Electronic Supplementary Information

Palladium(II) ligated with selenated NHC based (Se,C_{NHC},N^-) type pincer: An efficient catalyst for Mizoroki-Heck and Suzuki Miyaura Coupling in water

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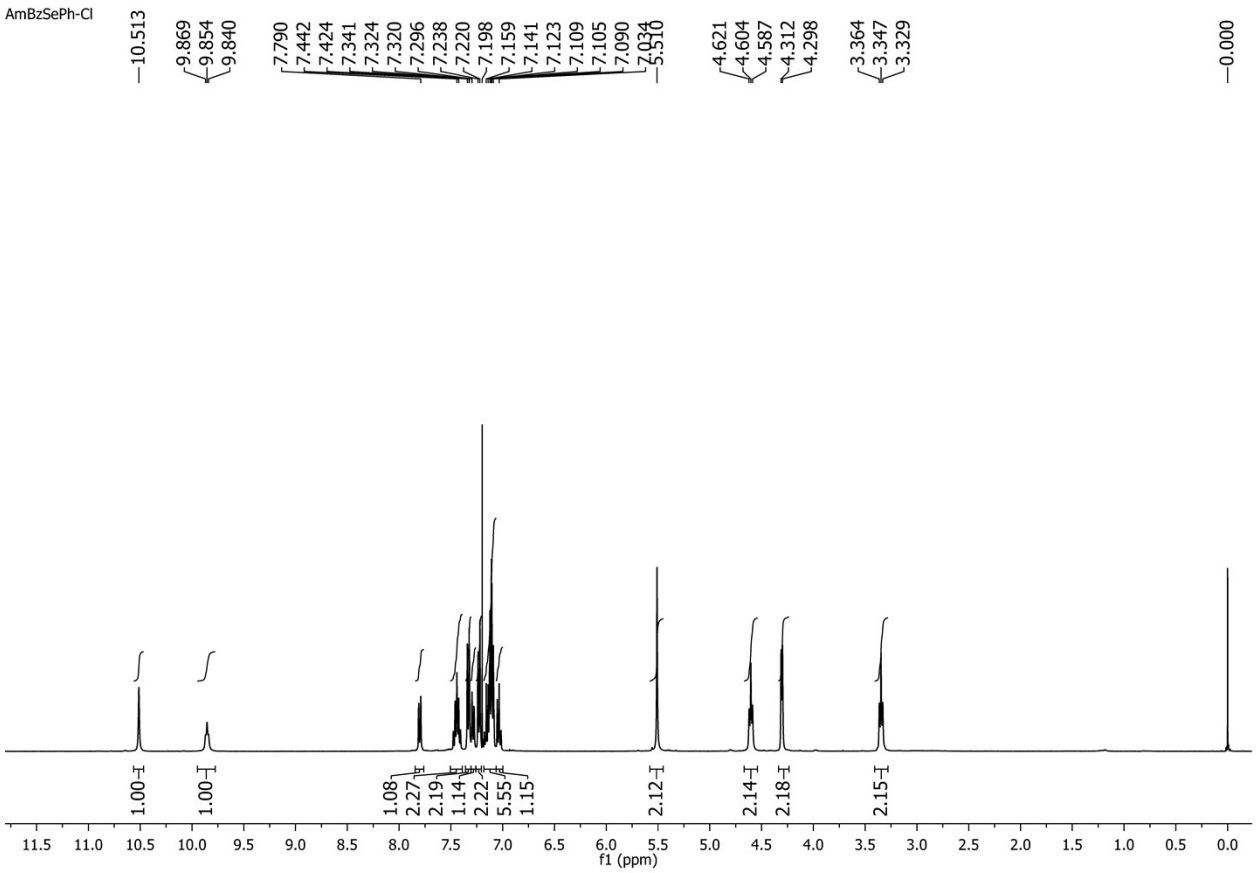


Figure S1. ^{1}H NMR of 1-[*N*-benzylacetamido]-3-[1-(2-phenylselenylethyl)]-benzimidazolium chloride (**L**) in $CDCl_3$.

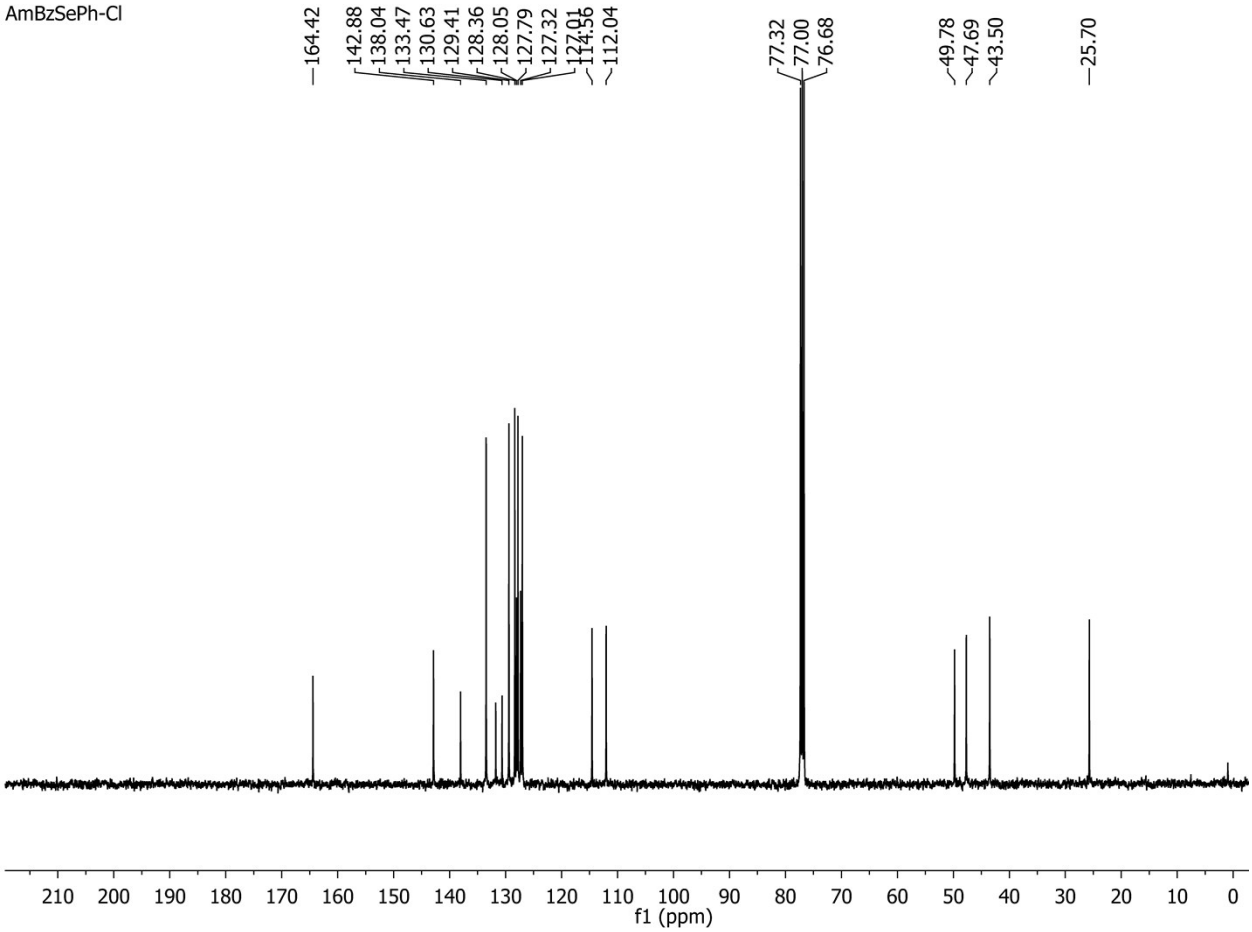


Figure S2. $^{1}H\{^{13}C\}$ NMR of 1-[*N*-benzylacetamido]-3-[1-(2-phenylselenylethyl)]-benzimidazolium chloride (**L**) in $CDCl_3$.

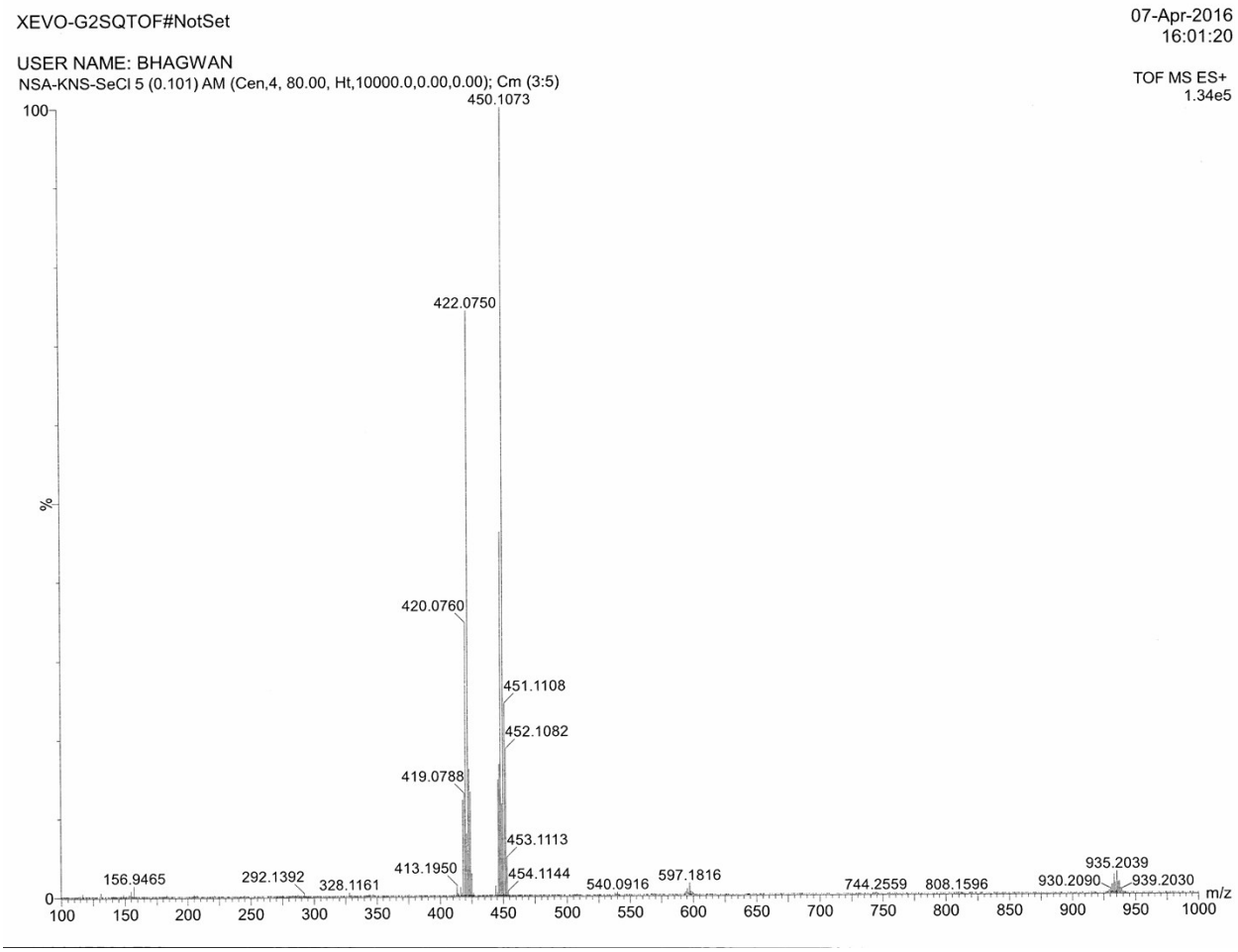


Figure S3. Mass spectrum of 1-[*N*-benzylacetamido]-3-[1-(2-phenylselenylethyl)]-benzimidazolium chloride (**L**).

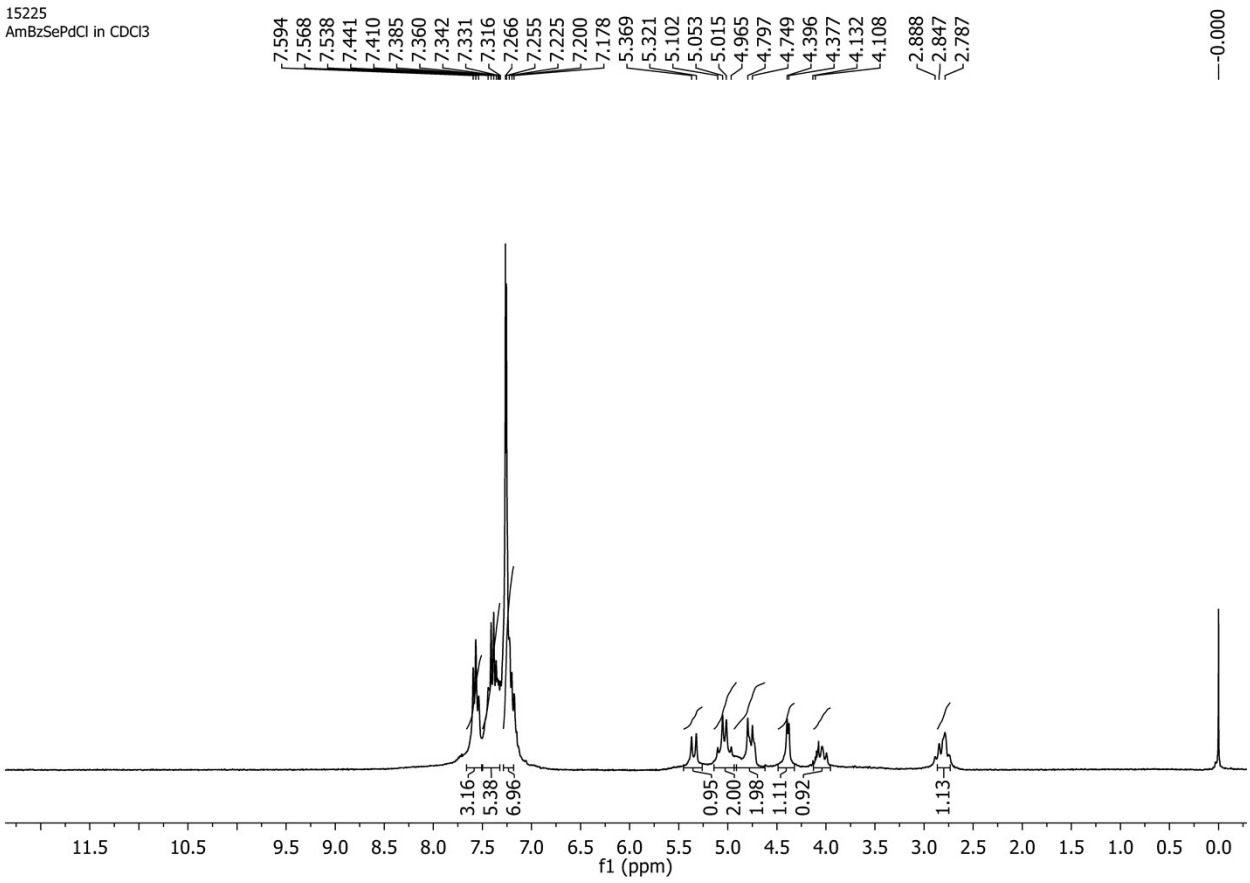


Figure S4. ^{1}H NMR of palladium(II) complex (**1**) in $CDCl_3$.

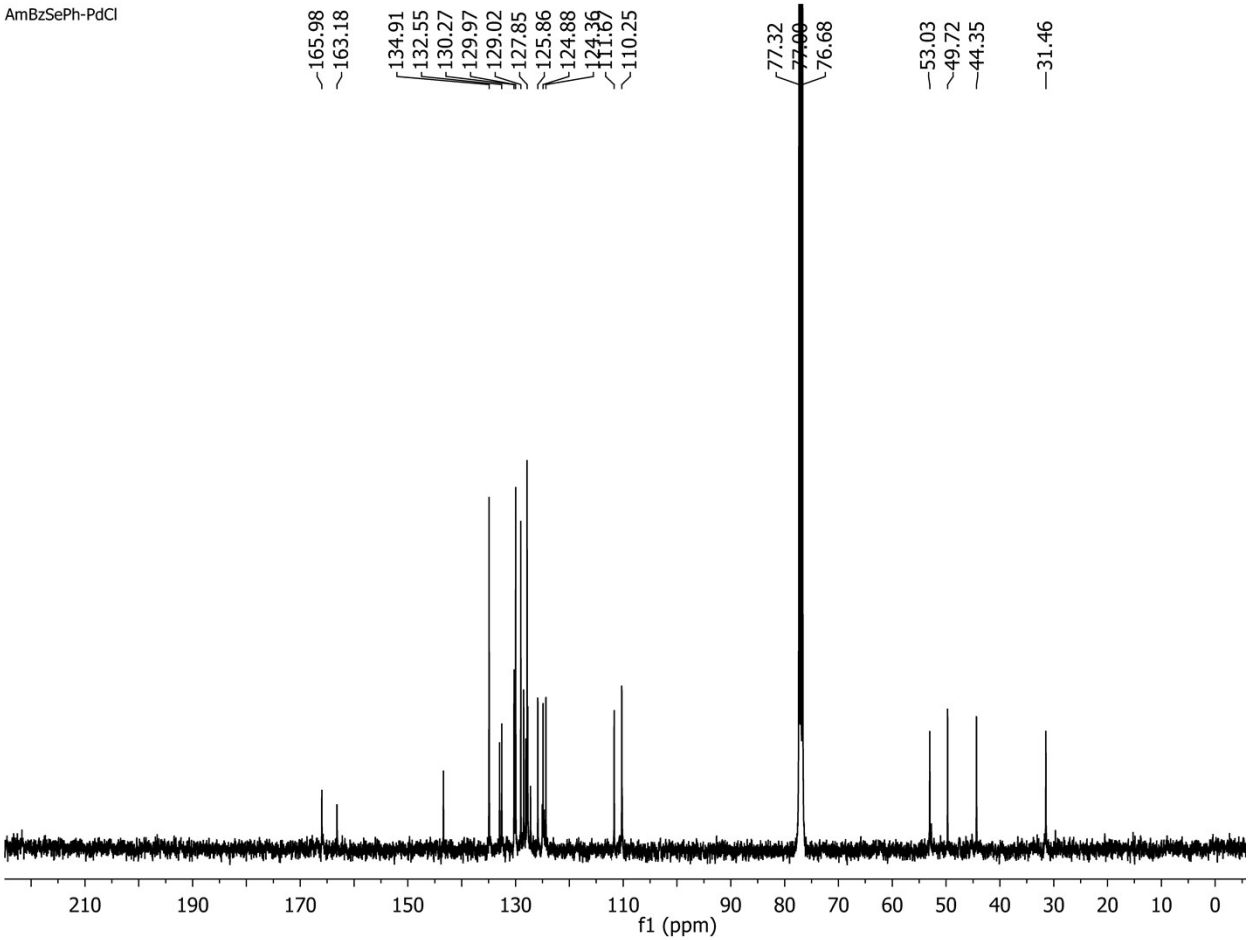


Figure S5. $^{1}H\{^{13}C\}$ NMR of palladium(II) complex (**1**) in $CDCl_3$.

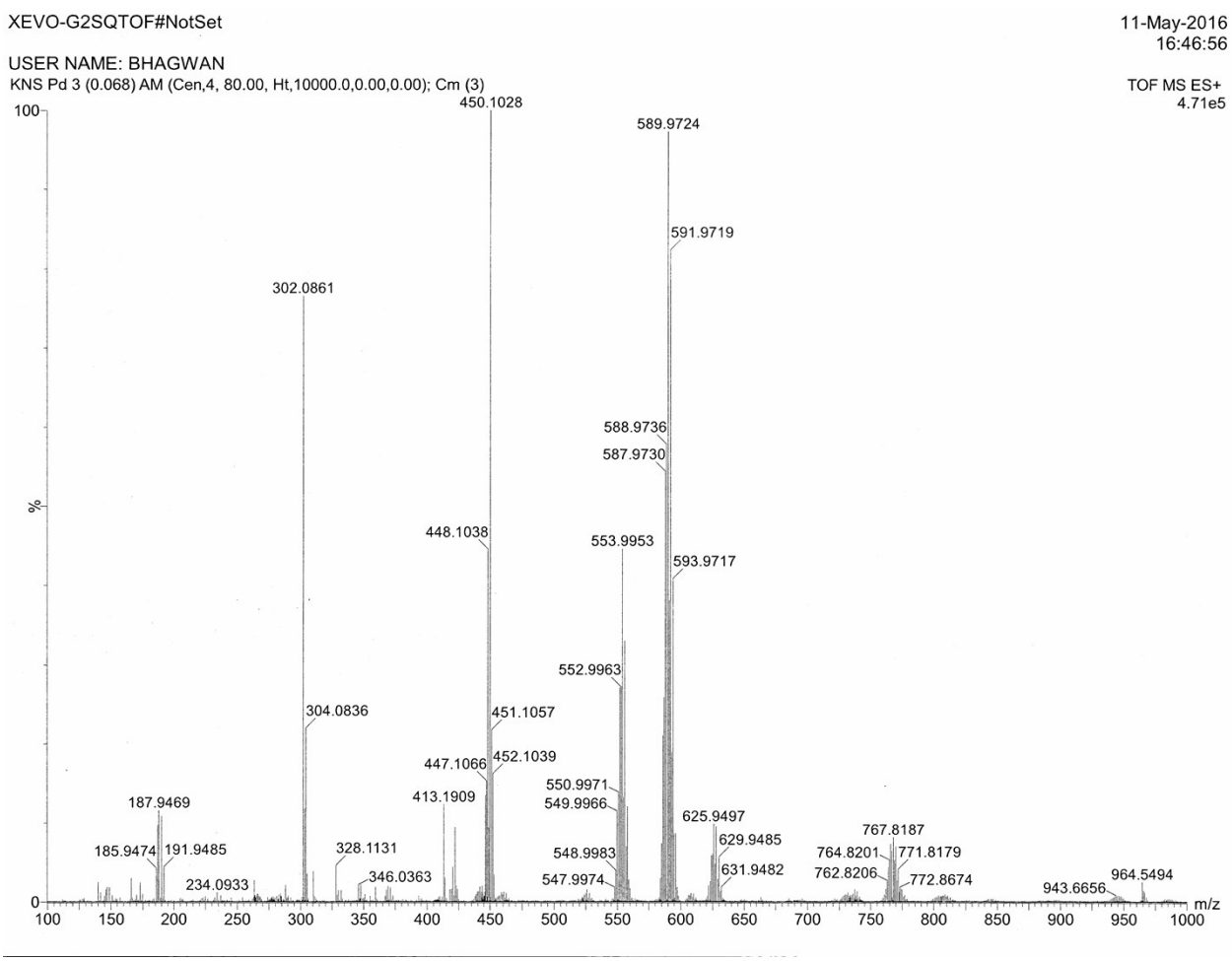


Figure S6. Mass spectrum of palladium complex (**1**).

Table S1. Crystal Data and Structural Refinement Parameters for 1

Compound	Complex **1**
Empirical formula	$C_{24}H_{36}ClN_3OPdSe$
Formula Wt.	603.37
Crystal size [mm]	0.31×0.24×0.18
Crystal system	Trigonal
Space group	R−3
Unit cell dimension	*a* = 27.3190(6)Å *b* = 27.3190(6)Å *c* = 19.5324(4)Å α = 90° β = 90° γ = 120°
Cell volume [Å^3]	12624.5(6)
Z	18
Density (Calc.) [Mg·m^{-3}]	1.429
Absorption Coeff. [mm^{-1}]	2.073
F(000)	5508
ϑ Range [°]	3.466–24.989
Index ranges	−32≤ *h* ≤ 32 −32≤ *k* ≤ 32 −23≤ *l* ≤ 23
Reflections collected	38573
Independent reflections (R_{int}.)	4927 (0.0628)
Max./Min. transmission	1.000/0.417
Data/restraints/parameters	4927/0/280
Goodness-of-fit on F^2	1.059
Final R indices [*I* >2σ(*I*)]	R_1 = 0.0578, wR_2 = 0.1750
R indices (All Data)	R_1 = 0.0724, wR_2 = 0.1876
Largest diff. peak/hole [e.Å^{-3}]	0.746/–0.664

Table S2. Selected Bond Lengths [Å] and Bond Angles [°] for 1

Bond length [Å]		Bond angle [°]	
Pd(1)—Se(1)	2.4046(8)	C(1)—Pd(1)—N(1)	85.5(2)
Pd(1)—C(1)	1.935(6)	C(1)—Pd(1)—Cl(1)	175.61(18)
Pd(1)—N(1)	2.026(5)	N(1)—Pd(1)—Cl(1)	93.58(17)
Pd(1)—Cl(1)	2.3710(17)	C(1)—Pd(1)—Se(1)	92.73(17)
Se(1)—C(5)	1.961(6)	N(1)—Pd(1)—Se(1)	177.45(15)
Se(1)—C(19)	1.932(7)	Cl(1)—Pd(1)—Se(1)	88.31(5)
N(1)—C(3)	1.292(10)	C(19)—Se(1)—C(5)	95.9(3)
N(1)—C(12)	1.484(9)	C(19)—Se(1)—Pd(1)	103.8(2)
N(2)—C(1)	1.336(8)	C(5)—Se(1)—Pd(1)	105.8(2)
N(3)—C(1)	1.364(7)	N(2)—C(1)—N(3)	107.6(5)
O(1)—C(3)	1.273(9)	N(2)—C(1)—Pd(1)	122.3(4)
C(3)—C(2)	1.533(10)	N(3)—C(1)—Pd(1)	130.1(5)
C(2)—N(2)	1.458(8)	C(3)—N(1)—C(12)	118.3(6)
C(5)—C(4)	1.505(10)	C(3)—N(1)—Pd(1)	124.7(5)
C(4)—N(3)	1.467(8)	C(12)—N(1)—Pd(1)	116.9(5)

Optimization of the reaction conditions for Heck coupling:

Table S3. Solvent Standardization for Mizoroki-Heck Coupling Catalyzed by 1

Entry	Base	Solvent	**1** (mol%)	Yield (%)
1	K_3PO_4	Water	0.2	94
2	K_3PO_4	DMF-water	0.2	94
3	K_3PO_4	DMF	0.2	75
4	K_3PO_4	DMSO	0.2	62
5	K_3PO_4	Dioxane	0.2	55

Reaction conditions: 4-Bromoacetophenone (0.199 g, 1.0 mmol), styrene (0.156 g, 1.5 mmol), K_3PO_4 (0.319 g, 1.5 mmol), TBAB (0.5 mmol), catalyst (0.002 mmol, 0.2 mol%), solvent (1.5 mL), Temp 120 °C, time 12 h and yields (isolated after purification).

