Supporting Information

A Thiourea-Functionalized Metal-Organic Macrocycle for Catalysis of Michael Additions and Prominent Size-Selective Effect

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1. Structural Figures and Characterizations of Catalysts

Figure S1. Molecular structure of Ni–**SPT** capsule within a unique unit. Selective bond distance (Å) and angle (°) in Ni–**SPT** (Symmetry code: #1 *y-2/3*, *x+2/3*, -z+1/6): Ni(1)-N(2) 2.005(4), Ni(1)-N(1) 2.111(4), Ni(1)-N(15)$^{\#1}$ 1.991(4), Ni(1)-S(1) 2.389(14), Ni(2)-N(7) 1.989(5), Ni(2)-N(9) 2.118(4), Ni(2)-S(3) 2.3992(18), N(2)-Ni(1)-N(16)$^{\#1}$ 102.15(17), N(2)-Ni(1)-N(1) 78.36(16), N(2)-Ni(1)-S(6)$^{\#1}$ 99.61(11), N(7)-Ni(2)-N(10) 172.60(18), N(7)-Ni(2)-S(4) 106.21(13).

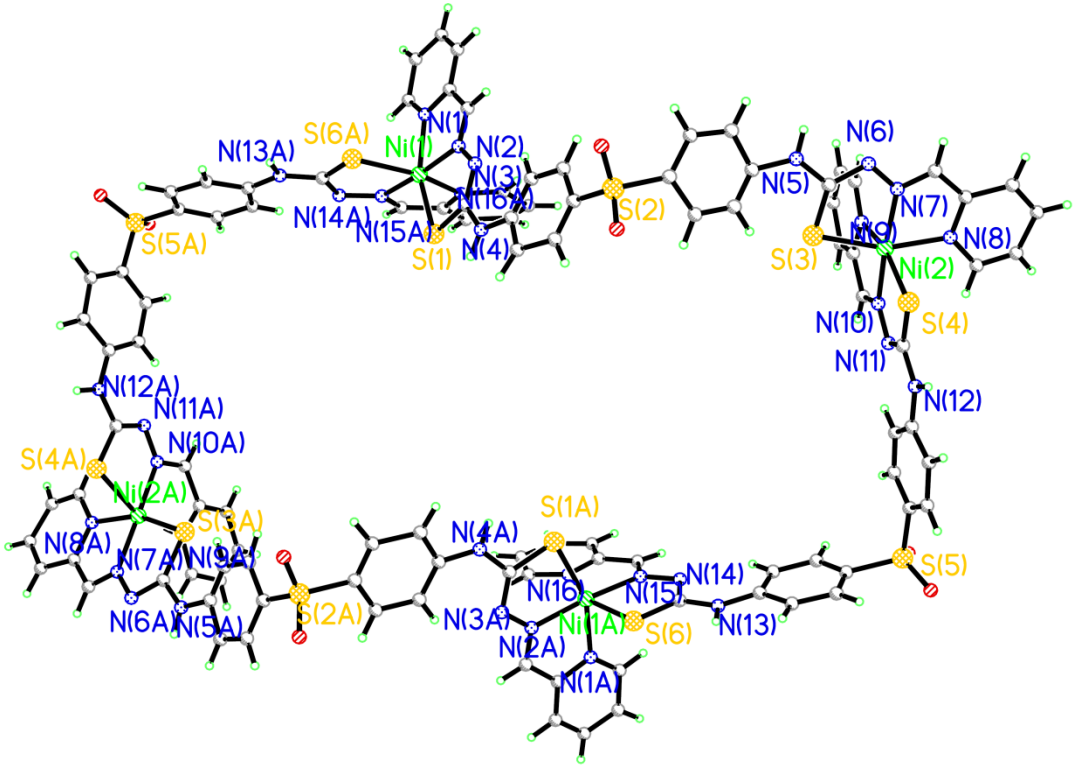


Figure S2. Packing mode of Ni–**SPT**, viewed along *b* axis.

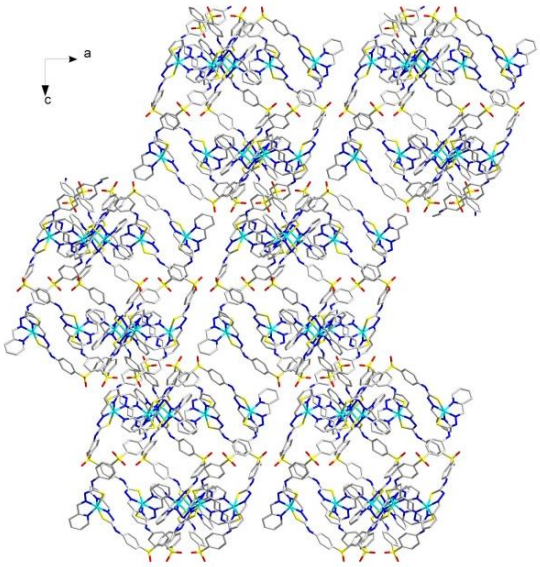


Figure S3. Packing mode of Ni–**SPT**, viewed along *c* axis.

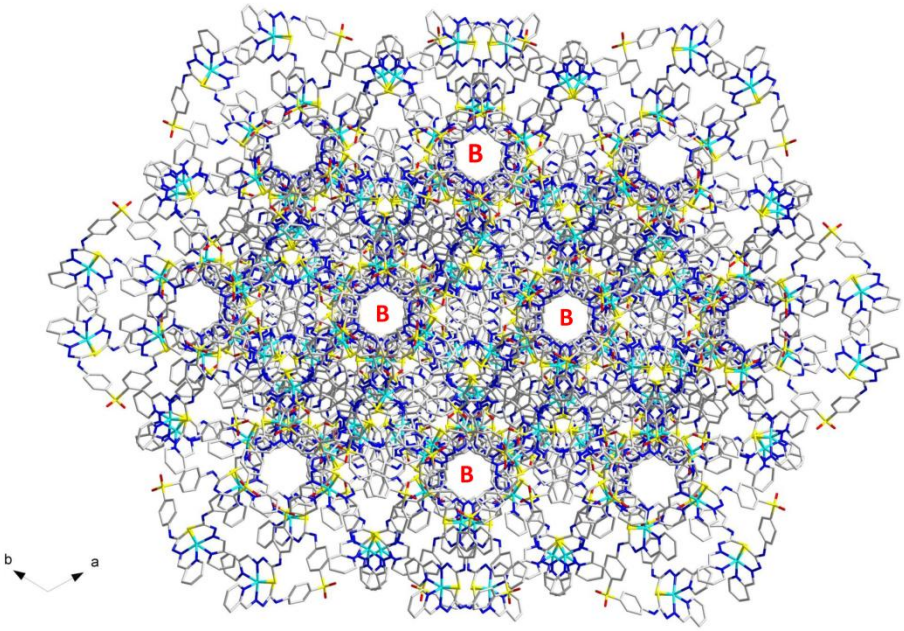


Figure S4. Molecular structure of Ni–**PDT**. Selective bond distance (Å) and angle (°) in Ni–**PDT**: Ni(1)-N(1) 2.099(7), Ni(1)-N(2) 2.011(6), Ni(1)-S(1) 2.432(2), Ni(2)-N(7) 1.973(7), Ni(2)-N(8) 2.099(7), Ni(2)-S(2) 2.413(2), S(1)-C(7) 1.699(8), C(1)-N(1) 1.357(11), N(2)-Ni(1)-N(9) 98.2(3), N(2)-Ni(1)-S(3) 100.14(17), N(7)-Ni(2)-N(16) 100.1(3), N(7)-Ni(2)-S(4) 99.73(19).

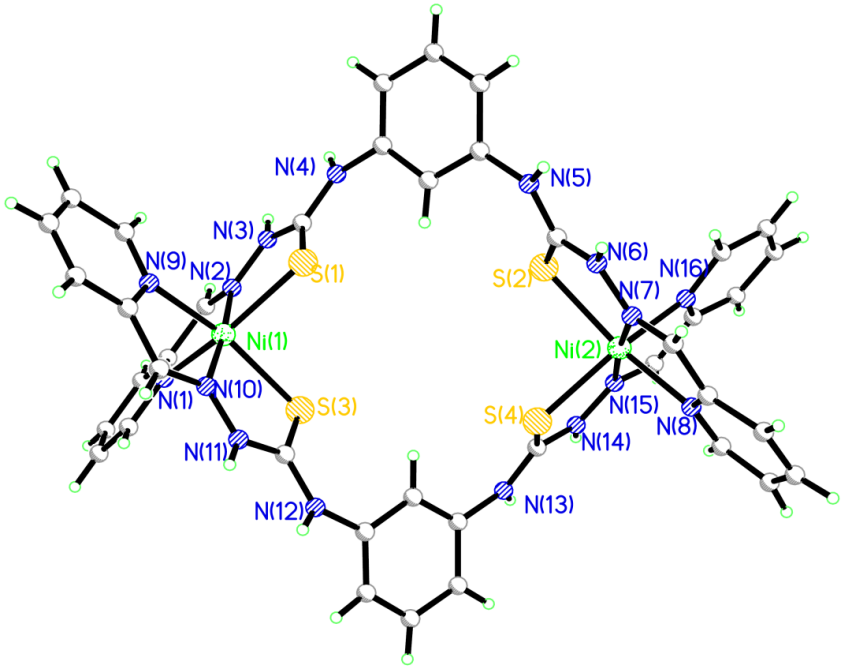


Figure S5.Space-filling structure of Ni–**PDT**.

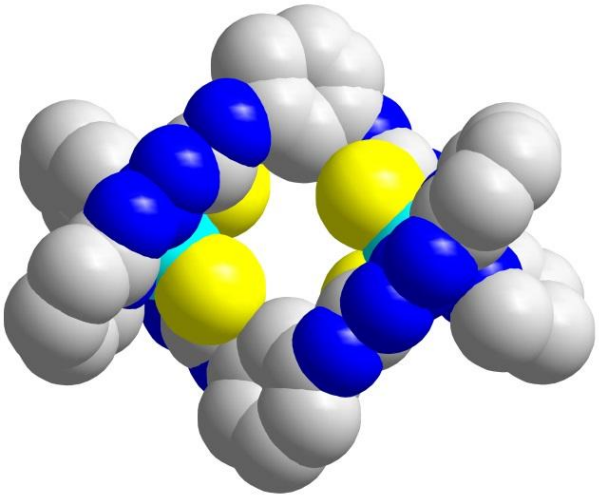
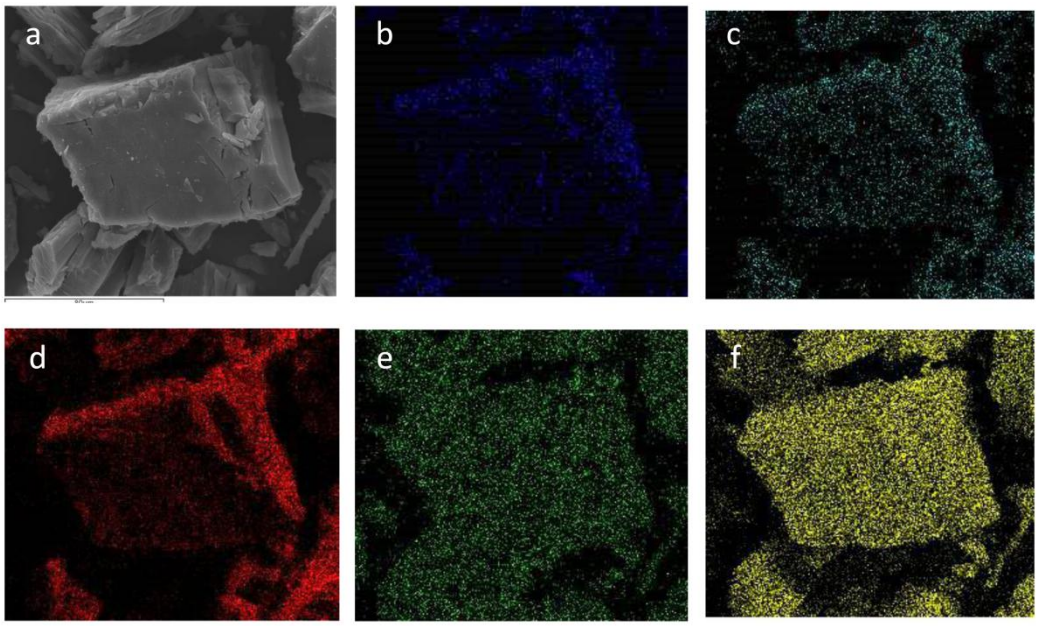


Figure S6. The element maps for the Ni−**SPT**: (a) SEM image; (b) N (blue); (c) O (indigo); (d) C (red); (e) Ni (green); (f) S (yellow).

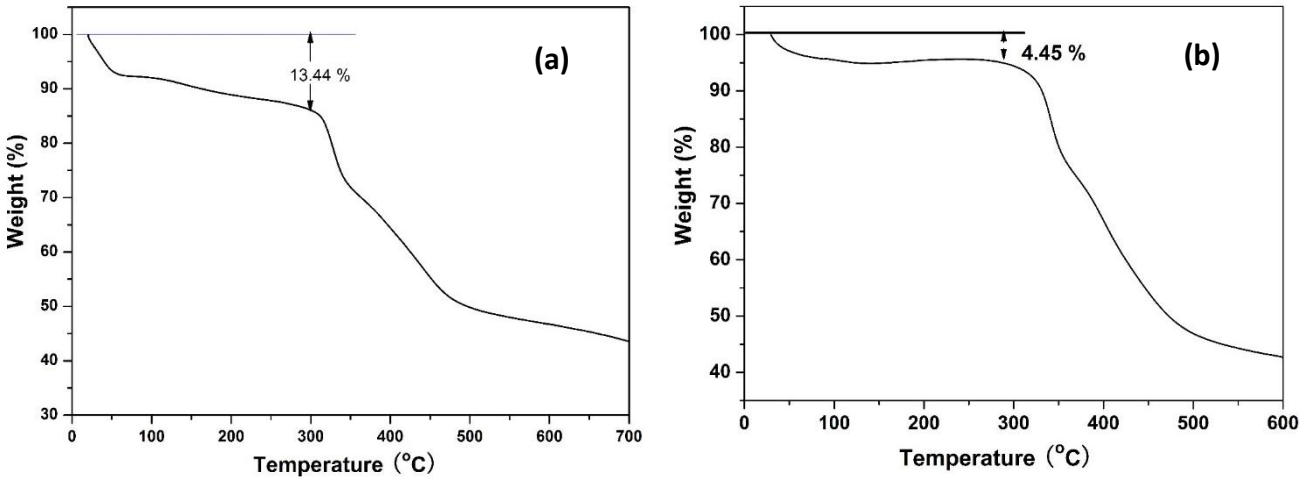


2. Catalysis Details

Typical procedure for solvent exchange of Ni−**SPT**

Before the catalysis experiments, solvent exchange studies were carried out to remove the inherent guest molecules. The sample was treated by soaking in a 5 mL CH_3CN solution shaking for 2 days and fully dried out the guest solvent molecules in a vacuum oven (100 ^oC, 6 hours). The TGA was used to demonstrate the solvent-exchange of Ni−**SPT**.

Figure S7. The TG curves of Ni−**SPT** before **(a)** and after **(b)** solvent exchange.



