

Supporting Information

Active Ruthenium Catalysts Based on Phosphine-modified Ru/CeO₂ for the Selective Addition of Carboxylic Acids to Terminal Alkynes

Masami Nishiumi, Hiroki Miura, Kenji Wada,* Saburo Hosokawa, and Masashi Inoue

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,

Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, JAPAN

Phone +81-75-383-2482, Fax +81-75-383-2479,

e-mail: wadaken@scl.kyoto-u.ac.jp

1. Characterization of the supported ruthenium catalysts by nitrogen gas adsorption.

BET surface areas of representative supported catalysts used in the present study were calculated based on the nitrogen adsorption isotherms, and the results are summarized in Table S1. The ceria-supported catalysts showed typical type IV nitrogen adsorption/desorption isotherms, which reflected their mesoporous nature.

Table S1. BET surface area of supported Ru catalysts

Entry	Sample ^[a]	BET surface area (m ² /g)
1	Ru/CeO ₂	102
2	Ru/ZrO ₂	82
3	Ru/MgO	148
4	Ru/TiO ₂	50
5	Ru/Al ₂ O ₃	142
6	Ru/SiO ₂	269
7	CeO ₂	86

^[a] Ru(acac)₃ was used as a Ru precursor.

2. Effects of phosphines for the modification of Ru/CeO₂.

The effects of phosphines used for modification on the yields and selectivity of adducts were examined (Table S2). Among the phosphines examined, dppb was found to be the most suitable for the selective preparation of **Z-3aa** (entry 5). Note that the suitable amount of dppb for the modification of Ru/CeO₂ is 2 to 3 equivalents (molar base) to Ru. Although catalysts modified with PPh₂(CH₂)₃PPh₂ (dppp) or PPh₂(CH₂)₅PPh₂ (dpppe) showed high selectivities for **Z-3aa**, the yields were quite low (entries 4 and 6). On the other hand, Ru/CeO₂ catalysts modified with 1,1-bis(diphenylphosphino)methane (dppm), P(ⁿBu)₃, or P(ⁿOct)₃ afforded **4aa**, the Markovnikov adduct, as a major product (entries 2, 8 and 9). Modification by other phosphines, PPh₃, *rac*-BINAP, and 1,2-bis(diphenylphosphino)ethane (dppe) completely suppressed the activity under the present conditions (entries 1, 3 and 7).

Table S2. Effects of phosphines for the modification of Ru/CeO₂.^[a,b]

Entry	Phosphine	Total yield (%) ^[c]	Selectivity (%) ^[d] Z-3aa : E-3aa : 4aa
1	PPh ₃	trace	—
2	dppm	68	26 : 8 : 66
3	dppe	0	—
4	dppp	7	86 : 14 : 0
5 ^[e]	dppb	>99	98 : 2 : 0
6	dpppe	7	100 : 0 : 0
7	<i>rac</i> -BINAP	trace	—
8	P(ⁿ Bu) ₃	57	11 : 7 : 82
9	P(ⁿ Oct) ₃	71	11 : 21 : 68

^[a] Reaction conditions: **1a** 1.0 mmol, **2a** 1.3 mmol, toluene 1.0 cm³, 2.0 wt% Ru/CeO₂ catalyst 125 mg (0.025 mmol as Ru, prepared from Ru(acac)₃), phosphine 0.050 mmol, at 80 °C for 24 h under Ar.

^[b] Ru/CeO₂ and phosphine were pretreated at 100 °C for 20 min under H₂ (1 atm).

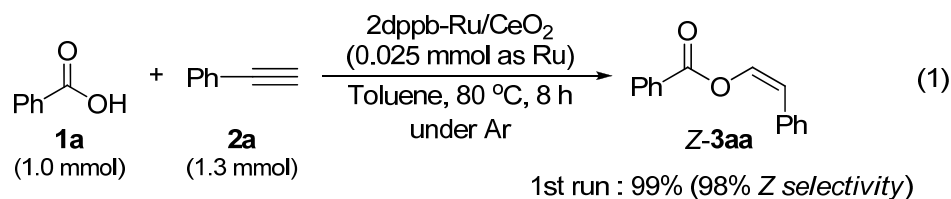
^[c] Total yield of **3aa** and **4aa** based on **1a**, determined by GLC.

^[d] Molar ratio of isomers determined by GLC.

^[e] Reaction time, 8 h.

3. Effects of the procedure for recycling of the dppb-Ru/CeO₂ catalyst on the activity.

The activities of recovered dppb-modified Ru/CeO₂ catalysts regenerated by various methods were examined. Table S3 shows the regeneration procedure and the activity of the recycled catalyst. The recovered dppb-modified Ru/CeO₂ catalyst, which had given vinyl esters **3a** in a yield of 99% in the first catalytic run, was used in the second run after thorough washing with diethyl ether (10 cm³, 3 times) followed by overnight drying in air at 80 °C. The total yield of **3a** in the second use was low, 24% (entry 1), probably because of the loss of most of the dppb ligand from the solid surface during washing. As shown in entry 2, reductive treatment of the washed catalyst in H₂ together with dppb increased its activity to give vinyl esters in a total yield of 40% with high selectivity for the *Z*-isomer of **3aa**. On the other hand, calcination of the washed catalyst in air at 400 °C for 30 min completely changed the product selectivity. As noted in entry 3, the total yield of vinyl esters was 40% and the *E*-isomer of **3aa** was produced as a major product with 70% selectivity. This selectivity is very similar to that with the fresh unmodified Ru/CeO₂ catalyst (entry 2 of Table 1), probably because calcination removes dppb from the coordination sites of ruthenium. Finally, the recycled catalyst, which was re-modified by dppb after thorough washing and subsequent calcination in air at 400 °C for 30 min, selectively afforded the *Z*-isomer of **3aa** in a high yield (total yield 99%), indicating that Ru/CeO₂ can be repeatedly used without a loss of effectiveness after a suitable regeneration procedure. Although a decreased amount of the Ru/CeO₂ catalyst was used, the *Z*-isomer of **3aa** was also obtained in a high yield and selectivity in the 3rd catalytic run.

Table S3. Recycling of the dppb-modified Ru/CeO₂ catalyst.^[a,b]

Entry	Recycling procedures	Catalyst	Total yield (%) ^[c]	Selectivity (%) ^[d] <i>Z-3aa</i> : <i>E-3aa</i> : <i>4aa</i>
1	Washing + drying	2 nd use	24	98 : 2 : 0
2 ^[e]	Washing + drying + dppb modification	2 nd use	40	98 : 2 : 0
3 ^[e]	Washing + drying + calcination	2 nd use	40	20 : 75 : 5
4	Washing + drying + calcination + dppb modification	2 nd use ^[f]	99	98 : 2 : 0
5	Washing + drying + calcination + dppb modification	3 rd use ^[g]	94	98 : 2 : 0

^[a] Reaction conditions: **1a** 1.0 mmol, **2a** 1.3 mmol, toluene 1.0 cm³, Ru/CeO₂ catalyst 125 mg (0.025 mmol as Ru, prepared from Ru(acac)₃), dppb 0.050 mmol, at 80 °C for 8 h under Ar.