Table S4. Optimization of catalyst loading for Mizoroki-Heck coupling catalyzed by **1**

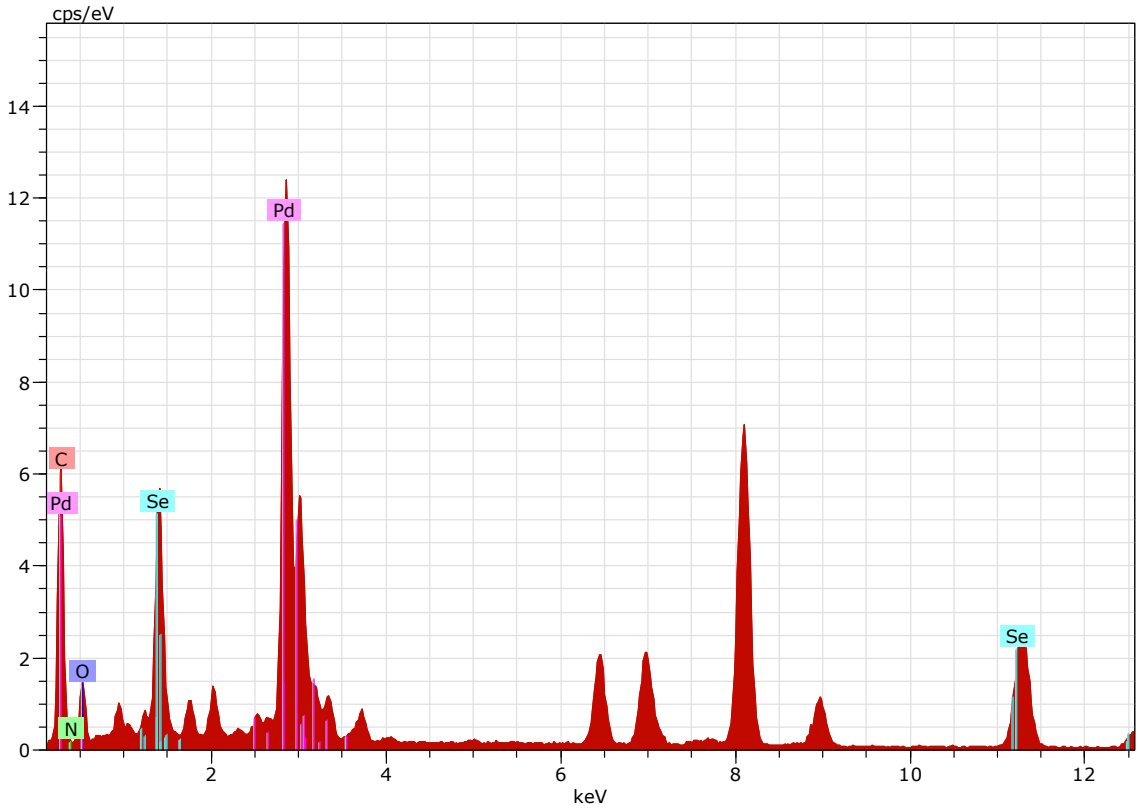
Entry	Base	Solvent	**1** (mol %)	Yield (%)
1	K_3PO_4	Water	0.2	94
2	K_3PO_4	Water	0.1	45
3	K_3PO_4	Water	0.05	24
4	K_3PO_4	Water	0.01	Trace

Reaction conditions: 4-bromoacetophenone (0.199 g, 1.0 mmol), styrene (0.156 g, 1.5 mmol), K_3PO_4 (0.319 g, 1.5 mmol), TBAB (0.161 g, 0.5 mmol), water (1.5 mL), Temp 120 °C, time 12 h and yields (isolated after purification).

Table S5. Base standardization for Mizoroki-Heck coupling catalyzed by **1**

Entry	Base	Solvent	**1** (mol %)	Yield (%)
1	-	Water	0.2	nd
2	K_3PO_4	Water	0.2	94
3	K_2CO_3	Water	0.2	82
4	Cs_2CO_3	Water	0.2	84
5	TEA	Water	0.2	78
6	KOH	Water	0.2	74

Reaction conditions: 4-Bromoacetophenone (0.199 g, 1.0 mmol), styrene (0.156 g, 1.5 mmol), base (1.5 mmol), TBAB (0.161 g, 0.5 mmol), water (1.5 mL), Temp 120 °C, time 12 h and yields (isolated after purification), nd (not detected)



Spectrum: Acquisition 669

Element	Series	Net unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Selenium	L-series	14864	17.84	17.84	22.64	5.45
Palladium	L-series	59356	82.16	82.16	77.36	24.76
Total:			100.00	100.00	100.00	

Figure S7. TEM-EDX analysis of in situ generated Pd-Se NPs from **1** during Heck coupling.

Table S6. Comparison of catalytic efficiency of present catalyst 1 with previous NHC based Pd catalytic systems for the Mizoroki-Heck coupling reactions

S. No.	Pd Catalyst	Aromatic halide	Olefins used	Pd mol%	temp/ time	Solvent / atm	Yield (%)	Ref
1	NHC/Phosphine (mixed) Pd(II)	Bromides	Styrene	1.0-3.0	130 °C/ 12-32 h	DMA N_2	98	[1]
2	Pd(II)-aNHC (PEPPSI-type Pd complex)	iodides, bromides	methyl acrylate	2.0	125 °C	DMF argon	98 (GC yield)	[2]
3	Pd(II) complex bearing ($PC_{NHC}P$) pincer	bromides	styrene, *n*-butyl acrylate	0.5	165 °C 1-20 h	DMA N_2	94	[3]
4	$PdCl_2(CH_3CN)_2$ and hydrazone as ligand	chlorides	styrene, *n*-butyl acrylate	5.0	120 °C 24-48 h	NMP argon	69	[4]
5	β-Diketiminatop-hosphane Pd Catalyst	chlorides	styrene, ethyl acrylate	1.0	100 °C 2-15 h	DMF-water air	94	[5]
6	$Pd(OAc)_2$ and Dave-Phos (6 mol%)	chlorides	styrene, alkyl acrylates	2.0	80 °C 24 h	1,4-dioxane argon	98	[6]
7	Pd(OAc) and NHC Ligand (0.05 mol%)	chlorides	styrene, *n*-butyl acrylate	0.025	135 °C 1-7 h	DMF air	62	[7]
8	Pd-NHC complex	bromides	*n*-butyl acrylate	5.0	150°C 30 min.	Ionic liquid argon	95	[8]
9	Pd(0)-phosphine-functionalized NHC	bromides chlorides	styrene, *n*-butyl acrylate	0.5-3.0	140 °C 2 h	neat N_2	94	[9]
10	$Pd(dba)_2$ with 1.0 mol% bis-NHC	iodides, bromides	styrenes, acrylates	1.0	60 °C 24 h	DMF N_2	98	[10]
11	**Pd(II) bearing (Se,C_{NHC},N^-) pincer ligand**	**chlorides**	**styrenes, acrylates**	**0.2**	**100 12 h**	**water air**	**94**	**Present catalyst**

NMR Spectroscopic analysis data of Mizoroki-Heck coupling products

(1) 4-Acetyl-4'-methyl-*trans*-stilbene[11] **(Table 1, Entry 1a/1b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.54 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.42 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.06 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.58 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 197.4, 142.1, 138.3, 135.6, 133.8, 131.3, 129.4, 126.7, 126.3, 126.2, 26.5, 21.2.

(2) 4'-Methyl-*trans*-4-stilbenecarboxaldehyde[6] **(Table 1, Entry 2a/2b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.97 (s, 1H), 7.83 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.61 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.43 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.07 (d, $^3J_{H-H}$ = 16.4 Hz, 2H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 191.6, 143.6, 138.5, 135.1, 133.7, 132.1, 130.2, 129.5, 126.8, 126.7, 126.2, 21.2.

(3) 4'-Methyl-*trans*-4-nitrostilbene[12] **(Table 1, Entry 3a/3b).** Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.58 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.43 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.06 (d, 1H, $^3J_{H-H}$ = 16.4 Hz), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 146.5, 144.0, 139.0, 133.3, 133.2, 129.6, 126.9, 126.6, 125.2, 124.1, 21.3.

(4) 4'-Methyl-*trans*-4-stilbenecarbonitrile[13] **(Table 1, Entry 4a/4b).** ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.46 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.34 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.121 – 7.071 (m, 3H), 6.945 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 142.0, 138.7, 133.4, 132.4, 132.3, 129.5, 126.8, 126.7, 125.6, 119.1, 110.2, 21.3.

(5) 4'-Methyl-*trans*-4-stilbenecarboxylic acid (Table 1, Entry 5a/5b). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.90 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.67 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.51 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.34 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 7.24 (d, $^3J_{H-H}$ = 16.4 Hz, 2H), 7.18 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 2.29 (s, 3H).

(6) 4-(trifluoromethyl)-4'-methyl-*trans*-stilbene[14] **(Table 1, Entry 6a/6b).** White solid ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 – 7.53 (m, 4H), 7.40 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.18 – 7.12 (m, 3H), 7.04 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 141.1, 138.3, 134.0, 131.2, 129.5, 126.7, 126.4, 126.2, 125.6–125.5 (m), 21.3.

(7) 4-Methyl-*trans*-stilbene[6] **(Table 1, Entry 7a/7b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (d, $^3J_{H-H}$ = 7.6 Hz, 2H), 7.42 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.35 (t, $^3J_{H-H}$ = 7.6 Hz, 2H), 7.25 (t, $^3J_{H-H}$ = 7.3 Hz, 1H), 7.17 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 7.08 (d, $^3J_{H-H}$ = 2.3 Hz, 2H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 137.51, 137.48, 134.51, 129.38, 128.63, 128.58, 127.66, 127.39, 126.40, 126.37, 21.25.

(8) 4,4'-Dimethyl-*trans*-stilbene[12] **(Table 1, Entry 8a/8b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37 (d, $^3J_{H-H}$ = 8.0 Hz, 4H), 7.123 (d, $^3J_{H-H}$ = 8.0 Hz, 4H), 7.007 (s, 2H), 2.33 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 137.2, 134.9, 129.3, 127.7, 126.3, 21.2.

(9) 4-Methoxy-4'-methyl-*trans*-stilbene[12] **(Table 1, Entry 9a/9b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.31 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.08 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 6.93 – 6.81 (m, 4H), 3.75 (s, 3H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 137.1, 134.9, 130.4, 129.5, 127.8, 127.7, 127.3, 126.6, 126.3, 114.2, 55.4, 21.3.

(10) (*E*)-2-(4-Methylstyryl)pyridine[15] **(Table 1, Entry 12a/12b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.595 (d, $^3J_{H-H}$ = 4.4 Hz, 1H), 7.675 – 7.632 (m, 1H), 7.483 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.379 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.196 – 7.177 (m, 2H), 7.150 – 7.110 (m, 2H), 2.369 (s, 3H). $^{13}C\{^1H\}$

NMR (101 MHz, $CDCl_3$) δ (ppm) 155.8, 149.6, 138.4, 136.5, 133.9, 132.7, 129.4, 127.0, 126.9, 121.9, 121.8, 21.3.

(11) (*E*)-3-(4-Methylstyryl)pyridine[16] **(Table 1, Entry 11a/11b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 – 8.69 (m, 1H), 8.47 – 8.45 (m, 1H), 7.82 – 7.79 (m, 1H), 7.42 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.18 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.13 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 7.00 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 148.4, 148.2, 138.2, 133.8, 133.1, 132.5, 130.7, 129.4, 126.5, 123.8, 123.5, 21.2.

(12) (*E*)-3-(4-Methylstyryl)quinoline (Table 1, Entry 12). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.08 – 9.07 (m, 1H), 8.08 – 8.06 (m, 2H), 7.76 – 7.73 (m, 1H), 7.65 – 7.61 (m, 1H), 7.51 – 7.47 (m, 1H), 7.43 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.25 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 7.17 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.12 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 149.3, 147.2, 138.1, 133.8, 131.9, 130.7, 130.3, 129.4, 129.1, 128.9, 128.0, 127.7, 126.8, 126.5, 124.0, 21.2.

(13) (*E*)-5-(4-Methylstyryl)pyrimidine (Table 1, Entry 13). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.07 (s, 1H), 8.85 (s, 2H), 7.43 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.23 – 7.19 (m, 3H), 6.94 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 156.9, 154.1, 139.0, 133.2, 132.7, 131.2, 129.6, 126.8, 120.0, 99.9, 21.3.

(14) (*E*)-2-(4-Methylstyryl)thiophene[17] **(Table 1, Entry 14a/14b).** Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.19 – 7.09 (m, 4H), 7.03 (d, $^3J_{H-H}$ = 3.2 Hz, 1H), 6.99 – 6.96 (m, 1H), 6.89 (d, $^3J_{H-H}$ = 16.0 Hz, 1H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 143.1, 137.5, 134.1, 129.4, 128.3, 127.5, 126.2, 125.7, 124.0, 120.8, 21.2.

(15) (*E*)-3-(4-Methylstyryl)thiophene[16] **(Table 1, Entry 15a/15b).** Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39 – 7.34 (m, 3H), 7.32 – 7.30 (m, 1H), 7.24 – 7.23 (m, 1H), 7.16 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.08 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 6.93 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 140.3, 137.3, 134.5, 129.4, 128.63, 128.58, 126.2, 126.1, 124.9, 121.9, 21.2.

(16) *trans*-Stilbene[6] **(Table 2, Entry 1a/1b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (dd, $^3J_{H-H}$ = 5.1, 3.4 Hz, 2H, 7.39 – 7.35 (m, 2H), 7.31 – 7.24 (m, 1H), 7.13 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 137.3, 128.7, 127.6, 126.5.

(17) 4-Acetyl-*trans*-stilbene[6] **(Table 2, Entry 2a/2b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.55 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.52 (d, $^3J_{H-H}$ = 7.2 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.30 – 7.27 (m, 1H), 7.20 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 7.10 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 2.58 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 197.4, 141.9, 136.6, 135.8, 131.3, 128.8, 128.7, 128.2, 127.3, 126.7, 126.4, 26.5.

(18) *trans*-4-Nitrostilbene[6] **(Table 2, Entry 3a/3b).** Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.61 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.54 (d, $^3J_{H-H}$ = 7.6 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.35 – 7.32 (m, 1H), 7.25 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 7.12 (d, $^3J_{H-H}$ = 16.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 146.7, 143.8, 136.1, 133.2, 128.8, 128.7, 127.0, 126.8, 126.2, 124.1.

(19) *trans*-4-Stilbenecarbonitrile[6] **(Table 2, Entry 4a/4b).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 – 7.62 (m, 2H), 7.59 – 7.56 (m, 2H), 7.54 – 7.52 (m, 2H), 7.41 – 7.37 (m, 2H), 7.34 – 7.32 (m, 1H), 7.21 (d, $^3J_{H-H}$ = 16.4 Hz, 1H), 7.09 (d, $^3J_{H-H}$ = 16.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 141.7, 136.2, 132.4, 132.3, 128.8, 128.6, 126.8, 126.7, 126.6, 119.0, 110.4.

(20) *n*-Butyl cinnamate[12] **(Table 2, Entry 6a/6b).** Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.669 (d, $^{3}J_{H-H}$ = 16.0 Hz, 1H), 7.500 – 7.491 (m, 2H), 7.347 (bs, 3H), 6.427 (d, $^{3}J_{H-H}$ = 16.0 Hz, 1H), 4.193 (t, $^{3}J_{H-H}$ = 6.5 Hz, 2H), 1.707 – 1.637 (m, 2H), 1.466 – 1.376 (m, 2H), 0.949 (t, $^{3}J_{H-H}$ = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 166.94, 144.41, 134.31, 130.08, 128.73, 127.91, 118.12, 64.27, 30.64, 19.08, 13.64.

(21) *n*-Butyl (*E*)-3-(4-nitrophenyl)acrylate[4] **(Table 2, Entry 7a/7b).** Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, $^{3}J_{H-H}$ = 8.7 Hz, 2H), 7.64 – 7.59 (m, 3H), 6.49 (d, $^{3}J_{H-H}$ = 16.0 Hz, 1H), 4.15 (t, $^{3}J_{H-H}$ = 6.8 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.40 – 1.31 (m, 2H), 0.88 (t, $^{3}J_{H-H}$ = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 166.0, 148.3, 141.5, 140.5, 128.5, 124.0, 122.5, 64.8, 30.6, 19.0, 13.6.

(22) Ethyl cinnamate[5] **(Table 2, Entry 8a/8b).** Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63 (d, $^{3}J_{H-H}$ = 16.0 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.29 – 7.27 (m, 3H), 6.38 (d, $^{3}J_{H-H}$ = 16.0 Hz, 1H), 4.19 (q, $^{3}J_{H-H}$ = 7.1 Hz, 2H), 1.26 (t, $^{3}J_{H-H}$ = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 166.48, 144.15, 134.07, 129.85, 128.50, 127.69, 117.89, 60.05, 13.97.

NMR Spectroscopic analysis data of Suzuki-Miyaura coupling products

(1) 4-Acetyl-1,1'-biphenyl[18] **(Table 3, Entry 1).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 7.68 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 7.62 (d, $^3J_{H-H}$ = 7.4 Hz, 2H), 7.46 (t, $^3J_{H-H}$ = 7.2 Hz, 2H), 7.40 (d, $^3J_{H-H}$ = 7.0, 1H), 2.63 (s, 3H).

(2) [1,1'-Biphenyl]-4-carbaldehyde[18] **(Table 3, Entry 2).** Light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.03 (s, 1H), 7.93 (d, $^3J_{H-H}$ = 8.3 Hz, 2H), 7.72 (d, $^3J_{H-H}$ = 8.2 Hz, 2H), 7.62 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.45 – 7.40 (m, 3H).

(3) (1,1'-Biphenyl)-4-carbonitrile[18] **(Table 3, Entry 3).** Pale yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 – 7.62 (m, 4H), 7.62 – 7.53 (m, 2H), 7.50 – 7.40 (m, 3H).

(4) 4-Methoxy-1,1'-biphenyl[18] **(Table 3, Entry 4).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 – 7.51 (m, 4H), 7.42 (t, $^3J_{H-H}$ = 7.7 Hz, 2H), 7.31 (dt, $^3J_{H-H}$ = 9.1, 4.2 Hz, 1H), 6.98 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 3.85 (s, 3H).

(5) 4-Nitro-1,1'-biphenyl[18] **(Table 3, Entry 5).** Pale yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.71 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.61 (d, $^3J_{H-H}$ = 7.6 Hz, 2H), 7.54 – 7.40 (m, 3H).

(6) 5-Phenylpyrimidine[18] **(Table 3, Entry 6).** Light tan solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.17 (s, 1H), 8.92 (s, 2H), 7.58 – 7.52 (m, 2H), 7.51 – 7.47 (m, 2H), 7.46 – 7.40 (m, 1H).

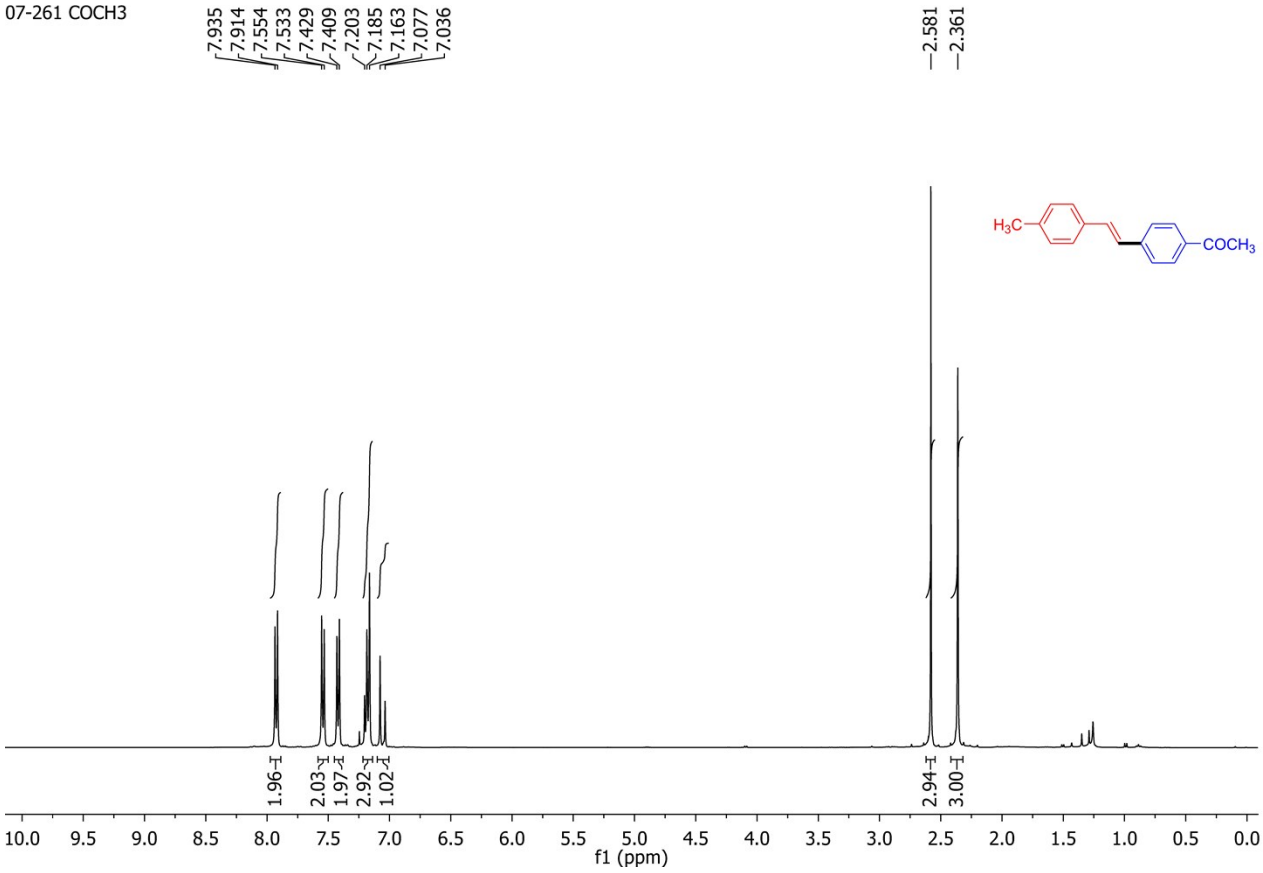
(7) 3-Phenylquinoline[19] **(Table 3, Entry 7).** Light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.17 (d, $^3J_{H-H}$ = 2.1 Hz, 1H), 8.24 (d, $^3J_{H-H}$ = 2.0 Hz, 1H), 8.14 (d, $^3J_{H-H}$ = 8.5 Hz, 1H), 7.82 (d, $^3J_{H-H}$ = 8.1 Hz, 1H), 7.72 – 7.63 (m, 3H), 7.57 – 7.45 (m, 3H), 7.40 (t, $^3J_{H-H}$ = 7.4 Hz, 1H).

(8) 4,4'-dimethyl-1,1'-biphenyl[20] **(Table 3, Entry 8).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 (d, $^3J_{H-H}$ = 8.1 Hz, 4H), 7.38 (d, $^3J_{H-H}$ = 8.3 Hz, 4H), 2.54 (s, 6H).

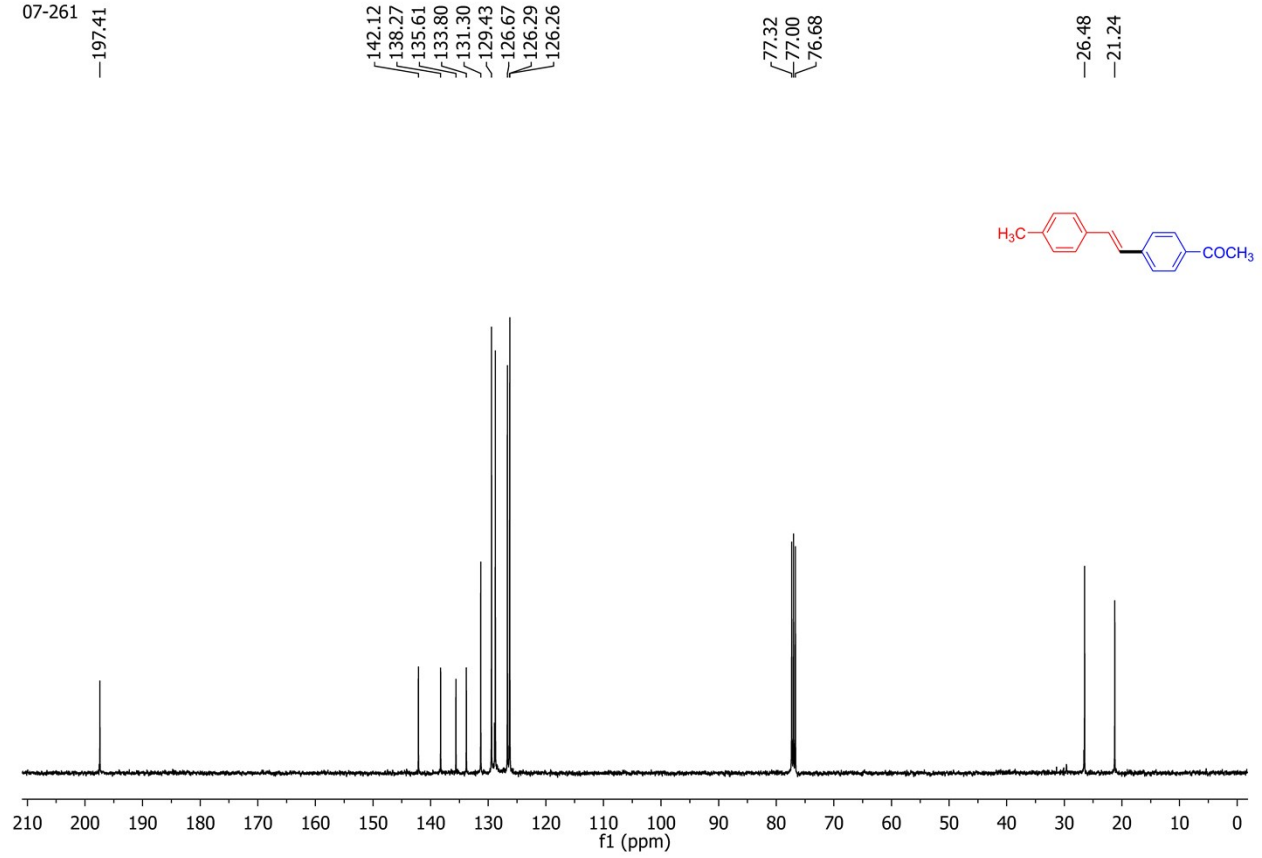
(9) 4-methyl-4'-nitro-1,1'-biphenyl[20] **(Table 3, Entry 9).** White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25 (d, $^3J_{H-H}$ = 8.7 Hz, 2H), 7.69 (d, $^3J_{H-H}$ = 8.7 Hz, 2H), 7.51 (d, $^3J_{H-H}$ = 8.1 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H).

