

Solid acids as cocatalysts on the chelation-assisted hydroacylation of alkenes and alkynes

Blanca I. Vergara-Arenas,^a Eréndira García-Ríos,^b Rubén Gaviño,^{*b} Jorge Cárdenas,^b Alfredo Martínez-García,^c Erick A. Juárez-Arellano,^c Adolfo López-Torres,^c José A. Morales-Serna^{*c}

^a Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco No. 186, Ciudad de México, C. P. 09340, México.

^b Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Ciudad de México, 04510, México.

^c Centro de Investigaciones Científicas, Instituto de Química Aplicada, Universidad del Papaloapan, Tuxtepec, Oaxaca, 68301, México. E-mail: joseantonio.moralesserna@gmail.com.

Table of contents

1. General information	S3
2. Experimental procedures	S3
2.1. Synthesis of sulphated zirconia (SZ)	S3
2.2. Synthesis of Al-MCM-41	S4
2.3. Modification of montmorillonite	S4
2.4. Characterization of sulfated zircon (SZ)	S4
2.5. Characterization of Al-MCM-41	S6
2.6. Characterization of modified montmorillonite	S8
2.7. Standard catalytic reaction procedure to hydroacylation reaction of aldehydes	S11
2.8. Standard catalytic reaction procedure to hydroacylation of benzylic alcohols	S11
3. Characterization of organic compounds	S12
4. NMR Spectrum	S15
5. References	S27

1. General information

Trifluoromethanesulfonic acid, zirconium *n*-propoxide (70% *n*-propanol), 2-propanol, sulfuric acid, cetyltrimethylammonium bromide, triethylamine, tetramethylammonium hydroxide, TEOS, aluminium nitrate nonahydrate, benzaldehyde, chloridotris(triphenylphosphine)rhodium(I), 2-amino-3-picoline, aniline, 1-butene, 1-pentene, 1-hexene, 1-nonene, 1-dodecene, phenylacetylene, 1-ethynyl-4-nitrobenzene, 1-ethynyl-3-nitrobenzene, 1-chloro-2-ethynylbenzene, 1-bromo-4-ethynylbenzene, *p*-anisaldehyde, acetaldehyde, toluene, hexane, and ethyl acetate were purchased from Sigma Aldrich. Microwave irradiation experiments were performed using a Discover System (CEM Corporation) single-mode microwave with standard sealed microwave glass vials. The organic reactions were monitored by TLC carried out on 0.25 mm Merck silica gel plates. The developed TLC plates were visualised under a short-wave UV lamp or by heating after they were dipped in Ce(SO₄)₂. Flash column chromatography (FCC) was performed using silica gel (230–400) and employed a solvent polarity correlated with the TLC mobility. Yields refer to the chromatographically and spectroscopically (¹H and ¹³C) homogeneous materials. NMR experiments were conducted on a Varian 300 or Bruker 500 MHz instruments in CDCl₃ (99.9% D) and CD₃OD (99.8% D) as solvents; the chemical shifts (δ) were referenced to CHCl₃ (7.26 ppm ¹H, 77.00 ppm ¹³C), CD₃OD (4.87 ppm ¹H, 49.00 ppm ¹³C), or TMS (0.00 ppm). The chemical shifts are reported in parts per million (ppm) and coupling constants *J* are given in hertz (Hz). The multiplicities are reported as: s – singlet, d – doublet, t – triplet, q – quartet, dd – doublet of doublets, dt – doublet of triplets, ddd – doublet of doublet of doublets, td – triplet of doublets or m – multiplet. The elemental analyses were carried out in an Elemental Analyzer Thermo Scientific/Flash 2000 equipment. The measurements of EPR were made with a Jeol JES-TE300 X band fashion spectrometer with a cylindrical cavity in the mode TE011. The external calibration of the magnetic field was carried out with a precision gaussmeter, Jeol ES-FC5. Powder X-ray diffraction (XRD) was performed using a Stoe Stadi-P Cu diffractometer with Cu Kα1 (using 40kV and 30mA). The nitrogen adsorption-desorption analysis of the materials was obtained at –196 °C on Micromeritics ASAP 2020 equipment. The chemical composition of natural montmorillonite and modified montmorillonite were determined by energy-dispersive X-ray spectroscopy (EDXS), using an electronic spectrometer microprobe EPMA, JXA8900-R, JEOL. FT-IR spectra were recorded on a Nicolet Magna 750 spectrometer and data collection was performed using DRIFT.

2. Experimental procedures

2.1. Synthesis of sulfated zirconia (SZ)

Zirconium *n*-propoxide (20 mL, 70% *n*-propanol) and 2-propanol (30 mL) were added to a 250 mL Erlenmeyer flask and stirred with a magnetic bar. Acid solution (1 mL 98% sulfuric acid in 3.2 mL

distilled water) was added dropwise to hydrolyse the zirconium *n*-propoxide to obtain a gel. The solid was filtered and dried at 80 °C until complete alcohol evaporation, then calcined in air at 600 °C for 6 h.¹

2.2. Synthesis of Al-MCM-41

Cetyltrimethylammonium bromide (7.3 g) was mixed with deionized water (200 mL) at 30 °C, then triethylamine (3.3 mL) was added. After stirring for 15 minutes, TMAOH (18 mL, 10 wt %), TEOS (22.4 mL) and Al(NO₃)₃·9H₂O (18.75 g) were added, and the solution was stirred for 1 hour. The resulting gel, with molar composition 1 TEOS : 0.2 CTMABr : 0.6 EA : 0.2 TMAOH : 0.05 Al(NO₃)₃·9H₂O : 150 H₂O, was placed in glass bottles and sonicated for 4 h. The precipitated solid was recovered by filtration and washed with deionized water, dried at 80 °C overnight and calcinated at 540 °C for 6 h under air flow.²

2.3. Modification of montmorillonite

50 g of natural montmorillonite was ground in a mortar and suspended in 1000 mL of deionized H₂O. The mixture was stirred for 24 h and the suspended montmorillonite was separated by centrifugation (600 rpm for 15 min). This process was repeated three times and then the montmorillonite was dried at 100 °C under vacuum for 72 h to obtain a white solid. 10 g of this solid was suspended in 300 mL of deionized H₂O and stirred for 72 h. Subsequently, a solution of CF₃SO₃H (100 mL, 0.18 M) was added, and the mixture was stirred for 24 h. The solid was recovered by vacuum filtration and washed with acetone (50 mL). Finally, the montmorillonite was dried at 100 °C under vacuum for 72 h to obtain a white solid.

2.4. Characterization of sulfated zirconia (SZ)

The figure S1 shows XRD corresponding to the crystalline tetragonal zirconia as the predominantly phase which is given by reflections in $2\theta = 30.21^\circ$ (1 1 1), 35.35° (2 0 0), 50.21° (2 2 0), 59.23° (3 1 1), 60.17° (2 2 2), 62.84° (2 0 2), 74.78° (4 0 0) and 81.78° (3 3 1).

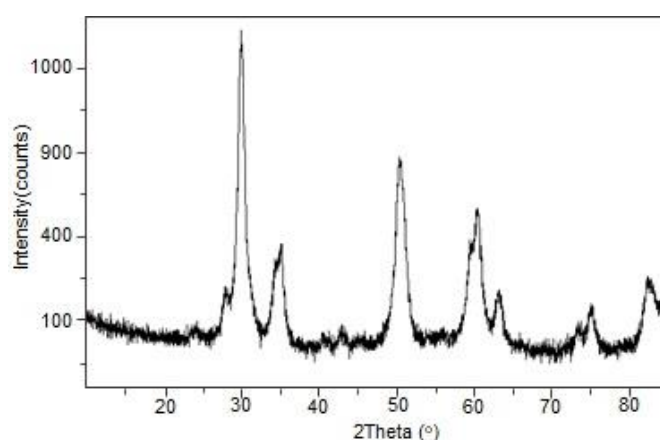


Fig. S1. XRD of SZ.

Supporting Information

Figure S2 shows the nitrogen adsorption-desorption isotherm of SZ, corresponding to type IV of the IUPAC classification, typical for mesoporous materials. The table S1 shows the SZ surface area, pore volume, and pore size were 90.75 m²/g, 0.12 cm³/g, and 52.73 Å, respectively.

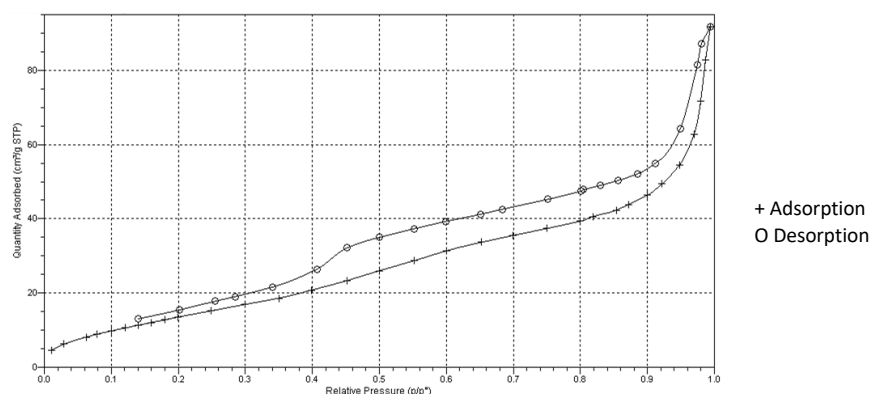


Fig. S2. Nitrogen adsorption-desorption isotherm of SZ.

Table S1. Textural properties of SZ

Entry	Parameter	SZ
1	BET Area (m ² /g)	90.75
2	Pore Volume (cm ³ /g)	0.12
3	Pore Size (Å)	52.73

Table S2 shows the chemical compositions of SZ determined by EDXS.

Table S2. Chemical analyses determined by EDXS

	Elemental concentration weight (%)			
	C	O	S	Zr
SZ	46.65	40.04	0.28	13.03

The micrograph of the SZ showing the presence of a porous material (Figure S3).

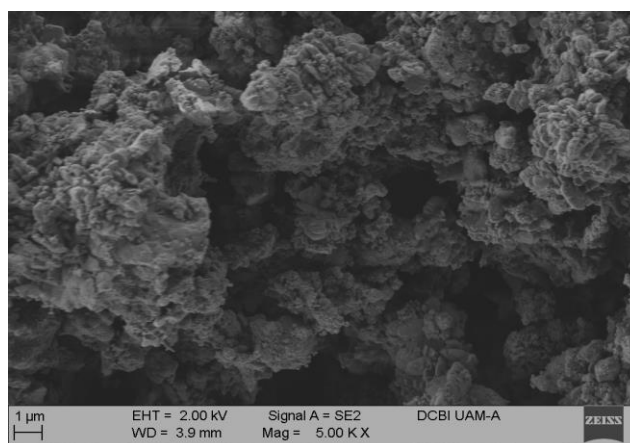


Fig. S3. TEM micrograph of SZ.

Supporting Information

The characteristic bands of FTIR of SZ are observed in the figure S4. Bands in 497 and 660 cm^{-1} , corresponding to S-O; 1045, 1303 and 1416 cm^{-1} , corresponding to S=O; cm^{-1} , and 3393 cm^{-1} , corresponding to OH group.

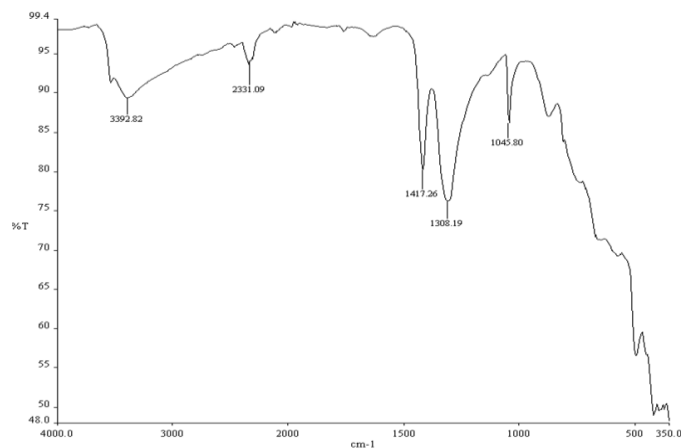


Fig. S4. FTIR spectrum of SZ.