^[b] Ru/CeO₂ and dppb were pretreated at 100 °C for 20 min under H₂ (1 atm).

^[c] Total yield of **3aa** and **4aa** based on **1a**, determined by GLC.

^[d] Molar ratio of isomers determined by GLC.

^[e] Reaction time, 24 h.

^[f] Recovered catalyst, 113 mg.

^[g] Recovered catalyst, 97 mg from entry 4.

4. Examination of the surface of Ru/CeO₂ catalyst by an XPS study.

The composition of the surface of the catalyst after the catalytic run and re-calcination was monitored by X-ray photoelectron spectroscopy (XPS). Due to the high volatility of phosphines, the spectrum just after phosphine-modification was not recorded. As summarized in Table S4, most of the surface of the used catalyst after thorough washing at room temperature was covered with carbonaceous materials. The amount of phosphorous species on the surface was small, 0.38 atom %, indicating that most of the phosphorous species was eliminated by washing. Note that the possible sublimation of phosphines during evacuation prior to the XPS study should be taken into account. After re-calcination, most of the surface carbonaceous species and remaining phosphorous species were eliminated. The surface ratio of ruthenium species was almost unchanged before and after the catalytic run and the subsequent regeneration procedure. Ru 3d_{5/2} peaks appeared at around 281 eV in all cases shown in Table S4, but it was difficult to precisely estimate the binding energies due to severe overlapping with the C 1s peaks.

Table S4. XPS analysis of the Ru(2.0 wt%)/CeO₂ catalyst prepared from Ru(acac)₃.^[a]

Remarks	C (%)	Ru (%)	P (%)	Ce (%)	O (%)
fresh catalyst	21.59	1.09	none	22.67	54.65
after 1 st use, washed ^[b]	41.28	0.98	0.38	13.63	43.73
after 1 st use, washed and re-calcined ^[c]	22.39	1.00	trace	21.76	54.79

^[a] Surface concentrations are shown as atomic %, measured at room temperature.

^[b] Washed three time with diethyl ether (5 cm³) at room temperature.

^[c] Calcined at 400 °C for 30 min in air.

5. DRIFT spectra of Ru/CeO₂ catalyst before and after dppb-modification.

Figure S1 shows changes in the diffuse reflectance infrared Fourier transform (DRIFT) spectrum of the Ru/CeO₂ catalyst prepared using Ru(acac)₃ followed by dppb-modification. Whereas fresh Ru/CeO₂ showed a band at 975 cm⁻¹ characteristic of the surface Ru=O species,^[1-3] such a band was not detected in the spectra of the dppb-modified catalyst or the used catalyst, which reflected the absence of Ru=O species. Note that dppb shows absorption bands at 845, 905, 995, 1025, 1065, and 1095 cm⁻¹. The spectrum of the used catalyst also showed significant bands probably due to adsorbed organic materials, mainly dppb.

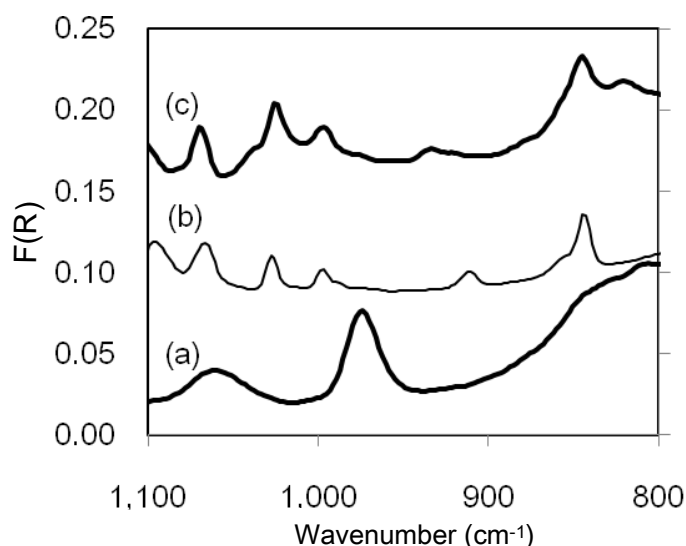
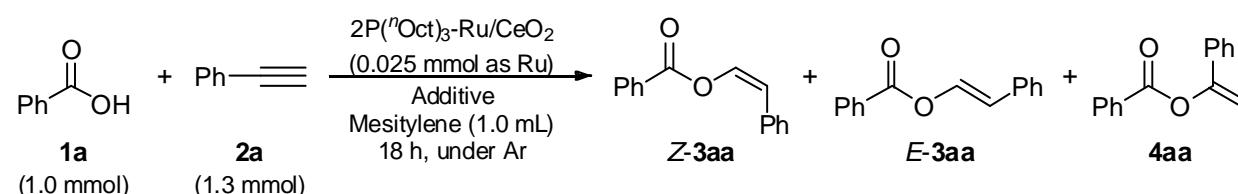


Figure S1 DRIFT spectra of Ru/CeO₂ catalysts prepared using Ru(acac)₃ as a precursor. (a) Fresh, (b) dppb-modified, and (c) used catalyst.

6. Effects of reaction temperatures, additives, and the amount of $P(^n\text{Oct})_3$ on the reaction using $P(^n\text{Oct})_3$ -modified Ru/CeO₂ catalyst.

As shown in entries 1 to 3 of Table S5, a reaction temperature of around 120 °C was found to be the most suitable for the reactions of **1a** and **2a** over the $P(^n\text{Oct})_3$ -modified Ru/CeO₂ catalyst (prepared from Ru(acac)₃). The effects of various additives are also summarized in Table S5. The addition of 0.10 mmol (4 eq. to Ru) of NH₄Cl was found to be suitable in terms of both the yield of vinyl esters and the selectivity of **4aa**. The addition of a larger or smaller amount of NH₄Cl decreased the total yield and the selectivity of **4aa**.

Table S5. Effects of reaction temperature and additives on the reaction catalyzed by $P(^n\text{Oct})_3$ -modified Ru/CeO₂.^[a,b]



Entry	Additive (mmol)	Reaction temp. (°C)	Total yield (%) ^[c]	Selectivity (%) ^[d] Z-3aa : E-3aa : 4aa
1 ^[e]	None	80	71	11 : 21 : 68
2 ^[e]	None	120	99	26 : 27 : 47
3 ^[e]	None	140	81	31 : 7 : 62
4	KI (0.10)	120	92	28 : 33 : 39
5	KBr (0.10)	120	99	26 : 15 : 59
6	KCl (0.10)	120	99	24 : 11 : 65
7	LiCl (0.10)	120	92	28 : 50 : 22
8	NaCl (0.10)	120	83	19 : 6 : 75
9 ^[f]	NH ₄ Cl (0.10)	120	>99	15 : 8 : 77
10	NH ₄ Cl (0.050)	120	69	29 : 28 : 43
11	NH ₄ Cl (0.20)	120	82	15 : 21 : 64
12	NH ₄ Cl (0.40)	120	88	39 : 20 : 41
13	Bu ₄ NCl(0.10)	120	97	9 : 30 : 61

^[a] Reaction conditions: **1a** 1.0 mmol, **2a** 1.3 mmol, mesitylene 1.0 cm³, 2.0 wt% Ru/CeO₂ catalyst 125 mg (0.025 mmol as Ru, prepared from Ru(acac)₃), $P(^n\text{Oct})_3$ 0.050 mmol, for 18 h under Ar.