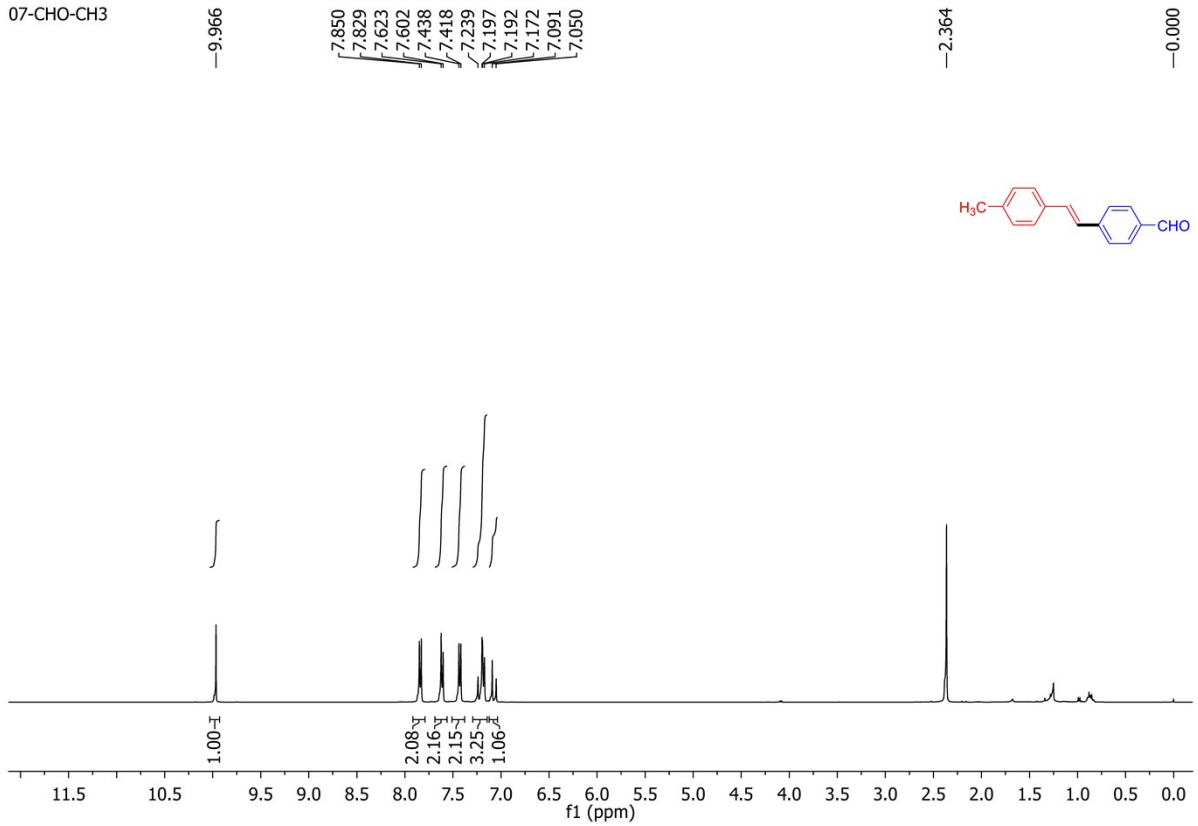
(10) 4-Fluoro-4'-nitro-1,1'-biphenyl[18] **(Table 3, Entry 10).** Light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 – 8.24 (m, 1H), 7.71 – 7.62 (m, 2H), 7.62 – 7.52 (m, 2H), 7.19 – 7.14 (m, 2H).

07-261 COCH3



07-261

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7.091
7.050
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0.000
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CHO
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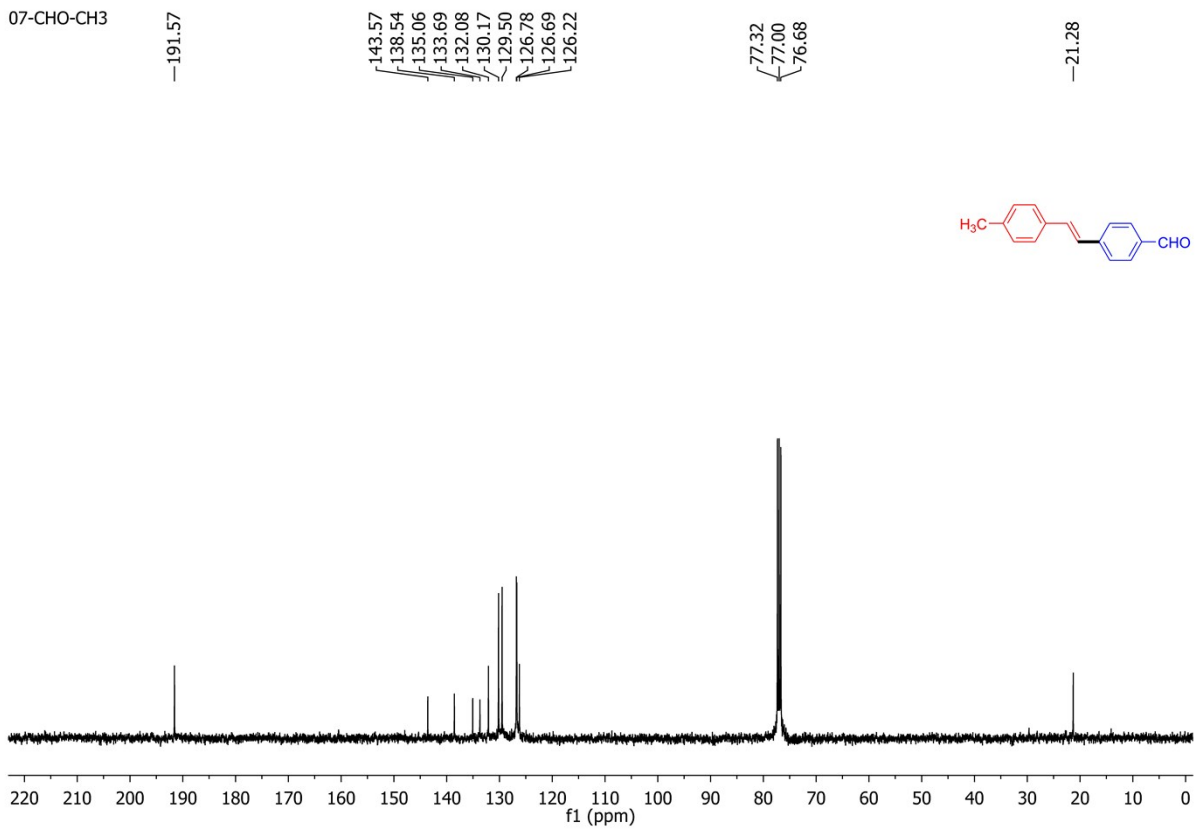
2.08
2.16
2.15
3.25
1.06
f1 (ppm)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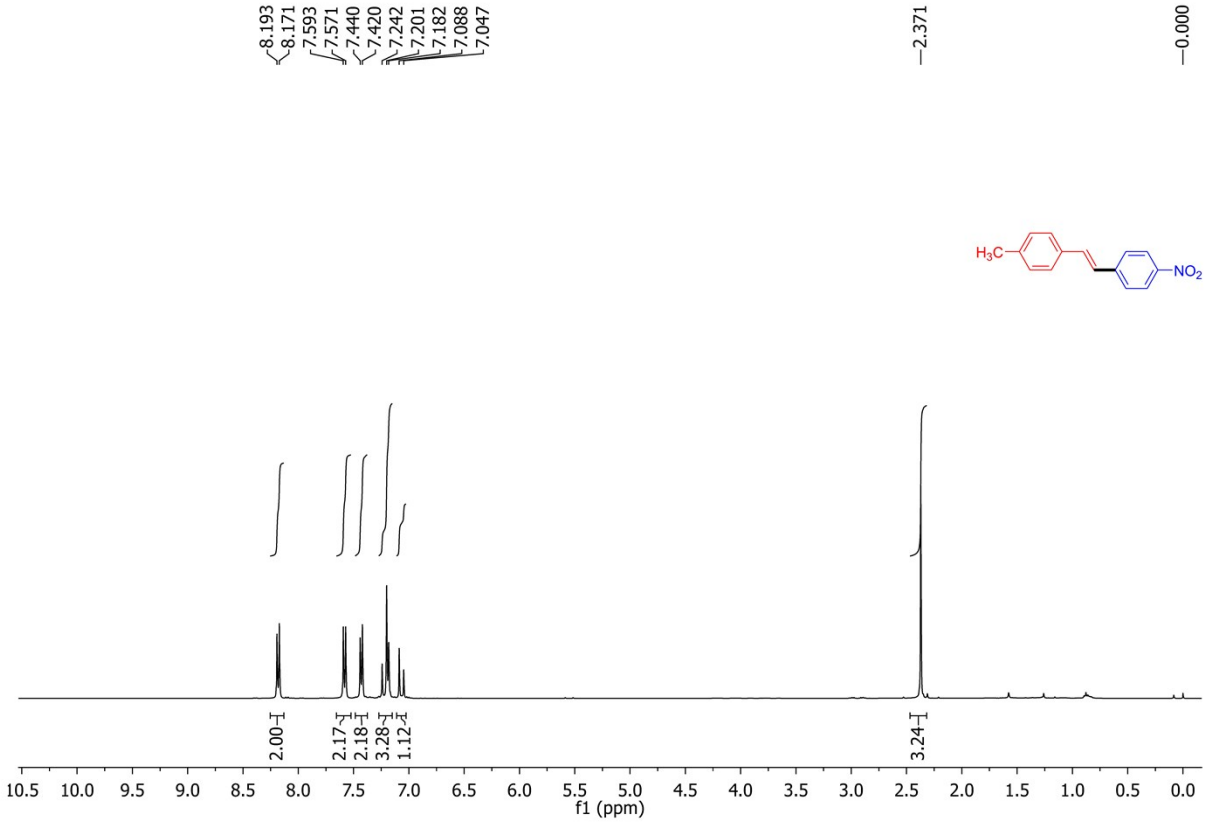
143.57
138.54
135.06
133.69
132.08
130.17
129.50
126.78
126.69
126.22
77.32
77.00
76.68
21.28
H3C
CHO
f1 (ppm)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7.201
7.182
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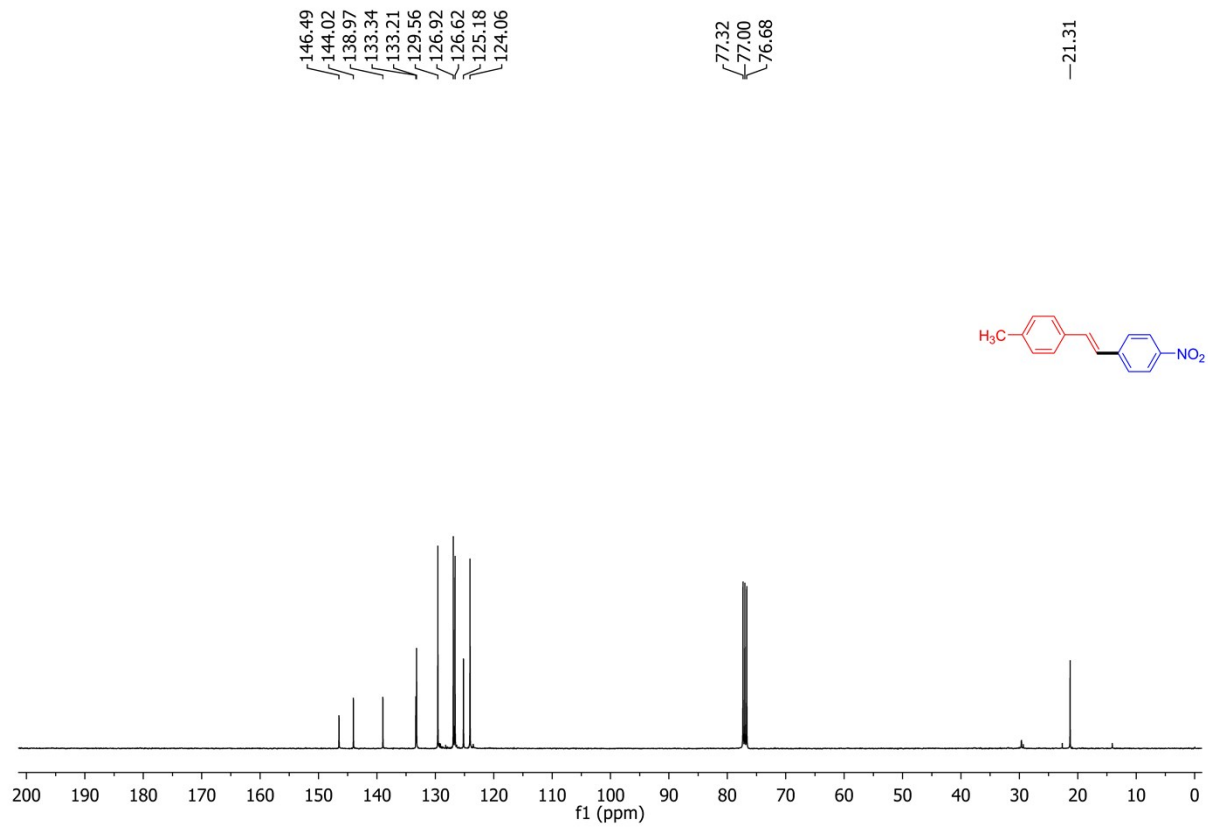
7.047
2.371
0.000
H3C
NO2
2.00
2.17
2.18
3.28
1.12
3.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.02
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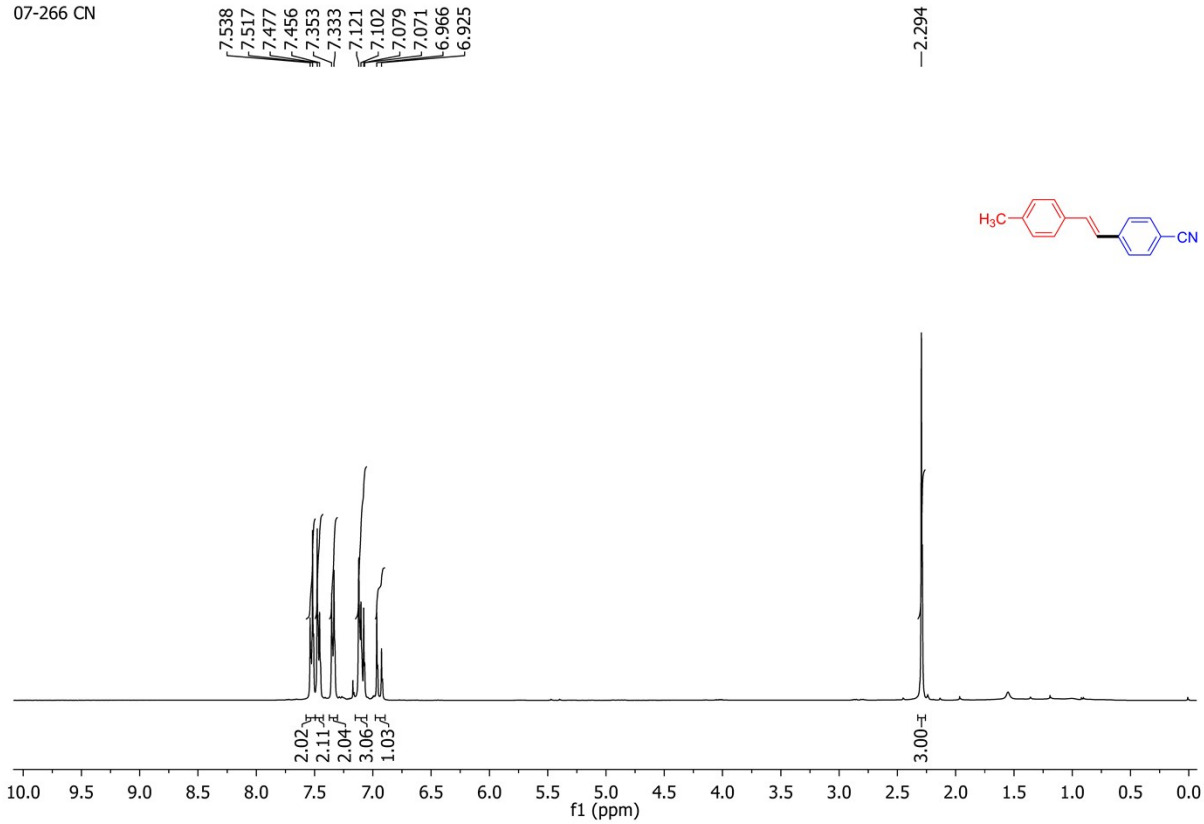
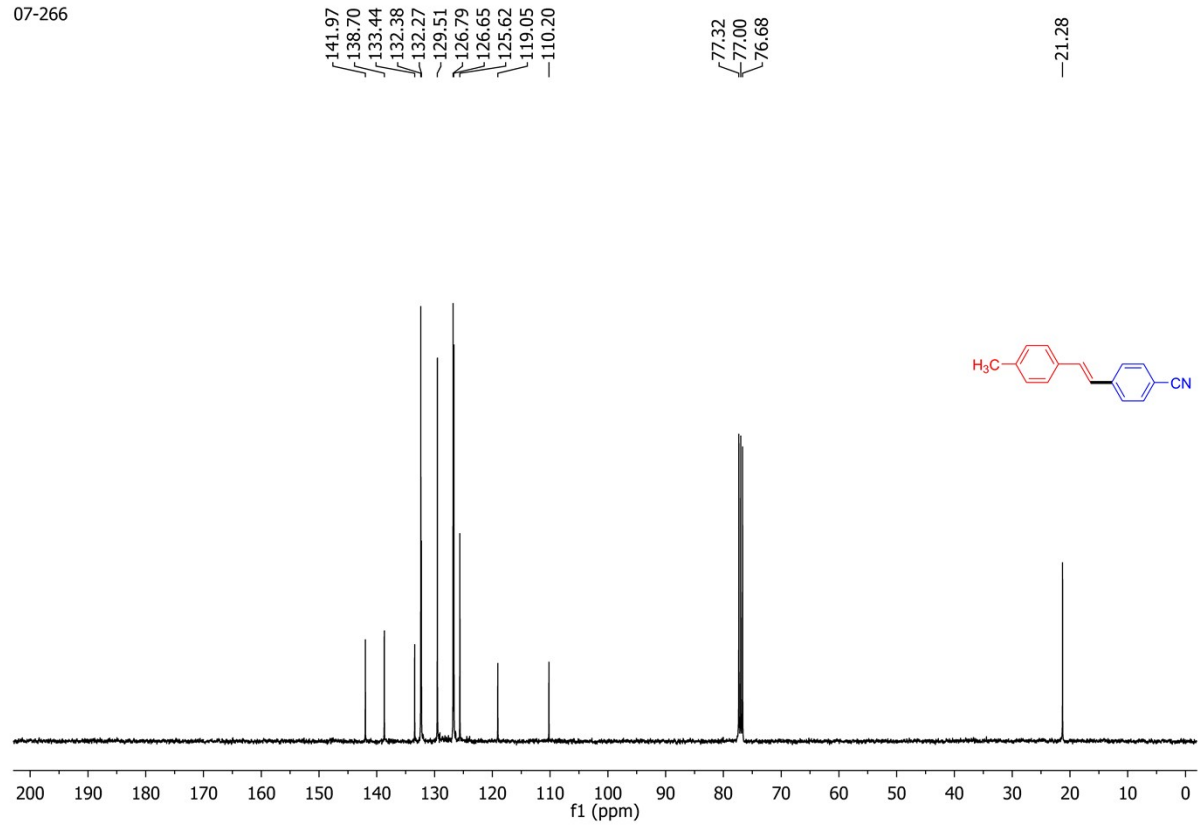
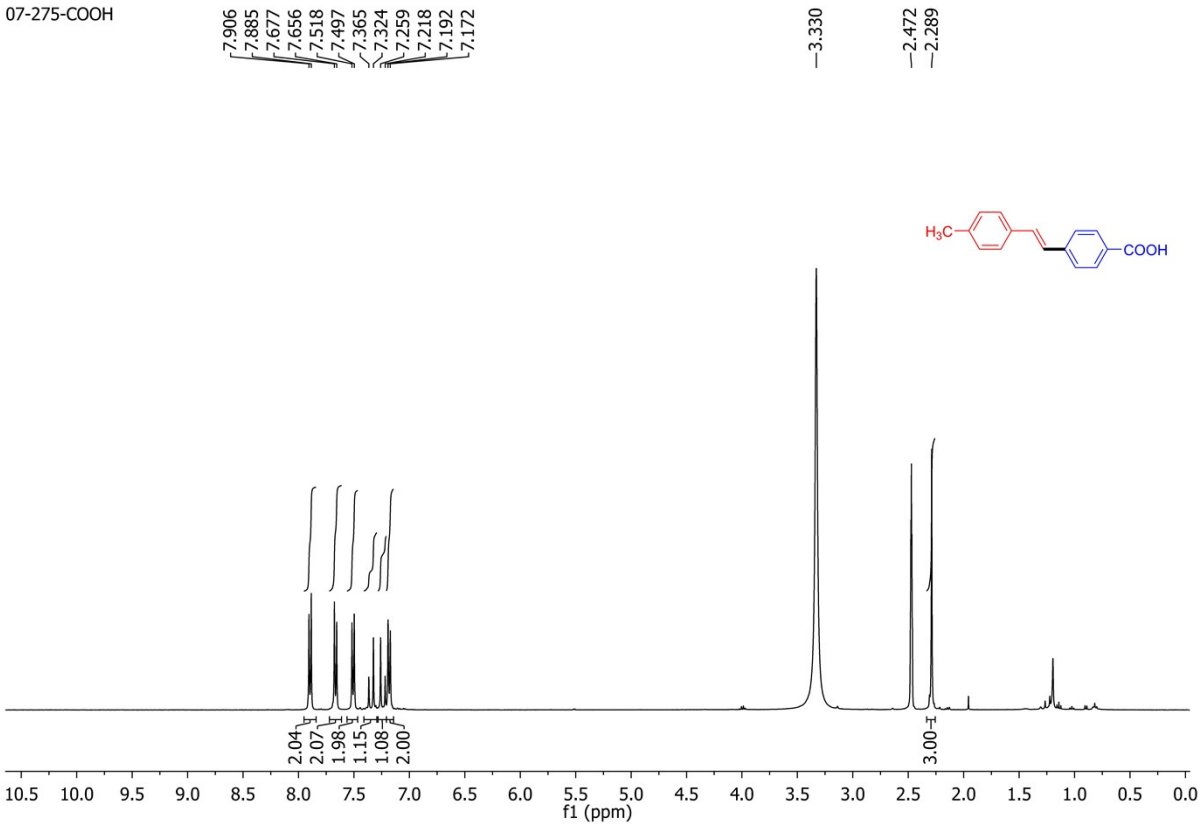
129.56
126.92
126.62
125.18
124.06
77.32
77.00
76.68
21.31
H3C
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

07-266 CN



07-266

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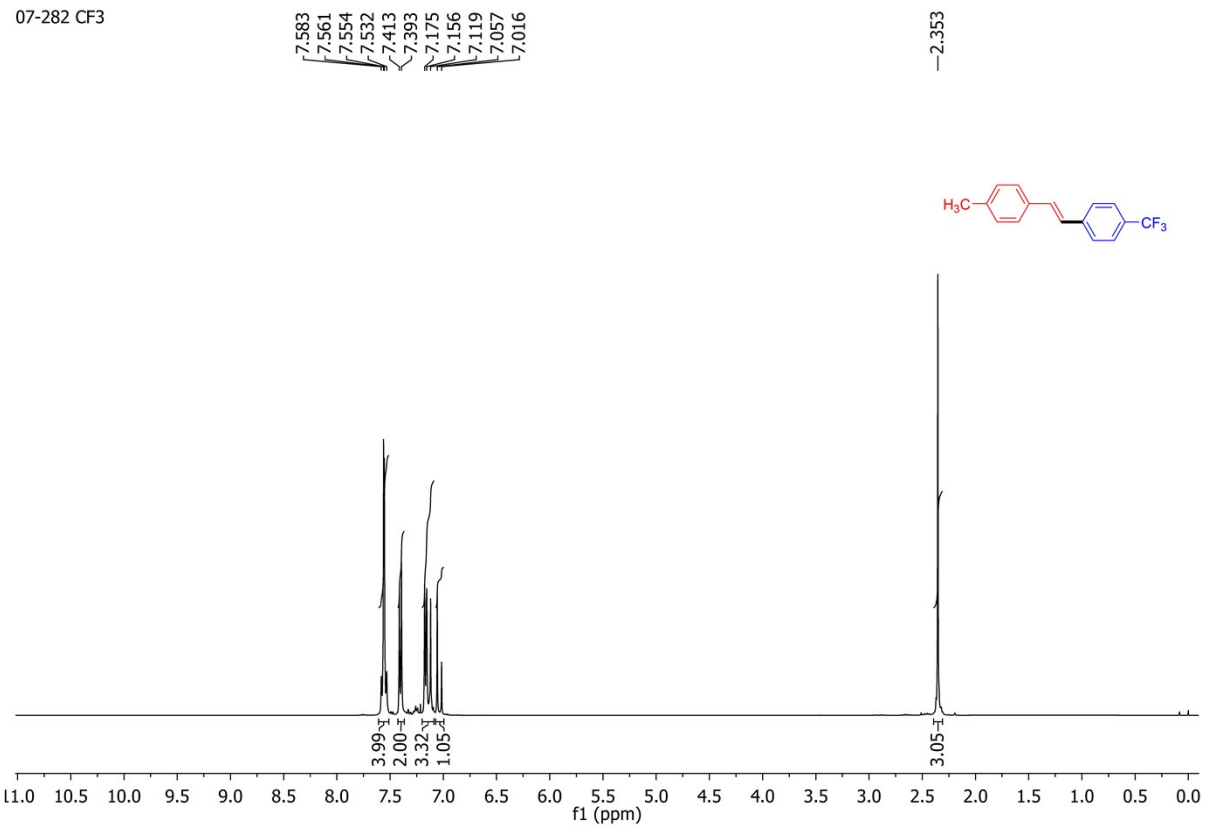
7.192
7.172
3.330
2.472
2.289
H3C
COOH
2.04
2.07
1.98
1.15
1.08
2.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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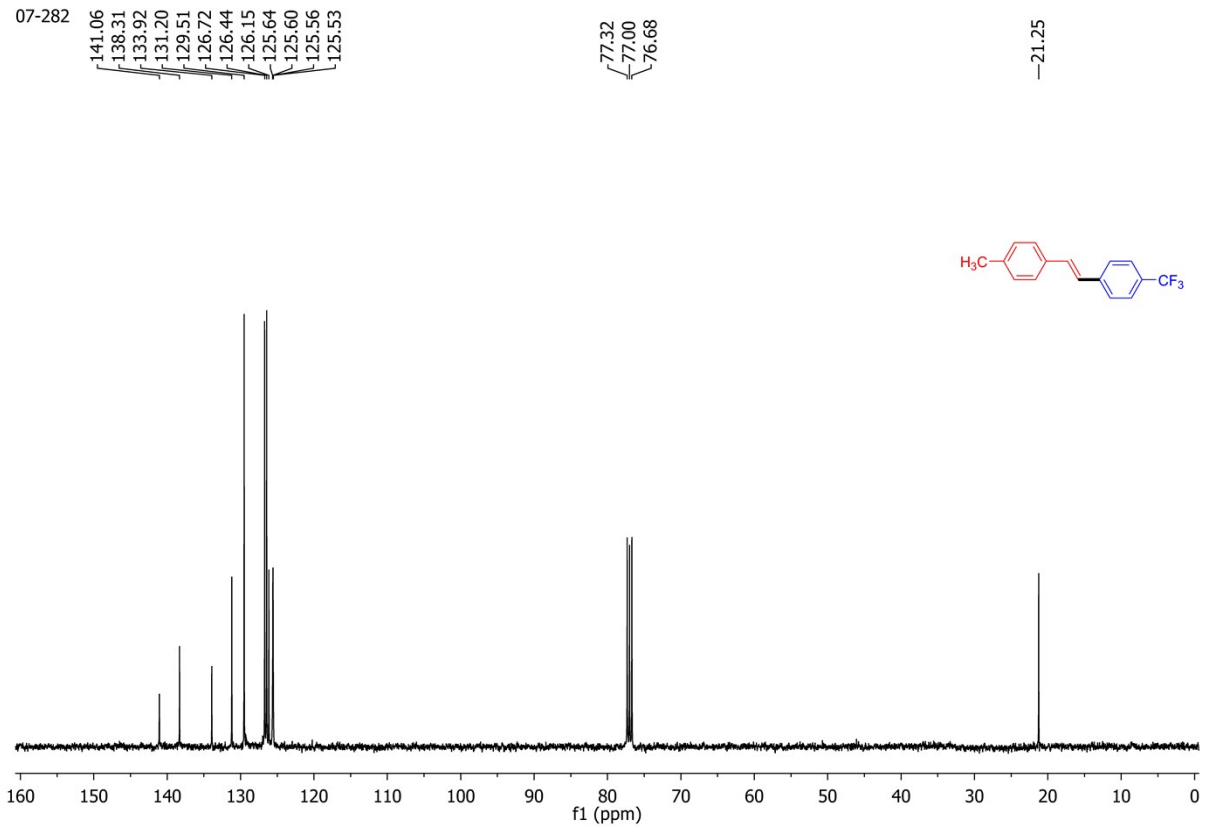
7.554
7.532
7.413
7.393
7.175
7.156
7.119
7.057
7.016
2.353
H3C
CF3
3.99
2.00
3.32
1.05
3.05
f1 (ppm)