Typical procedure for the Michael reactions of *β*-nitrostyrene to nitroolefins

Catalyst Ni–**SPT** (2.5 mol%) or Ni–**PDT** (5 mol%) was added to the dry toluene (0.4 mL) dissolving *β*-nitrostyrene (0.2 mmol, 1 eq), dimethyl malonate (0.4 mmol, 2 eq) and Et_3N (4 μL, 5 mol%) stirring at 25 ^oC. After 60 hours, dry dichloromethane (8 mL) was added. The catalyst was separated by centrifuge and the filtrate was concentrated in a vacuum. The yield of reaction was determined by ^1H-NMR analysis of the crude products. The residue was purified by column chromatography on silica gel (hexane / AcOEt = 5 / 1 as eluent) to afford the desired product.

Table S1. Control experiments for the Michael reaction of *β*-nitrostyrene and dimethyl malonate[a]

Entry	Catalysts	Adduct	Time (h)	Yield (%)[b]
1[c]	Ni–**SPT**	TEA	48	76
2	Ni–**SPT**	TEA	48	88
3[d]	Ni–**SPT**	TEA	48	98
4	Ni–**SPT**	-	48	trace
5	$NiSO_4$, Ligand **SPT**	TEA	48	33
6	Ligand **SPT**	TEA	48	24
7[e]	Ligand **SPT**	TEA	48	68
8	$NiSO_4$	TEA	48	22
9	-	TEA	48	26

[a] The reaction was conducted with **2a** (1 equiv), **3a** (2 equiv), and toluene in the presence of various catalysts (2.5 mol%) at room temperature. [b] Isolated yields were determined by ^1H-NMR analysis. [c] With 1.25 mol% catalyst. [d] With 5.0 mol% catalyst. [e] This reaction was conducted in a homogeneous phase using DMSO-d6 as solvent.

Table S2. Recycling studies of catalyst Ni–**SPT** for the heterogeneous reactions in optimum condition: Ni–**SPT**, 0.005 mmol; *β*-nitrostyrene, 0.2 mmol; dimethyl malonate, 0.4 mmol; Et_3N, 4 μL; 25 ^oC; 60 h

Entry	Yield (%)
Round 1	>99
Round 2	93
Round 3	89
Round 4	86
Round 5	84
Round 6	81

Figure S8. Leaching test was carried out by removing the catalyst after 4 h reaction under the optimal conditions, indicating that no active species has been leached into the reaction system.

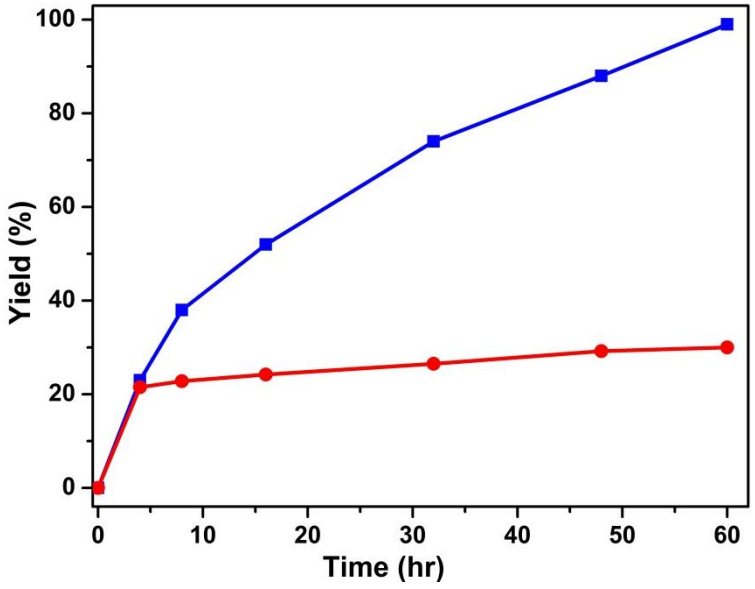


Figure S9. PXRD pattern of measured fresh Ni–**SPT** (a, red) and Ni–**PDT** (b, red), their calculated patterns based on the single-crystal simulation (a, b, black) and the samples after catalysis (a, b, blue).

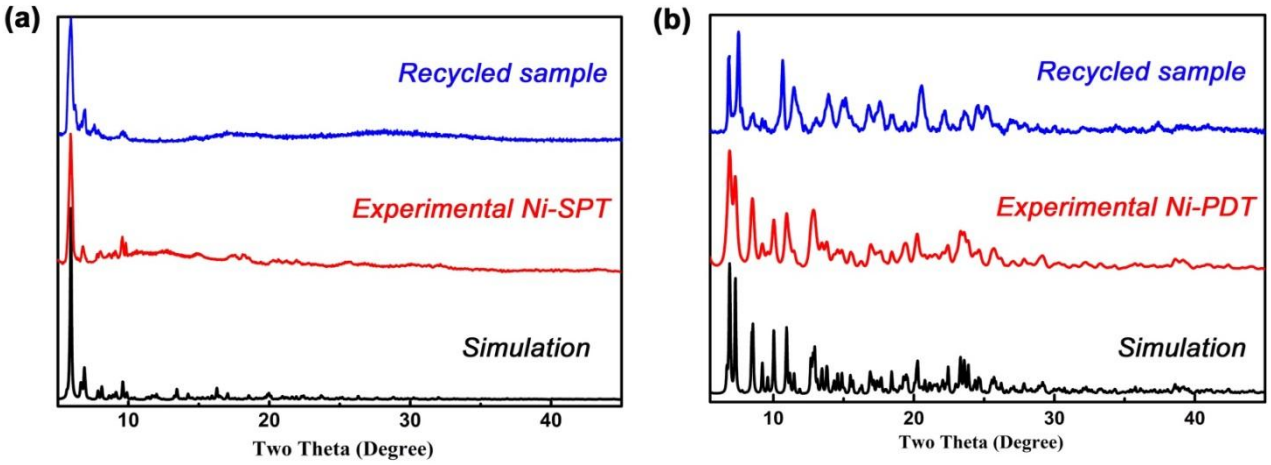


Figure S10. ^{1}H NMR ($CDCl_3$, 400 MHz) monitoring of the Michael reaction progress using catalyst Ni**–SPT**, showing the increasing tendency of the peaks at around 3.87, 4.25, 4.85, 7.23 and 7.35 ppm, while the gradual vanish of the peaks at around 7.40, 7.58 and 7.90 ppm, respectively, with the proceeding of the reaction.

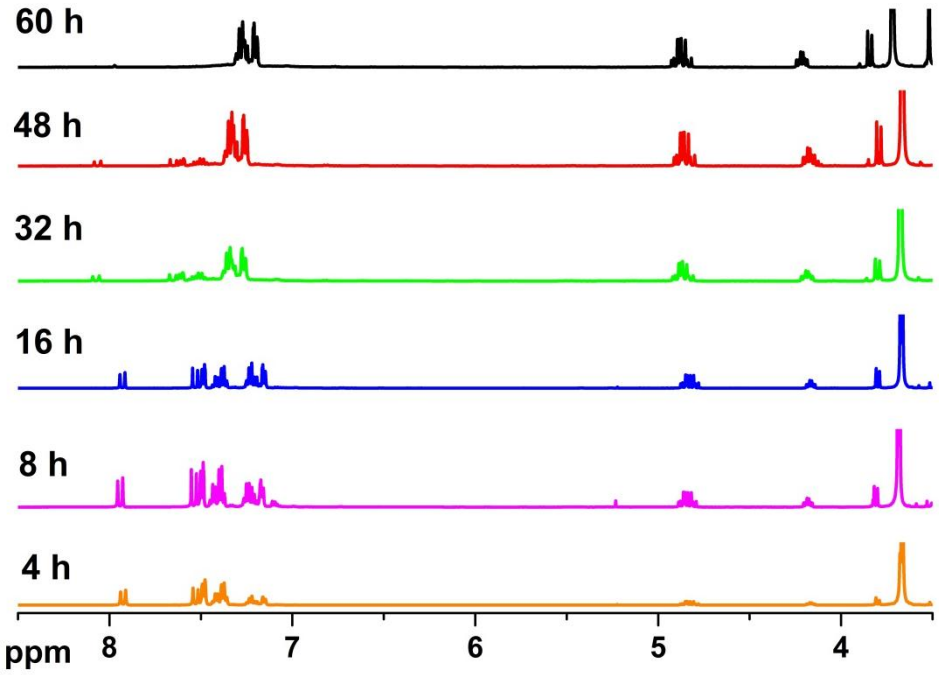


Figure S11. (a) Kinetic study on the Michael reaction, and the straight line indicates the reaction is first-order in **2a**; (b) The linear relationship of the calculated rate constants with the amount of catalyst Ni**–SPT**.

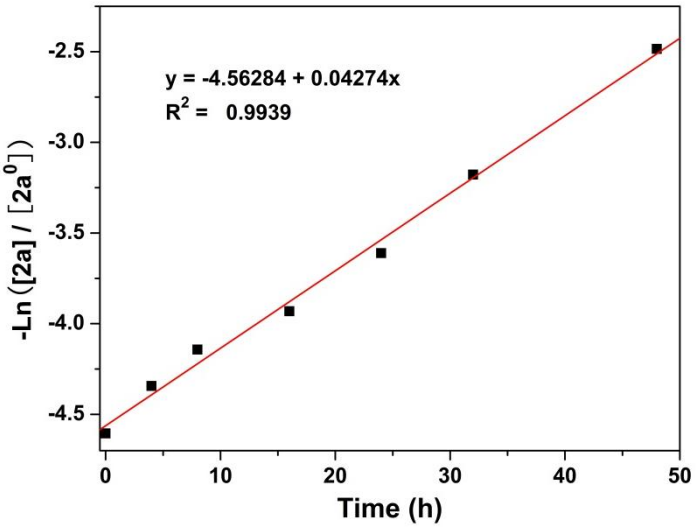
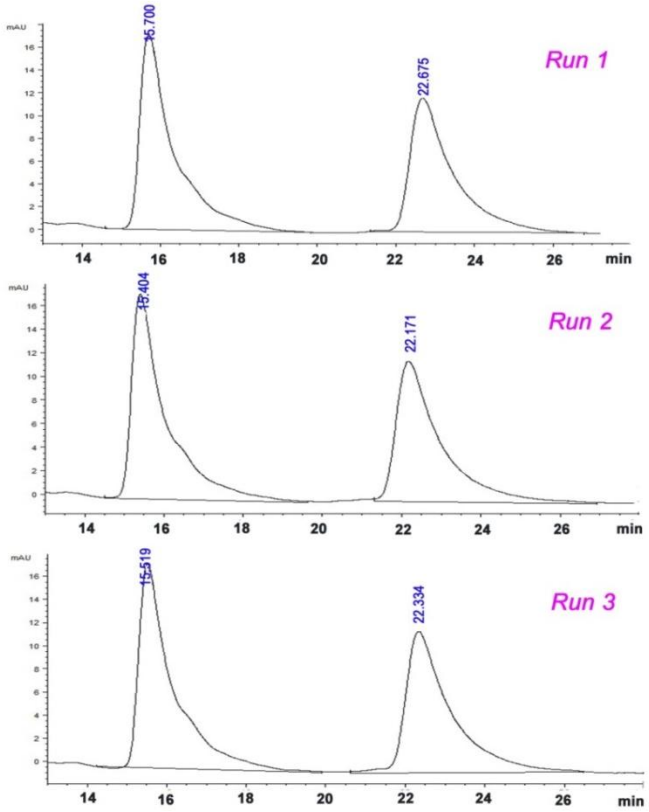
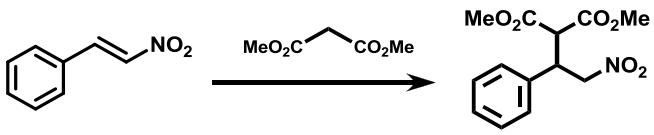


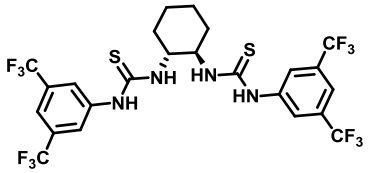
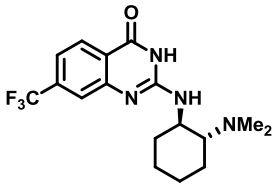
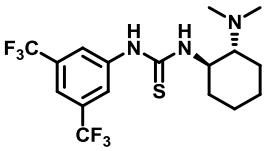
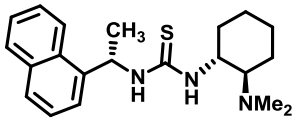
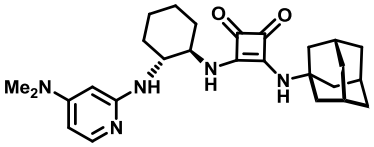
Figure S12. Chiral HPLC chromatograms of three runs for isolated catalytic product **4a** (Chiralcel AD, hexane/2-propanol = 90/10, flow rate: 1.0 mL/min, λ = 254 nm).



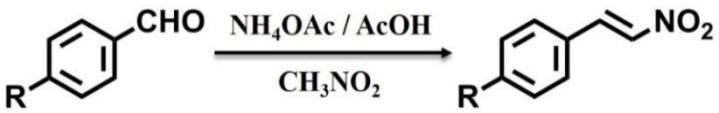
Entry	Major (%)	Minor (%)	ee (%)
4a-run 1	53.713	46.287	7.426
4a-run 2	53.157	46.843	6.314
4a- run 3	52.400	47.600	4.800
4a-average	53.090	46.910	6.180

Table S3. A selective summary of the reported different kinds of catalysts to the Michael reaction between *β*-nitrostyrene and dimethyl malonate that was performed in this paper (R.T.= room temperature).

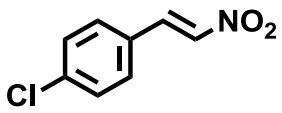


Entry	Catalysts	Homogeneous/ Heterogeneous	Temperature (^{o}C)	Time (h)	Yields (%)	ref
1	**CSF-IBOIHS (3)**	Homogeneous	R.T.	20	90	S1a
2		Homogeneous	-30	72	90	S1b
3		Homogeneous	R.T.	24	90	S1c
4		Homogeneous	R.T.	9	89	S1d
5		Homogeneous	20	24	78	S1e
6		Homogeneous	5	8	96	S1f
7	**Ni Cs-BINOL-salen**	Homogeneous	R.T.	48	60	S1g
8	**graphene oxide (GO)**	Heterogeneous	R.T.	48	50	S1h

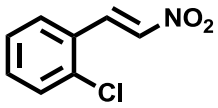
Typical procedure for the synthesis of para-substituted *β*-nitrostyrene



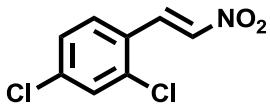
The synthesis of para-substituted *β*-nitrostyrene was according to the literature.[S2] To a solution containing ammonium acetate (2.4 eq) in 20 mL acetic acid was added nitromethane (6.9 eq) followed by para-substituted aldehyde (1 eq). The mixture was refluxed for six hours at 100 ^{o}C and then cooled to room temperature and stirred overnight. The resulting solution poured into ice water and extracted with EtOAc (3 × 50 mL) after adjusted to pH = 7 with NaOH (aq, 2M). The extract was washed with brine, dried over Na_2SO_4, filtered and concentrated to a yellow solid. The pure product was obtained by silica gel column chromatography (ethyl acetate and hexane as eluent).



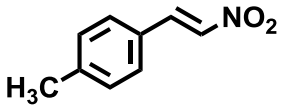
(*E*)-1-chloro-4-(2-nitrovinyl)benzene (**2b**). Yellow solid. Yield: 82 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.96 (d, *J* = 13.7 Hz, 1H), 7.56 (d, *J* = 13.7 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H).



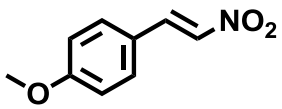
(*E*)-1-chloro-2-(2-nitrovinyl)benzene (**2c**). Yellow solid. Yield: 51 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 8.39 (d, *J* = 13.7 Hz, 1H), 7.62-7.56 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H).