^[b] Ru/CeO₂ and $P(^n\text{Oct})_3$ were pretreated at 100 °C for 20 min under H₂ (1 atm).

^[c] Total yield of **3aa** and **4aa** based on **1a**, determined by GLC.

^[d] Molar ratio of isomers determined by GLC.

^[e] Reaction time, 24 h.

^[f] Reaction time, 6 h.

As shown in Table S6, the optimum P(ⁿOct)₃/Ru molar ratio was found to be 2.

Table S6. Effect of the amount of P(ⁿOct)₃ on the Markovnikov addition^[a]

Entry	<i>x</i> ^[b]	Total yield (%) ^[c]	Selectivity (%) ^[d] Z- 3aa : E- 3aa : 4aa
1	1	61	15 : 28 : 57
2 ^[e]	2	>99	15 : 8 : 77
3	3	59	16 : 15 : 69
4	4	17	17 : 12 : 71

^[a] Reaction conditions: **1a** 1.0 mmol, **2a** 1.3 mmol, solvent 1.0 cm³, Ru/CeO₂ catalyst 0.025 mmol as Ru, NH₄Cl 0.10 mmol, at 120 °C for 24 h under Ar.

^[b] *x* = P(ⁿOct)₃/Ru (molar ratio).

^[c] Based on **1a**, determined by GLC.

^[d] Molar ratio of isomers determined by GLC.

^[e] Reaction time, 6 h.

Table S7 shows the effects of Ru precursors used for the preparation of Ru/CeO₂. The reaction in the presence of Ru/CeO₂ prepared using Ru complexes with chlorido ligands or RuCl₃ · *n*H₂O showed higher selectivity for the Markovnikov adducts.

Table S7. Effects of Ru precursors of Ru/CeO₂ on Markovnikov addition^[a]

Entry	Ru precursor	Total yield (%) ^[b]	Selectivity (%) ^[c] Z- 3aa : E- 3aa : 4aa
1 ^[d]	Ru(acac) ₃	>99	27 : 26 : 47
2	Ru ₃ (CO) ₁₂	>99	15 : 26 : 59
3	RuCl ₃ · <i>n</i> H ₂ O	79	9 : 13 : 78
4	[RuCl ₂ (<i>p</i> -cymene)] ₂	99	23 : 16 : 61
5	[RuCl ₂ (CO) ₃] ₂	99	13 : 16 : 71

^[a] Reaction conditions: **1a** 1.0 mmol, **2a** 1.3 mmol, solvent 1.0 cm³, Ru/CeO₂ catalyst 0.025 mmol as Ru, at 120 °C for 18 h under Ar.

^[b] Based on **1a**, determined by GLC.

^[c] Molar ratio of isomers determined by GLC.

^[d] Reaction time, 24 h.

7. Effects of solvent on the reaction using P(ⁿOct)₃-modified Ru/CeO₂ catalyst.

As shown in Table S8, aromatic solvents such as mesitylene, xylene, or toluene were found to be suitable. In polar solvents, the reaction did not proceed at all.

Table S8. Effect of solvent on the reaction using P(ⁿOct)₃-modified Ru/CeO₂ ^[a,b]

Entry	Solvent	Total yield (%) ^[c]	Selectivity (%) ^[d] Z- 3aa : E- 3aa : 4aa
1 ^[e]	Mesitylene	>99	15 : 8 : 77
2 ^[f]	Toluene	56	13 : 12 : 75
3	<i>o</i> -Xylene	50	12 : 12 : 76
4	1-Methyl-2-pyrrolidone	0	—
5	<i>N,N</i> -Dimethylformamide	0	—
6	<i>N,N</i> -Dimethylacetamide	0	—
7 ^[g]	CH ₂ Cl ₂	0	—

^[a] Reaction conditions: **1a** 1.0 mmol, **2a** 1.3 mmol, solvent 1.0 cm³, 2.0 wt% Ru/CeO₂ catalyst 125 mg (0.025 mmol as Ru, prepared from Ru(acac)₃), P(ⁿOct)₃ 0.050 mmol, NH₄Cl 0.10 mmol, at 120 °C for 18 h under Ar.

^[b] Ru/CeO₂ and P(ⁿOct)₃ were pretreated at 100 °C for 20 min under H₂ (1 atm).

^[c] Total yield of **3aa** and **4aa** based on **1a**, determined by GLC.

^[d] Molar ratio of isomers determined by GLC.

^[e] Reaction time, 6 h.

^[f] Reaction temp., 100 °C.

^[g] Bath temp., 90 °C; reaction time, 8 h.

8. $^{31}\text{P}\{^1\text{H}\}$ NMR study of the reaction mixture.

After the catalytic run shown in entry 9 of Table 1, the used dppb-modified Ru/CeO₂ catalyst was removed from the reaction mixture by cannula filtration (using No. 2 filter paper) at room temperature and then washed with toluene (5 cm³, three times). The combined filtrate and washings were condensed by evaporation and then subjected to $^{31}\text{P}\{^1\text{H}\}$ NMR measurement (161.9 MHz, in CDCl₃ at room temperature) with or without a known amount of OP(OPh)₃ as an internal standard. In the spectrum, there is a large singlet at -16.5 ppm due to dppb together with very small peaks of intractable phosphorous compounds. Similarly the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of washings of 2dppb-Ru/CeO₂ after heating in toluene (1.0 cm³) for 8 h without any substrates showed only a distinct peak due to dppb without any sign of other products, indicating that 91% of the dppb used for modification remained unchanged in the solution.