07-282
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129.51
126.72
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125.64
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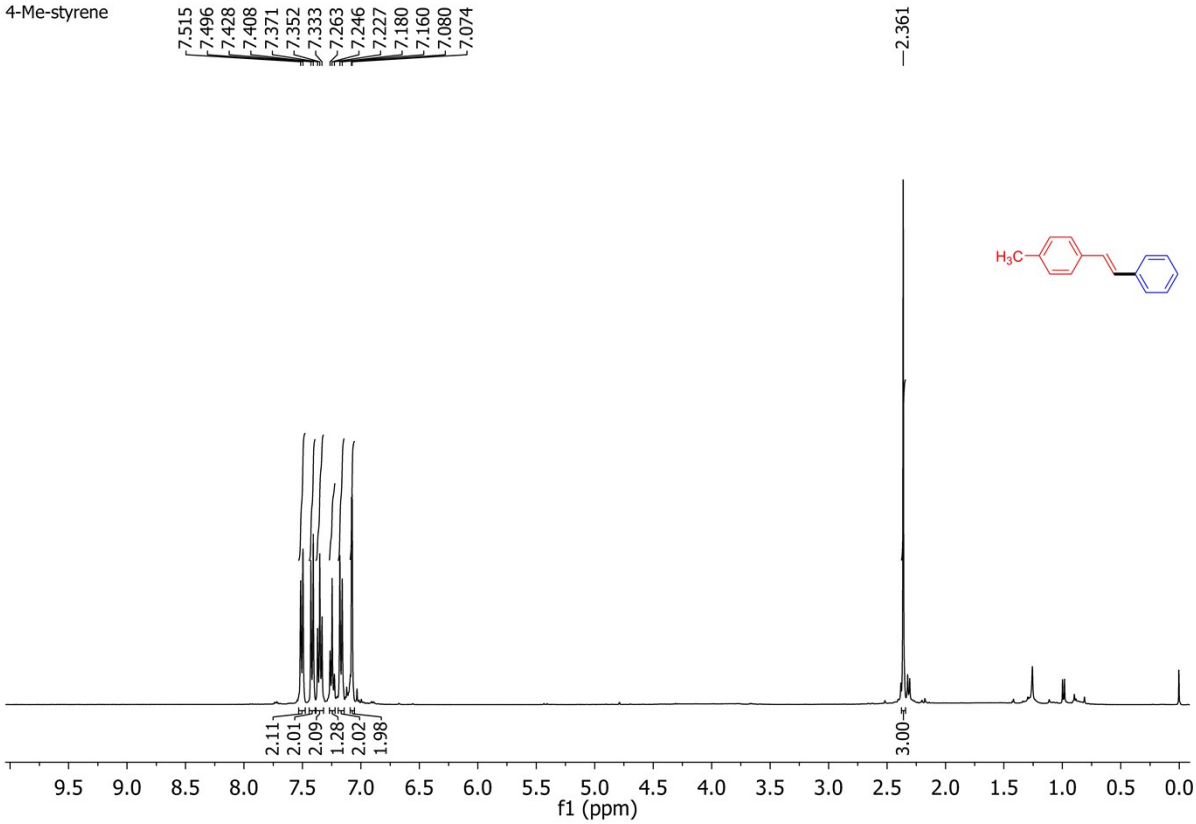
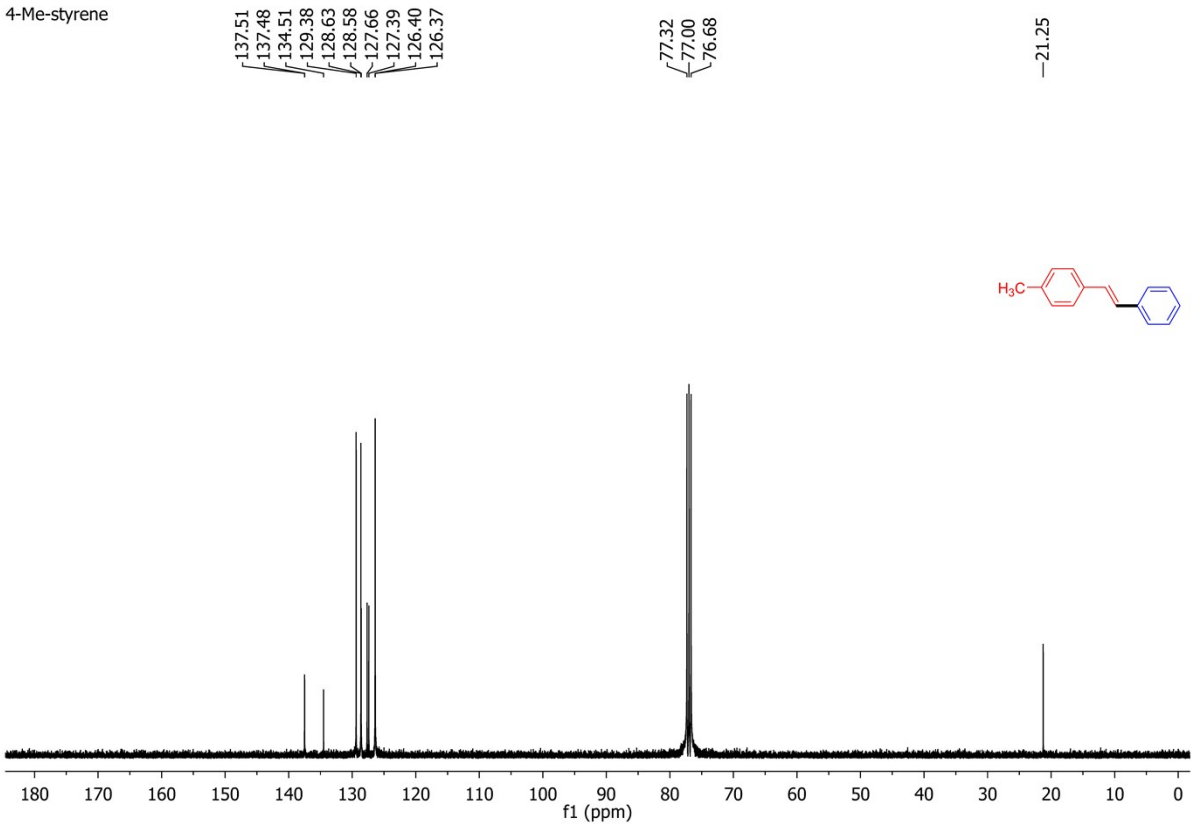
125.53
77.32
77.00
76.68
21.25
H3C
CF3
f1 (ppm)

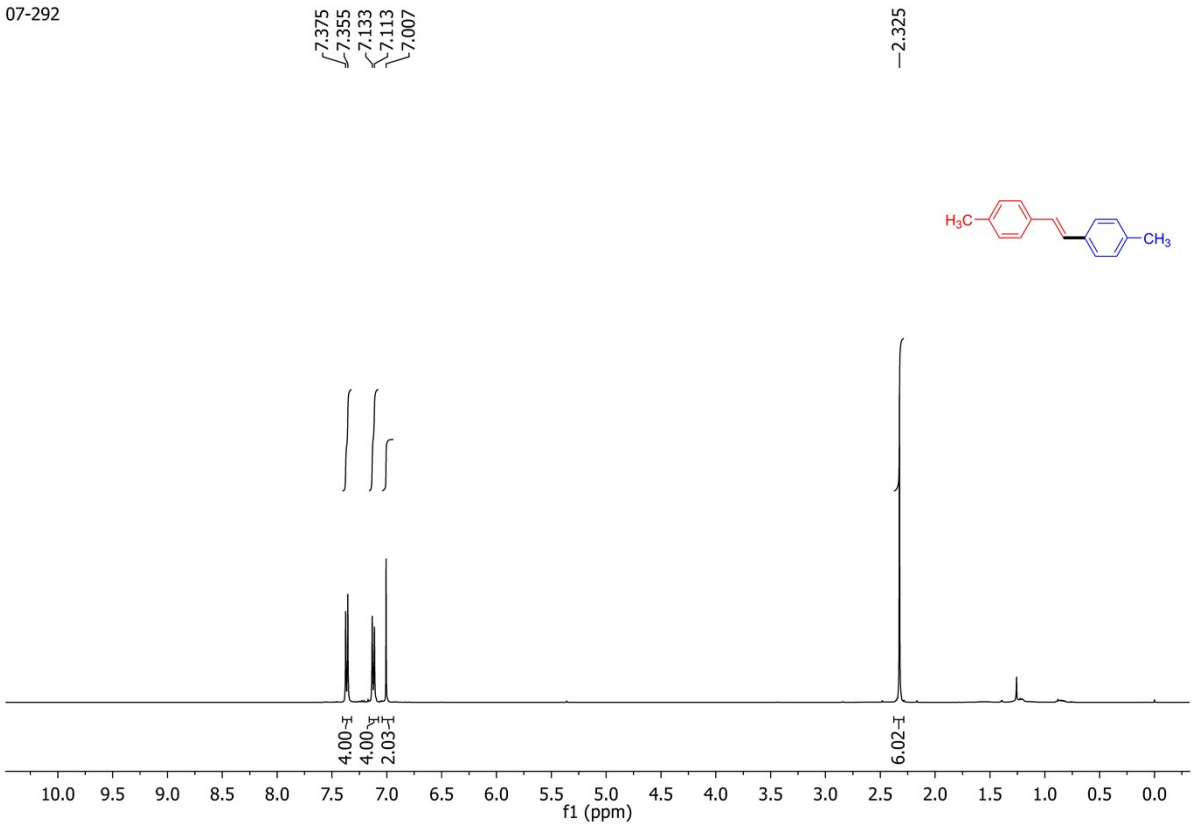
4-Me-styrene



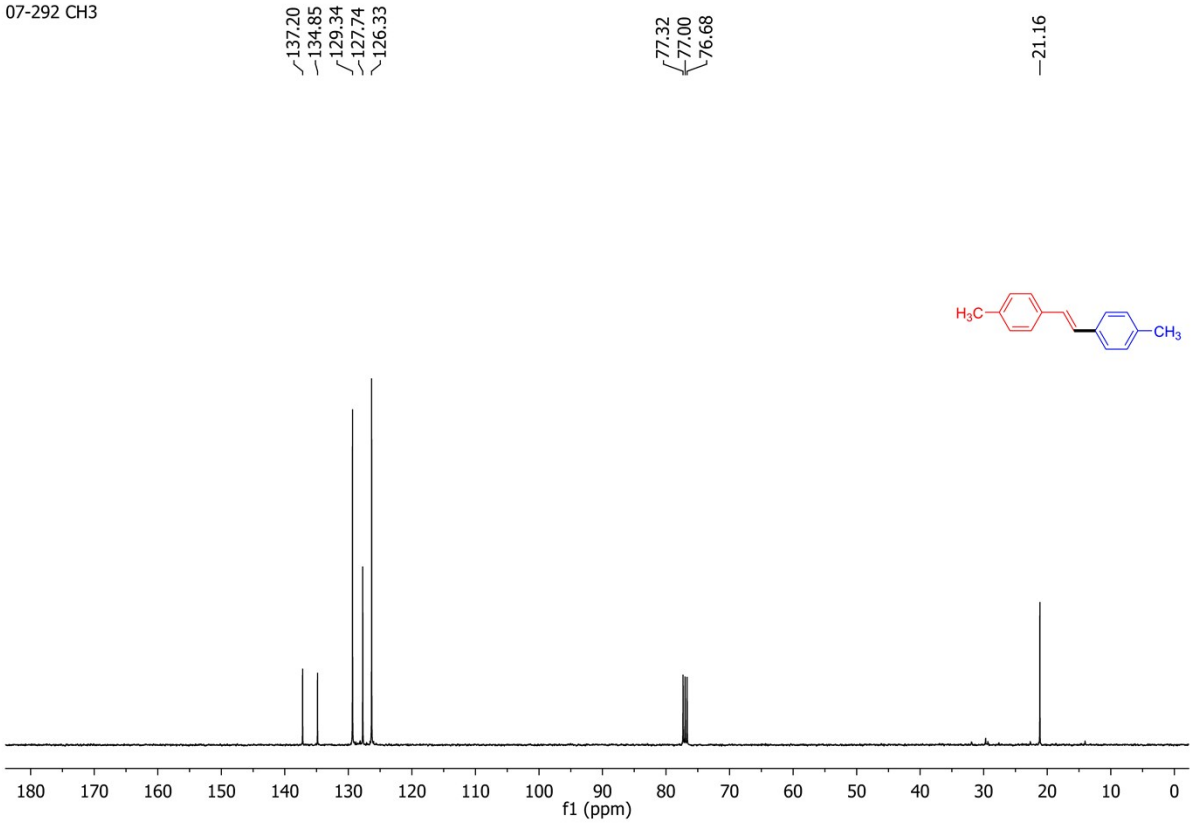
4-Me-styrene

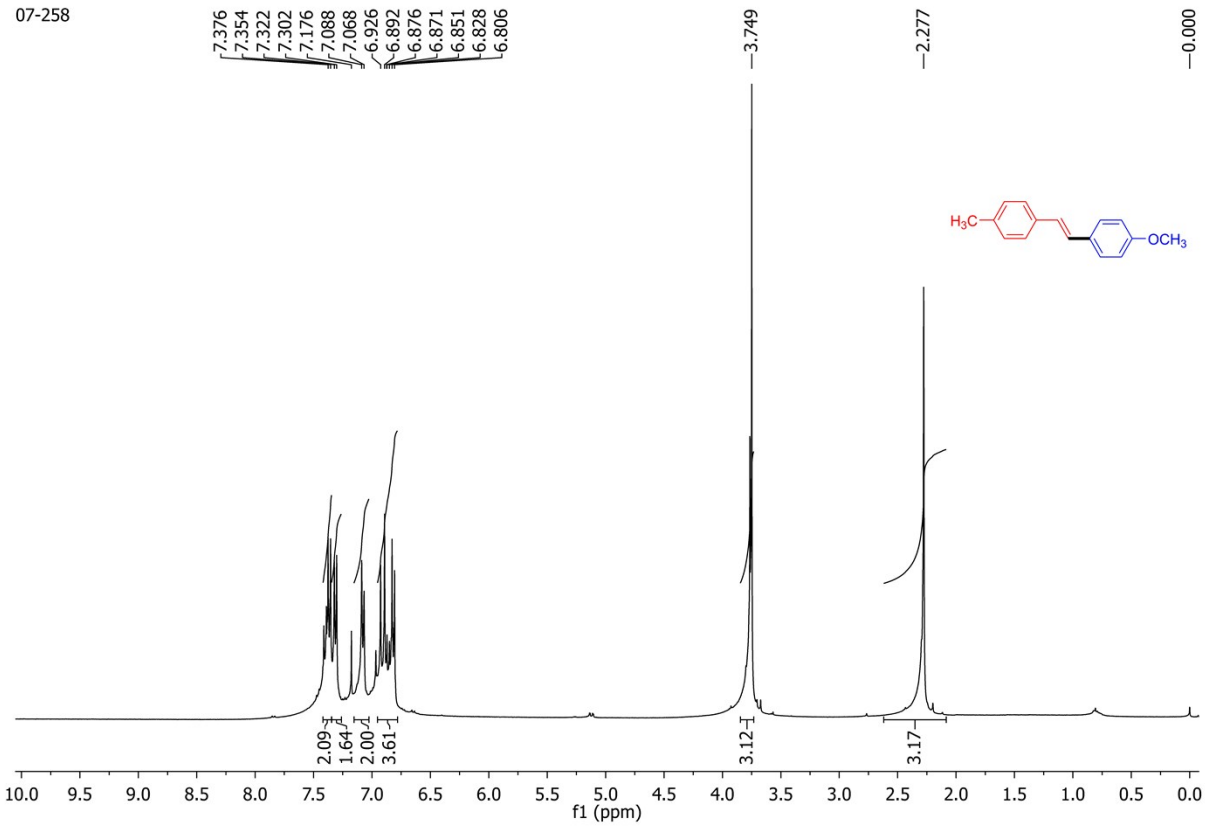


07-292



07-292 CH3

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7.068
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6.876
6.871
6.851
6.828
6.806
3.749
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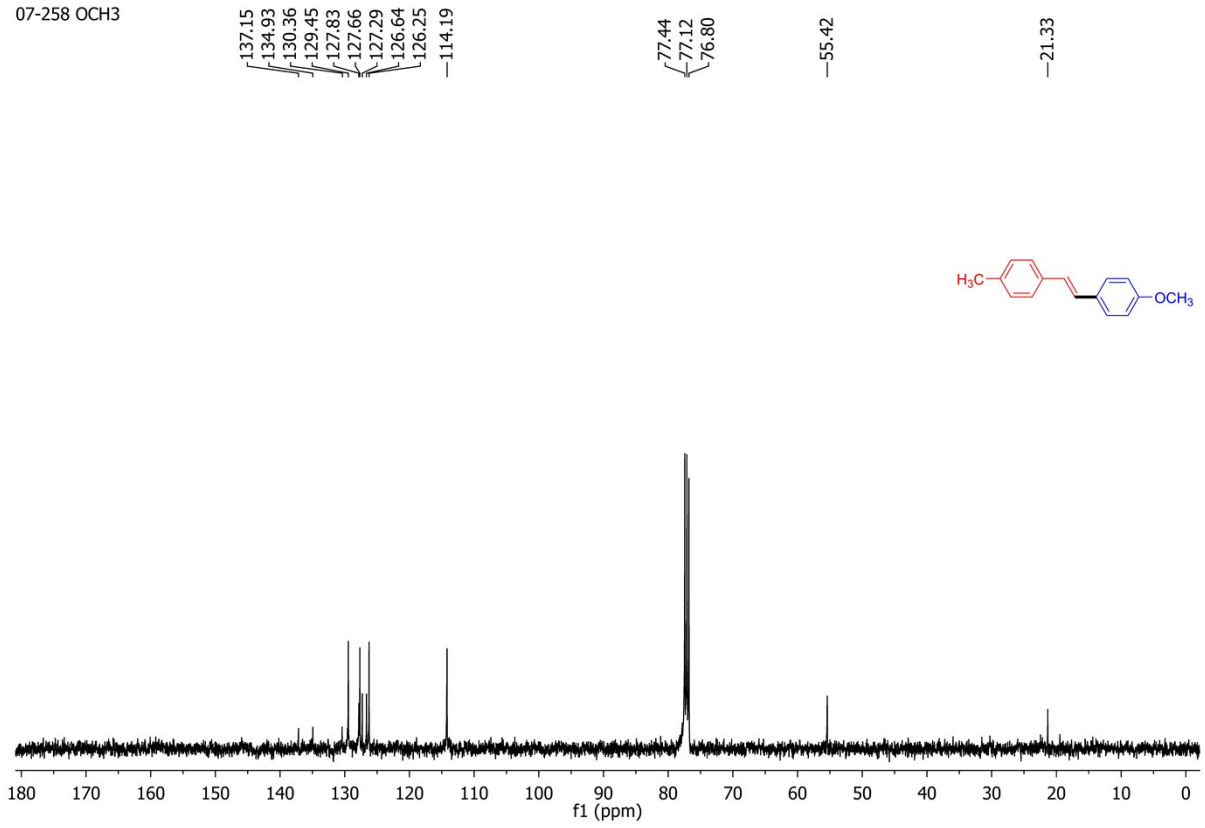
OCH3
2.09
1.64
2.00
3.61
3.12
3.17
f1 (ppm)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130.36
129.45
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127.66
127.29
126.64
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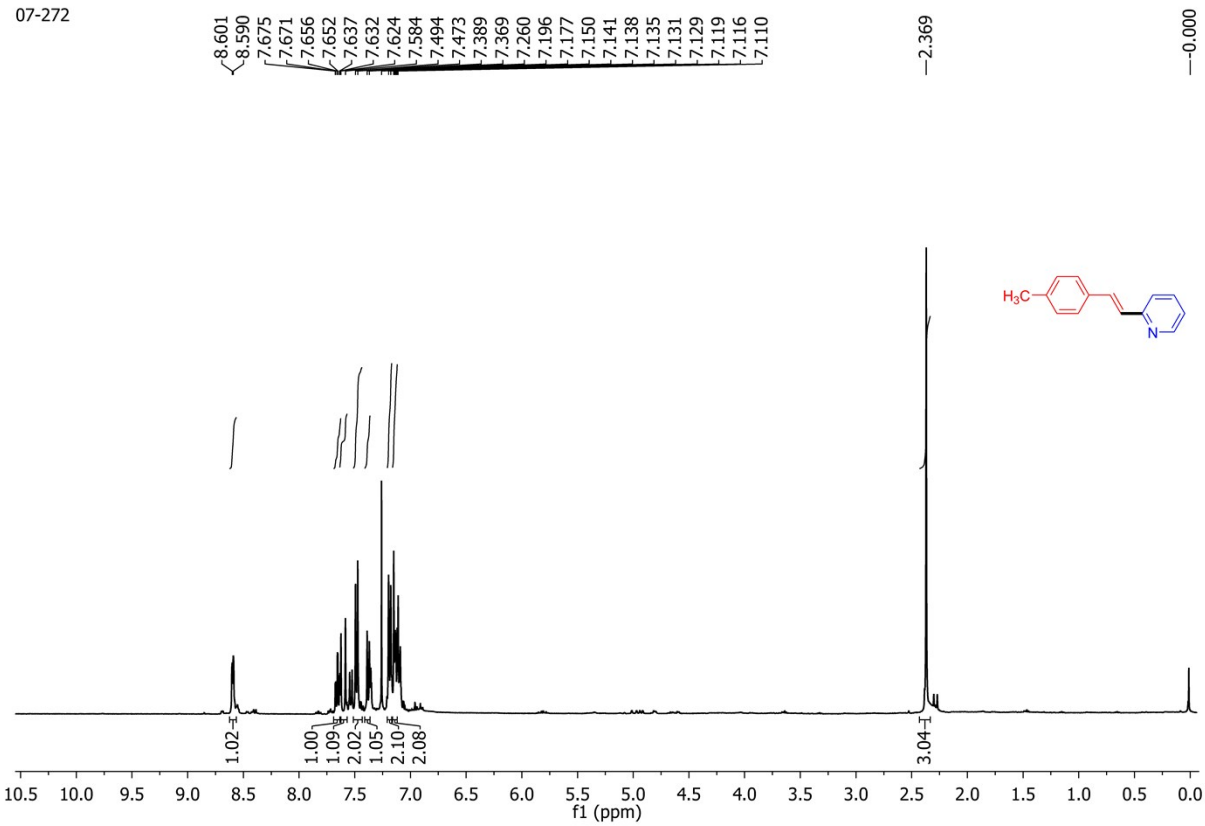
H3C
OCH3
f1 (ppm)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7.389
7.369
7.260
7.196
7.177
7.150
7.141
7.138
7.135
7.131
7.129
7.119
7.116
7.110
2.369
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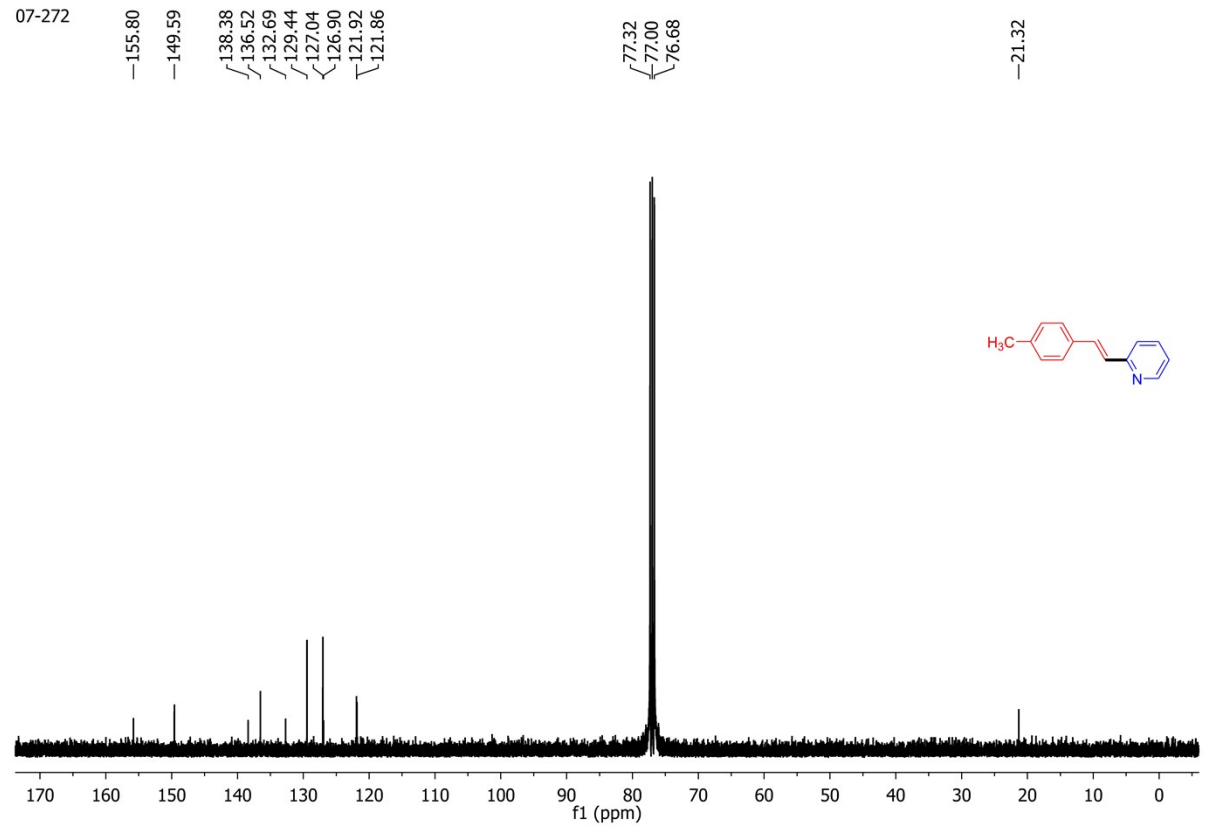
1.02
1.00
1.09
2.02
1.05
2.10
2.08
3.04
f1 (ppm)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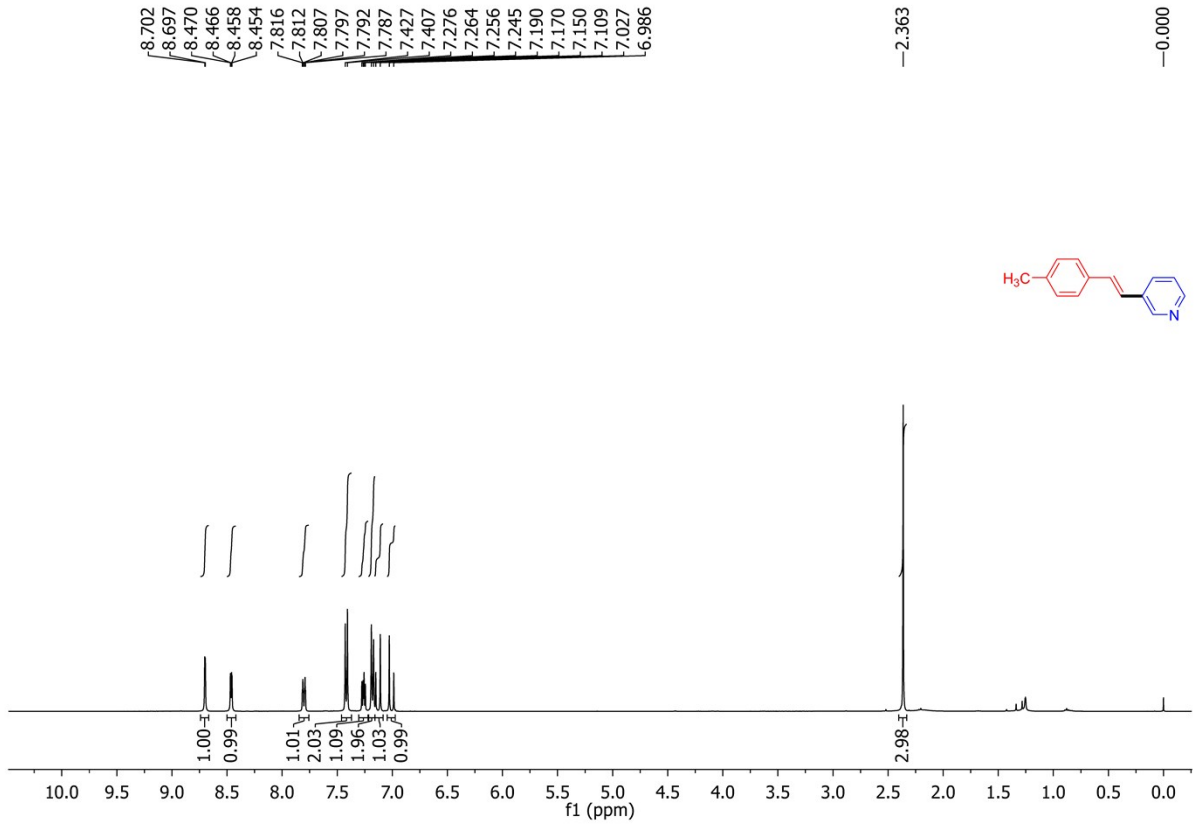
21.32
f1 (ppm)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7.407
7.276
7.264
7.256
7.245
7.190
7.170
7.150
7.109
7.027
6.986
2.363
0.000
H3C
N
1.00
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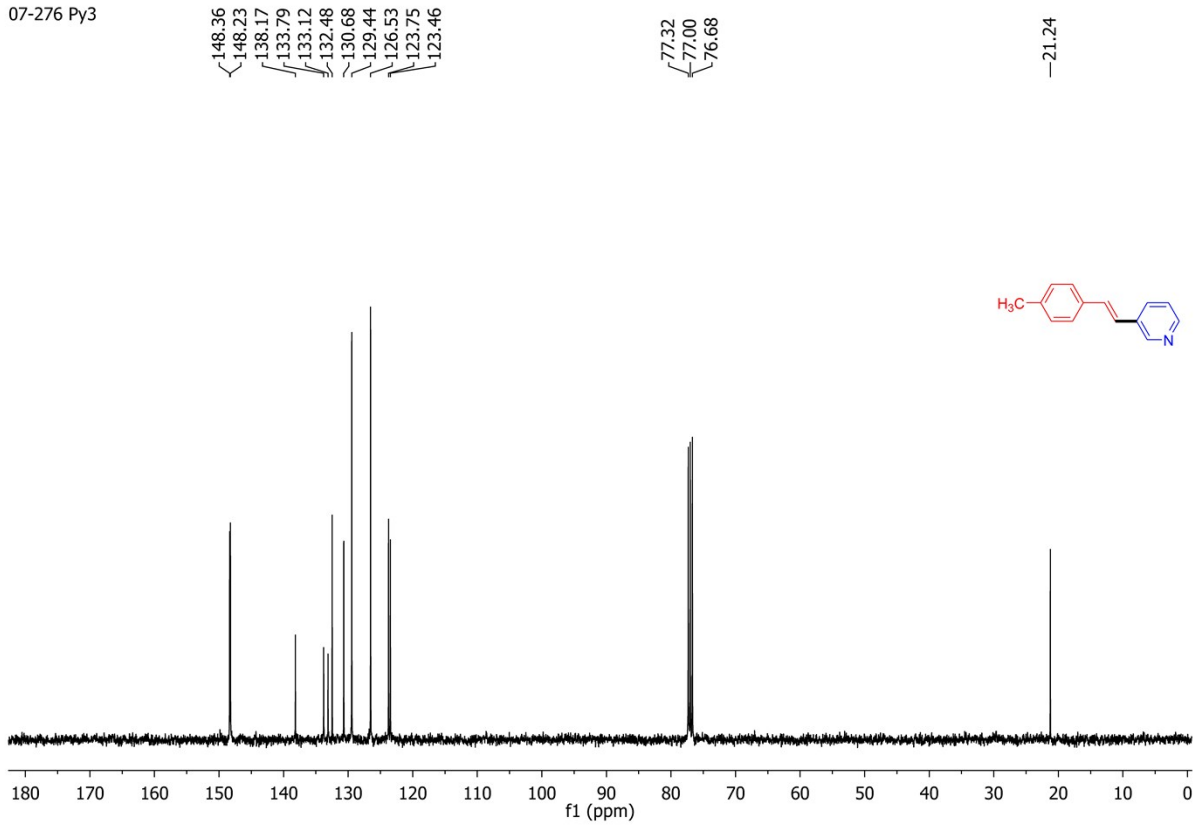
1.01
2.03
1.09
1.96
1.03
0.99
2.98
f1 (ppm)