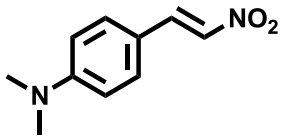
(*E*)-2,4-dichloro-1-(2-nitrovinyl)benzene (**2d**). Yellow solid. Yield: 62 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 8.33 (d, *J* = 13.7 Hz, 1H), 7.58 (d, *J* = 13.7 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 1H).



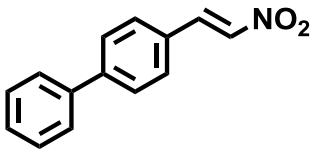
(*E*)-1-methyl-4-(2-nitrovinyl)benzene (**2e**). Yellow solid. Yield: 78 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.99 (d, *J* = 13.6 Hz, 1H), 7.57 (d, *J* = 13.6 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H).



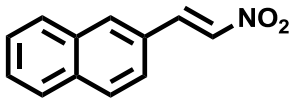
(*E*)-1-methoxy-4-(2-nitrovinyl)benzene (**2f**). Yellow solid. Yield: 75 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.98 (d, *J* = 13.5 Hz, 1H), 7.60-7.45 (m, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H).



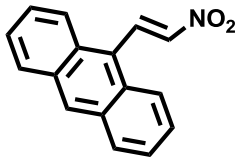
(*E*)-N, N-dimethyl-4-(2-nitrovinyl)aniline (**2g**). Yellow solid. Yield: 30 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.98 (d, *J* = 13.5 Hz, 1H), 7.51 (d, *J* = 13.4 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.09 (s, 6H).



(*E*)-4-(2-nitrovinyl)biphenyl (**2h**). Yellow solid. Yield: 60 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 8.05 (d, *J* = 13.7 Hz, 1H), 7.74-7.58 (m, 7H), 7.53-7.44 (m, 2H), 7.41 (t, *J* = 7.9 Hz, 1H).

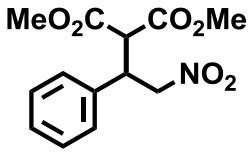


(*E*)-2-(2-nitrovinyl)naphthalene (**2i**). Yellow solid. Yield: 43 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 8.84 (d, *J* = 13.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.69-7.63 (m, 2H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H).

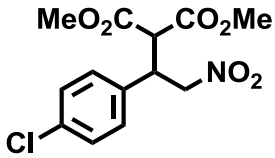


(*E*)-9-(2-nitrovinyl)anthracene (**2j**). Red solid. Yield: 52 %. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 8.98 (d, *J* = 13.8 Hz, 1H), 8.52 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 2H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.56 (dt, *J* = 14.8, 7.1 Hz, 5H).

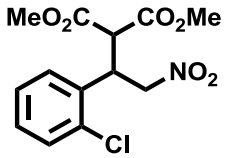
2. ^{1}H NMR Analysis for the Products and Substrates



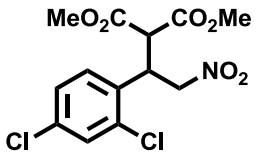
Dimethyl 2-(2-nitro-1-phenylethyl)malonate (**4a**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.38-7.27 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.99-4.79 (m, 2H), 4.25 (td, *J* = 9.0, 5.3 Hz, 1H), 3.87 (d, *J* = 9.1 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H).



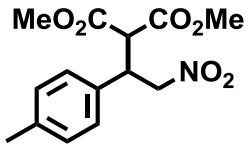
Dimethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (**4b**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 11.0 Hz, 2H), 4.97-4.77 (m, 2H), 4.23 (td, *J* = 9.0, 5.1 Hz, 1H), 3.83 (d, *J* = 9.0 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H).



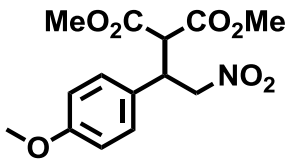
Dimethyl 2-(1-(2-chlorophenyl)-2-nitroethyl)malonate (**4c**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.45-7.36 (m, 1H), 7.25-7.17 (m, 3H), 5.10 (dd, *J* = 13.6, 8.7 Hz, 1H), 4.95 (dd, *J* = 13.7, 4.3 Hz, 1H), 4.75 (td, *J* = 8.4, 4.7 Hz, 1H), 4.12-4.08 (m, 2H), 3.71 (s, 3H), 3.62 (s, 3H).



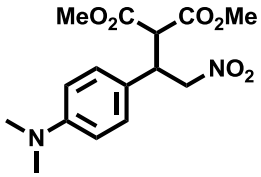
Dimethyl 2-(1-(2,4-dichlorophenyl)-2-nitroethyl)malonate (**4d**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.43 (s, 1H), 7.21 (q, *J* = 8.5 Hz, 2H), 5.09 (dd, *J* = 13.6, 8.8 Hz, 1H), 4.93 (dd, *J* = 13.7, 4.0 Hz, 1H), 4.75-4.65 (m, 1H), 4.06 (d, *J* = 8.3 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 3H).



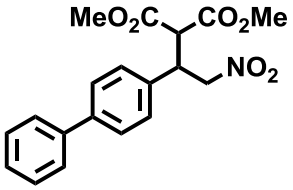
Dimethyl 2-(2-nitro-1-*p*-tolylethyl)malnoate (**4e**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.16-7.05 (m, 4H), 4.87 (qd, *J* = 13.1, 7.0 Hz, 2H), 4.27-4.15 (m, 1H), 3.84 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H), 2.30 (s, 3H).



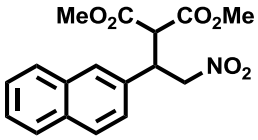
Dimethyl 2-(1-(4-methoxyphenyl)-2-nitroethyl)malonate (**4f**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.85 (qd, *J* = 13.0, 7.1 Hz, 2H), 4.18 (tt, *J* = 11.6, 5.8 Hz, 1H), 3.82 (d, *J* = 9.2 Hz, 1H), 3.76 (d, *J* = 5.1 Hz, 6H), 3.56 (s, 3H).



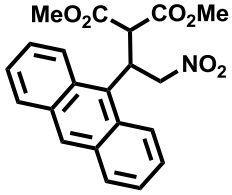
Dimethyl 2-(1-(4-(dimethylamino)phenyl)-2-nitroethyl)malonate (**4g**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 7.7 Hz, 2H), 4.84 (d, *J* = 42.3 Hz, 2H), 4.15 (d, *J* = 17.8 Hz, 1H), 3.82 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 3.58 (s, 3H), 2.93 (s, 6H).



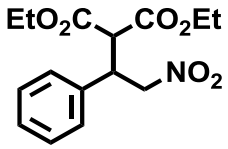
Dimethyl 2-(1-(biphenyl-4-yl)-2-nitroethyl)malonate (**4h**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.54 (d, *J* = 2.4 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.39-7.29 (m, 3H), 5.07-4.80 (m, 2H), 4.38-4.22 (m, 1H), 3.91 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H), 3.60 (s, 3H).



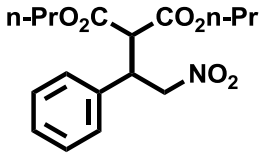
Dimethyl 2-(1-(naphthalene-2-yl)-2-nitroethyl)malonate (**4i**). White solid. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.48-7.35 (m, 2H), 5.19 (dd, *J* = 20.9, 8.0 Hz, 2H), 5.07 (dd, *J* = 12.8, 4.3 Hz, 1H), 4.11 (d, *J* = 7.4 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H).



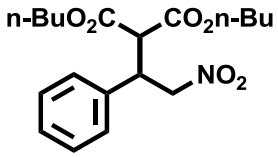
Dimethyl 2-(1-(anthracen-9-yl)-2-nitroethyl)malonate (**4j**). Yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 8.67 (d, *J* = 9.2 Hz, 1H), 8.46 (d, *J* = 17.1 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.96 (dd, *J* = 12.7, 8.8 Hz, 2H), 7.68-7.60 (m, 1H), 7.60-7.53 (m, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 6.17 (dt, *J* = 11.4, 5.8 Hz, 1H), 5.42 (dd, *J* = 14.0, 5.5 Hz, 1H), 5.10 (dd, *J* = 14.0, 6.1 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 3.87 (s, 3H), 3.07 (s, 3H).



Diethyl 2-(2-nitro-1-phenylethyl)malonate (**4k**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.25 (dddd, *J* = 13.8, 12.7, 6.6 Hz, 5H), 5.03-4.75 (m, 2H), 4.21 (dd, *J* = 12.8, 5.3 Hz, 3H), 3.99 (dd, *J* = 16.6, 4.7 Hz, 2H), 3.80 (d, *J* = 9.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H).



Dipropyl 2-(2-nitro-1-phenylethyl)malonate (**4l**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.34-7.22 (m, 5H), 4.90 (qd, *J* = 13.1, 7.0 Hz, 2H), 4.23 (tt, *J* = 12.0, 6.0 Hz, 1H), 4.19-4.06 (m, 2H), 3.91 (t, *J* = 6.7 Hz, 2H), 3.85 (d, *J* = 9.3 Hz, 1H), 1.73-1.61 (m, 2H), 1.52-1.41 (m, 2H), 0.94-0.86 (m, 3H), 0.83-0.75 (m, 3H).



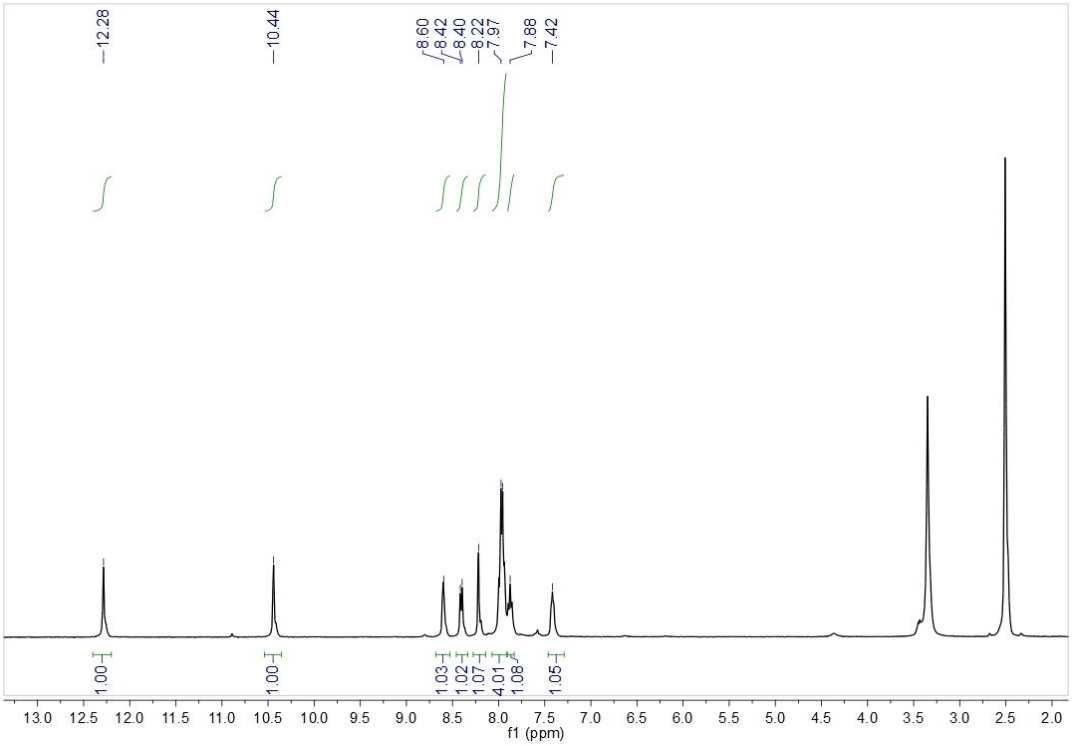
Dibutyl 2-(2-nitro-1-phenylethyl)malonate (**4m**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *ppm*): δ 7.36-7.19 (m, 5H), 4.97-4.83 (m, 2H), 4.22 (ddd, *J* = 9.2, 7.9, 4.6 Hz, 1H), 4.18-4.10 (m, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.87-3.81 (m, 1H), 1.68-1.57 (m, 3H), 1.47-1.38 (m, 2H), 1.37-1.31 (m, 2H), 1.31-1.24 (m, 2H), 1.21 (dd, *J* = 15.1, 7.8 Hz, 2H), 0.96-0.88 (m, 3H), 0.86-0.80 (m, 3H).

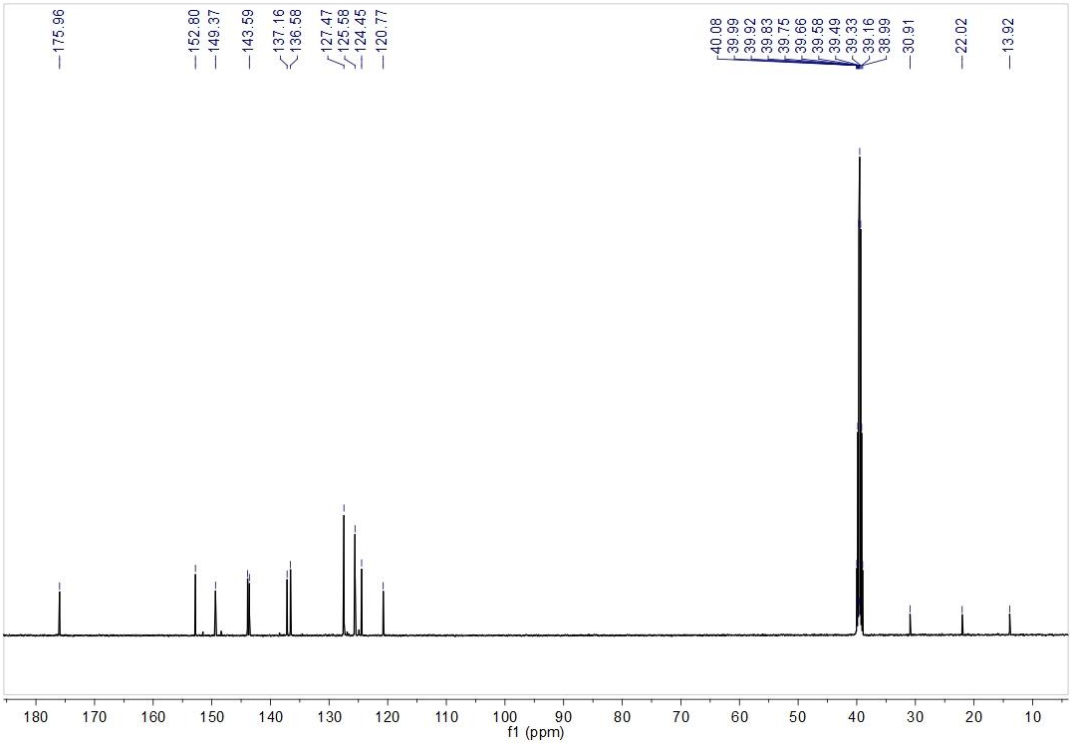
3. References

[S1] (a) X. M. Xu, T. Y. Cheng, X. C. Liu, J. Y. Xu, R. H. Jin, G. H. Liu, *ACS Catal*. 2014, **4**, 2137; (b) M. Hestericová, R. Šebesta, *Tetragedron*. 2014, **70**, 901; (c) G. Suez, V. Bloch, G. Nisnevich, M. Gandelman, *Eur. J. Org. Chem*. 2012, 2118; (d) T. Okino, Y. Hoashi, T. Furukawa, X. N. Xu, Y. Takemoto, *J. Am. Chem. Soc*. 2005, **127**, 119; (e) E. I. Jiménez, W. E. V. Narváez, C. A. Román-Chavarría, J. Vazquez-Chavez, T. Rocha-Rinza, M. Hernández-Rodríguez, *J. Org. Chem*. 2016, **81**, 7419; (f) M. Işık, M. Y. Unver, C. *J.* Tanyeli, *Org. Chem*. 2015, **80**, 828; (g) V. Annamalai, E. F. DiMauro, P. J. Carroll, M. C. Kozlowski, *J. Org. Chem*. 2003, **68**, 1973; (h) Y. M. Kim, S. Some, H. Lee, *Chem. Commun*. 2013, **49**, 5702.