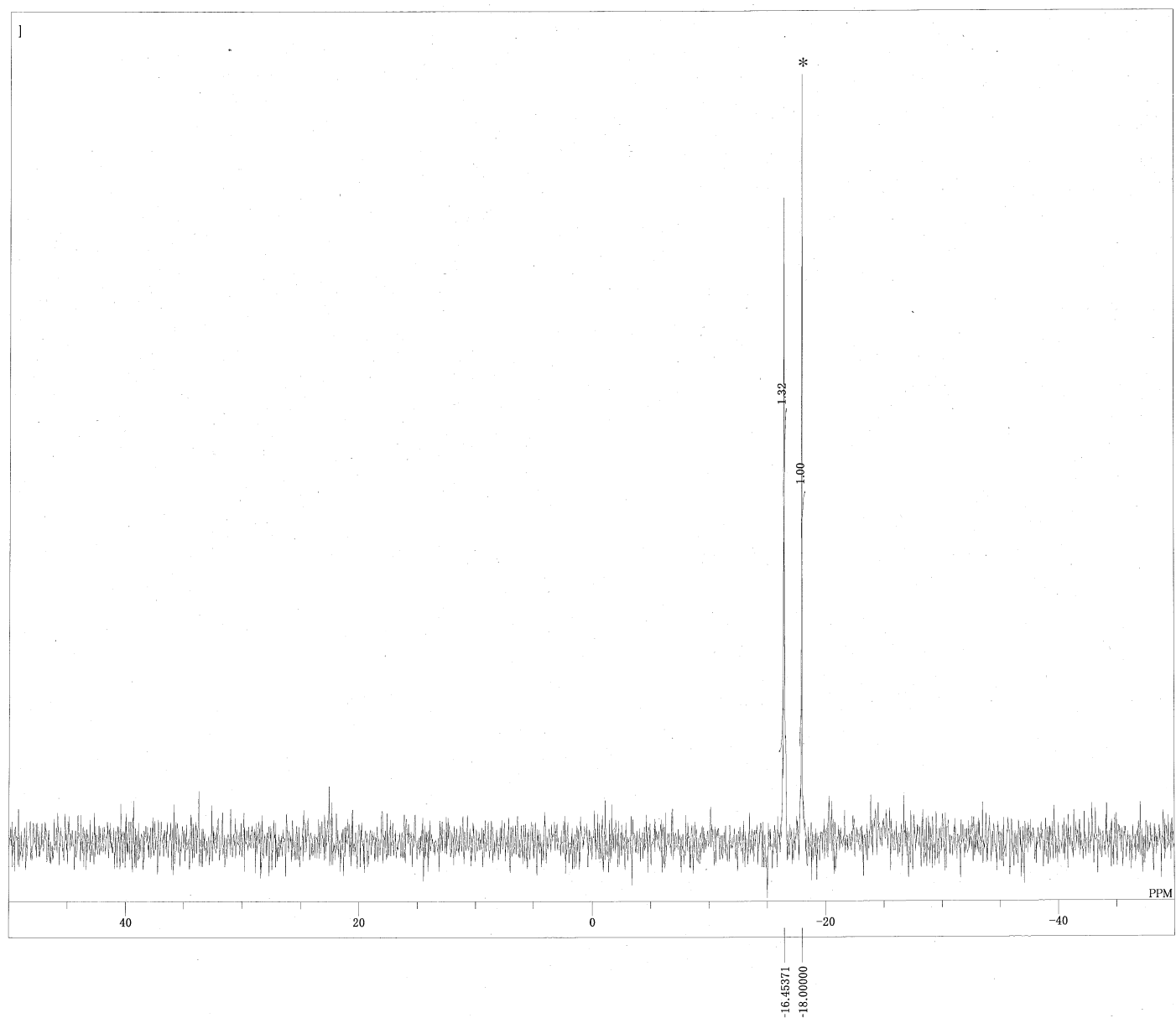
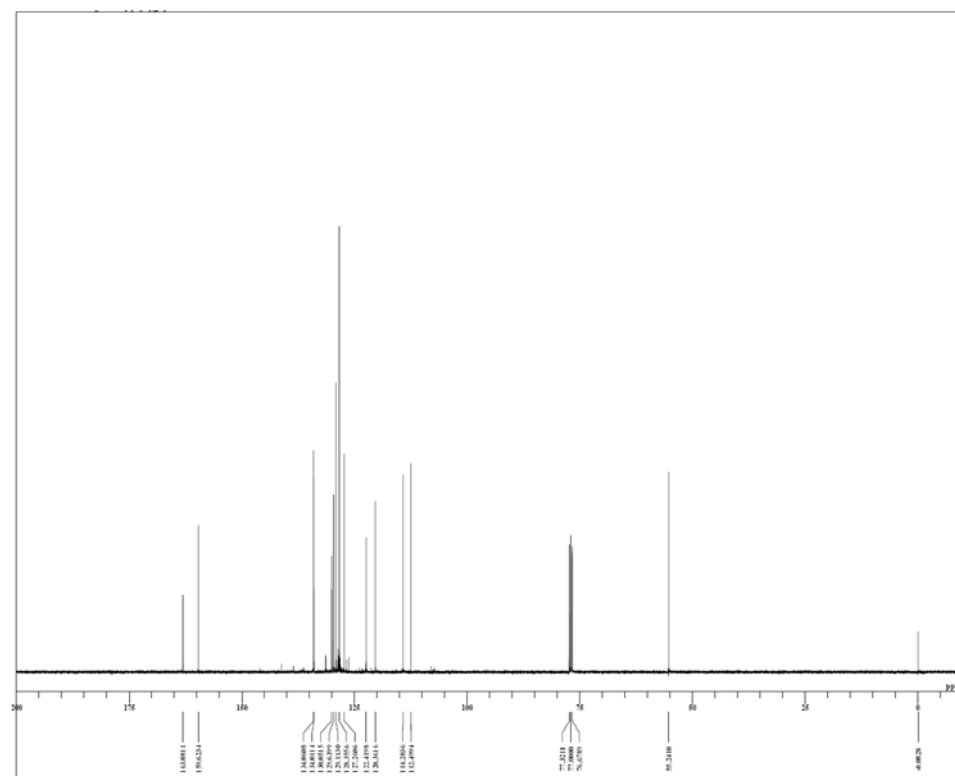
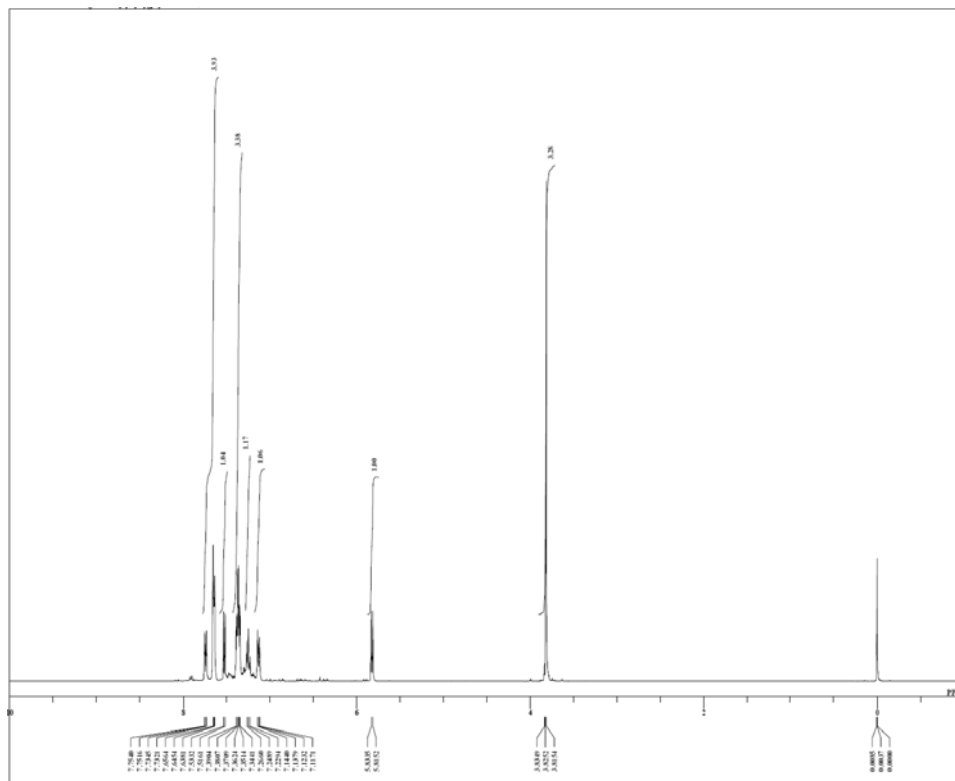
