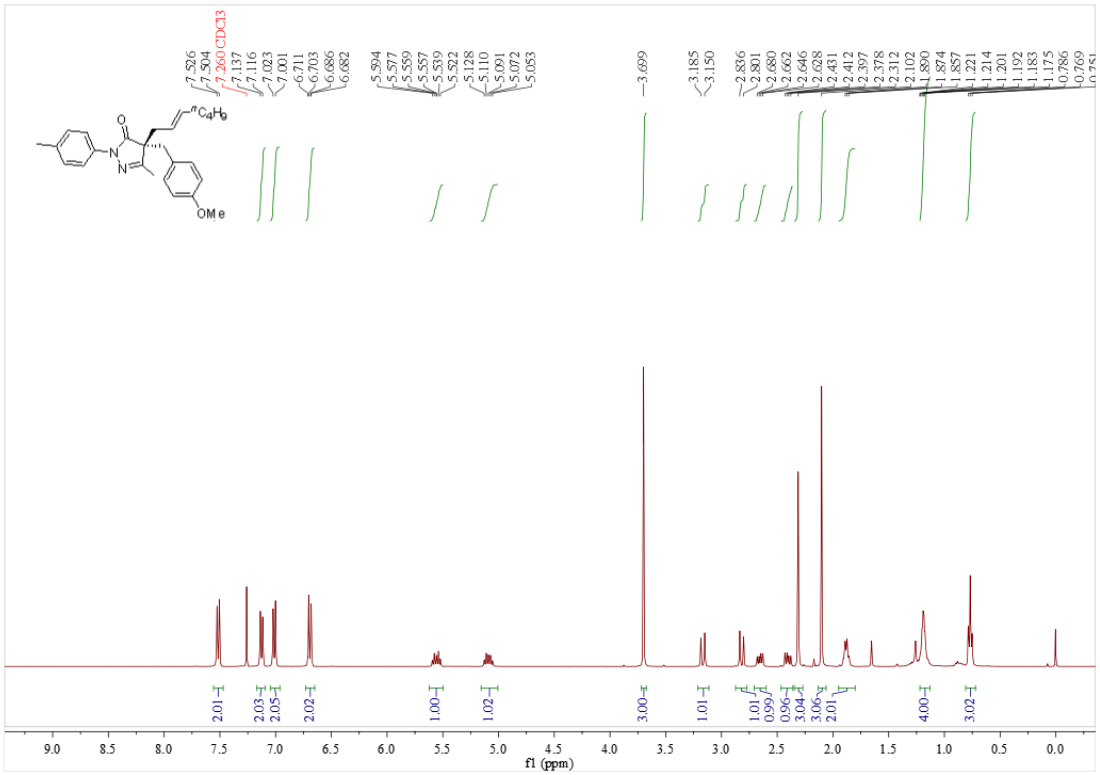

168.49
137.41
121.99
119.08
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.53
50.43
39.86
32.30
31.39
22.23
14.28
14.02
NC CO2Et
C4H9
C4H9
f1 (ppm)

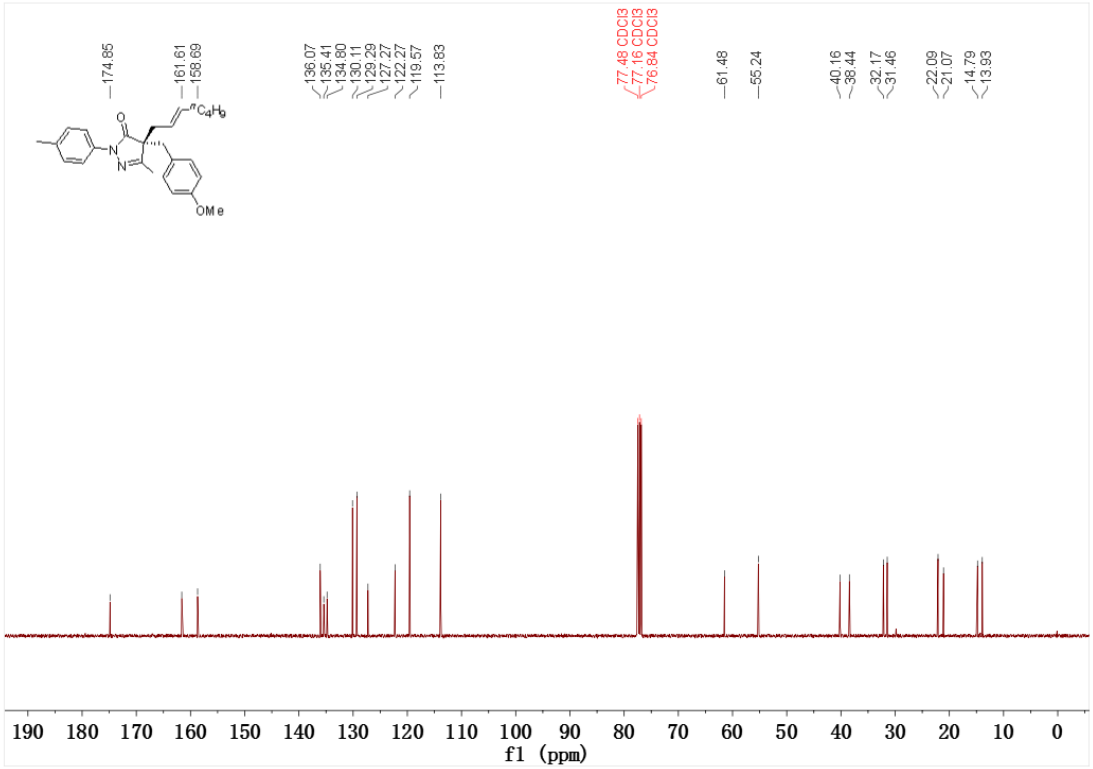
6a


7.531
7.510
7.260 CDCl3
7.140
7.119
6.994
6.987
6.972
6.954
6.948
5.595
5.577
5.559
5.557
5.539
5.522
5.128
5.110
5.091
5.072
5.053
3.214
3.179
2.844
2.809
2.687
2.670
2.653
2.636
2.438
2.419
2.404
2.385
2.314
2.222
2.095
1.905
1.889
1.873
1.856
1.220
1.212
1.200
1.191
1.182
1.173
1.149
0.785
0.768
0.750
1.96
2.03
4.05
1.00
1.00
1.00
1.01
0.99
1.04
2.97
2.99
2.03
4.04
3.03
f1 (ppm)

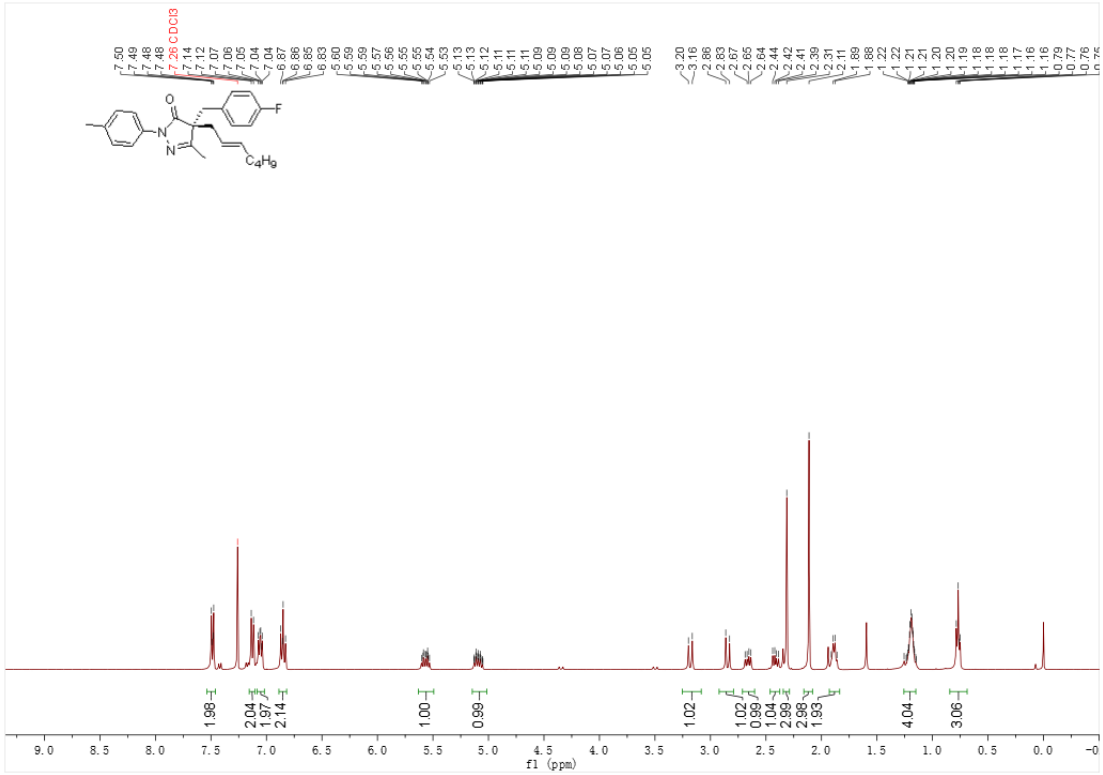

174.86
161.62
136.80
136.11
135.44
134.79
132.15
129.29
129.18
128.93
122.25
119.58
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.38
40.59
38.58
32.18
31.47
22.10
21.13
21.08
14.82
13.94
f1 (ppm)

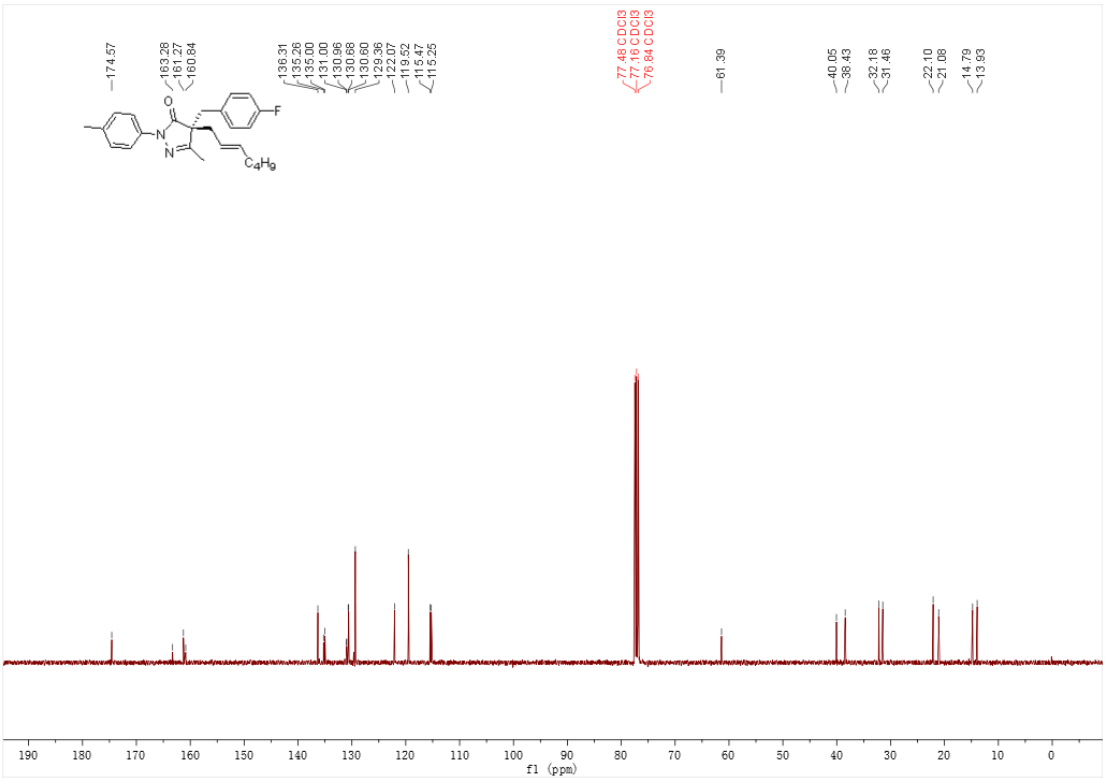
6b


7.526
7.504
7.260 CDCl3
7.137
7.116
7.023
7.001
6.703
6.686
6.682
5.594
5.577
5.559
5.557
5.539
5.522
5.128
5.110
5.091
5.072
5.053
3.699
3.185
3.150
2.836
2.801
2.680
2.662
2.646
2.628
2.431
2.412
2.397
2.378
2.312
2.102
1.890
1.874
1.857
1.221
1.214
1.201
1.192
1.183
1.175
0.786
0.769
0.751
OMe
2.01
2.03
2.05
2.02
1.00
1.02
3.00
1.01
1.01
0.99
0.96
3.04
3.06
2.01
4.00
3.02
f1 (ppm)