07-276 Py3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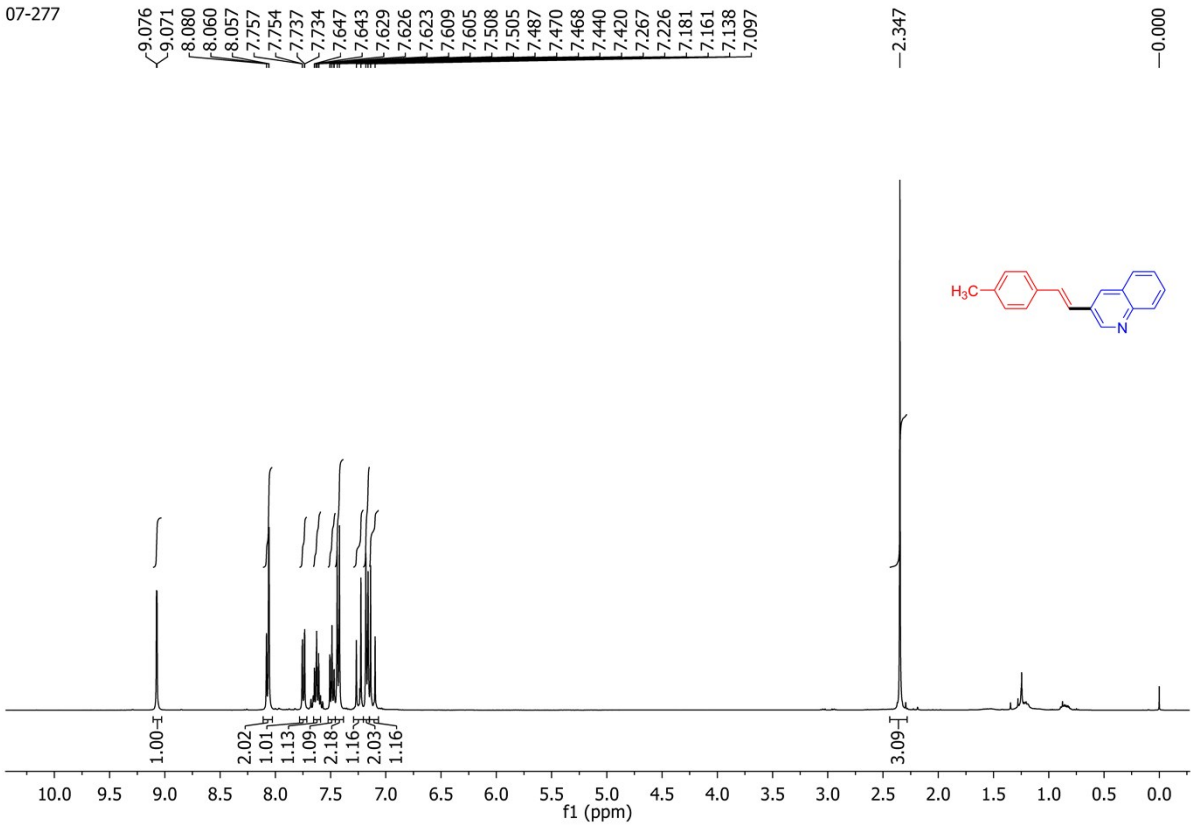
133.12
132.48
130.68
129.44
126.53
123.75
123.46
77.32
77.00
76.68
21.24
H3C
N
f1 (ppm)


07-277
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7.734
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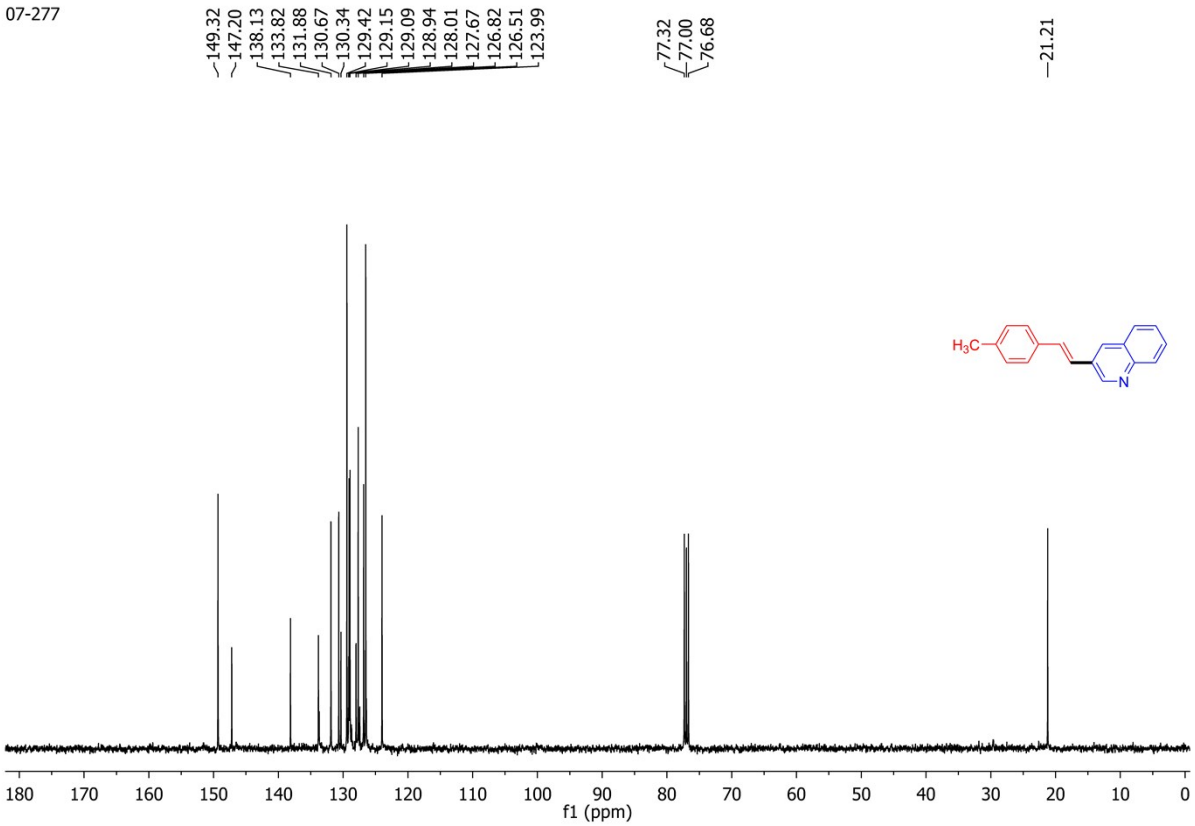
7.623
7.609
7.605
7.508
7.505
7.487
7.470
7.468
7.440
7.420
7.267
7.226
7.181
7.161
7.138
7.097
2.347
0.000
H3C
N
1.00
2.02
1.01
1.13
1.09
2.18
1.16
2.03
1.16
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


07-277
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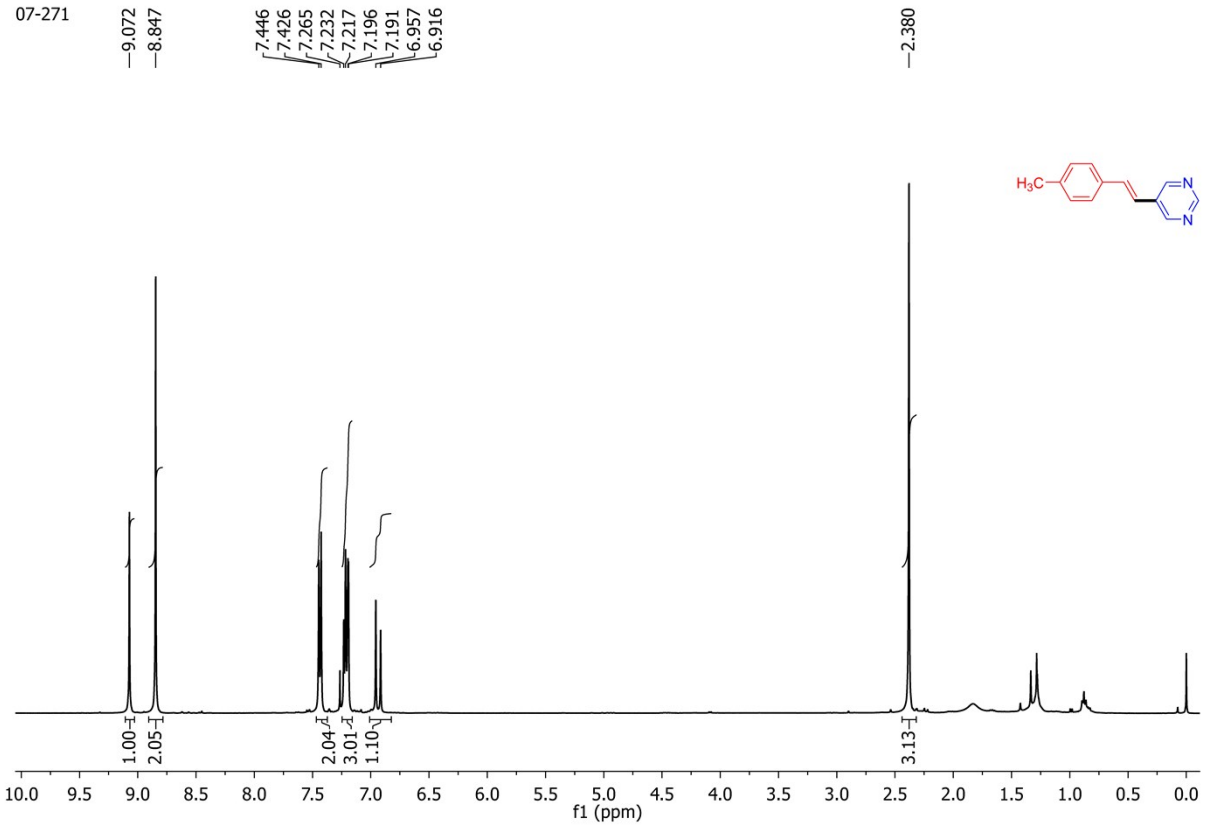
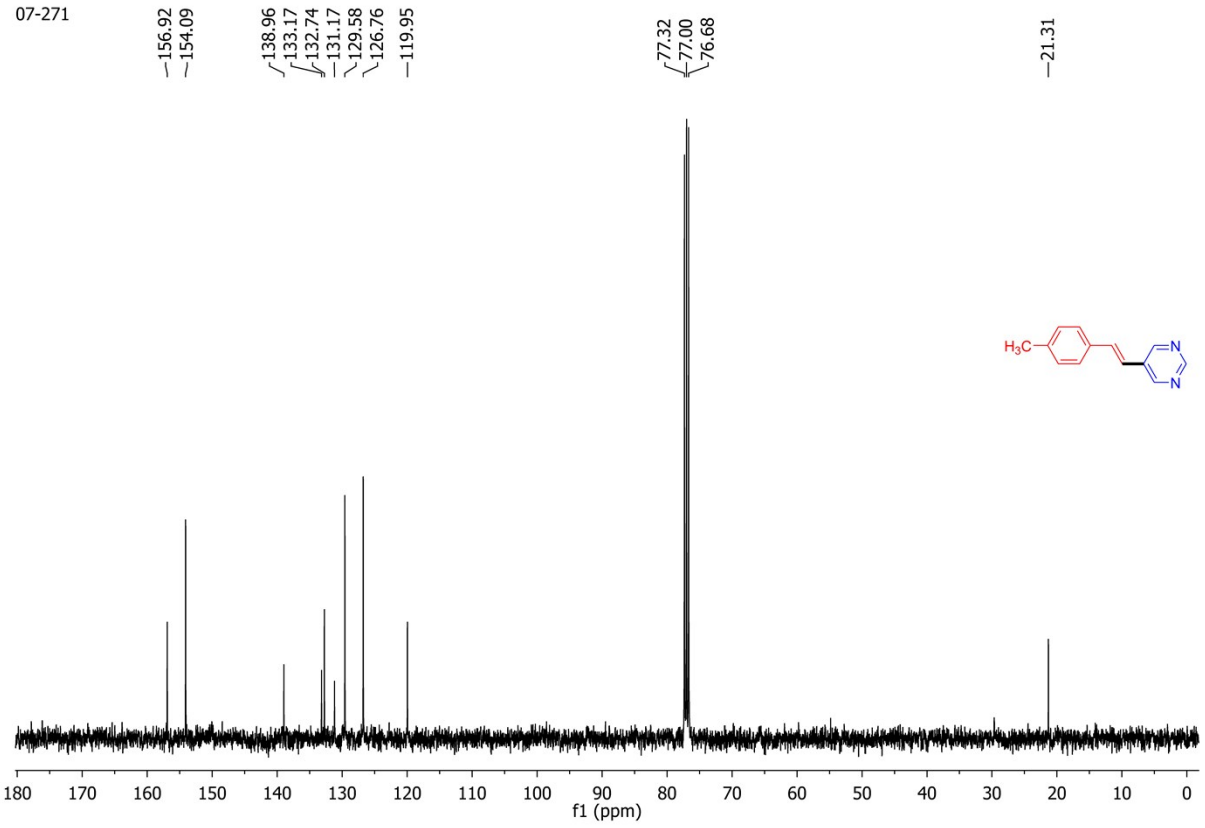
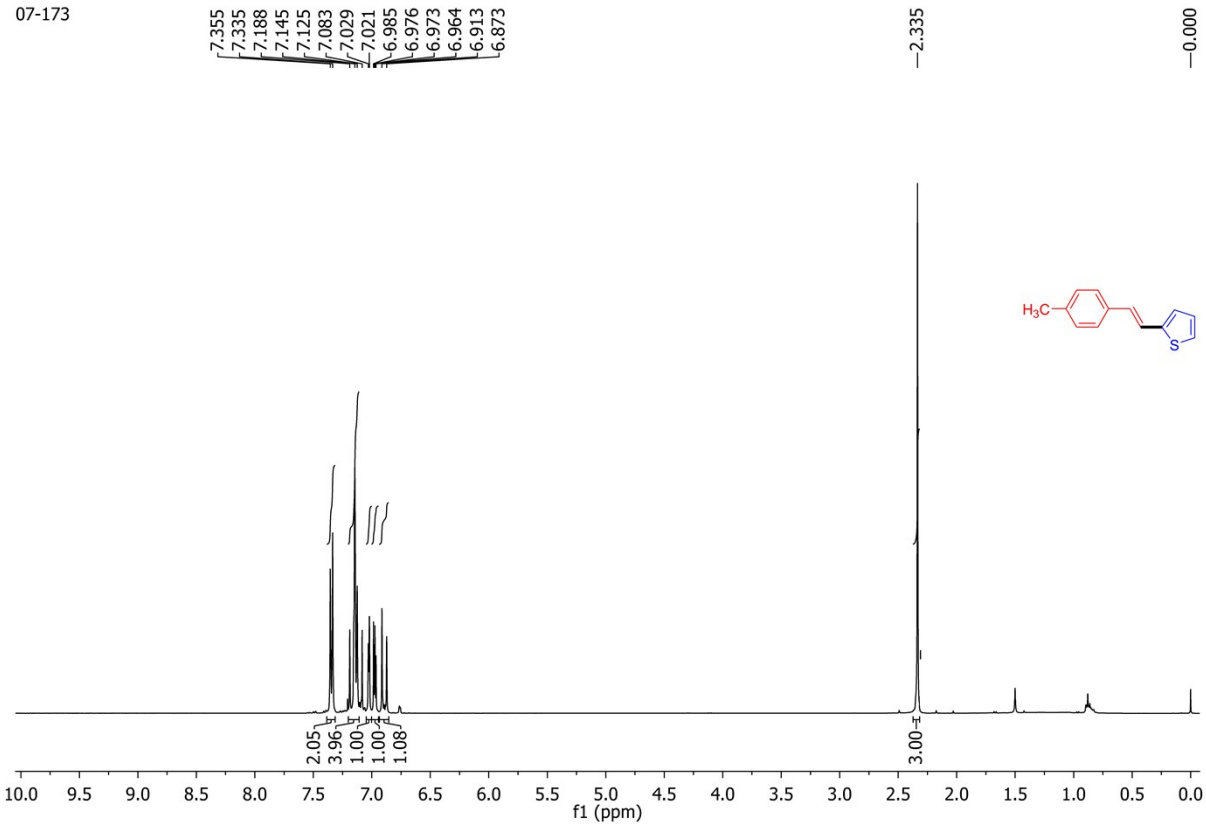
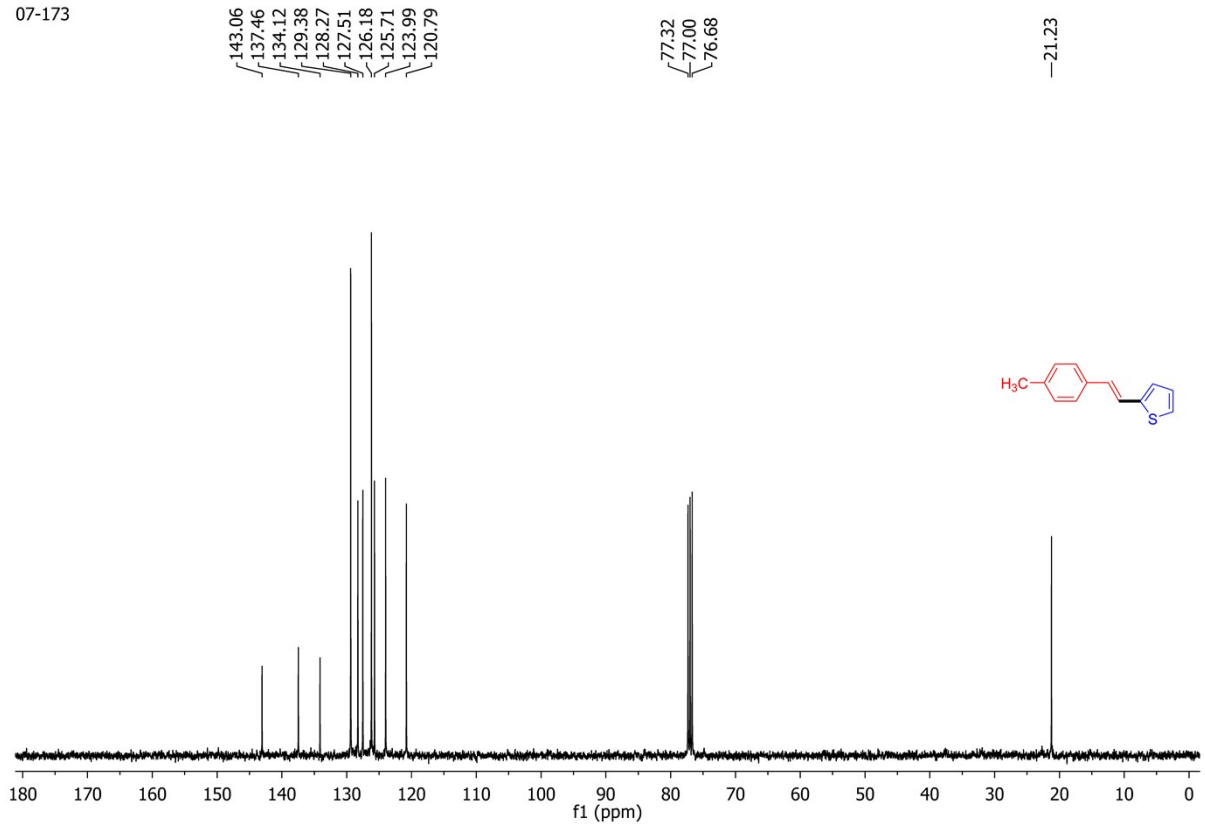
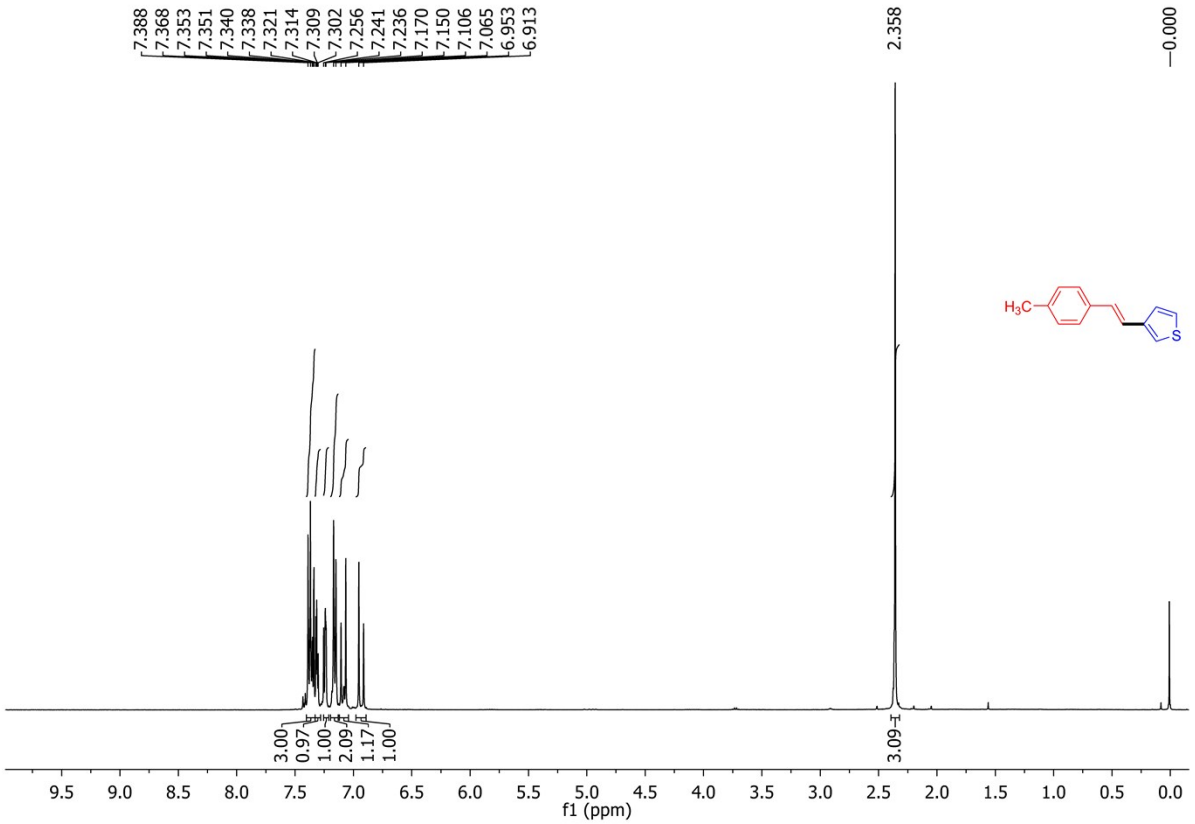
133.82
131.88
130.67
130.34
129.42
129.15
129.09
128.94
128.01
127.67
126.82
126.51
123.99
77.32
77.00
76.68
21.21
H3C
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