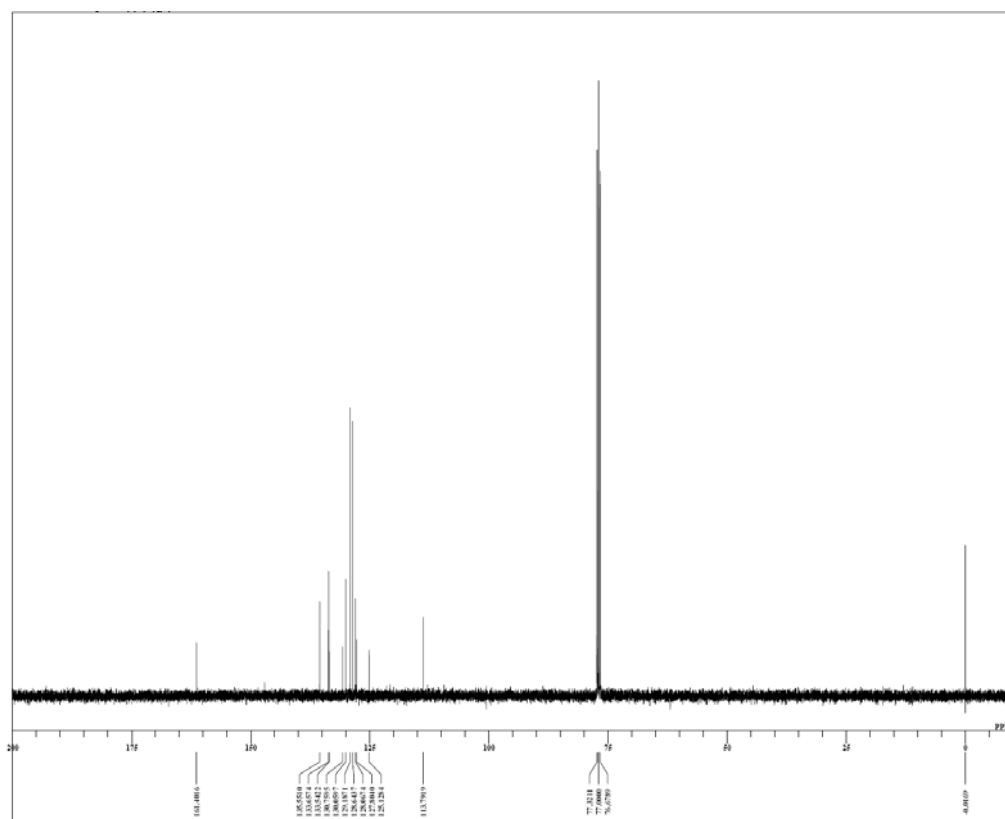
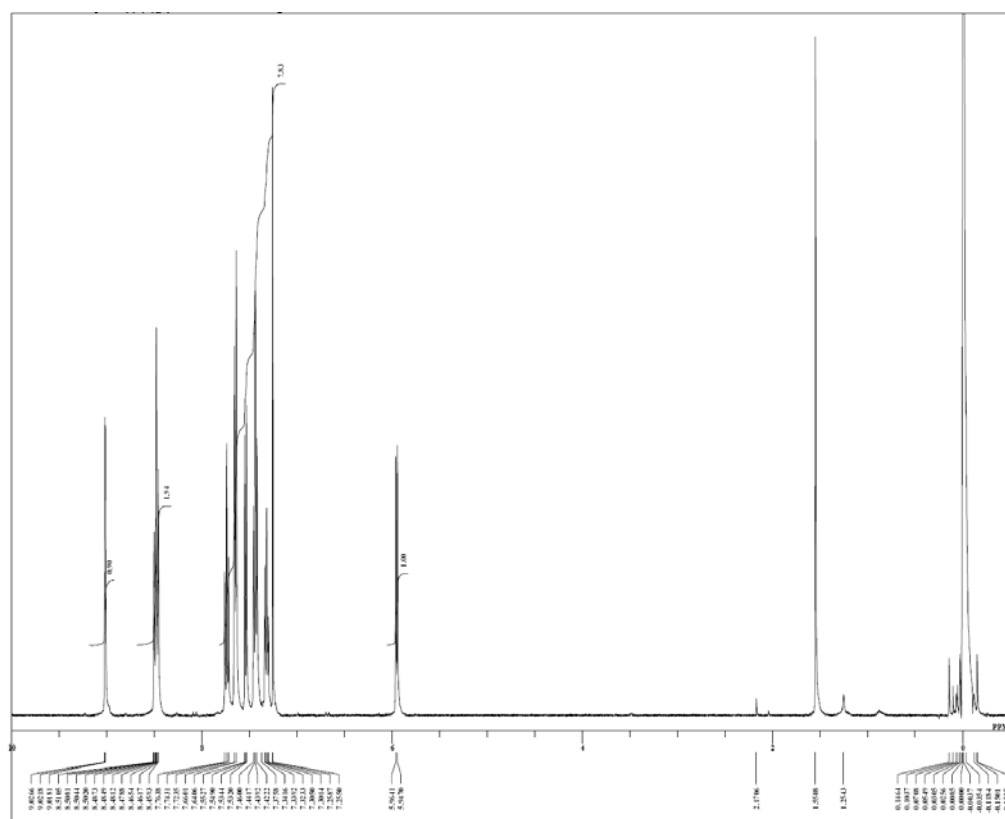