The acidity of SZ was determined by pyridine impregnation analysis in FTIR (Table S3).²

Table S3. Concentration of Brønsted and Lewis acids in SZ

A.I. (Bronsted) mmol	A.I. (Lewis) mmol	Bronsted mmol/g	Lewis mmol/g	Acid mmol/g
3.83	5.03	227	277	504

2.5. Characterization of Al-MCM-41

The Al-MCM-41 mesoporous materials exhibited reflections associated with the SiO crystal structure. The maxima correspond to typical diffraction by reflections 2.2° (1 0 0) and 4.0° (1 1 0) (Figure S5).

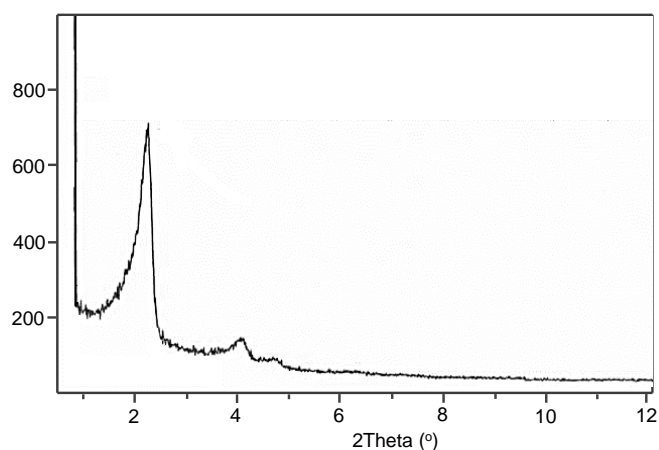


Fig. S5. XRD pattern of Al-MCM-41.

Supporting Information

The nitrogen adsorption-desorption isotherms of Al-MCM-41 (Figure S6) showed a profile corresponding to type IV of the IUPAC classification, typical for mesoporous materials. The Al-MCM-41 surface area, pore volume, and pore size were 1221.79 m²/g, 0.85 cm³/g, and 26.49 Å, respectively (Table S4).

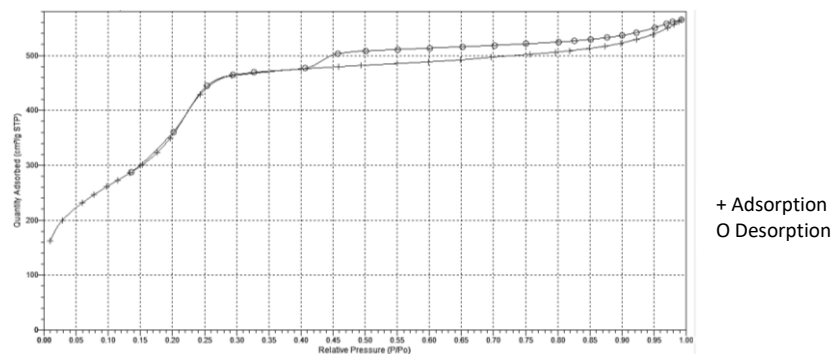


Fig. S6. Nitrogen adsorption-desorption isotherm of Al-MCM-41.

Table S4. Textural properties of Al-MCM-41

Entry	Parameter	Al-MCM-41
1	BET Area (m ² /g)	1221.79
2	Pore Volume (cm ³ /g)	0.85
3	Pore Size (Å)	26.49

Table S5 shows the chemical composition of Al-MCM-41 determined by EDXS.

Table S5. Chemical analyses determined by EDXS

	Elemental concentration weight (%)		
	O	Si	Al
Al-MCM-41	53.3	40.9	3.8

The figure S7 shows the micrograph of Al-MCM-41. The image shows a porous material, with uniform distribution.

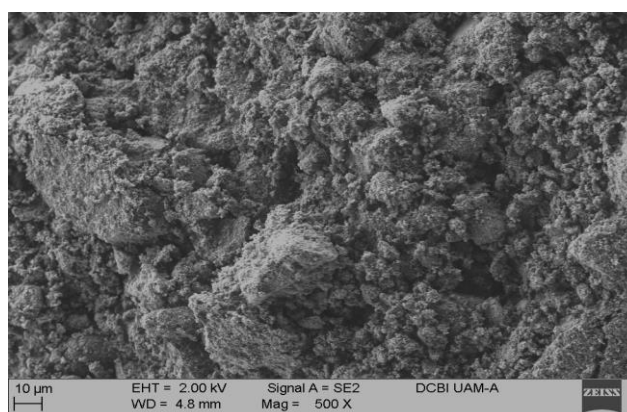


Fig. S7. TEM micrograph of Al-MCM-41.

In the FTIR spectrum of Al-MCM-41, the characteristic bands of MCM-41 are observed, 451.25 cm^{-1} , corresponding to O-Si-O; 780.07 cm^{-1} , corresponding to O-Si-O flexion; 1067.10 cm^{-1} , corresponding to Si-O; 1642.73 cm^{-1} , corresponding to Si-OH, and 3428.57 cm^{-1} , corresponding to Si-OH (Figure S8).

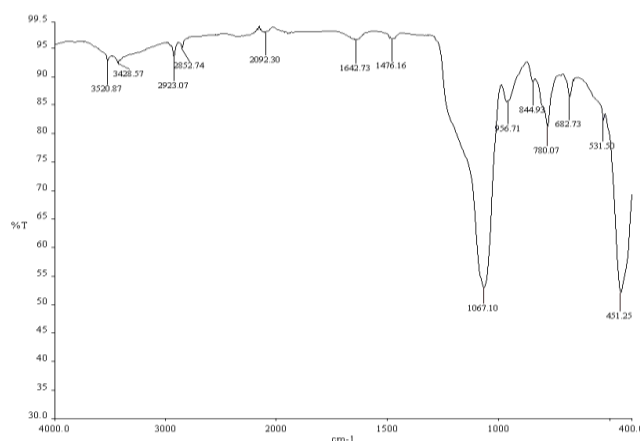


Fig. S8. FTIR spectrum of Al-MCM-41.

The acidity of Al-MCM-41 was determined by pyridine impregnation analysis in FTIR (Table S6).²

Table S6. Concentration of Brønsted and Lewis acids in Al-MCM-41

A.I. (Bronsted) mmol	A.I. (Lewis) mmol	Bronsted mmol/g	Lewis mmol/g	Acid mmol/g
3.15	3.88	218	249	467

2.6. Characterization of modified montmorillonite

The XRD patterns of montmorillonite exhibited reflections associated with bentonite crystal structure. Reflection relative to the planes (0 0 1), (1 0 0), (1 0 5), (2 1 0) and (3 0 0) confirmed the crystal structure of montmorillonite (Figure S9).

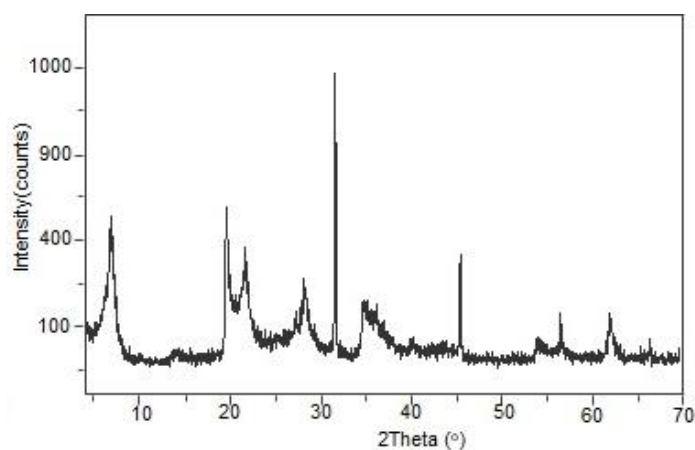


Fig. S9. XRD of modified montmorillonite.

The isotherms of montmorillonite corresponded to type IV (IUPAC classification) with H3 hysteresis, which is typical for mesoporous materials (Figure S10). The surface area, pore diameter and pore volume were calculated using Barret–Joiner–Halenda (BJH) model and the results are showed in table S7.

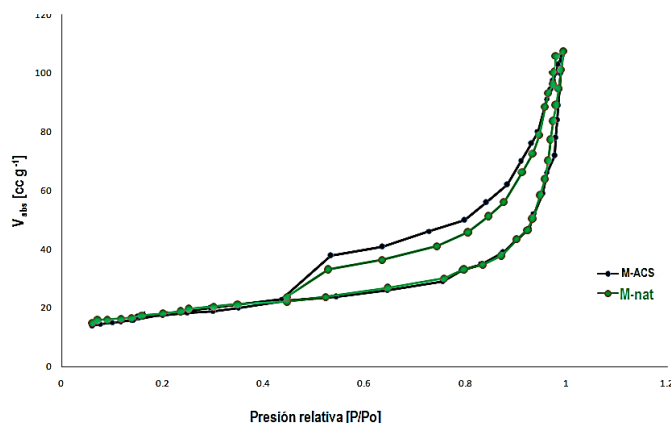


Fig. S10. Nitrogen adsorption-desorption isotherm of natural montmorillonite (M-nat) and modified montmorillonite (M-ACS).

Table S7. Textural properties of montmorillonite

Entry	Parameter	Natural montmorillonite	Modified montmorillonite
1	BET Area (m ² /g)	48.02	185.00
2	Pore Volume (cm ³ /g)	0.14	0.60
3	Pore Size (Å)	20.16	107.79

Table S8 shows the chemical composition of natural montmorillonite and modified montmorillonite determined by EDXS. The modified montmorillonite was found to contain S, which was provided by CF₃SO₃H used.³

Table S8. Chemical analyses determined by EDXS

	Elemental concentration weight (%)									
	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	SO ₃	TiO ₂	MnO	Fe ₂ O ₃
Natural montmorillonite	2.60	0.29	3.45	21.20	65.48	1.32	-	0.30	0.28	5.08
Modified montmorillonite	0.13	0.22	2.04	15.69	72.51	1.19	2.3	0.28	0.10	5.54

The micrograph of the montmorillonites showed the presence of stackings of clay layers distributed in a disorganized way. Such arrangements are typical of delaminated clays that confirmed the porosity data obtained (Figure S11).

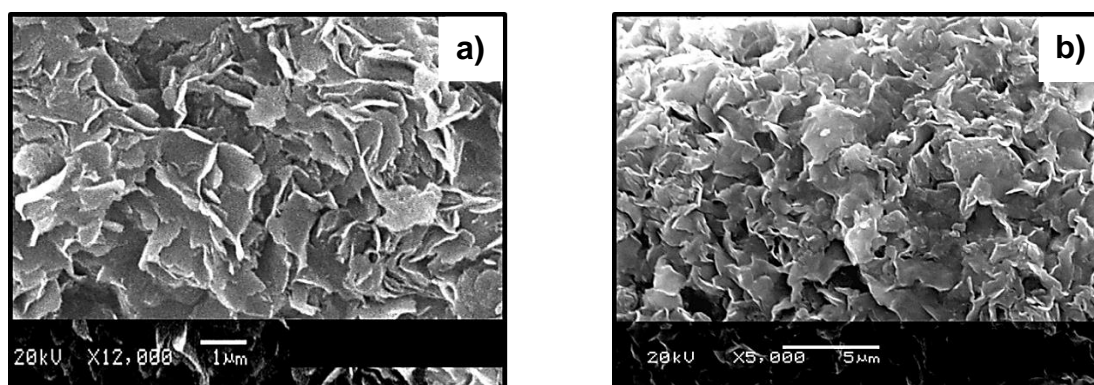


Fig. S11. TEM micrograph of a) natural montmorillonite and b) modified montmorillonite.

Figure S12 shows the IR spectrum of natural and modified montmorillonite. The characteristic vibrations of modified montmorillonites can be observed in 446 cm^{-1} , corresponding to Si-O-Si; 797 cm^{-1} , corresponding to Si-O; 844 cm^{-1} , corresponding to Al-Mg-O group; 1038 cm^{-1} , corresponding to Si-O group; 1188 cm^{-1} , corresponding H-SO₃; and broad band at 3622 cm^{-1} corresponding to hydroxy OH group.