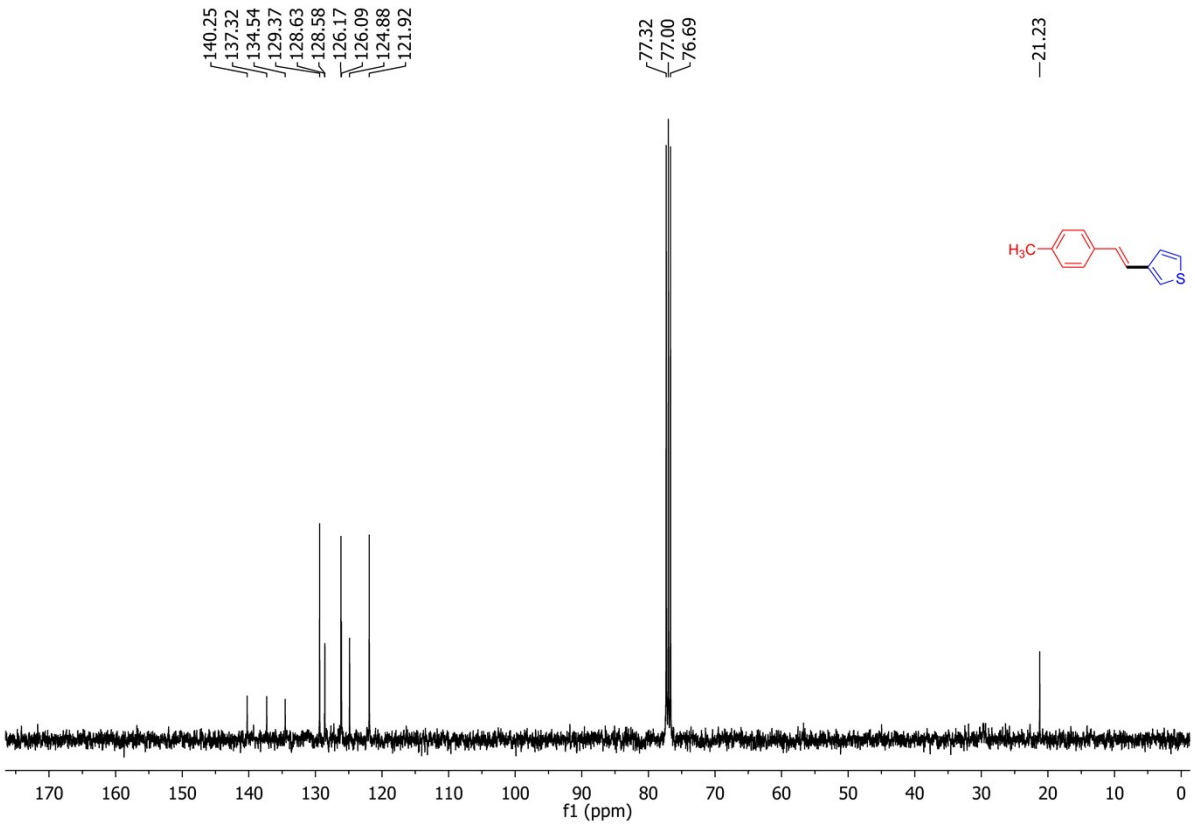

07-271
9.072
8.847
7.446
7.426
7.265
7.232
7.217
7.196
7.191
6.957
6.916
2.380
1.00
2.05
2.04
3.01
1.10
3.13
f1 (ppm)

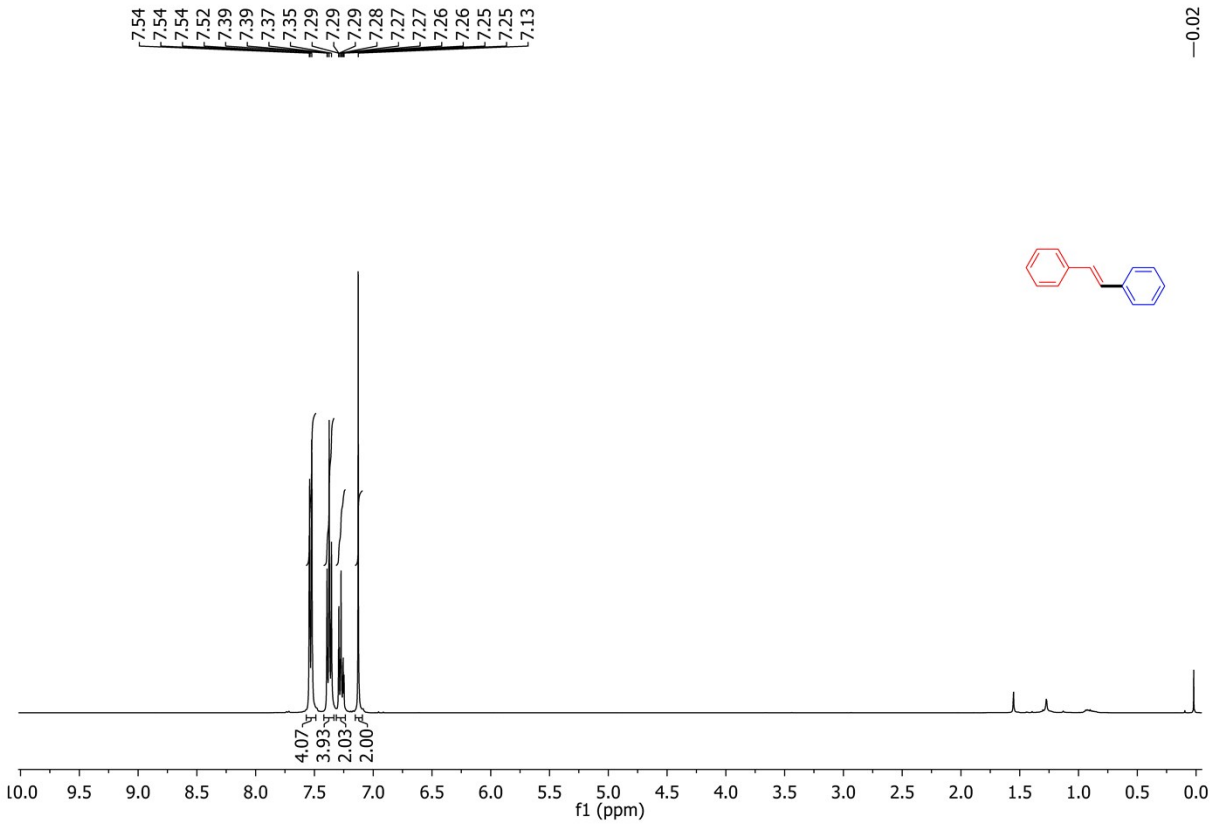

07-271
156.92
154.09
138.96
133.17
132.74
131.17
129.58
126.76
119.95
77.32
77.00
76.68
21.31
f1 (ppm)

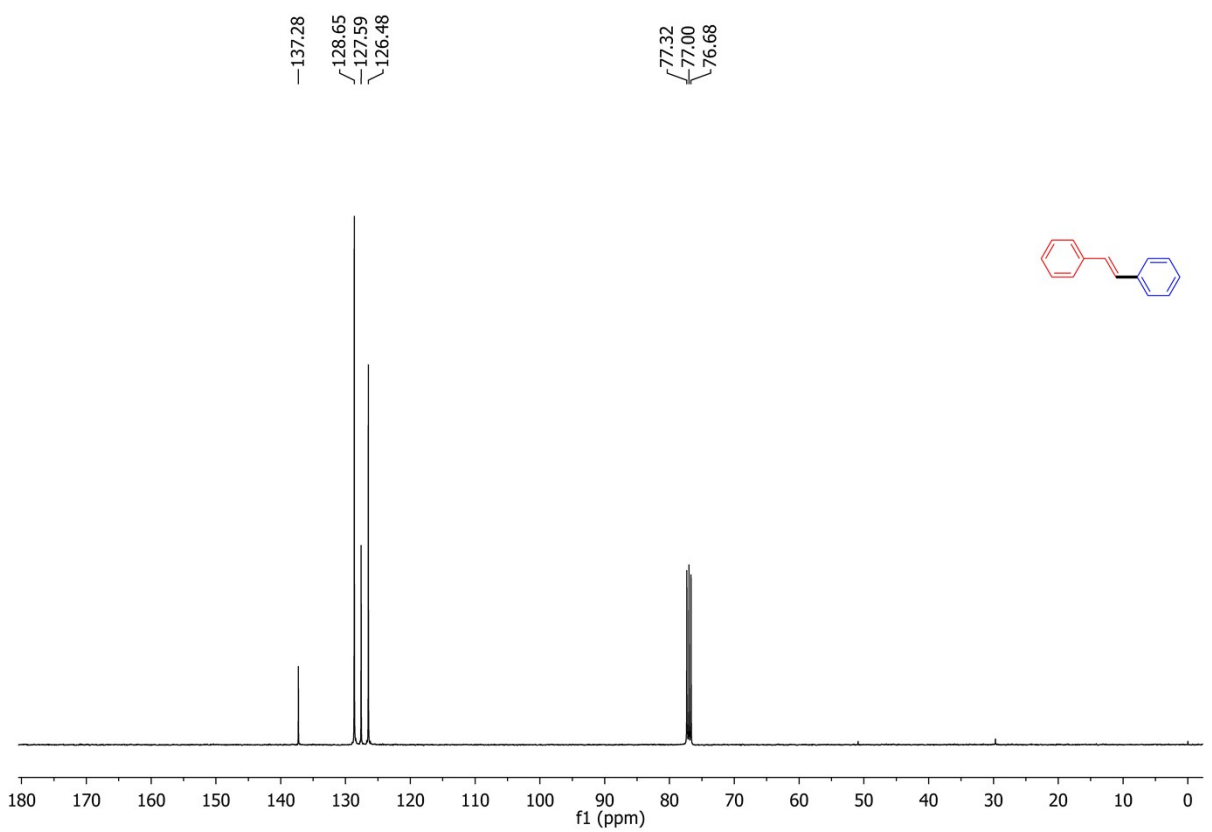

07-173
7.355
7.335
7.188
7.145
7.125
7.083
7.029
7.021
6.985
6.976
6.973
6.964
6.913
6.873
2.335
0.000
2.05
3.96
1.00
1.00
1.08
3.00
f1 (ppm)

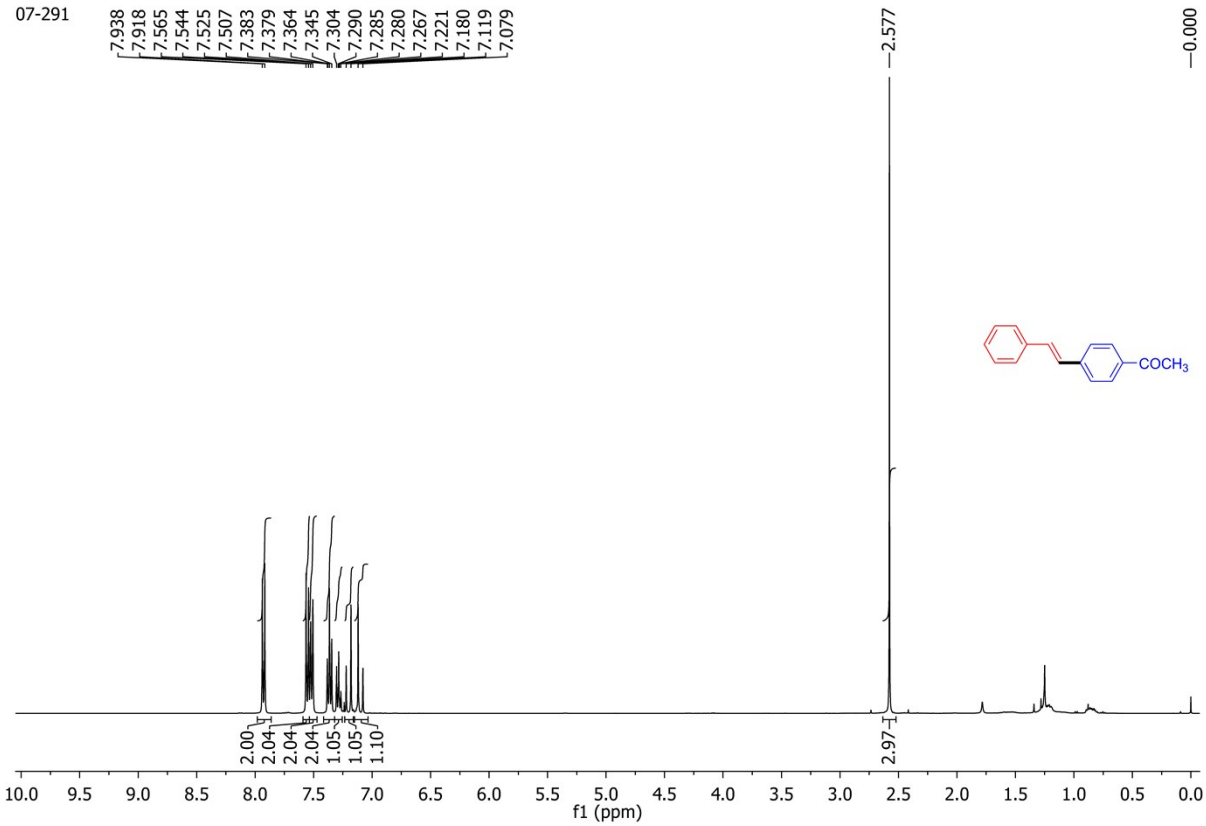

07-173
143.06
137.46
134.12
129.38
128.27
127.51
126.18
125.71
123.99
120.79
77.32
77.00
76.68
21.23
f1 (ppm)

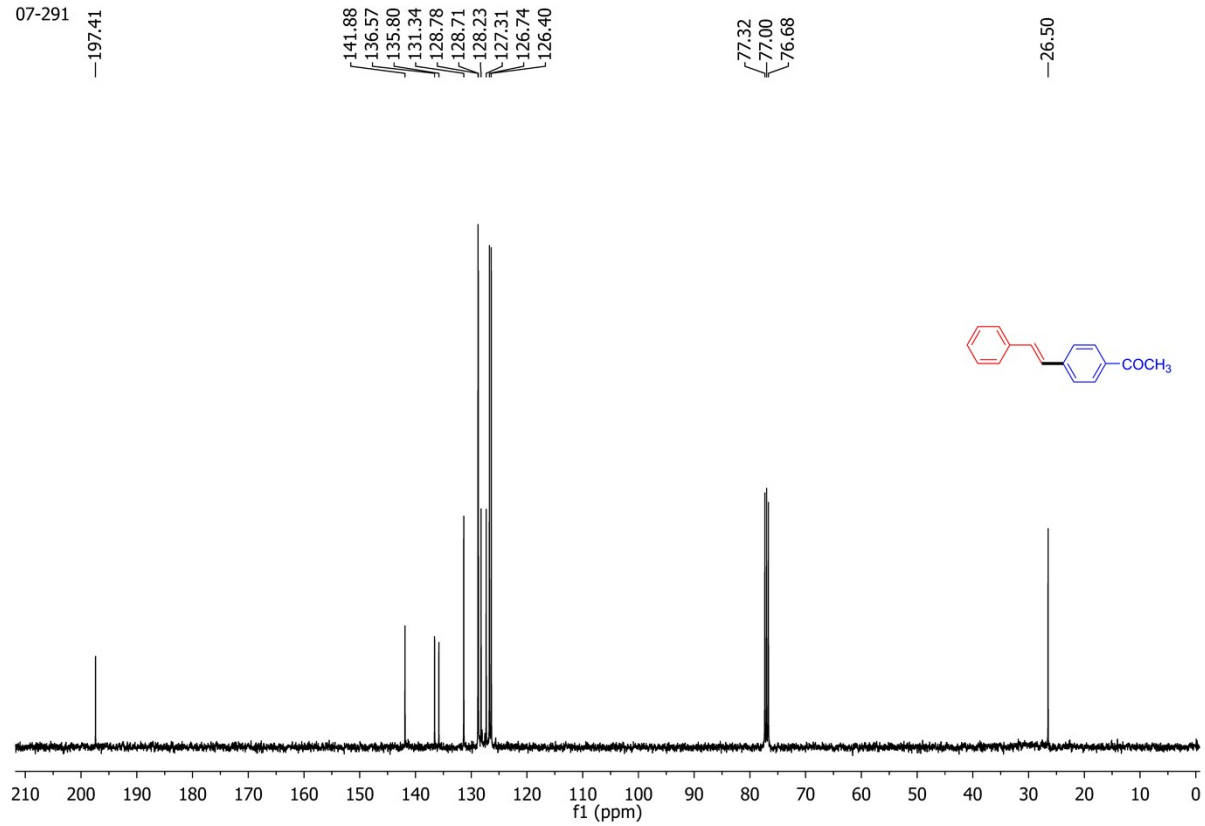

7.388
7.368
7.353
7.351
7.340
7.338
7.321
7.314
7.309
7.302
7.256
7.241
7.236
7.170
7.150
7.106
7.065
6.953
6.913
2.358
0.000
3.00
0.97
1.00
2.09
1.17
1.00
3.09
f1 (ppm)

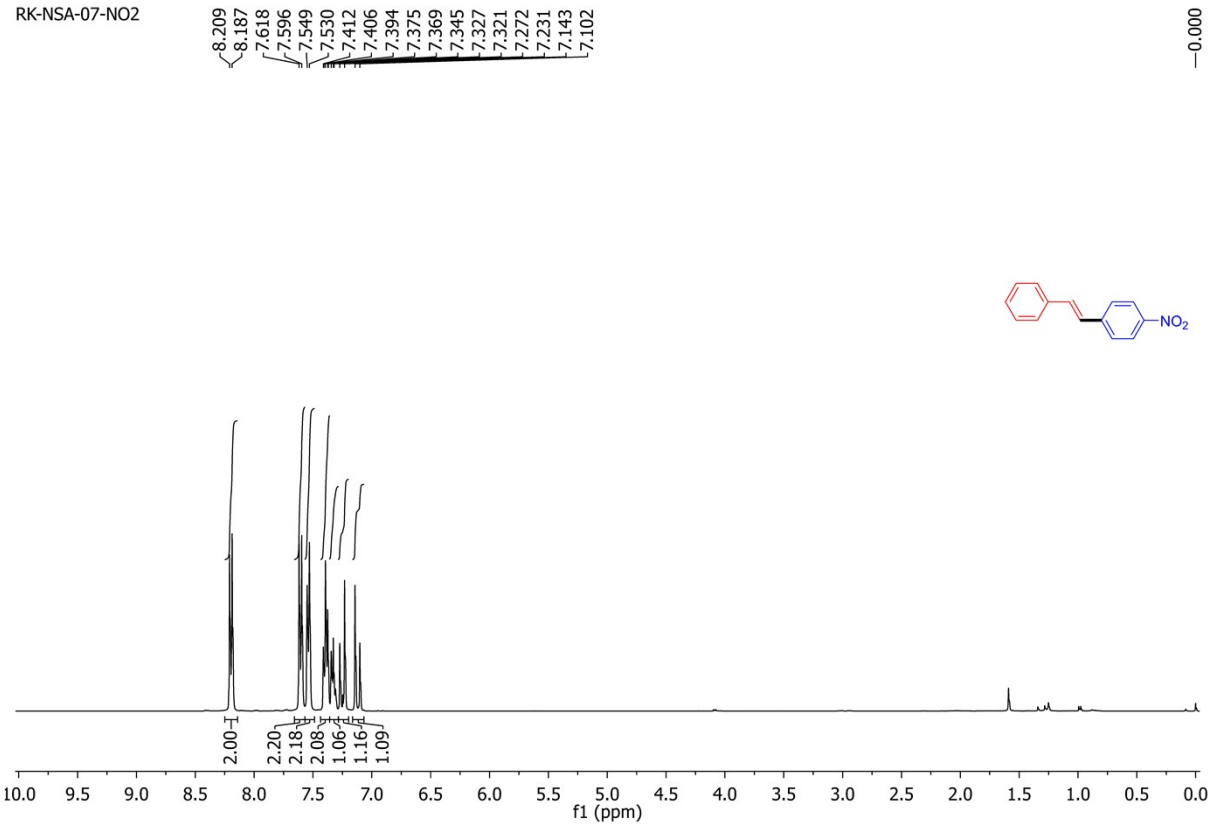

140.25
137.32
134.54
129.37
128.63
128.58
126.17
126.09
124.88
121.92
77.32
77.00
76.69
21.23
f1 (ppm)

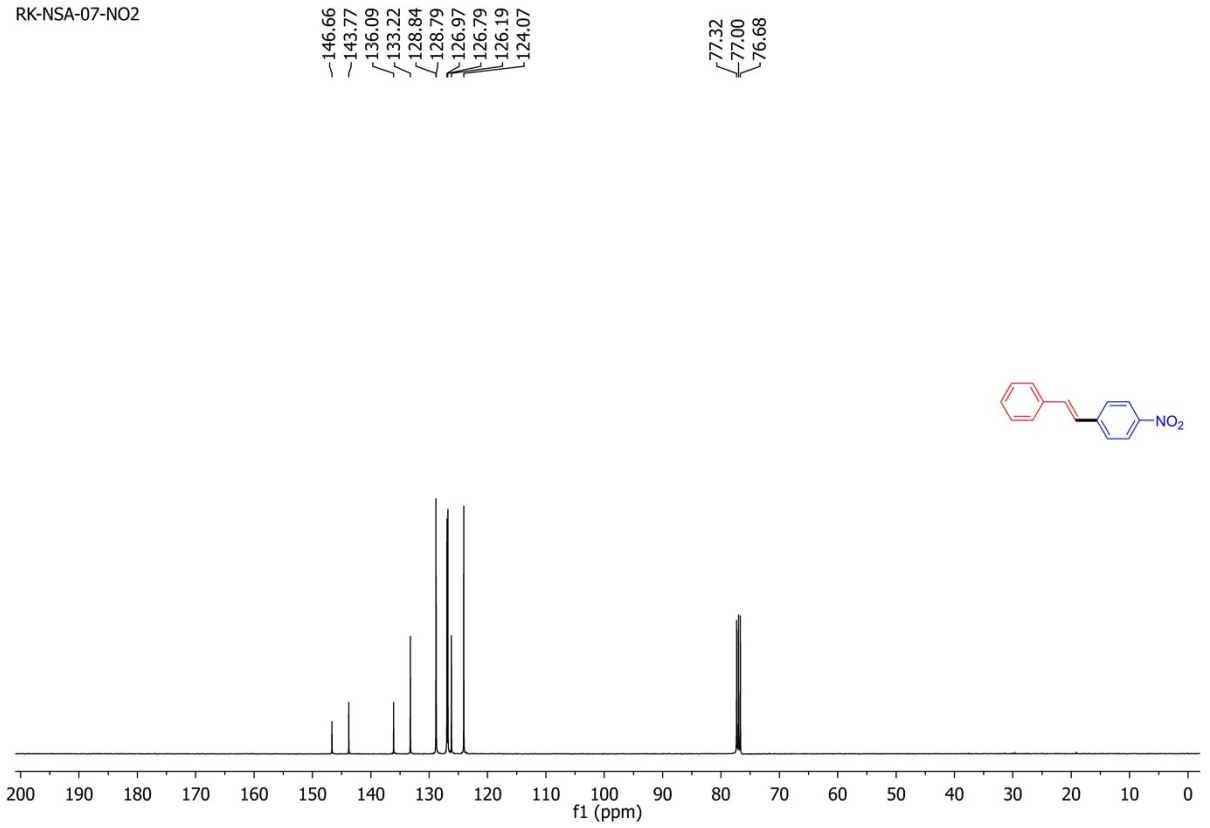

7.54
7.54
7.54
7.52
7.39
7.39
7.37
7.35
7.29
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.13
0.02
4.07
3.93
2.03
2.00
f1 (ppm)


137.28
128.65
127.59
126.48
77.32
77.00
76.68
f1 (ppm)