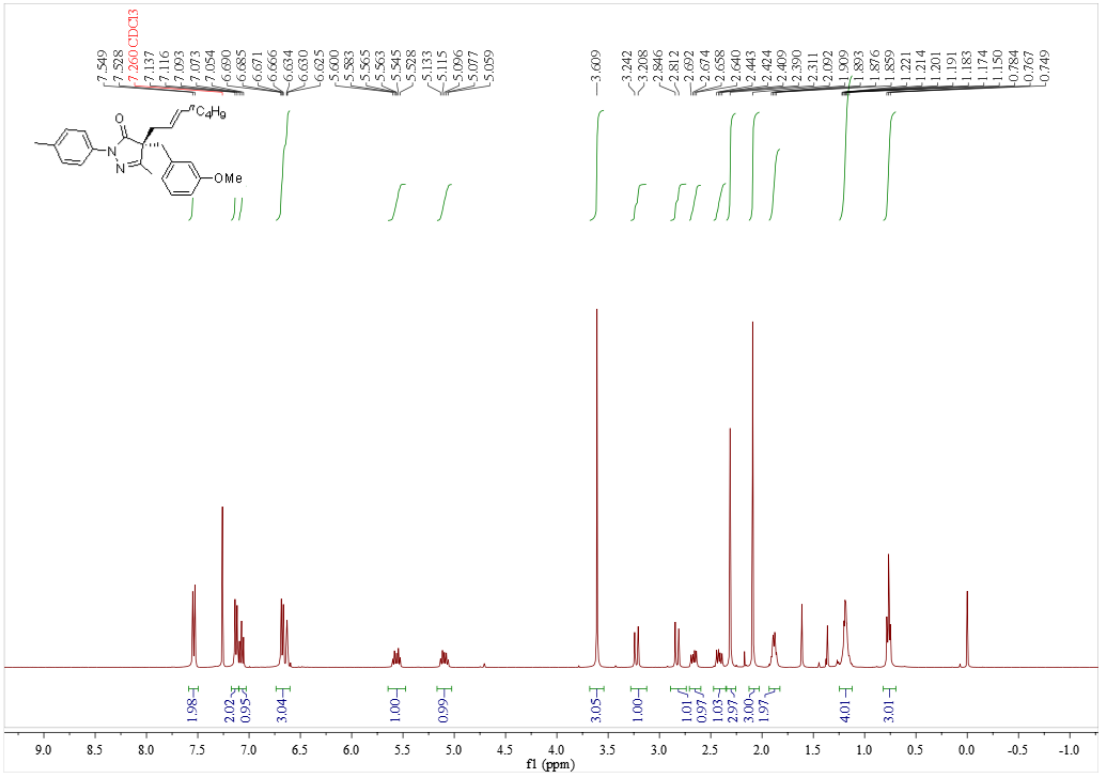

174.86
161.61
158.69
136.07
135.41
134.80
130.11
129.29
127.27
122.27
119.57
113.83
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.48
55.24
40.16
38.44
32.17
31.46
22.09
21.07
14.79
13.93
OMe
f1 (ppm)

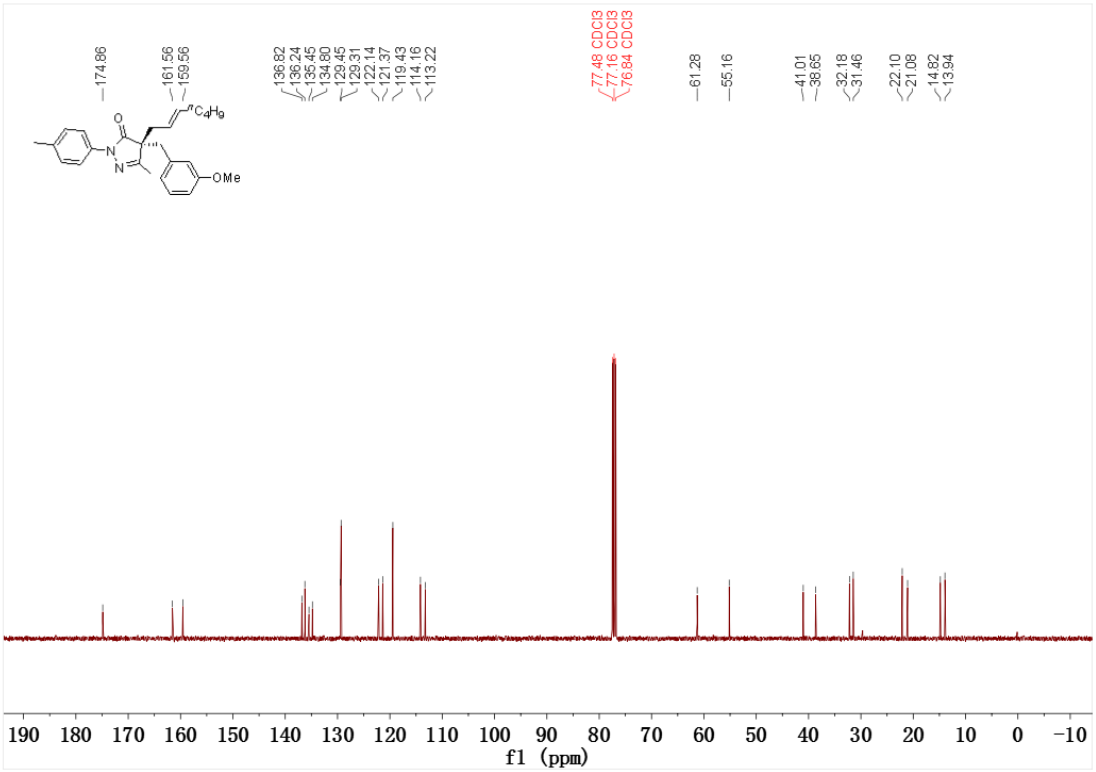
6c



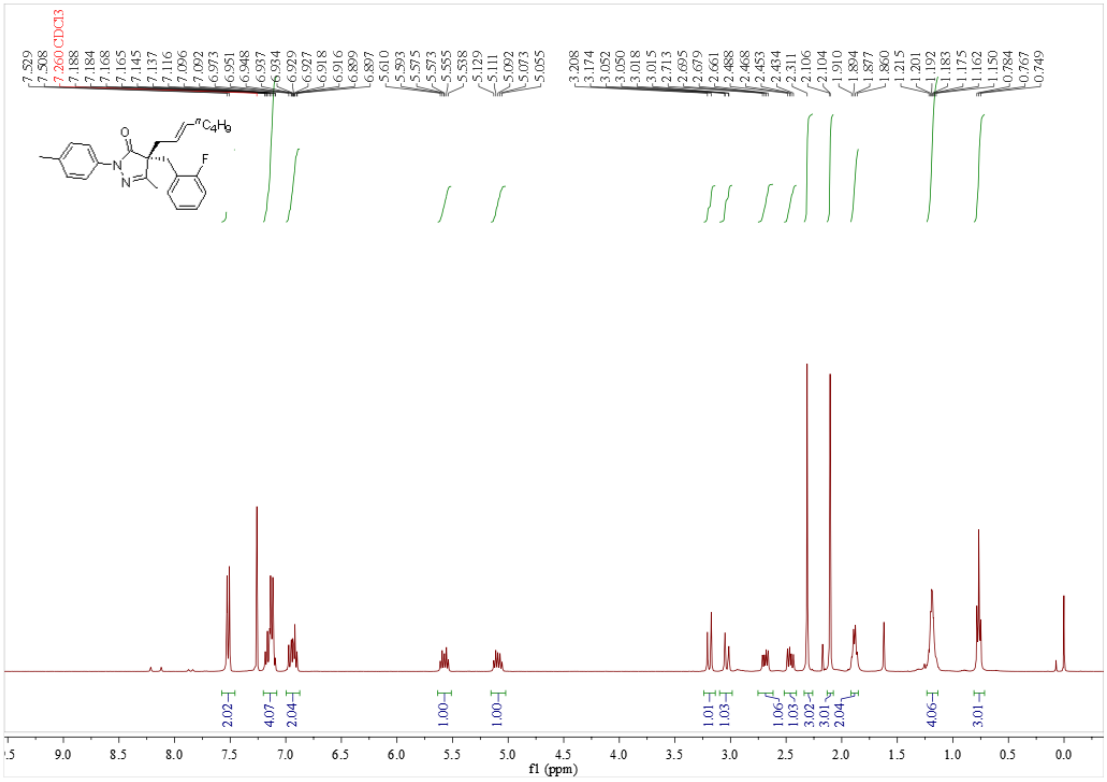


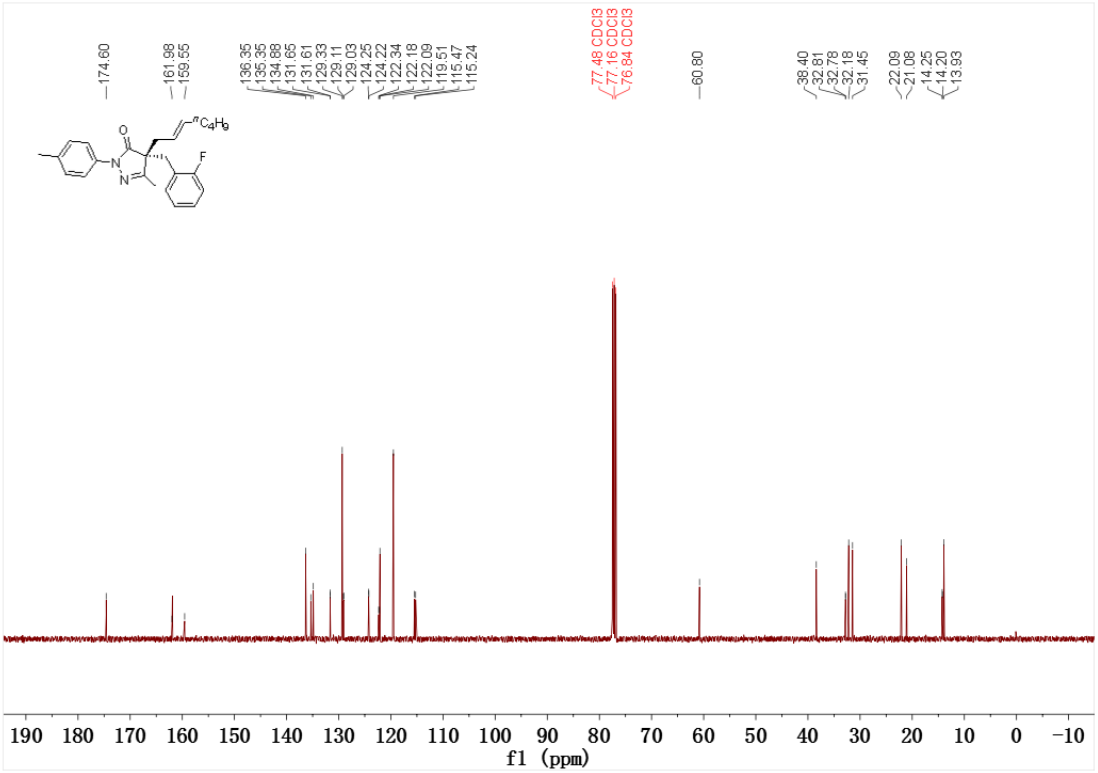
6d


7.549
7.528
7.260 CDCl3
7.137
7.116
7.093
7.073
7.054
6.690
6.685
6.671
6.666
6.634
6.630
6.625
5.600
5.383
5.565
5.563
5.545
5.528
5.133
5.115
5.096
5.077
5.059
3.609
3.242
3.208
2.846
2.812
2.692
2.674
2.658
2.640
2.443
2.424
2.409
2.390
2.311
2.092
1.909
1.893
1.876
1.859
1.221
1.214
1.201
1.191
1.183
1.174
1.150
0.784
0.767
0.749
OMe
1.98
2.02
0.95
3.04
1.00
0.99
3.05
1.00
1.01
0.97
1.03
2.97
3.00
1.97
4.01
3.01
f1 (ppm)


174.86
161.56
159.56
136.82
136.24
135.45
134.60
129.45
129.31
122.14
121.37
119.43
114.16
113.22
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.28
55.16
41.01
38.65
32.18
31.46
22.10
21.08
14.82
13.94
OMe
f1 (ppm)