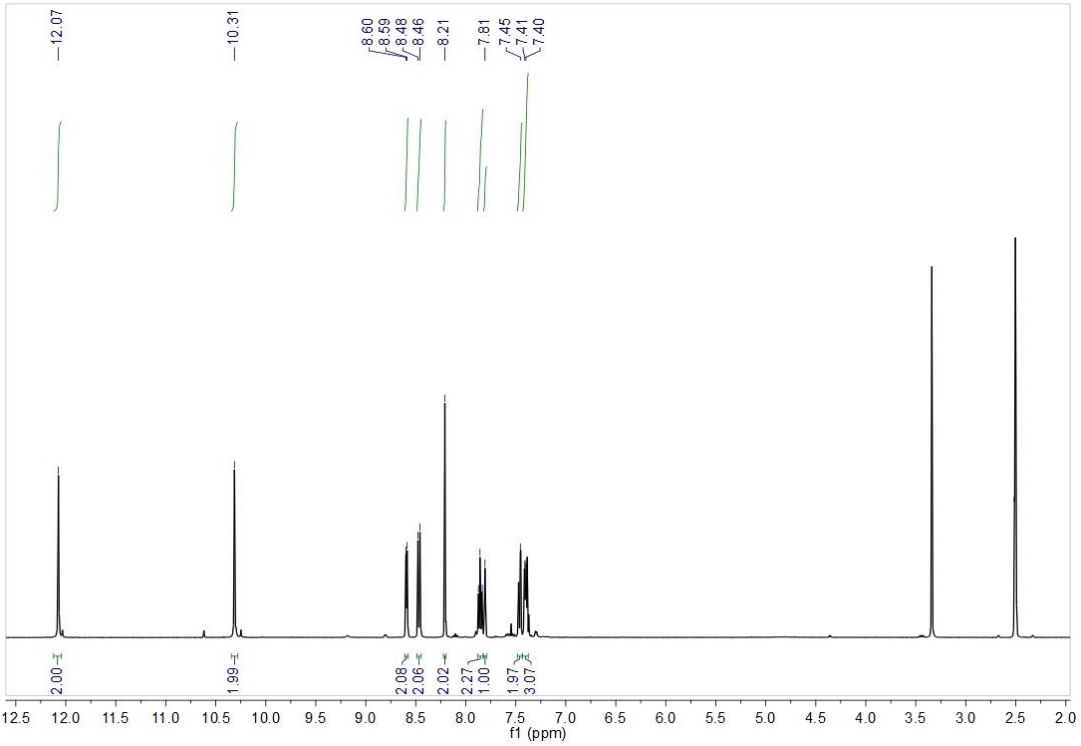
[S2] J. M. Lopchuk, R. P. Hughes, G. W. Gribble, *Org. Lett*. 2013, **15**, 5218.

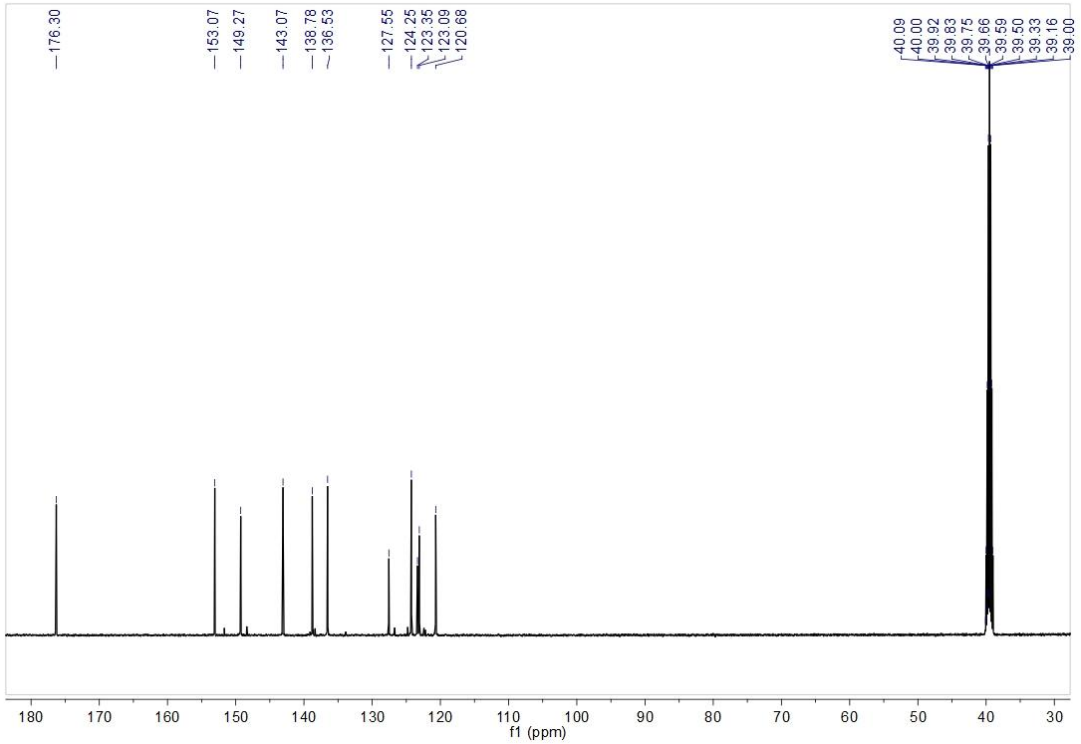
4.1. ^{1}H and ^{13}C NMR spectra of ligand **SPT**



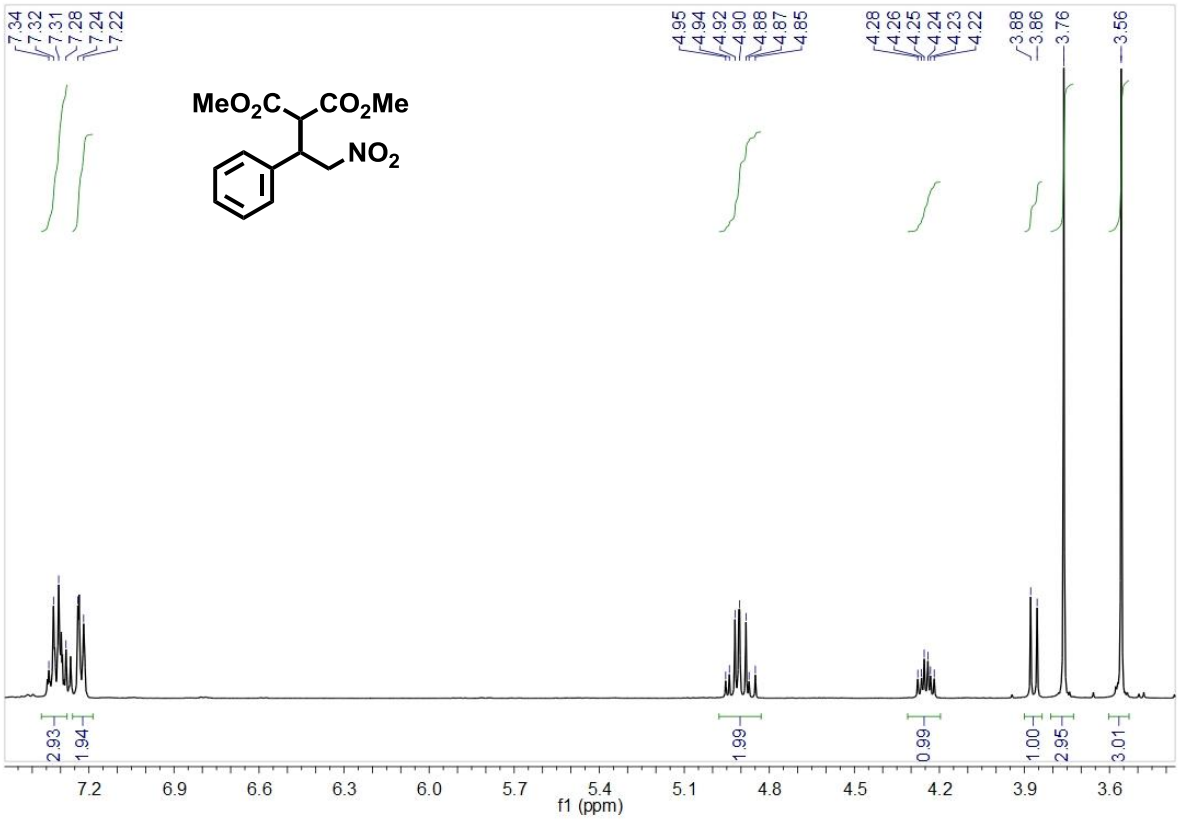


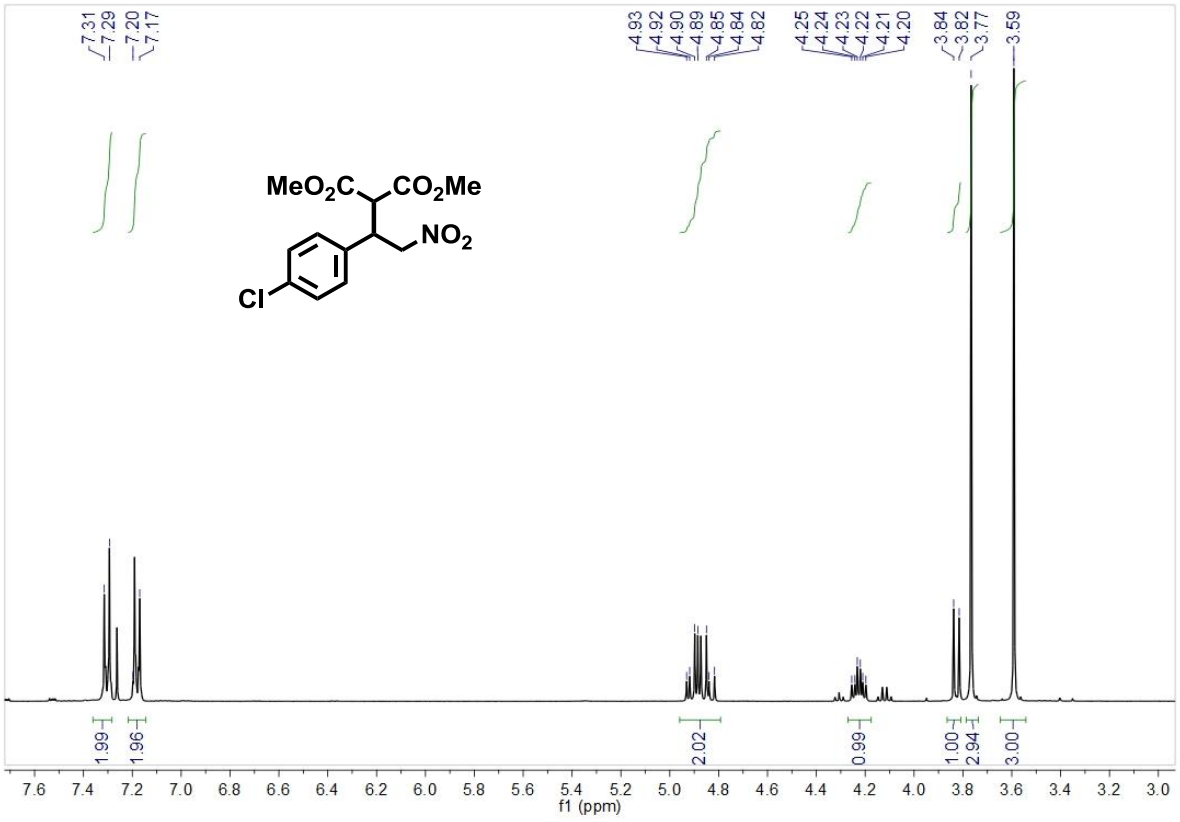
4.2. ^{1}H and ^{13}C NMR spectra of ligand **PDT**