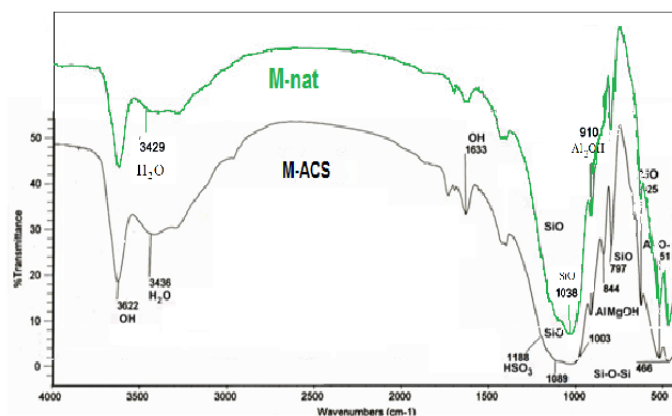


Fig. S12. FTIR spectrum of natural montmorillonite (M-nat) and modified montmorillonite (M-ACS).

Acidity was determined by the KOH titration method (Table S9).³

Table S9. Montmorillonite acidity

Acidity	%-weight
TA (meq KOH/g)*	0.099
H_0 **	≤ -0.20

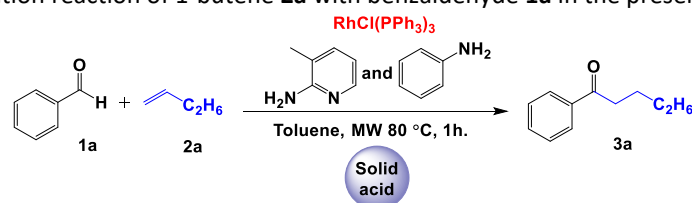
*TA: total acidity (KOH titration method)

** H_0 : Hammet acidity function (spectrophotometric method, with Hammett bases)

2.7. Standard reaction procedure to hydroacylation reaction from aldehydes

In a 10 mL tube of microwave with stir bar, 50 mg of solid acid, 1 mmol of aldehyde **1**, 1.5 mmol of alkene or alkyne **2**, 5% mmol of $\text{RhCl}(\text{PPh}_3)_3$, 20% mmol of 2-amino-3-picoline, 20% mmol of aniline and 3 mL of toluene were added. It was irradiated for 1 h in the microwave, at 80 °C. The mixture was dried in a rotavapor and purified for chromatography column.

Table S10. Hydroacylation reaction of 1-butene **2a** with benzaldehyde **1a** in the presence of solid acids.

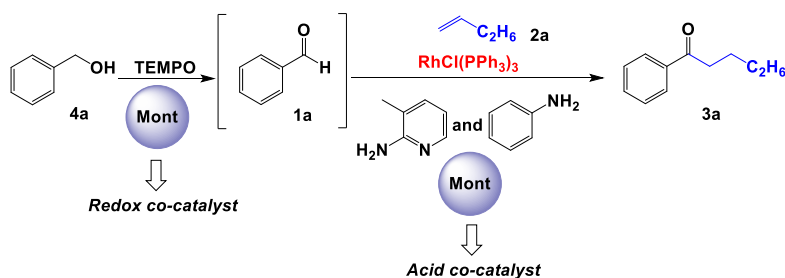


Entry	Solid acid	Solid acid loading mg	Time minutes	Solvent	Yield % ^a
1	Modified montmorillonite	50	30	Toluene	45
2	Modified montmorillonite	50	45	Toluene	63
3	Modified montmorillonite	50	60	Toluene	87
4	Modified montmorillonite	25	60	Toluene	49
5	Modified montmorillonite	50	30	DMSO	22
6	Modified montmorillonite	50	45	DMSO	35
7	Modified montmorillonite	50	60	DMSO	52
8	Modified montmorillonite	25	60	DMSO	20
9	SZ	50	30	Toluene	49
10	SZ	50	45	Toluene	72
11	SZ	50	60	Toluene	90
12	SZ	25	60	Toluene	46
13	SZ	50	30	DMSO	18
14	SZ	50	45	DMSO	25
15	SZ	50	60	DMSO	39
16	SZ	25	60	DMSO	21
17	Al-MCM-41	50	30	Toluene	41
18	Al-MCM-41	50	45	Toluene	64
19	Al-MCM-41	50	60	Toluene	85
20	Al-MCM-41	25	60	Toluene	43
21	Al-MCM-41	50	30	DMSO	21
22	Al-MCM-41	50	45	DMSO	30
23	Al-MCM-41	50	60	DMSO	49
24	Al-MCM-41	25	60	DMSO	27

^aYield of the isolated product after chromatographic purification.

2.8. Standard reaction procedure to oxidation of benzylic alcohols and hydroacylation

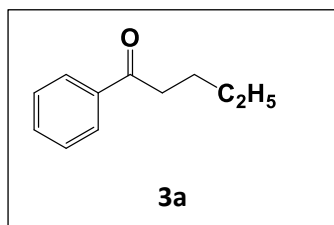
In a 10 mL tube of microwave with stir bar, 50 mg of solid acid, 1 mmol of alcohol **4a**, 1.5 mmol of alkene or alkyne **2a**, 10% TEMPO, 5% mmol of $\text{RhCl}(\text{PPh}_3)_3$, 20% mmol of 2-amino-3-picoline, 20% mmol of aniline and 3 mL of toluene were added. It was irradiated for 2 h in the microwave, at 80 °C. The mixture was dried in a rotavapor and purified for chromatography column.

Table S11. Hydroacylation of benzyl alcohol **4a**

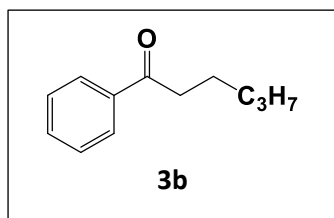
Entry	Solid acid	Solid acid loading mg	Time minutes	Solvent	Yield % ^a
1	Modified montmorillonite	50	30	Toluene	10
2	Modified montmorillonite	50	45	Toluene	24
3	Modified montmorillonite	50	60	Toluene	38
4	Modified montmorillonite	50	90	Toluene	52
5	Modified montmorillonite	50	120	Toluene	66
6	Modified montmorillonite	50	240	Toluene	65
6	Modified montmorillonite	50	30	DMSO	5
7	Modified montmorillonite	50	45	DMSO	10
8	Modified montmorillonite	50	60	DMSO	17
9	Modified montmorillonite	50	90	DMSO	28
10	Modified montmorillonite	50	120	DMSO	40

^aYield of the isolated product after chromatographic purification.

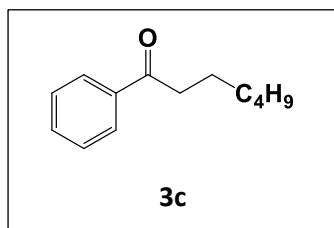
3. Characterization of organic compounds



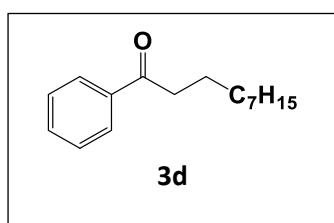
1-phenylpentan-1-one 3a. NMR ¹H (CDCl₃, 300 MHz): δ 7.96 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 2H), 7.54 (tt, *J* = 7.5, 2.4 Hz, 1H), 7.44 (m, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 1.71 (quint, *J* = 7.2 Hz, 2H), 1.40 (sext, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). NMR ¹³C (CDCl₃, 75 MHz): δ 200.6, 137.2, 132.9, 128.6, 128.1, 38.3, 26.5, 22.5, 14.0. Anal. calcd for C₁₂H₁₆O: C, 81.44; H, 8.70. Found: C, 81.39; H, 8.65.



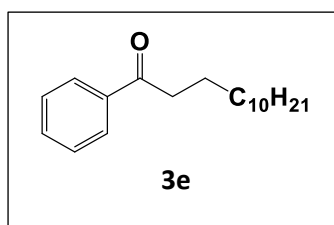
1-phenylhexan-1-one 3b. NMR ¹H (CDCl₃, 300 MHz): δ 7.96 (m, 2H), 7.52 (m, 1H), 7.43 (m, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 1.72 (quint, *J* = 7.5 Hz, 2H), 1.36 (m, 4H), 0.89 (t, *J* = 6.3 Hz, 3H). NMR ¹³C (CDCl₃, 75 MHz): δ 200.5, 137.2, 132.8, 128.5, 128.0, 38.6, 31.6, 24.1, 22.5, 13.9. Anal. calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.72; H, 9.09.



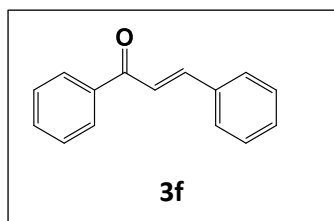
1-phenylheptan-1-one 3c. NMR ^1H (CDCl_3 , 300 MHz): δ 7.95 (ddd, $J = 8.1, 2.4, 1.2$ Hz, 2H), 7.52 (tt, $J = 7.2, 2.4$ Hz, 1H), 7.42 (m, 2H), 2.94 (t, $J = 7.5$ Hz, 2H), 1.72 (quint, $J = 7.5$ Hz, 2H), 1.33 (m, 6H), 0.88 (t, $J = 6.3$ Hz, 3H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 200.4, 137.2, 132.8, 128.5, 128.0, 38.6, 31.7, 29.0, 24.3, 22.5, 14.0. Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 81.97; H, 9.46.



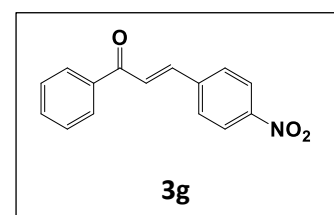
1-phenyldecan-1-one 3d. NMR ^1H (CDCl_3 , 300 MHz): δ 7.96 (ddd, $J = 8.1, 2.4, 1.5$ Hz, 2H), 7.54 (tt, $J = 7.5, 2.4$ Hz, 1H), 7.44 (m, 2H), 2.95 (t, $J = 7.8$ Hz, 2H), 1.73 (quint, $J = 7.8$ Hz, 2H), 1.30 (m, 12H), 0.87 (t, $J = 6.9$ Hz, 3H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 200.5, 137.0, 132.7, 128.4, 128.0, 38.5, 31.8, 29.4, 29.3, 29.2, 24.3, 22.6, 14.0. Anal. calcd for $\text{C}_{16}\text{H}_{24}\text{O}$: C, 82.70; H, 10.41. Found: C, 82.63; H, 10.34.



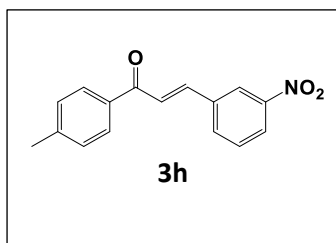
1-phenyltridecan-1-one 3e. NMR ^1H (CDCl_3 , 300 MHz): δ 7.96 (ddd, $J = 7.2, 2.4, 1.2$ Hz, 2H), 7.54 (tt, $J = 7.2, 2.4$ Hz, 1H), 7.44 (m, 2H), 2.95 (t, $J = 7.8$ Hz, 2H), 1.73 (quint, $J = 7.8$ Hz, 2H), 1.34 (m, 2H), 1.26 (m, 14H), 0.87 (t, $J = 6.9$ Hz, 3H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 200.7, 137.2, 132.9, 128.6, 128.1, 38.7, 32.0, 29.7, 29.6, 29.5, 29.4, 24.5, 22.8, 14.2. Anal. calcd for $\text{C}_{18}\text{H}_{28}\text{O}$: C, 83.02; H, 10.84. Found: C, 82.97; H, 10.77.



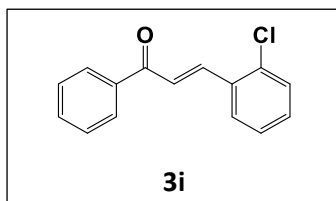
(E)-chalcone 3f. NMR ^1H (CDCl_3 , 300 MHz): δ 8.02 (dd, $J = 8.1, 2.7, 1.2$ Hz, 2H), 7.81 (d, $J = 15.6$ Hz, 1H), 7.63 (m, 2H), 7.53 (m, 5H), 7.42 (m, 2H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 190.6, 144.9, 138.3, 135.0, 132.9, 130.6, 129.0, 128.7, 128.6, 128.5. Anal. calcd for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 86.51; H, 5.81. Found: C, 86.47; H, 5.76.



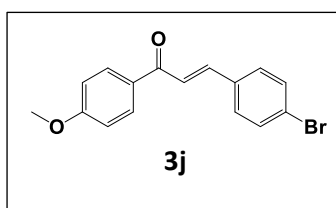
(E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one 3g. NMR ^1H (CDCl_3 , 300 MHz): δ 8.26-7.53 (m, 11H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 189.6, 148.5, 141.4, 141.0, 137.5, 133.3, 128.9, 128.8, 128.5, 125.7, 124.1. Anal. calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.09; H, 4.31; N, 5.45.