6e


7.529
7.508
7.260 CDCl3
7.188
7.184
7.168
7.165
7.145
7.137
7.116
7.096
7.092
6.973
6.951
6.948
6.937
6.934
6.929
6.927
6.918
6.916
6.899
6.897
5.610
5.593
5.575
5.573
5.555
5.538
5.129
5.111
5.092
5.073
5.055
3.208
3.174
3.052
3.050
3.018
3.015
2.713
2.695
2.679
2.661
2.488
2.468
2.453
2.434
2.311
2.106
2.104
1.910
1.894
1.877
1.860
1.215
1.201
1.192
1.183
1.175
1.162
1.150
0.784
0.767
0.749
2.02
4.07
2.04
1.00
1.00
1.01
1.03
1.06
1.03
3.02
3.01
2.04
4.06
3.01
f1 (ppm)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161.98
159.55
136.36
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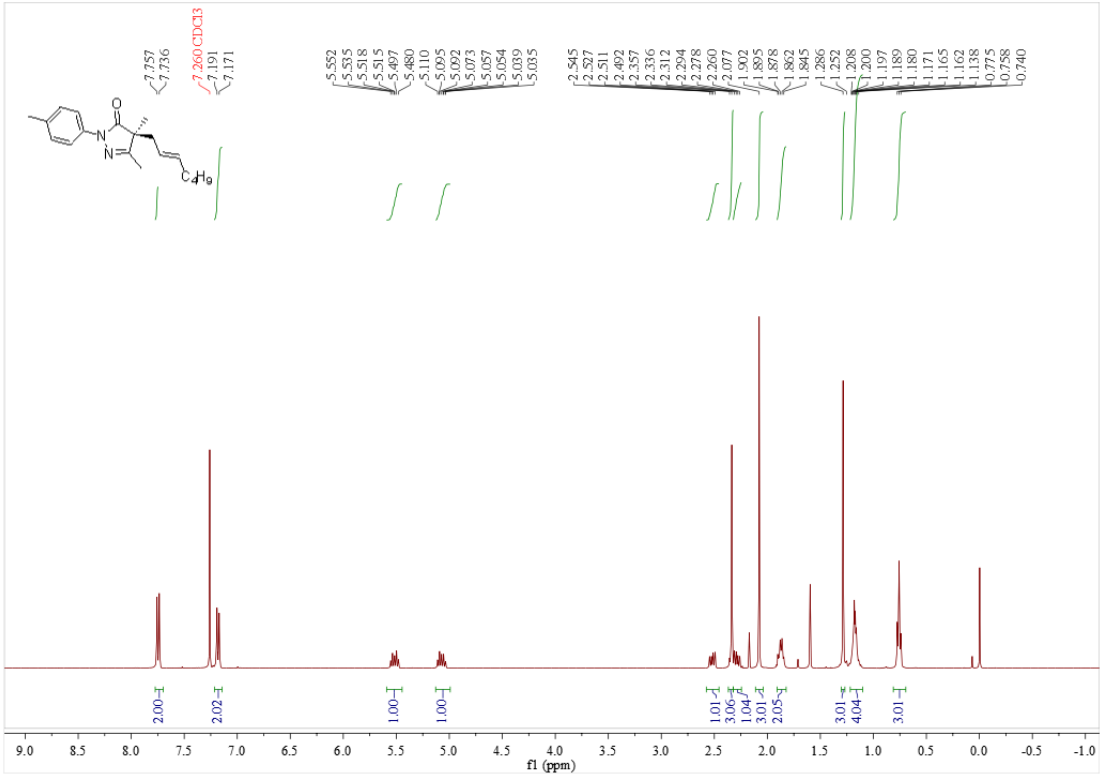
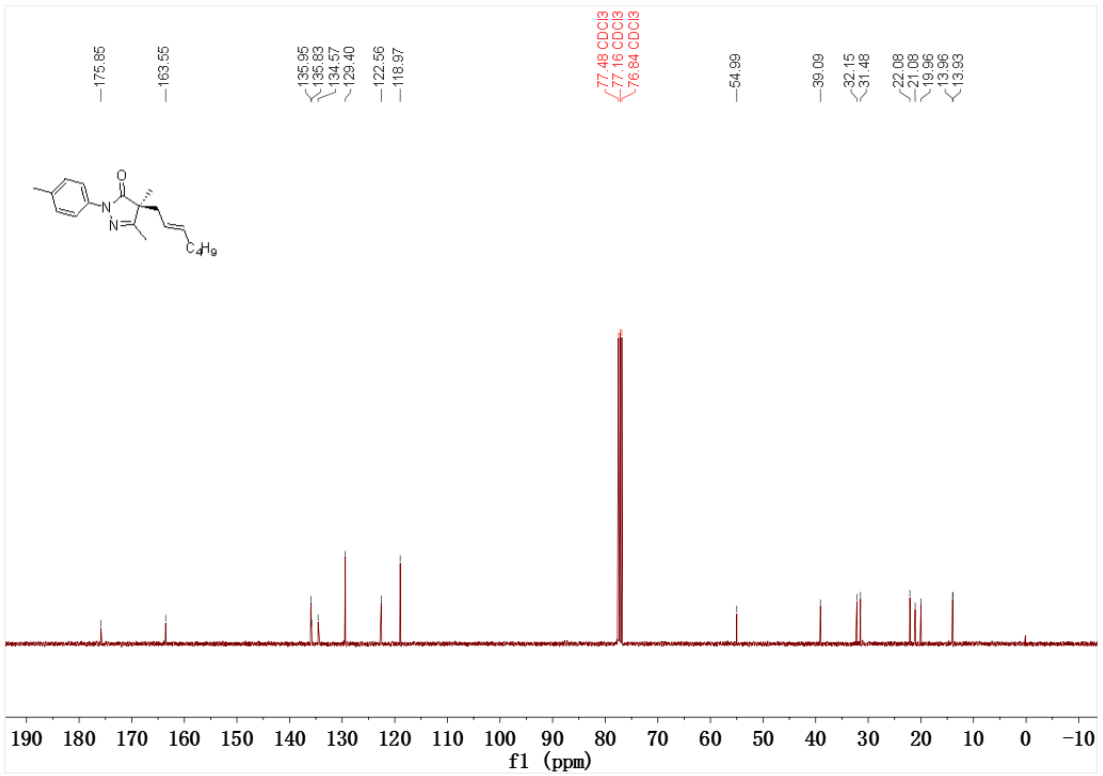
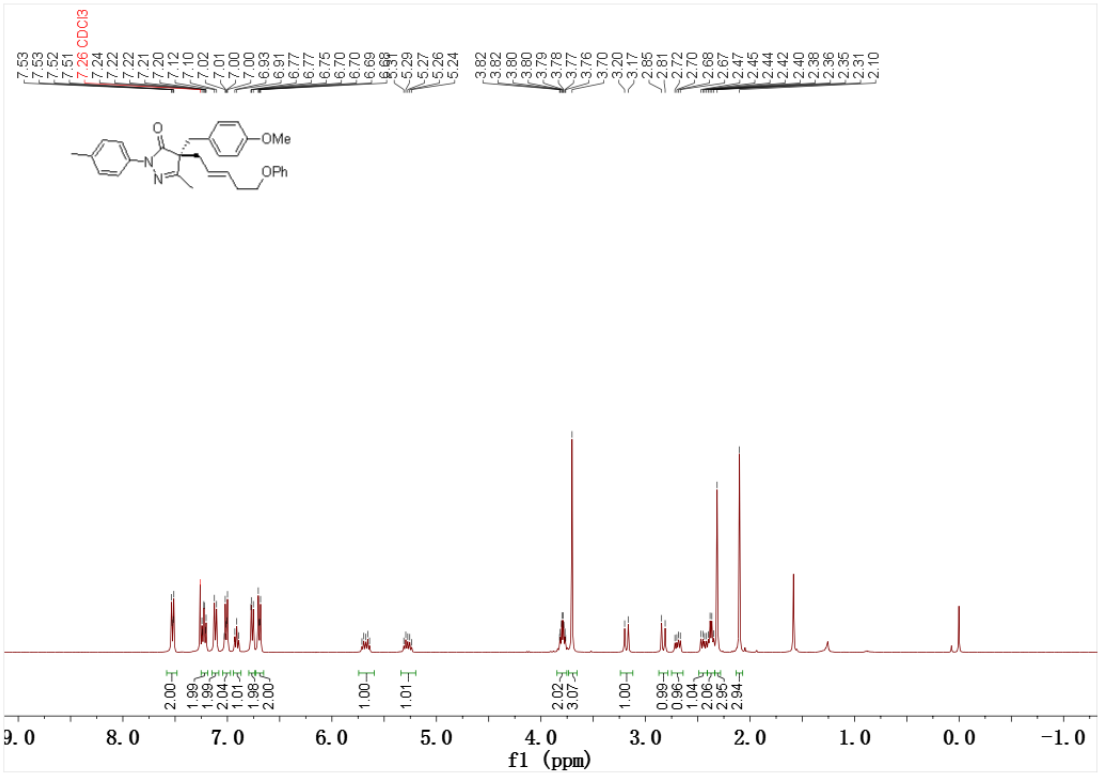
134.88
131.65
131.61
129.33
129.11
129.03
124.25
124.22
122.34
122.18
122.09
119.51
115.47
115.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
60.80
38.40
32.81
32.78
32.18
31.45
22.09
21.08
14.25
14.20
13.93
f1 (ppm)

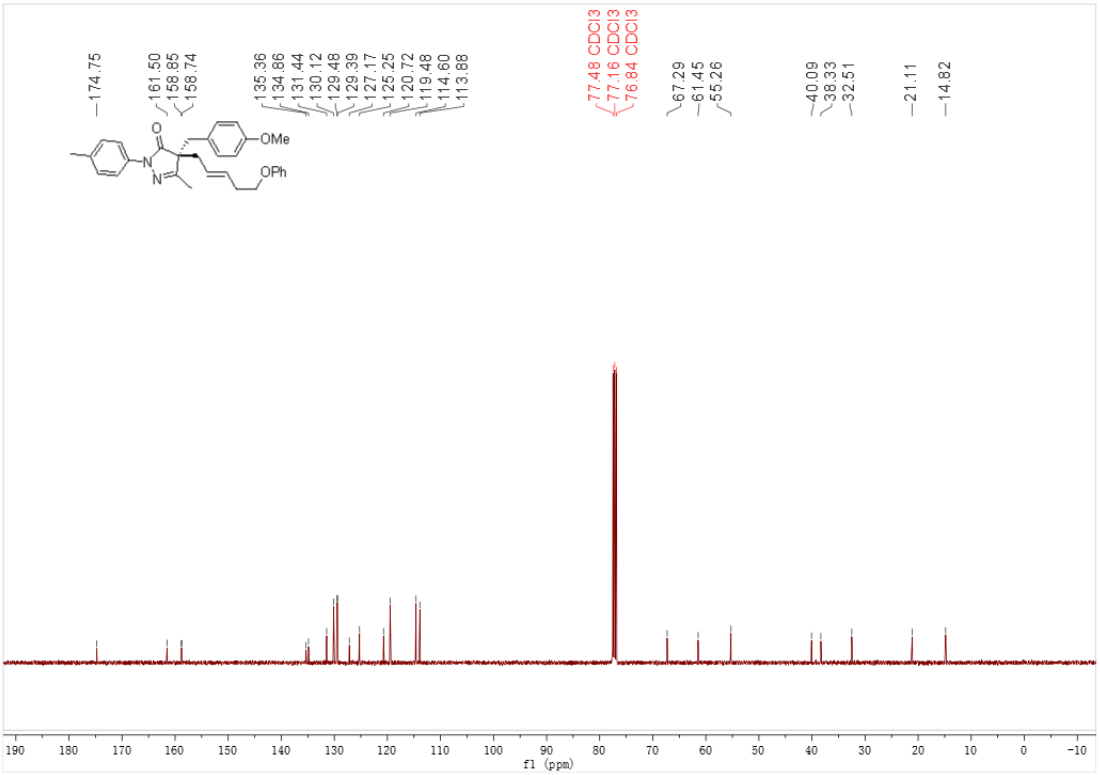
6f


7.757
7.736
7.260 CDCl3
7.191
7.171
5.552
5.535
5.518
5.515
5.497
5.480
5.110
5.095
5.092
5.073
5.057
5.054
5.039
5.035
2.545
2.527
2.511
2.492
2.357
2.336
2.312
2.294
2.278
2.260
2.077
1.902
1.895
1.878
1.862
1.845
1.286
1.252
1.208
1.200
1.197
1.189
1.180
1.171
1.165
1.162
1.138
0.775
0.758
0.740
2.00
2.02
1.00
1.00
1.01
3.06
1.04
3.01
2.05
3.01
4.04
3.01
f1 (ppm)

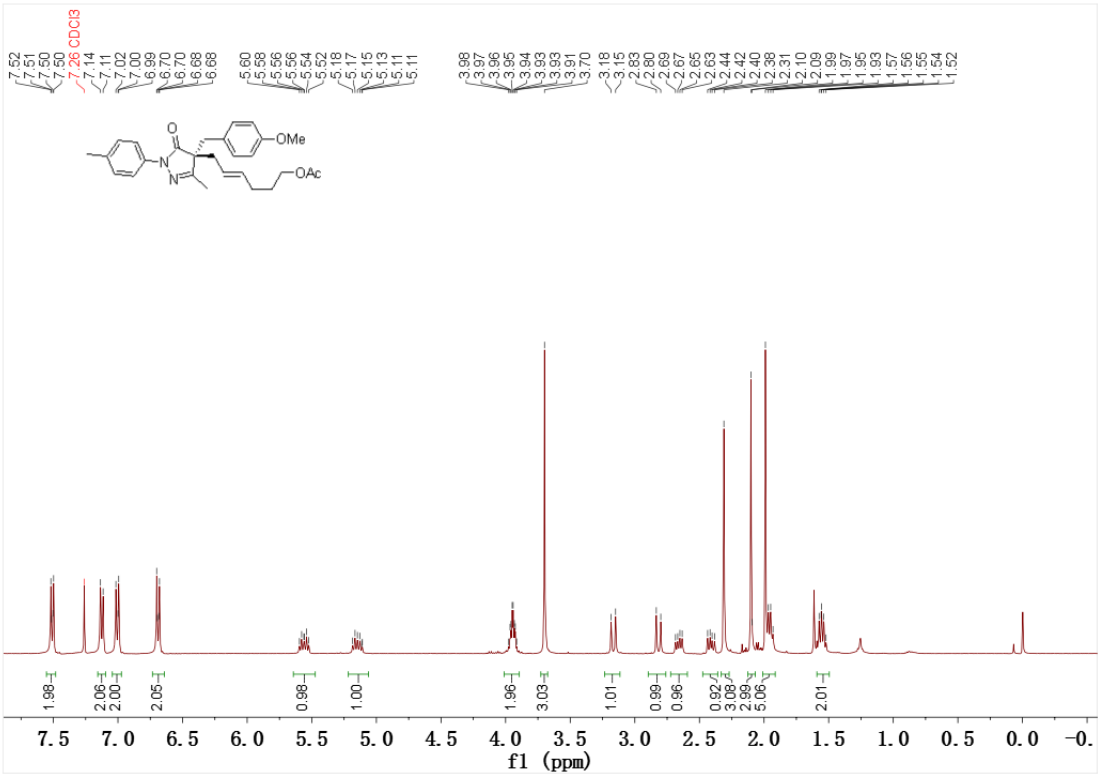

175.85
163.55
135.95
135.83
134.57
129.40
122.56
118.97
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
54.99
39.09
32.15
31.48
22.08
21.08
19.96
13.96
13.93
f1 (ppm)

