Polymer Bulletin 56, 331–338 (2006)
DOI 10.1007/s00289-006-0503-9

Polymer Bulletin

Coordination Cyclopolymerization Behavior of Diethyl Bis(2,3-butadienyl)malonate by Allylnickel Catalyst

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Received: 30 November 2005 / Accepted: 31 December 2005

Summary

The π-allylnickel-catalyzed coordination cyclopolymerization of a bis(allene) possessing a malonate moiety, diethyl bis(2,3-butadienyl)malonate, gave a polymer which is soluble in organic solvents. The polymer was composed of an almost comparable content of the 1,2- and the 2,3-polymerized units. The polymerization was supposed to proceed through the selective formation of a six-membered ring unit in the main chain by means of the cyclopolymerization of the bis(allene). That is, the intramolecular attack of the growing allylnickel species generated from the first allene moiety upon another one was supposed to give the 1,2-polymerized unit having the six-membered ring system while the intermolecular attack of the allylnickel species derived from the second allene provides the 2,3-polymized unit selectively as is the case of the monofunctional allenes. The effect of the polymerization conditions such as the concentration of the monomer on the polymerization behavior is also described.

Introduction

Cyclopolymerization of bifunctional monomers is an attractive method to obtain polymers bearing rigid cyclic structure and those having functional groups in the main chain. Many cyclopolymerization systems using the free radical, the ionic, and the coordination polymerization techniques have been reported [1]. In these systems, the appropriate design of monomers is essentially of importance to attain the predominant intramolecular reaction (i.e. the cyclopolymerization) than the intermolecular propagation (i.e. the crosslinking reaction). On the basis of the living polymerization techniques, the cyclopolymerization can be studied systematically. Nevertheless, the examples of the cyclopolymerizations based on the living systems are still limited so far [2].

We have been working on the development and applications of the living coordination polymerization of allene derivatives using allylnickel catalysts [3]. This method is one of the most promising tools for the precision synthesis of functional polymers, because it is applicable to monomers containing a large variety of functional groups and it can be carried out under a wide variety of polymerization conditions. In this paper, an α,ω-bis(allene) was designed and synthesized from a malonate ester, and its coordination polymerization was performed by [(π-allyl)NiOCOCF$_3$]$_2$ under various conditions to investigate the cyclopolymerization behavior.

Experimental Part

Measurements

Nuclear magnetic resonance (NMR) spectra were measured on a JEOL ECP-300 instrument using tetramethylsilane as an internal standard (300 MHz and 75 MHz for ^{1}H NMR and ^{13}C NMR, respectively). Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS liquid chromatograph equipped with Tosoh TSK-gel GMH$_{HR}$-M tandem columns using chloroform (CHCl$_3$) as an eluent at 35 °C. Polystyrene standards were used for calibration. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-14B equipped with an FID detector using *n*-eicosane as an internal standard (SE-30, 2 m, gradient temperature of 100-230 °C, heating rate; 10 °C/min). The slow addition of the monomer was performed using a micro-syringe pump (KD Scientific Model 100). The semi-empirical molecular orbital (MO) calculations were performed on a Wavefunction Spartan'02 for Macintosh program using the PM3 basis set.

Materials

Bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$) was obtained from Cica. Allyl trifluoroacetate was obtained from Aldrich and was distilled under nitrogen atmosphere before use. An allylnickel catalyst, [(π-allyl)NiOCOCF$_3$]$_2$ (**1**), was prepared as previously described [3]. Toluene was dried over sodium benzophenone ketyl and distilled under nitrogen before use. Ethanol was dried over magnesium ethoxide and distilled under nitrogen before use. Other reagents were used as received. All the polymerizations were carried out under nitrogen.