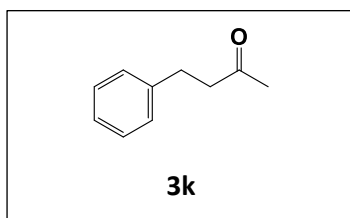
(E)-3-(3-nitrophenyl)-1-(p-tolyl)prop-2-en-1-one 3h. NMR ^1H (CDCl_3 , 300 MHz): δ 8.49 (dd, $J = 2.1, 1.8$ Hz, 1H), 8.24 (ddd, $J = 8.1, 2.1, 0.9$ Hz, 1H), 7.96 (AA'BB', d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.81 (d, $J = 15.9$ Hz, 1H), 7.65 (d, $J = 15.9$ Hz, 1H), 7.62 (dd, $J = 8.1, 7.8$ Hz, 1H), 7.33 (AA'BB', d, $J = 8.4$ Hz, 2H), 2.44 (s, 3H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 189.1, 148.8, 144.3, 141.2, 136.8, 135.1, 134.3, 130.1, 129.6, 128.8, 124.7, 124.6, 122.4, 21.8. Anal. calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_3$: C, 71.9; H, 4.9; N, 5.24. Found: C, 71.81; H, 4.83; N, 5.18.



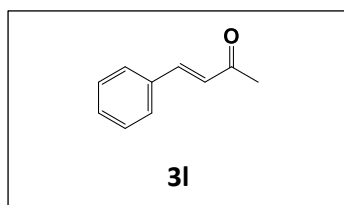
(E)-3-(2-chlorophenyl)-1-phenylprop-2-en-1-one 3i. NMR ^1H (CDCl_3 , 300 MHz): δ 8.17 (d, $J = 15.9$ Hz, 1H), 8.01 (d, $J = 7.5$ Hz, 2H), 7.74 (m, 1H), 7.51 (m, 5H), 7.32 (m, 2H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 190.5, 140.7, 138.0, 135.5, 133.3, 133.0, 131.2, 130.4, 128.8, 128.7, 127.9, 127.2, 124.9. Anal. calcd for $\text{C}_{15}\text{H}_{11}\text{ClO}$: C, 74.23; H, 4.57. Found: C, 74.17; H, 4.51.



(E)-3-(4-bromophenyl)-1-(p-tolyl)prop-2-en-1-one 3j. NMR ^1H (CDCl_3 , 300 MHz): δ 7.87 (AA'BB', m, 2H), 7.78 (d, $J = 15.1$ Hz, 1H), 7.62 (AA'BB', m, 2H), 7.59 (AA'BB', m, 2H), 7.34 (d, $J = 15.1$ Hz, 1H), 6.93 (AA'BB', m, 2H), 3.85 (s, 3H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 189.2, 161.7, 145.1, 137.1, 131.7, 130.2, 129.8, 127.4, 127.3, 119.0, 114.3, 55.2. Anal. calcd for $\text{C}_{16}\text{H}_{13}\text{BrO}$: C, 63.81; H, 4.35. Found: C, 63.76; H, 4.29.

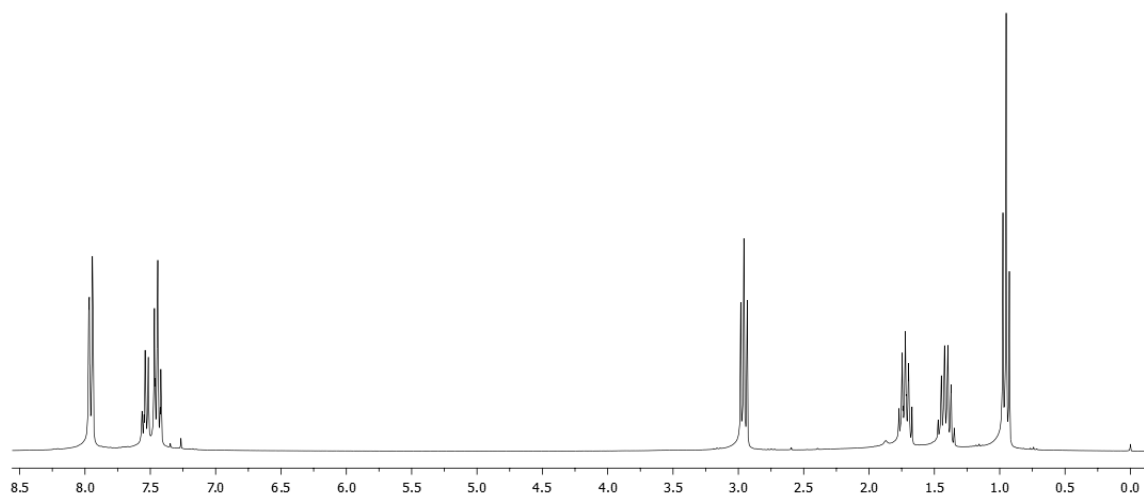


4-phenylbutan-2-one 3k. NMR ^1H (CDCl_3 , 300 MHz): δ 7.34 (m, 2H), 7.25 (m, 3H), 2.96 (t, $J = 8.0$ Hz, 2H), 2.79 (t, $J = 8.0$ Hz, 2H), 2.17 (s, 3H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 207.4, 140.8, 128.2, 128.0, 125.9, 44.79, 29.48. Anal. calcd for $\text{C}_{10}\text{H}_{12}\text{O}$: C, 81.04; H, 8.16. Found: C, 81.35; H, 8.46.

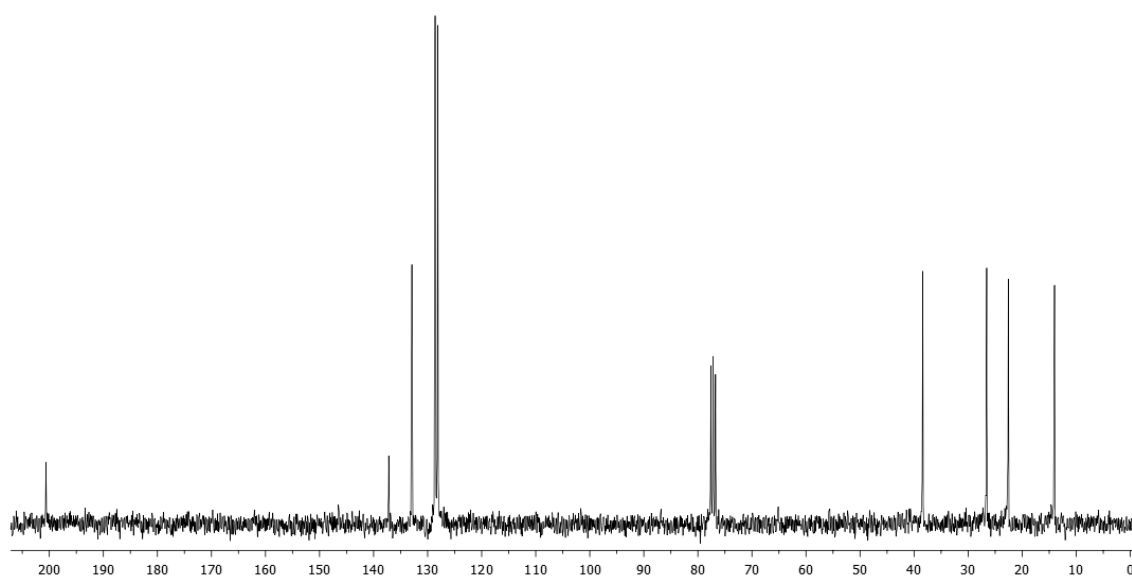


(E)-4-phenylbut-3-en-2-one 3l. NMR ^1H (CDCl_3 , 300 MHz): δ 7.54 (m, 2H), 7.52 (d, $J = 12.3$ Hz, 2H), 7.40 (m, 3H), 6.72 (d, $J = 12.3$ Hz, 2H), 2.38 (s, 3H). NMR ^{13}C (CDCl_3 , 75 MHz): δ 198.5, 143.6, 134.6, 130.6, 129.0, 128.5, 127.3, 27.5. Anal. calcd for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.90. Found: C, 82.29; H, 6.98.