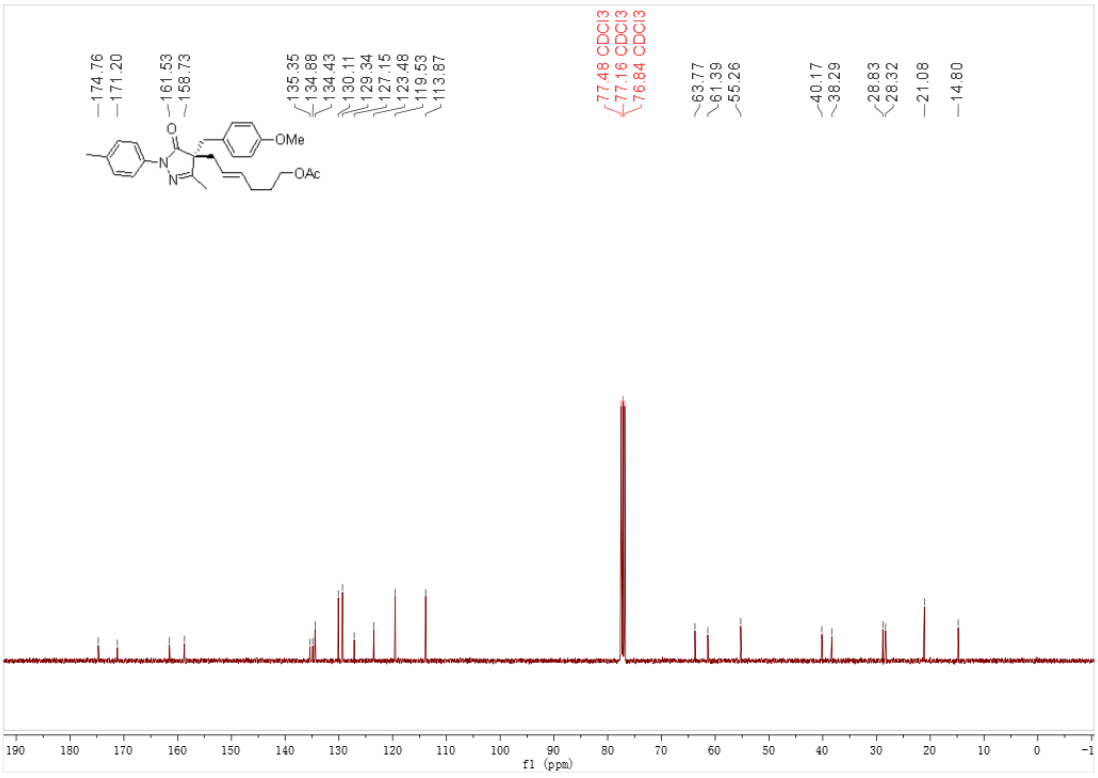
6g


7.53
7.53
7.52
7.51
7.26 CDCl3
7.24
7.22
7.21
7.20
7.12
7.10
7.02
7.01
7.00
7.00
6.93
6.91
6.77
6.77
6.75
6.70
6.70
6.69
6.68
5.31
5.29
5.27
5.26
5.24
3.82
3.82
3.80
3.80
3.79
3.78
3.77
3.76
3.70
3.20
3.17
2.85
2.81
2.72
2.70
2.68
2.67
2.47
2.45
2.44
2.42
2.40
2.38
2.36
2.35
2.31
2.10
OMe
OPh
2.00
1.99
1.99
2.04
1.01
1.98
2.00
1.00
1.01
2.02
3.07
1.00
0.99
0.96
1.04
2.06
2.95
2.94
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

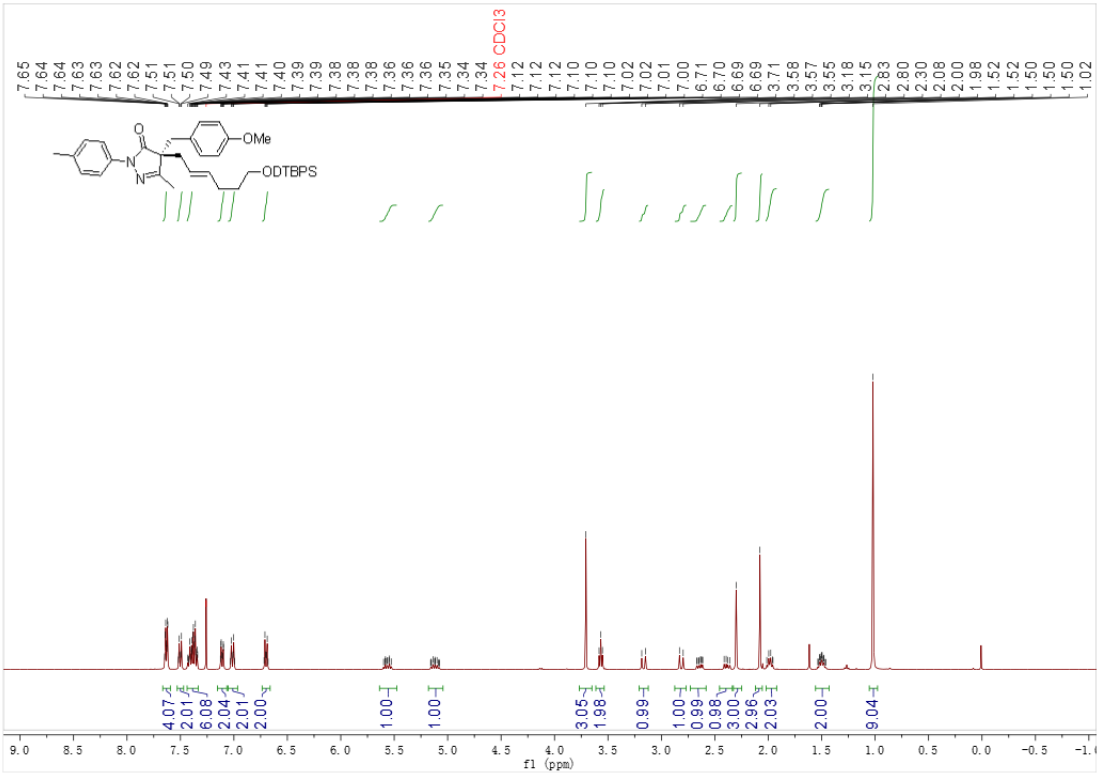

174.75
161.50
158.85
158.74
135.36
134.86
131.44
130.12
129.48
129.39
127.17
125.25
120.72
119.48
114.60
113.88
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.29
61.45
55.26
40.09
38.33
32.51
21.11
14.82
OMe
OPh
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

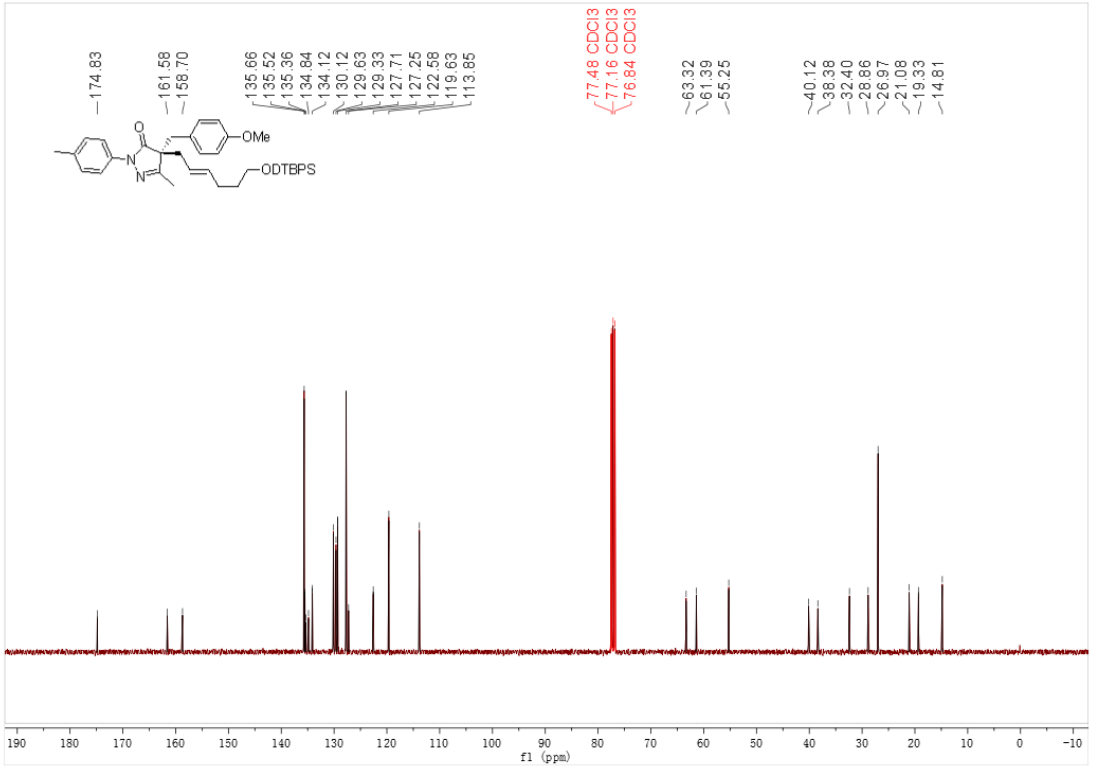
6h


7.52
7.51
7.50
7.50
7.26 CDCl3
7.14
7.11
7.02
7.00
6.99
6.70
6.70
6.68
6.68
5.60
5.58
5.56
5.56
5.54
5.52
5.18
5.17
5.15
5.13
5.11
5.11
3.98
3.97
3.96
3.95
3.94
3.93
3.93
3.91
3.70
3.18
3.15
2.83
2.80
2.69
2.67
2.65
2.63
2.44
2.42
2.40
2.38
2.31
2.10
2.09
1.99
1.97
1.95
1.93
1.57
1.56
1.55
1.54
1.52
O
N
OMe
OAc
1.98
2.06
2.00
2.05
0.98
1.00
1.96
3.03
1.01
0.99
0.96
0.92
3.08
2.99
5.06
2.01
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

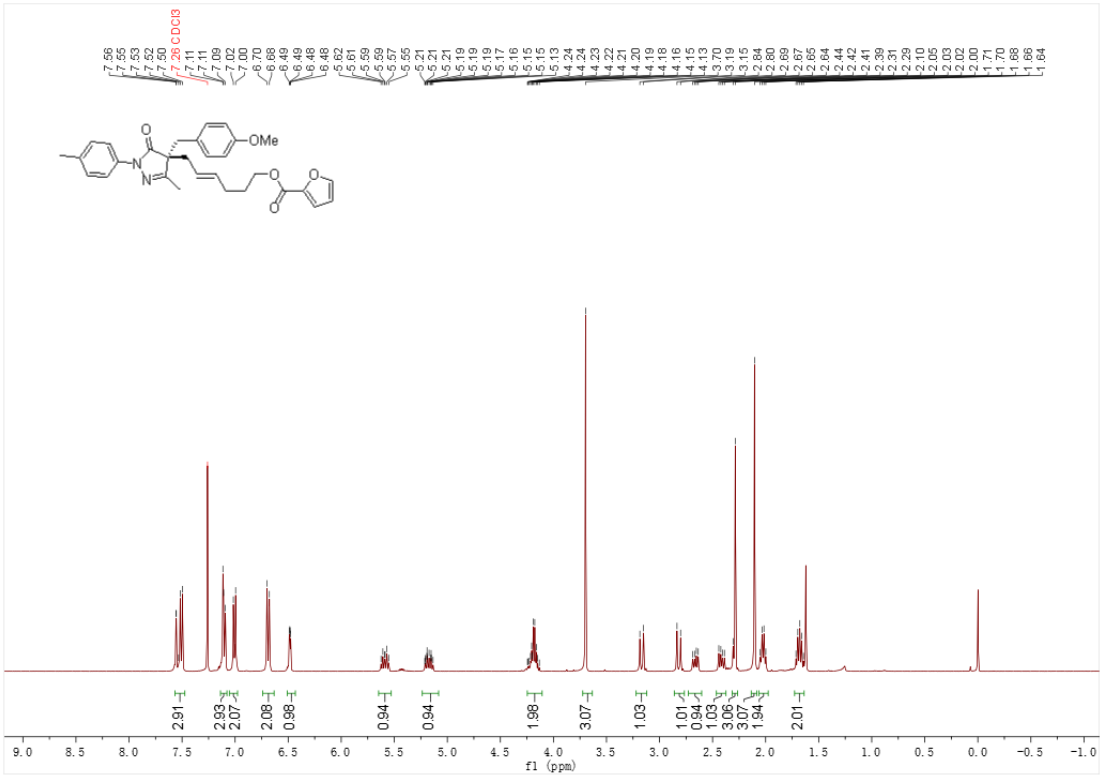

174.76
171.20
161.53
158.73
135.35
134.88
134.43
130.11
129.34
127.15
123.48
119.53
113.87
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.77
61.39
55.26
40.17
38.29
28.83
28.32
21.08
14.80
O
N
OMe
OAc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

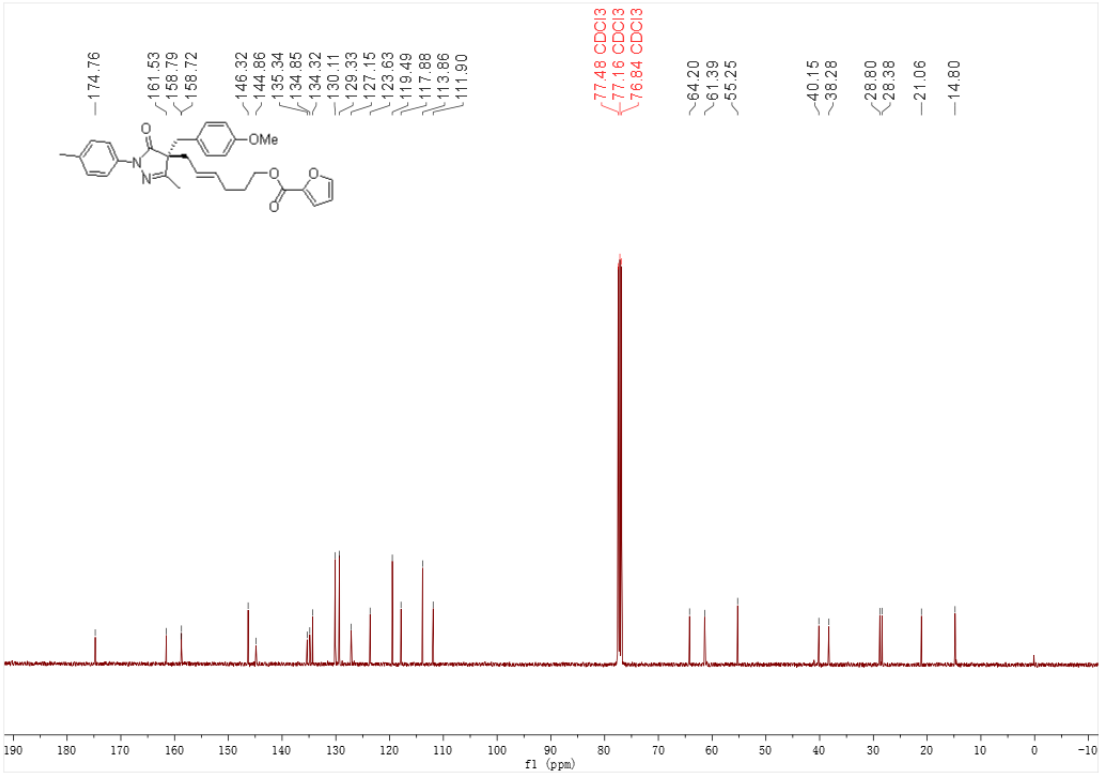
6i


7.65 7.64 7.64 7.63 7.63 7.62 7.62 7.51 7.51 7.50 7.49 7.43 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.38 7.36 7.36 7.36 7.35 7.34 7.34 7.26 CDCl3 7.12 7.12 7.12 7.10 7.10 7.02 7.02 7.01 7.00 6.71 6.70 6.69 6.69 3.71 3.58 3.57 3.55 3.18 3.15 2.83 2.80 2.30 2.08 2.00 1.98 1.52 1.52 1.50 1.50 1.50 1.02
OMe
ODTBPS
4.07 2.01 6.08 2.04 2.01 2.00 1.00 1.00 3.05 1.98 0.99 1.00 0.99 0.98 3.00 2.96 2.03 2.00 9.04
f1 (ppm)