Figure S2. ^{31}P { ^1H } NMR spectrum of the combined filtrate and washings. A peak marked with * is that of $\text{OP}(\text{OPh})_3$.

Z-3ca

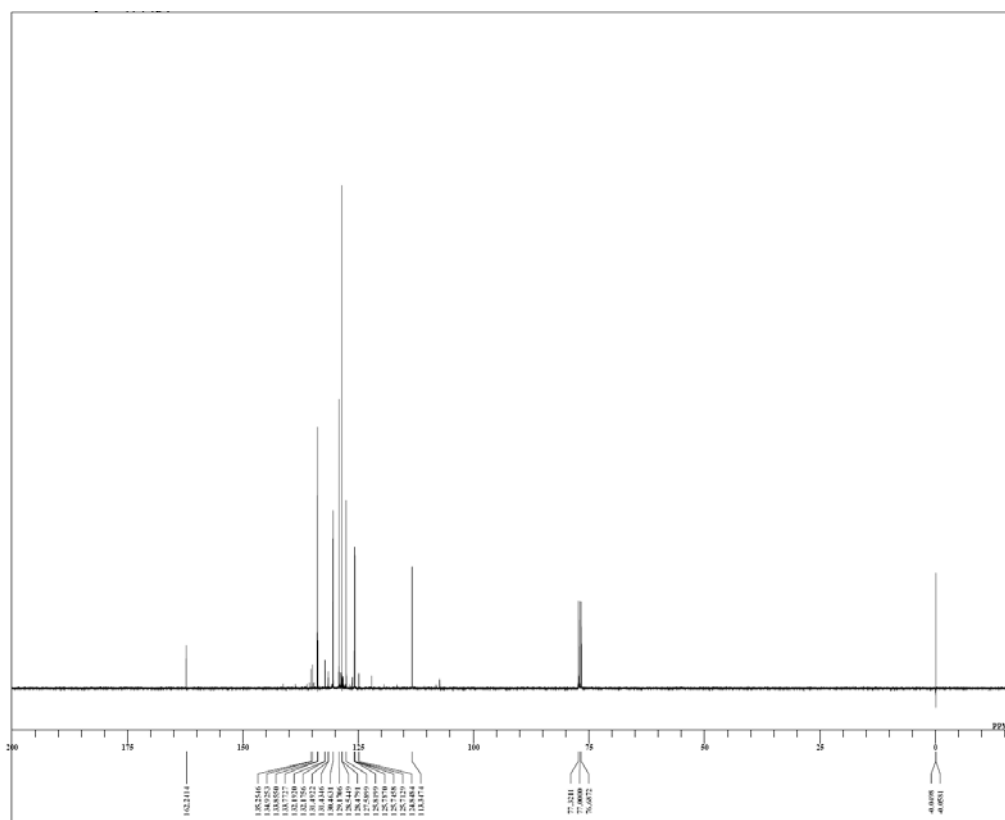
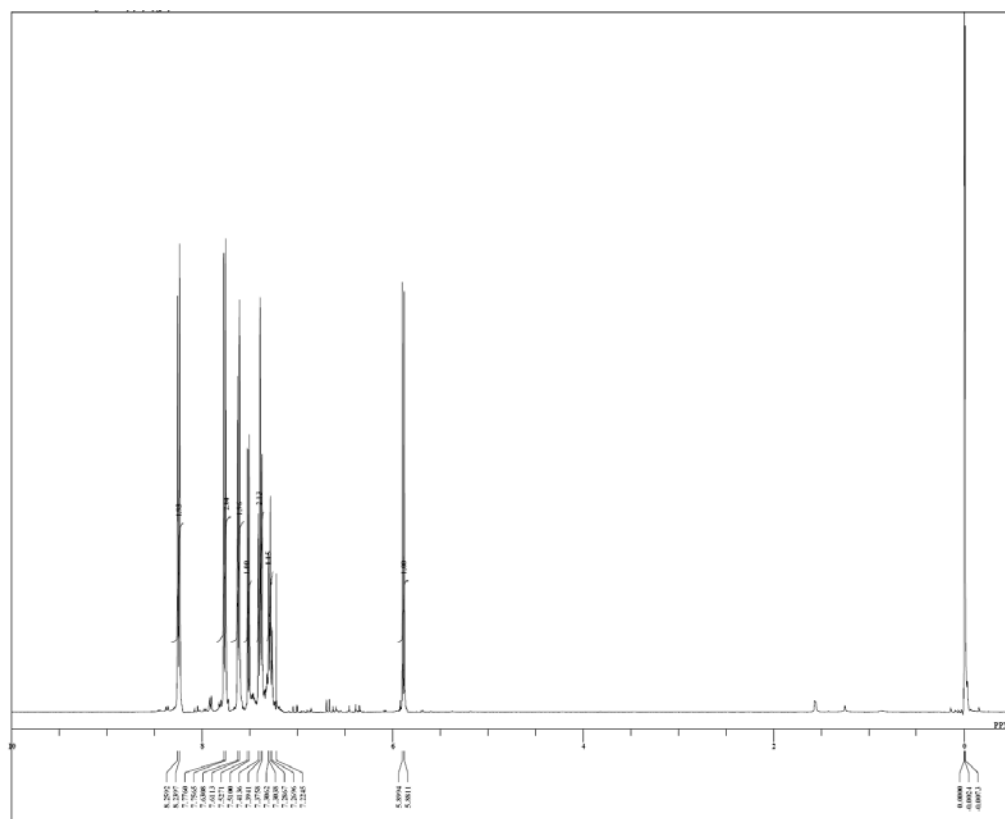