4. NMR Spectrum

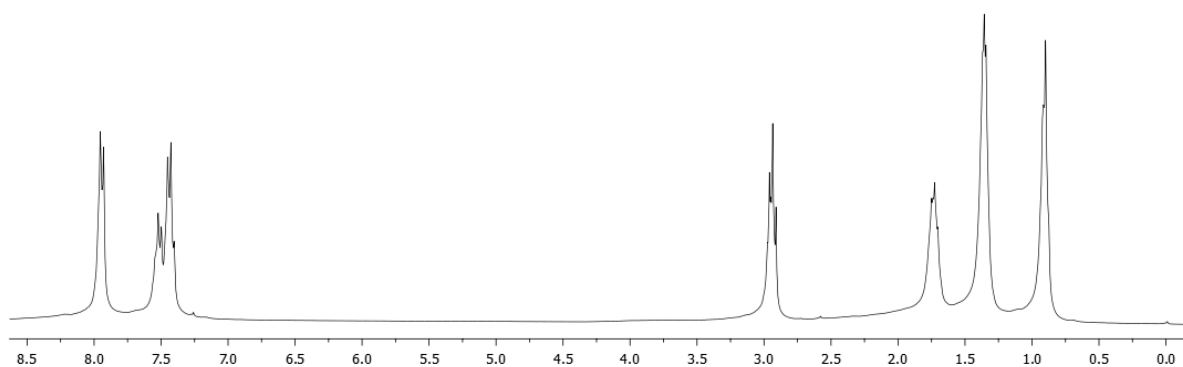


^1H NMR of **3a**

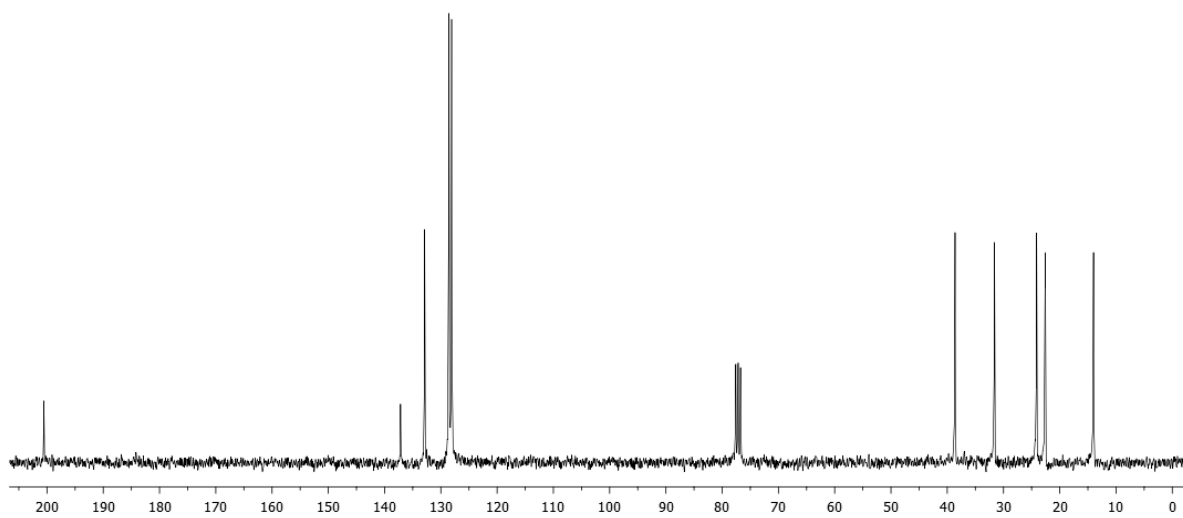


^{13}C NMR of **3a**

Supporting Information

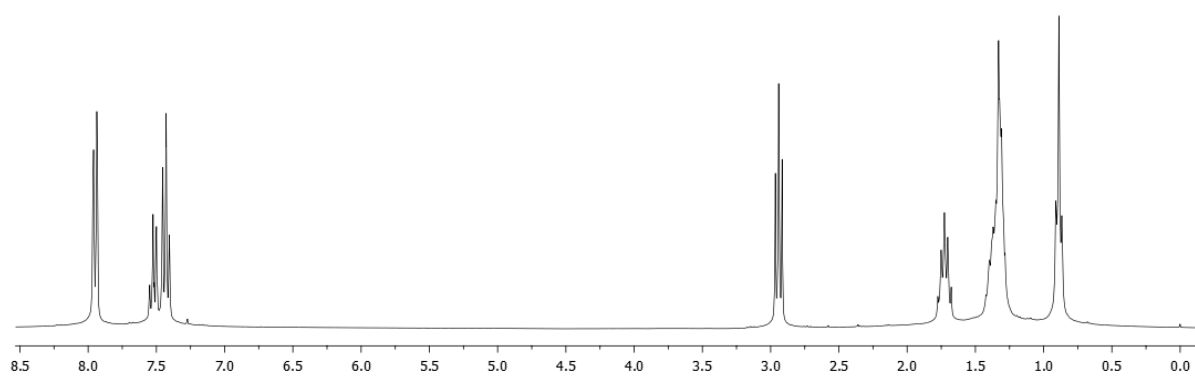


^1H NMR of **3b**

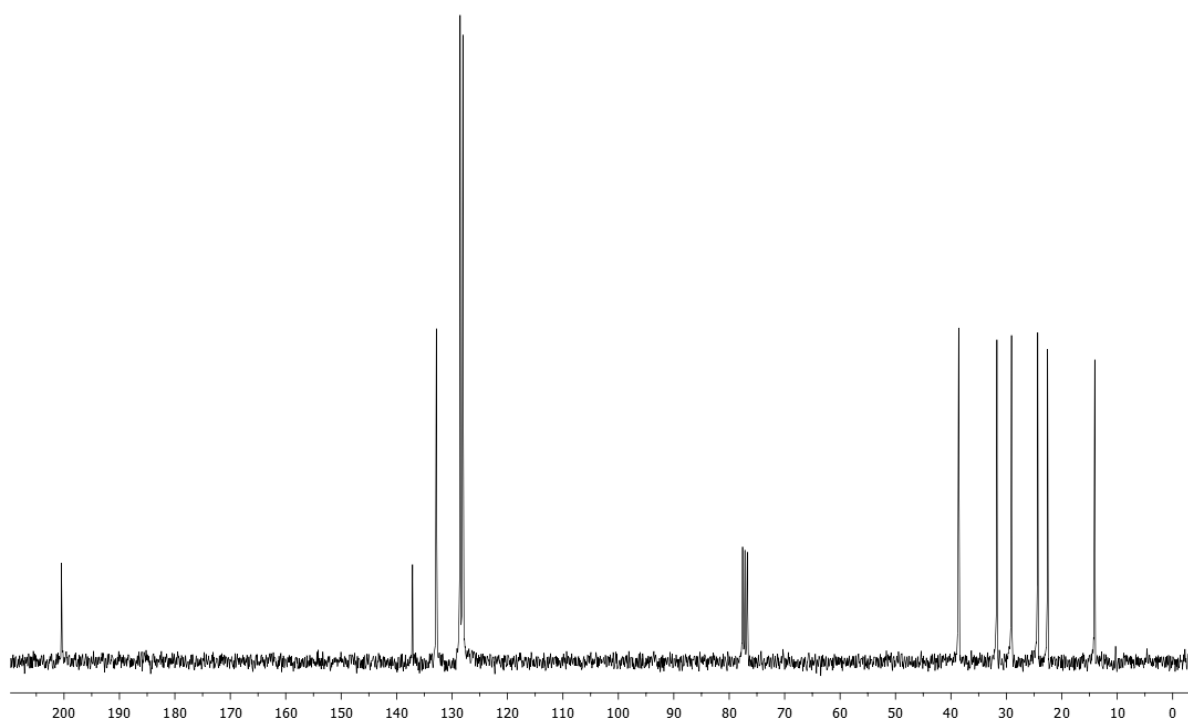


^{13}C NMR of **3b**

Supporting Information

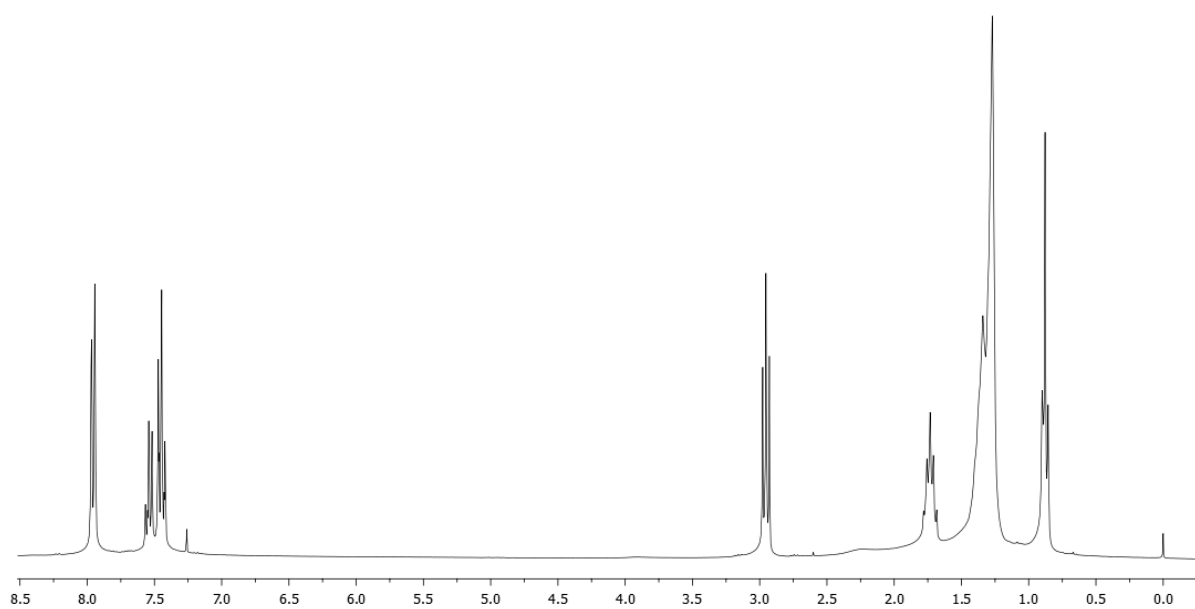


^1H NMR of **3c**

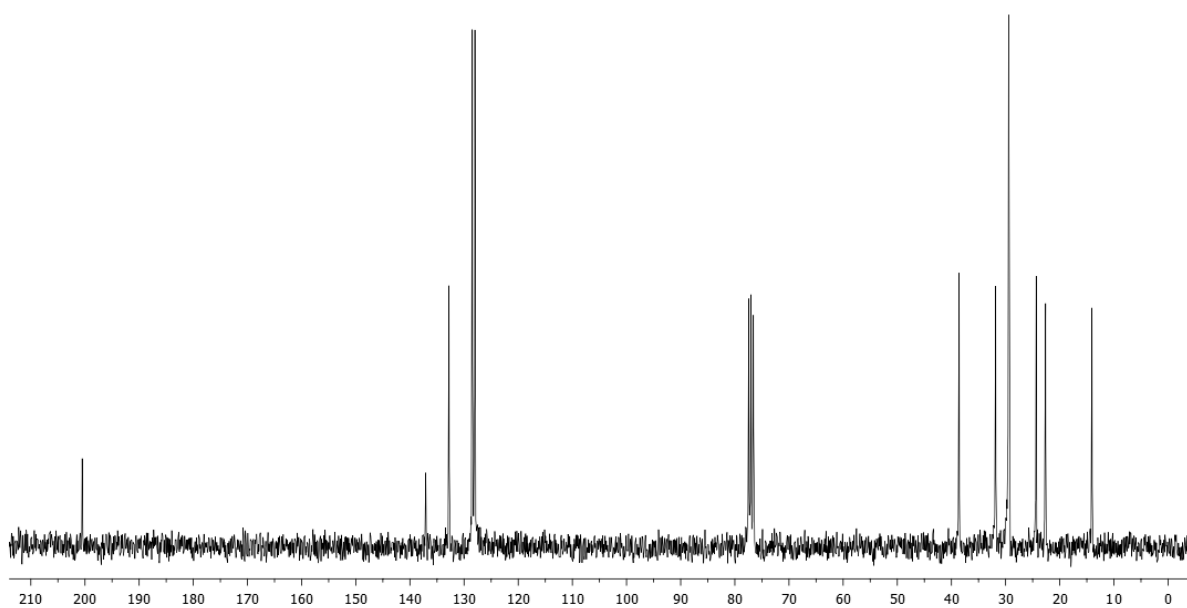


^{13}C NMR of **3c**

Supporting Information

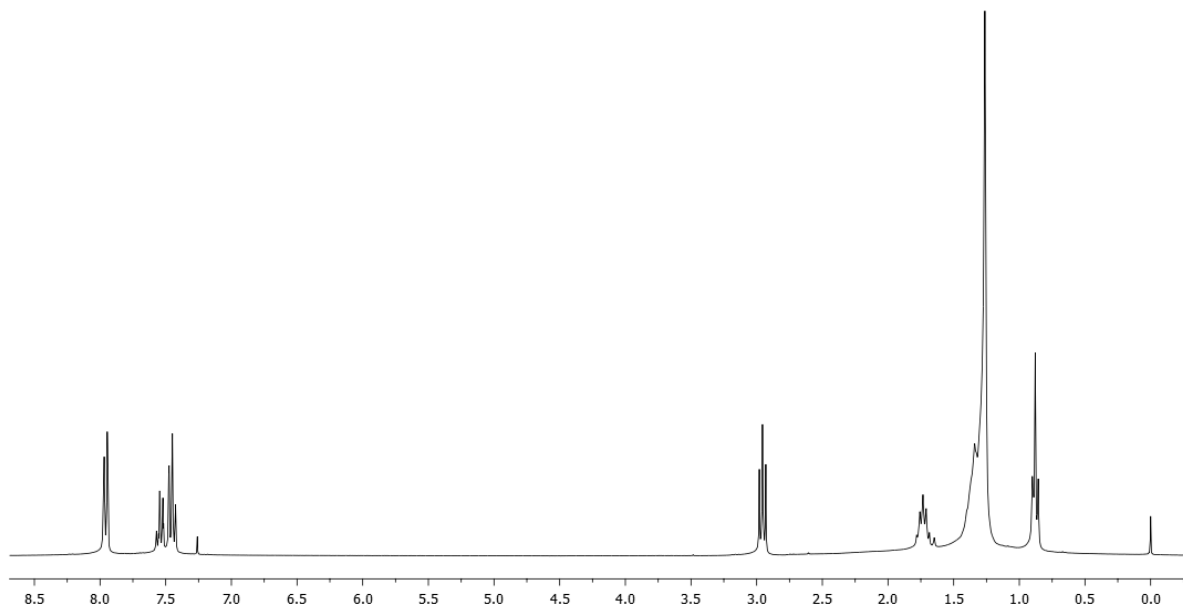


^1H NMR of **3d**

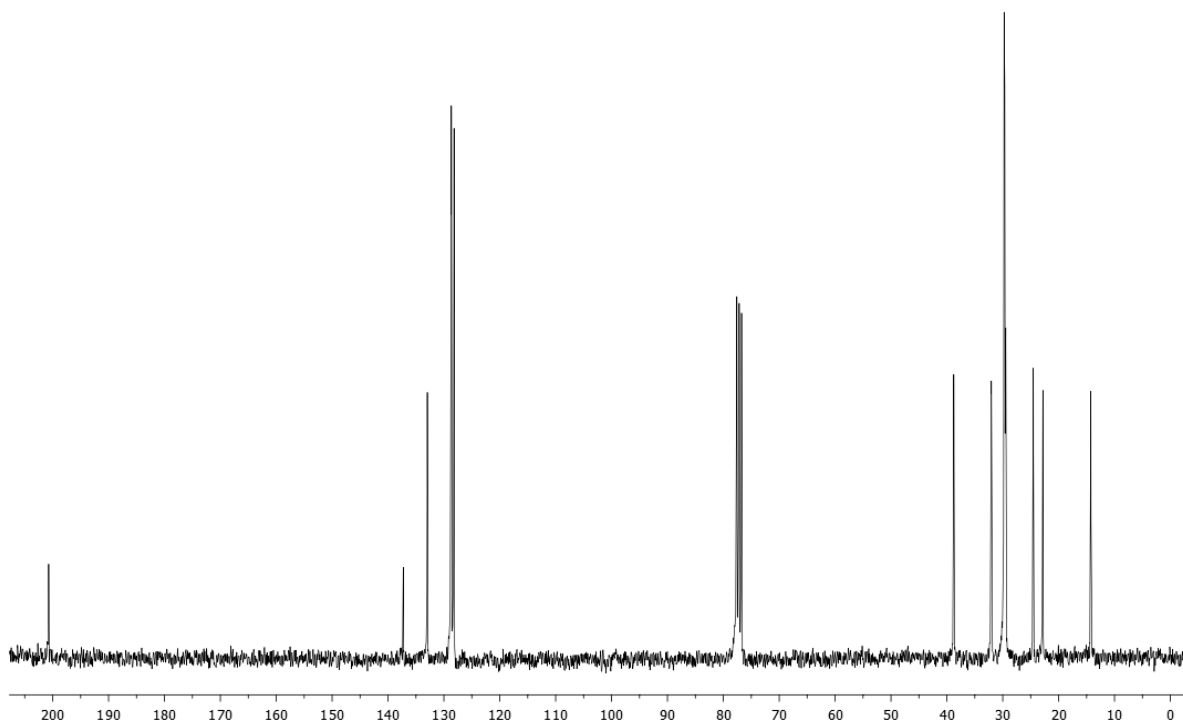