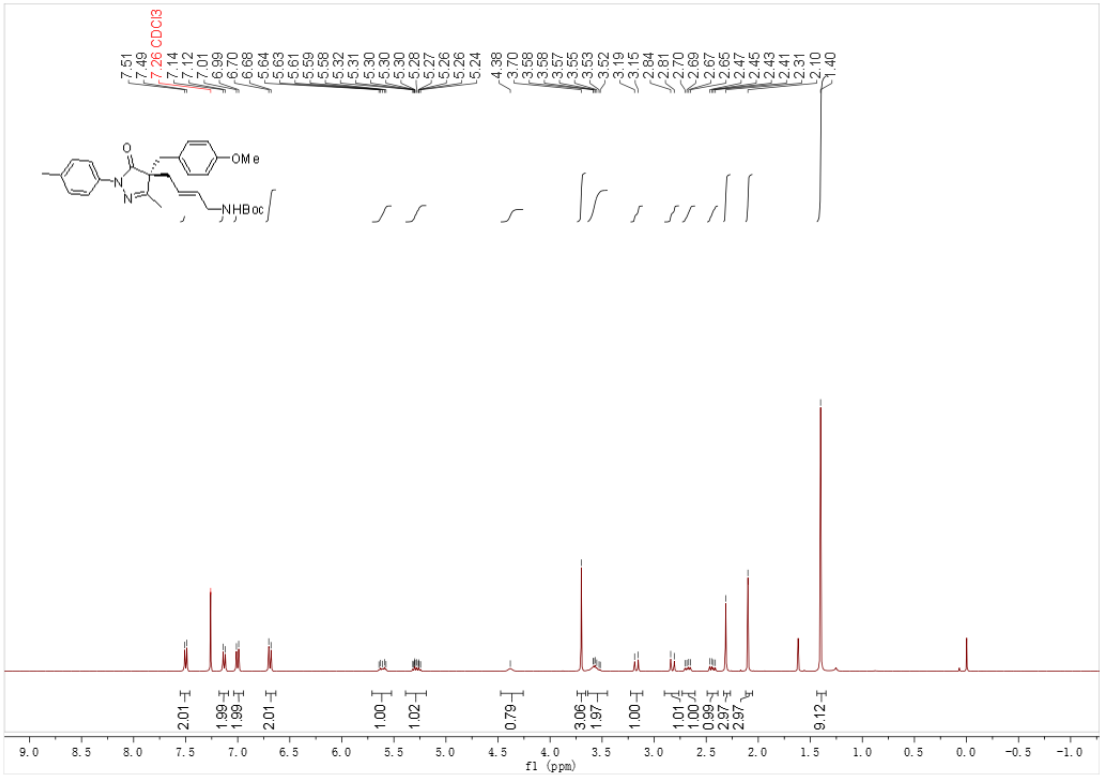

174.83 161.58 158.70 135.66 135.52 135.36 134.84 134.12 130.12 129.63 129.33 127.71 127.25 122.58 119.63 113.85
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
63.32 61.39 55.25 40.12 38.38 32.40 28.86 26.97 21.08 19.33 14.81
OMe
ODTBPS
f1 (ppm)

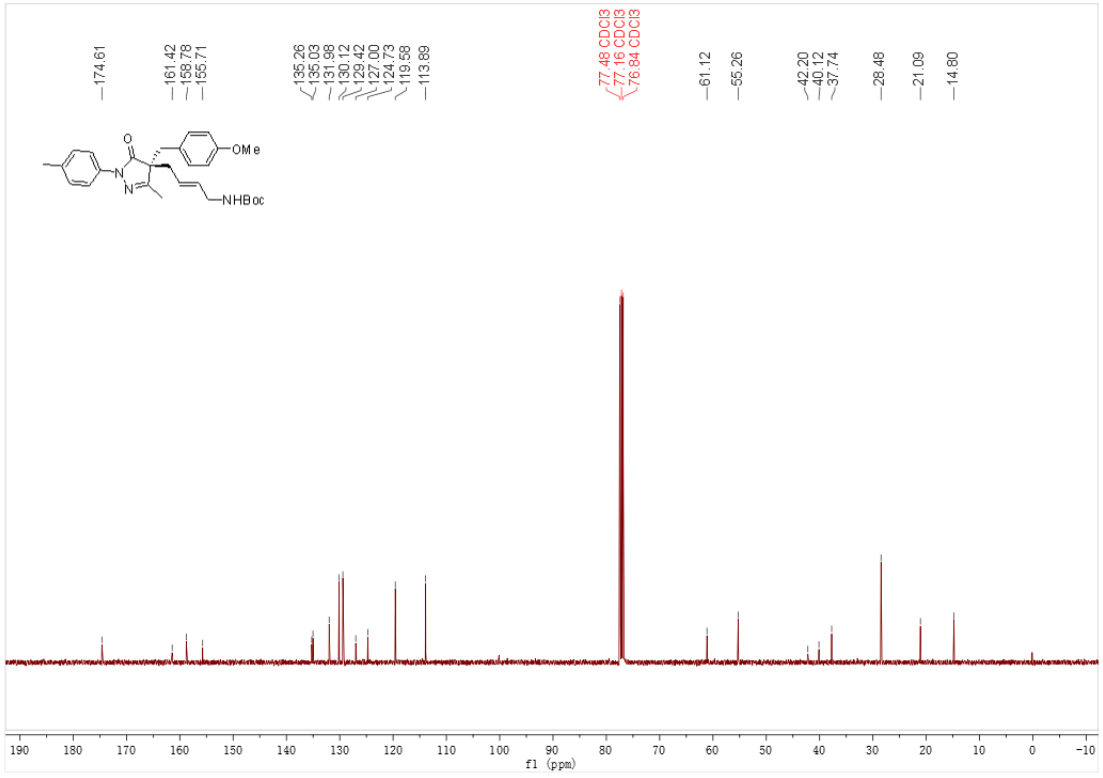
6j


7.26 CDCl3
OMe
f1 (ppm)

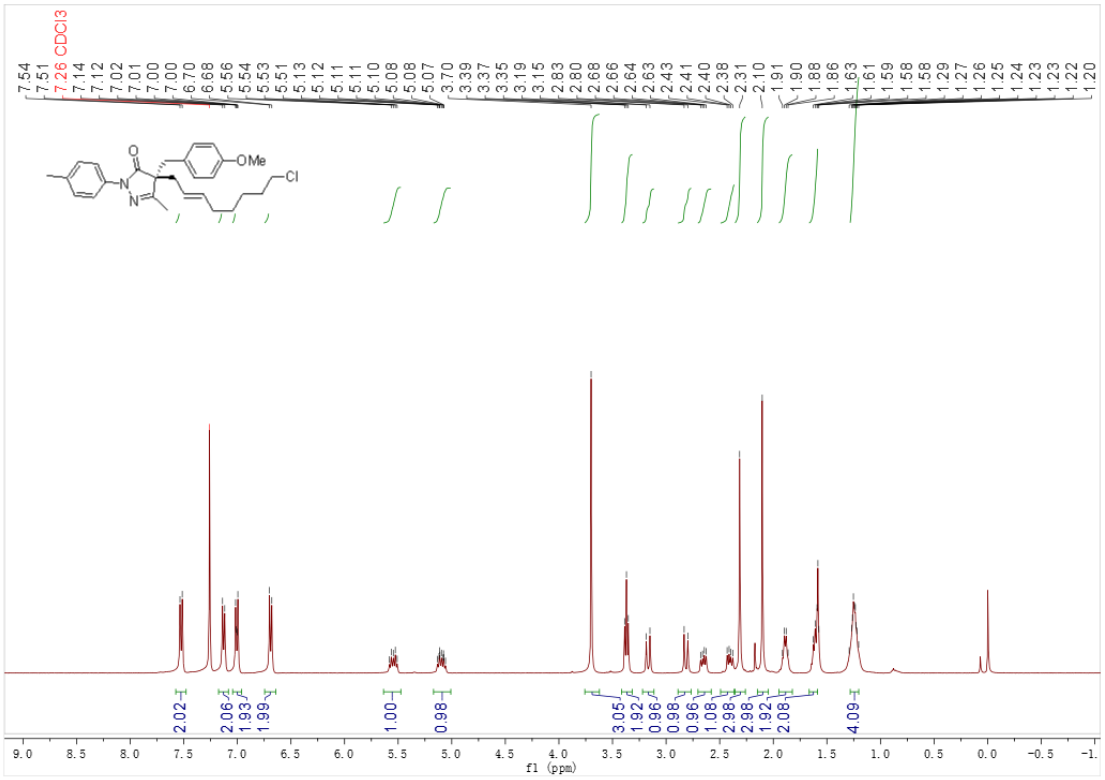

174.76
161.53
158.79
158.72
146.32
144.86
135.34
134.85
134.32
130.11
129.33
127.15
123.63
119.49
117.88
113.86
111.90
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
64.20
61.39
55.25
40.15
38.28
28.80
28.38
21.06
14.80
OMe
f1 (ppm)

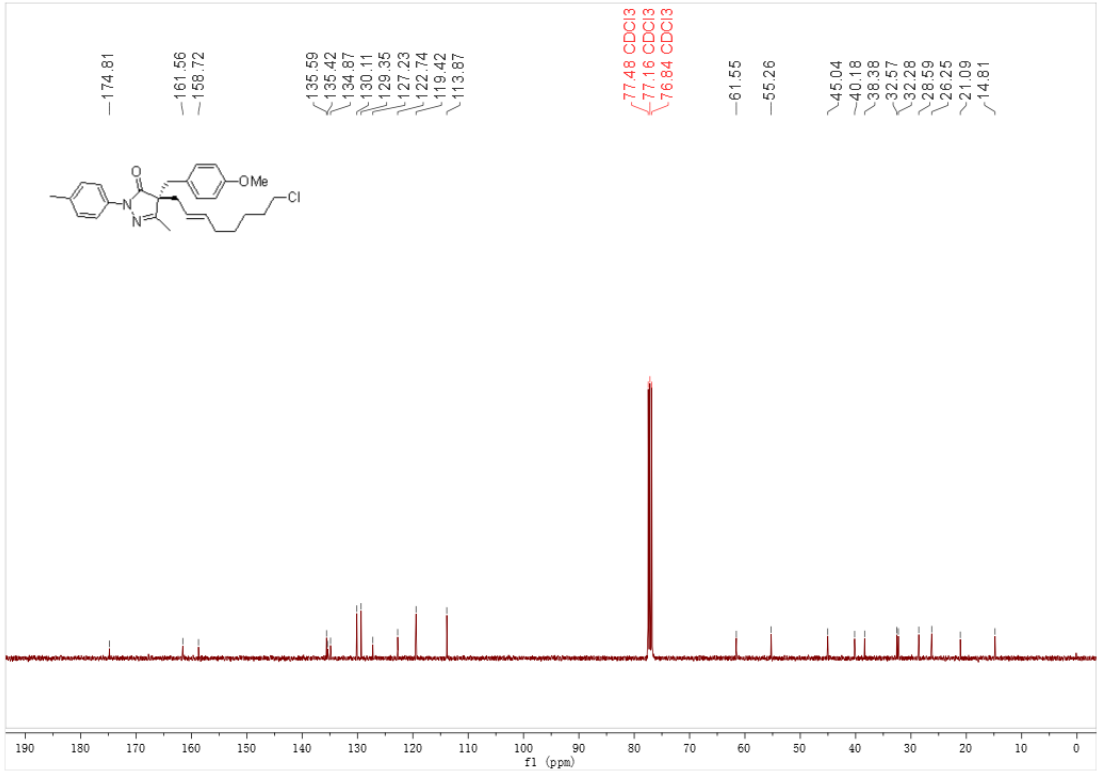
6k


7.51
7.49
7.26 CDCl3
7.14
7.12
7.01
6.99
6.70
6.68
5.64
5.63
5.61
5.59
5.58
5.32
5.31
5.30
5.30
5.30
5.28
5.27
5.26
5.26
5.24
4.38
3.70
3.58
3.58
3.57
3.55
3.53
3.52
3.19
3.15
2.84
2.81
2.70
2.69
2.67
2.65
2.47
2.45
2.43
2.41
2.31
2.10
1.40
OMe
NHBoc
2.01
1.99
1.99
2.01
1.00
1.02
0.79
3.06
1.97
1.00
1.01
1.00
0.99
2.97
2.97
9.12
f1 (ppm)