Z-3da

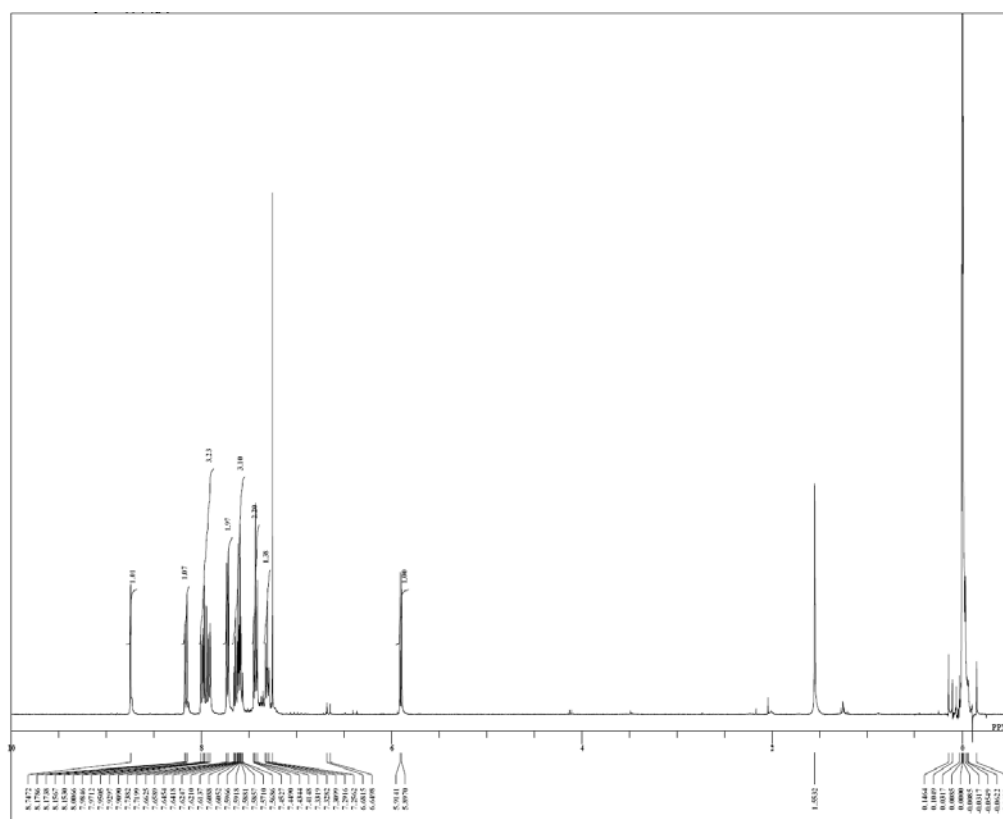


S14

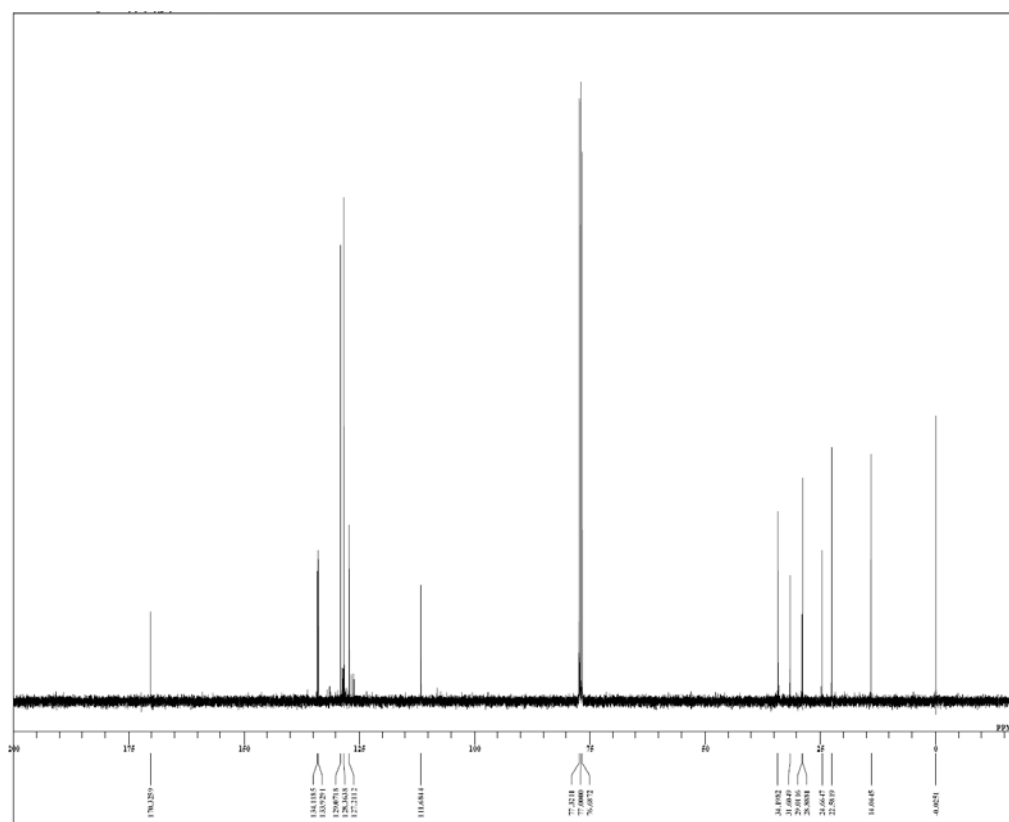
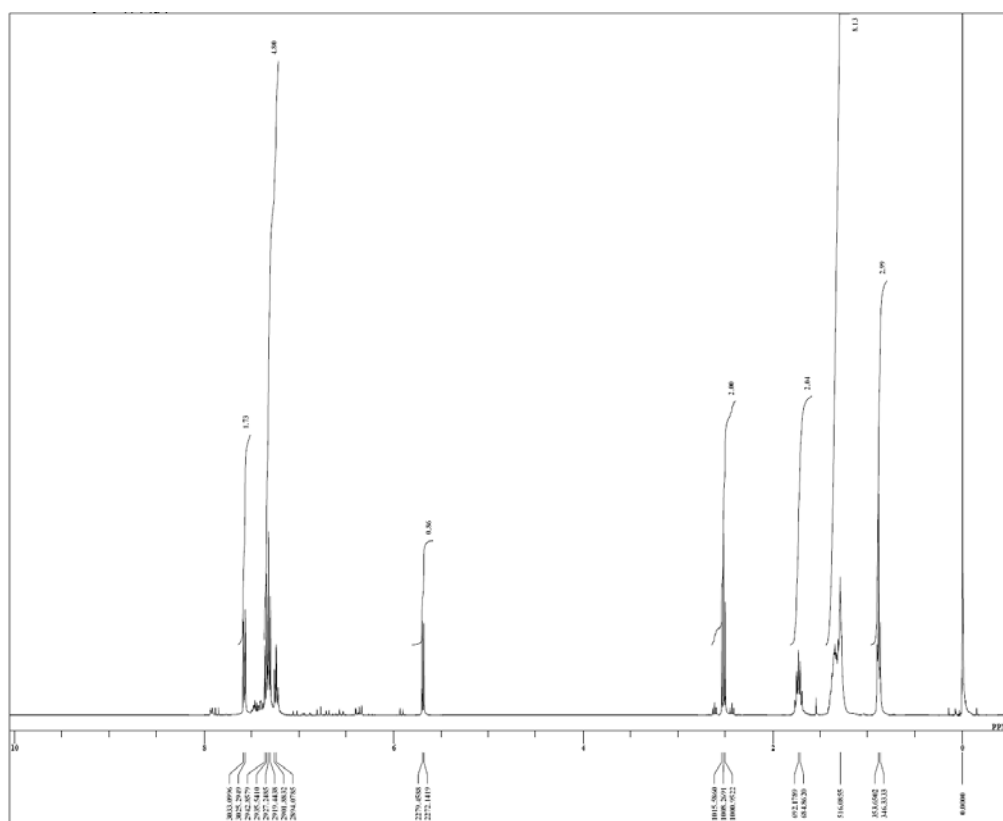
Z-3ea