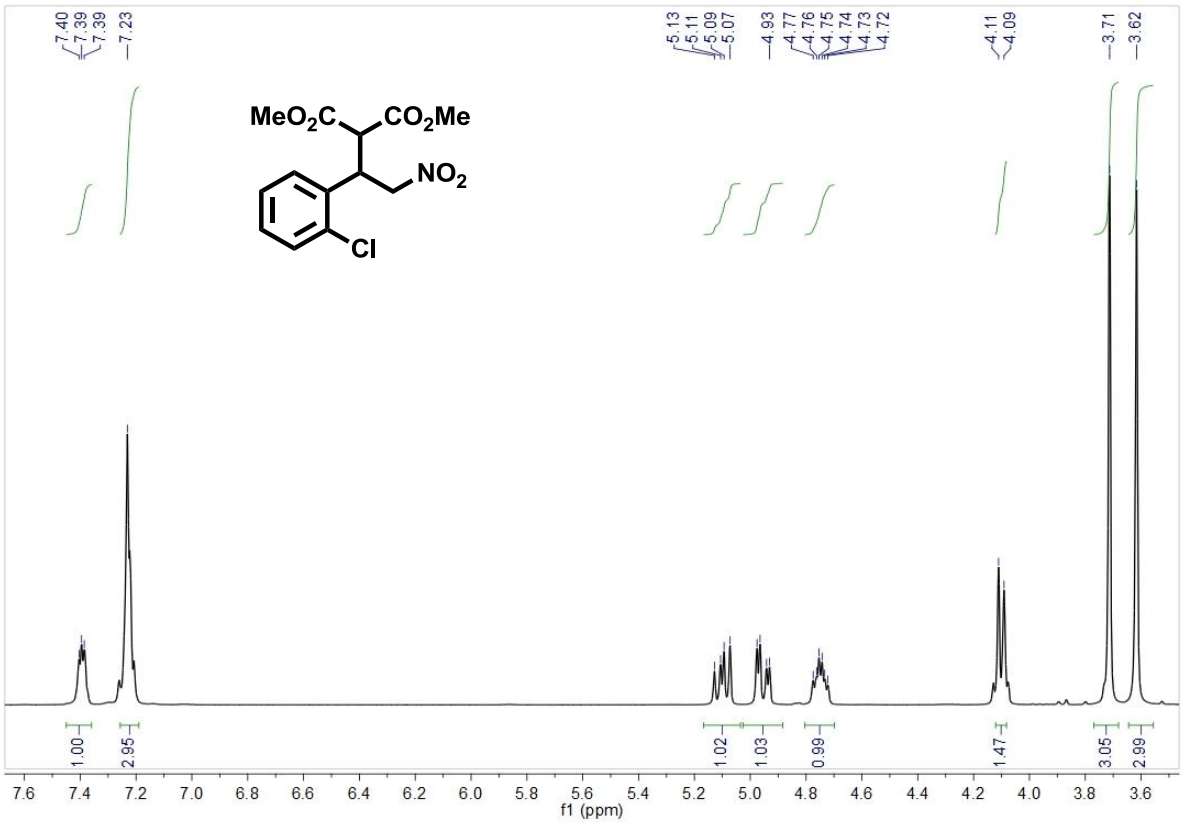




5.3. ^{1}H spectra for the Products and Substrates



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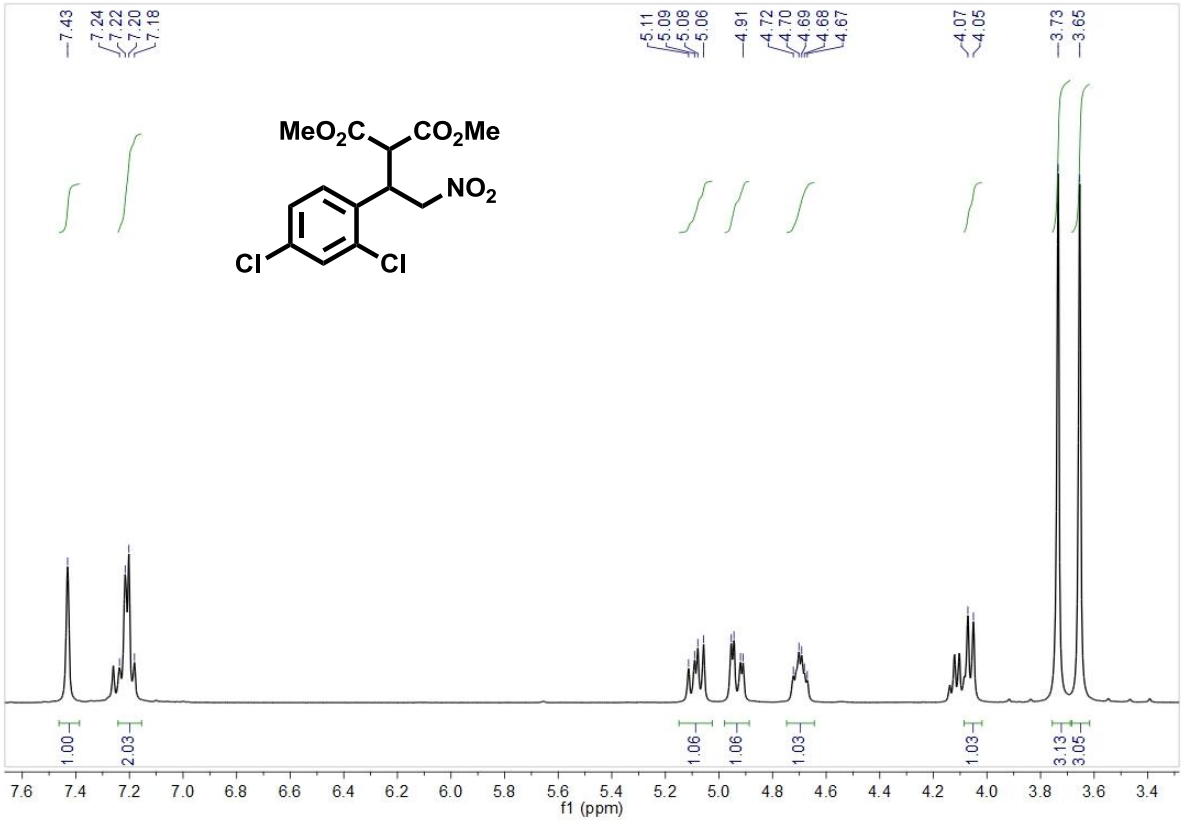
f1 (ppm)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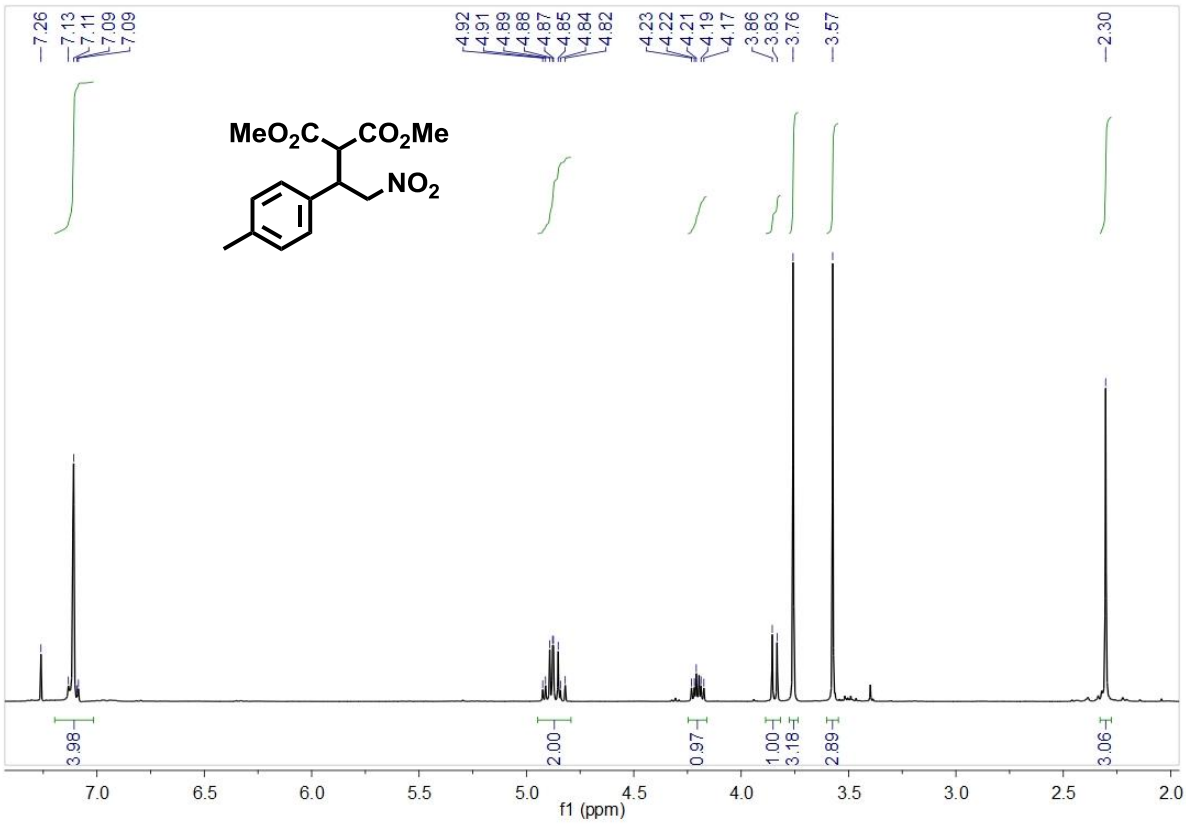
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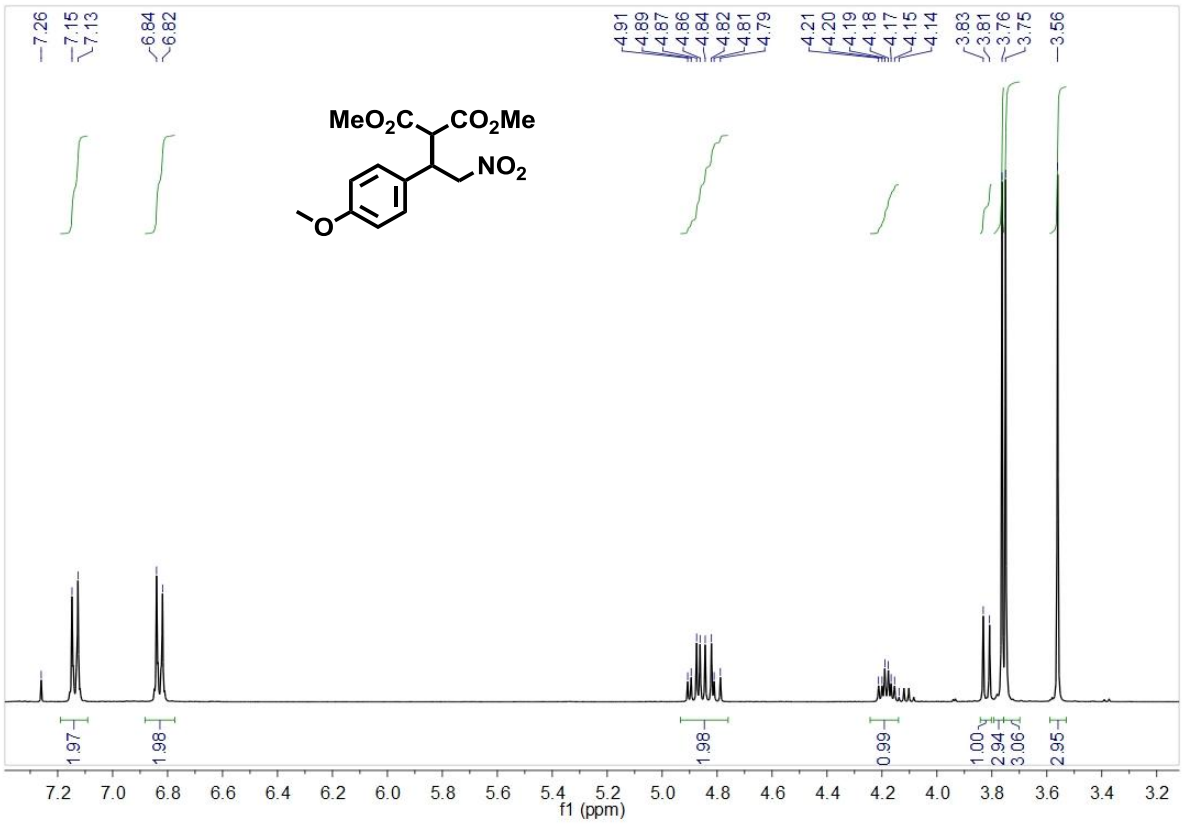
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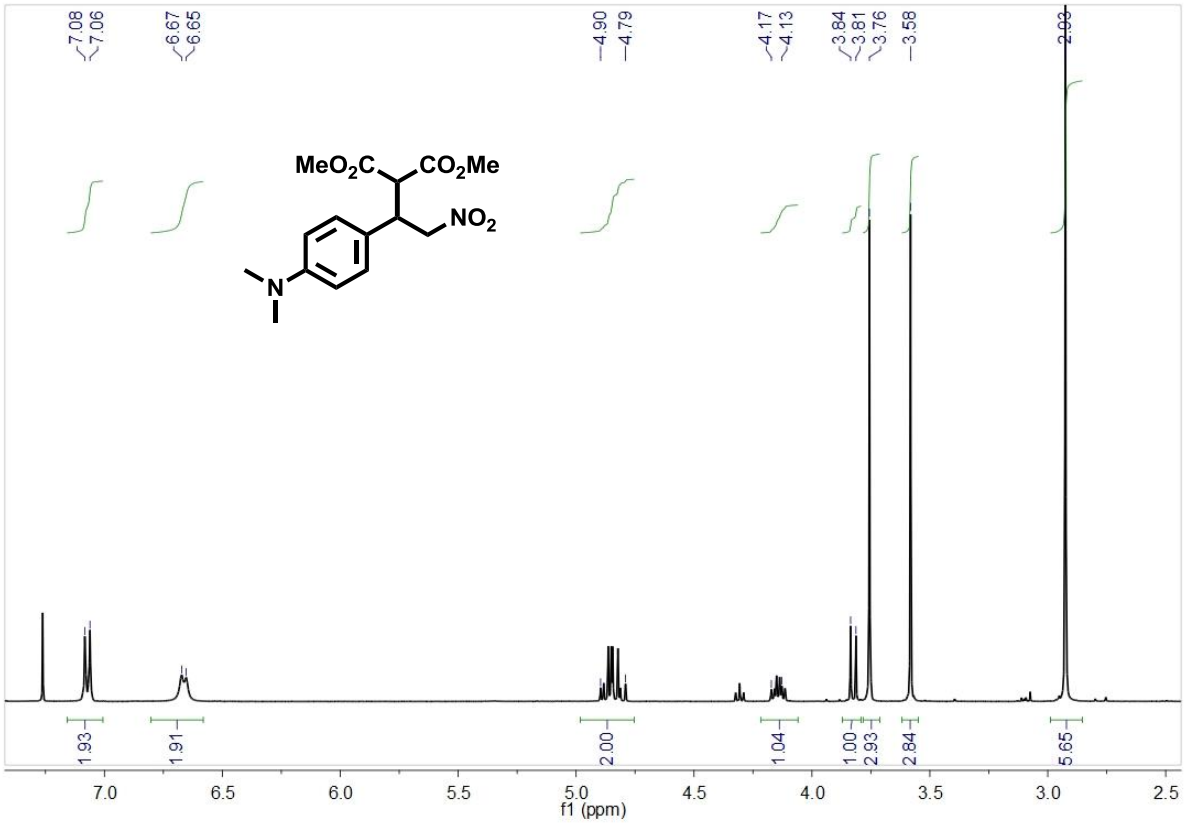
f1 (ppm)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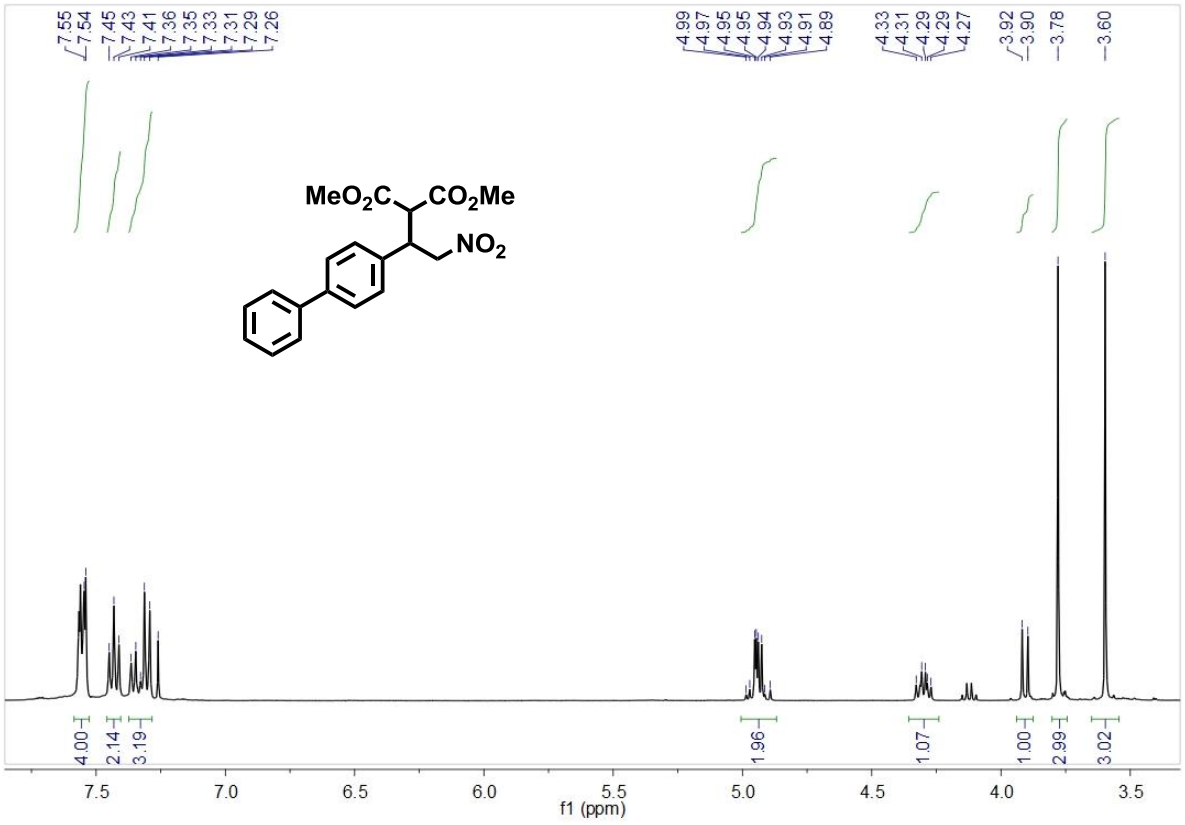
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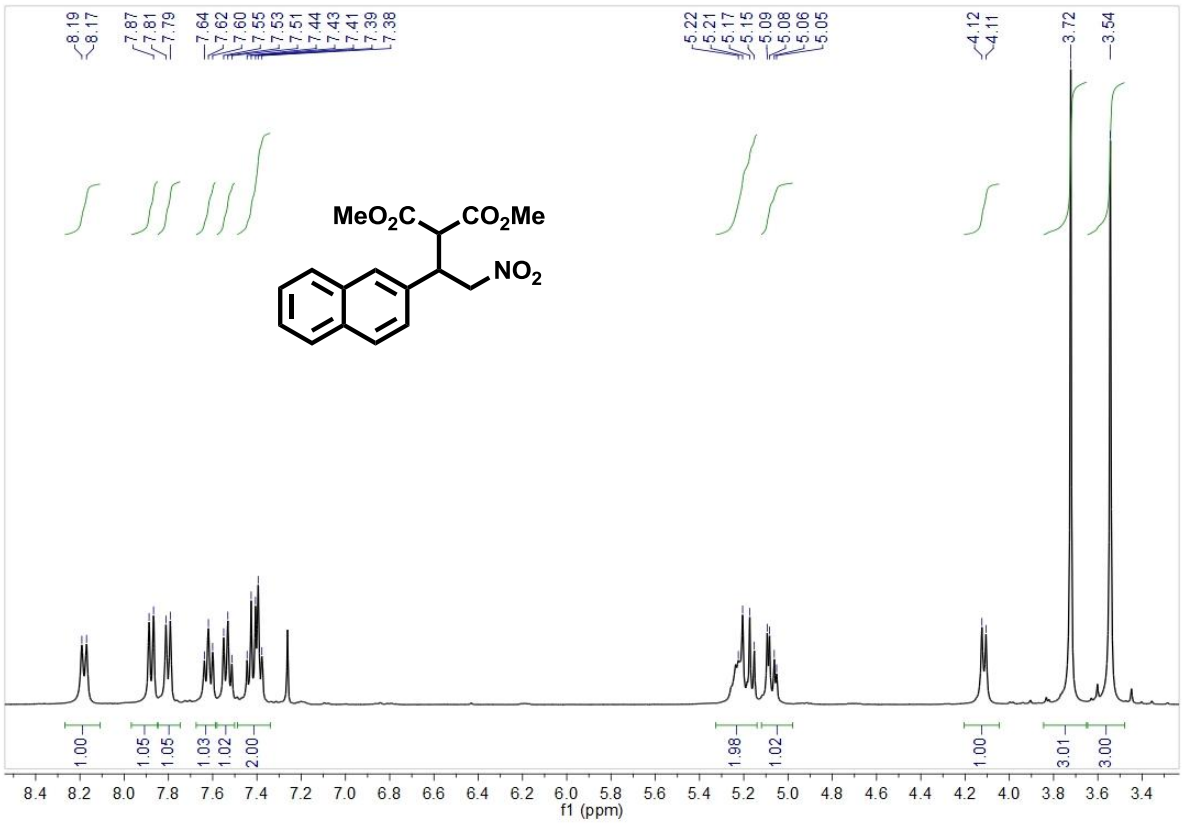