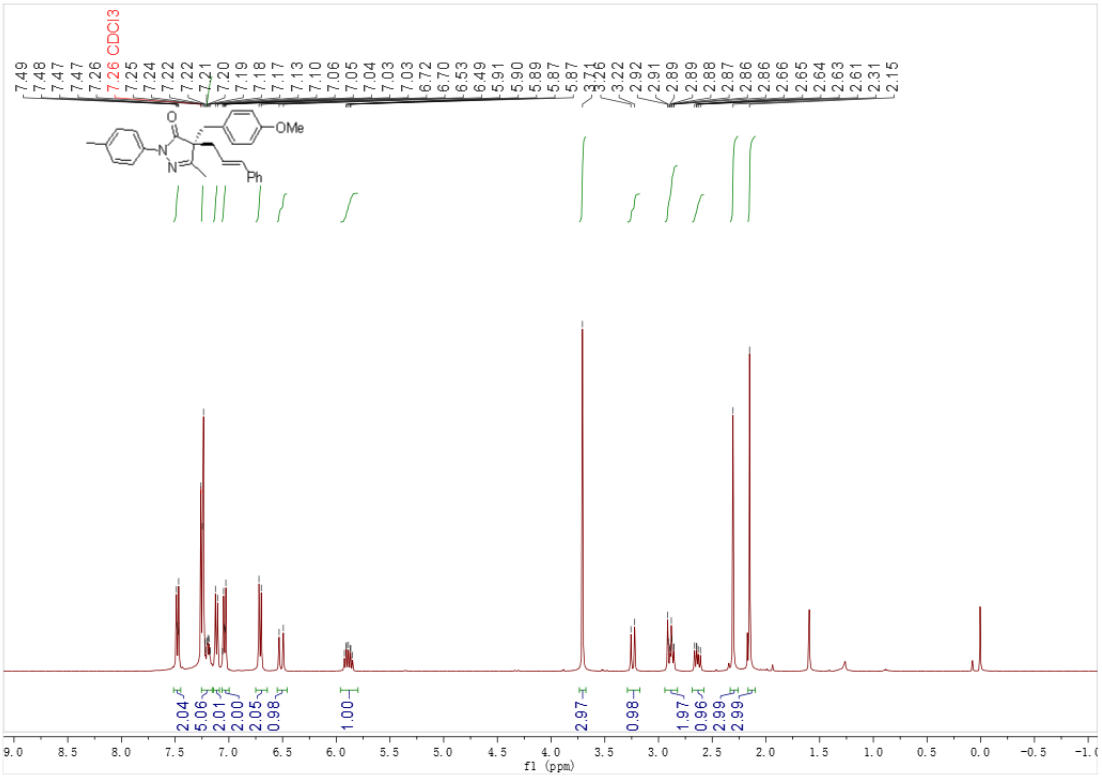

174.61
161.42
158.78
155.71
135.26
135.03
131.98
130.12
129.42
127.00
124.73
119.58
113.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.12
55.26
42.20
40.12
37.74
28.48
21.09
14.80
OMe
NHBoc
f1 (ppm)

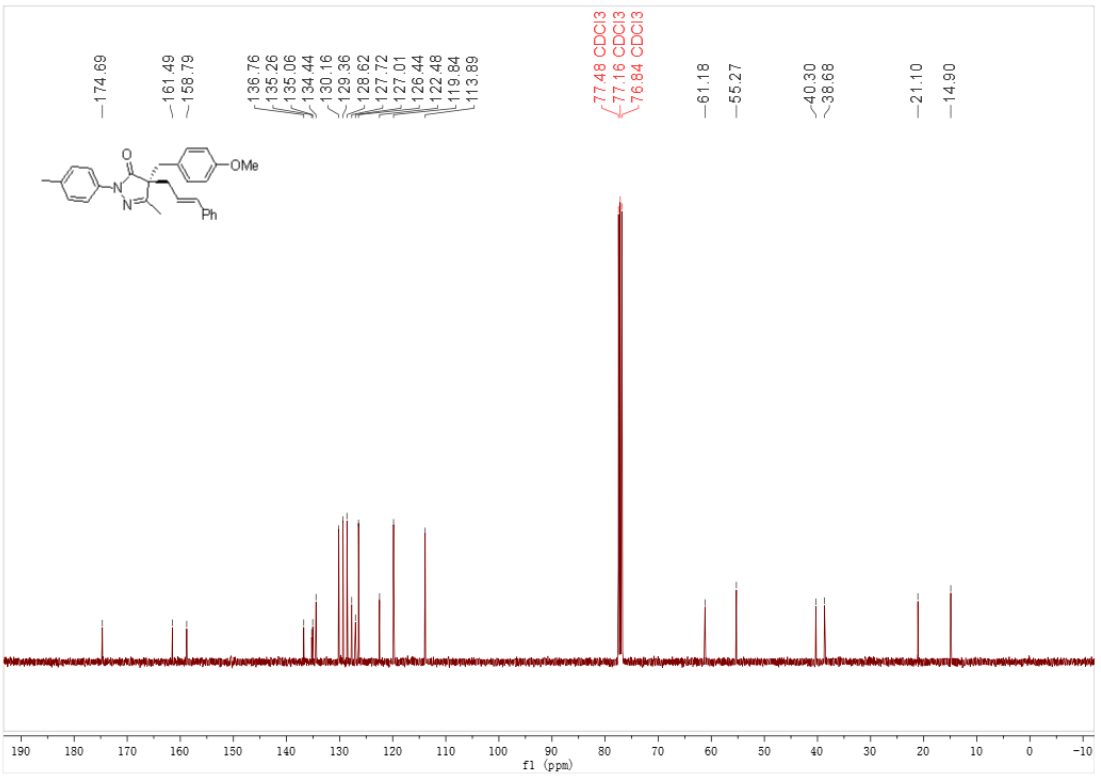
6l


7.54
7.51
7.26 CDCl3
7.14
7.12
7.02
7.01
7.00
7.00
6.70
6.68
5.56
5.54
5.53
5.51
5.13
5.12
5.11
5.11
5.10
5.08
5.08
5.07
3.70
3.39
3.37
3.35
3.19
3.15
2.83
2.80
2.68
2.66
2.64
2.63
2.43
2.41
2.40
2.38
2.31
2.10
1.91
1.90
1.88
1.86
1.63
1.61
1.59
1.58
1.58
1.29
1.27
1.26
1.25
1.24
1.23
1.23
1.22
1.20
OMe
Cl
2.02
2.06
1.93
1.99
1.00
0.98
3.05
1.92
0.96
0.98
0.96
1.08
2.98
2.98
1.92
2.08
4.09
f1 (ppm)


174.81
161.56
158.72
135.59
135.42
134.87
130.11
129.35
127.23
122.74
119.42
113.87
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.55
55.26
45.04
40.18
38.38
32.57
32.28
28.59
26.25
21.09
14.81
OMe
Cl
f1 (ppm)

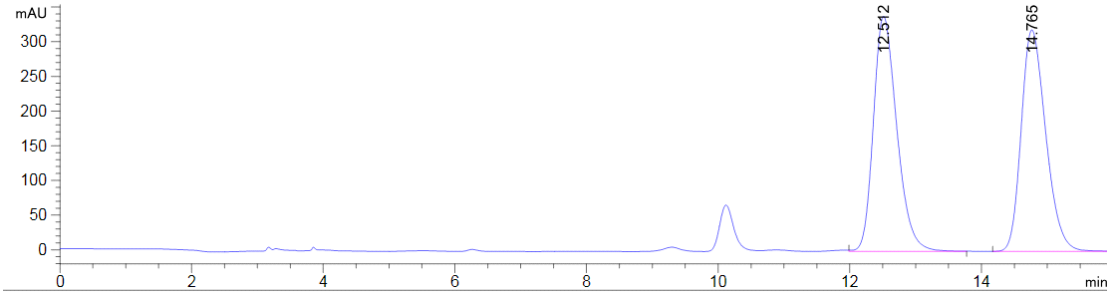
6m


7.49
7.48
7.47
7.47
7.26
7.26 CDCl3
7.25
7.24
7.22
7.22
7.21
7.20
7.19
7.18
7.17
7.13
7.10
7.06
7.05
7.04
7.03
7.03
6.72
6.70
6.53
6.49
5.91
5.90
5.89
5.87
5.87
3.71
3.26
3.22
2.92
2.91
2.89
2.89
2.88
2.87
2.86
2.86
2.66
2.65
2.64
2.63
2.61
2.31
2.15
OMe
Ph
2.04
5.06
2.01
2.00
2.05
0.98
1.00
2.97
0.98
1.97
0.96
2.99
2.99
f1 (ppm)

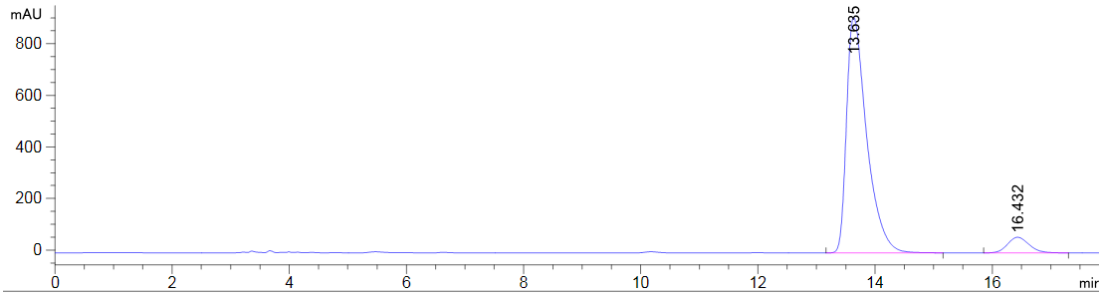

174.69
161.49
158.79
136.76
135.26
135.06
134.44
130.16
129.36
128.62
127.72
127.01
126.44
122.48
119.84
113.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.18
55.27
40.30
38.68
21.10
14.90
OMe
Ph
f1 (ppm)

HLPC

6a

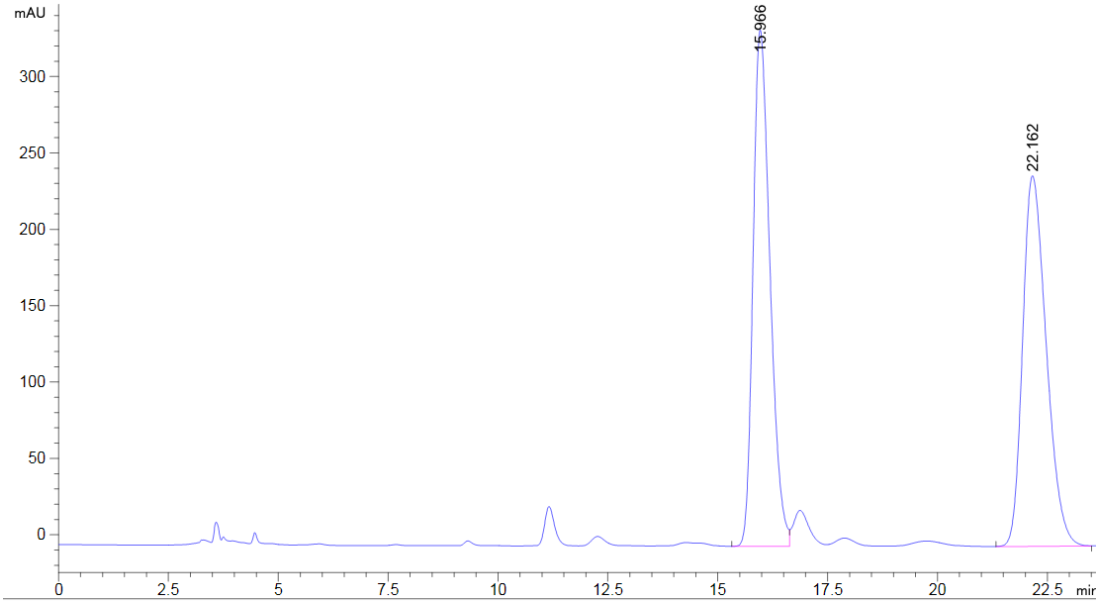


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.512	VB	0.3812	8381.63574	338.87540	50.3114
2	14.765	BBA	0.4026	8277.88672	319.17651	49.6886

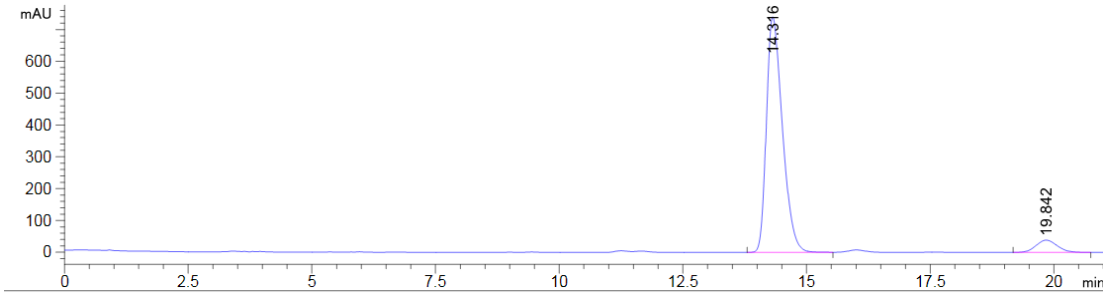


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.635	BB	0.3626	2.18324e4	913.78308	93.3440
2	16.432	BB	0.3952	1556.78015	60.92033	6.6560

6b

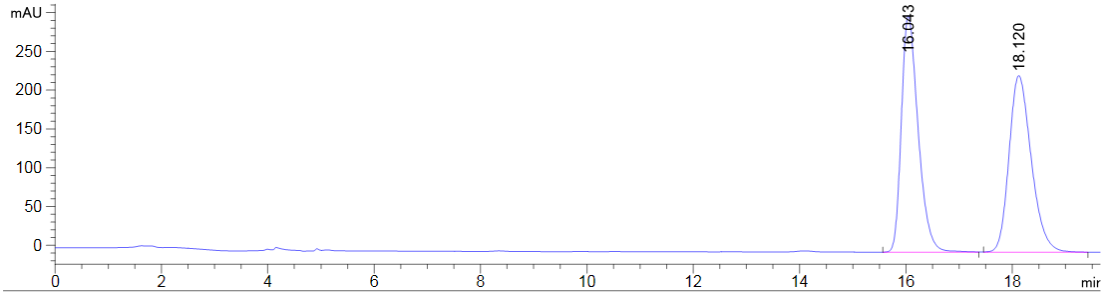


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.966	VV	0.4114	9062.98242	338.00037	49.9564
2	22.162	BB	0.5808	9078.79199	242.56079	50.0436