^{13}C NMR of **3d**

Supporting Information

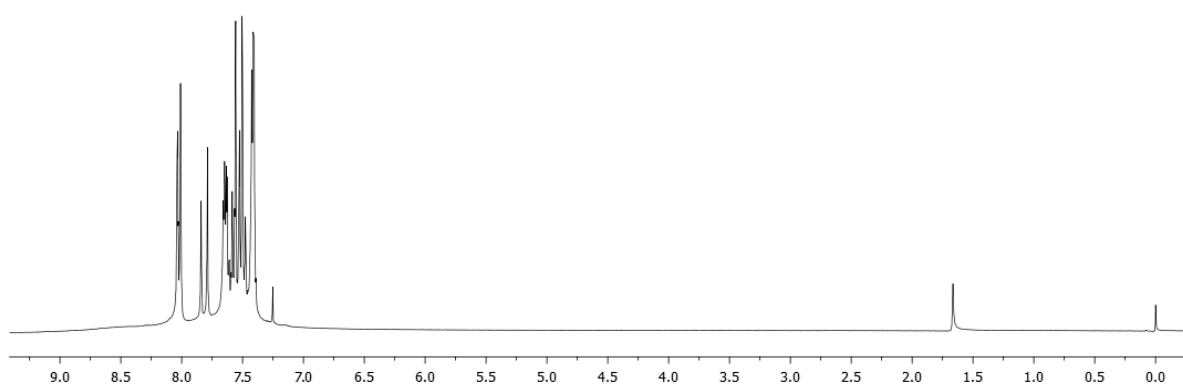


^1H NMR of **3e**

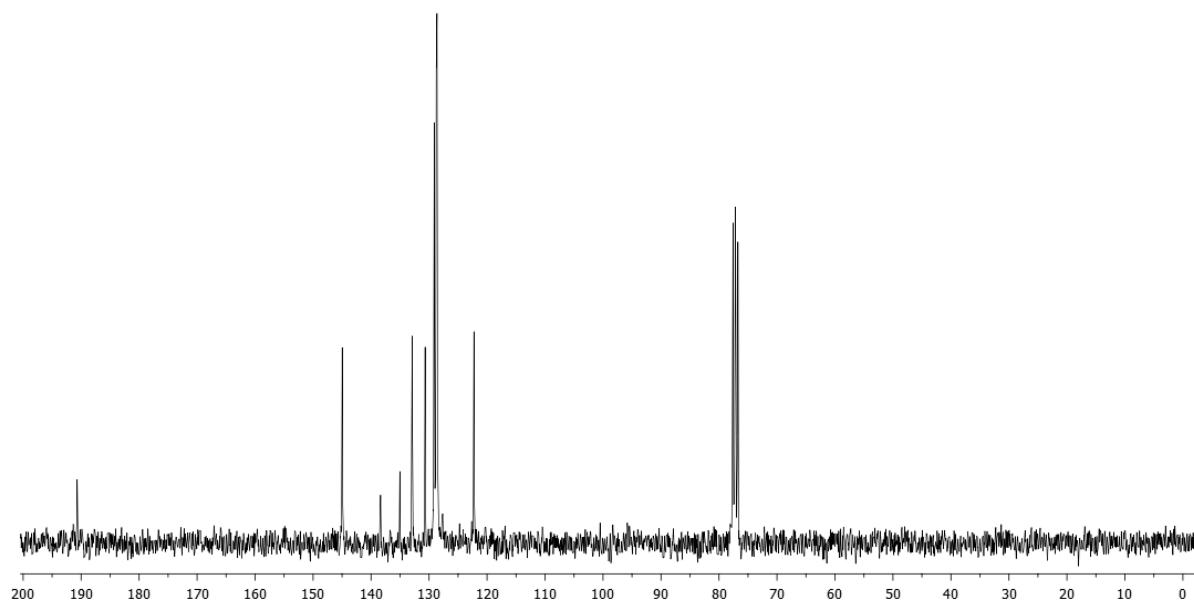


^{13}C NMR of **3e**

Supporting Information

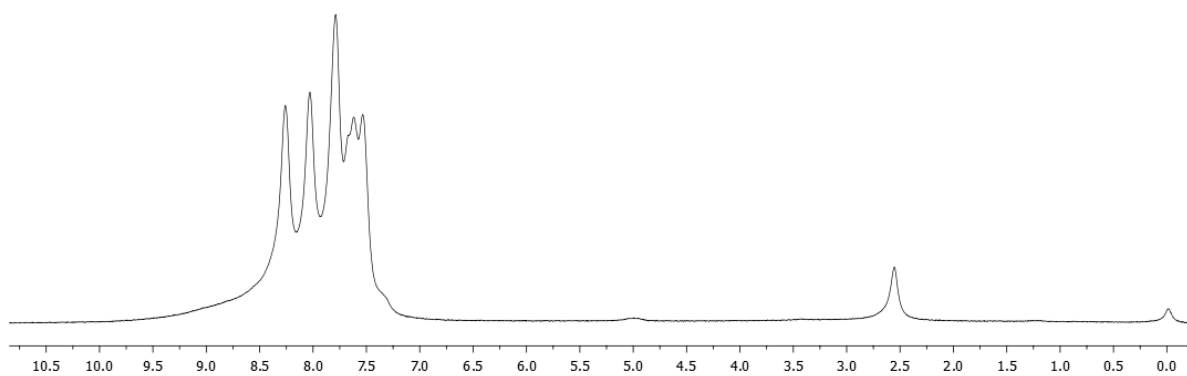


^1H NMR of **3f**

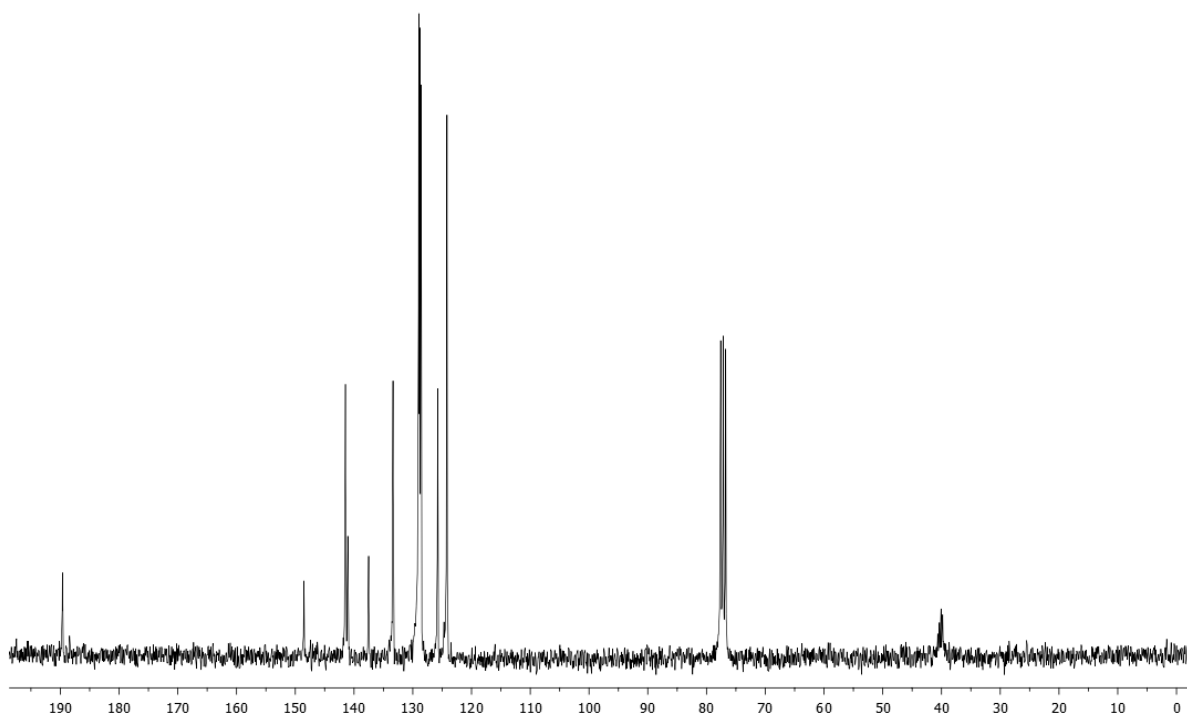


^{13}C NMR of **3f**

Supporting Information

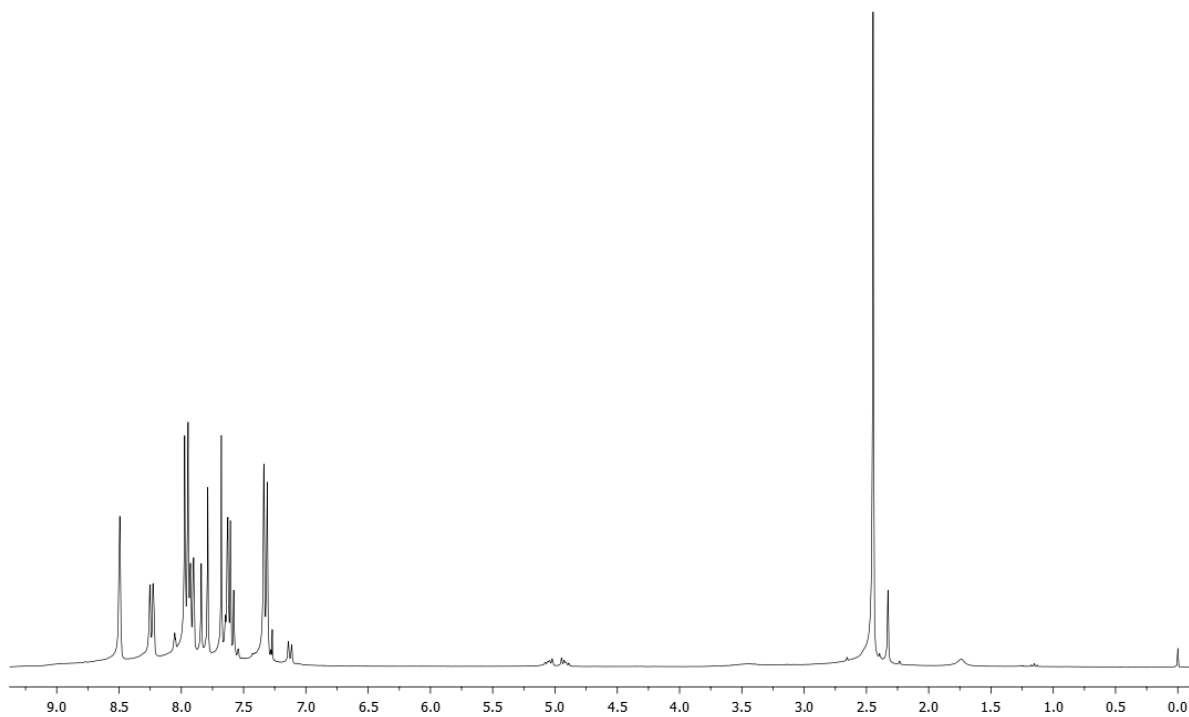


^1H NMR of **3g**

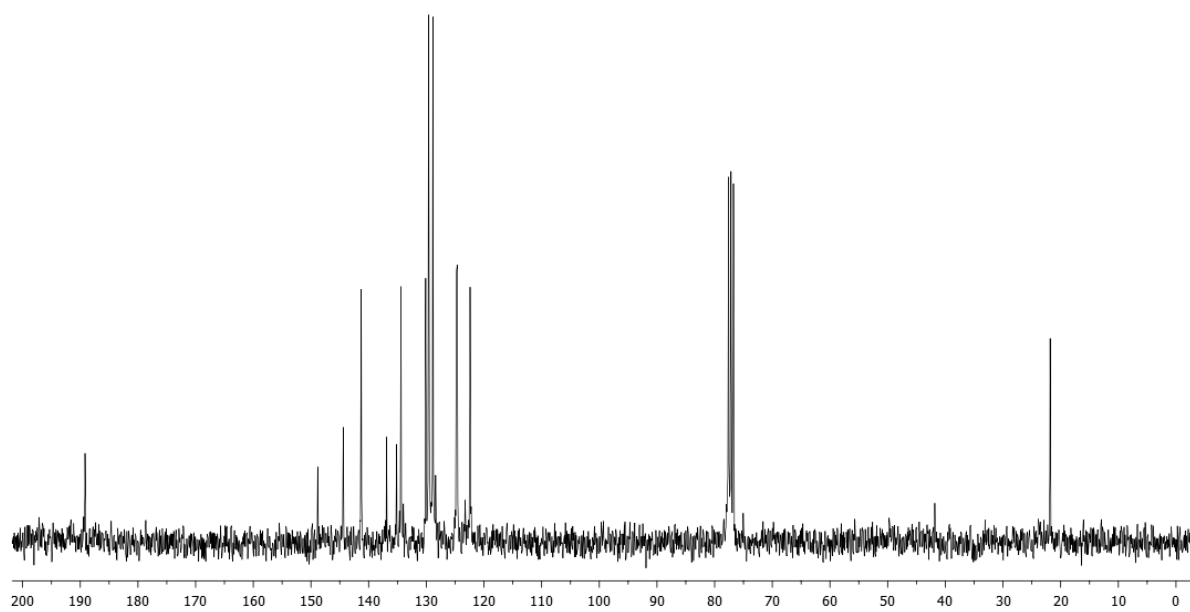


^{13}C NMR of **3g**

Supporting Information

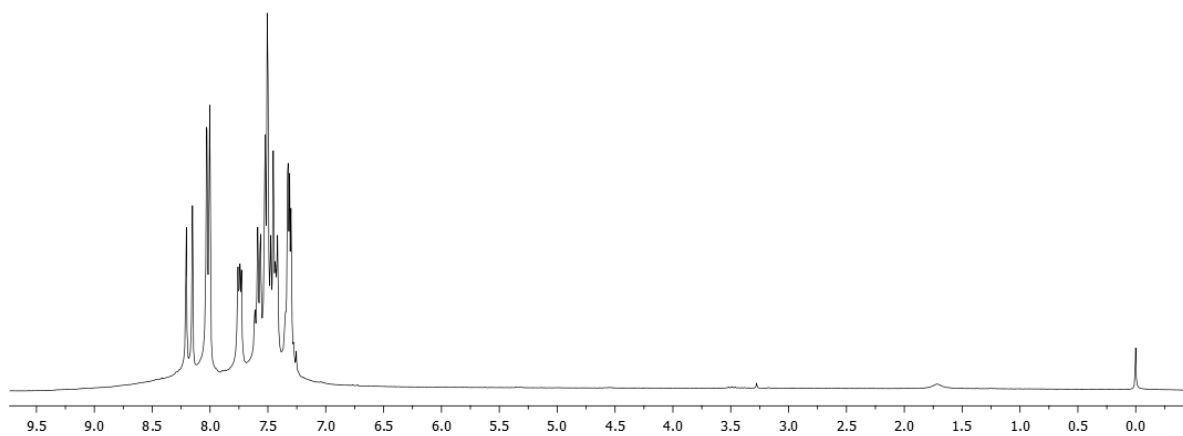


^1H NMR of **3h**