Synthesis of Diethyl Dipropargylmalonate

To a 200-mL two-neck round bottom flask equipped with a mechanical stirrer, a Dimroth condenser and a dropping funnel, were added diethyl malonate (16.3 g, 100 mmol) and an absolute ethanol (100 mL) solution of sodium ethoxide (prepared from 224 mmol of sodium). To the resulting solution, propargyl bromide (26.6 g, 224 mmol) was added slowly from the dropping funnel at 60 °C and the mixture was refluxed with stirring overnight. After removal of ethanol under reduced pressure, diethyl ether (ca 50 mL) was added to the residue and the organic layer was washed 3 times with water. After drying over MgSO$_4$, the volatile fractions were evaporated and the remaining oil was purified by distillation (82-83 °C/0.12 mmHg) to give diethyl dipropargylmalonate in a 91% yield (21.5 g, 91 mmol). ^{1}H NMR (CDCl$_3$, δ ppm): 1.21 (t, J = 7.2 Hz, 6H, —CH$_2$—CH_3), 1.99 (t, J = 2.3 Hz, 2H, —C≡CH), 2.94 (d, J = 2.4 Hz, 4H, —CH_2—C≡CH), 4.18 (q, J = 7.1 Hz, 4H, —O—CH_2—CH$_3$). ^{13}C NMR (CDCl$_3$, δ ppm): 13.9 (—CH$_2$—CH$_3$), 22.4 (—CH$_2$—C≡CH), 56.2 (>C(CH$_2$—C≡CH)$_2$), 62.0 (—O—CH$_2$—CH$_3$), 71.6 (—C≡CH), 78.4 (—C≡CH), 168.5 (—C(=O)—O—). IR (KBr disk, cm^{-1}): 3302, 3272, 2986, 2940, 1732, 1468, 1424, 1370, 1302, 1215, 1094, 1053, 1003, 957, 855, 801, 675, 637, 540, 461, 417.

*Synthesis of Diethyl Bis(2,3-butadienyl)malonate (**2**)*

To a 200-mL two-neck round bottom flask equipped with a Dimroth condenser, were added diethyl dipropargylmalonate (5.72 g, 24.2 mmol), paraformaldehyde (1.82 g, 60.5 mmol), CuI (5.07g, 26.6 mmol), diisopropylamine (10 mL) and 1,4-dioxane (100 mL) under nitrogen and the mixture was refluxed with stirring for 24 h. After removal of the volatile fractions under reduced pressure, diethyl ether (ca 40 mL) was added to the residue and the organic layer was washed 3 times with water. After drying over $MgSO_4$, the product was purified by silica gel column chromatography (eluent: CH_2Cl_2) to give **2** in a 57% yield (3.62 g, 13.7 mmol). ^{1}H NMR ($CDCl_3$, δ ppm): 1.25 (t, *J* = 7.2 Hz, 6H, —CH$_2$—C*H*$_3$), 2.65 (4H, —C*H*$_2$—CH=C=CH$_2$), 4.19 (q, *J* = 7.2 Hz, 4H, —O—C*H*$_2$—CH$_3$), 4.66 (4H, —CH=C=C*H*$_2$), 4.95 (2H, —C*H*=C=CH$_2$). ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (—CH$_2$—*C*H$_3$), 31.8 (—*C*H$_2$—CH=C=CH$_2$), 57.7 (>*C*(CH$_2$—CH=C=CH$_2$)$_2$), 61.3 (—O—*C*H$_2$—CH$_3$), 74.6 (—CH=C=*C*H$_2$), 84.2 (—*C*H=C=CH$_2$), 168.5 (—*C*(=O)—O—), 210.1 (—CH=*C*=CH$_2$). IR (NaCl, cm^{-1}): 2984, 2361, 1958, 1732, 1443, 1391, 1368, 1279, 1246, 1202, 1080, 1020, 853, 693, 556.

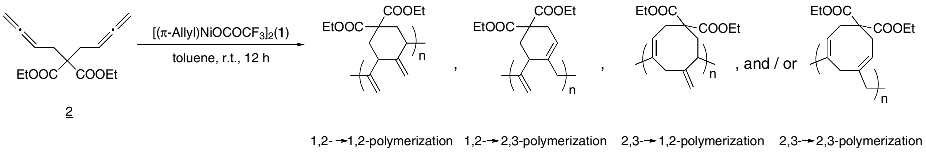
*Coordination Cyclopolymerization of **2** by **1** (Typical Procedure)*