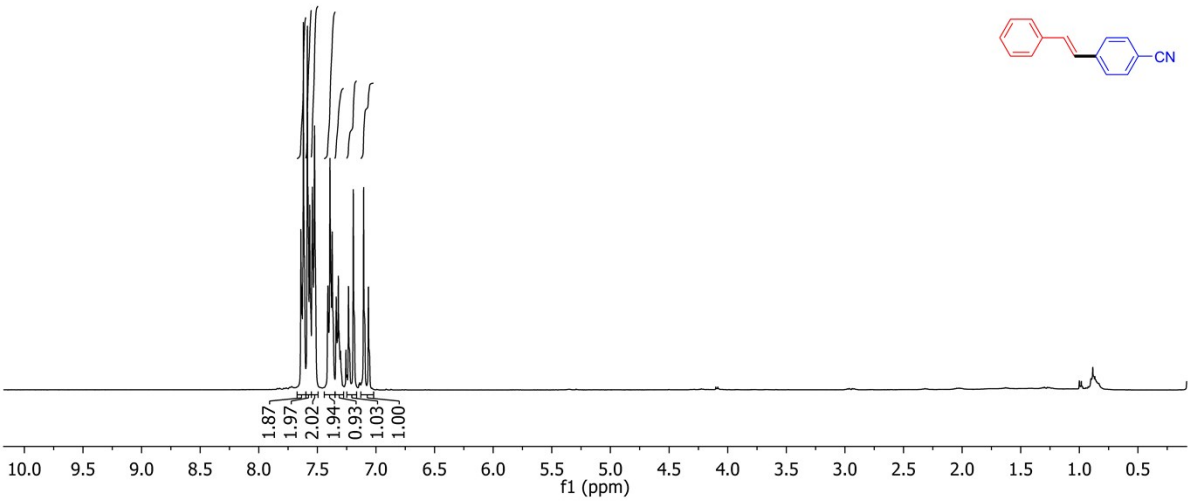

07-291
7.938
7.918
7.565
7.544
7.525
7.507
7.383
7.379
7.364
7.345
7.304
7.290
7.285
7.280
7.267
7.221
7.180
7.119
7.079
2.577
0.000
COCH3
2.00
2.04
2.04
2.04
1.05
1.05
1.10
2.97
f1 (ppm)

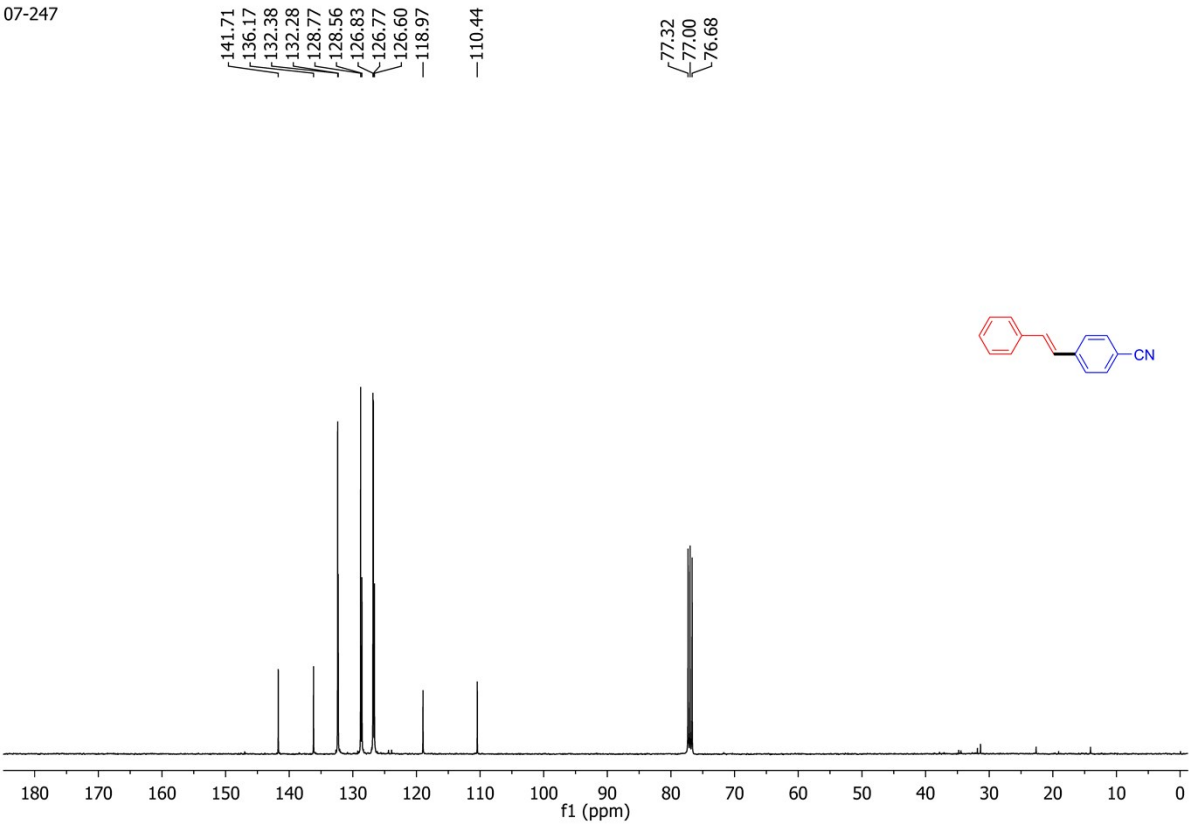

07-291
197.41
141.88
136.57
135.80
131.34
128.78
128.71
128.23
127.31
126.74
126.40
77.32
77.00
76.68
26.50
COCH3
f1 (ppm)


RK-NSA-07-NO2
8.209
8.187
7.618
7.596
7.549
7.530
7.412
7.406
7.394
7.375
7.369
7.345
7.327
7.321
7.272
7.231
7.143
7.102
0.000
NO2
2.00
2.20
2.18
2.08
1.06
1.16
1.09
10.0 9.5 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)

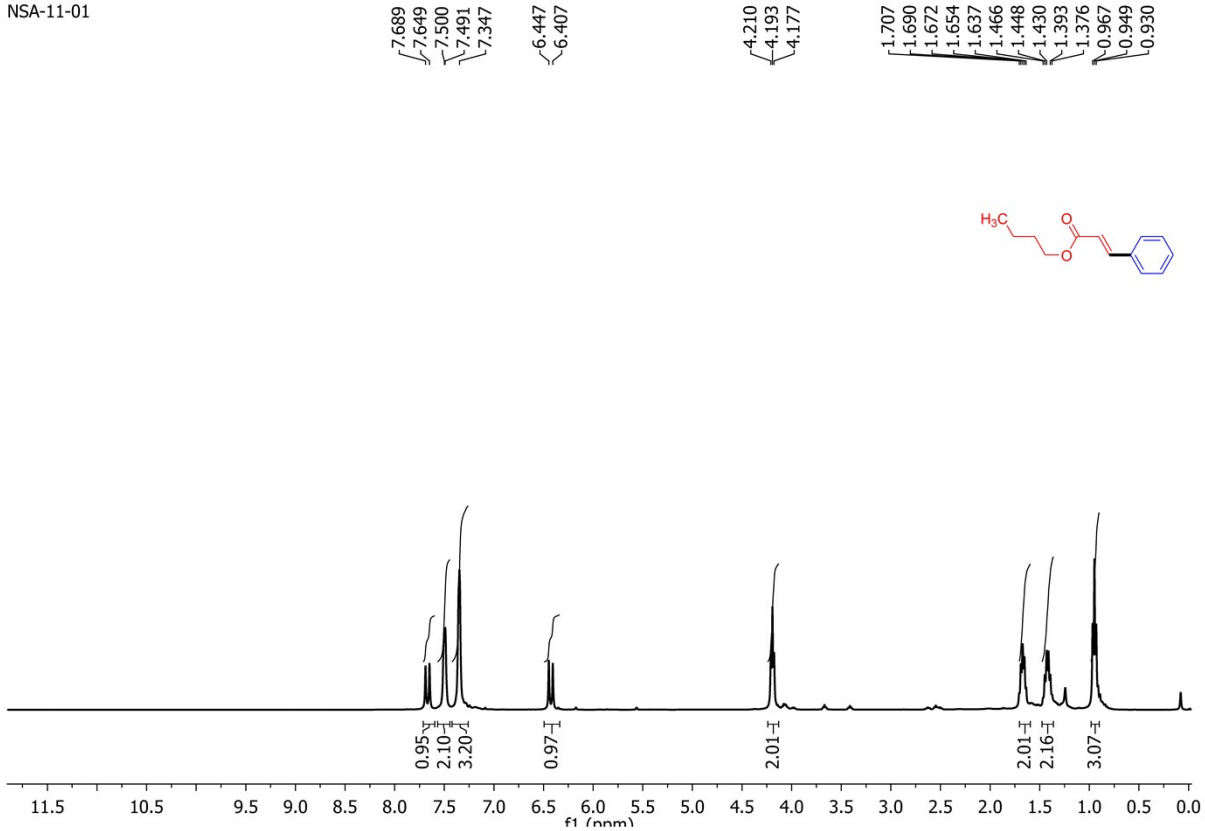

RK-NSA-07-NO2
146.66
143.77
136.09
133.22
128.84
128.79
126.97
126.79
126.19
124.07
77.32
77.00
76.68
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


07-247
7.64
7.64
7.63
7.62
7.61
7.59
7.58
7.56
7.54
7.54
7.52
7.41
7.41
7.39
7.37
7.37
7.34
7.33
7.32
7.26
7.23
7.19
7.11
7.06

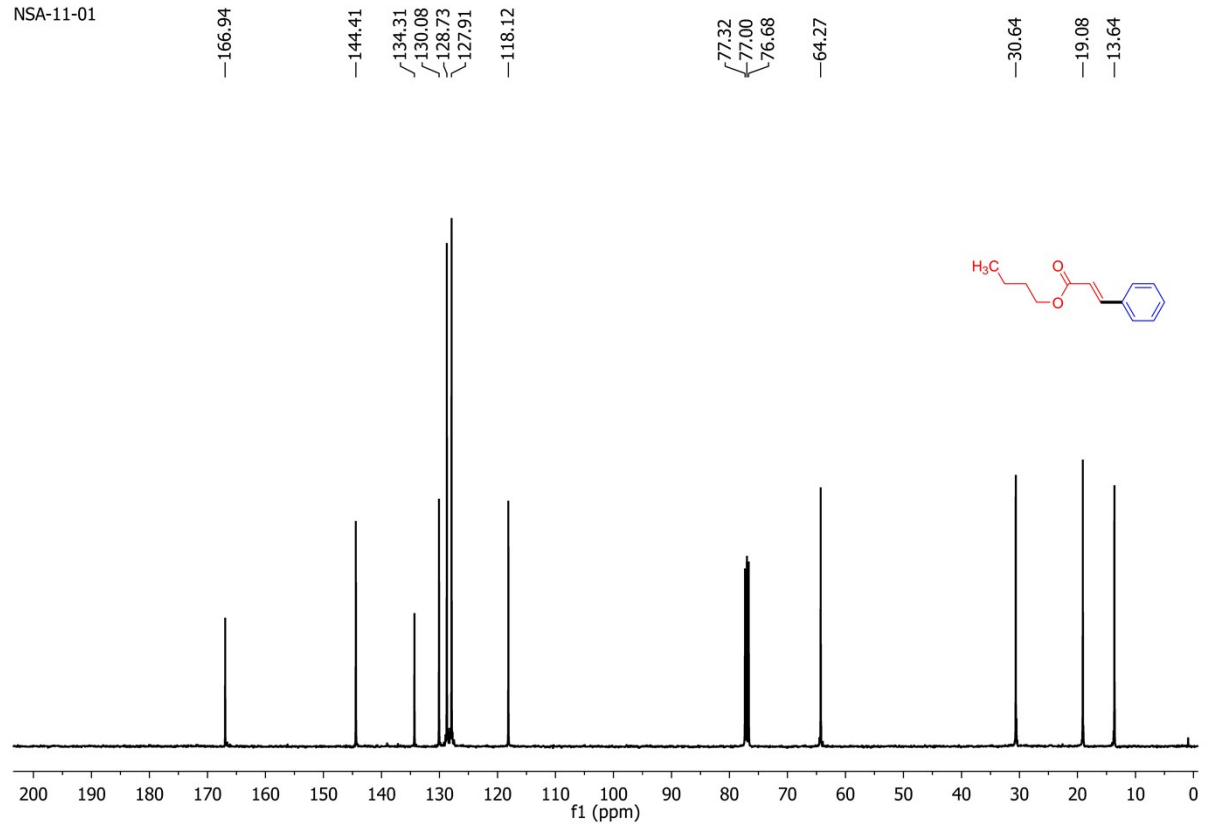

CN
1.87
1.97
2.02
1.94
0.93
1.03
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

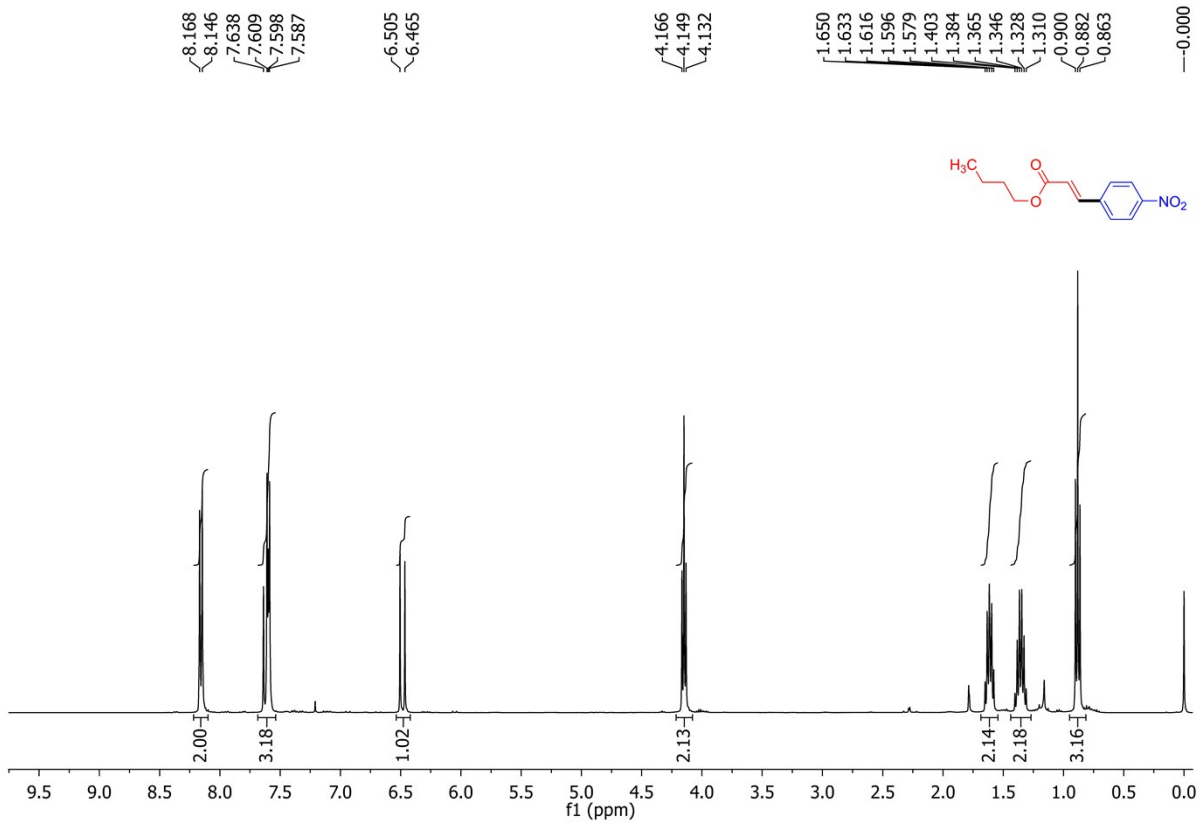

07-247
141.71
136.17
132.38
132.28
128.77
128.56
126.83
126.77
126.60
118.97
110.44
77.32
77.00
76.68
CN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

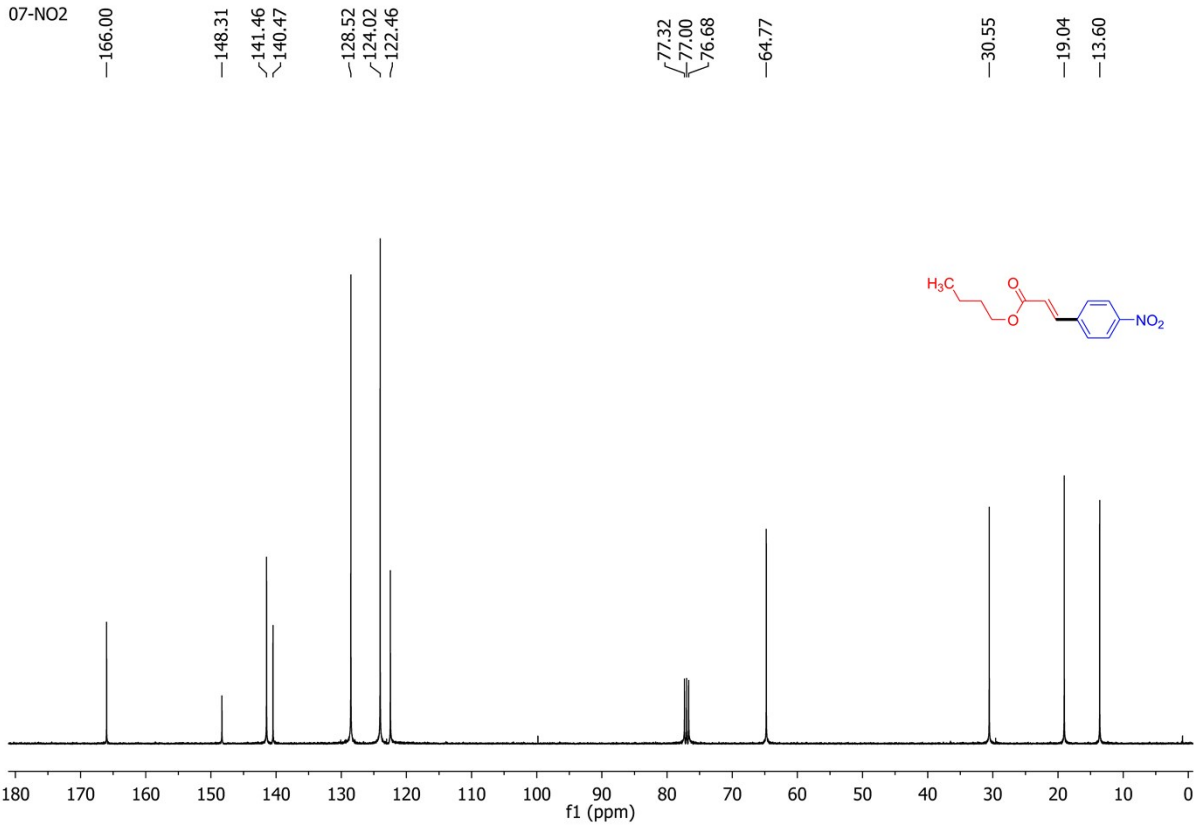
NSA-11-01

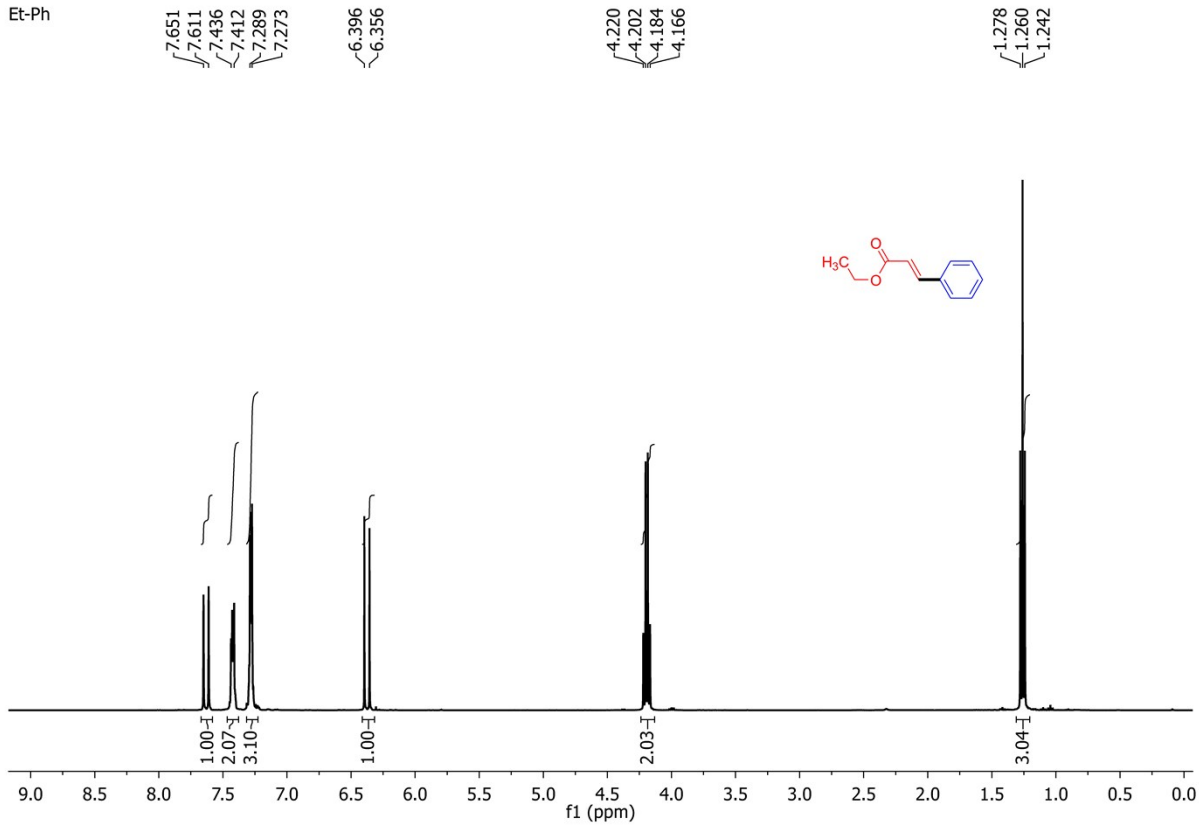


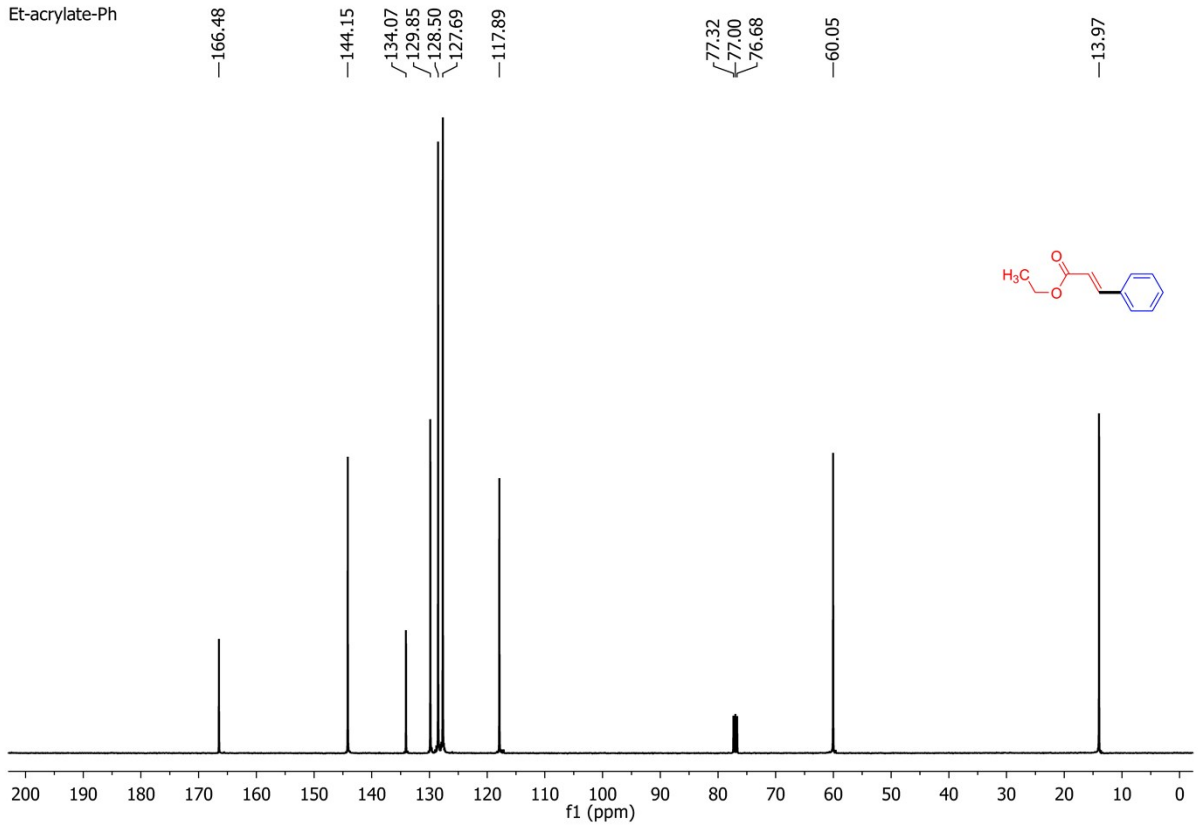
NSA-11-01



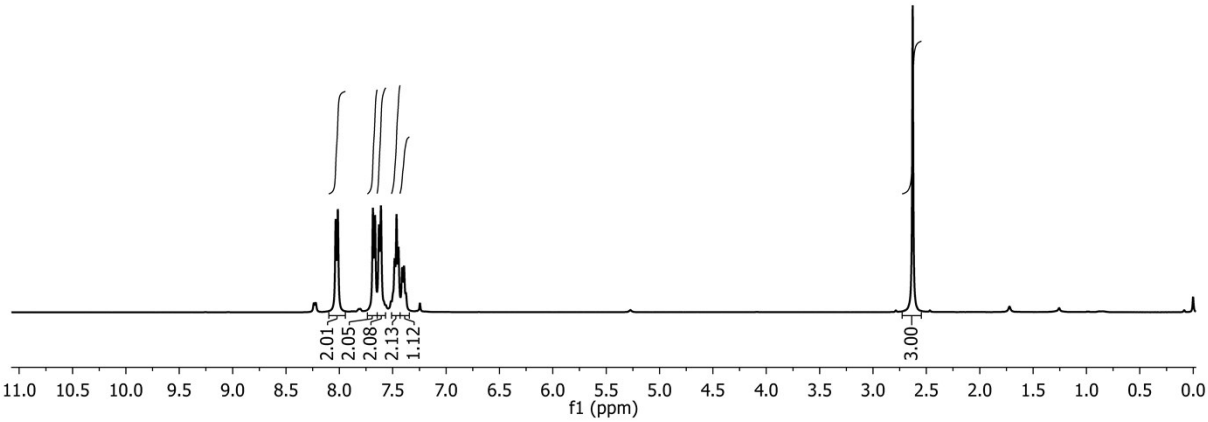

8.168
8.146
7.638
7.609
7.598
7.587
6.505
6.465
4.166
4.149
4.132
1.650
1.633
1.616
1.596
1.579
1.403
1.384
1.365
1.346
1.328
1.310
0.900
0.882
0.863
0.000
H3C
O
O
NO2
2.00
3.18
1.02
2.13
2.14
2.18
3.16
f1 (ppm)


07-NO2
166.00
148.31
141.46
140.47
128.52
124.02
122.46
77.32
77.00
76.68
64.77
30.55
19.04
13.60
H3C
O
O
NO2
f1 (ppm)

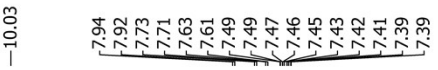

Et-Ph
7.651
7.611
7.436
7.412
7.289
7.273
6.396
6.356
4.220
4.202
4.184
4.166
1.278
1.260
1.242
1.00
2.07
3.10
1.00
2.03
3.04
f1 (ppm)

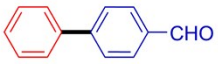

Et-acrylate-Ph
166.48
144.15
134.07
129.85
128.50
127.69
117.89
77.32
77.00
76.68
60.05
13.97
f1 (ppm)