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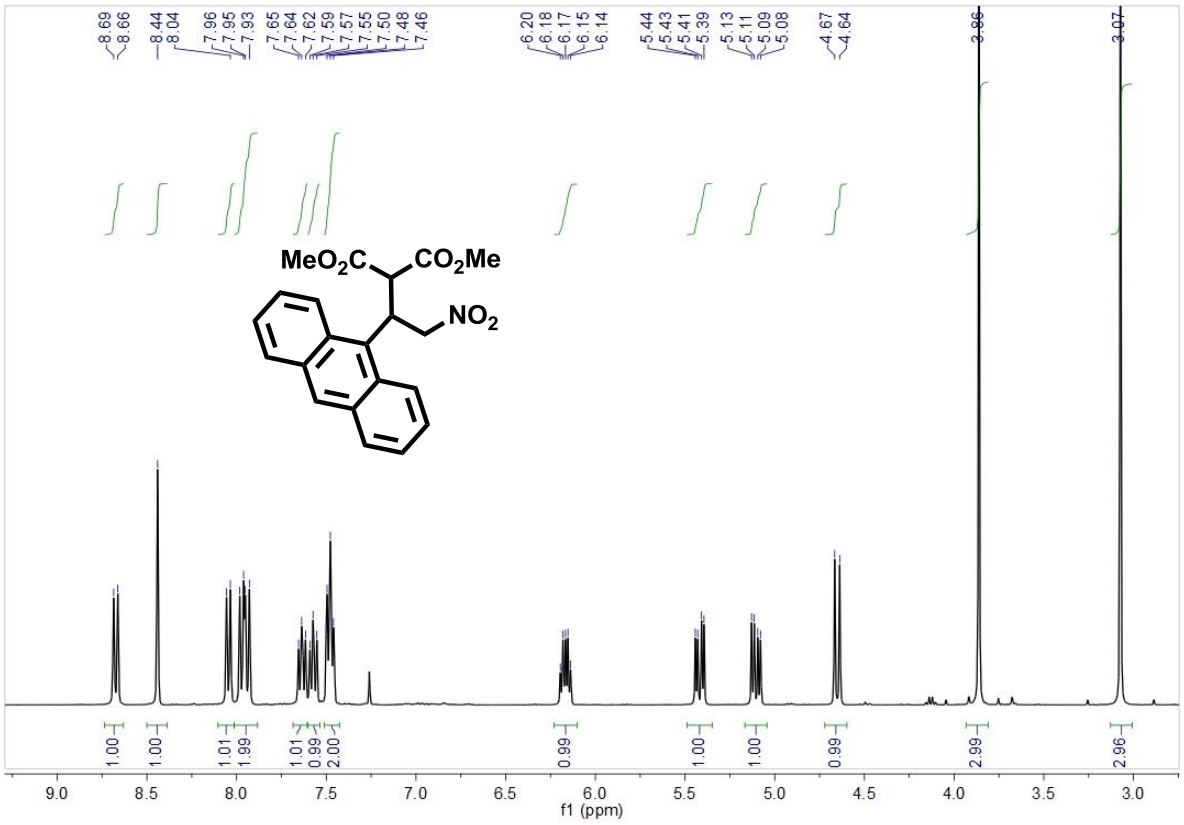
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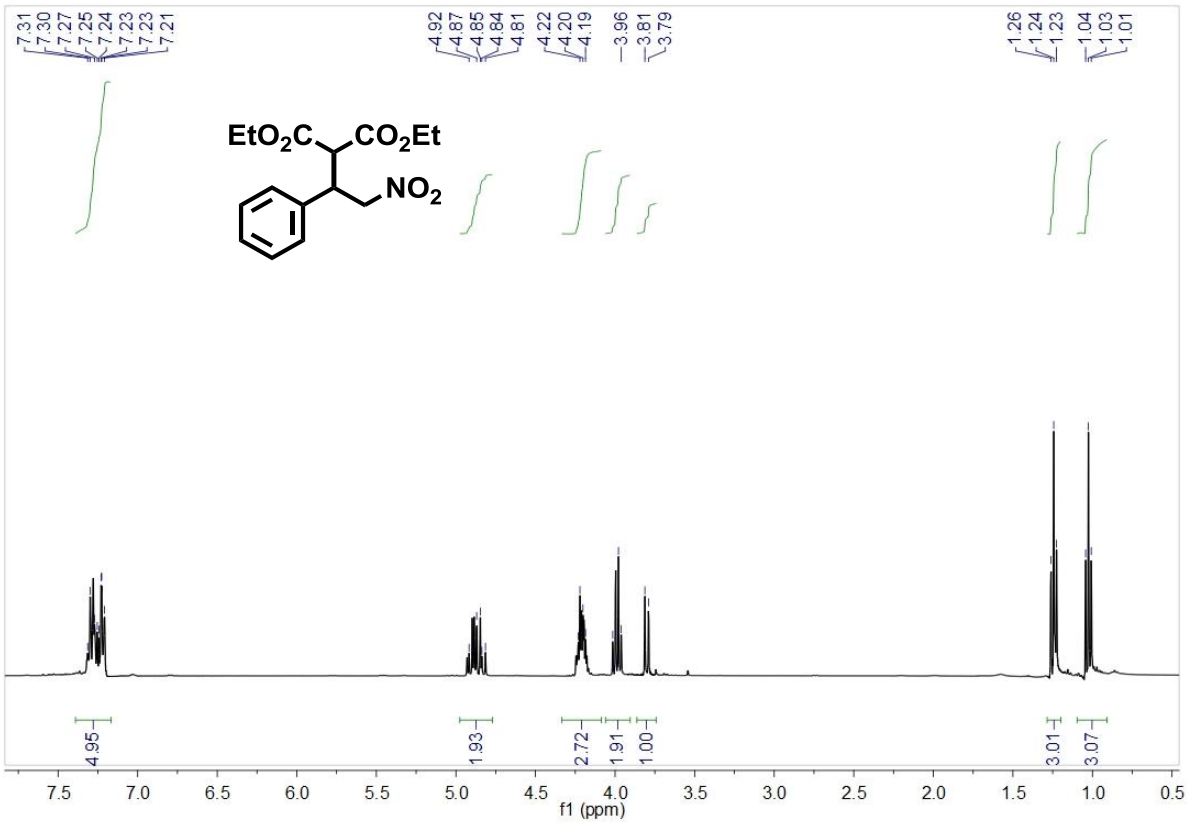
2.00
0.99
1.00
1.00
0.99
2.99
2.96
f1 (ppm)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7.30
7.27
7.25
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7.23
7.23
7.21
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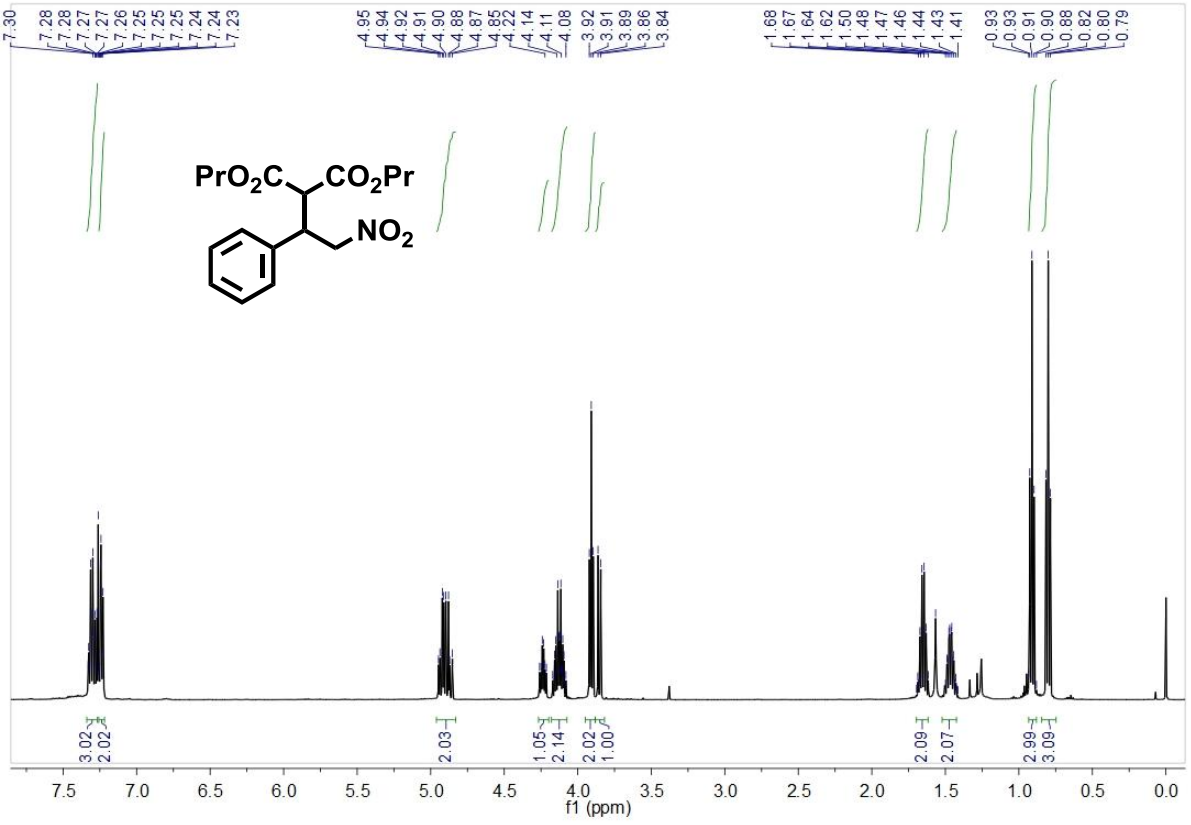
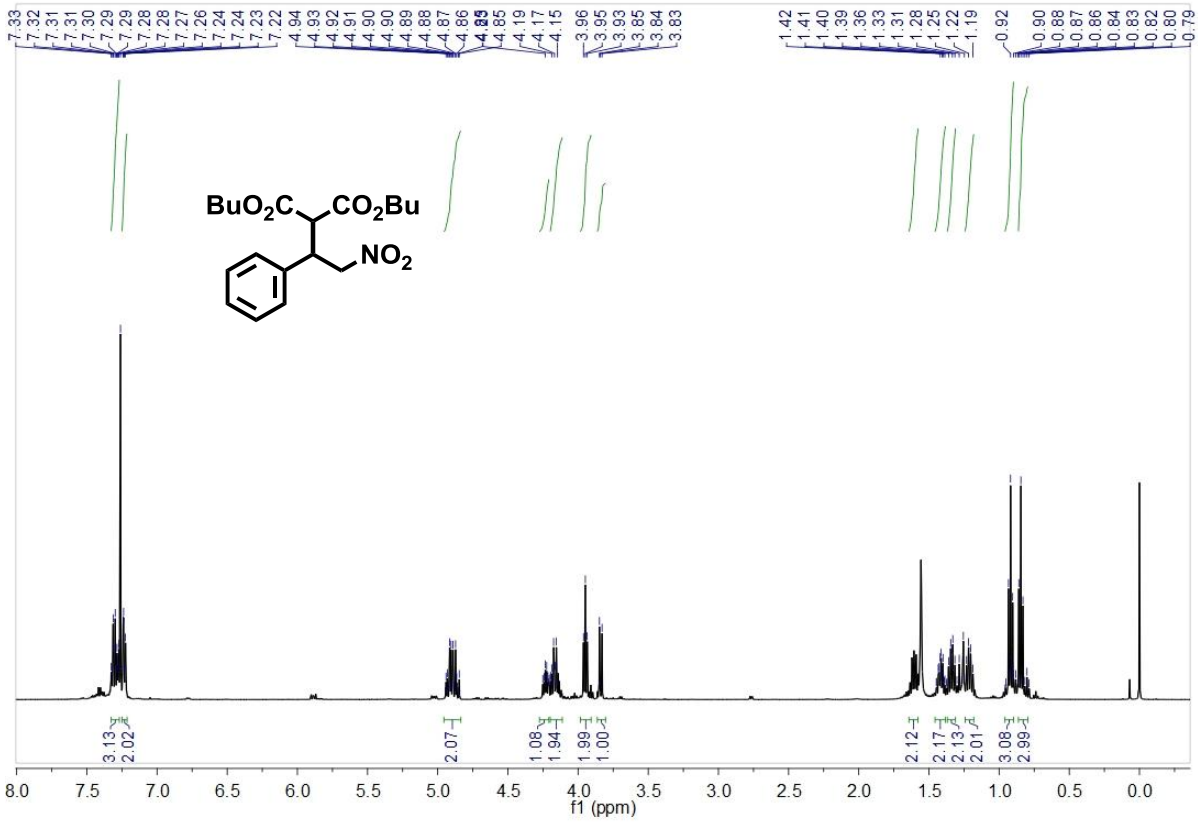
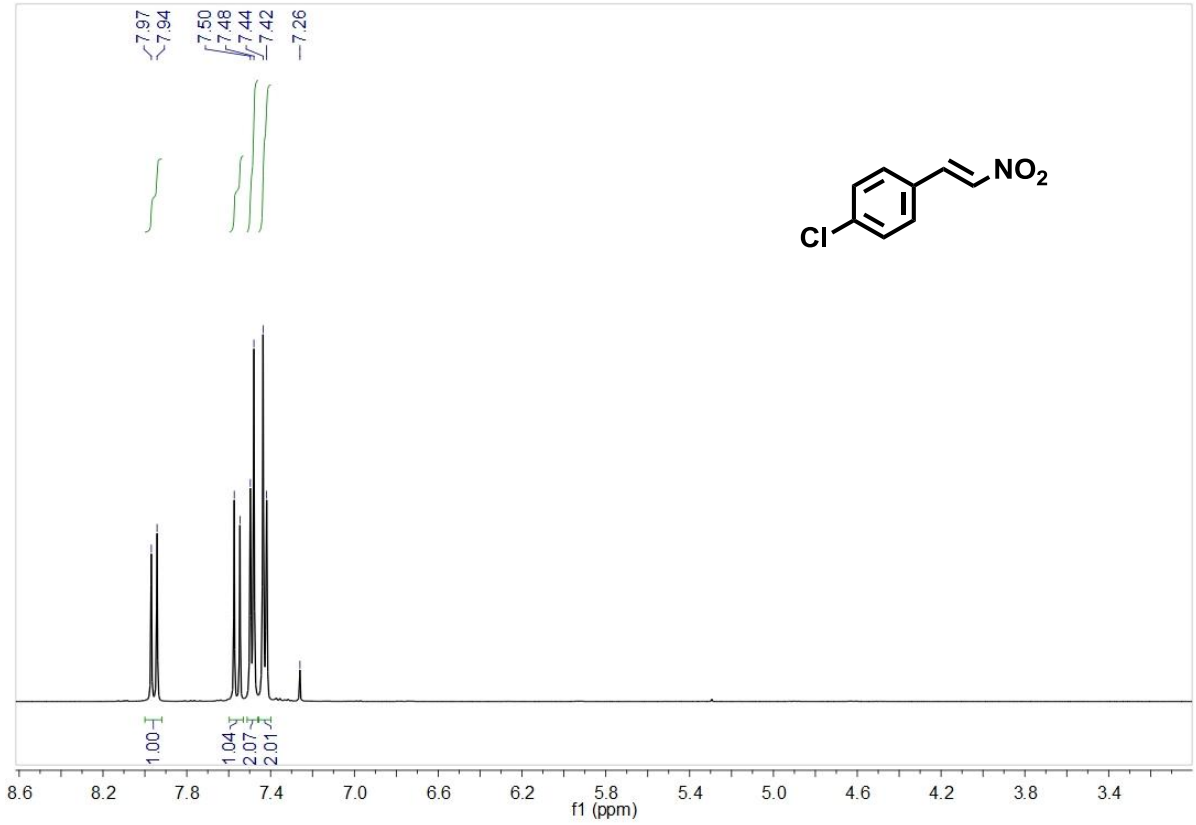
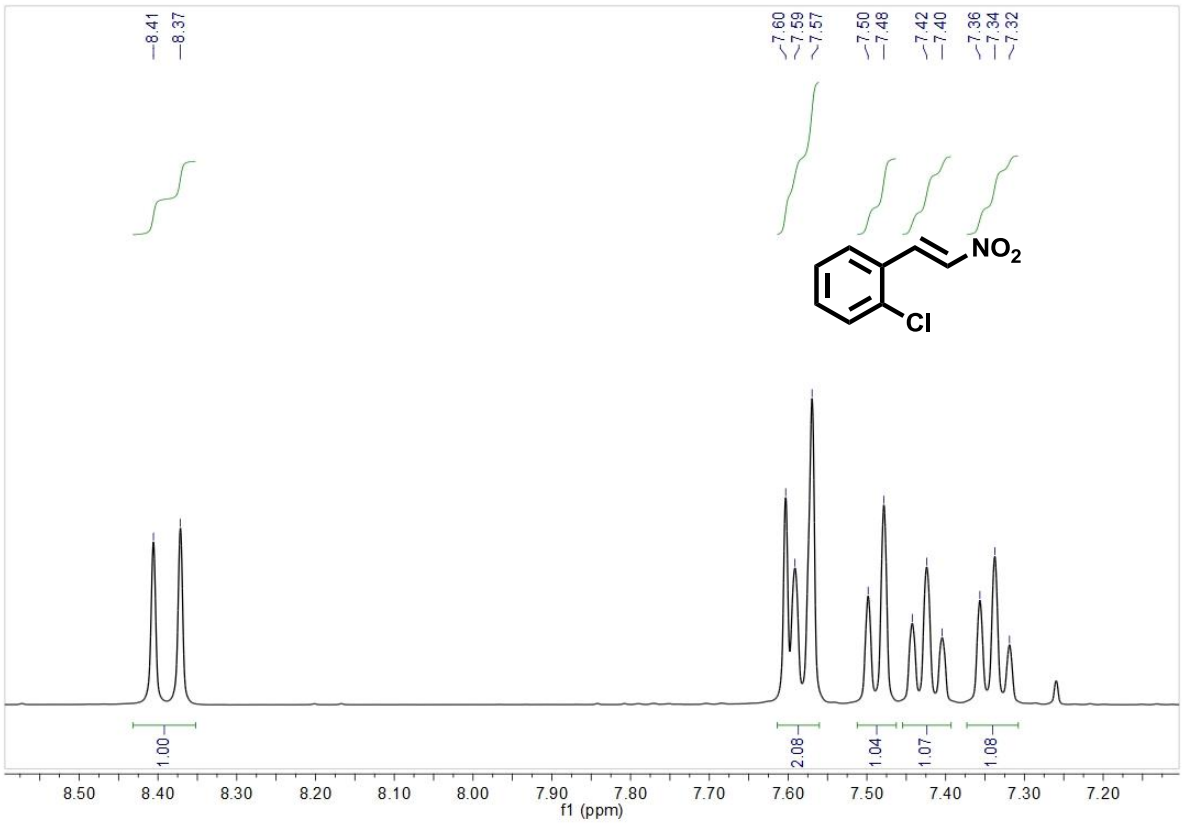
4.87
4.85
4.84
4.81
4.22
4.20
4.19
3.96
3.81
3.79
1.26
1.24
1.23
1.04
1.03
1.01
EtO2C
CO2Et
NO2
4.95
1.93
2.72
1.91
1.00
3.01
3.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