To a flask equipped with a thee-way stopcock and a magnetic stirrer bar, a toluene (7.0 mL) solution of **1** (2.3×10^{-2} mmol) was introduced under nitrogen. Then, **2** (0.19 g, 0.70 mmol, 30 equiv) was added and the mixture was stirred at ambient temperature for 24 h. The resulting solution was poured into methanol/H_2O (v/v = 2/1) to give a polymer in a 97 % yield (0.18 g). ^{1}H NMR ($CDCl_3$, δ ppm, also shown in Figure 1a): 1.16 (6H, —O—CH$_2$—C*H*$_3$), 1.78 (2H x 0.52, >CH—C*H*$_2$—C(C(=O)O)$_2$), 2.01-2.72 (2H x 0.48 + 1H x 0.52, —(C=)C—C*H*$_2$—C(=CH$_2$)—, —(CH$_2$=)C—C*H*—(=C)—), 3.31 (2H x 0.48, C—C*H*$_2$—CH=C<), 4.10 (4H, —O—C*H*$_2$—CH$_3$), 4.68 (2H x 0.52, >C=C*H*$_2$), 5.52 (1H x 0.48, >C=C*H*—); 1,2-:2,3-polymerizations = 52:48. ^{13}C NMR ($CDCl_3$, δ, ppm, Figure 1b): 14.1 (—O—CH$_2$—*C*H$_3$), 30.7 (C—*C*H$_2$—CH<), 37.3 (C—*C*H$_2$—CH=C<), 43.6 (—(CH$_2$=)C—*C*H—(=C)—), 52.8 (—(C=)C—*C*H$_2$—C(=CH$_2$)—), 58.0 (>*C*(C(=O)O—)$_2$), 61.1 (—O—*C*H$_2$—CH$_3$), 113.8 (>C=*C*H$_2$), 123.9 (>C=*C*H—C), 135.7 (>*C*H=CH—C), 147.5 (>*C*=CH$_2$), 171.5 (—*C*(=O)—O—). IR (NaCl, cm^{-1}): 2982, 2938, 1732, 1640, 1445, 1391, 1368, 1256, 1186, 1093, 1024, 899, 860, 802, 758, 704, 667, 557, 471, 458.

Results and Discussion

*Cyclopolymerization of **2***

The polymerization of the bis(allene) (**2**) ($[\mathbf{2}]_0$ = 0.1 M, 30 equiv) was performed by $[(\pi\text{-allyl})NiOCOCF_3]_2$ (**1**) in toluene at ambient temperature for 24 h to evaluate the possibility of the cyclopolymerization (Scheme 1). The polymerization proceeded in a homogeneous system and a polymer was obtained in a 97% yield by precipitated into methanol/H_2O (v/v = 2/1). This polymer (poly(**2**)) is soluble in organic solvents such as toluene, dichloromethane, chloroform, THF, and acetone. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of poly(**2**) were estimated by GPC to be 6,200 and 2.10, respectively.



Scheme 1. Possible paths for coordination cyclopolymerization of **2** by **1**.

*Structural Elucidation of Poly(**2**)*

In the ^{1}H-NMR spectrum of poly(**2**), the characteristic peaks due to the *exo*-methylene moiety in the 1,2-polymerized unit and the methine moiety in the 2,3-polymerized unit were observed at $\delta = 4.68$ ppm and 5.52 ppm, respectively (Figure 1a). The ratio of the 1,2- to the 2,3-polymerizations was determined as 52:48 from the intensity of these peaks. As described in the polymerization of monofunctional alkylallenes, the content of the 1,2-polymerized unit in the polymers obtained by **1** is below 9%, indicating that the polymer obtained from the bis(allene) has a remarkably higher content of the 1,2-polymerized unit. The ^{13}C NMR spectrum of poly(**2**) exhibited no peak at δ210 ppm for the unreacted allenyl group, indicating that both of the two allene moieties in **2** participated in the polymerization. Accordingly, the higher content of the 1,2-polymerized unit in poly(**2**) and the production of the entirely soluble product from the bifunctional monomer support that the cyclopolymerization takes place effectively under the examined conditions.