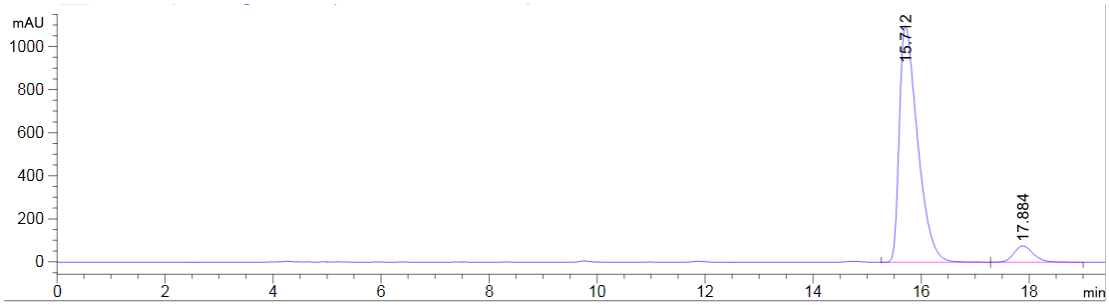


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.316	BB	0.3431	1.66399e4	740.33649	93.4342
2	19.842	BB	0.4741	1169.31226	38.58825	6.5658

6c

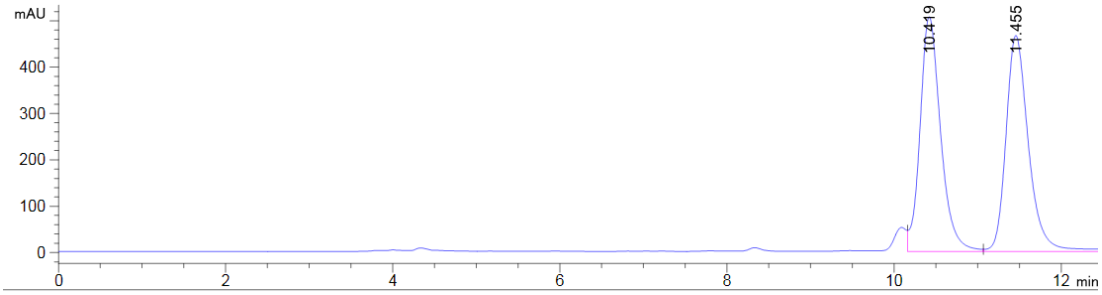


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.043	BB	0.3340	6690.11133	304.82538	50.2061
2	18.120	BB	0.4487	6635.17627	227.74876	49.7939

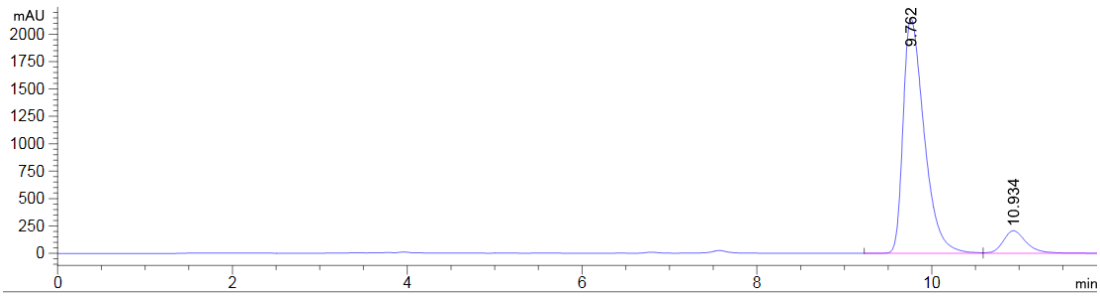


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.712	VV	0.3563	2.57975e4	1098.66211	93.0985
2	17.884	VB	0.3916	1912.40002	75.75890	6.9015

6d

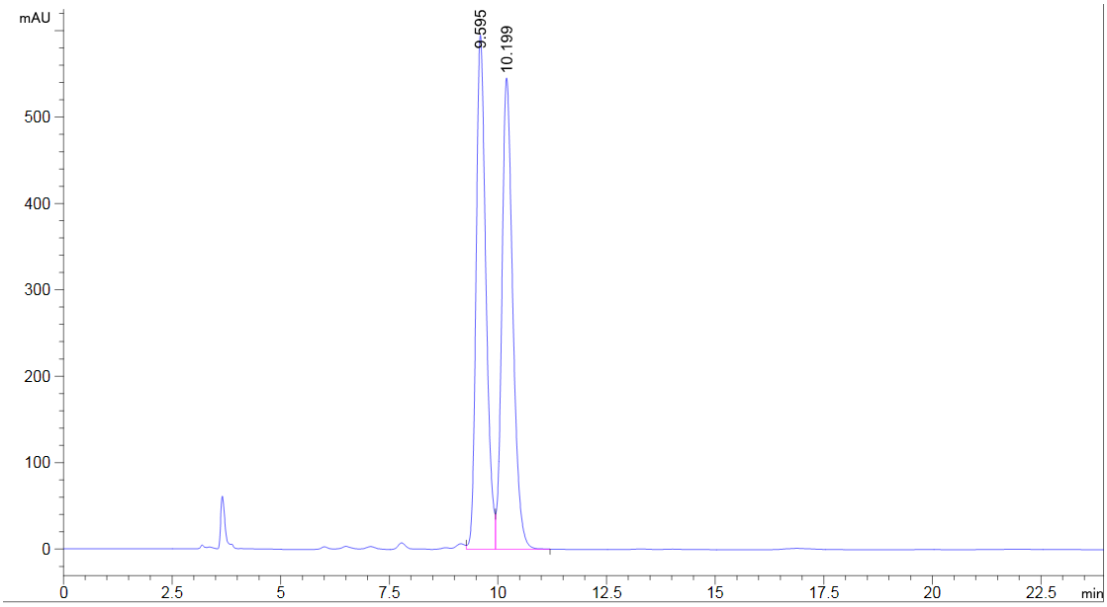


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.419	VV	0.2595	8648.52344	506.46478	49.7829
2	11.455	VBA	0.2845	8723.95117	466.13577	50.2171

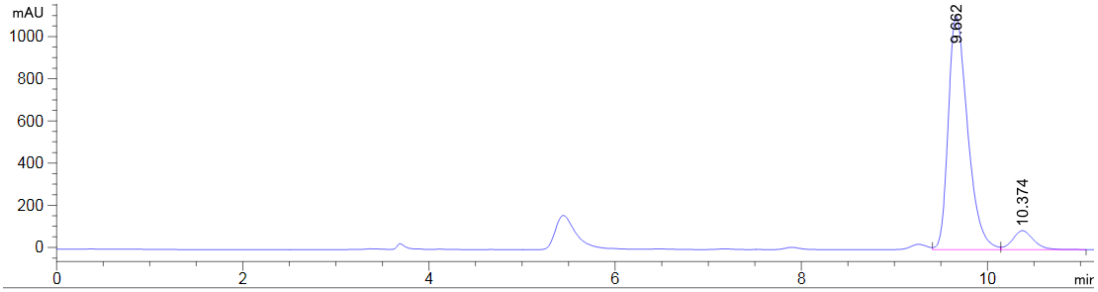


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.762	VV	0.2555	3.58048e4	2139.86255	90.4470
2	10.934	VBA	0.2795	3781.69751	205.41942	9.5530

6e

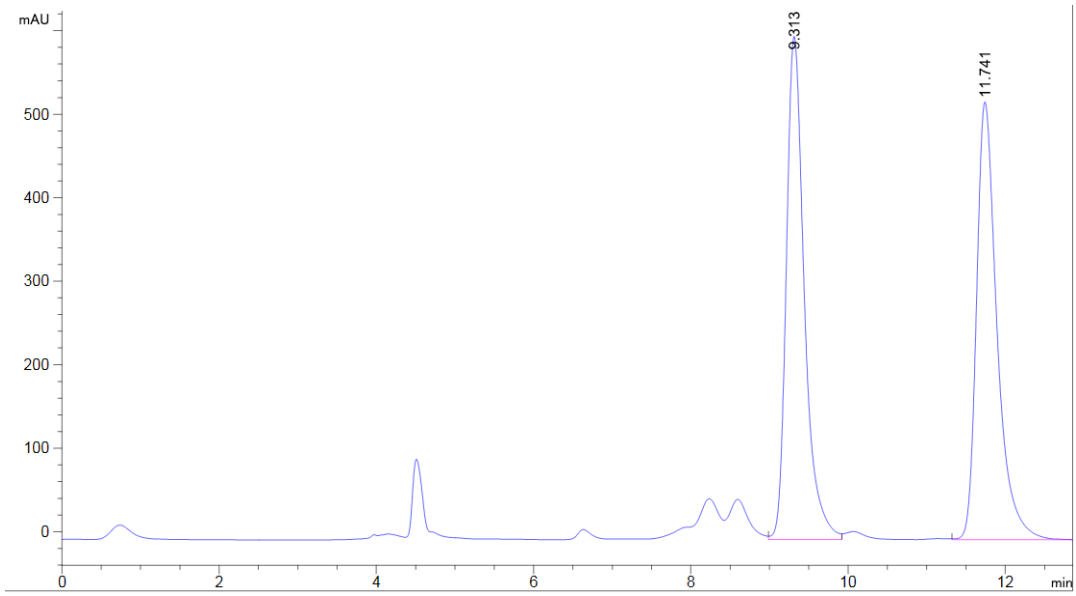


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.595	VV	0.2408	9363.39844	595.35602	49.4330
2	10.199	VB	0.2681	9578.18750	545.57678	50.5670

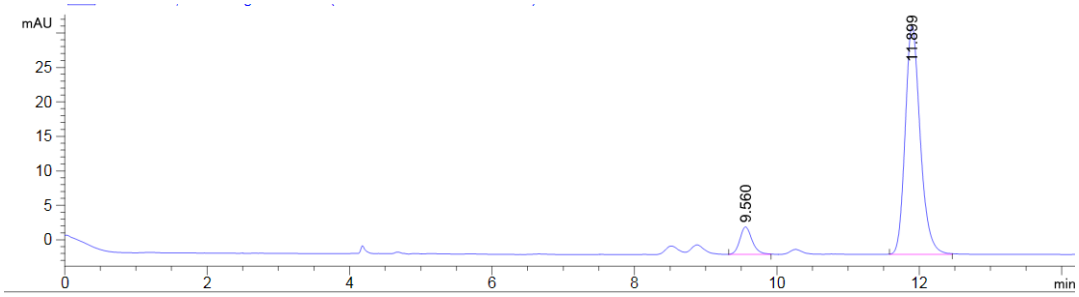


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.662	VV	0.2201	1.60407e4	1109.69275	91.9257
2	10.374	VB	0.2388	1408.92786	89.85838	8.0743

6f

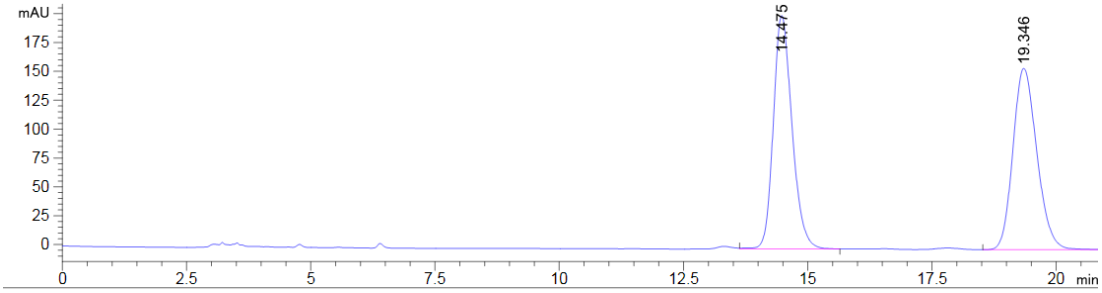


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.313	VV	0.2417	9600.73828	602.87439	50.2625
2	11.741	VBA	0.2731	9500.45605	524.38593	49.7375

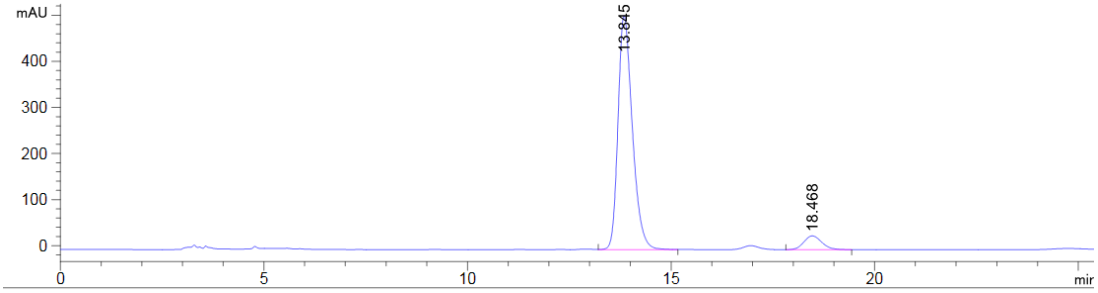


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.560	BB	0.1832	48.20747	4.00195	9.0355
2	11.899	BB	0.2255	485.32861	33.09159	90.9645

6g

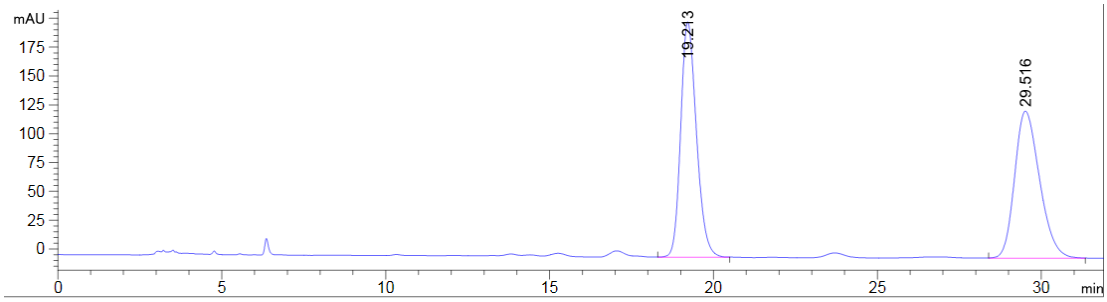


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.475	VB	0.4034	5311.08643	202.24413	50.2395
2	19.346	VBA	0.5187	5260.44092	157.07161	49.7605