7.30
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.24
7.23
4.95
4.94
4.92
4.91
4.90
4.88
4.87
4.85
4.22
4.14
4.11
4.08
3.92
3.91
3.89
3.86
3.84
1.68
1.67
1.64
1.62
1.50
1.48
1.47
1.46
1.44
1.43
1.41
0.93
0.93
0.91
0.90
0.88
0.82
0.80
0.79
PrO2C
CO2Pr
NO2
3.02
2.02
2.03
1.05
2.14
2.02
1.00
2.09
2.07
2.99
3.09
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)


BuO2C
CO2Bu
NO2
f1 (ppm)


NO2
Cl
f1 (ppm)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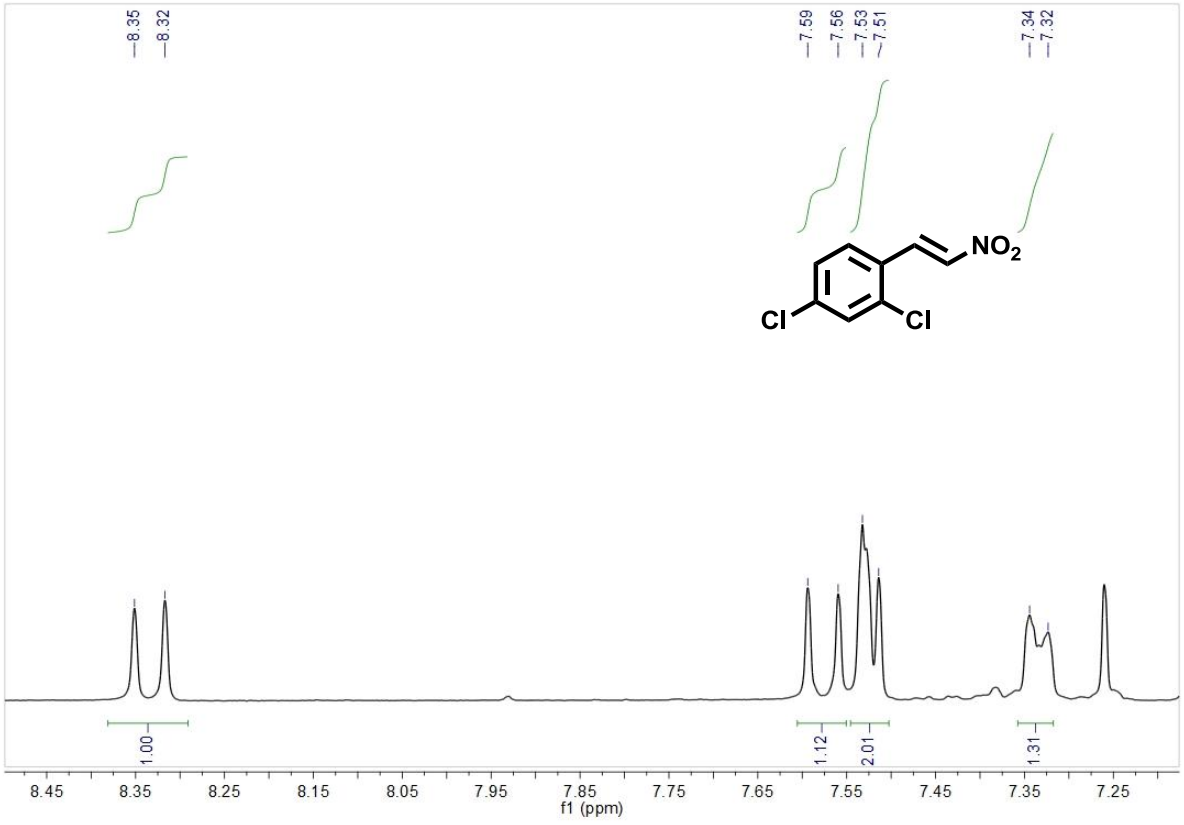
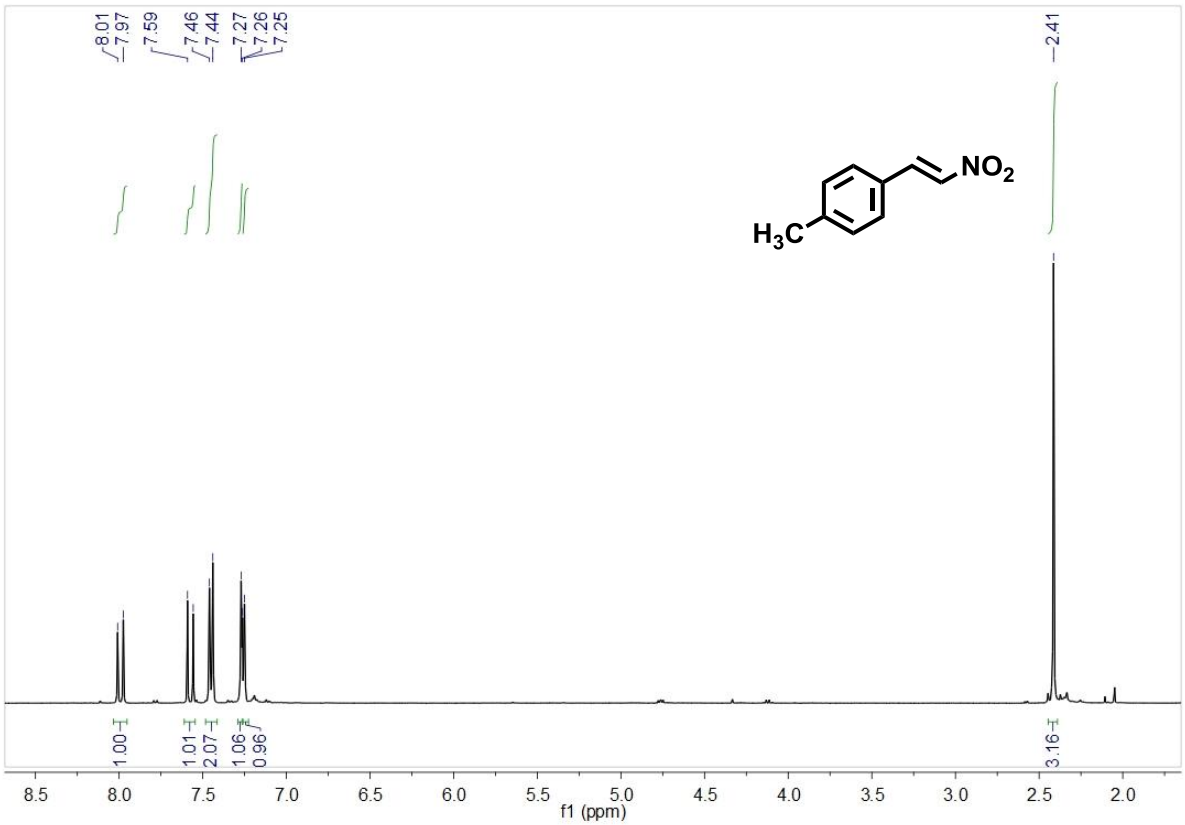
8.37
7.60
7.59
7.57
7.50
7.48
7.42
7.40
7.36
7.34
7.32
NO2
Cl
1.00
2.08
1.04
1.07
1.08
8.50
8.40
8.30
8.20
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
f1 (ppm)