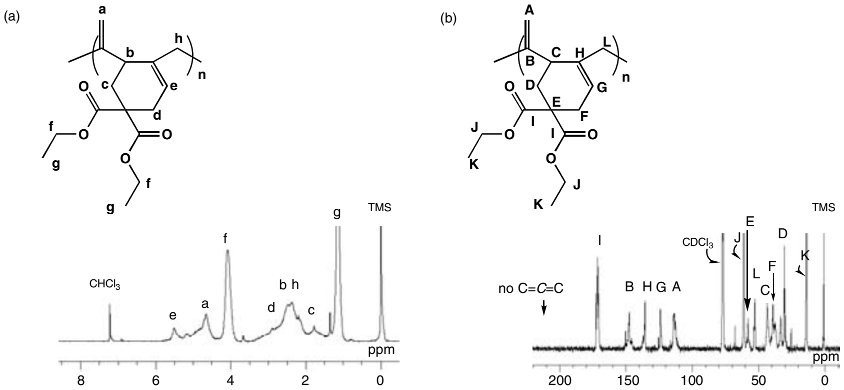


Figure 1. ^{1}H-NMR (a) and ^{13}C-NMR spectra (b) of poly(**2**) prepared by the polymerization of **2** by **1** ($[\mathbf{2}]_0 = 0.10$ M, $[\mathbf{1}]_0 = 3.3 \times 10^{-3}$ M).

Comparison of Heats of Formation for Possible Cyclic Units by MO Calculations

The origin of the higher content of the 1,2-polymerized unit in poly(**2**) was evaluated by the semi-empirical computational MO calculation using the PM3 basis set. As summarized in Figure 2, we first compared the heats of formation for the two possible intramolecular cyclization process of an 1:1 adduct of **1** and **2** [4]. Among the two possible ring-closing mechanisms for the intramolecular insertion of the second allene moieties, one leading to the 1,2-polymerized unit having the six-membered ring system (path A-1) was estimated to be thermodynamically more favorable than the other giving the 2,3-polymerized unit having the eight-membered ring system (path A-2). That is, the formation of the six-membered ring assists the formation of the 1,2-polymerized unit which is the less favorable process for monofunctional alkylallenes. In the next step, the intermolecular insertion of another monomer takes place, during which the formation of the 2,3-polymerized unit (path B-1) is more favorable than the 1,2-polymerized unit (path B-2) as is the case for the monofunctional alkylallenes. Because the content of the 1,2- and the 2,3-polymerized units in poly(**2**) are almost comparable in poly(**2**) (52:48), the cyclopolymerization most probably takes place in a highly selective fashion, resulting in the formation of the six-membered ring unit in the main chain.

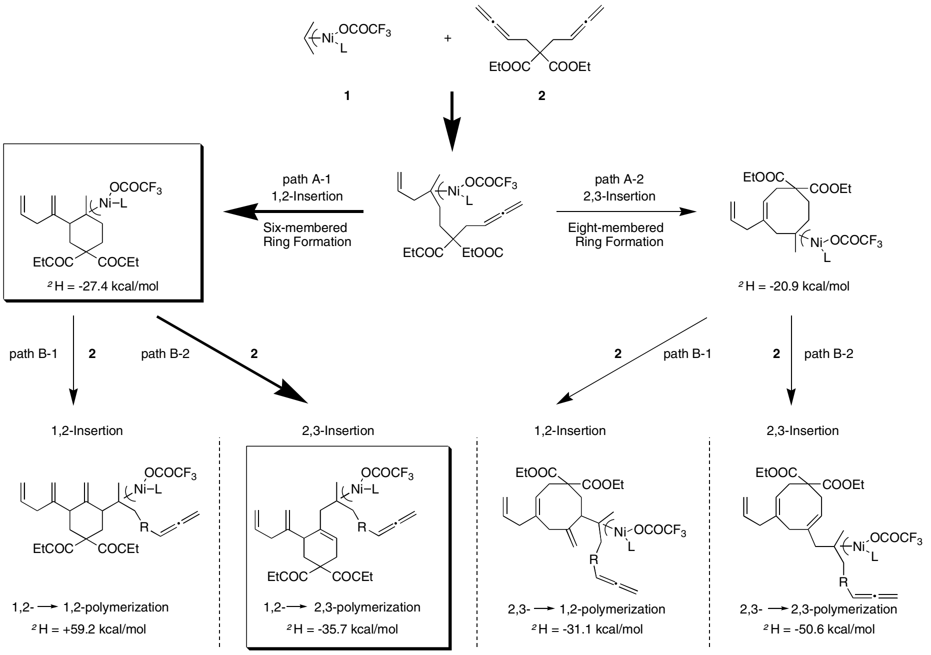


Figure 2. Heats of formation of plausible isomeric units in the cyclopolymerization process of **2** estimated by the semi-empirical computational MO calculation using PM3 basis set.