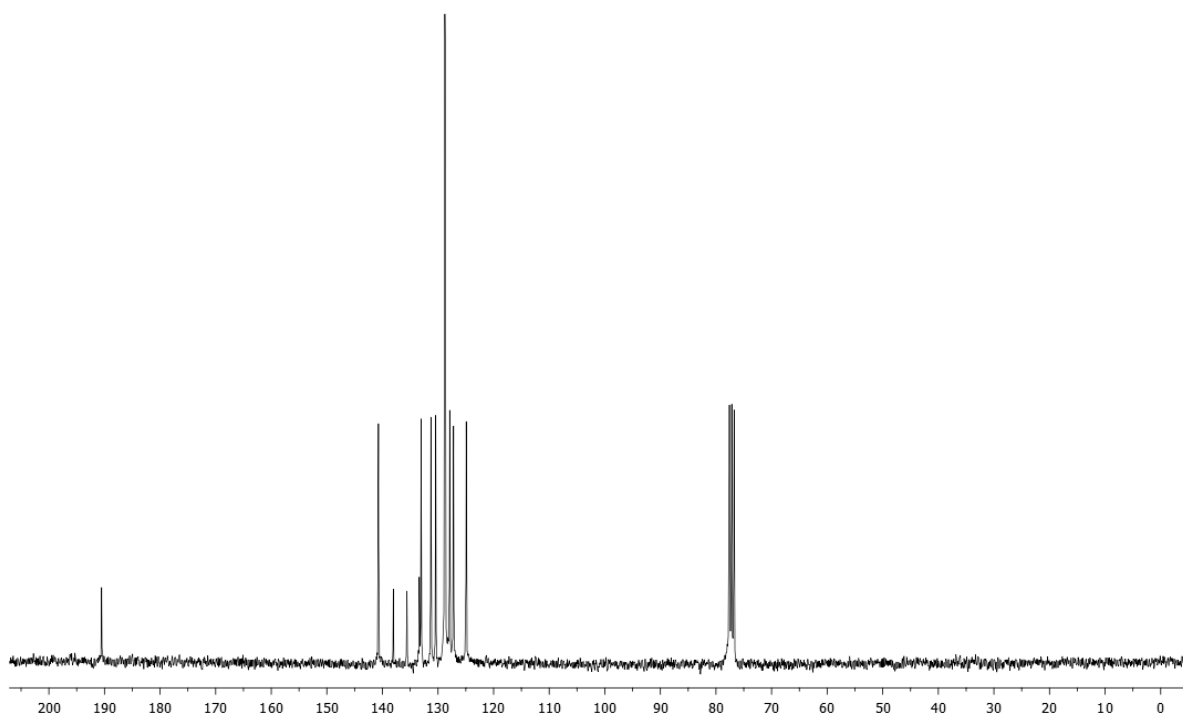


^{13}C NMR of **3h**

Supporting Information

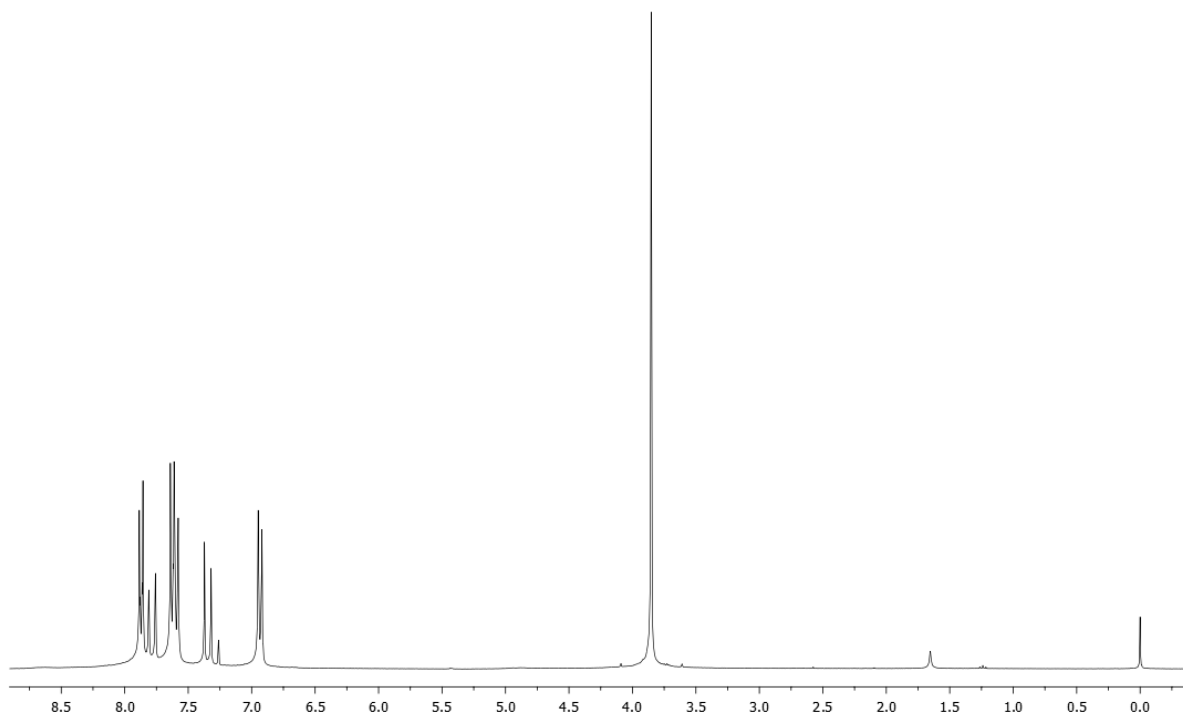


^1H NMR of **3i**

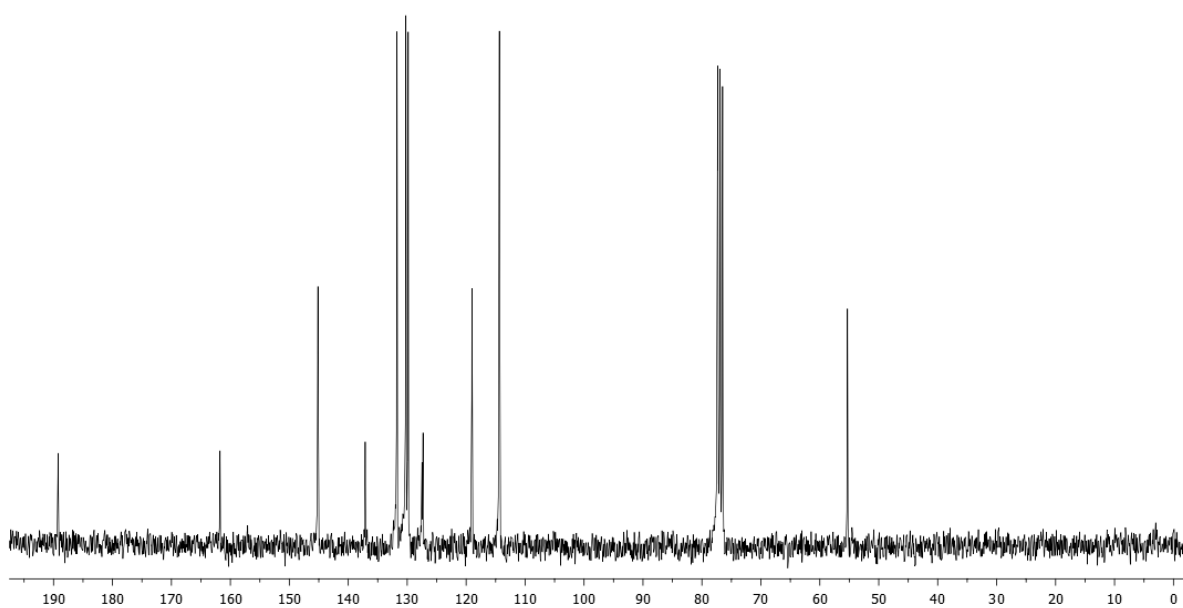


^{13}C NMR of **3i**

Supporting Information

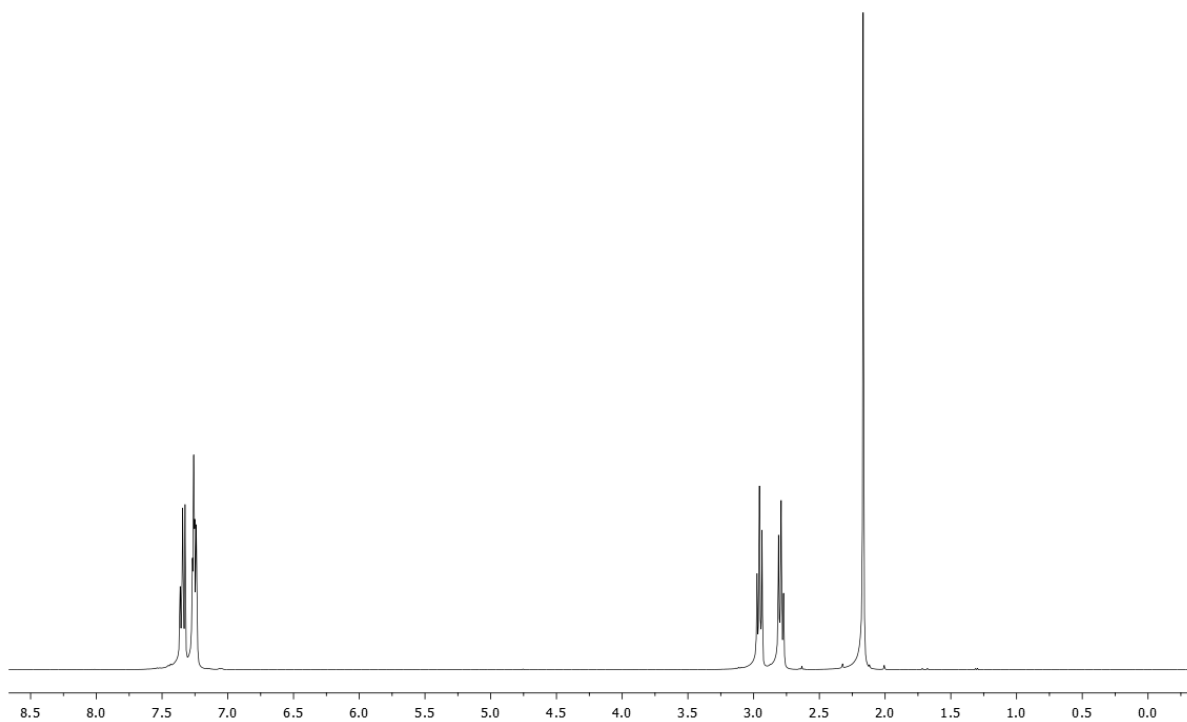


^1H NMR of **3j**

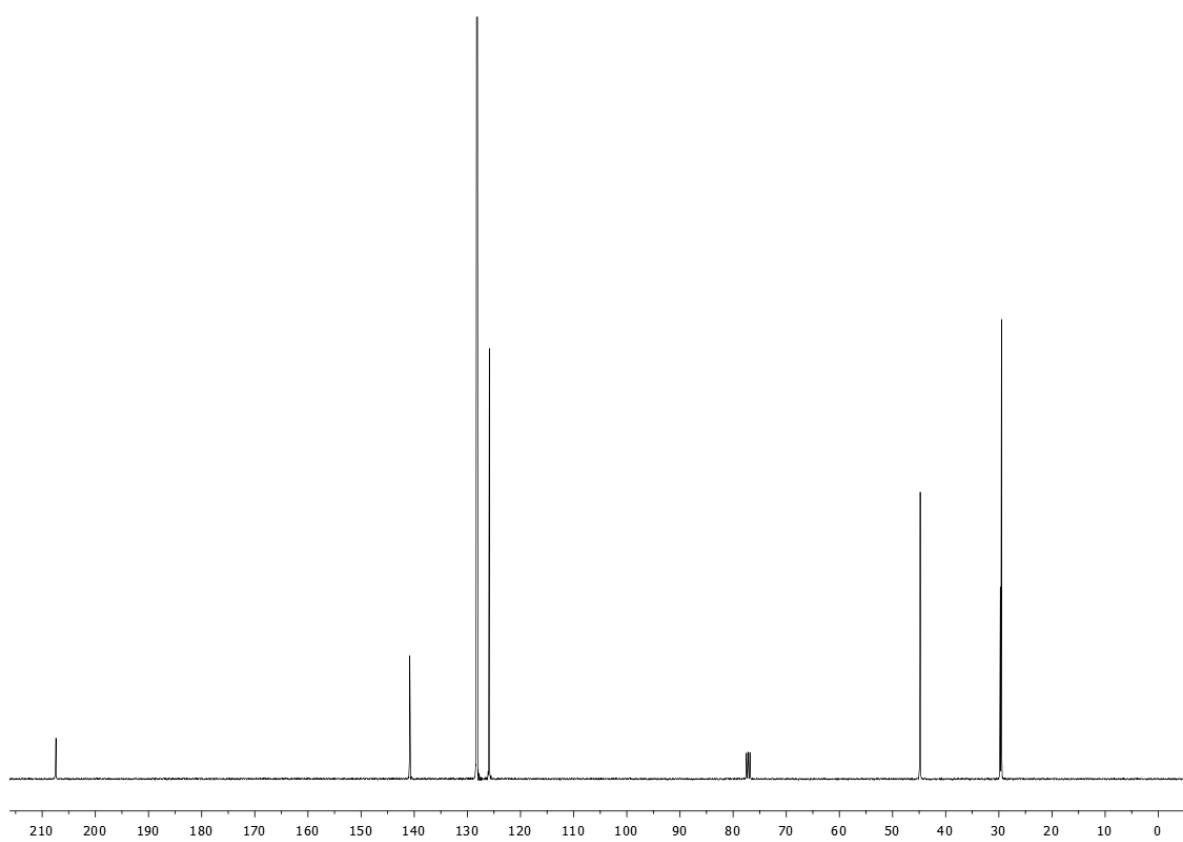


^{13}C NMR of **3j**

Supporting Information

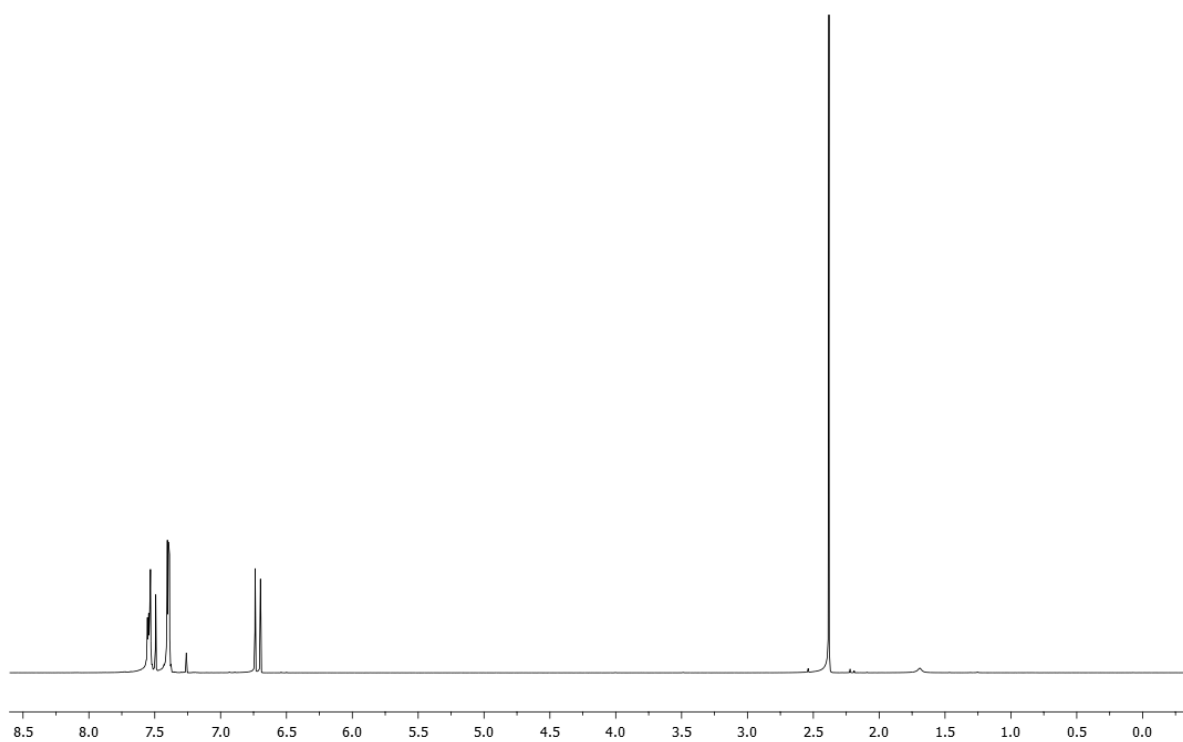


^1H NMR of **3k**

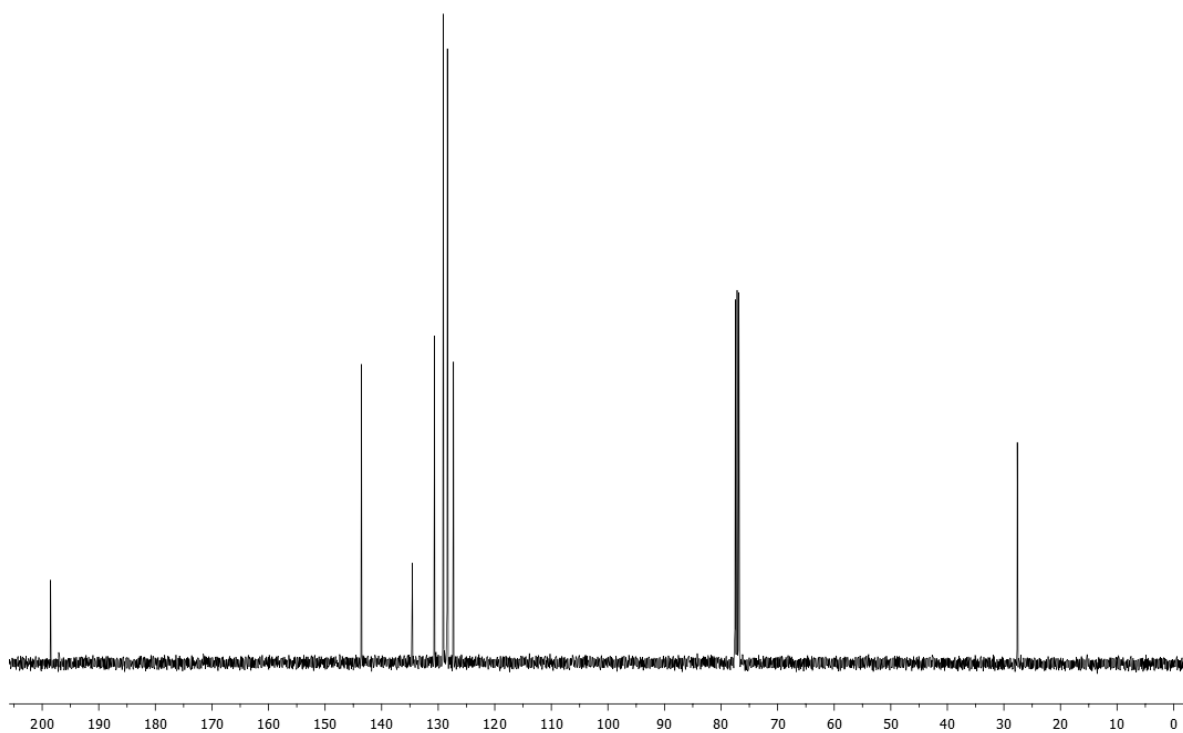


^{13}C NMR of **3k**

Supporting Information



^1H NMR of **3I**



^{13}C NMR of **3I**

5. References

- ¹ G. E. Negrón, L. N. Palacios, D. Angeles, L. Lomas and R. Gavino, *J. Braz. Chem. Soc.*, 2005, **16**, 490.
- ² B. I. Vergara-Arenas, L. Lomas-Romero, D. Ángeles-Beltrán, G. E. Negrón-Silva, A. Gutiérrez-Carrillo, V. H. Lara and J. A. Morales-Serna, *Tetrahedron Lett.*, 2017, **58**, 2690.
- ³ a) G. Granados-Oliveros, V. Gómez-Vidales, A. Nieto-Camacho, J. A. Morales-Serna, J. Cárdenas and M. Salmón, *RSC Adv.*, 2013, **3**, 937; b) R. Y. M. Vargas, H. I. Beltrán, V. E. Labastida, L. C. López and M. Salmón, *J. Mater. Res.*, 2007, **22**, 788.