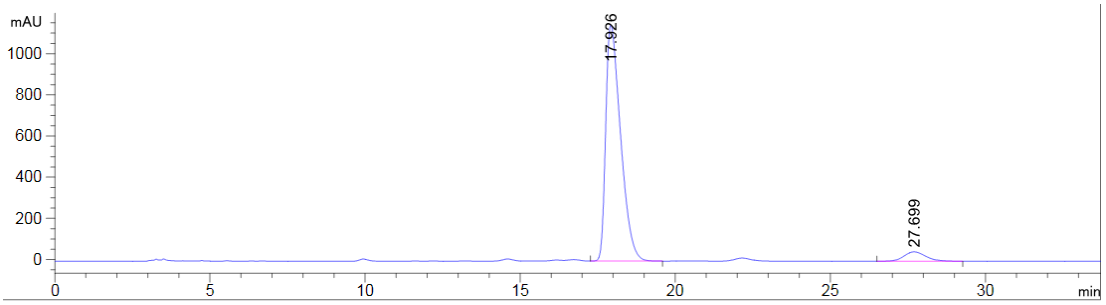


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.845	VB	0.3733	1.24054e4	507.76108	92.9943
2	18.468	BB	0.4749	934.55768	30.27428	7.0057

6h

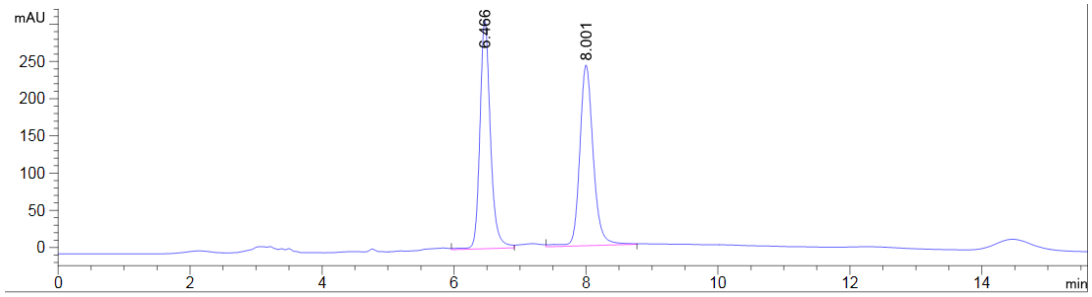


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.213	BB	0.5154	6802.65967	204.04944	50.2129
2	29.516	BB	0.8158	6744.98584	127.47701	49.7871

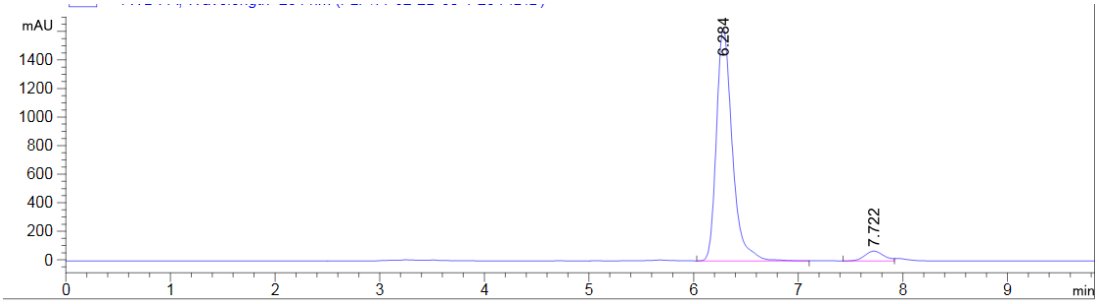


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.926	VB	0.5071	3.81911e4	1148.32312	94.3375
2	27.699	BB	0.7605	2292.38037	46.37625	5.6625

6i

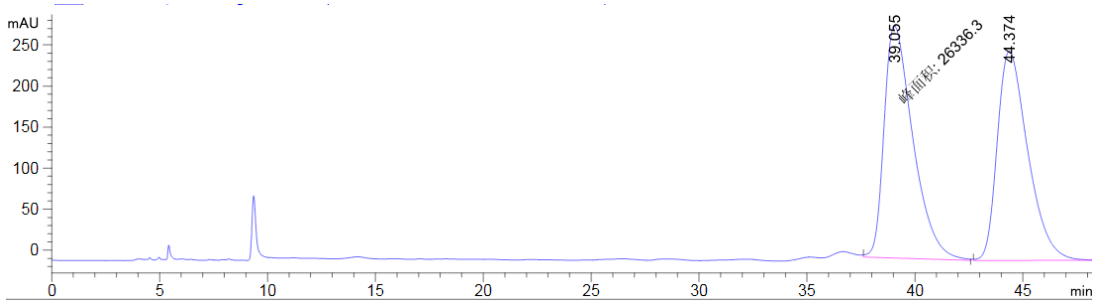


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.466	VV	0.1693	3402.89087	306.38257	49.7013
2	8.001	VB	0.2171	3443.79395	242.59251	50.2987

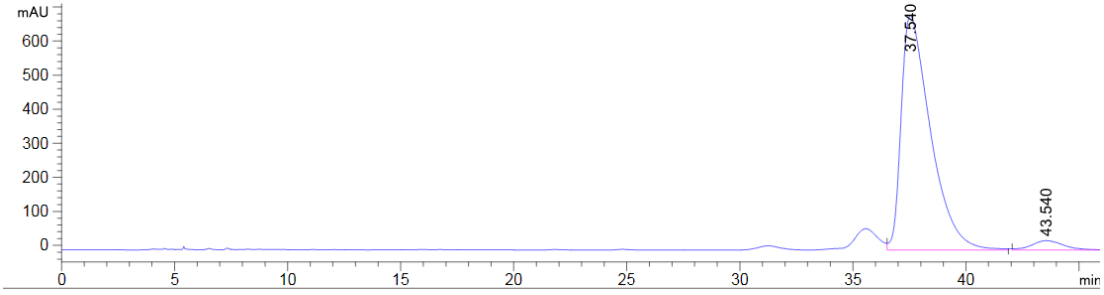


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.284	VV	0.1601	1.72356e4	1629.77844	95.0694
2	7.722	VV	0.1972	893.88660	69.46568	4.9306

6j

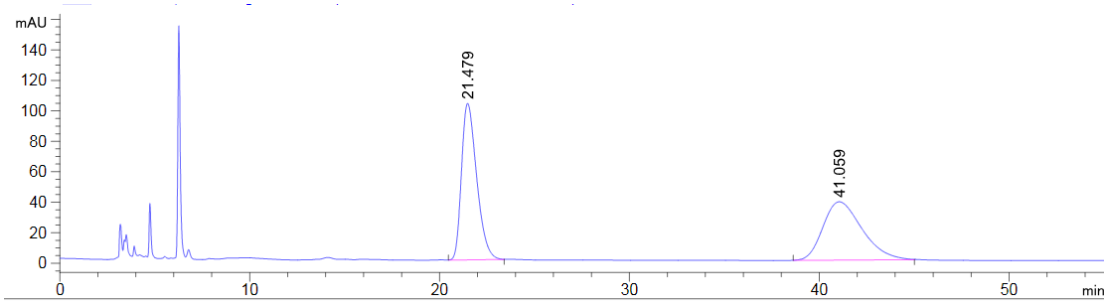


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.055	MM	1.5542	2.63363e4	282.42560	51.2272
2	44.374	BBA	1.4924	2.50745e4	255.07921	48.7728

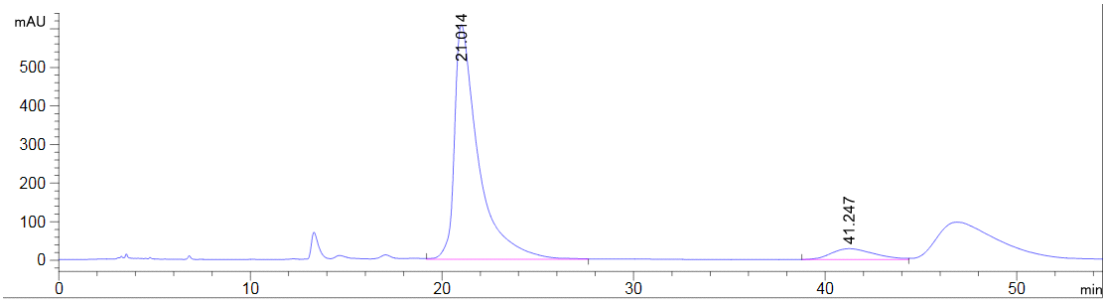


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.540	VB	1.3358	6.21904e4	689.70081	95.7455
2	43.540	BBA	1.4142	2763.43555	27.83394	4.2545

6k

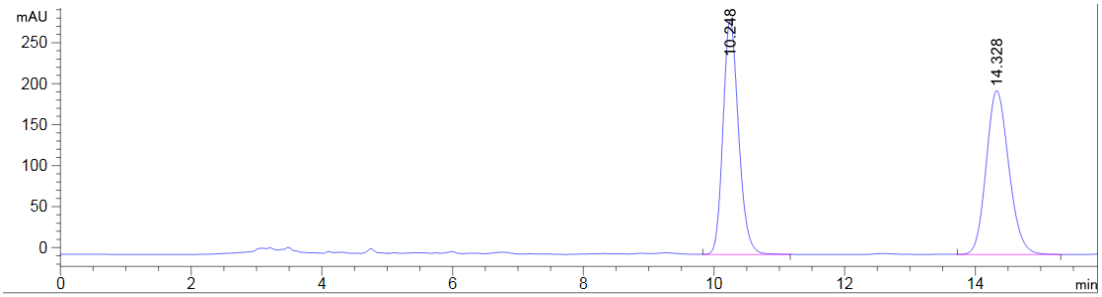


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.479	BB	0.8553	5704.35107	102.71274	50.9771
2	41.059	BB	2.1457	5485.67773	38.30735	49.0229

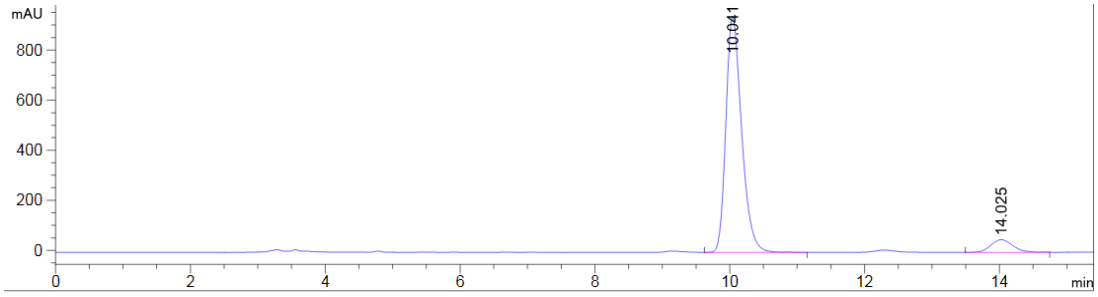


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.014	VB	1.2404	5.24241e4	607.63489	92.4116
2	41.247	BV	2.1230	4304.84033	27.93321	7.5884

6l

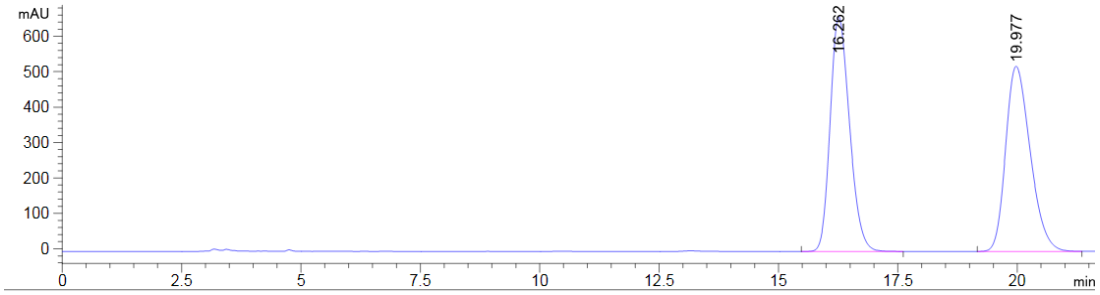


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.248	VB	0.2546	4733.66846	286.35538	49.5394
2	14.328	VB	0.3740	4821.69189	199.91748	50.4606

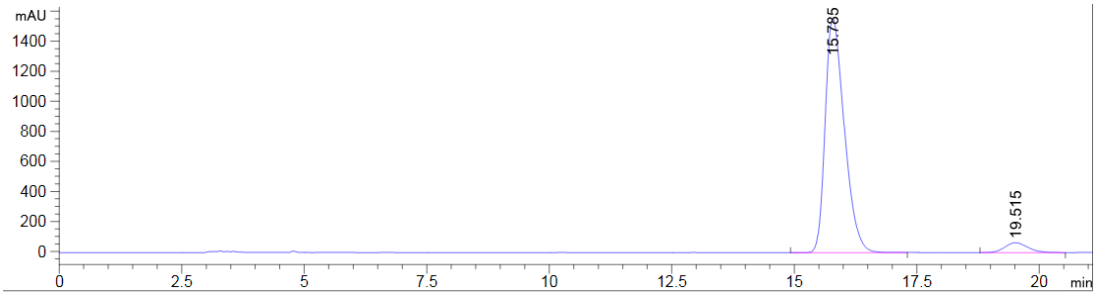


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.041	VB	0.2481	1.52767e4	941.64514	92.9749
2	14.025	BB	0.3530	1154.29407	50.58387	7.0251

6m



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.262	BB	0.4351	1.87182e4	663.37036	49.9858
2	19.977	BB	0.5529	1.87288e4	523.18054	50.0142



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.785	VB	0.4192	4.24255e4	1558.01331	95.1478
2	19.515	BB	0.5056	2163.55762	66.06246	4.8522