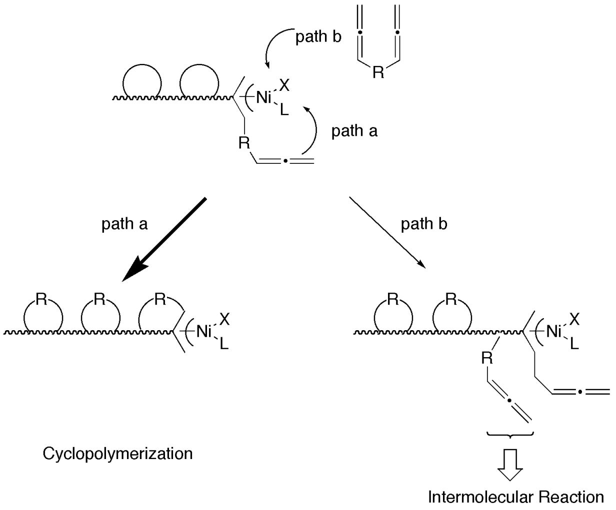
Effect of Polymerization Time, [M]/[I] Ratio, and Monomer Concentration

The monomer conversion and the molecular weight of poly(**2**) in the polymerization of **2** ([**2**] = 0.10 M, $[\mathbf{2}]_0/[\mathbf{1}]$ = 15) were investigated carefully by both GC and GPC after designated reaction periods (Table 1). After 10 min, the consumption of **2** was almost complete (>97%) and the molecular weight distribution of poly(**2**) was relatively narrow (M_n = 3,300, M_w/M_n = 1.65). After an additional 40 min, the molecular weight of poly(**2**) increased slightly and the molecular weight distribution became a little broader (M_n = 3,600, M_w/M_n = 1.97). Although the orange color of the growing allylnickel did not diminish throughout the reaction for 12 h, the molecular weight and the molecular weight distribution of poly(**2**) did not exhibit noticeable change. These results indicate that the intermolecular reaction of a small amount of the unreacted allenyl groups in the polymer occurred subsequently, which facilitates the intermolecular reaction (Scheme 2, path b). As expected, no peak for the unreacted allenyl group was detected in the ^{1}H NMR and ^{13}C NMR spectra after the polymerization for 12 h.

Table 1. Dependence of the conversion and the molecular weight on polymerization time.[a)]

Run	Time	Conversion (%)[b)]	M_n[c)]	M_w/M_n[c)]
1	1 min	62	1,400	1.23
2	10 min	97	3,300	1.65
3	30 min	>99	3,400	1.92
4	50 min	>99	3,600	1.97
5	12 h	>99	3,600	1.97

a) Conditions: $[\mathbf{2}]_0/[\mathbf{1}] = 15$, $[\mathbf{2}]_0 = 0.10$ M in toluene.
b) Determined by GC.
c) Estimated by GPC ($CHCl_3$, polystyrene Std).



Scheme 2. Plausible reaction paths for cyclopolymerization (path a) and intermolecular reaction (path b).

The polymerization of **2** was also carried out under various ratios of $[\mathbf{2}]_0/[\mathbf{1}]$ ($[\mathbf{2}]_0 = 0.10$ M) to give soluble polymers in high yields. By increasing the $[\mathbf{2}]_0/[\mathbf{1}]$ ratio, the molecular weight increased as is the case of the living polymerization of monofunctional allene derivatives, although its distribution was rather broad (Table 2).

Table 2. Dependence of molecular weight of poly(**2**) on $[\mathbf{2}]/[\mathbf{1}]$ ratio.