8.35
8.32
7.59
7.56
7.53
7.51
7.34
7.32
NO2
Cl
Cl
1.00
1.12
2.01
1.31
8.45
8.35
8.25
8.15
8.05
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)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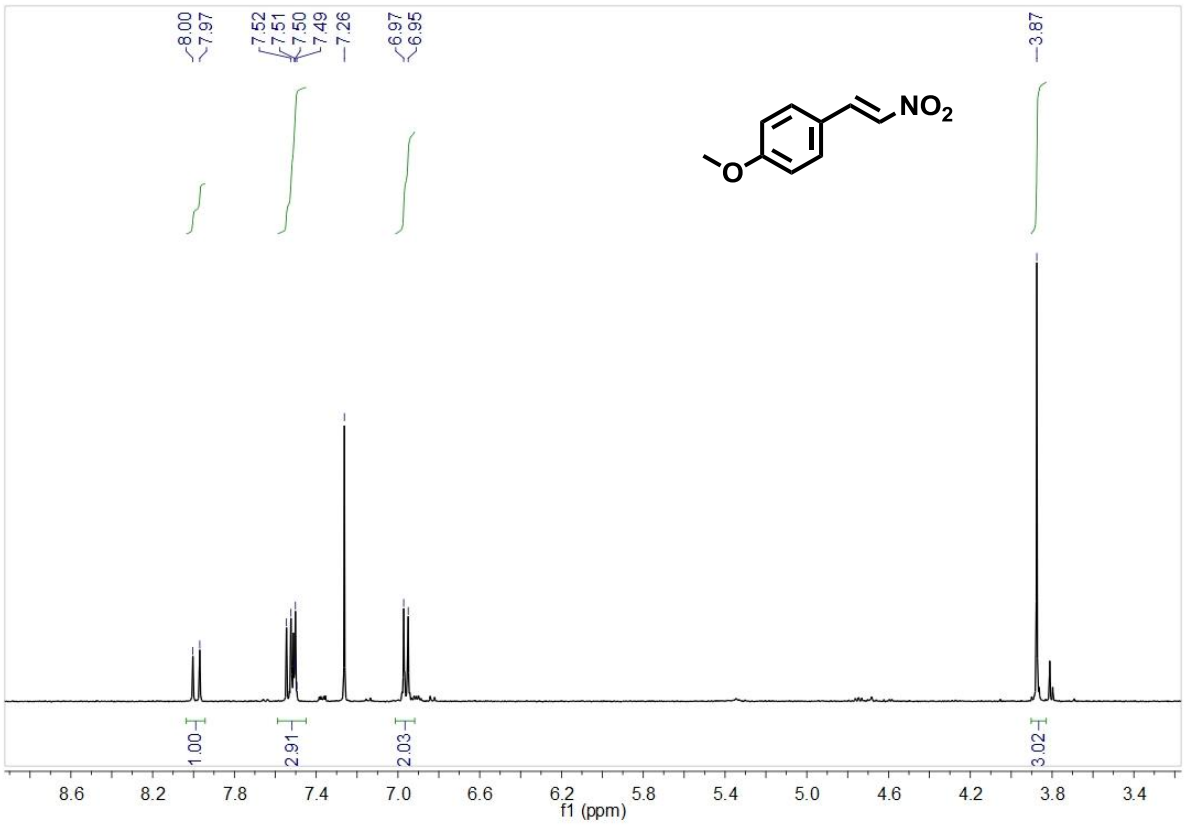
7.97
7.59
7.46
7.44
7.27
7.26
7.25
2.41
NO2
H3C
1.00
1.01
2.07
1.06
0.96
3.16
f1 (ppm)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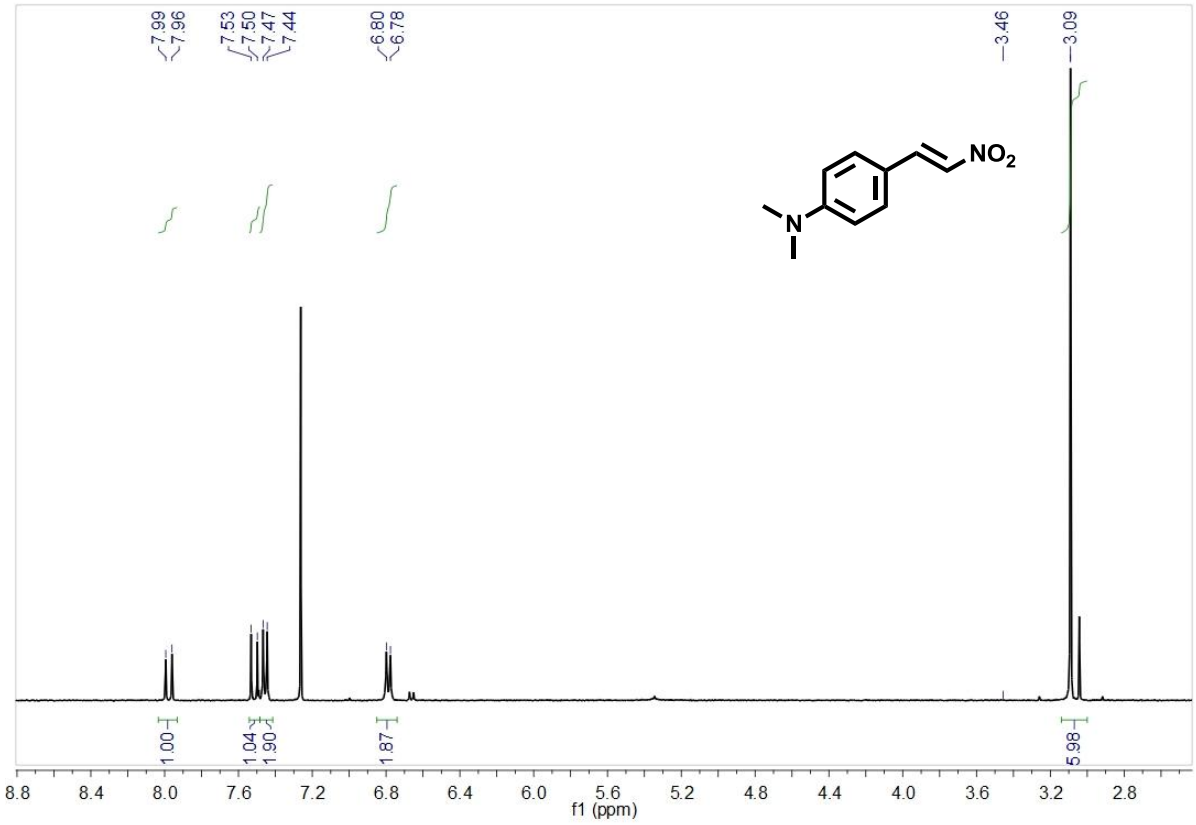
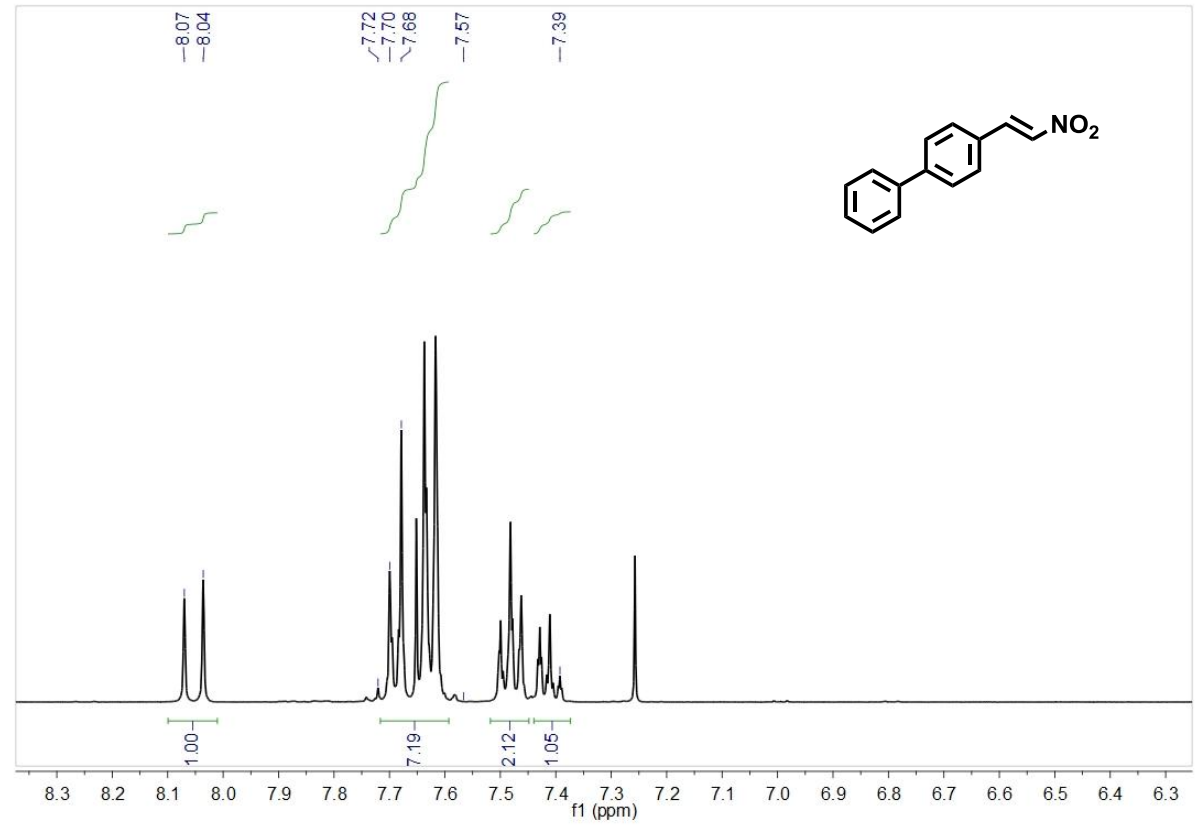
7.97
7.52
7.51
7.50
7.49
7.26
6.97
6.95
3.87
NO2
O
1.00
2.91
2.03
3.02
f1 (ppm)


7.99
7.96
7.53
7.50
7.47
7.44
6.80
6.78
3.46
3.09
NO2
N
1.00
1.04
1.90
1.87
5.98
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
f1 (ppm)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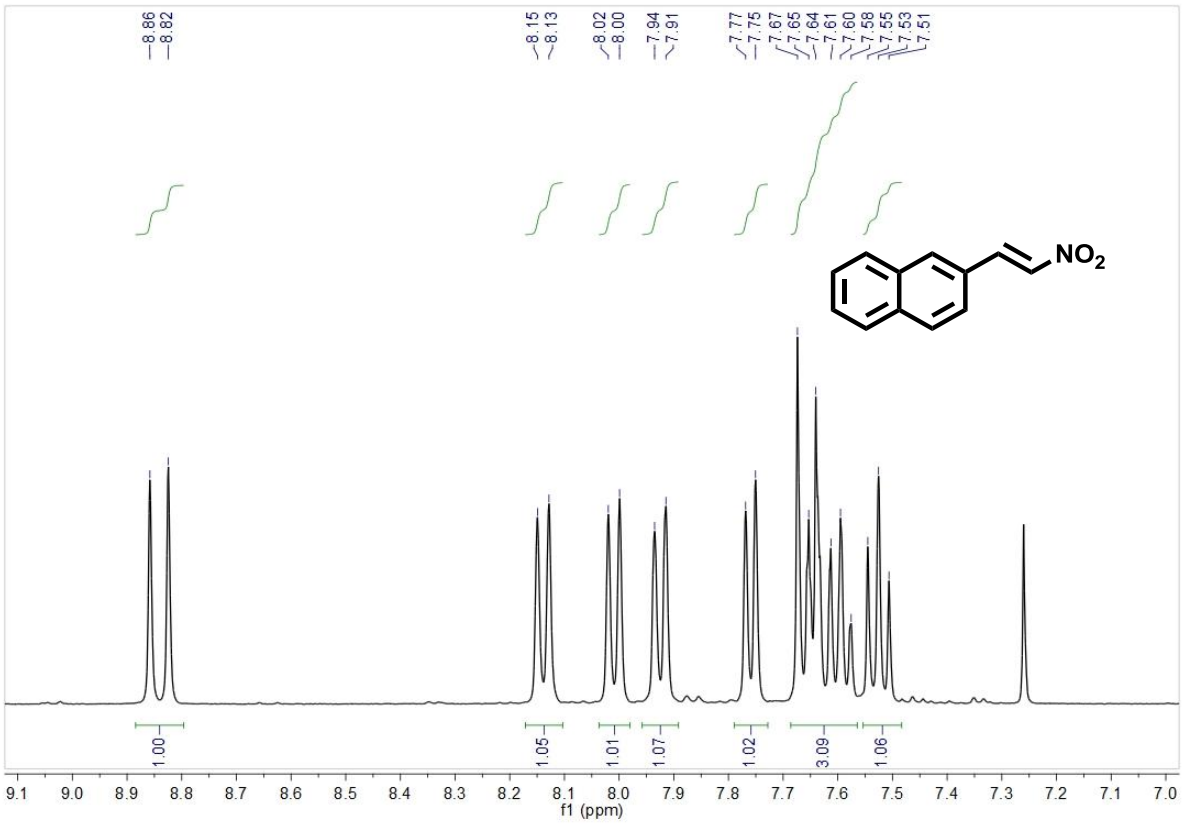
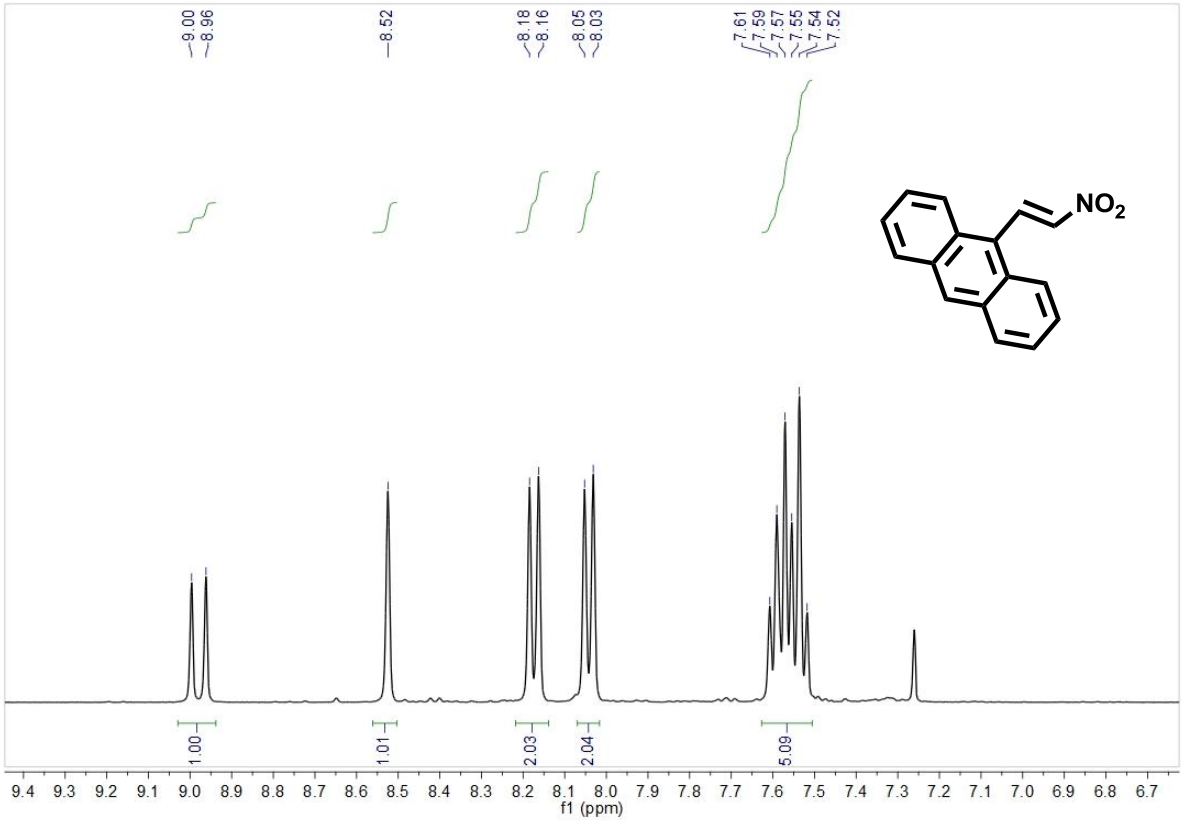
8.04
7.72
7.70
7.68
7.57
7.39
NO2
1.00
7.19
2.12
1.05
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
f1 (ppm)


8.86
8.82
8.15
8.13
8.02
8.00
7.94
7.91
7.77
7.75
7.67
7.65
7.64
7.61
7.60
7.58
7.55
7.53
7.51
NO2
1.00
1.05
1.01
1.07
1.02
3.09
1.06
f1 (ppm)


9.00
8.96
8.52
8.18
8.16
8.05
8.03
7.61
7.59
7.57
7.55
7.54
7.52
NO2
1.00
1.01
2.03
2.04
5.09
f1 (ppm)