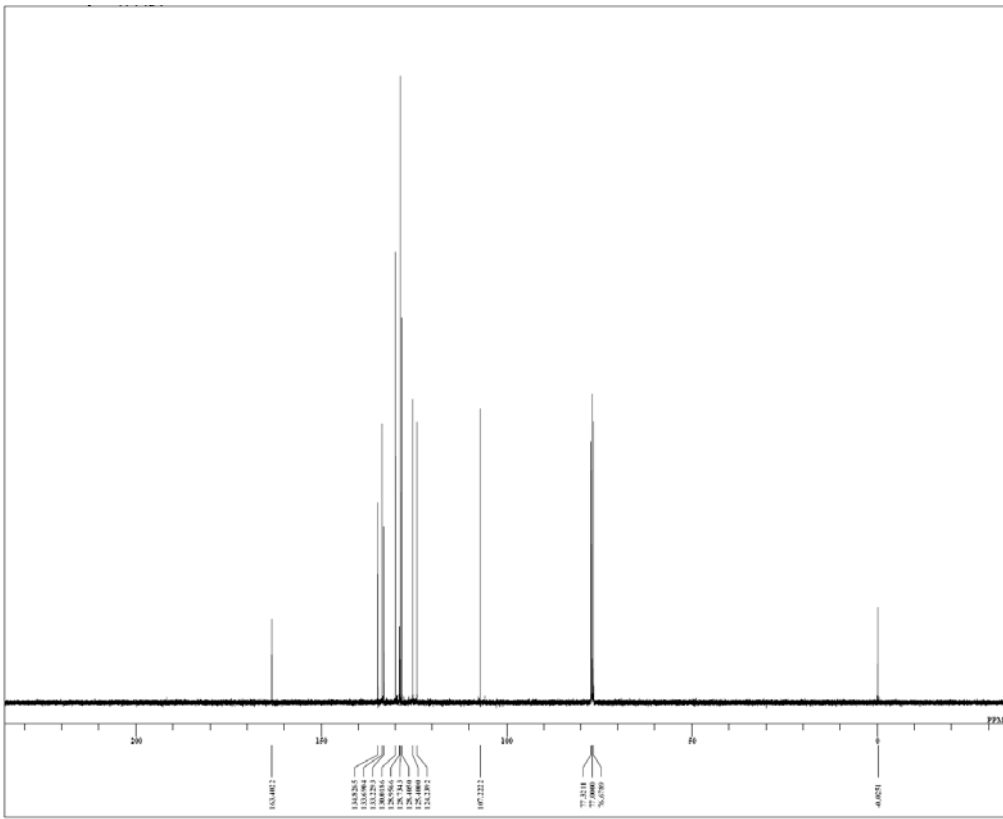
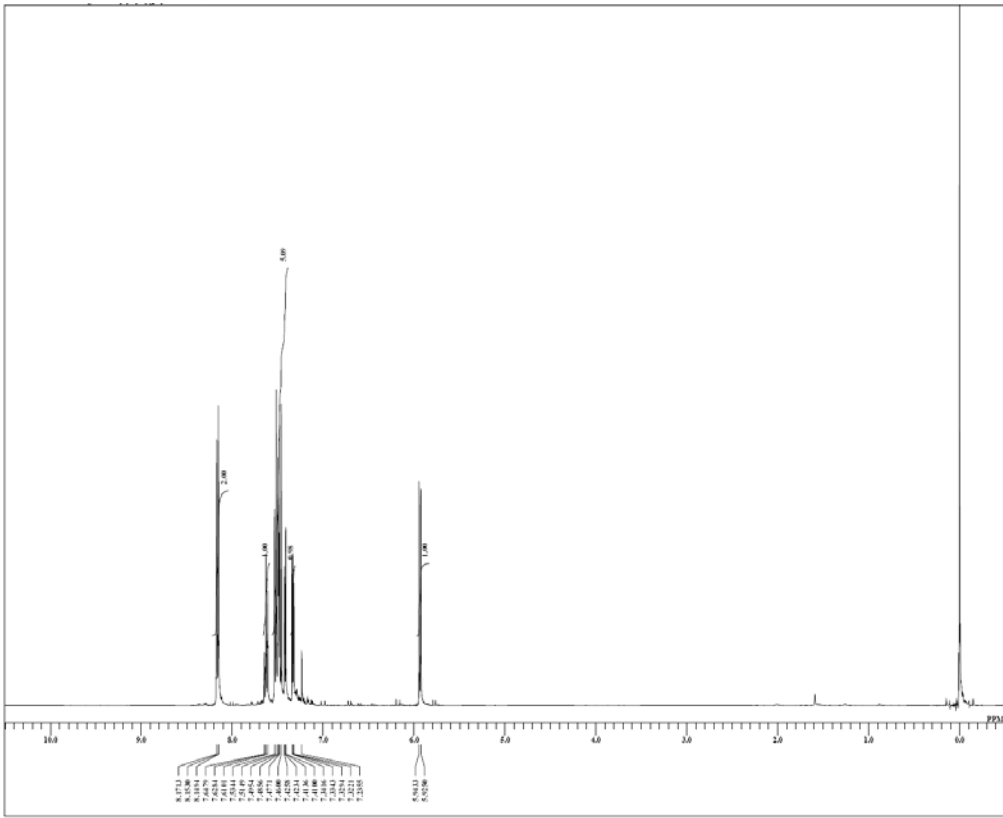
Z-3fa



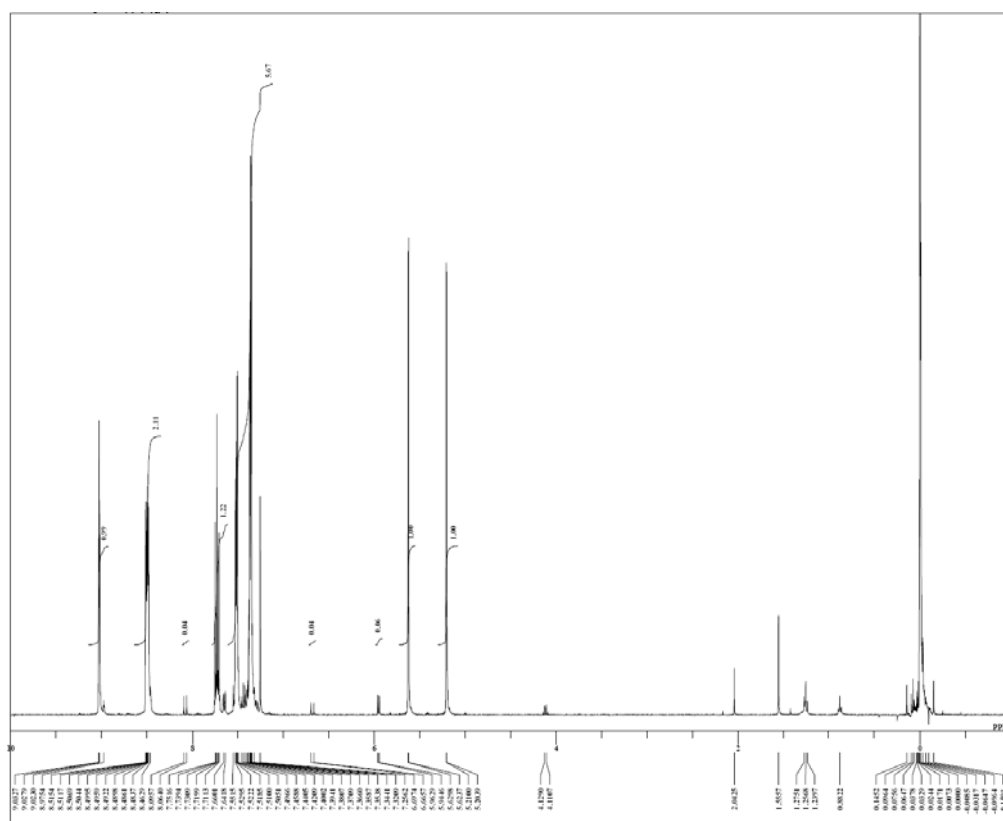
Z-3ha



Z-3ad



4da, E-3da and Z-3da (91:4:5)



9. References

- (1) (a) Miura, H.; Wada, K. ; Hosokawa, S.; Sai, M.; Kondo, T.; Inoue, M. *Chem. Commun.* **2009**, 4112–4114.
(b) Miura, H.; Wada, K. ; Hosokawa, S.; Inoue, M. *Chem. Eur. J.* **2010**, *16*, 4186–4189. (c) Miura, H.;
Wada, K. ; Hosokawa, S.; Inoue, M. *ChemCatChem* **2010**, *2*, 1223–1225.
- (2) Nishiumi, M.; Miura, H.; Wada, K. ; Hosokawa, S.; Inoue, M. *Adv. Synth. Catal.* **2010**, *352*, 3045–3052.
- (3) Hosokawa, S.; Nogawa, S., Taniguchi, M.; Utani, K.; Kanai, H.; Imamura, S. *Appl. Catal. A General* **2005**, *288*, 67–73.