Run[a)]	$[\mathbf{2}]_0/[\mathbf{1}]$	M_n[b)]	M_w/M_n[b)]	Yield (%)[c)]
1	15	3,600	1.97	91
2	30	6,200	2.10	97
3	50	9,500	1.90	92

a) Conditions: $[\mathbf{2}]_0 = 0.1$ M, in toluene at ambient temperature for 12 h.
b) Estimated by GPC ($CHCl_3$, polystyrene Std).
c) Isolated yield after precipitation with methanol/H_2O (v/v = 1/2)

In general, the cyclopolymerizations of bifunctional monomers are often carried out under dilute conditions to suppress the intermolecular reactions of the uncyclized propagating species [1]. In the present polymerization, the soluble polymer was constantly produced within the examined range of the initial monomer concentrations ($[\mathbf{2}]_0$ = 0.05 M-0.50 M, $[\mathbf{2}]_0/[\mathbf{1}]$ = 30) (Table 3). In these cases, however, the molecular weight distribution of poly(**2**) became broader and the molecular weight also became much larger at the higher initial concentration of **2**, suggesting that the present system implies the intermolecular cross-linking process as a side reaction which works much more obvious at the higher concentration of **2**.

Table 3. Coordination cyclopolymerization of **2** under varied initial concentrations.[a)]

Run	$[\mathbf{2}]_0$	Polymerization Time (h)	M_n[b)]	M_w/M_n[b)]	Yield (%)[c)]
1	0.50 M	16	7,200	3.20	99
2	0.30 M	24	6,800	2.52	96
3	0.10 M	30	6,200	2.10	97
4	0.05 M	72	4,000	2.05	98

a) Conditions: $[\mathbf{2}]_0/[\mathbf{1}]$ = 30, at ambient temperature.
b) Estimated by GPC ($CHCl_3$, polystyrene Std).
c) Isolated yield after precipitation with methanol/H_2O (v/v = 1/2).

Table 4. Effect of feeding rate of **2** in the coordination polymerization by **1**.

Run	Time Required for Monomer Addition (Feeding Rate)[a)]	M_n[b)]	M_w/M_n[b)]	Yield (%)[c)]
1	10 sec (0.10 mmol / sec)	6,200	2.15	97
2	10 h (0.10 mmol / h)	5,800	2.02	87
3	20 h (0.05 mmol/ h)	2,600	1.87	94
4	120 h (0.0083 mmol/ h)	2,200	1.73	98

a) The monomer (**2**) was added slowly by a micro-syringe pump except for fun 1 ($[\mathbf{2}]_0/[\mathbf{1}]$ = 30, $[\mathbf{1}]_0 = 3.3 \times 10^{-3}$ M) and the polymerization was carried out in toluene at ambient temperature.
b) Estimated by GPC ($CHCl_3$, polystyrene Std).
c) Isolated yield after precipitation with methanol/H_2O (v/v = 1/2).

In order to keep the monomer concentration low, the polymerization of **2** (30 equiv) was performed by the slow feeding of the monomer using a micro-syringe pump at various feeding rates ($[\mathbf{1}]_0 = 3.3 \times 10^{-3}$ M). As summarized in Table 4, the polymer having smaller molecular weight and narrower molecular weight distribution was obtained under the slower feeding rate of **2**.

Conclusions

The π-allylnickel-catalyzed coordination polymerization of a bis(allene), diethyl bis(2,3-butadienyl)malonate (**2**), was found to give a polymer in a high yield which is soluble in organic solvents. The polymer was found to have an almost comparable content of the 1,2- and the 2,3-polymerized units. The polymerization was supposed to proceed through the selective formation of a six-membered ring unit in the main chain by means of the cyclopolymerization of the bis(allene). The regulation of both the molecular weight and its distribution of the polymer was attainable more effectively under the lower concentration of **2**, suggesting that the cyclopolymerization proceeds much effectively. The cyclopolymerization behavior of other bis(allene)s and applications of the resulting cyclopolymers are currently being investigated.

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[4] In the absence of neutral ligands such as phosphines, many allylnickel complexes are known to exist as dimers where the anionic ligands serve as the bridging ligands for another nickel center. In the present polymerization system, the nickel complex may have any neutral ligands (L) on the nickel although we have not succeeded in attributing the structure yet. As to perform the MO calculations, we have pecked up the carbonyl group in the trifluoroacetate ester as L (for simplicity, CF_3COOCH_3 was used). We also checked some other candidates of L such as phosphine for the series of the MO calculations which also pointed out the same selectivity.