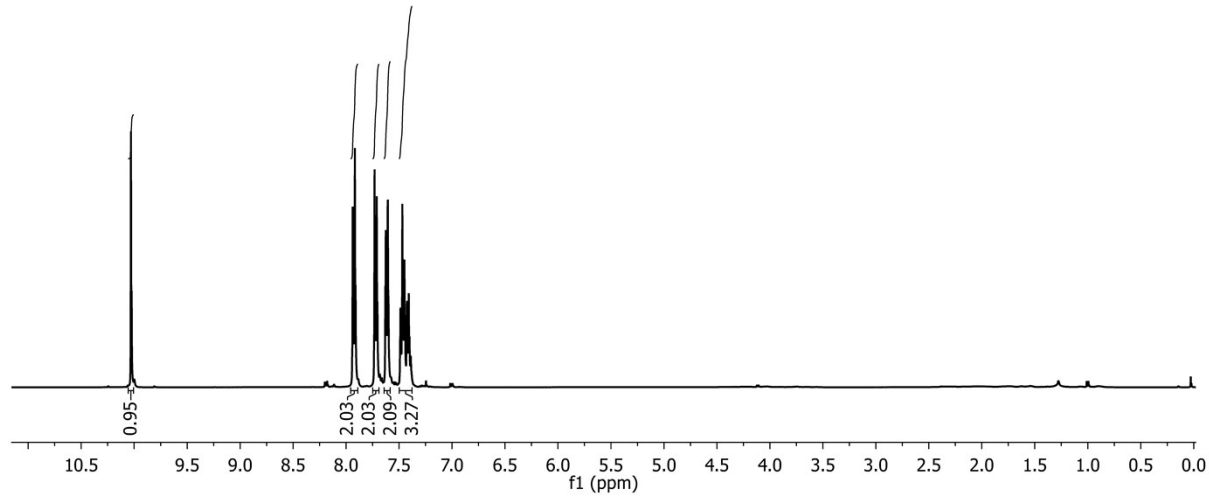
RK-NSA-I



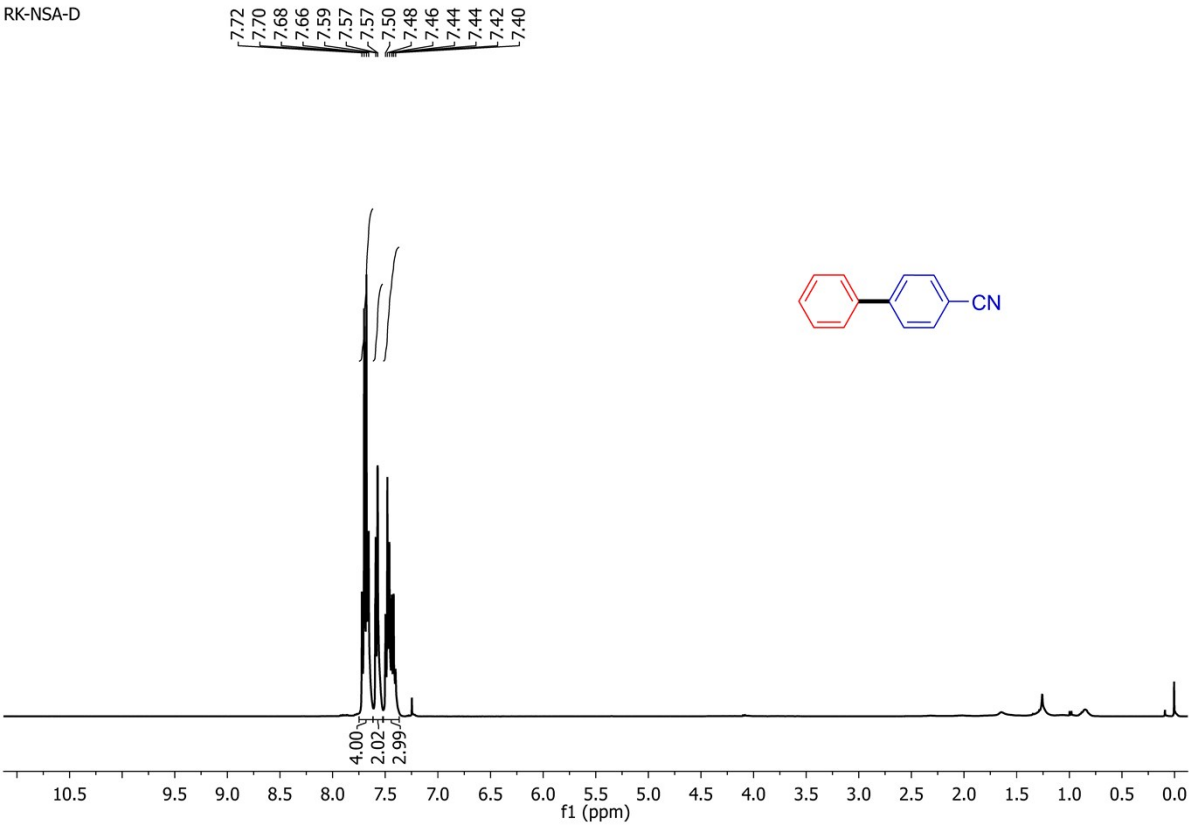
RK-NSA-F



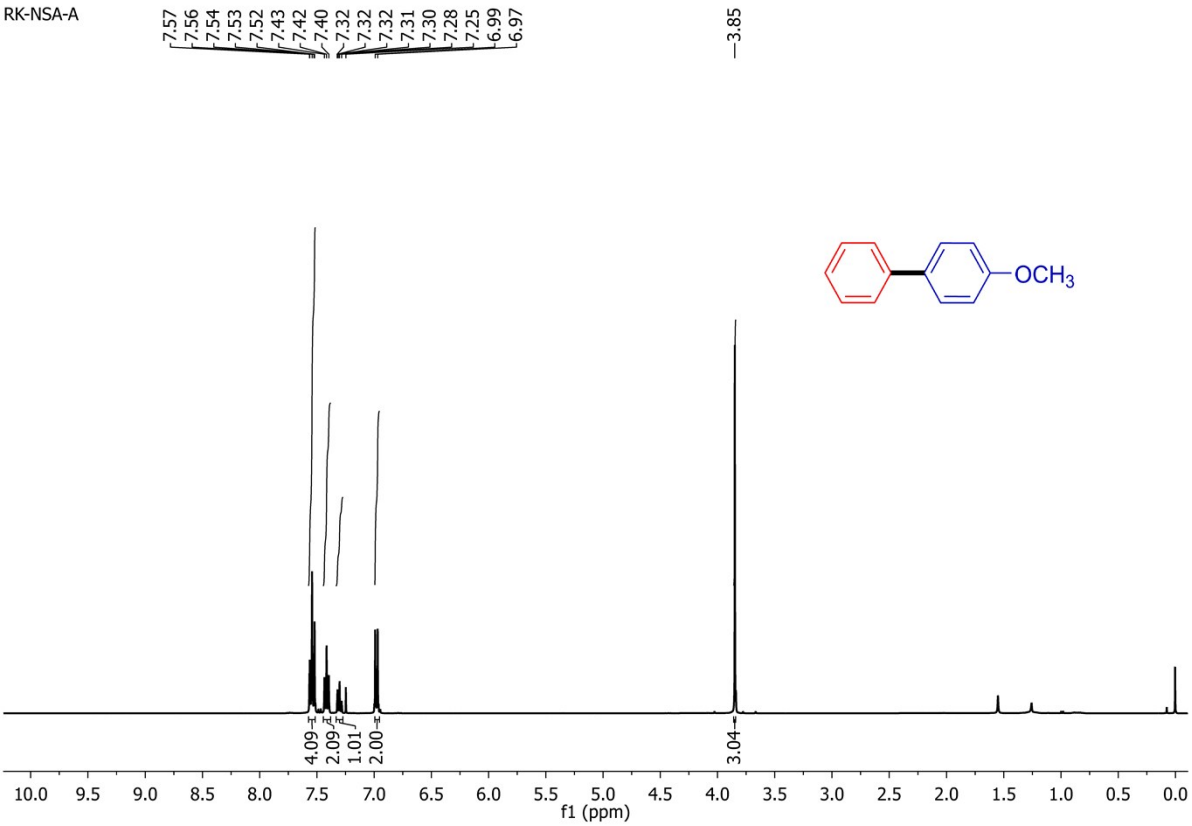




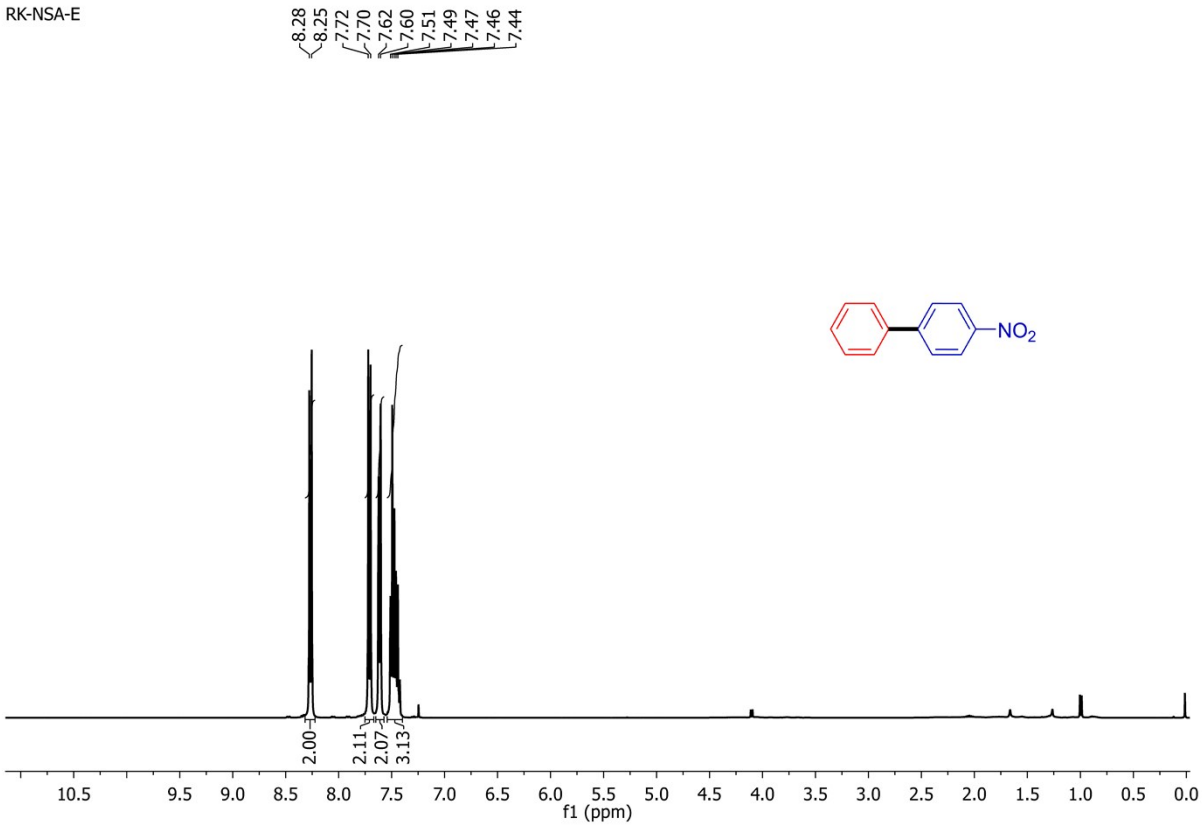
RK-NSA-D



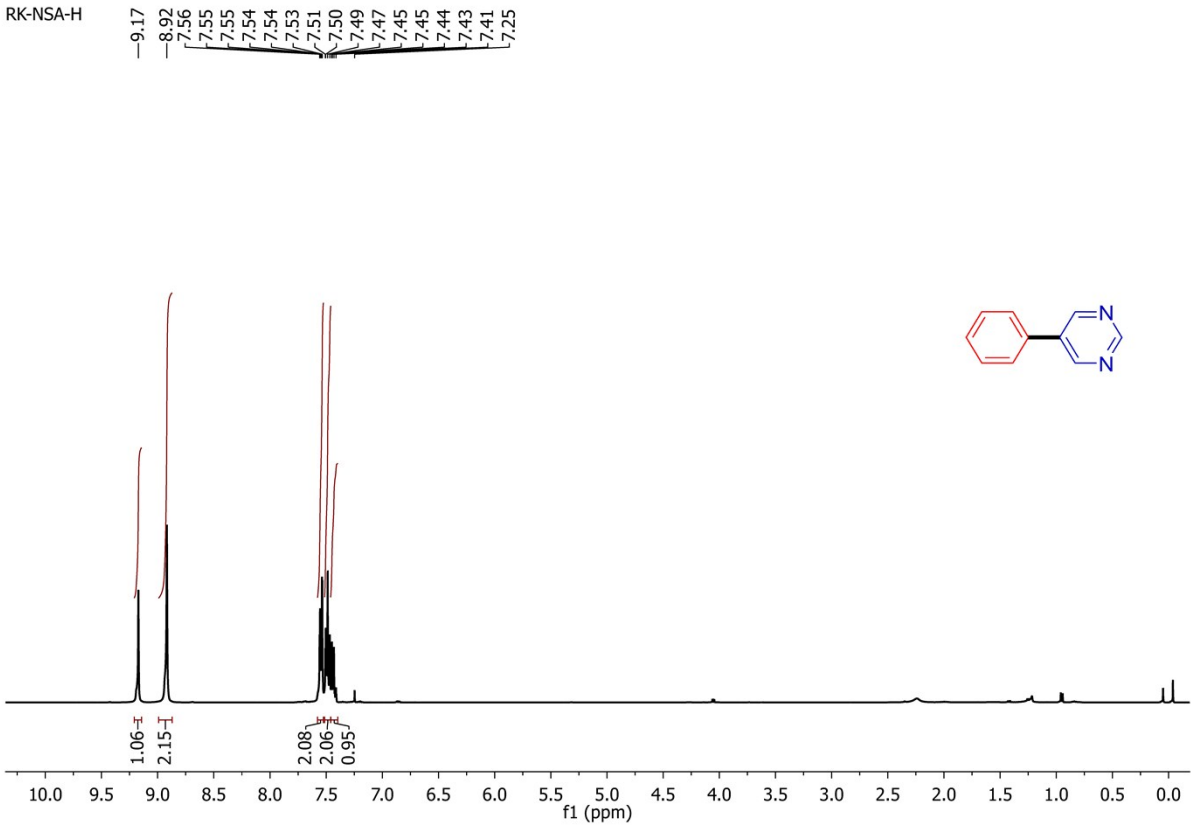
RK-NSA-A



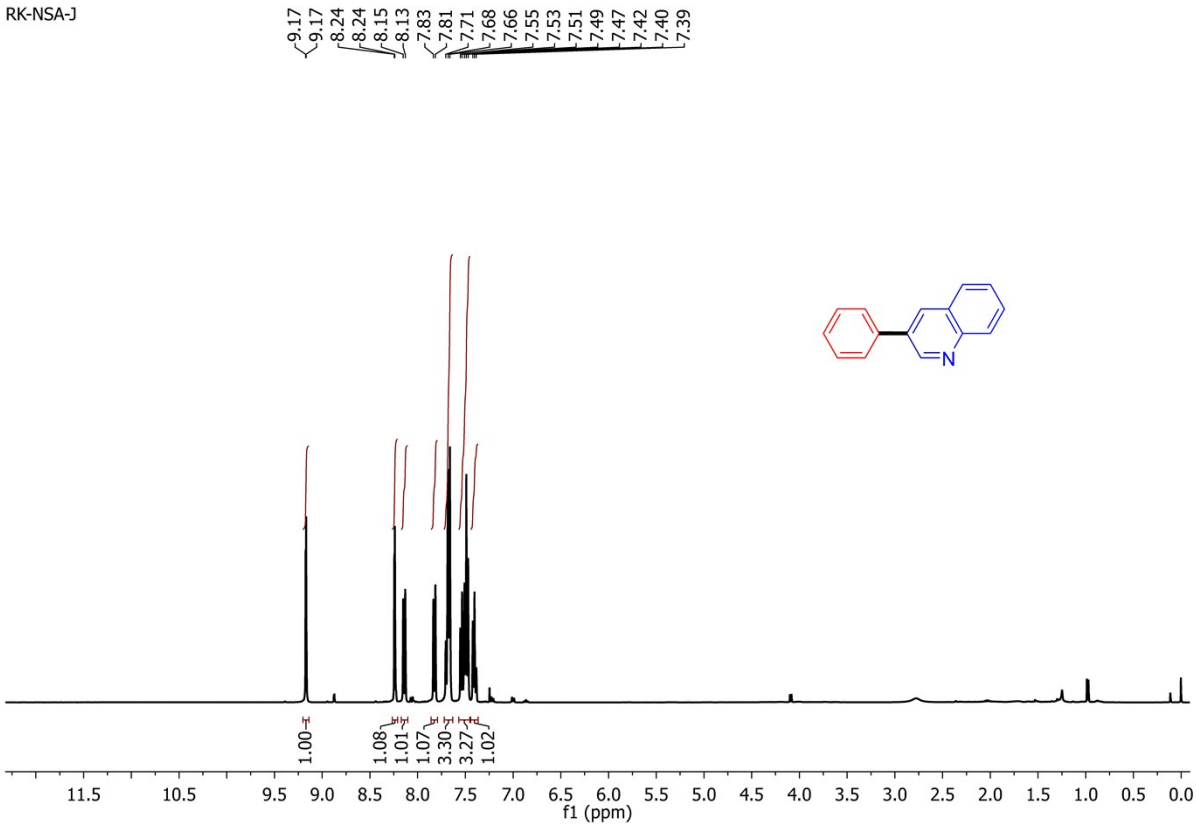
RK-NSA-E



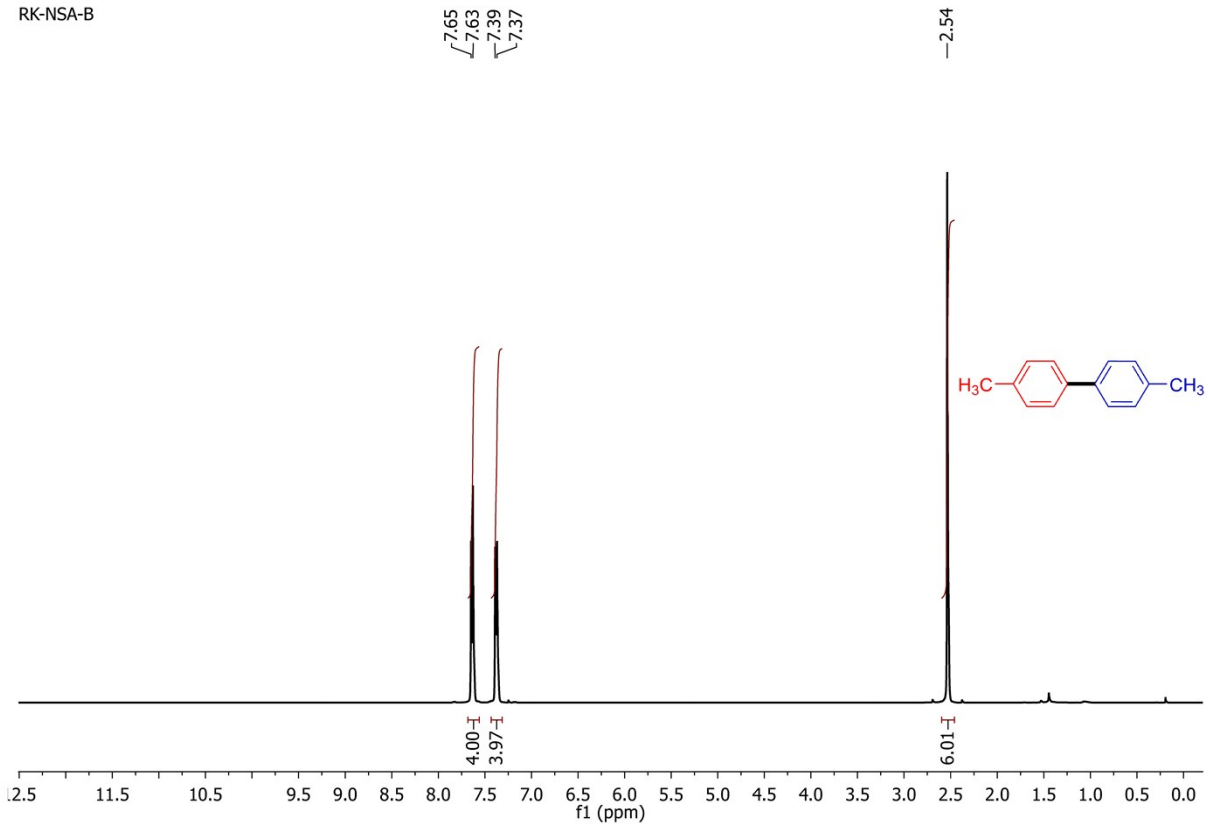
RK-NSA-H



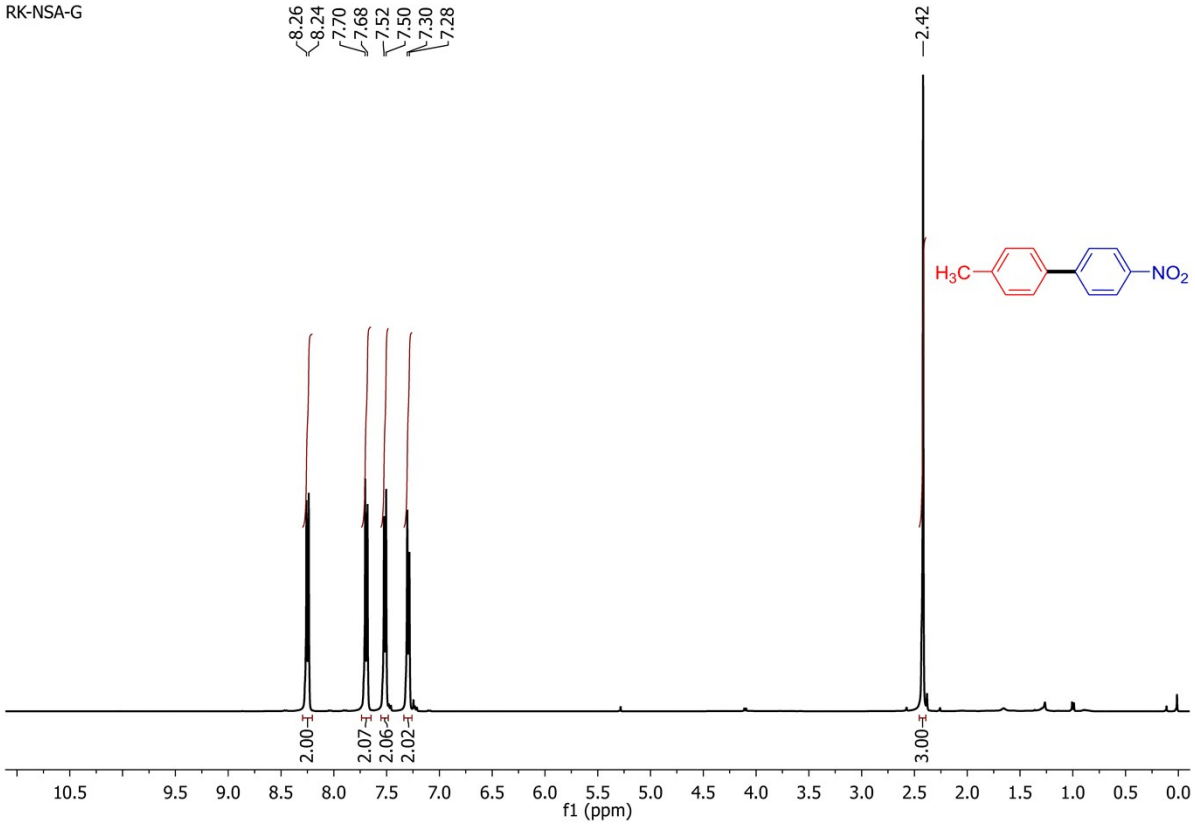
RK-NSA-J



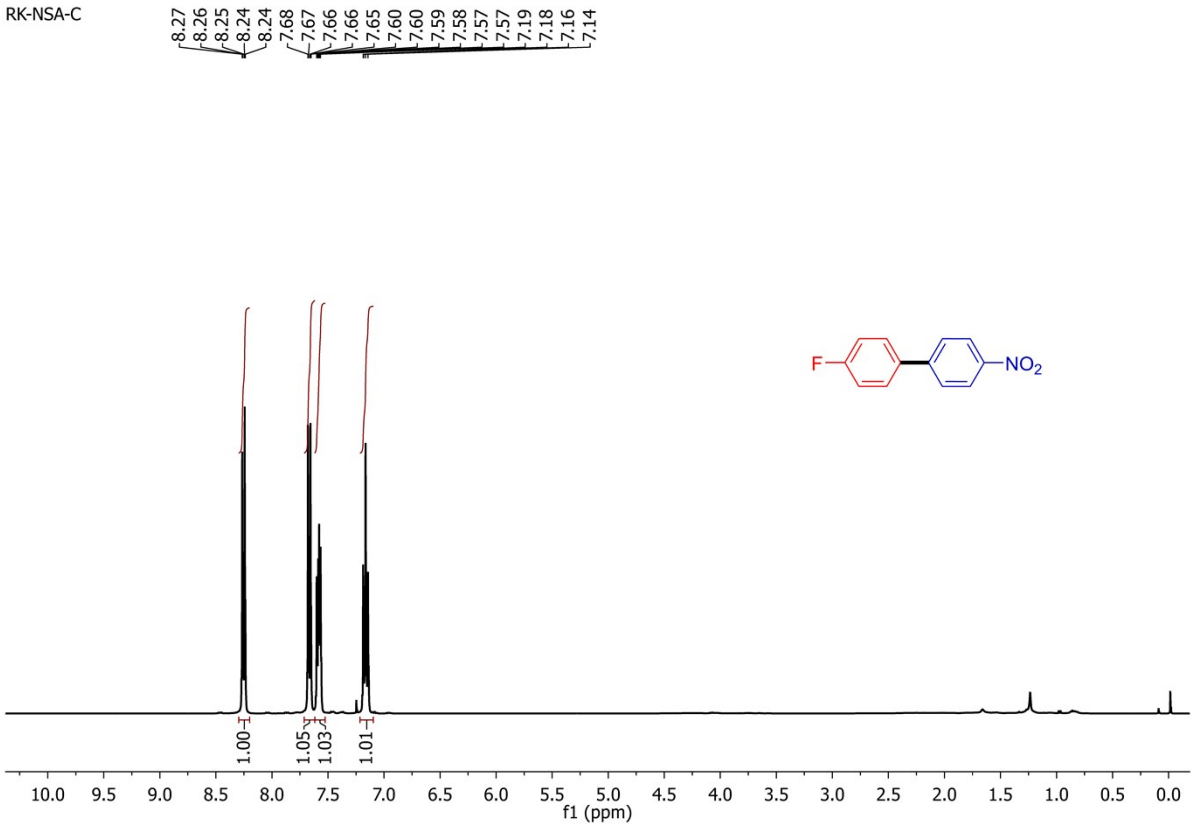
RK-NSA-B



RK-NSA-G



RK-NSA-C



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